UNIVERSITY OF SOUTHAMPTON

Faculty of Science

Department of Chemistry

ZEOLITE SUPPORTED PLATINUM
ELECTROCATALYSTS

By Jun Yao

Thesis submitted for the Degree of Doctor of Philosophy

January 2002
Recently, platinum exchanged zeolite modified catalysts have been shown to be interesting as electrodes, as the physical structure and chemical nature of the zeolite may influence the electron transfer at the electrode – solution interface of known chemical steps. Generally, the catalytic nature of zeolite can be modified by pre-exchanging metal ions to give the desired cationic form, and its catalytic activity can be increased by calcinating to lock the exchangeable metal ions into position.

In this project we have chosen Y zeolite as Pt support. The study found that the pre-treatment, such as, preparation methods, Pt(NH$_3$)$_4$(NO$_3$)$_2$ or Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ ion exchange and impregnation methods, calcination and reduction temperature and the stoichiometry of the titration method (O$_2$, H$_2$), is important for obtaining highly dispersed platinum-zeolite catalysts. The structure/reactivity relationship was investigated by altering the Pt loading from 1.5 wt.% to 5wt.% to show that the particle size increases with the metal loading. The investigation was carried by the use of X-ray absorption spectroscopy and in particular the extended X-ray adsorption fine structure (EXAFS) method. XAS data was collected in a gas treatment cell as well as in the electrochemical environment.

The materials are characterised by fabricating carbon composite electrodes, and the electrocatalytic activity is determined by cyclic voltammetry technique. We used the evidence of hydrogen adsorption in the cyclic voltammograms as the basis upon which to make the judgement. The experimental results show that the Pt nanoparticle supported on zeolite may be electrochemically reduced due to the hydrogen spillover function of the zeolite.

Based on the experimental results, we found that the use of the Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ ion-exchanged material, subjected to oxygen calcination – hydrogen reduction performs better than other catalysts prepared for a variety of electrochemical reactions.
ACKNOWLEDGEMENTS

Many people have helped me during my PhD study. Therefore, I would sincerely like to thank them for their kind support over the last three years.

Firstly, I would like to thank my research supervisor, Dr Andrea Russell for continued guidance, expertise and encouragement during my entire research period. My special thanks also go out to Prof. George Attard for giving me invaluable suggestions on how to improve my written work and for being my advisor during my time at the Dept. of Chemistry, University of Southampton.

Thanks are extended to everybody (Becky, Stephanie, Fabrice, Anne, Abbe and Chris) working in the Russell group over the last three years for their support and invaluable help. I would also like to thank Linda Carrette for her kind help and friendship. A big thank you goes to Dr Andrew Hector who carried out XRD experiments for me.

Thanks are also extended to Prof. Mark Weller’s group for allowing me to use their furnace room and equipment, especially Jon Read for his invaluable help when I need it.

I am grateful to Prof. George Attard’s group for allowing me to use BET instrument and useful help for the data analysis.

Thanks also go to Prof. Diek Koningsberger at the University of Utrecht in the Netherlands and Dr Debra Rolison at the Naval Research Laboratory, USA for inspiration and many useful discussions.

A big thank you goes to all the people in the technical workshop and the glassblowers for their useful help. Thanks to the people at Daresbury as well for their helpful assistance and suggestions to make our time there much easier.

I would like to say a big thank you to my parents and brother for their help, understanding and encouragement.
I would like to thank my husband, Dr Yufeng Yao for his support and encouragement throughout my study and my son, Weiyi Yao for sharing the long study period with great understanding.

Finally, I would like to thank EPSRC for funding this project.

To you all thanks.
List of Symbols and Acronyms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Coulombs</td>
</tr>
<tr>
<td>(\chi(k))</td>
<td>EXAFS function</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammogram</td>
</tr>
<tr>
<td>d</td>
<td>space between crystal planes in a crystal structure</td>
</tr>
<tr>
<td>E</td>
<td>cell potential</td>
</tr>
<tr>
<td>(E^o)</td>
<td>thermodynamic cell potential</td>
</tr>
<tr>
<td>eV</td>
<td>electron Volts = measure of energy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (96845 C mol(^{-1}))</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transformation</td>
</tr>
<tr>
<td>(\eta)</td>
<td>overpotential = deviation of the cell potential from the standard Electrode potential</td>
</tr>
<tr>
<td>j</td>
<td>current density/Acm(^{-2})</td>
</tr>
<tr>
<td>(I_o)</td>
<td>intensity of an X-ray beam before passing through the sample in an XAS experiment</td>
</tr>
<tr>
<td>iR</td>
<td>Ohmic potential drop in an electrochemical cell</td>
</tr>
<tr>
<td>(I_t)</td>
<td>intensity of an X-ray beam measured after passing through the sample in an XAS experiment</td>
</tr>
<tr>
<td>K edge</td>
<td>edge arising in an XAS experiment due to the excitation of an electron from the K shell to the continuum by the adsorption of energy</td>
</tr>
<tr>
<td>k</td>
<td>wave number in an EXAFS experiment</td>
</tr>
<tr>
<td>L(_n)</td>
<td>edge arising in an XAS experiment due to the excitation of an electron from the L shell to the continuum by the adsorption of energy</td>
</tr>
<tr>
<td>(\mu(\chi))</td>
<td>absorption coefficient = (\ln(I_o/I_t))</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MMS</td>
<td>Mercury/Mercurous Sulphate reference electrode (+0.65 V versus SHE)</td>
</tr>
<tr>
<td>N</td>
<td>co-ordination number = number of neighbours of a specific type around the absorber atom as calculated from the EXAFS analysis</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
</tbody>
</table>
PTFE: Poly-TetraFluoro Ethylene

R: molar gas constant (8.31 J mol⁻¹ K⁻¹)

R: co-ordination distance = distance between the absorber atom and the neighbour in question calculated by examining the EXAFS region

RE: Reference Electrode

SHE: Standard Hydrogen Electrode

WE: Working Electrode

wt.%: weight in percentage of the substance in the total catalyst

XAS: X-ray absorption Spectroscopy

XC-72R: Carbon support = C

XRD: X-Ray Diffraction

Ω: Ohm

ANCR: tetraamine platinum nitrate salt ion exchange, calcination and reduction

ANXCR: tetraamine platinum nitrate salt/ammonia nitrate salt ion exchange, Calcination and reduction

Pd: Palladium

HR: hydrogen reduction region

DL: double layer region

OR: the oxide region

HSP: hydrogen adsorption potential

Sₘ: the surface area of the material

BET: Brunauer, Emmett and Teller (names who developed surface area measurement)

V₀: the amount of gas required to fill the micropores

P/P₀: relative pressure

Vₘ: the volume of gas in a monolayer

V: the volume of gas adsorbed (in ml, S.T.P)

hν: the energy of incident photon

| f |: the wavefunction of photoelectron in the final state

ω: the frequency of the X-ray photon

| i>: the wavefunction of the photoelectron in its initial state

ρ( E_f ): the density of final state

XANES: X-ray Absorption Near Edge Structure
\( \lambda \) the wavelength of the beam
\( m \) the mass of the electron
\( j \) the \( j \)th co-ordination shell
\( 2\sigma_j^2 \) Debye Waller factor which represents a measurement of static and thermal disorder in the sample, and is temperature dependent
\( \Phi_k \) the backscattering phase shift
\( \theta \) the angle of incidence or reflection of the X-ray beam
\( T \) the temperature in Kelvin
\( \text{EASA} \) electrochemically active surface area
# Table of Contents

## Chapter 1: Introduction

1. **Electrode Modified Zeolites**  
   1.1. Electrode Modified Zeolites  
2. **The Nature of Zeolites**  
3. **Platinum and Palladium Supported on Zeolites**  
   1.3.1. Spillover of Hydrogen On the Pt Surface  
4. **Extended X-Ray Absorption Fine Structure and Metal Particles on Zeolites**  
5. **Thesis Plan**  
6. **References**

## Chapter 2: Experimental Methods and Techniques

2.1. **Catalyst Preparation**  
   2.1.1. Metal/Zeolite Ion-Exchange  
   2.1.1.1. The Ion-Exchange Procedure  
   2.1.1.2. The Theory of Metal/Zeolite Ion-Exchange  
   2.1.2. Calcination and Reduction  
   2.1.2.1. The Fluidised Bed Reactor  
   2.1.2.2. Calcination  
   2.1.2.3. Reduction  
   2.1.2.4. List of sample acronyms  
2.2. **Electrode Manufacture**  
   2.2.1. Nafion® Bound Electrodes  
   2.2.2. Nafion®  
   2.2.3. Electrode Preparation  
2.3. **Electrochemistry**  
   2.3.1. Introduction  
   2.3.2. Instrumentation  
   2.3.3. The electrochemical cell  
   2.3.4. Cyclic Voltammetry  
   2.3.5. Electrochemical Active Area  
   2.3.5.1. CO oxidation  
   2.3.5.2. Hydrogen  
   2.3.5.3. Polarisation  
   2.3.5.4. iR Drop  
2.4. **BET**  
   2.4.1. The Principle of BET Surface Area Measurement  
   2.4.2. BET surface area measurement  
2.5. **X-Ray Absorption Spectroscopy (XAS)**  
   2.5.1. Introduction  
   2.5.1.1. X-Ray Absorption Spectroscopy – Theory  
   2.5.2. Data Collection  
   2.5.2.1. The Cell & Powders
Chapter 3: Pt/Y Physical Characterization of Pt Particles Supported on Y Zeolite

3.1. Introduction

3.2. Results

3.2.1. The ex-situ EXAFS Results for 1.5 wt. % Pt/Zeolite Catalysts

3.2.1.1. The ex-situ EXAFS Results of the 1.5 wt% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} Edge in Air

3.2.1.2. The ex-situ EXAFS Results of 1.5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge following Hydrogen Chemical Reduction

3.2.1.3. The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge as prepared

3.2.1.4. The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge following Hydrogen Chemical Reduction

3.2.1.5. The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Fe K edge as prepared

3.2.1.6. The ex-situ EXAFS Results of 5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge as prepared

3.2.1.7. The ex-situ EXAFS Results of 5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge following Hydrogen Chemical Reduction

3.2.2. The results of BET surface area measurement

3.2.3. XRD Characterization

3.2.4. The Relationship between Pt loading and the Pt Particle Size

3.2.4.1. The actual Pt loading on zeolite determined by the edge jump

3.2.4.2. Estimation of Pt Particle Size

3.3. Discussion and Conclusion

3.4. References

Chapter 4: Electrochemical Characterization of Pt Particles Supported on Y Zeolite

4.1. Introduction

4.2. Brief Experimental Reminder

4.2.1. The Summary of the type of Pt Zeolite Electro catalysts

4.2.2. Nafion\textsuperscript{®} Bound Electrodes
Chapter 5: The Characteristics of Palladium Particles Supported on Y Zeolite

5.1. Introduction 175
5.2. Experimental 177
5.3. Results 178
  5.3.1. The Results of 40 wt.% Pd/C Electrode 178
  5.3.2. The Electrochemical Characteristics of 1.5 wt.% Pd/Y Zeolite 180
  5.3.3. The Results of Extended X-Ray Adsorption Fine Structure (EXAFS) 184
  5.3.4. The Results of in situ Extended X-Ray Adsorption Fine Structure (EXAFS) 187
5.4. Discussion and conclusion 191
5.5. References 195

Chapter 6: Conclusions 196

6.1. Utilization of Zeolite Supported Metal Particles 196
6.2. Hydrogen/Proton Transport 199
6.3. Electrooxidation of Small Spices 200
  6.3.1. Oxidation of Methanol 201
  6.3.2. Oxidation of Formic Acid 205
6.4. Conclusion and Future Directions 208
6.5. References 209
Chapter 1: Introduction

1.1 Electrode Modified Zeolites

Zeolite catalysts have been used in the petroleum industry for many years because of their catalytic activity and high selectivity for certain reaction. Recently, zeolites have become of interest in the electrochemical environment. Debra Rolison has published two excellent review articles on zeolite-modified electrodes and electrode modified zeolites [1, 2]. By the phrase zeolite modified electrodes she is referring to the situation where a conducting electrode surface is covered in a layer of zeolite material. Electrode modified zeolites describes the case where nanometer sized metal particles contained in the interior of the zeolite structure are used as electrodes. In this thesis the latter type of zeolite electrodes will be investigated.

Electrode modified zeolites have been of increased interest as the zeolite has particular chemical and physical characteristics which may influence the electrochemical reactions. They offer a crystallized structure with a great capacity for water and the ability to be completely hydrated and dehydrated without damage to the crystalline lattice [1]. Zeolites are dc electronic insulators and, therefore this cannot be used as direct electrode materials. However, they can act as an electron bank to contribute electrons to or garner electrons from a reactant [2, 3] in an electrochemical reaction. Aluminosilicate zeolites, such as the Y type zeolite used in this project, are ionic conductors. They are capable of solution – like ionic conduction [3]. This link in common with the electrochemical environment means that electrochemical reactions and the chemical and catalytic reactions of the aluminosilicate zeolites can occur in a charge – balanced ionic environment such as that found in electrochemical systems [1, 2].

The lack of dc electronic conduction of the zeolite causes some difficulty when trying to explain how electrochemical oxidation and reduction reactions may occur at metal particles trapped within the zeolite structure. The aim of this thesis is to investigate the electron transfer process at Pt and Pd particles supported on Y zeolite using electrochemical and X-ray absorption spectroscopic techniques, and thereby to
contribute to the understanding of how such processes can occur when the support is not conducting.

Rolison's approach to obtaining contact to the metal particles in the zeolite structure was to disperse the modified zeolite powder in an electrolyte solution of high ionic strength and to place this dispersion between two large feeder electrodes. The zeolite particles then were thought to act as microelectrodes [4, 5]. A complication of such dispersed electrodes is that the metal species may exchange out of the zeolite structure into the solution, thereby circumventing the problem of electronic conduction within the zeolite [1, 6]. In the work reported in this thesis electrodes were manufactured from Pt and Pd modified Y zeolites by mixing with carbon powder, which provided electronic conduction, and Nafion, which acted as a binding agent, similar to those prepared in polymer electrolyte membrane fuel cells. Thus, the metal particles were confined to the zeolite structure throughout the investigation.

1.2 The Nature of Zeolites

Zeolites, as heterogeneous catalysts, are widely used in commercially important reactions. Small quantities of zeolite occur naturally but a much larger amount can be synthesized on a commercial scale. They are manufactured by dispersing or imbedding the crystals in a matrix form. The general molecular formula of a zeolite can be expressed below [7]:

$$M_{p/n}(AlO_2)_p(SiO_2)_q \cdot yH_2O$$

In the formula, $n$ represents the charge number, while $p$ and $q$ describe the numbers of $[AlO_2]$ and $[SiO_2]$ respectively. $y$ represents the number of water molecule in the zeolite.

Natural and synthetic zeolite, for example, amorphous aluminosilicates are of practical importance as molecular sieves and catalysts. They are comprised of $[SiO_4]$ and $[AlO_4]$ tetrahedra interlinked together. The tetrahedron in a zeolite [8] is presented in figure
1.1. Each [AlO₄] tetrahedron has a negative charge, which is compensated using a charge-balancing cation (e.g., Na⁺ or H⁺), situated in the zeolite channel or cavity.

![Tetrahedral arrangement in zeolite](image)

Figure 1.1: tetrahedral arrangement in zeolite [8]

According to the different Si/Al ratios and different connecting forms, zeolites can be classified into types of X, Y, L, M, ZSM-5. Zeolite Y, which is used in this project, is a cage type with a channel. The formula of Y zeolite can be described as:

Na₅₆[Al₅₆Si₁₃₆O₃₅₄] • 264H₂O

The framework structure of Y-zeolite consists of sodalite cages that are interconnected via hexagonal prisms in a tetrahedral array as shown in figure 1.2 [9]. The large cavities in the zeolite are usually called the supercages, and they are interconnected forming the large channel that extends throughout the bulk of zeolites via rings that contain 12 numbered O atoms. This is a relatively large channel in a zeolite. The main channel is connected to the small channel system consisting of sodalite cages and hexagonal prisms via rings containing 6 numbered O atoms. Generally, the sodalite cage is also called the β cage. Both channels can contain an extra framework of metal cations. The proportion of metal cations in either channels or cages (supercage or sodalite cage or hexagonal prism) is dependent on the distribution of active sites in the zeolite. These active sites are formally named as Brønsted sites, and will be discussed further below. Conventional Brønsted sites are designated in figure 1.2 as I, II and III.
Figure 1.2: Framework structure of zeolite Y. There is two major channel systems. The large channel is formed from interconnecting supercages that extend throughout the bulk of zeolites; the small channel network comprises the sodalite cages and hexagonal prisms.[9]

There are 16 I sites either situated on the square face consisting of hexagonal cage on the external surface of zeolite or inside the hexagonal cage, and 32 II sites are either located on the hexagonal face consisting of sodalite cage or inside supercage. The rest of the III sites, approximately 8, are positioned on the square face located on the ring containing 12 numbered O atoms. The overall active sites in zeolite Y are up to 56. Nevertheless, the I site which is conventionally called a hexagonal prism is particularly stable for the exchanged metal ions when compared to the rest of active sites due to the high negative charge.

The catalytic performance of zeolites can be modified by pre-exchanging ions to give the desired cationic form [8] and calcinating at a certain temperature in order to lock the exchangeable metal ions into position to increase catalytic activity of zeolite. The versatile cation exchange nature of zeolites allows a great range of metal ions and complexes to be loaded on to zeolites. Amongst various metals, transition and noble metal ion exchanged zeolites, particularly platinum - exchanged zeolite have been found to be efficient for the catalytic reactions.

The Y zeolite has both Bronsted and Lewis acidic sites as depicted in figure 1.3 [8]. The negatively charged tetrahedral aluminium centers have strong bonds to hydrogen
ions. Hydrogen ions are associated with oxygen to form hydroxyl groups throughout the bulk of zeolite. Hence, the negatively charged sites are the active sites on the zeolite, and are also the classic Brønsted acid centers. The aluminium centers can be counterbalanced by charge-compensating mobile cations, i.e. sodium or platinum.

Figure 1.4 [3] shows a two-dimensional representation of the Al-O-Si linkages that create the framework structure of aluminosilicate zeolite. Figures 1.3 and 1.4, illustrate the overall structure of zeolite. The primary features are:

(i) The fixed anionic sites associated with Al atoms in the lattice require counterbalancing cations.

(ii) The presence of the terminating hydroxyl group.

![Diagram](image)

Figure 1.3: Nature of the acidic sites in zeolite and ion exchange [8].
1.3 Pt and Pd Particles Supported on Zeolites

Metal microstructures constrained within the supercages of zeolite can be varied in size from single atoms to particles on the order of 1-2 nm [4], forming clusters containing 10 to 25 atoms on average [10]. The surface area of a zeolite is primarily internal or intracrystalline. Consequently, only a small fraction of the metal is supported on the exterior of the zeolite [3, 4]. Although particles formed on the exterior are not constrained by the internal architecture of zeolite, they are still much smaller than the micrometer size [4, 11].

Platinum and Palladium are practically important elements in catalysts [12]. Generally, the catalytic activity of a Pt cluster or particle can be promoted during the reaction of interest after it is deposited on high surface area of Y zeolite. Various techniques are available to introduce the metals into zeolite, but most frequently used techniques are ion exchange and the incipient wetness impregnation methods. The ion exchange method introduces the desired cation into the specific active sites of the zeolite. Nevertheless, the impregnation method incorporates an equivalent number of cation
and anions into the zeolite structure at the same time. However, the ion exchange method is often preferred for zeolite-based catalysts [13].

The most commonly used Pt and Pd precursors for ion exchange are organometallic compounds. Because the metal zeolite catalysts prepared by this way usually exhibit a high dispersion due to the organic ligands that are removed rapidly at relatively low temperatures. Moreover, the effect of anions, which may poison Pt or Pd, such as chloride, can be eliminated via ion exchange, whereas these anions often remain if salt impregnation method is used during the catalyst preparation.

Generally, Pt(NH$_3$)$_4$(NO$_3$)$_2$ and Pd(NH$_3$)$_4$Cl$_4$ salts are used for metal catalyst preparation. The Pt(NH$_3$)$_4^{2+}$ and Pd(NH$_3$)$_4^{4+}$ ions are exchanged into the main channels and the supercages via an ion exchange step, whereas some of the Pt(NH$_3$)$_4^{2+}$ may be trapped on the external surface of the zeolite.

Highly dispersed metals can be obtained by calcination and reduction steps with oxygen and hydrogen, using a stoichiometric titration method in the gas phase under temperature control. The coordinating ligands can be removed by a suitable calcination step prior to reduction. This procedure is extremely important for metal/zeolite catalysts because this step may control the cation location and substantially affect the metal particle growth mechanism for the later reduction [13]. Thus, it is very important to define an optimum temperature for obtaining highly dispersed metal/zeolite catalysts.

When ammoniated ion precursors are used during the course of calcination step, a low heating rate and a high oxygen flow are favoured in order to obtain a homogenous distribution of metal on the zeolite. This can also prevent autoreduction of metal ions caused by ammonia ligands during the calcination step, as autoreduction may lead to a non-uniform distribution. For example, Exner et al. [14] found autoreduction phenomenon in their research work.

In general the reduction of Pt and Pd ions in the zeolite is carried out in flowing hydrogen after calcination. Ions located at different sites of the zeolite following the calcination step usually have different reducibilities due to the different structural
interactions between the zeolite and the Pt or Pd ions and differences in the accessibility of hydrogen. Pt and Pd ions in hexagonal prisms appear to be most difficult to reduce. This may be attributed to the fact that the kinetic diameter of the hydrogen molecule is larger than the 2.2 Å windows of hexagonal prisms. Consequently, the hydrogen hardly has access to these hidden sites. In addition, the zeolite structure may change after the calcination step, if dealumination occurs. This may severely affect the Pt reduction due to the loss of active sites on the zeolite structure.

A high degree of metal dispersion may be achieved in the presence of zeolitic protons or auxiliary metal ions, such as iron ions. These ions can act as chemical anchors for reduced Pt and Pd atoms or particles, and contribute to diminished sintering of the metal particles at relatively high temperatures. Metal loading and catalyst preparation conditions are very important. For example the presence of anchors [13], solution pH and ramp rate of temperature during the calcination step all have an effect on the particle size distribution. Some of these effects are briefly reviewed below.

Fe$^{2+}$ ions primarily ion exchanged into the zeolite cages can be calcined to Fe$^{3+}$ ions. The Fe$^{3+}$ ion has a high charge density, and it is favourable for this species to remain in the hexagonal prisms. Fe$^{2+}$ ions obtained after reduction are more likely to remain in the supercages and sodalite cages. The strong interaction of Fe$^{2+}$ with Pt prevents the sintering of Pt. Consequently a high dispersion of Pt on the zeolite and small particle sizes are obtained. This is demonstrated by our work with the use of X-ray adsorption spectroscopy, in particular with the use of in-situ and ex-situ extended X-ray adsorption fine structure (EXAFS). The catalytic performances of these catalysts in electrochemical environment are determined by using cyclic voltammetry (CV) technique.

Dalla Betta and Boudart [15] investigated the situation using different pre-treatment methods and pointed out the importance of pre-treatment condition for obtaining the highest platinum dispersion. They concluded that well – defined pre-treatment conditions of Pt – Y zeolite were required to obtain a homogeneous platinum dispersion and reproducible results. Hence, thermal treatments become one of most important stages in order to get higher dispersion and smaller platinum particle sizes.
Gallezot et al. [16] used Pt(NH₃)₄Cl₂ to exchange with Y – zeolite and found that thermal activation for removing H₂O and NH₃ molecules was a critical step, in particular when heavily metal loaded zeolites and/or large sample quantities were treated, as reduction and subsequent sintering of platinum is liable to occur. Higher water content in the inert gas, such as Ar and He, may also destroy the zeolite lattice, and thus, facilitate growth of larger particles [13]. The physisorbed water can be removed at 250 °C. The tetrammine complex also starts to be destroyed at 250 °C, and its destruction is completed at 300 °C to 360 °C.

Gallezot et al. [16] also investigated the Pt calcinations and reduction under different temperature ranges and found that most of the Pt was located in the supercages at 300 °C. Platinum agglomerates fitting into supercages between 6 – 13 Å were formed on reducing at 300 °C, and remained stable up to 800 °C. On the contrary to the situation at 300 °C, most of Pt ions were found in the sodalite cages at 600 °C or above. A certain amount of Pt was encapsulated within the zeolite pore structure. They also found that hydrogen chemisorption and the stoichiometry of the titration were critical steps for very small particles.

Rolison et al. [4] investigated the catalytic effect of different thermal treatments on the particle size using XPS. It was apparent that Pt was strewn through the zeolite with flowing oxygen at 600 °C or above, and even migrated into the smaller sodalite cages. The particle size approached 2 nm on zeolite crystals with flowing hydrogen at 300 °C. Callezot et al. [16] also found that Pt particles remained in the supercages with oxygen at 300 °C, and formed 0.6 – 1.3 nm particles after reduction at 300 °C [17]. The results demonstrate that platinum particles are within the zeolite framework, and the location critically depends on the pre-treatment condition.

The calcination temperature is crucial for the location of Pt on the zeolite. Pt ions are mostly located in the supercage cages when metal ions are calcined at 350 °C and 400 °C, whereas half the Pt ions could migrate to sodalite cages if the calcination temperature is raised to 450 °C or above [18]. Consequently, a higher temperature is required to reduce the proportion of the metal ions located in the small cages as compared to those of metal ions located in the supercages. After calcination the Pt ions
are more stable in the sodalite cages, and in particular in the hexagonal prisms due to their higher negative charge density. However, the ammonia ligands can be completely removed from the Pt in the supercages at 300 °C or above. This is in contrast to the catalyst prepared with the Pd ammonia compound.

As reported from the paper by Homeyer and Sachtler [13, 19], it is apparent that complete ammonia ligand removal leaves the Pd ion in the sodalite cages. Calcination at 250 °C results in cis-diammine Pd ions. These ions remain in the supercages. After calcination at a temperature above 300 °C, the migration of Pd ion, which is coordinated to one or two ammonia ligands into sodalite cages, occurs. The third ammonia ligand is oxidized at 340 °C, and a complete removal of fourth-coordinated ammonia ligand happens at 400 °C. When calcination is raised up to 500 °C, some of Pd ions are found to occupy the hexagonal prisms.

The location of the Pd ions depends on the reduction temperature. As the reduction temperature is increased, Pd atoms may migrate from the sodalite cages back to the supercages, and form multi-atomic particles [20]. Homeyer and Sachtler have reported that the majority of Pd is released from sodalite cages to supercages at 350 °C via hydrogen reduction [19], and reduction temperature greater than 350 °C is required to cause the Pd atoms to migrate from the hexagonal prisms to the supercages. The Pd particle size in the sodalite cages or hexagonal prisms is small, as it is defined according to the aperture of cage. However, these small particles can act as nucleation sites to form new particles whose size is still smaller than the dimension of supercages, and thus, further increase the metal dispersion on the zeolite.

In contrast to Pd, Pt ions are much more stable in the small cages, even under high reduction temperatures at 500 °C. As presumed by Sachtler [13], the reason the Pt atoms are less mobile than Pd atoms in migrating out of the sodalite cages is caused by the larger size of Pt in combination with its higher polarizability because of the d electron configuration.

Sachtler and co-workers [18, 21] indicate that the Pt and Pd particle sizes obtained from ion-exchanged catalysts are fairly uniform, and the particles are highly dispersed.
throughout the zeolite crystallite. However, the calcination and reduction temperatures are very important.

1.3.1 Spillover of Hydrogen on the Pt surface

Pt has been demonstrated to be the best catalyst for a variety of electrochemical reaction in the acid electrolyte solution. Conventionally, Pt was dispersed on the high surface area support. This leads to the formation of small Pt particle size and creates a highly-utilised catalyst surface area. However, the adsorptive and electrochemical properties of supported catalysts are different from those of the individual components due to the strong interaction of metal – support in the supported catalyst system [22]. It has reported that the phenomenon of hydrogen spillover was discovered on the Pt/C, Pt/SiO₂ and Pt/Al₂O₃ catalyst system. During the spillover process, species, such as H⁺ ion, adsorbed on the Pt active surface can diffuse onto the surface of the inert support. The research [22, 23] done by other group has shown that spillover hydrogen is very important for catalysis of electrochemical reactions with the use of these catalysts.

Spillover is a phenomenon associated with transport of an active species from one site to another [24]. Spillover hydrogen has been found in the Pt/zeolite catalyst system in gas phase. The research work done by Fujimoto [24] has revealed that spillover hydrogen could occur from Pt sites to zeolite acidic site (Brønsted and Lewis). The spillover hydrogen on the Pt/Yzeolite electrode in the electrochemical environment has not been investigated substantially. We presume that the principle of spillover hydrogen for the Pt/zeolite catalyst system in the liquid phase is similar to those found for the catalysts in the gas phase and in the Pt/C Pt/SiO₂ and Pt/Al₂O₃ catalyst system.

1.4 Extended X-Ray Absorption Fine Structure and Metal Particles on Zeolites

Extended X-ray adsorption fine structure (EXAFS) is a unique technique for probing the structure of materials. It permits the in situ study of heterogeneous electrocatalysts [25] because X-rays can penetrate pressurised environments and liquid electrolytes. This technique specifically probes short-range order because the free path of an
electron is very short (< 5 Å). EXAFS can provide information, such as coordination numbers, bond distances and the chemical identity of nearest neighbours. It is ideal for structural studies of ions in solution and poorly crystallized materials used as electrocatalysts and heterogeneous catalysts. In addition, the electronic properties of highly dispersed metal particles on a variety of supports can be determined by using this method. The details of the method will be described in chapter 2.

EXAFS has proved to be very useful in characterising Pt/zeolite catalysts. The following represents a brief review of the literature. Byannov et al. [10] discovered that the disorder of Pt within the framework of zeolite had a dramatic effect on the electronic structure of Pt. They also found that acidity of the zeolite framework has an effect on the X-ray absorption white line, but increasing acidity of the zeolite framework results in no measurable systematic effects on the spatial structure of the clusters. Their work suggests that the Pt clusters on the zeolite might undergo a metal – insulator transition at temperature below 80 K [26].

Yokoyama et al.[27] have shown that the Pt-Pt bond distance of the platinum cluster encaged in the supercages of the zeolite was found to be shorter than that of the bulk metal. They concluded that the charge transfer from the Pt clusters to the substrate was stronger in Pt/Na Y than other Pt catalyst, such as Pt/SiO₂, and Pt cluster in the Na Y zeolite was more cationic than those on the SiO₂-support. They explained that the contraction of Pt-Pt bond distance in the zeolite supported Pt was due to the increase of Pt-Pt bonding energy caused by electron deficiency. Generally, thermal disorder is associated with metal particle dispersion and the particle size, and the thermal disorder value increases as the Pt particle size increases. However, in their study they found that the small disorder value obtained was due to the increase of the Pt-Pt bonding energy.

Pandya et al [28] investigated the Pt particle size at different reduction temperature by using EXAFS technique. The results have shown that the Pt particle size was small, approximately 11.3 Å and an average number of 20 to 30 atoms per particle was obtained when the Pt/Y zeolite was reduced at 300 °C. They suggested that such particles were able to reside in the supercages, and there was no metal support interaction to be observed, as the crystallinity was lost as indicated by XRD. Furthermore, they claimed that the particle size was increased to 16 Å upon the
increase of reduction temperature to 500 °C. Thus, the Pt particle size formed at 500 °C (high reduction temperature) was larger than those observed at the low reduction temperature (300 °C).

The research work done by Koningsberger et al. [29] with the use of EXAFS technique has shown that the metal particles in Pt/Na Y catalysts were small with first Pt-Pt co-ordination numbers around 5.5, and the average metal particle size was approximately 15 atoms. Moreover, they suggested that Pt-Pt distance of 2.75 Å was characteristic of metallic Pt. With the use of the EXAFS technique, they studied the phenomenon of hydrogen chemisorption on the Pt surface and found that a longer Pt-H bond was associated to the weaker chemisorbed hydrogen. By further investigation into the metal zeolite structural interaction, they concluded that the zeolite oxygen atom had a significant effect on the charge transfer. Increasing electronegativity of the nearby support oxygen atoms lead to increase zeolite alkalinity. Consequently, the change in electronegativity of the support oxygen atoms can result in a charge transfer from or to the metal particles. This particularly accounted for the PtHY zeolite catalyst, as H⁺ ions exchanged into zeolite structure may result in an increase in the O, Si and Al binding energy.

1.5 Thesis Plan

As stated at the beginning of this introduction, the aim of the work presented in this thesis is to contribute to the understanding of how electron transfer reactions can occur at small metal particles supported on zeolites under electrochemical control. To accomplish this Pt and Pd modified zeolites were prepared and electrodes were manufactured from these materials. The preparation methods and electrode manufacturing techniques are described in Chapter 2. Also described in Chapter 2 are the other experimental methods employed in this study. The structure of the Pt particles supported on and in Y zeolite was investigated using X-ray absorption spectroscopy for both the as prepared and chemically reduced, reduced under flowing hydrogen, materials, as well as XRD and BET measurements. This structural investigation is presented in Chapter 3. The results of the structural investigation are compared with those obtained in an electrochemical environment in Chapter 4. Also in Chapter 4 the electrochemical responses of a variety of Pt modified Y zeolite materials
are presented. In Chapter 5 the Pd on Y zeolite system is investigated. Comparison of the Pt and Pd systems enables the influence of the location of the supported metal particles in (or on) the zeolite structure on the electrochemical behaviour to be determined. Chapter 6 contains the general conclusions of the thesis as well as a preliminary investigation of the oxidation of small organic molecules using Pt on Y zeolite electrode materials.
1.6 References


Chapter 2: Experimental Methods and Techniques

2.1 Catalyst Preparation

The materials used in the experiments are listed in the table below.

<table>
<thead>
<tr>
<th>Chemical Reagents</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Y zeolite</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetraammine platinum (II) nitrate</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Ammonium nitrate 98 wt.%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Ammonium tetrachloropalladate(II) Permian, 99.998% (metals basis)</td>
<td>Alfa</td>
</tr>
<tr>
<td>Nafion® Perfluorinated Ion-Exchange resin</td>
<td>Aldrich</td>
</tr>
<tr>
<td>5 wt.% solution in Aliphatic Alcohols and H2O</td>
<td>Aldrich</td>
</tr>
<tr>
<td>0.1 N silver nitrate solution in water. The solution is in ASTM reagent grade.</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Iron (II) Sulphate</td>
<td>Alfa</td>
</tr>
<tr>
<td>Toray Carbon Paper THPH-090</td>
<td>E-TEK Inc.</td>
</tr>
<tr>
<td>20 wt.% Wet Proofed</td>
<td></td>
</tr>
<tr>
<td>XC-72R inactivated</td>
<td>Johnson Matthey</td>
</tr>
</tbody>
</table>

Water purified by a Barnstead system and high purity concentrated sulphuric acid (98.99%) were used to prepare the electrolyte solution, 2.5 mol dm$^{-3}$ H$_2$SO$_4$. Deaeration of the solution was carried out by bubbling high purity nitrogen (>99.9%) through the electrolyte solution.
2.1.1 Metal/Zeolite Ion-Exchange

2.1.1.1 The Ion-Exchange Procedure

(a) Platinum Salt/Zeolite Ion-Exchange

Various techniques are available for the preparation of metal loaded zeolite catalysts. In general, the ion exchange and impregnation methods are often used. However, the former method is preferred to introduce the metal ions into zeolite. [1, 2]

The ion exchange method of platinum with sodium Y zeolite followed the procedure developed by many researchers, such as, Boyan [3]and Lalchan [4].

In this project, 1.5 wt.% or 5 wt.% Pt loading on zeolite was made using two different forms of platinum salt, either Pt(NH₃)₄(NO₃)₂ and Pt(NH₃)₄Cl₂, or Pt(NH₃)₄(NO₃)₂/NH₄NO₃ and Pt(NH₃)₄Cl₂/NH₄NO₃. For simplicity, we have given each ion exchange condition an acronym. Exchange with Pt(NH₃)₄(NO₃)₂ is named as PtAN, with Pt(NH₃)₄(NO₃)₂ and excess NH₄NO₃ is PtANX, and with Pt(NH₃)₄Cl₂ is PtACl. The ion exchange procedure was similar in all cases. For most of the ion exchanges the pH of the solution was neutral. The exchange with PtAN to give 1.5 wt.% Pt loading is described below as an example.

An appropriate quantity of Pt(NH₃)₄(NO₃)₂ was dissolved in about 200 ml of triply distilled water at 0.004 mol dm⁻³, and was agitated in ultrasonic bath for 20 minutes. The sodium Y (Na Y) zeolite powder was dispersed in 1 dm³ of triply distilled water in a water-jacketed reactor. Meanwhile, the platinum solution was added slowly by pumping the dilute platinum salt solution at 0.1 ml/min into the vessel containing the Na Y zeolite slurry (1 g/100 ml). The temperature of the ion-exchange solution was maintained at 70 °C by using a water pump with heater. The hot water was pumped through the water jacket of the reactor continuously. The suspension was stirred for several hours up to several days. The time was dependent on whether platinum exchange was complete as determined by UV spectroscopy. The sample was filtered, and washed with copious amounts of triply distilled water. The washed sample was repeatedly re-suspended in water, stirred, and filtered until the filtrate was free of the [Pt(NH₃)₄]²⁺ complex. This can be verified by loss of the [Pt(NH₃)₄]²⁺ adsorption peak.
at 290 nm in the UV spectrum [4]. Finally, the sample was placed in an oven overnight at 110 to 120 °C.

In the case of the PtANX ion exchange with zeolite, excess NH₄NO₃ was added to the suspended zeolite to provide a NH₄NO₃ concentration of 0.063 mol dm⁻³ prior to the addition of the Pt salt.

(b) Pd Salt/Zeolite Ion Exchange

Samples containing 1.5 wt.% Pd loading on Y zeolite were also made using the ion exchange method. The ion exchange procedure was identical to that described for the platinum zeolite exchanges above. The ion exchange was carried out in the neutral condition, around pH 7. The Pd salt used was Pd(NH₄)₄Cl₄. Attention must be paid to this ion exchange process, as we know that chloride is a potent poison to many electrochemical reactions. After exchange, the sample was washed with a sufficient amount of water until the filtrate was free of Cl⁻ ions. The presence of Cl⁻ ions was monitored using 1N AgNO₃ solution. AgNO₃ was added dropwise to the filtrate, forming a white precipitate when Cl⁻ was present. An experimental diagram set up for the ion exchange is shown in figure 2.1.
As mentioned previously, most of the Pt zeolite samples were exchanged in the neutral condition, pH=7, accompanied by washing with copious amounts of purified water. The Fe/zeolite exchange was conducted under acidic conditions, 2.5 mol dm$^{-3}$ H$_2$SO$_4$ was added dropwise to the exchange solution to adjust the pH to 3.8. Subsequently, the zeolite was dispersed in the solution, and stirred constantly. After the temperature of the exchange solution had reached 70 °C, the iron salt (0.051 mol dm$^{-3}$) was added dropwise at 0.1 ml/min. The exchange was carried out for at least 24 hours. After the ion exchange was finished, the sample was washed with copious amounts of purified water to remove SO$_4^{2-}$ ions and any remaining H$^{+}$ ions. The sample was dried overnight in the oven at 110 °C.

The iron-exchanged zeolite sample was then divided into two groups. One group, which was named FeNYZ, was re-suspended in 1 dm$^3$ purified water for exchange with Pt(NH$_3$)$_4$(NO$_3$)$_2$ directly. The second sample, named FeNYZSE, was first calcined and
reduced at 550 °C and subsequently ion-exchanged with Pt(NH₃)₄(NO₃)₂ salt. The ion-exchange process and conditions of the Pt nitrate salt with FeNYZ or FeNYZSE were identical to those for Pt zeolite exchange. After calcination and reduction, the two samples were re-named as PtFeAN and PtFeSEAN, respectively.

(d) Pt Salt – Zeolite Impregnation

The Pt salt impregnation procedure was carried out according to the Mitchell method[1, 2, 5]. The method used in this study is simple and fast. Firstly, a sufficient quantity of Pt(NH₃)₄(NO₃)₂ equivalent to 1.5 wt.% Pt loading on Na Y zeolite was dissolved in purified water. The water volume was controlled such that the catalyst was just immersed under water. This mixture was left overnight until incipient wetness was achieved and the sample was dried in the oven at 110 °C for 10 hours. Finally, the sample was calcined at 350 °C and reduced at 400 °C. The impregnation method should have left a shell distribution of Pt on zeolite, as shown in figure 2.2.

![Pt distribution on Na Y zeolite following impregnation](image)

Figure 2.2: Pt distribution on Na Y zeolite following impregnation

2.1.1.2 The Theory of Metal/Zeolite Ion-Exchange

(a) NH₄⁺/Na Y Zeolite Ion-Exchange

The zeolite structures and their nature have been introduced in chapter one. Their catalytic behaviour can be modified using many techniques, such as, ion exchange or impregnation. However, the mechanisms of ion replacement on the structure are identical for all techniques. In this section, the mechanism of the ion exchange process is described. In the excess nitrate ion-exchange method, Pt(NH₃)₄(NO₃)₂/NH₄NO₃, NH₄⁺ ions diffuse into the channel to exchange with sodium ions. They have an affinity with the negative charges situated on the alumina tetrahedra. The NH₄⁺ is decomposed to evolve NH₃ when the sample is heated to 300 °C and above, and H⁺ sites on the zeolite, which are academically named as
Brønsted acidic sites, are generated. This is a reversible reaction. The detailed procedure is shown in figure 2.3 [6].

![Figure 2.3: NH₄⁺/Na Y Zeolite ion exchange](image)

H⁺ sites interact with the oxygen associated with the alumina–silica framework to form hydroxyl groups. H⁺ sites and hydroxyl groups are very important in later thermal treatments, such as, calcination and reduction process. These ions influence the metal particle size, electronic properties, loading on the zeolite, and, thus, the catalytic performance as demonstrated in the literature [7, 8, 9, 10]. It was discovered that ions, for example, H⁺ and hydroxyl, could assist in anchoring the reduced metal particles to the cage walls of the zeolite, thus preventing migration of the metal ions into the sodalite cages and hexagonal prisms. Finally, the metals are highly dispersed on the zeolite surface or within the supercages.
(b) $\text{Pt}^{2+}$ and $\text{Pd}^{4+}$/Zeolite Ion Exchange

The general route of Pt$^{2+}$ zeolite ion exchange is the same as that for the NH$_4^+$ exchange described previously. Figure 2.4 shows a route of platinum–zeolite exchange[11].

After ion-exchange, one Pt$^{2+}$ replaces two Na$^+$ ions to interact with two negative charges sited on two [AlO$_4$]$^-$ ions separately, and the Pt$^{2+}$ ion bridges two of the [AlO$_4$]$^-$ sites as shown in the diagram.

The route of Pd$^{4+}$ zeolite exchange is similar to that of Pt$^{2+}$, and is shown in figure 2.5.
Ion exchange with the zeolite using certain metals, for example, Co, Ni, Ca, or Fe prior to the introduction of Pt/Pd ions is particularly useful in determining the exchange sites that will be occupied by the noble/metal ions. The metal ions can block the hexagonal prisms and sodalite cages to prevent migration of the noble metal ions through the channels [7, 12] and also helps to assist the reduction of metals less easily reduced. It is very important to have zeolitic protons present on the cages, especially in the supercages because of the structure of zeolite. The blockage of sodalite cages and hexagonal prisms by a suitable metal can force protons to stay in the supercages. As explained above, the protons act as chemical anchors for the reduced Pt or Pd. Hence, highly dispersed Pt or Pd samples can be obtained by a pre-exchange with another metal in which most of the Pt or Pd ions remain in the supercages.

In this project, Fe$^{2+}$ was chosen to block the small cages because it has a highly positive charge density. Hence, it binds strongly to these sites. According to the studies done previously [7, 8, 9, 10], Fe$^{2+}$ ions not only block the hidden sites and small cages, but also assist in anchoring the reduced metal particles to the zeolite cage walls. This behaviour is similar to that of H$^+$ ions.

The ion exchange of Fe$^{2+}$ should be conducted in acidic solution (pH=3.8 in this experiment) to prevent the hydrolysis of iron, which could lead to blockage of the supercages. However, the heating rate and temperature during the calcination and reduction steps must also be controlled carefully to assist the migration of blocking ions to the small cages.

The exchange process involves an ion exchange step (1) and a migration step (2) as follows:

\[
[\text{Fe(H}_2\text{O)}]^2+ + \text{Na}_{\text{SUP}}\text{Na}_{\text{SH}} Y \rightarrow 2\text{Na}^+ + \text{Fe(H}_2\text{O)}_{\text{SUP}}\text{Na}_{\text{SH}} Y \quad (2.1.1.2.1)
\]

\[
\text{Fe(H}_2\text{O)}_{\text{SUP}}\text{Na}_{\text{SH}} Y \rightarrow \text{Na}_{\text{SUP}}\text{Fe}_{\text{SH}} Y + \text{H}_2\text{O} \quad (2.1.1.2.2)
\]

where, [Fe(H$2$O)]$^{2+}$ is the solvated ion in solution, SUP represents the supercages, and SH represents the sodalite cages and hexagonal prisms.
The Pt\(^{2+}\) ion exchange procedure was carried out following the Fe\(^{2+}\) ion exchange, as described in section 2.1.1.1 (c). The product of this exchange method mostly consists of Pt sited in the supercages. The quantities of Fe\(^{2+}\) and Pt\(^{2+}\) adding during the ion exchange were calculated according to the molecular formula of the Na Y zeolite, and the number of Al\(^+\) sites.

2.1.2 Calcination and Reduction

The calcination and reduction steps involve the removal of Pt co-ordinating ligands and are crucial in the formation of the Pt or Pd particle structure, size and dispersion on the zeolite substrate [13, 14, 15].

In this project, the calcination and reduction procedures developed by Gallezot and co-workers [13] for the synthesis of platinum microstructures in Na Y zeolite, are followed and are described below.

2.1.2.1 The Fluidised Bed Reactor

The calcination and reduction was performed in a fluidised bed reactor, which was installed in a vertical tube furnace, a schematic of which is shown in figure 2.6.

The reactor can be described in three parts: the reactor bed, gas feeds, and the gas vent. The reactor bed is a 10 \(\mu\)m pore glass frit and is situated at the heart of the reactor. Samples were placed on the bed to be calcined by O\(_2\) or reduced by H\(_2\). The gas feeders were separated into two parts. One part was connected to the bottom tube of the reactor to provide the maximum contact of the Pt zeolite catalyst with various gases. The other was connected to one of the side tubes at the top of reactor, which is named an insert rig. This design allows heat loss and hence, controls the reactor temperature. The gas mixture passes through the sample on the fluidised bed and flows out of the vent line on the top of the insert rig to the waste gas exhaust line. The reactor material can endure a maximum temperature of around 1000 °C.
2.1.2.2 Calcination

2 g of the ion-exchanged zeolite were placed in the reactor to cover the bed, and the reactor was installed in the furnace vertically. Firstly, the inert gas argon was introduced into the reactor from the bottom gas line. The flow rate of argon was controlled at 250 ml/min. Meanwhile, the furnace was heated to 150 °C at 1 °C/min., and left at this temperature overnight under flowing argon. Subsequently, the reactor was cooled down to room temperature whilst the argon flow was maintained. The water absorbed on the Pt ion-exchanged samples was removed following this procedure. The next step was to introduce O₂ into the reactor and heat the sample to a specific temperature. It should be emphasised that the heating rate and temperature used to decompose the ammoniated ion precursor, such as [Pt(NH₃)₄]²⁺ or [Pd(NH₄)₄]⁴⁺ in the calcination period, are extremely important for the later reduction procedures, because Pt²⁺ or Pd⁴⁺ ions, which were initially exchanged to the main channel system
in the supercage, can be mobile to the small channel systems and cages during the calcination period. From the theory, ammonia ligands, attached to the Pt, start to be destroyed at 250 °C [13], and physically adsorbed water on the zeolite is completely removed at this temperature. When the temperature reached 350 °C, a complete oxidation phenomenon of the amine ligands occurs. This can be identified by the change in colour from off white to dark grey, which indicates the presence of Pt oxide particles in the supercages of zeolite. Therefore, a slow heating rate and a suitable calcination temperature are necessary for obtaining a fine Pt particle size and a better dispersion on its support. For the Pt samples, a slow heating rate of 0.3 °C/min with a mild O2 flow of 200 ml/min was used. The temperature was increased to 350 °C and maintained for 2 hours. A calcination temperature of 350 °C was chosen because of concern that Pt could move into the small cages at higher temperatures. At the same time, physisorbed water can be removed completely from the zeolite structure at this calcination temperature [16].

Finally, the samples were cooled down to room temperature under flowing argon in preparation for the reduction procedure. The reduction reaction was carried out with the 5%H2/95%N2 gas mixture and is described in detail in section 2.1.2.3

There are several reasons for choosing this calcination procedure. Firstly, the use of an inert medium, such as argon for the sample purge, provides good dehydration. It is important to reduce the relatively high water content existing in the zeolite framework to prevent formation of polynuclear platinum amine complexes, which is caused by the interaction of Pt(NH3)4(OH)2 with OH groups formed on zeolite. This process would favour the undesirable lattice–fragmentation reaction according to the formula shown as follows [6]:

\[
\begin{align*}
\left[ \text{Na}^+ \rightarrow \text{Al-O-Si} \right] + 2 \text{H}_2 \text{O} & \leftrightarrow \left[ \text{H}_3 \text{O}^+ \rightarrow \text{Al-O-Si} \right] + \text{NaOH} \\
\text{H}_3 \text{O}^+ \rightarrow \text{Al-O-Si} & \leftrightarrow \left[ \text{Al-O-Si} \right] + \text{H}_2 \text{O}
\end{align*}
\]

(2.1.2.2.1)

(2.1.2.2.2)
\[
\begin{align*}
\text{Pt(NH}_3\text{)}_4\text{(NO}_3\text{)}_2 + 2\text{NaOH} & \rightarrow \text{Pt(NH}_3\text{)}_4(\text{OH})_2 + 2\text{NaNO}_3 \\
\text{(2.1.2.2.3)} \\
\text{Pt(NH}_3\text{)}_4(\text{OH})_2 + \text{HO-}\text{Si} & \rightarrow \text{Pt(NH}_3\text{)}_4\text{Si(OH)}_2 + \text{H}_2\text{O} + \text{OH}^- \\
\text{(2.1.2.2.4)}
\end{align*}
\]

As reported by Exner et al [17], relatively high water content in the zeolite framework favours the lattice fragmentation reaction according to reaction formula (2.1.2.2.5). This procedure will facilitate the growth of big metal particles exceeding the size of supercages.

\[
\begin{align*}
\text{(SiO — Al} & + 5\text{H}^+ + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 8(\text{SiOH}) \\
\text{(2.1.2.2.5)}
\end{align*}
\]

The formula above shows that water adsorbed on the zeolite can act as acidic sites to interact with oxygen on the zeolitic framework, and form OH groups, which contribute to formation of the undesired phenomenon.

Secondly, the procedure enables the prevention of autoreduction of the metal ions by the ammonia ligands [14, 17]. Autoreduction may cause a nonuniform distribution of particles on the zeolite and produce large metal particles as previously reported [17, 18, 19, 20]. As a result of the autoreduction, protons are formed inside the zeolite cages in addition to the metal particles. This creates an uncontrolled reduction atmosphere inside the zeolite cages during the calcination step [20].

In the absence of autoreduction, divalent Pt will produce PtO after calcination with O\(_2\) by the following mechanism:

\[
\begin{align*}
\text{[Pt(NH}_3\text{)}_4]^{2+} & \rightarrow \text{Pt}^{2+} + 4\text{NH}_3 \text{ (gas)} \\
\text{(2.1.2.2.6)} \\
2\text{Pt}^{2+} + \text{O}_2 \text{ (gas)} & \rightarrow 2\text{PtO} \\
\text{(2.1.2.2.7)}
\end{align*}
\]

Autoreduction can change the Pt oxidation state dramatically. The originally divalent ion [Pt(NH\(_3\))\(_4\)]\(^{2+}\) may be partially reduced to Pt\(^0\) before being oxidized to PtO\(_2\) with tetravalent Pt\(^{4+}\) rather than the desired divalent species. This oxidation state requires a higher temperature for the later reduction and high reduction temperatures may induce
migration of Pt into small cages. Consequently, the activation energy of reduction is even higher for the isolated Pt ions inside the sodalite cages or hexagonal prisms. Eventually, this could lead to a decrease in the zeolite pore size or damage to its structure.

In contrast to Pt atoms or particles, which appear to be less mobile in comparison to other metals, Pd appears to be much more sensitive to its calcination temperature. Hence, the calcination temperature was varied to investigate the mobility of Pd within the zeolite framework. Samples were prepared at 250 °C, 300 °C and 400 °C. Homeyer and Sachtler [21] determined that the ammonia ligands attached to Pd start to decompose at 250 °C and were completely decomposed by 400°C. The Pd calcined at over 300 °C can migrate through the channel from the supercages to the sodalite cages or hexagonal prisms, and can return to the supercages depending on the reduction temperature. In this case, the incompletely decomposed Pd particles in the supercage can’t break out the windows of 2.2 Å (between the supercage and the sodalite cages), and therefore can’t move to the sodalite cages and hexagonal prisms because of the large particle size achieved under 300 °C during the calcination period. Generally, the Pd ions remain in the supercages at temperatures below 300 °C [20]. The phenomenon of Pd migration from supercages to sodalite cages begins at 300 °C, following the complete removal of the ammonia ligands. Surprisingly, the Pd become mobile from sodalite cages, and even from hexagonal prisms, to the supercages, once again, when the reduction temperature is between 350 °C to 400 °C. This phenomenon is very different from that of Pt according to the literature [20]. A Pt particle can remain immobile and stable in the hexagonal prism when the calcination and reduction temperature reaches 500 °C.

2.1.2.3 Reduction

(a) Reduction

The reduction steps either followed the calcination step or direct reduction of the sample, in which no calcination process was involved.
In both cases, the sample was heated in the reactor to the reduction temperature at a rate of 5 °C/min with a gentle flow of 5%H₂/95%N₂ gas mixture at 1L/min and this temperature was maintained for 12 hours. The sample was cooled to room temperature under flowing argon before being transferred to a sealed glass container to minimise re-oxidation of the catalyst.

The reduction temperatures chosen for the Pt samples in this project were 300 °C, 400°C, and 500 °C. The temperature was varied to investigate the Pt distribution on the zeolite. Bergeret, Gallezot and Kleine [22, 23] discovered using TEM techniques that the reduction step could cause agglomeration of the Pt or Pd atoms in the supercages depending on the temperature. These particles will extend over several cages at higher temperatures.

The Pt ions will mostly be trapped in the sodalite cages or hexagonal prisms at temperatures of 500 °C and above. Hence, it is difficult for the Pt ions to migrate back into the supercages or to reduce isolated Pt atoms that remain in the sodalite cages unless very high temperatures are used. The formula for Pt reduction is as follows:

$$\text{PtO} + \text{H}_2 \text{(gas)} \rightarrow \text{Pt} + \text{H}_2\text{O}$$  \hspace{1cm} (2.1.2.3.1)

Attention should be paid to the reoxidation of Pt atoms by the protons in the same cages. Sachtler [24] and Tzou et al [20, 25] have observed this phenomenon for Pt/Na Y at 400 °C. The protons oxidised the Pt atoms to Pt ions and formed hydrogen gas.

$$\text{Pt}^0 + 2\text{H}^+ \rightarrow \text{Pt}^{2+} + \text{H}_2 \text{(gas)}$$  \hspace{1cm} (2.1.2.3.2)

Homeyer and Sachtler [20, 24, 26] have also reviewed the mechanism of metal particle formation on zeolite Y during H₂ reduction. They found that the location and particle sizes of Pt or Pd were mainly dependent on the calcination procedure. During the calcination step, the oxidation of the amine and ammonium ligands in [Pt(NH₃)₄]²⁺ or [Pd(NH₄)₄]⁴⁺ leads to a significant migration of Pt or Pd between the cages.

For the Pd reduction experiment, 360 °C was chosen as the reduction temperature for all of the samples. Zhang et al [12, 20, 27, 28] found that the zeolitic protons are an important factor for obtaining a high degree of metal dispersion. They indicated that the presence of zeolitic protons could act as chemical anchors for the reduced Pd atoms or particles. Ideally, the ammonium ligands attached to Pd are decomposed between
250 °C and 300 °C. Unfortunately, this is not always the case. On occasion, the ammonium ligands are only partially decomposed during the calcination stage. The remaining ammonium ligands released during the reduction process could neutralize the acidic sites. Thus, this phenomenon may prevent those protons from acting as chemical anchors, thereby contributing to a lower degree of metal dispersion. However, the Pd dispersion initially formed on the zeolite and its mobility still depends on the calcination temperature. This variable was explored by varying both the calcination and reduction temperatures.

(b) Direct Reduction

The direct reduction reaction was also carried out in the fluidised bed reactor. Initially, the samples were heated to 150 °C in argon following at 250 ml/min, and held at that temperature overnight under argon purge with same flow rate. The reactor was cooled to room temperature, and the samples were heated to 400 °C under mixed gas, such as, 5%H₂/95%N₂ flowing at 11/min. Once the temperature reached 400 °C, the samples were held at that temperature for a further twelve hours under the 5%H₂/95%N₂ gas flow. Finally, the reactor was cooled to room temperature under flowing argon. The samples were collected into sealed glass containers for later use.

Several research groups have shown [7, 20, 21, 23] that Pt atoms have less mobility to migrate out of the sodalite cages to supercages in comparison to Pd during the calcination and reduction period. They concluded that this might be caused by the large size of Pt in combination with its higher polarisablity due to the d electron configuration. They also indicated that this could lead to an increased interaction between the metal and proton.

2.1.2.4 List of sample acronyms

The composition and preparations of powder samples are given in table 2.1. Using these powders, electrodes were prepared for cyclic voltammetry.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation Method</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain carbon: XC-72R</td>
<td>As Received (Johnson Matthey)</td>
<td>XC-72R</td>
</tr>
<tr>
<td>Plain zeolite: Na-Y Al_{56}Si_{138}O_{380} \cdot 250H_2O</td>
<td>As Received (Aldrich)</td>
<td>Na Y</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH_3)_4(NO_3)_2 exchange, calcined at 350 °C under O_2, reduced at 400 °C under 5% H_2/95% N_2 gas mixture</td>
<td>15PtANCR4</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH_3)_4(NO_3)_2 exchange, calcined at 350 °C under O_2, reduced at 300 °C under 5% H_2/95% N_2 gas mixture</td>
<td>15PtANCR3</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH_3)_4(NO_3)_2/NH_4NO_3 exchange, calcined at 350 °C under O_2, reduced at 400 °C under 5% H_2/95% N_2 gas mixture</td>
<td>15PtANXCR4</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH_3)_4(NO_3)_2/NH_4NO_3 exchange, calcined at 350 °C under O_2, reduced at 300 °C under 5% H_2/95% N_2 gas mixture</td>
<td>15PtANXCR3</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ exchange, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANCR4</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ exchange, calcined at 350 °C under O$_2$, reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANCR3</td>
</tr>
<tr>
<td>5wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANCR4</td>
</tr>
<tr>
<td>5wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANXCR3</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ exchange, direct reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANDR3</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange, direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANXDR4</td>
</tr>
<tr>
<td>Table continued</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange, direct reduced at 300°C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANXDR3</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, nitrate ion-exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ exchange, direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANDR4</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ exchange, direct reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANDR3</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANXDR4</td>
</tr>
<tr>
<td>5 wt.% Pt/Na-Y zeolite, excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ exchange direct reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>5PtANXDR3</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite nitrate exchange, impregnation method, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ impregnation, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANIMPGCR4</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite nitrate exchange, impregnation method, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ impregnation, calcined at 350 °C under O$_2$, reduced at 300 °C under 5% H$_2$/95% N$_2$ gas</td>
<td>15PtANIMPGCR3</td>
</tr>
<tr>
<td>Table continued</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite nitrate Exchange, impregnation method, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$(NO$_3$)$_2$ impregnation, direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANIMPGDR4</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, Pt chloride ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$ exchange, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCICR4</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, Pt chloride ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$ exchange, calcined at 350 °C under O$_2$, reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCICR3</td>
</tr>
<tr>
<td>1.5 wt.% Pt/Na-Y zeolite, Pt chloride ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$ exchange, direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIDR4</td>
</tr>
<tr>
<td>1.5 wt% Pt/Na-Y zeolite, Pt chloride ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$ exchange, direct reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIDR3</td>
</tr>
<tr>
<td>1.5 wt% Pt/Na-Y zeolite, Pt chloride with excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$/NH$_4$NO$_3$ exchange, calcined at 350 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIXCR4</td>
</tr>
<tr>
<td>Sample Description</td>
<td>Treatment Details</td>
<td>Code</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.5 wt% Pt/Na-Y zeolite, Pt chloride with excess ammonium nitrate ion exchange, calcined reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$/NH$_4$NO$_3$ exchange, calcined at 350 °C under O$_2$, reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIXCR3</td>
</tr>
<tr>
<td>1.5 wt% Pt/Na-Y zeolite, Pt chloride with excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$/NH$_4$NO$_3$ exchange, direct reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIXDR4</td>
</tr>
<tr>
<td>1.5 wt% Pt/Na-Y zeolite, Pt chloride with excess ammonium nitrate ion exchange, direct reduced sample</td>
<td>Pt(NH$_3$)$_4$Cl$_2$/NH$_4$NO$_3$ exchange, direct reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PtANCIXDR3</td>
</tr>
<tr>
<td>1.5 wt% Pd/Na-Y zeolite, Pd chloride ion exchange, calcined reduced sample</td>
<td>Pd(NH$_3$)$_4$Cl$_4$ exchange, calcined at 250 °C under O$_2$, reduced at 360 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PdANC25R36</td>
</tr>
<tr>
<td>1.5 wt% Pd/Na-Y zeolite, Pd chloride ion exchange, calcined reduced sample</td>
<td>Pd(NH$_3$)$_4$Cl$_4$ exchange, calcined at 400 °C under O$_2$, reduced at 400 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PdANCR400</td>
</tr>
<tr>
<td>1.5 wt% Pd/Na-Y zeolite, Pd chloride ion exchange, calcined reduced sample</td>
<td>Pd(NH$_3$)$_4$Cl$_4$ exchange, calcined at 300 °C under O$_2$, reduced at 300 °C under 5% H$_2$/95% N$_2$ gas mixture</td>
<td>15PdANCICR3</td>
</tr>
</tbody>
</table>
1.5 wt.% Pd/Na-Y zeolite, Pd chloride ion exchange, calcined reduced sample & Pd(NH$_3$)$_4$Cl$_4$ exchange, calcined at 300 °C under O$_2$, reduced at 360 °C under 5% H$_2$/95% N$_2$ gas mixture & 15PdANC30R36

### 2.2 Electrode Manufacture

#### 2.2.1 Nafion® Bound Electrodes

Support substrates that consist of a porous structure with a high surface area can improve the usage of the active metal of supported catalysts. In electro-catalysis, such porous structural electrodes provide significant mass transport advantages.

A few requirements must be considered when these electrodes are manufactured [29]. Firstly, the catalyst dispersion must be uniform throughout the electrode to obtain the high surface area distribution of the metal on the electrode. Secondly, the porous structure must be optimised to avoid the electrolyte blocking the porous electrode structure, and to avoid inaccurate assessment of the behaviour of the catalyst. Thirdly, the mass transfer of the electroactive species to and from the electrode surface must be efficient. Finally, the electrode must be mechanically and chemically stable for electrochemical testing.

Porous electrodes are widely used in electrochemistry in combination with solid conductive polymer electrolytes, such as, Nafion® and PTFE. These polymer electrolytes are used to bind the catalyst material to a current collector. As their side chains have the sulphonic acid groups, proton can transfer from solution to the electrode. Thus, this three phase boundary is particular useful for the reaction using gaseous species as a reactant.

In this project, Nafion® was used as binder in the electrode manufacture.
2.2.2 Nafion®

Nafion is a perfluorinated sulphonic acid based conductive electrolytic polymer. This binder consists of a PTFE-like backbone to which sulphonic acid groups are attached, as shown below in figure 2.7 [30].

The Nafion® structure can be divided into two different regions:

(a) the PTFE backbone which is hydrophobic

(b) the side chains which are hydrophilic and transport protons

Figure 2.7: the Diagram of Nafion® Structure [30]

There are advantages of using Nafion® to fabricate electrodes. Firstly, it can be solubilized in organic solvents under specified conditions of temperature and pressure[31]. Hence, this material can be cast into films on the electrode surface by evaporation of the solvent. Secondly, Nafion® can also be dissolved in most of the non-aqueous solvents suitable for electrochemistry. Third, the cationic electro-active species that are exchanged into the Nafion® films can exhibit electrochemical
behaviour similar to their behaviour in the solution. Finally, another very important factor, Nafion® is known to be chemically and electrochemically stable and it has an excellent ionic transport capability. The conductive ion, $\text{H}^+$ can easily pass through the pore of zeolite to the reactive sites. Therefore, Nafion® was chosen for use as the binder in the Pt/zeolite catalyst electrode fabrication for this project.

2.2.3 Electrode preparation

The electrode fabrication procedure was identical for all the catalyst types. The catalyst powder and XC-72R were ground together with a mortar and pestle. The appropriate amount of Nafion®, 15wt.% in the electrode, was added dropwise to a small volume of water and the solution was added to the powder mixture. The resultant thin paste was agitated in an ultrasonic bath for several hours until well mixed. The paste was spread onto carbon paper, typically 9 cm², with a spatula. The carbon paper acted as the current collector. The sheet was hot pressed at 100 °C and at 75 kg cm⁻² pressure for 3 mins. The electrodes were cut from the compressed sheet to the required size, discs of 1.3 cm² diameter for cyclic voltammetry and 2.5 cm² for XAS.

2.3 Electrochemistry

2.3.1 Introduction

Electrochemistry is the study of phenomena produced by charge separation [32]. Generally, the electrode process at one electrode, which is called the working electrode, is investigated. The potential of the working electrode is controlled with respect to a reference electrode, at which no current is passed. The current of the electrochemical cell is passed between the working electrode and an auxiliary electrode, which is called the counter electrode. The electron transfer between the working electrode and the counter electrode must be equal and opposite to maintain the overall charge balance. The current flows through the external electrical circuit. Thus, the cell contains three electrodes to measure the electrochemical processes.
Under conditions of equilibrium, the Nernst equation describes the variation of electrode potential for each electrochemical reaction [33] with the activities of the oxidised $a_O$ and reduced species $a_R$ in the equation below:

$$E_{eq} = E^o + RT/nF \ln(a_O/a_R)$$  \hspace{1cm} (2.3.1.1)

where $E^o$ refers to the standard electrode potential of the electrochemical reaction in Volts when all species have unit activity. $R$ is the molar gas constant, 8.31 J mol$^{-1}$K$^{-1}$, $T$ is the temperature in Kelvin, $n$ is the number of electrons in the electrochemical process. $F$ is the faradic constant, 96485 C mol$^{-1}$.

### 2.3.2 Instrumentation

The electrochemical experiments were conducted using a computer-controlled potentiostat (Autolab PGSTAT20). The use of such a system enabled a wide variety of electrochemical experiments to be conducted; for example, cyclic voltammetry, linear sweep voltammetry, polarisation, and iR drop measurements. Figure 2.8 shows a schematic of a working potentiostat system based on the Autolab system.

![Schematic of a working potentiostat system in Autolab](image)

A voltage is applied between the working electrode and the reference electrode. The current is passed through the working electrode via the counter electrode.
The voltage across the working electrode to reference electrode can be described as follows [33].

\[ E = (\phi_{WE} - \phi_S) + (\phi_S - \phi_{RE}) + iR \]  

(2.3.2.1)

The first term is the driving force for the interface of the working electrode with solution. The second term is the potential drop at the reference electrode/solution interface. The term \( iR \) is the voltage drop caused by the resistance in the whole system.

### 2.3.3 The electrochemical cell

The cyclic voltammetric experiment was carried out in a glass-jacketed cell of the type shown in Figure 2.9 [30]. The working electrode was held in a Delrin holder, which was sealed by using a PTFE o-ring and cap. For some experiments, a gas feed electrode holder was used to allow gas to be fed through the back of the electrode as shown in figure 2.10 [29]. The counter electrode was platinum gauze with larger surface area to provide the reverse reaction response to the working electrode, and ensure that polarisation occurring at the counter electrode could be neglected. Therefore, the response of the cell could be assumed to be primarily occurring at the working electrode [30]. The \( \text{Hg/Hg}_2\text{SO}_4 \) (MMS) reference electrode was chosen over the \( \text{Hg/Hg}_2\text{Cl}_2 \) (calomel) reference electrode for two reasons. Firstly, MMS has a high non-polarisation performance, and secondly, to eliminate the possibility of contamination by chloride ions. Chloride ions are a known poison to the electrodes used in this work. The reference electrode was placed in a Luggin capillary and the tip of the Luggin capillary was positioned as close as possible to the working electrode. This avoided large \( iR \) losses between the two electrodes. The MMS reference electrodes were calibrated versus a dynamic hydrogen electrode in 0.5 mol dm\(^{-3}\) sulphuric acid.

The electrolyte volume used was either 150 cm\(^3\) or 180 cm\(^3\) subject to the experimental conditions, and 2.5 mol dm\(^{-3}\) sulphuric acid was used as the electrolyte solution. During the experiment, the electrolyte solution was continually purged with nitrogen and thoroughly stirred to remove all dissolved oxygen from the cell. After purging with \( \text{N}_2 \) for about 10 minutes, the CV for the electrode of interest was recorded.
Figure 2.9 Schematic of the glass cell and electrode holder [30]

Figure 2.10 Schematic of the glass cell and gas feed electrode holder [29]
2.3.4 Cyclic Voltammetry

Cyclic voltammetry (CV) provides a quick and easy method to determine the electroactivity of species in solution and on the electrode surface. It monitors the response of an electrochemical system by the measurement of the current as the potential is changed. The working electrode is controlled by a potentiostat, and is changed continuously at a constant scan rate (dE/dt) by a potential ramp from a waveform generator [34] as shown in figure 2.10. The outcome of the measurement depends on the chosen potential regions. Ideally, only the oxidation or reduction of the electroactive species of interest at the electrode material should be detected. Thus, within the chosen potential region, neither solvent, nor electrolyte decomposition occurs [32].

Cyclic voltammetry is introduced as one of the most simple and useful techniques to study the electro-activities of the catalysts of interests contained in the electrodes. In order to help the analysis of the experimental results, a 40 wt.% Pt/XC-72 is described and is shown in figure 2.11.

![Cyclic Voltammetry Diagram]

Figure 2.11: The typical CV of a 40 wt.% Pt/XC-72R electrode made with 15 wt.% Nafion® (0.02 V/s) in 2.5 mol dm⁻³ H₂SO₄.
The CV can be divided into three parts: hydride region of the cathodic sweep (-0.34 V to -0.65 V) and anodic sweep (-0.65 V to -0.22 V), oxide region of the anodic sweep (0.12 V to 0.5 V) and cathodic sweep (0.5 V to -0.26 V), and the double layer of the anodic sweep (-0.22 V to 0.12 V) and cathodic sweep (-0.26 V to -0.34 V).

The hydride region for the CV of the 40 wt.% platinum starts at the point of hydrogen adsorption potential (HSP), sweeps in a negative direction to -0.65 V, and cycles back to the hydrogen reduction region (HR). Two significant features, hydrogen adsorption and desorption, are observed. The peaks are assigned to hydrogen atoms at two different surface sites on platinum. On the cathodic sweep, peak A is said to be caused by the strongly adsorption of H ions due to their high adsorption energy on the plane of the platinum and electron conduction between the two elements. The second peak B is attributed to the weakly adsorption of hydrogen. It is thought that the H ion is just adsorbed on the platinum atom or particle surface with covalent bonding. The peak C is due to the hydrogen evolution. On the anodic sweep, there are two peaks due to hydrogen desorption. D is thought to be hydrogen re-oxidation, E represents the H desorption process. The whole process is expressed as follow:

\[
\text{Cathodic reaction} \quad H^+ + e^- \rightarrow \text{H_{adsorption}} \quad (2.3.4.1)
\]

\[
\text{Anodic reaction} \quad \text{H_{adsorption}} \rightarrow \text{H}^+ + e^- \quad (2.3.4.2)
\]

\[
\text{Hydrogen evolution} \quad 2\text{H}_{\text{adsorption}} \leftrightarrow \text{H}_2(g) \quad (2.3.4.3)
\]

\[
\text{Overall reaction} \quad 2H^+ + 2e^- \rightarrow \text{H}_2(g) \quad (2.3.4.4)
\]

Continuing the sweep from the hydrogen desorption region (HR) in a positive direction to 0.5 V, an increase in current occurs at 0.12 V, the oxide region (OR). This is due to the formation of platinum oxide species at the electrode surface. The anodic sweep is terminated at 0.5 V to avoid oxygen evolution. In the cathodic sweep, from 0.5 V to -0.26 V, there is the oxide-stripping peak, which is due to the reduction of the surface oxide layer. This process is not fully reversible as evidenced by the hysteresis displayed in the CV. The equations of the platinum surface oxidation/reduction are summarised as follows.
Pt + H₂O $\rightarrow$ OHPt + H⁺ + e⁻  \quad (2.3.4.5)

OHPt $\rightarrow$ PtO + H⁺ + e⁻  \quad (2.3.4.6)

PtO + H⁺ $\rightarrow$ Pt + OH⁻  \quad (2.3.4.7)

PtO + 2H⁺ $\rightarrow$ Pt + H₂O  \quad (2.3.4.8)

There is a double layer region (DL) from -0.26 V to -0.34 V on the cathodic sweep, -0.22 V to 0.12 V on the anodic sweep. This is due to charge separation at the plane of the metal with the electrolyte solution.

Figure 2.12 shows the typical CV of a 1.5 wt% Pt/Na Y zeolite electrode measured using the catalyst fabricated with the Pt(NH₃)₄(NO₃)₂ exchanged sample, calcined reduced at 400 °C. In this study, only the hydride region is investigated because evidence of the activity of the Pt particle may be found from the hydrogen adsorption/desorption. Although only one well-resolved hydrogen adsorption peak is observed in the hydride region, this does not necessarily mean that there is no weakly bound site existing on the platinum surface. The energy of adsorption for weakly and strongly bound hydrogen may be close. The peaks observed in the CV reveal that there is electrocatalytic activity on the platinum supported on or in the zeolite structure.

Figure 2.12: The typical CV of PtANCR4, 1 mV/s, in 2.5 mol dm⁻³ H₂SO₄
2.3.5 Electrochemical Active Area

2.3.5.1 CO oxidation

CO is commonly regarded as a poison species to the platinum surface in electrochemistry. However, over the years, CO has been used as a chemical reagent to detect the amount of Pt active surface area on the electrode. Typically, the surface area measurements were performed in a glass-jacketed cell as shown in figure 2.9. The potential was swept from -0.65 V to 0.5 V with N₂ purging. This procedure was to ensure that the clean platinum CV in sulphuric acid can be obtained prior to exposure to CO. CO was introduced to the cell under potential control. The CO potential deposition region was chosen at around -0.55 V to -0.6 V, to prevent hydrogen adsorption. The solution was purged with CO until the H_ads peak was suppressed. The electrolyte solution was purged with N₂ for another 45 mins to remove any remaining CO in the solution. The potential was swept from -0.55V to 0.5 V, reversed to -0.65 V, and cycled until the CV was obtained corresponding to that of the platinum electrode devoid of CO. A stripping peak occurs around 0.1V to 0.45 V vs MMS as shown in figure 2.13. The mechanism of CO adsorption and stripping from Pt surface may follow the formula presented as follows [35].

\[
\text{Pt(H}_2\text{O)} \rightarrow \text{Pt - H + Pt - OH} \quad (2.3.5.1.1)
\]

\[
\text{Pt(OH) + Pt(CO)} \rightarrow 2\text{Pt + CO}_2 + \text{H}^+ + \text{e}^- \quad (2.3.5.1.2)
\]

The overall reaction is presented as follows:

\[
\text{CO + H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2.3.5.1.3)
\]

The Pt surface area can be determined from the charge in coulombs passed during CO oxidation, which was obtained by measuring the area under the CO stripping peak. The charge may be converted to the active Pt surface area by assuming a surface platinum atom density of 0.95×10^{15} atoms cm\(^2\) in agreement with the crystallite size associated with hydrogen chemisorption data for a less well dispersed catalyst [36].

The surface of active platinum particles in cm\(^2\) per gram can be obtained via the Pt active surface area in cm\(^2\) divided by the platinum loading on the electrode and the actual electrode surface area exposed to the electrolyte solution.
Figure 2.13: CO stripping and after stripping CV of a PtANXCR4 electrode in 2.5 mol dm$^{-3}$ H$_2$SO$_4$ at 2 mV s$^{-1}$. The dotted line presents the CO stripping CV, and the solid line presents the after CO stripping CV.

However, using CO adsorption to measure the surface area of zeolite supported catalysts is not always reliable due to the combination of CO with zeolite protons, which will sometimes lead to changes of oxidation state for the entrapped metal, such as, Pt or Pd [20].

Fortunately, the results obtained by other researcher have shown that the effect of CO interacting with zeolite proton could be negligible at low temperatures. CO only induces a relaxation of the Pt – Pt bond in the small particles after removing adsorbed hydrogen. There was no Pt agglomeration observed by XRD [37].

### 2.3.5.2 Hydrogen Adsorption and Desorption

Hydrogen adsorption measurements are widely used in determining the real surface area of platinum [38] because the ratio of hydrogen atoms to surface platinum atoms is close to unity [36]. The measurement to obtain the real surface area is more accurate in comparison to the CO measurements for the highly dispersed small platinum atoms or
particles. The measurement was carried out in the glass cell used for the CO experiment. After three electrodes (reference electrode, counter electrode, and working electrode) were connected to the potentiostat within the Autolab, N₂ was introduced into the electrolyte solution (2.5 mol dm⁻³ H₂SO₄) to remove any O₂ in the solution. Thus, a fresh Pt surface was maintained. The three potential regions chosen for the cyclic voltammetric measurements were -0.65 V to 0 V and -0.65 V to 0.5 V respectively. The adsorption peak area was calculated automatically with the aid of the computer system. Hence, preliminary information of the catalytic activity of a Pt/zeolite system may be obtained.

Electrocatalytic properties on electrodes are dependent on the number of available surface sites. The charge can be converted to the real active Pt surface area by assuming the distribution of crystal faces exposed and which atoms in these faces would be adsorbed with hydrogen [38]. The charge may be converted to the active Pt surface area by assuming a hydrogen monolayer of 1.12×10¹⁵ atom cm⁻² [36, 39].

2.3.5.3 Polarisation

The polarisation measurements are often used in determining the performance of an electrocatalyst electrode. The electrode measurements are conducted galvanostatically in the same cell as described in section 2.3.3. Thus, the required potential to maintain a chosen steady state current density is determined for range of current densities. The diagram shown in figure 2.14 [30] represents the polarisation curve measured at the working electrode for an oxidation reaction. The shape of the polarisation curve may be divided into three parts. The first offset curve from the standard electrode potential E⁰ is called the charge transfer overpotential. It is the deviation of the open circuit potential (Eₑ) from the standard potential E⁰. The second offset is to tilt the polarisation curve away from horizontal. This is caused by the resistance of the electrode and cell, and is called the ohmic overpotential or iR drop. Finally, the non-linear shape of the polarisation curve at the high current end of the measurement is attributed to the effects of mass transfer at the electrode surface. This is called the mass transfer overpotential. Therefore, the overpotential of a polarisation can be expressed as follows [33]:

\[ \eta = E - E_e \]
As expressed, it is the deviation of the electrode potential from the standard potential. The polarisation overpotential can also be defined as:

$$\eta = \eta_{\text{rest}} + \eta_{\text{ohmic}} + \eta_{\text{kinetic}}$$

Figure 2.14: Diagram of a polarisation curve of an electrode for an oxidation reaction[30]

2.3.5.4 iR Drop

iR measurements were carried out using a potentiostat within the Autolab system. Normally, current is stepped from a given value to zero, and the voltage response versus time is recorded. The voltage difference divided by current gives the resistance across the system. However, when the practical experiment was carried out with the aid of an Autolab system, the potential was used to step from a chosen value, which should be within the investigated potential region of a cyclic voltammogram. The Ohmic resistance across system was measured automatically with the aid of the computer software. By obtaining the average of ohmic resistance data, the potentials obtained from the polarization measurements were then corrected. The equations for the polarization correction are represented as follows.
\[ \bar{R} = \frac{(R_1 + R_2 + R_3 + \ldots + R_n)}{n} \quad (2.3.5.4.1) \]
\[ i_i = \frac{V_i}{R_i} \quad (2.3.5.4.2) \]
\[ V_{avirpot} = V_i \pm i_i R \quad (2.3.5.4.3) \]

\( i_i \) is the current from each measurement. \( V_i \) is the potential applied during each measurement. \( R_i \) is the ohmic resistance obtained from each measurement using a potential step. \( V_{avirpot} \) is an average potential after the polarisation correction due to the ohmic resistance \((iR)\) in the electrochemical cell. \( i_i \bar{R} \) is subtracted for anodic reactions and added for cathodic reactions.

### 2.4 BET

#### 2.4.1 The Principle of BET Surface Area Measurement

Gas adsorption measurements are widely used for determining the surface areas and pore size distribution of a variety of adsorbent materials. Adsorption at the gas/solid interface also forms an essential part of many fundamental and applied investigations of the nature and behaviour of solid surfaces [40].

The standard procedure for the determination of surface area of finely-divided porous materials, was established by Brunauer, Emmett and Teller (BET) in 1938, using nitrogen adsorption. This method enables the volume of gas required to form a monolayer to be determined, from which the surface area can be calculated. The BET equation is an extension of the Langmuir isotherm [41] and is based on the following assumptions [40].

- Uniform energy of the adsorbent surface
- The sites for multilayer formation are provided by adsorbed molecules in the first layer
- Equal heats of adsorption \((H_{vap})\) for the adsorbate of the second and higher adsorbed layers
Identical adsorption and desorption characteristics

However, it is now generally recognised that the physisorption of gas molecules in very narrow pores does not involve the usual initial stage of monolayer coverage, but instead takes the form of pore filling at low relative pressure.

The exact conditions \( P/P^0 \) and \( T \) to the onset of a particular adsorption mechanism are dependent on the nature of the particular adsorbant-adsorbate interactions, and the ratio of the pore width to molecular diameter rather than on the absolute value of the diameter [42]. Generally, pore filling can take place in two stages:

(a) a primary process involving enhanced adsorbant-adsorbate interactions in very narrow pores, and

(b) a secondary, or co-operative process in the wider pores. The magnitude of the enhancement of adsorption energy is dependent on the pore shape.

The equation of the characteristic curve for the adsorption of gases on zeolites proposed by Dubinin and Astakhov, [43] can be expressed as follows:

\[
\frac{V}{V_o} = \exp\left[-\left(\frac{A}{bE_o}\right)^n\right]
\]  

(2.4.1.1)

Where \( V \) is the amount of gas adsorbed at relative pressure, \( P/P_o \), \( V_o \) is the amount of gas required to fill the micropores. \( A \) is the affinity defined as:

\[
A = RT \ln\left(P/P_o\right)
\]  

(2.4.1.2)

However, the usual BET equation is given as follow:

\[
\frac{P}{V(P_o-P)} = \frac{1}{(V_mC)}(P/P_o)
\]  

(2.4.1.3)

Where \( C \) is a constant given by \( C = \exp\left[(q_t q_u)/RT\right] \), in which \( q_t \) and \( q_u \) are the heats of adsorption for the monolayer and the multilayers converted respectively [44]. \( V \) is the volume of gas adsorbed (in ml, S.T.P) at the relative pressure \( P/P_o \), and \( V_m \) is the volume of gas in a monolayer. The BET equation can also be rearranged to give as follow:
Equation (2.4.1.3) predicts that a plot of $P/[V(P_0-P)]$ versus $P/P_0$ will be linear with a slope of $(C-1)/(V_mC)$ and an intercept of $1/V_mC$.

It should be noted that, due to the unrealistic assumption made in deriving the BET equation, the BET isotherm is only linear for relative pressures between 0.05 and 0.34[45] as shown in the figure 2.15 (a) and (b) below. Thus, to calculate the monolayer coverage, a BET plot is constructed for relative pressures only between these limits.

Figure 2.15: the typical BET plot of $P/[V(P_0-P)]$ versus $P/P_0$
The surface area of the material, $S_m$ is calculated using the following equation:

$$S_m = V_m N_A S_A$$  \hspace{1cm} (2.4.1.5)

where $N_A$ is Avogadro’s number and $S_A$ is the surface area occupied by one adsorbate molecule. The most commonly used adsorbate is nitrogen whose $S_A$ is taken to equal 16.2 Å$^2$ [40]. Sometimes, other gases, e.g. CO, are also utilised to measure the surface areas of special elements. Although it is necessary to make unrealistic assumptions about the nature of the interaction between the adsorbate and adsorbant to derive the BET isotherm, it is still possible to obtain accurate and reproducible surface area measurements for most materials.

### 2.4.2 BET surface area measurement

Experimentally, nitrogen is the most widely used adsorbate with procedures for measuring isotherms and surface area at 77 K. The BET equipment used for the zeolite surface area measure was a micromeritics Gemini 2375 system. The measurements were taken according to the procedure that follows.

1. Each sample was weighed accurately into a clean glass sample holder and then connected to the vacuum system.

2. Another empty glass tube was connected to the analysis port for comparison with the sample.

3. The sample was then allowed to degas at a room temperature under a pressure of 500 Torr.

4. Two liquid nitrogen traps were installed for analysis. Both the empty tube and the degassed sample were cooled to 77 K.

5. The gas used as adsorbent was introduced into the system, and maintained until the experiment was completed.

The BET measurement System automatically collects the isotherm data, performs the required calculations, and presents the results in the form chosen.
2.5 X-Ray Absorption Spectroscopy (XAS)

2.5.1 Introduction

Heterogeneous catalysts consisting of small metal particles dispersed on high surface area materials, such as zeolites, are very important to the catalytic reactions in many chemical processes. Their activity is known to be mainly a surface property [46]. Thus, knowledge of the metal dispersion and interaction between the catalytically active phase and support becomes fundamental to quantitatively understanding the mechanism of the catalyst in an electrochemical study. The preparative procedures that could change the metal dispersion state were investigated in combination with the metal/support interaction.

The electrocatalysts used in this study consist of small Pt particles dispersed on a zeolite support, an amorphous polymer material, which contains different pore sizes. The Pt concentration on this kind of system is very low, around 1.5 wt.% Pt and 5 wt.% Pt loading.

Detailed information of such catalyst system is difficult to obtain by using standard techniques, such as, X-ray diffraction, which is usually used to study bulk structure of the crystalline solid and the long – range order [47]. However, the Extended X- ray Absorption Fine Structure (EXAFS) technique using synchrotron radiation source has overcome these difficulties. Hence, the detailed local environment could be obtained, in particular, for a highly dispersed catalyst system with small particle size and low concentration.

EXAFS studies are not only limited to the materials with long-range order, but also can be applied to those materials having the short-range order characteristics of electron scattering, such as amorphous materials, solutions and supported catalysts containing small particles because the EXAFS oscillations are produced by atoms close to the emitting atom [48]. The technique is element specific due to the difference of the unique absorption edge of each element, which corresponds to the binding energy of the inner shell electron excited by the absorption process [48, 49]. Therefore, the local structure and chemical information contributing to the specific process may be probed according to each type of atom separately.
The XAS experiments are performed with the use of a synchrotron radiation source because of its very brightness and better collimation giving rise to very high fluxes on small targets. The synchrotron radiation sources can produce radiation, which is on the order of $10^6$ times more intense, in comparison to conventional sources, and is continuously tuneable from the far infrared (meV) to hard X-ray energies (keV) [48]. Thus, the data acquisition times are dramatically decreased. In addition, this kind of X-ray radiation source is highly polarized with the electric field vector, which is parallel to the acceleration vector [50].

The technique is particularly useful for the study of small metal clusters supported on amorphous materials with the use of in-situ methods in electrochemistry.

However, XAS is an averaging technique. It is not possible to independently obtain the information for two or more coordination sites with the use of different element at the same time, whereas it is still a powerful technique for obtaining local structural information for many catalysts, particularly for those very dilute, highly dispersed catalyst systems with small particle size.

### 2.5.1.1 X-Ray Absorption Spectroscopy – Theory

The XAS technique involves the determination of the X-ray absorption coefficient of a specific element as a function of photon energy that is in proximity to the absorption edge in a condensed and dilute medium or a gaseous medium. The measurements can be performed either in-situ or ex-situ. The photoelectron wave, caused by the excitation of a core electron is outgoing and then backscattered by surrounding atoms in the medium. X-ray absorption in the photon range up to 50 KeV is dominated by electron absorption where the photon is completely absorbed by a core electron, and a core hole is produced [50]. The process results in the interference effects that modulate X-ray adsorption observed [48]. The local scattering of X-ray interference produces the EXAFS itself. The electron wave function beyond the absorption threshold is considered as a spherical photoelectron wave. Figure 2.16(a) represents a schematic of a photoelectron ejection from 2p orbit into the Fermi level or continuum state. The wave radiates from the absorbing atom is shown in figure 2.16(b).
The figure 2.16: (a) the typical diagram representing the process, which a photoelectron is ejected from their orbit into a Fermi level or continuum state [48] (b) the Schematics of the Electronic Process of a Photon [51]

The X-ray photon energy is absorbed by atoms of a specific element, and an electron is ejected with kinetic energy after overcoming the binding energy. The kinetic energy of electron $E_k$ is given by [48]

$$E_k = h\nu - E_{\text{binding}}$$

(2.5.1.1.1)

where $h\nu$ represents the energy of incident photon, and $E_{\text{binding}}$ is the binding energy of electron.

The parameter used to describe the absorption of photons by a medium is the absorption coefficient, which can be expressed according to the Beer–Lambert law[52].

$$I_t = I_0 \exp(-\mu\chi)$$

(2.5.1.1.2)

where, $\chi$ is the thickness of the sample, $\mu$ represents the mass absorption coefficient, $I_0$ is the intensity of the incident beam, and $I_t$ is the intensity of the transmitted photon. The extent of absorption, and thus the absorption coefficient strongly depends on the photon energy. X-ray photons can be sufficiently energetic to excite core electrons, either into empty valence states or at higher energies into the ionisation continuum if
the correct energy is applied to cause an excitation within the medium [48]. Thus, a sharp increase in absorption coefficient vs energy, \( \mu(E) \), is observed. This is called the absorption edge, which occurs close to the ionisation potential of the core level. The edges are labelled according to the quantum number \( J \) and orbital angular momentum \( l \) of the electron ejected. For instance, K is a single edge corresponding to the excitation of an electron from \( n=1 \) and orbital angular momentum 0. Therefore, K arises from 1s. The L edge consists of three sub-edges \( L_1 \), \( L_2 \) and \( L_3 \) due to corresponding to \( n=2 \) and having orbital angular momentum 0 and 1. The \( L_1 \), \( L_2 \) and \( L_3 \) is raised from the 2s, 2p\(_{1/2}\) and 2p\(_{3/2}\) orbitals respectively.

The absorption coefficient seen in the absorption spectrum can be defined according to Fermi’s golden rule in terms of a dipole matrix element between an initial core state and the final state at an atom [51].

\[
\mu(E) = 4N_0 \pi^2 e^2 \omega/c \left| \langle f | \mathbf{k} | i \rangle \right|^2 \rho(\mathbf{E}_f) \tag{2.5.1.1.3}
\]

where, \( \omega \) is the frequency of the x-ray photon, \( | i \rangle \) is the waveform of the photoelectron in its initial state, \( \langle f | \) is the the waveform of the photoelectron in the final state, \( \rho(\mathbf{E}_f) \) is the density of final state, \( N \) represents the number of atoms per unit volume, and \( \mathbf{k} \) is a unit vector in the direction of electric field.

However, important information about the initial state and final state produced in the transitions is provided during the XAS study. The magnitude of the final state waveform depends on the overlap between the initial core level wave function and the final state wave function. An XAS spectrum for a single absorption threshold is shown in figure 2.17 [48].
The EXAFS structure arises due to the presence of atoms around the core, which absorbs a photon. The wave function produced by the adsorption of a photon, forward scatters away from atomic core where excitation occurred, and is backscattered by the surrounding atoms in the system. Hence, interference of the ejected electron between the outgoing wave and the backscattered wave produces the extended oscillations as shown in figure 2.18 [48].
The wave function of the ejected electron at a final state is dependent on the interference due to the backscattered waves either constructively or destructively with outgoing wave according to the phase shift. Figure 2.19 shows schematically the interference of the ejected electron that can produce an EXAFS spectrum [53].

(a)

(b)

Figure 2.19: (a) the plot of a constructive interference of the ejected electron (b) the plot of a destructive interference of the ejected electron [53]
I. Pre-edge

II. Absorption edge

III. X-ray absorption near edge structure (XANES)

IV. Extended X-ray absorption fine structure (EXAFS)

Figure 2.20 shows a typical EXAFS spectrum, which can be divided into four parts. The first part (I) is the pre-edge of an absorption spectrum. The second part (II) represents an adsorption edge. The third part (III) is the X-ray absorption near edge structure (XANES), which provides information about the surface structure, such as oxidation state of the metal in the potential dependent studies of electrochemical systems. The oscillations starting at about 50 eV (part IV) are defined as the extended X-ray absorption fine structure (EXAFS). This structure is contributed by the interference effects in the wave function of the excited electron. The whole spectrum is expressed as adsorption coefficient vs photon energy.

The absorption coefficient in the EXAFS region is given by [51]

\[ \mu_{\text{total}} = \mu_0 (1 + \chi) \]  

(2.5.1.1.4)
where $\mu_0$ is a smooth atomic like absorption coefficient, which represents the absorption cross EXAFS region of a free atom. Hence, the function of EXAFS in the form of $\chi(E)$ can be defined as [51]

$$\chi(E) = \frac{[\mu(E) - \mu_0(E)]}{\mu_0(E)}$$ (2.5.1.1.5)

The difference of $\mu - \mu_0$ depends on the local structure of the absorbing atom and represents the EXAFS [49]. Furthermore, the EXAFS is normalised to a per atom basis using the absorption coefficient difference ($\mu - \mu_0$) and dividing by $\mu_0$.

The EXAFS spectrum is the superimposition of contributions from different co-ordination shells to the backscattering process. Structural information can only be extracted from EXAFS after conversion from energy space to wave vector space [49] using the relationship as follows:

$$\lambda = 2\pi/k$$ (2.5.1.1.6)

$$k = \left[\frac{2m}{\hbar^2}(E - E_0)\right]^{1/2}$$ (2.5.1.1.7)

$$\hbar = \frac{\hbar}{2\pi}$$ (2.5.1.1.8)

where $k$ is in Å⁻¹, $m$ is the mass of the electron, and $E_0$ is defined as the threshold energy of the core shell for an excited atom. Hence, $E_0$ is close to the energy at the absorption edge.

The theoretical expression for core level absorption that relates the measured EXAFS to structural parameters can be written as a function of wavevector as follows [51]:

$$\chi(k) = \sum_j A_j(k) \sin[2k R_j + \phi_j(k)]$$ (2.5.1.1.9)

where $j$ is the jth co-ordination shell. $R_j$ represents the average distance between the absorbing atom and neighbouring atoms in the jth shell. $\phi(k)$ is the backscattering phase shift, which is dependent on the absorber – scatterer pair and distance between them. The detailed formula can be expressed as:
\[ \phi_{j}(k) = 2\phi_{\text{absorber}}(k) + \phi_{\text{backscatter}}(k) \quad (2.5.1.10) \]

The formula reflects the sum of the phase shifts induced for the outgoing and backscattered electron wave functions by the core atomic potentials of the emitting atom and backscattered atom [48]. \( \chi(k) \) also contains an amplitude part. It can be expressed as:

\[ A_{j}(k) = \frac{N_{j}}{kR_{j}^{2}} S_{0}^{2} F_{j}(k) \exp(-2k^{2} \sigma_{j}^{2}) \exp\left(-\frac{2R_{j}}{\lambda(k)}\right) \quad (2.5.1.11) \]

\( N_{j} \) is the number of neighbouring atoms of type \( j \) with backscattering amplitude, \( F_{j}(k) \) which is dependent on the neighbouring atom. Therefore, it is element specific. The product of \( F_{j}(k) \) gives the maximum amplitude. \( S_{0} \) is an amplitude reduction term which takes into account many body effects such as shake-up and shake-off process due to multi-electron excitation and energy loss [54]. \( e^{-2\sigma_{j}^{2}k^{2}} \) is the Debye Waller factor which represents a measure of static and thermal disorder in the sample, and is temperature dependent. The thermal disorder is usually considered as harmonic in nature.

The Debye Waller factor is the mean square deviation from ideal distance due to structural disorder. It describes the amplitude correction of the EXAFS oscillations due to thermal displacement of the backscatter relative to the emitting atom. \( \lambda_{j}(k) \) is the mean free path length of the photo-electron and accounts for the damping of the amplitude caused by the neighbouring environment surrounding the absorber. The range of travel of photo-electrons in the energy region of interest is limited by this term. It also contributes to the short-range description of the EXAFS phenomenon.

The final expression for the EXAFS function during data analysis can be written as:

\[ \chi_{k} = \sum_{j=1}^{\text{shell}} \frac{N_{j}}{kR_{j}^{2}} S_{0}^{2} F_{j}(k) e^{-2k^{2} \sigma_{j}^{2}} e^{-2R_{j}/\lambda(k)} \sin\left[2k R_{j} + 2\phi_{\text{absorber}}(k) + \phi_{\text{backscatter}}(k)\right] \quad (2.5.1.12) \]
2.5.2 Data Collection

2.5.2.1 The Cell & Powders

Experimentally, the cell employed in EXAFS studies of electrochemical systems depends on whether the transmission or fluorescence mode of detection is used. In the transmission mode, the cell must be designed to minimize absorption losses, which are caused by the window material, electrolyte, and the electrode itself [54]. Generally, low absorbing materials, such as polyethylene and polyamide (kapton) are used as a thin film to make the cell window. The thickness of electrolyte layer needs to be very small. The catalyst quantity used to make electrodes must be calculated to produce a sufficiently large absorption edge, typically $\mu \chi > 0.3$. Figure 2.21 shows the transmission cell employed for XAS experiments at Daresbury Laboratory.

![Transmission Cell](image)

Figure 2.21: The transmission cell employed for XAS experiments at Daresbury Laboratory [55]

In using a cell of this type, the WE is placed in the middle of one acrylic disc, in which a hole was cut in order to allow passage of the X-rays through the electrode. A gold wire current collector was placed underneath the working electrode to make a contact in the cell system. Several layers of filter paper soaked in 1 mol dm$^{-3}$ H$_2$SO$_4$ were placed over the electrode to prevent the electrode drying out whilst the cell was being
put together. Filter papers also help seal the cell against leaks, and help prevent bubble formation in the front of the window because bubbles could lead to a severe drop in the adsorption coefficient. Platinum gauze was used as the counter electrode, and was placed in the electrolyte at a separate acrylic disc. Finally, two acrylic discs, which consist of the whole cell, were compressed together. X-rays pass through the cell via kapton windows and the sample. The electrolyte was purged through the cell continuously via tubing during the measurement. This procedure ensures the removal of gas bubbles from the cell, and supplies a uniform composition of electrolyte to the electrode. The MMS reference electrode was connected to the cell via a salt bridge. Figure 2.22 shows the detailed configuration used for in-situ XAS measurement in the electrochemical cell.

![Diagram of electrode configuration](image)

**Figure 2.22:** A detailed electrode configuration used for in-situ XAS measurement on the electrochemical cell

When the concentration of the catalyst is too low for transmission XAS, i.e., the absorption edge \( \mu \chi < 0.1 \), the structural information cannot be extracted. Therefore, the
fluorescence detection mode is employed. The window for the fluorescence cell has to be very thin for the reasons described for the transmission cell. Thus, the materials used for the transmission mode cell can still be used for the fluorescence cell.

The fluorescence cell employed for XAS measurement at Daresbury Laboratory was made using the same material as for the transmission experiment. The WE was placed on the bottom of a hole in one acrylic disc with a gold wire to make contact to the working electrode. This acrylic disc was thinner than the other side. The depth of hole made for the WE is around 0.8 cm. A PTFE washer was placed on the top of electrode. The counter electrode and MMS reference electrode (via a salt bridge) were placed in the other acrylic disc, whose thickness was the same as that of the transmission cell. The side of the cell comprising of the WE was placed towards the detector at an angle of 45°. The procedure afterwards is the same as that of the transmission experiment. The advantage of this cell configuration is that an electrode containing a low quantity of catalyst can be measured.

In this project, EXAFS measurements for 1.5 wt.% Pt/zeolite samples were performed in the fluorescence mode due to the low concentration of Pt. Powders were used for ex-situ XAS experiments. Pellets were made by mixing the catalyst powder with boron nitride or polyethylene to give the overall loading of 0.73 mg/cm² of the element of interest. The pellet was then placed between two pieces of plastic, and sealed with scotch tape, both of which have low X-ray absorption. For the Pt samples, only the Pt L_{III} edge was investigated.

A gas treatment cell was also employed for powder sample XAS measurement. The body of cell is cylinder like, and was made by glass. During the experiment, the pellets were firstly compressed in the steel made disc holder, and then, were vertically placed in the bottom of cell. Subsequently, hydrogen gas was introduced to the cell from the top valve after vacuum procedure. Consequently, the cell was left for the gas purge for 45 minutes approximately before it was sealed off. Two kapton windows were located on the each side of cell on the bottom where pellet was suited. This design permits that X-rays to pass through the two kapton windows and sample.
2.5.2.2 Synchrotron

The XAS measurements were performed using the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The source can provide $10^6$ times more intensity than a conventional source in the hard X-ray region [48]. Hence, the experiment can be carried out in a much shorter time. The radiation from the synchrotron source ranges from the far infrared energies (MeV) to hard x-ray energies (KeV). An electron beam is produced by a 12 MeV linear accelerator, and the electrons are injected tangentially into the small booster, in which they are accelerated. The electrons are injected in bunches, separated by the radio frequency, and are steered round ring by dipole magnets. When the electrons gain energy up to around 600 MeV, the electrons are injected tangentially into the main storage ring where the electron energy is raised to 2 GeV. At this energy, the velocities of the electrons are boosted to close to the speed of light.

The beams with different energy used for various kinds of measurements are conducted to the different beam lines at the SRS by magnets. In general, a beam line set up includes in a mirror, a monochromator and two or three detectors, as shown in figure 2.23.

![Diagram of beamline set up at the SRS](image)

Figure 2.23: the beamline set up at the SRS

The incident beam from the storage ring is focused by a mirror onto the monochromator via a slit, which is used to limit the beam size and improve the energy resolution of the monochromator [56]. The monochromator contains crystals of a defined orientation. Two paralleled crystals are used to select the desired energy. The
output beam is parallel to the input beam with a slight vertical offset. The offset distance $h$ is given as follows:

$$h = 2d \cos \theta$$

(2.5.2.2.1)

where $d$ is the lattice separation of the monochromator crystal, and $\theta$ is the Bragg angle.

The first crystal is cooled with the aid of water because it takes the full flux of the incident beam. The two crystals can be rotated around an axis with the aid of a motor, which can accurately adjust the Bragg angle according to the requested absorption edge of the specific element. The second crystal is used to remove harmonics of higher orders that can affect the amplitude of the EXAFS. A percentage of harmonic beam is removed by detuning the second crystal, 50% detuning was used for the Pt L$_{III}$ and L$_{II}$ absorption edges.

Each ion chamber comprises two kapton windows located at each side of the ion chamber to seal the ion chamber tightly. This design allows X-ray to pass through, and the intensities of incident and transmitted beam are measured using the gas–filled ion chambers. The gas fill is a measured quantity of Ar, Xe or Kr made up to atmospheric pressure with He [57]. The gas mixture in the ion chamber $I_0$ is ionised by the incident radiation before the X-ray passes through the sample. Therefore, the $I_0$ is measured as an ion count by ion chamber 1. The transmitted intensity $I_t$ is recorded by ion chamber 2. A third ion chamber placed after ion chamber 2 may be used to collect a reference spectrum at the same time in order to correct any instabilities in the energy calibration during the experiment. The reference sample is usually a foil made of the metal of interest in the catalyst or a uniform pellet made from a known powder sample containing the element of interest. The ions formed by the absorption of photon produce electrons, $e^-$, which flow between two metallic plates with a 500 V potential difference between them, and are monitored as current, which is proportional to the photon flux. The current is converted to a readable voltage by Keithley amplifiers [57].

The gas mixtures in the ion chambers are varied depending on the absorption edge of a specific element. However, the first ion chamber should absorb 80% of the beam, and the second ion chamber absorbs 20% of the remaining beam.
2.5.2.3 Data Collection Mode (Transmission and Fluorescence)

Transmission Mode

Transmission mode is only used for concentrated samples. A schematic of a beam line constructed for transmission experiments has been shown in figure 2.23. In transmission mode, the data are usually plotted as $\ln(I/I_0)$ vs energy according to Beer’s Law given as follows: [54]

$$
\mu \chi = \ln(I_0/I)
$$

(2.5.2.3.1)

where $\mu$ is the linear absorption coefficient, $\chi$ is the sample thickness, $I_0$ is the incident beam intensity, and $I$ refers to the transmitted photon intensity. The X-ray intensities are measured using ionisation chambers in conjunction with high gain electrometers.

Fluorescence Mode

The fluorescence mode is employed when the sample is in a dilute form such that the signal to noise ratio is too low to give reliable results in the transmission mode. The intensity of the fluorescence signal strongly depends on the number of core holes generated and, thus, the absorption coefficient. Hence, fluorescence is much more sensitive in comparison to the transmission mode. To maximise the fluorescence signal detected, the sample is positioned at an angle of 45° to the incident beam and the detector is situated at 90° as shown in figure 2.24 [53].

![Fluorescence Detector](Figure 2.24: Schematic of the Configuration for Fluorescence Measurement)
The intensity of incident beam is measured using an ion chamber as described in the transmission mode, and the intensity of fluorescence signal emitted from the sample is measured using a solid state detector as this gives the best possible resolution. A filter is placed in the front of detector to reduce Compton scattering. The material of the filter used is made from the Z-1 or Z-2 element, where Z represents the atomic number of the element of interest [54].

The intensity strength of the fluorescence signal depends on the atomic number of the absorber when a heavy element is measured. Figure 2.25 shows the process of fluorescence radiation. Fluorescence occurs due to the energy emitted when a core hole, generated by the absorption of an X-ray photon, is filled by an electron from a higher level. Hence, the energy of the radiation is characteristic of the absorbing element [53, 55].

![Figure 2.25: Schematic of the Generation of Fluorescence](image)

2.5.3 Data Analysis

The aim of data analysis is to extract structural information from EXAFS, such as, the interatomic distance, number, and type of backscattering neighbours. The data analysis procedure involves several steps. In this project, the data processing and analysis were completed with the use of Daresbury’s software: EXCALIB, EXBROOK and EXCURV 98 software. The various steps of the data analysis procedure are described in figure 2.26 below.
Figure 2.26: Plots depicting the various processes involved in extraction of the EXAFS function. (a) and (b)=pre-edge subtraction (c)=background subtraction (d)=a single absorption threshold (e)=final Chi data (f)=Chi data, phase uncorrected (g)=Fourier transform, phase uncorrected
1. Energy calibration and generation of the XAS spectrum

The data collected on stations 9.2, 9.3 and 16.5 at the SRS, Daresbury Laboratory is stored as detector intensities as a function of monochromator angle in millidegrees. The EXCALIB program was used to convert these to \( \log(I/I_0) \) for transmission and \( (I/I_0) \) for fluorescence as a function of energy in eV. Multiple data files could also be averaged using this program to improve signal to noise ratio.

2. Pre-edge subtraction and post edge subtraction

The XAS spectrum is characterised by a near-linear decay in the absorption as the energy increased. This near-linear decline in absorption is most easily seen in the pre-edge region at energies below the absorption-edge. A polynomial is fit through this region and the result is subtracted from the data (Frame a of the diagram). This is called pre-edge subtraction. This step and the remaining steps up to data analysis were conducted using the EXBROOK program.

The outgoing wave of atom may not be backscattered by the neighbouring atoms. This results in a smoothly varying atomic background, which is defined as \( \mu_o \) above the edge in the absorption spectrum. To remove this smooth atomic background from experimental data, a polynomial spline of a given order is employed. The spline contains several parameters: \( SM \), a smoothing parameter; \( W \), a weighting factor; and the start and end energy that determine the number of points of the spline [58]. These parameters are adjusted to give the best fitting to the background subtraction. The formula of the post edge subtraction may be represented as follows:

\[
\Delta \mu = \mu_{\text{total}}(E) - \mu_o(E) \quad (2.5.3.1)
\]

The EXAFS is generated by subtracting the spline curve from the edge as shown in frame b of the diagram.
3. Normalisation

To obtain useful information from the XAS spectrum, the spectrum must be normalised to yield the absorption on a per atom basis. This is accomplished by the so-called edge jump. This is the amplitude of the atomic background after the edge.

\[ \chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \]  

(2.5.3.2)

The procedure is illustrated in frame c of the diagram.

As a result of the normalisation procedure, the XAS spectrum now provides the average local atomic information of specific element in the sample.

4. Conversion to wave vector form

In order to extract atomic structural information, the EXAFS must be expressed as a function of the wave vector \( k \). To achieve this, the x-axis must be converted from photon energy (eV) to the wave vector of a photoelectron, \( k \) (Å\(^{-1}\)) [50]. However, the choice of \( E_0 \) is important because it affects the phase of the EXAFS oscillation at low \( k \) values [54]. The formula of \( k \) wave vector is given by:

\[ k = \frac{1}{\hbar}[\frac{2m(h\nu - h\nu_{E_0})}{2m(h\nu - h\nu_{E_0})}]^{1/2} \]  

(2.5.3.3)

where \( k \) is in Å\(^{-1}\), and \( h\nu \) is in eV. \( h\nu_{E_0} \) is the threshold energy of the core shell for an excited atom. The value of \( E_0 \) is chosen to be the point of inflection at the absorption edge as shown in frame d of the diagram.

5. Extraction the final EXAFS function

The EXAFS function, \( \chi(k) \), is extracted from the XAS spectrum by choosing a minimum energy and discarding the points below this energy. The result is shown in
If averaging of several fills has not been completed in the first step using EXCALIB, it may be done by averaging several final EXAFS spectra.

6. K-Weighting

Equation (2.5.1.1.11) has predicated that the amplitude of EXAFS oscillation decreases with k. To compensate for this effect on the EXAFS amplitude at high k values, the χ function may be multiplied by a factor of k^n, where n is 0, 1, 2, or 3 [59]. K weighting is used to distinguish high or low Z (atomic number) scatters. k^2 and k^3 weighting effects the high energy part of spectrum, thus, emphasises the high z element contributions to the spectrum, whilst k^1 weighting emphasises the low z element contributions to the EXAFS spectrum [58].

7. Fourier transforms and fitting

Fourier transforms

The use of Fourier transforms in the analysis of EXAFS data was a major breakthrough in the EXAFS data analysis because it offers better visualization during the extraction of structural information. The formula of Fourier transform is shown as follows [54].

\[
FT(r) = \frac{1}{\sqrt{2\pi}} \int_{\text{min}}^{\text{max}} k^n \chi(k) \exp(-2\pi i kr) \, dk \quad (2.5.3.4)
\]

The function displays peaks that correspond to interatomic distances between the central atom and the individual coordination shells in R-space (Å). The Fourier transform is illustrated in panel g of the diagram. The peak height is proportional to the number of neighbours in the shell, and the peak width indicates the structural disorder [58].

Fitting for phase

The EXAFS function χ(k) is composed of amplitude and phase components as described in section 2.5.1.1. The phase component is expressed as follows.

\[
\sin[2kR_j + \phi(k)]
\]
Where $\Phi(k)$ is the backscattering phase shift as described previously. The phase shift depends on the identity of the absorber and backscatters. Backscattering phase shifts may be extracted from the EXAFS of reference compounds with well-characterised structures. However, it is now considered best practice to calculate such phase shifts theoretically. Accurate determination of the phase shifts is important for correct determination of the interatomic distances when fitting the EXAFS data.

**Fitting for amplitude**

The amplitude of an electron wave is affected by the interference of outgoing and backscattering electron waves. This effect can be accounted for in the EXAFS equation by an amplitude term $A_j(k) = \frac{N_j}{kR_j^2} S_j^2 F_j(k) \exp(-2k^2\sigma_j^2) \exp(-\frac{2R_j}{\lambda(k)})$ as described previously. The accurate fitting of amplitude is important as the types and numbers of backscattering atoms around a given absorber can be obtained. As in the case of the phase shift theoretical calculations are preferred to obtained the value of $F_j(k)$ for the absorber – backscatterer pair. In the data analysis presented in this thesis, the Fourier transforms and fitting were conducted using EXCURVE98.

### 2.5.4 X-Ray Diffraction (XRD)

XRD is usually used to study the long-range order of materials, such as, single crystals, or adsorbates on surfaces [49]. During the measurement, X-rays are scattered by the electron distribution around nuclei in the solid [48]. At certain angles re-emitted X-rays from different planes can interact either constructively or destructively [59]. The patterns are determined according to the Bragg angles of diffraction and reflection from the lattice planes in the crystal.

With the use of Bragg’s law, the Bragg angle $\theta$ is defined as follows: [59]

$$n\lambda = 2d \sin \theta$$

where, $d$ represents the spacing of the lattice planes, $\theta$ is the angle of incidence or reflection of the X-ray beam, $\lambda$ is the wavelength of the beam, and $n$ is an integer representing the order of diffraction. The number of orders is limited by the maximum
θ used in the experiment. The term 2dsinθ is the path length difference of the reflected beams from each plane. Thus, information regarding the crystal lattice size and symmetry can be obtained by the analysis of the position of diffracted beam.

The process of XRD is presented as a schematic in figure 2.27 [29, 60].

![Schematic of the process of XRD](image)

Figure 2.27: Schematic of the process of XRD [29, 60]

The powder XRD experiments were carried out in Southampton. All measurements were made using a Siemens D5000 diffractometer by Dr. Andrew Hector. A Cu source was used to generate Kα X-rays, which have a wavelength of 1.45 Å. The sample powder was finely ground, and pressed onto a quartz holder to obtain a uniform distribution. The holder was then placed into position. The X-rays were filtered, and then, sent through the sample.

The data collected from the detector was opened in a data acquisition program called EVA. It assigns the peaks to a two-theta value corresponding to a lattice spacing value, d. The peaks are related to each other via intensities compared to the highest peak. The data obtained from the composition of the sample was compared with known/theoretical values from the standard database.

As the metal particle size is very small (1nm) and highly dispersed inside the zeolite, it is difficult to obtain structural information via this technique. Hence, XRD data obtained for the Pt/zeolite samples was used to compare with that of plain zeolite, and to see whether there is a structural modification of the zeolite during the thermal treatment.
2.6 References


51. Russell A.E., Private Communication.


55. The cell photo taken from beam line at Daresbury Laboratory.


3.1 Introduction

A quantitative characterisation of the Pt dispersion on the Y zeolite is extremely important in understanding interactions between the metal particles and the support so that the preparative procedure of the catalysts may be optimised. Since catalytic activity is known to be mainly a surface property, considerable effort has gone into the development of preparative procedures that maximize Pt dispersion on the support [1].

As discussed in chapter 2, the role of the calcination and reduction procedures is crucial for obtaining highly dispersed Pt/zeolite catalysts. The research work done by Gallezot et al. has explored the calcination of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) - exchanged Na Y zeolite at different temperatures and has offered the ability to vary the position of the Pt aggregates formed after gas-phase reduction with H\(_2\) [2]. Scheme 1 displays the synthesis of nanoscale particles in the Y zeolite support. In the experiment, ion exchange equilibria are used to load the desired metal into the zeolite lattice and, then, gas-phase reactions are carried out to form the metal or metal oxide [3].

Scheme 1: Location of Pt after different calcination and reduction conditions [3]
The structure and dispersion of small Pt particles on Y zeolites have been studied extensively with the use of EXAFS techniques, which provide valuable information about the metal-support bonding [4]. The EXAFS region starting at 50 eV above the edge (shown in chapter 2) gives information regarding the nearest neighbours around the absorber atom, for example, the identity and number of the neighbours and the distances between the absorber and neighbouring atoms. The information about the coordination numbers and bond distances may be used to derive the size and shape of the metal particles [5, 6]. Meanwhile, the chemical state of the absorber atom may be characterized by analysis of the near edge region of the spectrum.

The results published by other groups show that metal microstructure constrained within the zeolite supercages can be varied in size from single atoms to particles in the order of 1-2 nm [7], forming clusters containing 10 to 25 atoms on average. The surface area of the zeolite is primarily internal or intracrystalline. Accordingly, only a small fraction of the metal may be supported on the exterior of zeolite. Although particles formed on the exterior are not constrained by the internal architecture of zeolite, they are still much smaller than the micrometer size [7, 8].

The metal-support interaction altering the catalytic behaviour may change the electronic properties of the supported metal cluster. Some authors have reported that there was an electron deficiency of the Pt cluster within the zeolite support due to the influence of the acidic sites on zeolite structure. However, there are several possible explanations for the metal-support interaction proposed in the literature [9]. Firstly, the formation of a metal-proton adduct accounts for the electron deficiency of particles observed on acidic zeolites [10, 11]. Secondly, charge transfer between the metal atoms and the nearest neighbouring zeolite oxygen atoms plays a certain role [12]. The polarization of metal particles by nearby cations may result in electron deficient metal atoms on the support [13]. Furthermore, the catalytic activity and spectroscopic properties of supported metal catalysts may be greatly affected by the charge compensating cations, such as \( \text{H}^+ \) or \( \text{K}^+ \) [9, 14].

In order to determine the structure and any metal zeolite interactions, which have been reported extensively in the literature, numerous techniques, such as EXAFS, BET and XRD techniques were used to characterise the various samples prepared.
BET surface area measurements in combination with XRD powder diffraction techniques were used to determine the actual zeolite surface area and structural changes caused by metal deposition. The XRD technique was mainly used to investigate those catalysts whose zeolite surface areas were dramatically reduced after loading with the metals according to the results obtained from BET surface area measurement.

Different metal loadings, such as 1.5 wt% Pt/Y zeolite or 1.5 wt% Pt/Fe/Y zeolite (details can be seen in chapter 2) and 5 wt.% Pt/Y zeolite prepared by the ion exchange procedure and the impregnation method, were investigated to examine the effect of the preparative procedure on the metal dispersion and structure.

3.2 Results

3.2.1 The ex-situ EXAFS Results for 1.5 wt. % Pt/Zeolite Catalysts

The X-ray absorption data discussed in this chapter was collected using station 16.5 of the Synchrotron Radiation Source (SRS) at Daresbury, UK. The transmission mode was used during the data collection. The details have been described in section 2.5 of chapter 2.

The catalyst powders used during the EXAFS measurements are 1.5 wt.% Pt / zeolite catalysts, Pt(NH₃)₄(NO₃)₂ or Pt(NH₃)₄(NO₃)₂/NH₄NO₃ salts ion exchanged, calcined at 350 °C and reduced at 400 °C. The sample (15impgan4r4), prepared with Pt(NH₃)₄(NO₃)₂ salt impregnated with zeolite, calcined at 350 °C and reduced at 400 °C, was employed as well.

Primarily, catalyst powders were ground with polyethylene or boron nitride powder and pressed to produce a pellet, and then, placed between two pieces of plastic as described in section 2.5.2 of chapter 2. The EXAFS data was initially recorded in air and then in a hydrogen atmosphere (chemical reduction). The chemical reduction was
conducted in a gas treatment cell for two hours at room temperature and the EXAFS data was collected with the sample mounted in this gas treatment cell.

The EXAFS spectrum of each sample was recorded at the Pt L\textsubscript{III} edge, and the data were analysed as described in chapter 2, section 2.5.3. All data shown below are $k^3$ weighted to emphasise the data quality and the backscattering from high Z neighbours.

3.2.1.1 The ex-situ EXAFS Results of the 1.5 wt\% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} Edge in Air

The results of the analysis of the EXAFS data obtained for the 1.5 wt. \% Pt/zeolite catalyst powders without hydrogen chemical reduction are presented in table 3.1. The raw EXAFS data and their Fourier transforms are shown in figure 3.1. The data was useful out to $k=18$ Å\textsuperscript{-1} for the 15impgncr4 catalyst, 16 Å\textsuperscript{-1} for the 15anrr4 catalyst, and 14.5 Å\textsuperscript{-1} for the 15anxcr4 catalyst. All data were fitted in r-space, and $k^3$ weighting was used as described above.
Figure 3.1: Chi data and Fourier transforms for the 1.5 wt.% Pt/Y zeolite catalysts, oxygen phase corrected. The data were collected at room temperature in air. The solid line represents the experimental data, and dashed line represents the fitted data. (a) =15ancr4, catalyst Pt(NH₃)₄(NO₃)₂ ion-exchanged with Y zeolite (b)=15anxcr4 catalyst, Pt(NH₃)₄(NO₃)₂/NH₄NO₃ ion-exchanged with Y zeolite (c)=15impGANCR4 catalyst, Pt(NH₃)₄(NO₃)₂ impregnated with Y zeolite
Before describing the fits to the data. It is worthwhile to examine the plots of the EXAFS functions and their Fourier transforms. As can be seen in the panels in the left hand column of figure 3.1 (the $\chi(k)$ plots), the period of the EXAFS oscillations for the three samples is different. The EXAFS of the 15ancr4 catalyst has a short period, indicating neighbours at longer distances. Also, the amplitude of the oscillations is fairly constant in the $k^2\chi(k)$ plot, suggesting high Z neighbours. Comparing the $k^2\chi(k)$ plots for the 15impgancr4 and 15anxcr4 samples, there is increasing evidence of neighbours at shorter distances (longer period oscillations) that are low Z elements (the amplitude decays at higher k values). These differences are reflected in the Fourier transform (FT) plots. The FT of the 15ancr4 EXAFS is dominated by a peak around 2.7 Å, and shows evidence of higher shells (peaks between 4 and 6 Å). The FTs for the other two samples have their main peak around 2 Å, and little evidence of higher shells.

The dashed lines in figure 3.1 are the fits to the data. These lines follow the data very well, reflecting the goodness of the fit. Pt neighbours were required in fitting the EXAFS data for each of the samples. Surprisingly, the Pt distances in the first shell for two of the catalysts are lengthened to 3.06 Å (15anxcr4 sample) and 3.05 Å (15impgancr4 catalyst), as compared to the distance obtained for the 15ancr4 catalyst, for which the data analysis has predicted a 2.76 Å Pt-Pt distance in the first shell.

Table 3.1: The results of fit for each Pt shell

(a) The result of fit of the Pt L_{III} EXAFS data for the 15ancr4 catalyst in air

<table>
<thead>
<tr>
<th>15ancr4</th>
<th>N</th>
<th>2$\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>$E_{\text{ef}}$/eV</th>
<th>$R_{\text{exaf}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.23±0.09</td>
<td>0.0086±0.0012</td>
<td>2.02±0.006</td>
<td>-12.95±0.62</td>
<td>30.68</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>3.13±0.62</td>
<td>0.0135±0.0003</td>
<td>2.76±0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.75±0.54</td>
<td>0.0191±0.0032</td>
<td>3.90±0.017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>3.12±0.75</td>
<td>0.0164±0.0020</td>
<td>4.81±0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 5 Pt</td>
<td>6.83±2.01</td>
<td>0.0235±0.0036</td>
<td>5.44±0.019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(b) The result of fit of the Pt L\textsubscript{III} EXAFS data for the 15anxcr4 catalyst in air

<table>
<thead>
<tr>
<th>15anxcr4</th>
<th>N</th>
<th>2σ\textsuperscript{2} / Å\textsuperscript{2}</th>
<th>R/Å</th>
<th>E\textsubscript{ef} /eV</th>
<th>R\textsubscript{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.60±0.08</td>
<td>0.0089±0.0009</td>
<td>2.02±0.006</td>
<td>-11.58±0.85</td>
<td>36.09</td>
</tr>
<tr>
<td>Shell 2 O</td>
<td>1.08±0.13</td>
<td>0.0052±0.0015</td>
<td>2.59±0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.28±0.28</td>
<td>0.0193±0.0023</td>
<td>3.06±0.012</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of fit of the Pt L\textsubscript{III} EXAFS data for the 15impgancr4 catalyst in air

<table>
<thead>
<tr>
<th>15impgancr4</th>
<th>N</th>
<th>2σ\textsuperscript{2} / Å\textsuperscript{2}</th>
<th>R/Å</th>
<th>E\textsubscript{ef} /eV</th>
<th>R\textsubscript{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.74±0.08</td>
<td>0.0102±0.0008</td>
<td>2.02±0.005</td>
<td>-10.17±0.70</td>
<td>38.42</td>
</tr>
<tr>
<td>Shell 2 O</td>
<td>0.91±0.10</td>
<td>0.0029±0.0009</td>
<td>2.58±0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.64±0.32</td>
<td>0.0218±0.0024</td>
<td>3.05±0.012</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N = coordination number
2σ\textsuperscript{2} = Debye-Waller Factor
R = coordination distance
R\textsubscript{exafs} = goodness fit value
E\textsubscript{ef} = energy in fermi level

The data analysis reveals that the 15anxcr4 and 15impgancr4 catalysts are exceedingly oxidized, as indicated by the two O-Pt neighbouring shells. However, only one Pt-O shell is observed for the 15anxcr4 catalyst in the data fit, and the O coordination number, approximately 1.23, is smaller than those for either 15anxcr4 catalyst (2.68) or 15impgancr4 catalyst (2.65). The Pt-O distance in the first Pt-O shell is same (2.02 Å) for three catalysts, and the Pt-O distance in the second Pt-O shell for the 15anxcr4 and 15impgancr4 catalysts is approximately 2.58 Å. The greater degree of oxidation of the 15anxcr4 and 15impgancr4 samples may account for the longer Pt-Pt distance discussed above.

The Pt coordination number for the 15anxcr4 catalyst was extended up to the forth shell, in an attempt to determine the morphology of these Pt particles, but simply one Pt-Pt shell was obtained for the 15anxcr4 catalyst and 15impgancr4 catalysts through the data analysis. The results indicate that the particle size for the catalyst prepared by the
Pt(NH$_3$)$_4$(NO$_3$)$_2$ salt ion-exchanged, calcined at 350 °C and reduced at 400 °C, is much larger in comparison to those for the catalysts prepared by Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ salt ion-exchanged with the same thermal treatment conditions. The particle size of 15anxcr4 catalyst prepared by the ion exchange method is the smallest compared to the rest of catalysts (see chapter 2).

However, the amplitude of an EXAFS function in k-space depends on both N and the Debye Waller factor ($2\sigma^2$). Consequently, the amplitudes of the peaks for the Fourier transform of an EXAFS function depend on both N and $2\sigma^2$ as well [15]. Thus, the coordination number N is coupled to the Debye Waller factor number and, therefore, the absolute values of the coordination numbers obtained must be used with caution.

### 3.2.1.2 The ex-situ EXAFS Results of 1.5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt L$_{III}$ edge following Hydrogen Chemical Reduction

The EXAFS data displayed in table 3.2 were collected after the catalysts were purged with hydrogen in a gas cell at room temperature. The EXAFS data and Fourier transforms presented in figure 3.2. The EXAFS data was useful out to k=18 Å$^{-1}$ for the 15impgancr4 and 15anxcr4 catalysts, and k=15 Å$^{-1}$ for the 15anxcr4 catalyst.

Comparing the plots shown in figure 3.1 and 3.2, it can be easily seen that treatment of the catalyst samples with hydrogen has a dramatic effect on the local structure of the Pt particles. Both the EXAFS and FT’s following hydrogen treatment indicate that the particles are now much more metallic in nature with a shell structure that reflects the f.c.c. structure of bulk Pt. The data analysis discloses that Pt coordination number (N) in the Pt-Pt first shell for each catalyst increases significantly after catalyst powder was purged by H$_2$ for 2 hours at room temperature. The first shell Pt-Pt coordination number for the 15anxcr4 catalyst (up to 6.19) is the largest with this value decreasing to 6.00 for the 15anxcr4 and 4.28 for the 15impgancr4 catalysts, respectively. Moreover, the value of the distance (R) obtained in the first Pt-Pt shell for each catalyst, approximately 2.75 Å, is consistent with that previously reported by other authors [9, 16]. This value is less than the 2.78 Å of bulk Pt and reflects the small particle size.
The fit for the 15ancr4 catalyst was extended up to 4th shell, and the Pt-Pt coordination number for the 15anxcr4 and 15mpgan4cr4 catalysts was only fitted up to the 2nd shell. Once again, data analysis reveals that there is a Pt-O coordination number (0.71) observed for the reduced 15mpgan4cr4 catalyst. This indicates that it was not possible to fully reduce the Pt particles in this sample at such low temperature and may be related to the smaller particle size as indicated by the smaller first shell Pt-Pt coordination number.

Table 3.2: The results of fit for each Pt shell

(a) The result of fit for the 15ancr4 catalyst, which data was collected at Pt L₃ edge at room temperature following hydrogen chemical reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{el}$/eV</th>
<th>$R_{exafs}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 1 Pt</td>
<td>6.33±0.23</td>
<td>0.0123±0.0003</td>
<td>2.75±0.003</td>
<td>-10.87±0.91</td>
<td>27.99</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>0.88±0.26</td>
<td>0.0070±0.0019</td>
<td>3.91±0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>3.34±0.66</td>
<td>0.0097±0.0014</td>
<td>4.78±0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>6.40±2.38</td>
<td>0.0178±0.0039</td>
<td>5.42±0.021</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit for the 15anxcr4 catalyst, which data was collected at Pt L₃ edge at room temperature following hydrogen chemical reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{el}$/eV</th>
<th>$R_{exafs}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15anxcr4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 1 Pt</td>
<td>6.00±0.15</td>
<td>0.0144±0.0009</td>
<td>2.75±0.002</td>
<td>-9.84±0.54</td>
<td>24.35</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.56±0.49</td>
<td>0.0175±0.0029</td>
<td>3.90±0.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of fit for the 15mpgan4cr4 catalyst, which the data was collected at Pt L₃ edge at room temperature following hydrogen chemical reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{el}$/eV</th>
<th>$R_{exafs}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15mpgan4cr4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 1 O</td>
<td>0.71±0.09</td>
<td>0.0162±0.0033</td>
<td>2.00±0.013</td>
<td>-10.05±0.57</td>
<td>24.55</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>4.28±0.12</td>
<td>0.0147±0.0002</td>
<td>2.75±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>2.03±0.69</td>
<td>0.0256±0.0048</td>
<td>3.89±0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.2: Chi data and their Fourier transforms for the 1.5 wt.% Pt/Y zeolite catalysts, phase corrected. The data were collected at room temperature with hydrogen chemical reduction. The solid line represents the experimental data, and dashed line represents the fitted data. (a) =15an4cr catalyst (b) =15anxcr4 catalyst (c) =15impagancr4 catalyst
3.2.1.3 The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Pt L_{III} edge as prepared

This study is focused on the effects of auxiliary Fe ions, which have been exchanged onto the zeolite prior to the ion exchange of platinum with zeolite. In order to investigate the chemical structure of platinum in detail, the extended X-ray absorption fine structure measurements at the Pt L_{III} were used to detect Pt structure changes. The 15Ptfeancr3 catalyst, prepared by Pt(NH₃)₄(NO₃)₂ salt ion-exchanged with Y zeolite, calcined at 300 °C and reduced at 300 °C, and the 15Ptfeancr4 catalyst, prepared by Pt(NH₃)₄(NO₃)₂ salt ion exchanged with Y zeolite, calcined at 350 °C and reduced at 400 °C, were investigated. The fits (dashed curves) obtained in the curve fitting are presented in figure 3.3, and the parameters are displayed in table 3.3. For 15Ptfeancr3 and 15Ptfeancr4 catalysts, the Chi data were used over the range of wave vectors 2.5 to 16.5 Å⁻¹ and 3.5 to 16 Å⁻¹, respectively.

The CHI data for the two samples are of a poorer quantity than the CHI data for the 1.5 wt. % Pt/zeolite catalysts with several obvious glitches in the data. Curve fittings give rise to an average Pt-O bond distance of 1.99 Å for the 15Ptfeancr3 catalyst and 1.94 Å for the 15Ptfeancr4 catalyst. The distances are slightly shortened as compared to that of 1.5 wt% Pt/zeolite catalysts previously reported (section 3.1.1.1). The fit for the 15Ptfeancr4 catalyst was extended up to the fourth shell. This leads to an improvement in the R_{exafs} value (47.73). The amplitude of the peak at the Pt-Pt distance of 3.99 Å in the Pt-Pt second shell for the 15Ptfeancr4 catalyst is larger than that for the 15Ptfeancr3 catalyst.

On addition of the secondary metal a slight contraction in the coordination distance of the Pt-Pt first shell is observed for two catalysts. Rebecca Mathew demonstrates this phenomenon in her study [17]. The Pt-Pt distance has largely shortened to 2.57 Å for the 15Ptfeancr3 catalyst and 2.56 Å for the 15Ptfeancr4 catalyst respectively, in comparison to that of 2.76 Å for the 1.5 wt. % Pt/zeolite catalysts.

The coordination number is significantly decreased compared to the value obtained for the 1.5 wt. % Pt/zeolite catalysts without Fe ions. This value is sensitive to the reduction temperature and increases upon increasing the temperature to 400 °C. A
second coordination number, approximately 1.00, is observed in the Pt-Pt coordination shell for the 15Ptfeancr4 catalyst. The data analysis reveals that Pt-Fe coordination numbers observed for two catalysts are very similar, approximately 0.54 for the 15Ptfeancr3 catalyst, and 0.65 for the 15Ptfeancr4 catalyst.

Table 3.3: The results of fit for each Pt shell

(a) The result of fit of Pt L_{III} edge EXAFS data for the 15Ptfeancr3 catalyst at room temperature in air

<table>
<thead>
<tr>
<th>15Ptfeancr3</th>
<th>N</th>
<th>$2\sigma^2$ / Å$^2$</th>
<th>R/Å</th>
<th>$E_{ef}$/eV</th>
<th>$R_{exafs}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.92±0.15</td>
<td>0.0046±0.0019</td>
<td>1.99±0.014</td>
<td>-6.67±2.64</td>
<td>59.71</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.26±0.31</td>
<td>0.0153±0.0018</td>
<td>2.57±0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Fe</td>
<td>0.54±0.24</td>
<td>0.0147±0.0064</td>
<td>2.59±0.033</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of Pt L_{III} edge EXAFS data for the 15Ptfeancr4 catalyst at room temperature in air

<table>
<thead>
<tr>
<th>15Ptfeancr4</th>
<th>N</th>
<th>$2\sigma^2$ / Å$^2$</th>
<th>R/Å</th>
<th>$E_{ef}$/eV</th>
<th>$R_{exafs}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.75±0.18</td>
<td>0.0116±0.0049</td>
<td>1.94±0.027</td>
<td>4.22±3.45</td>
<td>47.73</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.55±0.20</td>
<td>0.0128±0.0009</td>
<td>2.56±0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Fe</td>
<td>0.65±0.22</td>
<td>0.0193±0.0052</td>
<td>2.44±0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>1.00±0.49</td>
<td>0.0126±0.0035</td>
<td>3.99±0.025</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.1.4 The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge following Hydrogen Chemical Reduction

Figure 3.4 shows CHI data and Fourier transform collected for the 15Ptfeancr3 and 15Ptfeancr4 catalysts following the hydrogen chemical reduction. The useful data range extends to $k=17$ Å$^{-1}$ for the 15Ptfeancr3 catalyst and 18 Å$^{-1}$ for the 15Ptfeancr4 catalyst respectively. The $\chi(k)$ data shows that the noise level is reduced following hydrogen chemical reduction, in comparison to the data illustrated in figure 3.3. The data analysis shows that $R_{\text{exafs}}$ value is improved significantly for two reduced catalysts, as can be seen in table 3.4.
The amplitude of the main peaks in the Fourier transform for the 15Ptfeancr4 catalyst are slightly larger than that for the 15Ptfeancr3 catalyst. However, data analysis reveals that coordination number in the Pt-Pt first shell, approximately 3.82, is identical for the two catalysts. The difference may be attributed to the Fe coordination number, approaching 1.35 for the 15Ptfeancr3 catalyst and 1.51 for the 15Ptfeancr4 catalyst respectively. The value of the Pt-Pt distance (R) around 2.70 Å or 2.71 Å in the Pt-Pt first shell is almost same for the two catalysts within the fitting error and is contracted compared to the catalyst without Fe. The Pt-Fe distances are also in agreement within the errors of the fits.

Table 3.4: The results of fit for each Pt shell

(a) The result of fit of Pt L\textsubscript{III} edge data for the 15Ptfeancr3 catalyst following hydrogen chemical reduction at room temperature

<table>
<thead>
<tr>
<th>15Ptfeancr3</th>
<th>N</th>
<th>2σ\textsuperscript{2} / Å\textsuperscript{2}</th>
<th>R/Å</th>
<th>E\textsubscript{ct} / eV</th>
<th>R\textsubscript{exafs}(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Fe</td>
<td>1.35±0.38</td>
<td>0.0381±0.0054</td>
<td>2.62±0.026</td>
<td>-9.64±1.10</td>
<td>36.90</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>3.82±0.30</td>
<td>0.0195±0.0007</td>
<td>2.71±0.005</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of Pt L\textsubscript{III} edge data for the 15Ptfeancr4 catalyst following hydrogen chemical reduction at room temperature

<table>
<thead>
<tr>
<th>15Ptfeancr4</th>
<th>N</th>
<th>2σ\textsuperscript{2} / Å\textsuperscript{2}</th>
<th>R/Å</th>
<th>E\textsubscript{ct} / eV</th>
<th>R\textsubscript{exafs}(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Fe</td>
<td>1.51±0.46</td>
<td>0.0383±0.0065</td>
<td>2.59±0.030</td>
<td>-7.35±1.44</td>
<td>41.21</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>3.82±0.36</td>
<td>0.0186±0.0008</td>
<td>2.70±0.006</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.4: Chi data and Fourier transforms for the 1.5 wt.%Pt/Fe/Y zeolite catalysts, phase corrected. The data were collected at room temperature following hydrogen chemical reduction. The solid line represents the experimental data, and dashed line illustrates the fitted data. (a) =15Ptfeancr3 catalyst (b) =15Ptfeancr4 catalyst

3.2.1.5 The ex-situ EXAFS Results of 1.5 wt.% Pt/Fe/Zeolite Catalyst Powders Collected at Fe K edge as prepared

Figure 3.5 illustrates the fitting results of the Chi data and Fourier transform for the 15Ptfeancr3 and 15Ptfeancr4 catalysts. The two sets of data were collected at Fe K edge at room temperature using the as prepared catalysts. The data is only useful out to \( k = 10.5 \, \text{Å}^{-1} \) for the two catalysts, and was fitted in r-space, Å, and the parameters obtained are shown in table 3.5. The \( k^3 \) weight was used for the fit as described previously.

Comparing the \( \chi(k) \) spectra in figure 3.5 (Fe K edge) with those shown in figure 3.4 (Pt L_{III} edge) it is apparent that the coordination around the Fe atoms has much more oxygen character than seen for the Pt. This is reflected in the Fourier transforms.
Notice that the maximum peak is now closer to 2 Å for the Fe K edge data, rather than the 3 Å for the Pt L\textsubscript{III} edge data. The fits to the Fe K edge data shown in table 3.5 confirm the domination of the oxygen neighbours.

The fits for the 15Ptfeancr3 and 15Ptfeancr4 data sets are very similar. The only appreciable differences are in the number of metal (Fe-Fe or Fe-Pt) neighbours and the Fe-Pt distance. The effect of increasing the reduction temperature is to increase the number of Fe-Pt neighbours and to shorten the Fe-Pt distance. This contraction is in agreement with the results obtained at the Pt L\textsubscript{III} edge for the Fe distance. However, the values of distance obtained for the Pt do not agree with those obtained at the Pt L\textsubscript{III} edge. The data quality, however, does not enable a fit with a very good $R_{\text{exafs}}$ value to be obtained. Thus, the errors in the fit parameters are likely to be larger than those calculated by the fitting program. In using these parameters, attention should be paid to trends rather than the absolute values.

Table 3.5: The results of fit for each Pt shell

(a) The result of fit of Fe K edge data for the 15Ptfeancr3 catalyst, at room temperature in air

<table>
<thead>
<tr>
<th>15Ptfeancr3</th>
<th>N</th>
<th>$2\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>$E_{\text{ef}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>2.04±0.17</td>
<td>0.0147±0.0026</td>
<td>1.95±0.013</td>
<td>6.11±1.41</td>
<td>39.90</td>
</tr>
<tr>
<td>Shell 2 Fe</td>
<td>0.92±0.18</td>
<td>0.0170±0.0035</td>
<td>2.45±0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>0.95±0.50</td>
<td>0.0199±0.0155</td>
<td>2.92±0.063</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 O</td>
<td>4.35±0.54</td>
<td>0.0065±0.0047</td>
<td>3.36±0.024</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of Fe K edge data for the 15Ptfeancr4 catalyst at room temperature in air

<table>
<thead>
<tr>
<th>15Ptfeancr4</th>
<th>N</th>
<th>$2\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>$E_{\text{ef}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.40±0.30</td>
<td>0.0236±0.0069</td>
<td>1.91±0.022</td>
<td>15.22±2.30</td>
<td>50.35</td>
</tr>
<tr>
<td>Shell 2 Fe</td>
<td>1.27±0.22</td>
<td>0.0146±0.0026</td>
<td>2.38±0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.90±0.70</td>
<td>0.0235±0.0100</td>
<td>2.72±0.043</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 O</td>
<td>4.84±0.91</td>
<td>0.0121±0.0064</td>
<td>3.24±0.030</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.5: Chi data and Fourier transforms for the 1.5 wt. %Pt/Fe/Y zeolite catalysts, phase corrected. The data were collected at Fe K edge at room temperature in air. The solid line represents the experimental data, and dashed line illustrates the fitted data. (a) =15Ptfeancr3 catalyst (b)=15Ptfeancr4 catalyst

3.2.1.6 The ex-situ EXAFS Results of 5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt L\textsubscript{III} edge as prepared

This study attempts to determine the influence of Pt loading and deposition method on the particle size. The catalysts used are 5 wt.% Pt loading on Y zeolite, prepared by Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2} salt or Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2}/NH\textsubscript{4}NO\textsubscript{3} salt ion exchanged, calcined at 350 °C and reduced at 400 °C, or direct reduced at 400 °C, respectively. The EXAFS data were collected at Pt L\textsubscript{III} edge at room temperature.
Figure 3.6 illustrates the Chi data and their Fourier transforms. The useful data range extends to $k=18\ \text{Å}^{-1}$ for the $5\text{ancr4}$ catalyst, and to $k=17\ \text{Å}^{-1}$ for the $5\text{anxcr4}$ and $5\text{andr4}$ catalysts. The $\chi(k)$ data shows clearly that the noise level is reduced in comparison to the data for the 1.5 wt.% Pt loading catalysts. The data analysis discloses that $R_{\text{exafs}}$ value indicating in the table 3.6 is improved significantly for three catalysts when EXAFS data were fit up to fifth shell. Note that the fifth shell distance is by definition twice first Pt-Pt shell distance.

The value of the distance in the Pt-Pt first shell, around $2.76\ \text{Å}$, for the $5\text{ancr4}$ catalyst is identical for the $5\text{andr4}$ catalyst. The Pt-Pt distance in the Pt-Pt first shell for the $5\text{anxcr4}$ catalyst is slightly contracted to $2.75\ \text{Å}$. This distance is in agreement with the value observed for the 1.5 wt.% Pt loading catalysts discussed previously. The Pt-O distance is the same for all the samples within the fitting errors.

A significant increase in the Pt-Pt coordination number is observed with the use of direct reduction method. No large difference on Pt-O coordination number is observed for the $5\text{ancr4}$ and $5\text{andr4}$ catalysts. A slightly increase in the Pt-O coordination number is observed for the $5\text{anxcr4}$ catalyst.

Table 3.6: The results of fit for each Pt shell

(a) The result of fit of Pt L_{III} edge data for the $5\text{ancr4}$ catalyst at room temperature in air

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>$2\sigma^2$/Å²</th>
<th>R/Å</th>
<th>$E_{\text{ef}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.40±0.05</td>
<td>0.0060±0.0018</td>
<td>2.03±0.009</td>
<td>-10.91±0.37</td>
<td>27.58</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>5.79±0.13</td>
<td>0.0163±0.0002</td>
<td>2.76±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.93±0.30</td>
<td>0.0167±0.0016</td>
<td>3.90±0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>4.72±0.49</td>
<td>0.0162±0.0010</td>
<td>4.80±0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 5 Pt</td>
<td>5.79±1.14</td>
<td>0.0210±0.0027</td>
<td>5.44±0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(b) The result of fit of Pt L\textsubscript{III} edge data for the 5anxcr4 catalyst at room temperature in air

<table>
<thead>
<tr>
<th>5anxcr4</th>
<th>N</th>
<th>$2\sigma^2 / \text{Å}$</th>
<th>R/Å</th>
<th>$E_{\text{ef}}/\text{eV}$</th>
<th>$R_{\text{exafs}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.95±0.06</td>
<td>0.0123±0.0014</td>
<td>2.00±0.006</td>
<td>-10.78±0.43</td>
<td>19.69</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>4.35±0.11</td>
<td>0.0159±0.0002</td>
<td>2.75±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.54±0.34</td>
<td>0.0190±0.0023</td>
<td>3.90±0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>4.08±0.62</td>
<td>0.0192±0.0015</td>
<td>4.79±0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 5 Pt</td>
<td>5.44±1.06</td>
<td>0.0210±0.0021</td>
<td>5.42±0.011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of fit of Pt L\textsubscript{III} edge data for the 5andr4 catalyst at room temperature in air

<table>
<thead>
<tr>
<th>5andr4</th>
<th>N</th>
<th>$2\sigma^2 / \text{Å}$</th>
<th>R/Å</th>
<th>$E_{\text{ef}}/\text{eV}$</th>
<th>$R_{\text{exafs}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.30±0.09</td>
<td>0.0093±0.0062</td>
<td>2.02±0.028</td>
<td>-11.97±0.46</td>
<td>14.67</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>8.00±0.14</td>
<td>0.0128±0.0001</td>
<td>2.76±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>3.36±0.45</td>
<td>0.0144±0.0014</td>
<td>3.91±0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>5.31±0.48</td>
<td>0.0093±0.0008</td>
<td>4.79±0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 5 Pt</td>
<td>7.30±0.85</td>
<td>0.0105±0.0011</td>
<td>5.46±0.008</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.6: Chi data and their Fourier transforms for the 5 wt.% Pt/Y zeolite catalysts, phase corrected. The data were collected at room temperature at Pt L_{III} edge in air. The solid line represents the experimental data, and dashed line illustrates the fitted data. (a) =5anr4 catalyst (b) =5anxcr4 catalyst (c) =5andr4 catalyst
3.2.1.7 The ex-situ EXAFS Results of 5 wt.% Pt/Zeolite Catalyst Powders Collected at Pt $L_{\text{III}}$ edge following Hydrogen Chemical Reduction

Figure 3.7 illustrates the EXAFS data and the Fourier transforms of these data. The data were collected at Pt $L_{\text{III}}$ edge following hydrogen chemical reduction at room temperature. The results of fitting the EXAFS data are presented in table 3.7.

For the 5anxcr4 and 5andr4 catalysts the Chi data at the Pt $L_{\text{III}}$ edge was useful over the range of wave vectors from 2 to 16.5 Å$^{-1}$, respectively. For the 5anxcr4 sample the Chi data was useful out to 14.5 Å$^{-1}$.

The figure shows that the curves of the fits match the raw data very well. The quality of fit is indicated by the goodness fit value $R_{\text{exafs}}$ which is smaller than 35 for all three catalysts. The data analysis reveals that Pt coordination number in the Pt-Pt first shell for the 5andr4 catalyst, approximately 8.13, is greater than those of 5anxcr4 and 5andr4 catalysts. The multiple-shell fitting for Pt neighbours is up to the fourth Pt-Pt shell.

Surprisingly, Pt-O coordination number, approximately 0.55 is observed for the 5anxcr4 catalyst after it was chemically reduced by hydrogen at room temperature. The result is in common to the phenomenon observed for the 15impganxcr4 catalyst. The value of Pt-O distance, approximately 1.93 Å, is consistent with the values found for other oxidised catalysts presented earlier. The values of Pt distance in the Pt-Pt first shell, approximately 2.76Å for the 5anxcr4 and 5anxcr4 catalysts and 2.75 Å for the 5andr4 catalyst, are consistent with those shown previously in this report.
Table 3.7: The results of fit for each Pt shell

(a) The result of fit of Pt L_{III} edge data for the 5ancr4 catalyst following hydrogen chemical reduction at room temperature.

<table>
<thead>
<tr>
<th>5ancr4</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{\text{cf}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>7.47±0.27</td>
<td>0.0124±0.0003</td>
<td>2.75±0.003</td>
<td>-10.99±0.8</td>
<td>24.19</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>0.47±0.16</td>
<td>0.0118±0.0068</td>
<td>3.88±0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>4.53±0.95</td>
<td>0.0083±0.0019</td>
<td>4.79±0.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>6.57±1.50</td>
<td>0.0114±0.0023</td>
<td>5.45±0.014</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of Pt L_{III} edge data for the 5anxcr4 sample following hydrogen chemical reduction at room temperature.

<table>
<thead>
<tr>
<th>5anxcr4</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{\text{cf}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.56±0.12</td>
<td>0.0149±0.0080</td>
<td>1.93±0.020</td>
<td>-8.64±0.56</td>
<td>19.14</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>6.02±0.14</td>
<td>0.0126±0.0002</td>
<td>2.75±0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>1.81±0.50</td>
<td>0.0168±0.0021</td>
<td>3.89±0.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>4.33±0.70</td>
<td>0.0149±0.0015</td>
<td>4.78±0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 5 Pt</td>
<td>5.93±1.18</td>
<td>0.0173±0.0024</td>
<td>5.42±0.025</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of fit of Pt L_{III} edge data for the 5andr4 sample following hydrogen chemical reduction at room temperature.

<table>
<thead>
<tr>
<th>5andr4</th>
<th>N</th>
<th>$2\sigma^2$ / Å²</th>
<th>R/Å</th>
<th>$E_{\text{cf}}$/eV</th>
<th>$R_{\text{exafs}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>8.31±0.15</td>
<td>0.0108±0.0001</td>
<td>2.76±0.001</td>
<td>-11.08±0.44</td>
<td>15.50</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>3.03±0.43</td>
<td>0.0131±0.0010</td>
<td>3.91±0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>6.28±0.57</td>
<td>0.0112±0.0006</td>
<td>4.79±0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>7.49±0.98</td>
<td>0.0133±0.0009</td>
<td>5.45±0.006</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.7: Chi data and their Fourier transforms for the 5 wt.%Pt/Y zeolite catalysts, phase corrected. The data were collected at Pt L_{III} edge at room temperature with hydrogen chemical reduction. The solid line represents the experimental data, and dashed line illustrates the fitted data. (a) =5anr4 catalyst (b)=5anxer4 catalyst (c)=5andr4 catalyst
3.2.2 The results of BET surface area measurement

Volumetric uptake plots for the various catalysts investigated and a comparison of the calculated surface areas is shown in figure 3.8 and table 3.8, respectively. The values for the plain zeolite sample and a plain untreated XC-72R carbon powder are also shown in the table.

As can be seen in the table, the surface area for plain zeolite is greater than that obtained for any of the Pt zeolite catalysts. This reflects the blocking of pores upon the deposition of the Pt onto the zeolite. The extent of pore blocking/loss of surface area is greatest of the 15anr4 catalyst. In general, loading with 1.5 wt.% ~ 5 wt.% Pt decreases the surface area to 540-590 m²g⁻¹. Addition of Fe (98.0 wt.%) causes a further decrease to 350-375 m²g⁻¹.

By comparison of the BET results with the EXAFS analysis some conclusions regarding the location of the Pt may be made. This will be discussed at the end of this chapter.

Table 3.8: BET surface areas for various catalysts calculated for the N₂ uptake curves presented in figure 3.8.

<table>
<thead>
<tr>
<th>Acronym Name</th>
<th>Surface Area m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain zeolite powder</td>
<td>632.3 ± 0.1 %</td>
</tr>
<tr>
<td>Plain untreated XC-72R carbon powder</td>
<td>200 ± 0.1 %</td>
</tr>
<tr>
<td>15anr4 catalyst</td>
<td>168 ± 10.0 %</td>
</tr>
<tr>
<td>15anxcr4 catalyst</td>
<td>539 ± 1.0 %</td>
</tr>
<tr>
<td>15mpganr4 catalyst</td>
<td>376± 2.5 %</td>
</tr>
<tr>
<td>15Pfteancr3 catalyst</td>
<td>371± 5.0 %</td>
</tr>
<tr>
<td>15Pfteance4 catalyst</td>
<td>346± 3.0 %</td>
</tr>
<tr>
<td>5anr4 catalyst</td>
<td>553 ±1.0 %</td>
</tr>
<tr>
<td>5anxcr4 catalyst</td>
<td>563± 1.5 %</td>
</tr>
<tr>
<td>5andr4 catalyst</td>
<td>592±6.9 %</td>
</tr>
</tbody>
</table>
Figure 3.8: Volumetric uptake of nitrogen at 77 K for the catalysts. The blue points represent the adsorption volume and the red points represent the desorption volume. The units of $\text{vol Ads (ccg}^{-1}$) are cm$^3$ g$^{-1}$. 
3.2.3 XRD Characterisation

The XRD spectra were only collected for the catalysts where the BET surface areas were significantly less than that of the plain zeolite material. The main propose of these measurements was to examine if the crystalline structure of the zeolite changes during the thermal treatment and metal desorption. Consequently, detailed data analysis to obtain the unit cell parameters was not carried out. Figure 3.9 presents the XRD patterns for the 15anxcr4 and 5anxcr4 catalysts. The XRD pattern for plain zeolite was determined as well in order to compare it with those as prepared, and is shown in figure 3.10. The data were collected as a function of the angle 2θ as a function of over the range 5° ~ 44° at room temperature.

The full analysis of the XRD patterns for samples such as the zeolites used in this project is very complex and beyond the scope of this thesis. Instead, the qualitative features of the XRD patterns are compared to determine whether the metal deposition process causes a loss of the zeolite structure.

The figures show that the intensity of XRD pattern for plain zeolite is the largest in comparison to 15anxcr4 and 5anxcr4 catalysts. A loss of intensity is observed in the XRD pattern for each catalyst. The intensity of the XRD pattern for the Pt excess nitrate salt ion-exchanged 15anxcr4 catalyst is decreased dramatically as compared to that of 5anxcr4 catalyst and plain zeolite sample, as indicated at a 2θ angle of around 10°.

Figure 11 presents the XRD pattern for the 15ancr4 and 15impgancr4 catalysts, and figure 12 shows the XRD pattern for the 15Ptfeancr3 and 15Ptfeancr4 catalysts respectively. The XRD patterns were collected over a 2θ range of 10° ~ 45° in air at room temperature. It is apparent that the data quality of XRD patterns presented in figure 3.11 and 3.12 are poorer as compared to the features shown in figure 3.9 and 3.10. This is due to a shorter data collection time, 1 hr, rather than 8 hrs.

When the XRD patterns for the plain zeolite, figure 3.9, and the metal loaded zeolites, figures 3.10, 3.11 and 3.12, are compared the main differences are a loss in intensity of the diffraction peaks and a slight shift in their position. The loss in intensity indicates a
loss in crystallinity, whilst the decrease in the 2θ position of the peaks suggests an increase in the lattice constant. However, the presence of the XRD peaks and the similarity to that obtained for the plain zeolite indicates that the structural changes upon metal loading are not severe.

Figure 3.9: XRD pattern for plain Na Y zeolite
Figure 3.10: XRD pattern for the 5anxcr4 and 15anxcr4 catalysts
Figure 11: XRD pattern for the 15ancr4 and 15impancr4 catalysts
Figure 12: XRD pattern for the 15Pfeanrc3 and 15Pfeanrc4 catalysts
3.2.4 The Relationship between Pt loading and the Pt
Particle Size

3.2.4.1 The actual Pt loading on zeolite determined by the edge jump

The actual Pt loading on zeolite may be calculated by the use of the edge jump obtained from the EXAFS data background subtraction with the aid of the EXBROOK program. As introduced in section 2.5.1.1 of chapter 2, the total linear absorption coefficient \( \mu \) (cm\(^{-1}\)) for the primary beam is defined by the natural log of the ratio emergent \( (I) \) and incident intensity \( (I_o) \). Consequently, the edge step of a specific element can be expressed as follows:

\[
\ln(I/I_o) = \mu \chi
\]  

(3.2.4.1.1)

Here, \( \chi \) (cm) represents the thickness of the material used during the course of measurement. Since the reduction of intensity is determined by the quantity of matter traversed by the primary beam, the absorber thickness is often expressed on a mass basis, in gram per square cm, and subsequently, the mass absorption coefficient \( \mu/\rho \) (cm\(^2\)/g) is defined, where \( \rho \) is the density of the absorber. Thus:

\[
\mu \chi = (\mu/\rho)(m/S)
\]  

(3.2.4.1.2)

where \( m \) = total mass of the element interested and \( S = \) cross sectional surface area of the pellet.

The value of mass absorption coefficient \( \mu/\rho \) can be obtained from the literature for each element. For Pt at the L\(_{\text{III}}\) edge at room temperature the \( \mu/\rho \) is known to be 179 (cm\(^2\)/g) [20]. The die used to prepare the pellet was the diameter of 1.3 cm, and gives the value of the area for the sample pellet of 1.327 cm\(^2\). Consequently, the mass of Pt contained in the pellet can be obtained from the following formula:

\[
m = (\mu \chi) \ast (S)/(\mu/\rho)
\]  

(3.2.4.1.3)
Consequently, the Pt mass quantity on the zeolite can be calculated by the formula below:

\[
Pt \text{ wt.\%} = \frac{[\mu S]}{[\mu M]}/\text{M} \times 100\%
\]

(3.2.4.1.4)

where M is the total mass of Pt/zeolite sample in the pellet.

Table 3.9 displays the calculated loading of Pt on the zeolite in weight percentage (%) for the catalysts discussed previously.

<table>
<thead>
<tr>
<th>Acronym Name</th>
<th>Edge jump</th>
<th>The total mass of Pt/zeolite sample used (mg)</th>
<th>Calculated mass quantity in wt. percentage (%)</th>
<th>Mass quantity as proposed wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>0.5138</td>
<td>250</td>
<td>1.52</td>
<td>1.5</td>
</tr>
<tr>
<td>15anxcr4</td>
<td>0.3084</td>
<td>298</td>
<td>0.77</td>
<td>1.5</td>
</tr>
<tr>
<td>15impganr4</td>
<td>0.6789</td>
<td>300.2</td>
<td>1.68</td>
<td>1.5</td>
</tr>
<tr>
<td>15Ptfeanr3</td>
<td>0.6248</td>
<td>312</td>
<td>1.49</td>
<td>1.5</td>
</tr>
<tr>
<td>15Ptfeane4</td>
<td>0.6227</td>
<td>300</td>
<td>1.54</td>
<td>1.5</td>
</tr>
<tr>
<td>5ancr4</td>
<td>1.0467</td>
<td>100</td>
<td>7.76</td>
<td>5.0</td>
</tr>
<tr>
<td>5anxcr4</td>
<td>0.6352</td>
<td>102</td>
<td>4.71</td>
<td>5.0</td>
</tr>
<tr>
<td>5andr4</td>
<td>1.0102</td>
<td>101.2</td>
<td>7.40</td>
<td>5.0</td>
</tr>
</tbody>
</table>

As can be seen in the table, the value of Pt loading on zeolite in percentage for the 15ancr4 and 15Ptfeanr3 or 15Ptfeane4 catalysts are close to the values of 1.5 wt.% Pt loading on zeolite as proposed. Nevertheless, the calculation shows that the loss of Pt quantity for the 15anxcr4 catalyst is significant during the preparative process, as demonstrated by the value approximately 0.77 wt.% indicated in the table 3.9. The Pt loading on zeolite for the 15impganr4 catalyst prepared by the impregnation method, approximately 1.68 wt.%, is 0.18 wt.% higher than the value of 1.5 wt.% on zeolite as proposed. Moreover, Pt loading on zeolite for the 5ancr4 and 5andr4 samples is 7.76 wt.% and 7.40 wt.% respectively. The value is significantly greater than the theoretical 5 wt.% Pt loading and reflects an error in preparation of the ion exchange solutions or in the hydration of the zeolite powder used. The calculation reveals that the value of Pt loading on zeolite for the 5anxcr4 catalyst, around 4.71, is close to the prepared value of 5 wt.% Pt loading on zeolite.
3.2.4.2 Estimation of Pt Particle Size

As introduced in the section 2.5.1 of chapter 2, the average Pt nearest-neighbour coordination number $\bar{N}_i$ and the Pt-Pt distance in each shell are directly determined in the fitting the spectra. The cluster size and geometry may be estimated by the use of the mean first-nearest-neighbour coordination number $\bar{N}_i$ of atoms in a cluster according to the method given by Benfield [18]. In this method, $\bar{N}_i$ is regarded as a function of cluster edge length, and the formulae for $\bar{N}_i$ have been derived for two geometrical models, icosahedral and cuboctahedral. Benfield suggested that an icosahedral cluster might be more metallic than a cuboctahedral model with the same number of atoms. Consequently, we assume that the Pt structure for the Pt/zeolite catalysts discussed in this chapter have an icosahedral model.

The icosahedron proposed by Benfield is represented in figure 14 [18]. The model consists of concentric shells of atoms. It assumes that the central atom is counted as the first shell. Subsequently, $m$ complete shells in a cluster consist corresponds to the edge length of $m$ atoms. The total number of atoms in a cluster is calculated numerically with the aid of formula shown as follows:

$$N_{\text{total}} = \frac{1}{3}(2m-1)(5m^2 - 5m + 3)$$  \hspace{1cm} (3.2.4.2.1)

Moreover, the mean first-nearest-neighbour coordination number, $\bar{N}_i$, for the icosahedron in terms of cluster edge length $m$ atoms is given by the following formula:

$$\bar{N}_i (\text{icos}) = \frac{6[(m-1)(20m^2-25m+12)]}{[(2m-1)(5m^2-5m+3)]}$$  \hspace{1cm} (3.2.4.2.2)

Table 3.10 displays the value of $\bar{N}_i$ and the corresponding total atomic number of atoms in the cluster for the catalysts following $H_2$ chemical reduction. The reduced data were chosen, as there is less interference from the presence of oxygen neighbours in the first coordination shell. The presence of oxygen neighbours will cause an underestimation of the particle size, as these replace some of the Pt neighbours and lower the $N_i$(Pt-Pt) value. It should be noted that this model has serious limitations, as the formula for $\bar{N}_i$ is very dependent on the particle shape chosen. For example a disc
shaped particle of the same diameter will have a smaller average \( N_j \) than a spherical particle. However, the assumption that the particles may be represented by icosahedra is supported by previously published TEM images [19]. The values obtained for the number of atoms in the cluster should be treated as the lower limits. Studies of f.c.c. and b.c.c. dispersed metal particles have confirmed that use of the \( N_j \) values results in underestimation of the particle size [13, 18, 20].

Table 3.10: the value of Pt particle on zeolite

<table>
<thead>
<tr>
<th>Acronym Name</th>
<th>( N_j ) from refinement</th>
<th>Total atoms in the cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>6.33</td>
<td>13</td>
</tr>
<tr>
<td>15anxcr4(^b)</td>
<td>6.00</td>
<td>13</td>
</tr>
<tr>
<td>15impgancr4</td>
<td>4.28</td>
<td>13</td>
</tr>
<tr>
<td>15Ptfeancr3</td>
<td>5.17(^a)</td>
<td>13</td>
</tr>
<tr>
<td>15Ptfeance4</td>
<td>5.33(^a)</td>
<td>13</td>
</tr>
<tr>
<td>5ancr4</td>
<td>7.47</td>
<td>55</td>
</tr>
<tr>
<td>5anxcr4(^p)</td>
<td>6.02</td>
<td>13</td>
</tr>
<tr>
<td>5andr4</td>
<td>8.31</td>
<td>55</td>
</tr>
</tbody>
</table>

\(^a\) \( N_j = N_j \) (Pt-Pt) + \( N_j \) (Pt-Fe)

\(^b\) Oxygen neighbours present in the first coordination shell.

Figure 3.14: the icosahedron structure with 147 atoms (\( m=4 \)), atom 6 represents the vertex atom with 6-coordinate, atom 8 shows edge atom with 8-coordinate, atom 9 represents the atom with 9-coordinate in the triangular face [18].
For the 15Ptfeancr3 and 15Ptfeancr4 catalysts the sum of the $N_j$ (Pt-Pt) and $N_j$ (Pt-Fe) coordination numbers was used. Nevertheless, the calculation shows that the particle size for the 15Ptfeancr3 and 15Ptfeancr4 catalyst is smaller than the other catalysts. This is reflected in the shorter Pt-Pt distance obtained when fitting the EXAFS data, approximately 2.70 Å rather than the 2.75 Å obtained for the other catalysts.

### 3.3 Discussion and Conclusion

We have estimated Pt particle size of the catalysts as prepared according to the method given by Benfield. The particle size is proportional to the number of atoms in the cluster. These values have been presented in table 3.10. It is apparent that the Pt particles for the 5andr4 and 5anr4 catalysts, consisting of 55 atoms as estimated in the cluster are the largest, as compared to 5anxcr4 catalyst and 1.5 wt.% Pt/zeolite catalysts which give 13 atoms in the clusters. A Pt-Pt distance in the Pt first shell, approximately 2.76 Å, is observed for the 5andr4 and 5anr4 catalysts, whilst a Pt-Pt distance, around 2.75 Å, is observed for the 5anxcr4 catalyst. These values are in good agreement with the results obtained by Koningsberger group, who suggested that this distance was characteristic of metallic Pt [9, 16]. Moreover, the fit of the EXAFS data up to the Pt-Pt fourth shell predicts that the Particle size is around 1.0 ~ 1.1 nm in diameter for the 5anr4 and 5andr4 catalysts. The Pt particle size for the 5anxcr4 catalyst is much smaller than those of 5anr4 and 5andr4 catalysts.

A significant decrease of Pt particle size is observed upon reducing the value of Pt loading from 5 wt.% to 1.5 wt.% The Pt particle size, consisting of 13 atoms in a cluster, for the 15anxcr4 catalyst is slightly smaller than that for the 15anr4 catalyst, for which the fit of data was extended to forth shell (section 3.2.1.2). The decrease of Pt particle size for the 15anxcr4 and 5anxcr4 catalysts prepared with $[\text{Pt(NH}_3\text{)}_4]^{2+}/\text{NH}_4^+$ ion exchange indicates that there is a different structural interaction occurring between Pt and the zeolite compared to the 15anr4 and 5anr4 catalysts prepared with just $[\text{Pt(NH}_3\text{)}_4]^{2+}$. The Pt-Pt distances in the first shell for the as prepared 1.5 wt.% catalysts are 2.76 Å for the 15anr4 catalyst and 3.06 Å for the 15anxcr4 catalyst. The longer distance indicates that these particles are more oxidised in the as prepared state. However, the Pt-Pt distances after hydrogen chemical reduction are all still 2.75 Å, indicating that the smaller Pt particles are also metallic in nature following reduction.
The smallest particles were found for the 15impgancr4 catalyst prepared by using [Pt(NH$_3$)$_4$]$^{2+}$, with Pt particles consisting of 13 atoms in the cluster. Once again, the as prepared catalyst has a first shell Pt-Pt distance of 3.05 Å, whilst following hydrogen chemical reduction the Pt-Pt distance is decreased to 2.75 Å.

The EXAFS analysis provides an indication of the average metal particle size. However, it does not indicate where the particles are located on the zeolite structure. BET surface area measurements, however, give evidence of pore blocking within the zeolite support and, thereby, some evidence of the location of the metal particles. In addition, the powder XRD results allow changes in the crystallinity of the zeolite support upon metal deposition to be observed.

A slight decrease of the BET surface area is observed for the 5 wt.% Pt loading catalysts (5andr4, 5ancr4, and 5anxcr4), see table 3.8. An XRD pattern was collected for the 5anxcr4 catalyst (see figure 3.10). Comparing this pattern to that of the plain zeolite, it can be seen that the positions of the peaks are slightly shifted to larger angles, but the d values are similar. Therefore it may be concluded that the deposition of the metal has not significantly affected the zeolite structure. The decrease in the surface area may then be attributed to blocking of the smaller pores in the zeolite.

The BET surface areas for the 1.5 wt.% Pt loading catalysts (15anxcr4, 15anxcr4, 15impgancr4) depend on the deposition method, see table 3.8. The largest surface area is retained with the 15anxcr4 deposition method, 539 m$^2$ g$^{-1}$, compared to 376 m$^2$ g$^{-1}$ for the 15impgancr4 and 168 m$^2$ g$^{-1}$ for the 15anxcr4. The XRD patterns for each of the 1.5 wt.% catalysts also show that the crystal structure of the zeolite support is not significantly changed. The actual loading of the metal on the zeolite is only 0.77 wt.% for the 15anxcr4, whilst the loadings for the 15impgancr4 and 15anxcr4 catalysts are much closer 1.5 wt%, being 1.68 wt.% and 1.52 wt.%, respectively.

The main effect of the addition of excess NH$_4$NO$_3$ is to replace the Na$^+$ ions on the zeolite structure with NH$_4^+$. During the calcination step the NH$_4^+$ ions are converted to H$^+$. The Na$^+$ ions are strongly affiliated to the Al atoms on the zeolite cage walls. The H$^+$ ions are also affiliated to the Al atoms, but also form hydrogen bonds to the O atoms on the zeolite cage walls. The presence of the H$^+$ ions helps anchor the Pt
particles to the zeolite cage walls. This helps to keep the Pt in the supercages of the zeolite [21]. Restricting the Pt particles to the supercages, rather than the sodalite cages helps to preserve the BET surface area of the catalyst. The competition between the Pt\(^{2+}\) and the NH\(_4^+\) ion exchange processes may account for the decrease in the loading (yield) observed for the 15anocr4 catalyst.

For the case of 15imp ganocr4 catalyst the BET surface area is significantly less than that of the plain zeolite. This indicates that the pore structure of the zeolite is blocked by the Pt particles. However, the average particle size obtained from the EXAFS analysis indicates that the particles are the smallest observed in this study as the first mean coordination number, approximately 4.28 (although consisting of 13 atoms in the cluster), is smaller than those obtained from others. As described in the chapter 2, impregnation is expected to result in a shell distribution of the Pt particles on the zeolite structure. Thus, the very small Pt particles formed may be aggregating at the openings of the pores, effectively blocking them.

The smallest BET surface area was obtained for the 15anocr4 catalyst. In this deposition method a shell distribution is not predicted. However, without the H\(^+\) ions to anchor the Pt particles to the zeolite cage walls, the particles become mobile during the reduction process and may migrate to block the pore openings.

The effect of ion exchange with Fe\(^{2+}\) ions prior to ion exchange with Pt\(^{2+}\) is similar to that of the presence of excess H\(^+\) ions. The Fe\(^{2+}\) helps to anchor the Pt particles to the cage walls, restricting the mobility of the Pt during the reduction process. The particle sizes obtained for the 15Ptfeanocr3 and 15Ptfeanocr4 catalysts were both very small, consisting of 13 atoms on average in the cluster, respectively. The BET surface areas 371 m\(^2\)/g and 346 m\(^2\)/g for the 15Ptfeanocr3 and 15Ptfeanocr4 catalysts, respectively, reflect a 50% decrease in the surface area compared to the plain zeolite. This reduction in surface area, however, is not attributed to the Pt particles; rather it may be accounted for by the Fe species [21].

The study carried out by Sachtler et. al [21] has shown that Fe\(^{3+}\) cations incorporated into the zeolite by ion exchange are oxidized to Fe\(^{3+}\) during the calcination period. The Fe\(^{3+}\) ions are more favourably located in the small cages (sodalite cages and hexagonal
prisms) due to the high charge density. Thus, when Pt$^{2+}$ is subsequently exchanged the presence of the Fe$^{3+}$ in the smaller cages helps to confine the Pt$^{2+}$ to the supercages. Furthermore, the Fe$^{3+}$ remaining in the supercages can be reduced to Fe$^{2+}$ at the temperature we have chosen.

In summary, the results presented in this chapter demonstrate that the deposition method and the Pt loading have a significant effect on the particle size for the catalysts prepared. In addition, the distribution of the Pt particles on and in the zeolite support is also affected by the deposition method. The different Pt particle sizes and distributions may result in changes in the catalytic and electrochemical activities of the catalysts. The electrochemical response will be examined in chapter 4 and the catalytic behaviour in chapter 5.
3.4 References


Chapter 4: Electrochemical Characterization of Pt Particles Supported on Y Zeolite

4.1 Introduction

Zeolite and zeolite supported platinum catalysts are widely used in commercially important reactions, which are related to the petroleum industry. Recently, such kinds of catalysts have been of increased interest in terms of their electrochemical properties and application as electrocatalysts.

From the perspective of zeolite science, zeolites are dc electronic insulators and, therefore, cannot be used as direct electrode materials, but they can act as an electron bank to contribute electrons to or garner electrons from a reactant [1, 2]. However, zeolites are ionic conductors due to the influence of the Bronsted sites. Thus, they are capable of solution – like ionic condition [1, 2]. This link in common with the electrochemical environment means that electrochemical reactions of Y zeolite, similar to that of chemical and catalytic reactions can occur in a charge – balanced ionic environment. Their physical structure and chemical nature can affect electron transfer reaction between Pt and their support. Beyond the fundamental study of the interaction nature of platinum with zeolite, the influence of known chemical steps that are coupled to electron transfer steps may be fully investigated at the electrode–solution interface. Meanwhile, it is possible to find new chemical steps arising from the interaction of the electron – transfer reactants or products with the zeolite in an electrochemical interphase that does not usually appear at the electrode – solution interface in the absence of the zeolite [2].

In this project, we choose the Y type of zeolite as the Pt support, as it has the function of thermal stability at high temperature and a particular cage structure with pore opening suitably used at electrochemistry interfaces. The intrinsic properties of the Pt/zeolite electrocatalysts in the form of electrodes were initially characterised using cyclic voltammetry (CV) techniques as these can provide a quick and easy method to determine the electrochemical activity of species in solution and on the electrode.
surface. The detailed structural characterisation of Pt particles has been probed by the use of in-situ X-ray adsorption spectroscopy (XAS) and in particular the fine structure known as Extended X-ray Absorption Fine Structure (EXAFS). The experiments were carried out using the synchrotron radiation source based at Daresbury National Laboratory. Until now, no literature record can be found to elucidate the structure and electronic properties of Pt by using cyclic voltammogram and in-situ EXAFS techniques in an electrochemical environment.

The 1.5 wt.% Pt loading and 5 wt.% Pt loading Pt/zeolite samples used in the following discussion were mostly made by the ion – exchange method. However, the impregnation method was also employed to prepare a 1.5 wt.% Pt/zeolite sample in order to investigate the effect on Pt particle size and dispersion with the use of different metal deposition methods. The CV measurements were conducted in acid electrolyte solution. Particular attention was paid to the hydrogen adsorption/desorption features of the Pt cyclic voltammogram.

### 4.2 Brief Experimental Reminder

#### 4.2.1 The Summary of the type of Pt Zeolite Electrocatalysts

Preparation of the platinum microstructure in Y zeolite was carried out following the procedure developed by Gallezot and co-workers [3] and described in detail in chapter 2. The 1.5 wt.% Pt/zeolite and 5 wt.% Pt/zeolite catalysts were prepared by using Pt(NH$_3$)$_4$(NO$_3$)$_2$ salt or Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ salt ion-exchanged with zeolite, and then were calcined at 350 °C and reduced in a fluidised bed reactor at 400 °C. The impregnation method was used to prepare the 1.5 wt.% Pt loading sample calcined at 350 °C and reduced at 400 °C. The temperature was varied, either at 300 °C or 400 °C to reduce 1.5 wt.% Pt /Fe/zeolite sample, in which iron was used to block the small zeolite cages according to the ratio of Pt loading with Al$^+$ sites (Brønsted site).

#### 4.2.2 Nafion® Bound Electrodes

There are two types of polymer binders available for the electrode fabrication, PTFE and Nafion®, each of which give rise to different cyclic voltammogram. The PTFE
binder was used initially in the experiment. However, PTFE doesn't give a clear CV in the hydride region due to the high resistance of the PTFE bound electrodes. Hence, Nafion bound electrodes were chosen throughout all the electrochemical measurements presented in this thesis.

The procedure to make electrodes was identical for all types of Pt zeolite catalysts. The catalyst powder (100mg for Pt/zeolite) was first ground with a mortar and pestle, and then, the ground XC-72R carbon powder (100mg, untreated XC-72R), that is used to enhance the electrode performance and to facilitate the spreading of catalyst, was added to mix with the catalyst powder. Meanwhile, the appropriate amount of Nafion® (5 wt.% solution in lower alcohols from Aldrich) to form 15 wt.% in the electrode was added to 1 ml water. The solution was added to the powder mixture and stirred thoroughly to give a thin paste that was then agitated in an ultrasonic bath for 2 hours. The resulting thick paste was then spread on to carbon paper (E-TEK TGHP-90) with a spatula and hot pressed at 100 °C at 75 kg/cm^2 for 3 minutes. The carbon paper has the function of collecting current in the electrochemical experiment. The electrodes were cut from the compressed sheet to the require size, 1 cm^2 for cyclic voltammetry measurements.

The electrodes used for the in-situ EXAFS measurement were fabricated by using Nafion® as binder as well. The quantity of catalyst in the electrode (1.8 cm^2 area) was dependent on the type of EXAFS measurement.

4.2.3 The Electrochemical Experimental Procedure

The electrochemical experiment was carried out in a glass cell shown in figure 2.9 in section 2.3.3 of chapter 2, which is fitted with three electrodes; reference electrode, counter electrode and working electrode.

The counter electrode (CE) was high surface area platinum gauze. This design is to ensure that polarization at the counter electrode could be minimised. The reference electrode (RE) was an Hg/Hg_2SO_4 (MMS) electrode, immersed in an electrolyte, such as sulphuric acid. The RE potential was calibrated periodically by comparison to Pt
gauze in H₂(g) purged acid solution. The working electrode sealed in a PTFE ring was positioned as close as possible to the luggin capillary of the reference electrode.

2.5 mol dm⁻³ H₂SO₄ made with purified water from the Barnstead system (18 MΩ cm), either 150 cm³ or 180 cm³, was used to fill the electrochemical cell. Subsequently, an inert gas, N₂ was introduced to purge the electrolyte solution thoroughly during the course of experiment. Therefore, oxygen can be removed from the cell to prevent current produced by the reduction of oxygen. Cyclic voltammograms were recorded between −0.65 V to 0.5 V using a computer-controlled potentiostat (Autolab PGSTAT20). All potentials quoted were with respect to MMS reference electrode, and CVs were recorded at 1 mV/s due to the low quantity of Pt loading (0.1667 g cm⁻² maximum) and high capacitance.

Carbon monoxide (CO) is a well-known poison to the Pt surface, as it can be strongly adsorbed on the Pt surface to form a monolayer, either chemically or electrochemically. Thus, it is used practically to measure Pt surface area. The experiment was conducted in the same glass cell illustrated above. The saturated CO solution was prepared by passing CO gas through the electrolyte solution in the cell. The potential was held to set at −0.55 V for 45 minutes. Following the CO purge, N₂ was introduced into the cell continuously to purge electrolyte solution for further 30 minutes in order to remove any remaining CO in the solution. Cyclic voltammetry was carried out by sweeping potential from negative potential at −0.55 V towards to positive potential at 0.5 V, and then back between −0.65 V to +0.50 V until a cyclic voltammogram (CV) corresponding to that of a clean platinum electrode (without CO exposure) was obtained.

4.3 Results

4.3.1 The Results of 40 wt.% Pt/C Electrode

A brief study for a 40 wt.% Pt/XC-72R electrode was undertaken to be able to compare the features of 1.5 wt.% Pt/zeolite and 5 wt.% Pt/zeolite electrodes. The typical features of a cyclic voltammogram (CV) for a 40 wt.%Pt/XC-72R electrode can be distinguished in figure 4.1 and figure 4.2, overleaf. The two, separated, quasi-reversible
peaks at negative potentials represent hydrogen adsorption and desorption on the Pt surface.

A set of cyclic voltammograms with the scan rates at 20 mV/s and 1 mV/s were recorded to determine the influence of sweep rate on the peaks. A sweep rate of 1 mV/s (fig.4.2) gives a clear separation of the peaks at the hydrogen absorption and desorption region as well as that of oxidation region. The resistance of the electrode distorts the voltammogram less at slow sweep rates as indicated by the slope of the CV at negative limit of the anodic sweep. Therefore, a scan rate of 1 mV/s was adopted for all Pt/zeolite samples in the experiments because the electrochemical phenomena of the electrode solution interface and dynamic process may be observed sufficiently for the electrodes comprising small amounts of Pt. The significance of the two peaks observed at -0.43 V and -0.59 V (cathodic sweep) has already been discussed in the cyclic voltammogram section in chapter 2. The additional peak at -0.63 V observed in the anodic sweep is attributed to the re-oxidation of H₂ formed during the cathodic sweep and trapped within the porous electrode structure.

Figure 4.1: Cyclic Voltammogram of 40 wt.% Pt on XC-72R, electrode, scan rate of 20 mV/s in 2.5 mol dm⁻³ H₄SO₄. Arrows indicate features discussed in the text.
Figure 4.2: Cyclic Voltammogram of 40 wt. % Pt on XC-72R electrode, scan rate of 1 mV/s in 2.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\). Arrows indicate features discussed in the text.

The total electrochemically accessible platinum surface area on the electrode may be measured with the use of CO adsorption and electrooxidation, as the ratio of adsorbed CO to Pt sites was found to be unity at full CO coverage [4]. It has been reported that the number and size of the voltammetric peaks of CO recorded on the cyclic voltammetry were dependent upon the coverage of adsorbed CO [4, 5, 6]. The variation in the voltammetric peak heights is reflected by the transition in the number of electrons per site required to oxidize the adsorbed CO [7].

A typical CO oxidation and stripping CV on a carbon supported Pt electrode is shown in figure 4.3. The dotted line represents the cyclic voltammogram of CO stripping off the Pt surface. The current corresponding to the hydrogen desorption is not found, as hydrogen adsorption is suppressed with the coverage of CO on the Pt surface. A CO stripping peak to form carbon dioxide (CO\(_2\)) is observed at 0.25 V. On the cathodic sweep, the oxide reduction and stripping peak was observed at 0.1 V and hydrogen adsorption wave occurs. The solid line represents the CV after CO stripping.
Figure 4.3: Cyclic voltammogram of a 40 wt.% Pt on XC-72R electrode, scan rate of 20 mV/s in 2.5 H$_2$SO$_4$ mol dm$^{-3}$ with CO purge. The dotted line represents the CO stripping off from Pt surface; the solid line shows the CV after CO stripping.

The mechanisms of CO adsorption and oxidation at Pt surfaces have been studied intensively by the use of various techniques. It has been revealed from the literature that there are two types of CO adsorption on the Pt surface known as linear or bridge bonded CO [4]. It may be possible to transfer one type to another depending on the potential and concentration of CO in the solution due to a competition process of hydrogen and CO adsorption on the Pt surface. However, it is more favorable for the linear bonded CO to occur at high CO coverage, while the amount of bridged CO increases with surface roughness [8]. Adsorption of CO is supposed to follow the simple Langmuir-type process.

The mechanism of CO oxidation is very complicated. It has been proposed that the formation of oxides on the platinum was involved in the reaction due to the fact that the oxidation of CO happens at potentials where the formation of platinum oxides occurs [9]. However, for the purposes of the investigation presented in this thesis it is sufficient to know that 2 electrons are transferred in the electrooxidation of one CO
molecule and that the CO stripping peak obtained from the 40 wt% Pt/C electrode in this case represents an electrode area of 43.76 m²/g.

4.3.2 Electrochemistry of the Support

The electrodes of 1.5 wt.%Pt/zeolite and 5 wt.% Pt/zeolite, were prepared by mixing the catalyst powder with untreated XC-72R plain carbon powder and 15 wt.% Nafion, which is used to assist the electrode fabrication. Therefore, it is important to study the property of cyclic voltammetry (CV) for the plain carbon powder (XC-72R) as well as that of Na Y zeolite powder mixed with carbon powder prior to the cyclic voltammogram measurements for Pt/zeolite catalysts. Figure 4.4 displays the CV of plain carbon powder (XC-72R), while figure 4.5(a) and 4.5(b) show the CV of the mixture of plain zeolite/plain carbon powder (XC-72R) at different scan rates. It can be seen clearly that the phenomena of electron transfer at potential range from -0.75 V to -0.4 V are very similar for both electrodes. There are no hydrogen adsorption/desorption peaks observed. The current observed at negative limits in figure 4.4(a) and figure 4.5(a) is attributed to hydrogen evolution at the carbon electrode and carbon/zeolite electrode. An increase in the capacitance is observed for the Y zeolite/carbon electrode (figure 4.5) compared to the carbon electrode. A small contribution from a redox couple around -0.1 V up to 0.8 V is attributed to a redox process associated with the zeolite structure or functional groups on the carbon surface upon the incorporation of zeolite and carbon powder.

However, compared to the 40 wt.% Pt/XC-72R electrode described above, the hydrogen/oxygen evolution currents are dramatically decreased for these two types of electrodes. Restricting the potential window to –0.65 V on the cathodic sweep and 0.5 V on the anodic sweep ensures that hydrogen and oxygen evolution on the support minimised.
Figure 4.4: CV for carbon electrode, scan rate of 20 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The potential region of CV (a) is from $-0.75$ V to 0.8 V, and the potential region of CV (b) is from $-0.65$ V to 0.5 V.
Figure 4.5: the CV for zeolite/XC-72R electrode, scan rate of 20mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The potential of CV (a) is from −0.75 V to 0.8 V, and the potential of CV (b) is from −0.65 V to 0.5 V.

4.3.3 The 1.5 wt.% Pt/Y Zeolite Role of Deposition Method

Transition metal ion exchanged zeolites have been found to be particularly efficient for various catalytic reactions because the well-defined pore structure of the zeolite provides a compartmentalized environment that prevents cluster agglomeration at
certain temperatures and the subsequent decline in catalytic activity that accompanies
the agglomeration [10]. In this way, the metal atom or cluster may be immobilised
within the microspore structure during the catalytic reaction. However, most studies
have been devoted to elucidate the morphology and electronic properties of zeolite-
supported Pt cluster in the gas/solid environment of heterogeneous catalysis. The
detailed mechanism of the structural interaction between Pt (within 20 Å) and the
zeolite support is still unclear. Hence, it is interesting to undertake a further
investigation to determine the structural interaction of zeolite with platinum clusters, of
diameter less than 20 Å in an electrochemical environment.

(a) Cyclic Voltammogram

The cyclic voltammograms (CV) in figure 4.6(a) and 4.6(b) were recorded by using an
electrode fabricated with the 15anocr4 catalyst powder. The catalyst was prepared by
Pt(NH3)4(NO3)2 salt ion exchanged with Na Y zeolite, calcined at 350 °C and reduced
at 400 °C. The potential region was primarily chosen from -0.65 V to 0 V, as attention
was paid to the oxidation of the Pt particles, which might change the particle size and
surface structure. This study is focused on the hydride region as the evidence of activity
for Pt particles may be found.

It can be seen from the CV that two significant features are observed between -0.53 V
to -0.65 V, hydrogen absorption and desorption peaks. On the positive going sweep,
there is one peak at -0.64 V due to re-oxidation of H2 trapped in the porous electrode
structure following hydrogen evolution at -0.65 V on the cathodic sweep and a second
peak at -0.56 V due to H desorption.

On the negative going sweep, the peaks at -0.61 V for both of the CVs in figure 4.6 (a)
and (b) are attributed to hydrogen adsorption. Unlike the CV for Pt/XC-72R (figure
4.2), there is only one well resolved hydrogen adsorption and desorption peak observed
for the Pt/zeolite electrodes.
When the potential window from 0 V was expanded further to 0.5 V, an oxidation current was obtained, as can be seen in figure 4.6(b) in the anodic sweep between 0.2 V and 0.5 V.

![Cyclic voltammogram](image)

Figure 4.6: the Steady state cyclic voltammogram of a 1.5 wt.% Pt/Y zeolite electrode (15ancr4) in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. CV (a) is scanned at 2 mV/s from −0.65 V to 0 V and CV (b) is scanned at 1 mV/s from −0.65 V to 0.5 V.
However, a small peak is observed at $-0.05$ V (cathodic sweep), which is attributed to removal of the Pt oxides formed on the anodic sweep. Compared to the 40 wt.% Pt/XC-72R electrode, the relative currents for the $H_{ads}$ and oxide stripping are very different. This difference as well as the lack of a second H adsorption peak may be related to the much smaller Pt particles size on the zeolite than on the carbon support.

Koningsberger and coworkers [11] have shown that the addition of a large excess of NH$_4$NO$_3$ to the ion exchange solution resulted in smaller and better dispersed Pt clusters inside zeolite cages. We have examined the effect of such a catalyst preparation on the electrochemical response.

Figure 4.7 displays a comparison of the CVs obtained from the 15ancr4 electrode and 15anxcr4 electrode, which were made by Pt(NH$_3$)$_4$(NO$_3$)$_2$ or Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ ion-exchanged with Y zeolite, calcined at 350 °C and reduced at 400 °C. The basic cyclic voltammograms recorded for the two catalysts comprise both Pt features (hydride + oxide regions).

The electrode performance of the 15anxcr4 electrode was determined in a similar way to that of 15ancr4 electrode. The potential window was first set from $-0.65$ V to 0 V (a), and then, expanded further from 0 V to 0.5 V (b). Generally, exchange with excess NH$_4$NO$_3$ provides the most well resolved hydrogen features, as can be verified from the CVs in figure 4.7. When the potential window was restricted to $-0.65$ V to 0 V the peak potentials for the H adsorption are nearly the same for the two catalysts (fig4.7a). Hydrogen evolution is more facile on the 15ancr4 electrode, greater current observed at $-0.65$ V and more H$_2$ re-oxidation on the anodic sweep. Neither catalyst shows a clearly resolved H desorption peak in the anodic scan.

Increasing the anodic limit to 0.5 V has little effect on the H adsorption peak for the 15ancr4 catalyst as discussed previously. In contrast, the peak for H adsorption shifts to more positive potentials (fig 4.7 b), from $-0.62$ V to $-0.59$ V.
Figure 4.7: The steady state cyclic voltammogram for the 1.5 wt.% Pt/Y zeolite electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The thick line represents the CV for the 15anxcr4 electrode, and the thin line shows the CV for the 15anxcr4 electrode. The potential region in figure (a) was from -0.65 V to 0 V. The potential region in figure (b) was from -0.65 V to 0.5 V.
The conventional impregnation method was also used to prepare a group of 1.5 wt.% Pt/Y zeolite catalysts, named as 15imp gan cr4. In general, the method provides a shell distribution of Pt on the support surface. However, the distribution of Pt ion on zeolite is dramatically affected by the solution pH. The increasing acid strength could increase the dispersion of Pt on zeolite structure and reduce the particle size. However, this may also force Pt ions to remain in the small zeolite cages, such as the sodalite cages and hexagonal prisms. Thus, a well-controlled pH of impregnation solution is important for the Pt location on Y zeolite. In this case, a solution pH of 7 is used for the sample preparation, as a pH greater than 7 may lead to hydrolysis of the Pt(NH3)4(NO3)2 salt. Figures 4.8(a) and 4.8(b) show a comparison of CVs indicating the difference of hydride region for all three electrodes (15imp gan cr4, 15an cr4 and 15an xcr4 catalysts).

The cyclic voltammograms in figure 4.8 indicate that there is a larger shift of the hydrogen adsorption peak potential for the 15imp gan cr4 electrode. The peak potential for H adsorption is positively shifted to -0.594 V in comparison to the rest of electrodes during cycles from -0.65 V to 0 V, and increased H2 evolution is also observed. H desorption is more evident with this catalyst and is seen as a shoulder at -0.57 V on the anodic sweep.

The characteristics are obtained for three samples in the positive potential region when the potential window shown in figure 4.8 was extended from 0 V further to 0.5 V. The hydrogen adsorption peak for the 15imp gan cr4 shifts slightly to -0.60 V, in contrast to the positive shift observed for the 15an xcr4 catalyst. Increased oxide formation/oxygen evolution is observed at the anodic limit for the 15imp gan cr4 sample.
Figure 4.8: Effect of Pt deposition method on the steady state CV features for 15impgr4, 15ancr4 and 15anxcr4 electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The black line represents the CV of 15ancr4 electrode, the green line shows a CV of 15anxcr4 electrode, and the red line presents the CV of a 15impgr4 electrode.
(b) The Results of Extended X-Ray Adsorption Fine Structure (EXAFS)

As discussed in chapter 2, the structure of the supported Pt particles may be investigated by using X-ray absorption spectroscopy (XAS) and in particular the extended X-ray absorption fine structure (EXAFS). The in-situ EXAFS data illustrated in this section for the 15ancri4 and 15anxcri4 catalysts were collected at the L_{III} edge under potential control. The in-situ measurement for the 15impgancr4 catalyst has not been carried out due to the time constraints and failures of the synchrotron ring. The in situ EXAFS data was collected at -0.65 V vs MMS for all of the samples. The EXAFS data was analysed according to the procedure described in section 2.5.3. The resulting CHI-data obtained for the 15ancri4 and 15anxcri4 samples are displayed in figure 4.9(a) and 4.9(b).

The fluorescence mode was used during the data collection, as the quantity of Pt loading on the zeolite support is very low. The raw EXAFS (Chi) data is shown in figure 4.9. Fluorescence EXAFS data is usually of a poorer quality than transmission data and this is evident in the increased noise. The Chi data is useful out to k=14 Å⁻¹ for both catalysts. The data were fitted in r-space. A k³ weighting was used as the EXAFS is dominated by high Z neighbours. The fits are shown as the dashed lines in the diagrams and summarised in tables 4.1 (a) and 4.1 (b).

The data for the 15ancri4 sample was only fitted for two shells, as a result of the poor data quality. The figures in the forms of CHI data and Fourier transform show that the fit matches the general form of the raw data quite well. However, the goodness fit (R_{exa}) value, approximately 58 for the 15ancri4 sample, is very large because of the noise on the data. No improvement was observed when either the background subtraction or parameters in each shell were adjusted.
Figure 4.9: Chi data and Fourier transforms for the 1.5 wt.%Pt/Y zeolite catalysts, phase corrected. The data were collected at -0.65 V vs MMS reference electrode under potential deposition. The solid line represents the experimental data, and dotted line represents the fitted data. (a)=15ancr4, (b)=15anxcr4

Table 4.1: The results of fit for each Pt shell

(a) The result of fit for the 15ancr4 sample, which the data was collected at -0.65 V at room temperature.

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>2σ² / Å²</th>
<th>R/Å</th>
<th>E_{ef}/eV</th>
<th>R_{exaf}(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 1 Pt</td>
<td>7.45±0.84</td>
<td>0.0151±0.0011</td>
<td>2.77±0.011</td>
<td>-8.64±2.77</td>
<td>58.87</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>2.05±0.66</td>
<td>0.0112±0.0030</td>
<td>3.85±0.021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 O</td>
<td>0.75±0.50</td>
<td>0.0012±0.0010</td>
<td>2.19±0.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(b) The result of fit for the 15anxcr4 sample, which the data was collected at \(-0.65\) V at room temperature.

<table>
<thead>
<tr>
<th>15anxcr4</th>
<th>N</th>
<th>2σ² / Å²</th>
<th>R / Å</th>
<th>E&lt;sub&gt;ef&lt;/sub&gt; / eV</th>
<th>R&lt;sub&gt;exafs&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>6.38±0.49</td>
<td>0.015±0.0008</td>
<td>2.77±0.007</td>
<td>-10.06±1.32</td>
<td>44.99</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.48±0.67</td>
<td>0.0096±0.0045</td>
<td>3.90±0.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>5.15±2.23</td>
<td>0.0168±0.0052</td>
<td>4.80±0.026</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fit results in tables 4.1(a) and (b) reveal that the Pt coordination numbers in the Pt-Pt first and second shell for the 15ancr4 catalyst, approximately 7.45 and 2.05, are higher than the values of 6.38 and 1.48 obtained for the 15anxcr4 catalyst. An improvement in the fit of raw data is obtained upon adding a Pt-O shell although the goodness fit value R<sub>exafs</sub> is still higher than 50. The EXAFS raw data for the 15anxcr4 catalyst is fitted for 2 shells initially, and gives a goodness fit value R<sub>exafs</sub> >50. Subsequently, an improvement on the fit is obtained by adding a third Pt-Pt shell. This can be justified by the goodness fit value R<sub>exafs</sub> declining to 44.99. The value of distances (R) in the Pt-Pt first shell observed for two catalysts, approximately 2.77 Å, are consistent with that of bulk Pt.

The results indicate that Pt particle size of the 15ancr4 catalyst may be larger than that of the 15anxcr4 catalyst if it presumes that the geometries of Pt structure for these two catalysts follow the model discussed in chapter three. The oxygen coordination number observed for the 15ancr4 catalyst upon the electrochemical reduction may be attributed to the Pt in direct contact the zeolite structure. Nevertheless, it may be also related to Pt oxide located on the small cages, such as the sodalite cages and hexagonal prisms, as BET surface area measurement and XRD pattern results in chapter three have shown that zeolite pore structure was lost significantly. This may indicate that the oxidised Pt ion is encaged in the small cages where H₂ molecules find it difficult to reach during the reduction process.
(C) Oxidative stripping of adsorbed CO

Oxidative stripping of adsorbed carbon monoxide was carried out to determine the utilised Pt surface area. The detailed experimental method has been explained in section 2.3.5. Figure 4.10 shows the CVs of CO oxidation obtained for the 1.5 wt.% Pt loading samples. The active Pt surface area in m²/g for the catalysts previously discussed was calculated by determining the area under CO oxidation stripping peak and the actual Pt loadings using the edge step of the XAS data. The Pt surface area measurement for the 40 wt.% Pt/XC-72R electrode is also presented in figure 4.10 in order to compare with the surface area of 1.5 wt.% Pt loading catalysts.

As can be seen in figure 4.10, the CO stripping peak is observed in the first anodic sweep for all of the catalysts following the CO adsorption process. The peak potentials range from 0.17 V to 0.32 V for the Pt/zeolite catalysts and are positive shifted, as compared to the peak potentials at -0.04 V and 0.17 V for the Pt/XC-72R catalyst electrode. These differences indicate that CO is more strongly bound to the Pt particles supported on the zeolite substrate.

The CO determined Pt surface area for various catalysts are summarised in table 4.2. The figures show that CO oxidation and stripping peak for the 15anxcr4 catalyst is the most clear, and the surface area, 96.80 m²/g, is the largest as compared to the others. However, it seems that the 40 wt.% Pt/XC-72R electrode, which has the highest Pt loading on the carbon support, does not offer a high surface area (43.76 m²/g), as compared with the 1.5 wt.% Pt/zeolite loading samples. The value of the surface area for the 15anxcr4 catalyst, around 40.02 m²/g, is slightly higher than the values of 35.47 m²/g for the 15XC-72R catalyst prepared with 40 wt.% Pt loading catalyst with extra plain carbon. The lowest surface area is found for the 15impganxcr4 catalyst.
Figure 4.10: the CO oxidation and stripping CV for the electrode, a=15ancr4 catalyst, scan rate of 2 mV/s. b=15anxcr4 catalyst, c=15impgocr4 catalyst, d=1.5 wt.% Pt/XC-72R made by 40 wt.% Pt/XC-92R with extra carbon, named as 15Pt/XC-72R. Solid line represents the CO stripping CV, and the dash dot line represents the after CO stripping CV, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$.

Table 4.2. The data of the active Pt surface area as determined by CO under potential deposition at $-0.55$ V at room temperature in the 2.5 mole dm$^{-3}$ H$_2$SO$_4$ electrolyte solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under CO peak / C</th>
<th>mass of catalyst on electrode(mg)</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>$1.62 \times 10^{-2}$</td>
<td>0.133</td>
<td>1.52</td>
<td>40.02</td>
</tr>
<tr>
<td>15anxcr4</td>
<td>$1.974 \times 10^{-2}$</td>
<td>0.067</td>
<td>0.77</td>
<td>96.80</td>
</tr>
<tr>
<td>15impganocr4</td>
<td>$9.655 \times 10^{-3}$</td>
<td>0.147</td>
<td>1.68</td>
<td>21.58</td>
</tr>
<tr>
<td>15Pt/XC-72R</td>
<td>$1.404 \times 10^{-2}$</td>
<td>0.130</td>
<td>1.49</td>
<td>35.47</td>
</tr>
<tr>
<td>40Pt/ XC-72R</td>
<td>$1.971 \times 10^{-1}$</td>
<td>1.480</td>
<td>40.00</td>
<td>43.76</td>
</tr>
</tbody>
</table>

The charge associated with hydrogen adsorption can also be used to determine the active electrode area. These measurements were made and the results are summarised in table 4.3.
Table 4.3. The active Pt hydrogen adsorption area

(a) The potential was cycled from −0.65 V to 0 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>4.688 x 10⁻³</td>
<td>0.133</td>
<td>1.52</td>
<td>19.65</td>
</tr>
<tr>
<td>15anxcr4</td>
<td>5.203 x 10⁻³</td>
<td>0.067</td>
<td>0.77</td>
<td>43.28</td>
</tr>
<tr>
<td>15impghanr4</td>
<td>1.438 x 10⁻²</td>
<td>0.147</td>
<td>1.68</td>
<td>54.54</td>
</tr>
</tbody>
</table>

(b) The potential region was set from −0.65 V to 0.5 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>1.224 x 10⁻²</td>
<td>0.133</td>
<td>1.52</td>
<td>51.29</td>
</tr>
<tr>
<td>15anxcr4</td>
<td>1.245 x 10⁻²</td>
<td>0.067</td>
<td>0.77</td>
<td>103.57</td>
</tr>
<tr>
<td>15impghanr4</td>
<td>2.227 x 10⁻²</td>
<td>0.147</td>
<td>1.68</td>
<td>84.83</td>
</tr>
</tbody>
</table>

It is apparent in table 4.3 that the active Pt surface area for various electrode changes dramatically depending upon the potential range. When potential is cycled between −0.65 V to 0.5 V, the largest value of hydrogen adsorption active Pt surface area, approximately 103.57 m²/g is obtained for the 15anxcr4 electrode. However, when the electrode is cycled between −0.65 V to 0 V, in which a largest active hydrogen adsorption surface area of Pt is observed for the 15impghanr4 electrode. The electrochemical active hydrogen adsorption surface area of Pt for the 15ancr4 electrode is the smallest when the electrode is cycled in both potential regions.

The several issues are raised and it is apparent that Pt particle size and the dispersion state on the zeolite may play an important role for the hydrogen adsorption as compared to the surface area determined by CO.

The electrochemical results indicate that 15anxcr4 catalyst is thought to provide the most promising catalyst for further investigation. Vaarkamp et al.[12] have suggested that the Pt particle or cluster may be well anchored on the zeolite cage wall by the extra
protons situated on the zeolite Bronsted sites. Thus, we propose that a certain particle size may be maintained during the electrochemical reactions.

4.3.4 5 wt.% Effect of Loading

A further study into the Pt zeolite system was carried out with the increase of Pt loading from 1.5 wt.% to 5 wt.% on zeolite. The procedure to prepare 5 wt.% Pt loading on Na Y zeolite was the same as those for the 1.5 wt.% Pt loading samples described in section 2.1. The electrodes with 3.77 mg cm\(^{-2}\) Pt loading were prepared by the usual way, as have been narrated in section 4.2.2. The catalysts chosen for investigation were 5 wt.% Pt/zeolite, ion-exchanged with either Pt(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) salt or Pt(NH\(_3\))\(_4\)(NO\(_3\))\(_2\)/NH\(_4\)NO\(_3\) compound, calcined at 350 °C and reduced at 400 °C. Furthermore, a electrode made by 5 wt. % Pt/zeolite catalysts, Pt(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) salt ion-exchanged and direct reduced at 400 °C, was chosen as well in order to compare the effect of deposition methods on Pt particle size.

(a) Cyclic voltammogram

The study of the 5 wt% Pt/zeolite catalyst was undertaken to compare the results of 1.5wt.% Pt/zeolite electrodes in response to the same potential region shown in 4.3.3. A Pt/XC-72R electrode (acronym as 5Pt/XC-72R) prepared by the mixture of 40 wt. % Pt/XC-72R with extra XC-72R carbon to give the same mass of Pt per cm\(^2\) electrode area, was also investigated.

Figure 4.11 shows the CV for the 5Pt/XC-72R electrode. The potential regions chosen are the same as to those for the 1.5 wt. % Pt/zeolite electrodes. Both CV’s show a hydride region when potential was swept from -0.65 V to 0 V or from -0.65 V to 0.5 V respectively. A well-resolved hydrogen adsorption peak is observed at -0.563 V (figure 4.11a) or -0.574 V (figure 4.11b) on the cathodic sweep, and there is one peak at -0.640 V in both CVs due to re-oxidation of H\(_2\) trapped in the porous electrode.
structure following hydrogen evolution at $-0.65$ V on the cathodic sweep. Subsequently, two hydrogen desorption peaks presenting weakly or strongly bound hydrogen desorption are found at the different potential on the anodic going sweep. The small current change either at $-0.552$ V in figure 4.11 (a) or at $-0.549$ V in figure 4.11(b) is response to a weakly bound hydrogen desorption site. Furthermore, a small current occurring at $-0.428$ V in figure 11 (a) and in figure 4.11 (b) is related to strongly bound hydrogen desorption peak. An oxidation region is observed following the anodic sweep from $-0.65$ V to 0.5 V, as indicated by the increase of current starting from potential at 0.172V, and a clear oxidation stripping peak is observed at 0.137 V on the cathodic sweep. A thick double region in both CVs indicates that the capacitance of electrode is high, and the resistance caused by mass transfer between electrodes and solution is high.

Diagram is continued in next page
Figure 4.11: the steady state cyclic Voltammogram of Pt/XC-72R electrode, prepared by 40 wt.% Pt/XC-72R with extra XC-72R plain carbon, acronym as 5Pt/XC-72R, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The potential region of CV 4.11 (a) is from −0.65 V to 0 V, and that of CV 4.11 (b) is from −0.65 V to 0.5 V.

Figure 4.12 displays a typical CV of 5 wt.% Pt/zeolite, Pt(NH$_3$)$_4$(NO$_3$)$_2$/NH$_4$NO$_3$ salt ion exchanged, calcined 350 °C and reduced at 400 °C. The chosen potential region is same as that for the CV obtained for the 5Pt/XC-72R catalyst.
Figure 4.12: the steady state cyclic Voltammogram of 5anxcr4 electrode, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The potential region of CV 4.12 (a) is from $-0.65$V to 0V, and that of CV 4.12 (b) is from $-0.65$V to 0.5V.

The CVs show hydrogen adsorption peaks at $-0.613$ V (Figure 4.12a) and $-0.610$ V (figure 4.12b) when the potential was cycled from $-0.65$ V to 0 V or from $-0.65$ V to 0.5 V respectively. As compared to the hydrogen adsorption potential for the Pt/XC-72R catalyst (figure 4.11), the hydrogen adsorption potential for the 5anxcr4 electrode is shifted negatively. The hydrogen desorption peak is not well resolved in either of the
CVs and appears as a shoulder on the $\text{H}_2$ re-oxidation peak. When the anodic limit was extended to 0.5 V some evidence of Pt oxide formation and reduction is seen in the anodic and cathodic sweeps, respectively.

Figure 4.13 shows a set of cyclic voltammograms illustrating the effect of different platinum deposition method. The cyclic voltammograms comprise both hydrogen adsorption peaks and some evidence of oxide formation and reduction.

![Cyclic Voltammograms Illustrating the Effect of Different Platinum Deposition Method](image)

Figure 4.13: Effect of Pt deposition method on the steady state CV features for the 5anocr4, 5anxcr4 and 5andr4 electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ $\text{H}_2\text{SO}_4$. The black solid line represents the CV of 5andr4 electrode, the blue line shows a CV of 5anocr4 electrode, and the red line is the CV of 5anxcr4 electrode.
It is apparent that the position of the hydrogen adsorption peak in figure 4.13 (a) shifts to more negative potentials in the order 5ancr4 (-0.60 V) > 5anxcr4 (-0.61 V) > 5andr4 (-0.63 V). The hydrogen desorption peaks in the anodic scan reflect these changes with the peak for the 5ancr4 catalyst being the most well resolved from the H₂ re-oxidation peak.

When compared to the CVs for the 1.5 wt.% Pt/zeolite catalysts, the effect of increased Pt loading is to increase the resolution and area of the hydrogen adsorption and desorption peaks. Slight shifts in peak potentials are observed, but these are not greater than ~10 mV.

(b) The Results of Extended X-Ray Adsorption Fine Structure (EXAFS)

The EXAFS data for a group of 5 wt % Pt/zeolite catalyst were collected in the same way employed for the 1.5 wt % Pt/zeolite group, as discussed previously. The data at the Pt L₃ edge were collected at −0.65 V vs. MMS reference electrode in 1 mol dm⁻³ H₂SO₄ electrolyte at room temperature. As described previously, the data analysis was carried out in r space with a fit weighting of k³. The Chi data and Fourier transforms are shown in figure 4.14. The real data is shown as a solid line and the fits as dashed lines. The results of the fits for three samples are listed in tables a, b and c. Four Pt-Pt distances were fitted, in contrast to the 1.5 wt.% data described previously. This increase may be justified by the presence of peaks between 4 and 14 Å in the FTs and confirmed by the large improvement in the goodness of fit, R_exafs. The greater noise level in the 5anxcr4 data is reflected in the larger goodness fit value of approximately 32.24. In addition much larger Debye Waller factors were found for the 5anxcr4 catalysts. This may be attributed to the much lower coordination number around the absorber atom. Shell 1 has 5.7 neighbours compared to 6.8 or 8.2 for the other catalysts. The large values of the Debye Waller factors also contribute to large errors in the coordination numbers for this sample.
The influence of deposition method on the Pt particle size may be indicated from the Pt-Pt coordination number as well as the Pt distance in each shell. In fact, the coordination number obtained for the 5andr4 sample is the largest up to the Pt-Pt fourth shell. However, the detailed relationship between the Pt-Pt coordination number in each shell and particle size depend upon the shape or morphology of the Pt particle [13].

Furthermore, it can be seen in table 4.4 that the Pt-Pt bond distances in each shell for all samples are shortened in comparison to that obtained for the model Pt reference compound. In particular, the value of distance and Pt-Pt coordination number observed for the 5anxcr4 sample is small, when compared to those for the 5ancr4 and 5andr4 catalysts. Thus, it indicates that the Pt particle size on Y zeolite for the 5anxcr4 sample may be smaller than the others.

The data analysis shows that the electrodes are fully reduced at -0.65 V, as evidenced by the fact that the Pt-O neighbouring atom has not been found during the course of the data analysis. This is consistent with the result observed from the cyclic voltammogram at -0.65 V, where there is a hydride region observed.

Table 4.4: Results of the fits for the 5 wt.% Pt/zeolite catalysts
(a) The result of fit for the 5ancr4 sample. The data was collected at -0.65 V at room temperature.

<table>
<thead>
<tr>
<th>5ancr4</th>
<th>N</th>
<th>2σ²/Å²</th>
<th>R/Å</th>
<th>E_{ef}/eV</th>
<th>R_{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>6.78±0.17</td>
<td>0.0088±0.0002</td>
<td>2.76±0.003</td>
<td>-9.95±0.75</td>
<td>18.46</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.29±0.22</td>
<td>0.0042±0.0013</td>
<td>3.89±0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>3.10±0.34</td>
<td>0.0032±0.0008</td>
<td>4.78±0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>6.3±0.98</td>
<td>0.0087±0.0013</td>
<td>5.43±0.009</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(b) The result of the fit for the 5anxcr4 sample. The data was collected at -0.65 V at room temperature.

<table>
<thead>
<tr>
<th>5anxcr4</th>
<th>N</th>
<th>$2\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>$E_{el}$/eV</th>
<th>$R_{exafs}$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>5.71±0.30</td>
<td>0.0120±0.0005</td>
<td>2.75±0.005</td>
<td>-8.08±1.31</td>
<td>32.24</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>1.50±0.51</td>
<td>0.0101±0.0029</td>
<td>3.87±0.017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>4.07±1.21</td>
<td>0.0122±0.0027</td>
<td>4.77±0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>5.40±2.02</td>
<td>0.0162±0.0035</td>
<td>5.40±0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of the fit for the 5andr4 sample. The data was collected at -0.65 V at room temperature.

<table>
<thead>
<tr>
<th>5andr4</th>
<th>N</th>
<th>$2\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>$E_{el}$/eV</th>
<th>$R_{exafs}$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>8.19±0.27</td>
<td>0.0112±0.0003</td>
<td>2.75±0.003</td>
<td>-8.56±0.81</td>
<td>27.09</td>
</tr>
<tr>
<td>Shell 2 Pt</td>
<td>2.74±0.38</td>
<td>0.0066±0.0011</td>
<td>3.87±0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pt</td>
<td>5.53±0.53</td>
<td>0.0049±0.0008</td>
<td>4.78±0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 4 Pt</td>
<td>7.86±1.15</td>
<td>0.0088±0.0013</td>
<td>5.43±0.010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.14: CHI data and Fourier transform for the 5 wt.%Pt/Y zeolite catalysts, phase corrected. The data were collected at -0.65 V vs. MMS reference electrodes in 1.0 mol dm$^{-3}$ H$_2$SO$_4$. (a)=5an0<r, (b)=5anxc<r, (c)=5and<. The solid line represents the experimental data, and dashed line represents the fitted data.
(C) Pt Area Determination Using CO Oxidation Stripping

As previously clarified in chapter 2 and in section 4.3.3, the electrochemical active surface area of Pt is determined by CO absorption on the Pt surface and then oxidatively stripping it off under potential control. Figure 4.15 displays the cyclic voltammograms of CO oxidation and stripping off from the Pt surface for the 5 wt.% Pt/zeolite catalysts. The electrochemically active Pt surface area (m²/g) under CO stripping peak is listed in table 4.5. The electrochemical active Pt surface area for a similarly loaded 40 wt.% Pt/XC-72R catalyst electrode was determined as well in order to compare with the surface area for the 5 wt.% Pt/zeolite catalysts.

(The figures are continued in next page.)
Figure 4.15: the steady state CVs of CO oxidation and stripping from Pt surface for the 5 wt.% Pt/zeolite electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. Black line represents the CV of CO oxidation and stripping from Pt surface, and red line represents the CV after CO stripping. (a)=$\text{5anxcr4}$ catalyst, (b)=$\text{5anrc4}$ catalyst, (c)=$\text{5andr4}$ catalyst, (d) = prepared by 40 wt.% Pt/XC-92R with extra carbon, named as 5Pt/XC-72R.
Table 4.5: The data of electrochemical active Pt surface area as determined by CO under potential deposition at -0.55 V in 2.5 mole dm$^{-3}$ H$_2$SO$_4$ electrolyte solution at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under CO peak / C</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>5anxcr4</td>
<td>2.425x10$^{-2}$</td>
<td>0.328</td>
<td>4.71</td>
<td>24.29</td>
</tr>
<tr>
<td>5anccr4</td>
<td>3.278x10$^{-2}$</td>
<td>0.533</td>
<td>7.76</td>
<td>20.20</td>
</tr>
<tr>
<td>5andr4</td>
<td>5.781x10$^{-3}$</td>
<td>0.658</td>
<td>7.40</td>
<td>2.89</td>
</tr>
<tr>
<td>5Pt/XC-72R</td>
<td>3.748x10$^{-2}$</td>
<td>0.436</td>
<td>5.00</td>
<td>28.24</td>
</tr>
</tbody>
</table>

Figure 4.15 shows a set of CO oxidation CVs for the 5 wt.% Pt catalysts, and the values of actual Pt surface area via CO measurement are presented in table 4.5. It is apparent that the Pt active surface area of the 5Pt/XC-72R electrode, around 28.24 m$^2$/g, is the largest, whereas the value of the active Pt surface area for the 5anxcr4 electrode, approximately 22.94 m$^2$/g, is slightly larger than the value of 20.20 m$^2$/g for the 5anccr4 electrode. The data reveals that the value of the active Pt surface area for the 5andr4 electrode, approximately 2.89 m$^2$/g, is the lowest, as compared with others. The results show that CO surface area determined in the electrochemical circumstance for the 5anxcr4 electrode is not significantly increased upon adding excess ammonia salt, in comparison to that for the 5anccr4 electrode prepared with Pt ammonia nitrate. As compared the value obtained for the 1.5 wt.% Pt loading electrode, the CO adsorption Pt surface area is decreased dramatically. This predicates that the particle sizes of the 5 wt.% Pt loading catalysts are larger than those of 1.5 wt.% Pt loading catalysts, as evidenced by the EXAFS results.

One issue raised is that the extra protons may restrict Pt mobility throughout the zeolite cage or channel during the calcination and reduction step. Two explanations are provided for this observation. Firstly, all Pt ions and excess ammonia nitrate were initially incorporated into different site of zeolite cages including sodalite cage or hexagonal prisms by a dynamic process. As mentioned in chapter 2, the Pt distribution and particle size on the zeolite are primarily dependent upon calcination temperature, and then the reduction temperature. Generally, Pt is most likely to stay in the
supercages below 420 °C. However, for the 5anxcr4 catalyst the presence of an acidic proton functional group on the zeolite support enhances the structural interaction by anchoring Pt on to the zeolite cage wall. Thus, Pt is prohibited to migrate throughout zeolite channel. Meanwhile, some Pt particles may be encapsulated, and are hardly detected by electrochemical metal surface area measurement (EMSA) due to the problem caused by CO diffusion. It is assumed that Pt/zeolite catalyst made by the Pt nitrate salt ion exchanged deposition method may be mobile freely through zeolite channels or cages during the course of the calcination and reduction period because of the lack of protons on the Pt/zeolite catalyst system. Pt loading may play a certain role for the variety of Pt particle size due to the limitation of the number of Bronsted sites on zeolite and the size of zeolite cage. Overall, the increase of Pt loading may aid to increase the particle size, and furthermore, lead to blocking of the zeolite channel and cage.

The hydrogen adsorption area measurement may be used to estimate the changes in the activity for the 5 wt.% Pt/zeolite catalysts as prepared by different deposition methods. A summary of data for the active Pt hydrogen adsorption area is presented in table 4.6, and the comparison for all samples is illustrated in figure 4.20. The chosen potential is from −0.65 V to 0 V and −0.65 V to 0.5 V, respectively.

Table 4.6. The data of active Pt hydrogen adsorption surface area

(a) The active Pt hydrogen adsorption area was determined by cycling potential from −0.65 V to 0 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>5anxcr4</td>
<td>2.064×10⁻²</td>
<td>0.414</td>
<td>4.71</td>
<td>27.79</td>
</tr>
<tr>
<td>5ancr4</td>
<td>1.699×10⁻²</td>
<td>0.677</td>
<td>7.76</td>
<td>13.99</td>
</tr>
<tr>
<td>5andr4</td>
<td>6.066×10⁻³</td>
<td>0.652</td>
<td>7.40</td>
<td>5.19</td>
</tr>
</tbody>
</table>
(b) The active Pt hydrogen adsorption area was determined by cycling potential from -0.65 V to 0.5 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>5anxcr4</td>
<td>2.422 x 10⁻²</td>
<td>0.414</td>
<td>4.71</td>
<td>32.61</td>
</tr>
<tr>
<td>5aner4</td>
<td>2.210 x 10⁻²</td>
<td>0.677</td>
<td>7.76</td>
<td>21.47</td>
</tr>
<tr>
<td>5andr4</td>
<td>1.409 x 10⁻²</td>
<td>0.652</td>
<td>7.40</td>
<td>12.05</td>
</tr>
</tbody>
</table>

The table 4.6 presents the active hydrogen adsorption Pt surface area for various catalyst when the electrodes are cycled between two potential regions, -0.65 V to 0.5 V or -0.65 V to 0 V. The results show that the active hydrogen adsorption Pt surface area for the 5anxcr4 electrode, around 27.79 m²/g (from -0.65 V to 0 V) and 32.61 m²/g (from -0.65 V to 0.5 V) is the largest in contrast to the result observed for the 5andr4 electrode, which the active hydrogen adsorption Pt surface areas, approximately 5.19 m²/g (-0.65 V to 0 V) and 12.05 m²/g (-0.65 V to 0.5 V), are the lowest.

### 4.3.5 Addition of Iron

Many studies have revealed that zeolites of different structures and pore opening widths had exhibited different reduction profiles for the same metal precursors and the same pretreatment conditions. We have chosen Na Y zeolite to be used as the support in this project as it is known to have a faujasite structure with different channel and cage sizes. The research work done by other groups [14, 15] indicated that a homogeneous Pt particle distribution inside different Y zeolite cages could be obtained by Pt(NH₃)₄²⁺ ion exchange with the zeolite, due to the large pore window diameters (0.9 nm) and three-dimensional accessibility in the faujasite structure, as compared to other types of zeolites. However, as a prepared catalyst, the location of the Pt and the dispersion on Y zeolite are decided by a variety of factors, such as the solution concentration during the ion exchange, pH value and thermal processing. It has been demonstrated that the ultimate metal location and dispersion were dependent on calcination temperature. Subsequently, the finial particle size is determined with the reduction temperature. [16, 17]
Ion exchange is normally carried out with a dilute solution. Therefore, the majority of Pt ions may be primarily ion-exchanged into zeolite supercages, as the concentration gradient between solution and zeolite is small. During the calcination step, a high calcination temperature of 300 °C or above is required for the complete removal of amine ligands, but this procedure may lead to induced migration of the bare ions into small cages. Meanwhile, the high negative charge density in the small cavities may provide the main driving force for the migration of multivalent metal ions from supercages to sodalite cages, in particular to the hexagonal prisms [18]. Pt particle size is also affected significantly by the reduction temperature, as ions located at different sites on the zeolite have generally different reducibilities due to the different degrees of accessibility of the reducible gas (H₂) to Pt sites. Although Pt atoms in the small cages may be forced to move back to zeolite supercages the temperature required is so high that large particles are formed. [15,19].

In order to avoid these undesirable phenomena, an effective method, which permits complete amine destruction and prevents migration of the Pt ions into sodalite cages and hexagonal prisms, was employed. Therefore, the metals, such as Mg²⁺, Ca²⁺, or Fe ion, was chosen to ion exchange with the zeolite prior to the Pt or Pd and zeolite ion exchange process was carried out [19, 20]. However, in this project only Fe²⁺ ion was chosen to use in the experiment. Fe²⁺ exchanged into zeolite channel and cage can be oxidized to Fe³⁺ ion during the calcination step, Fe³⁺ can block the hexagonal prisms and sodalite cages due to the high charge density. Moreover, Fe²⁺ ions obtained after reduction process will remain in the supercages and assist in anchoring the reduced Pt particles to zeolite cage wall [21].

Figure 4.16 displays the comparison of cyclic voltammograms obtained for the 15Ptfeancr3 and 15Ptfeancr4 samples, prepared by the use of Fe to block zeolite small cages at first prior to Pt(NH₃)₄(NO₃)₂ salt ion exchanged with zeolite. 15Ptfeancr3 was calcined at 300 °C and reduced at 300 °C, whilst 15Ptfeancr4 sample was calcined at 350 °C and reduced at 400 °C. The Pt loading for both samples is 1.5 wt.% Pt on zeolite and 98.5 wt.% Fe.
The CV shows that the Pt performance indicated by hydride region for the 15Ptfeanr4 electrode is better (more well resolved hydrogen adsorption and desorption peaks at more positive potential) than that for the 15Ptfeanr3 electrode in both of two potential regions, -0.65 V to 0 V and -0.65 V to 0.5 V. This implies that the resolution of hydrogen adsorption and desorption is dramatically improved when reduction temperature was raised from 300 °C to 400 °C. The two quasi-reversible peaks observed at potential 0.014V and -0.032 V are attributed to the Fe²⁺/Fe³⁺ redox couple of the Fe exchanged on the zeolite.

The resolution and potential of peaks on the hydride region obtained for the sample reduced at different temperatures may predict the Pt dispersion state inside zeolite cages. Reduction at 400 °C should produce small metal particles in the zeolite supercages. Mobility of the Pt is reduced at 300 °C. Pt particles in the supercages should be more accessible to the solution and more easily reduced.
Figure 4.16: the Comparison of the steady state cyclic voltammograms for the 15Ptfeancr3 electrode with the 15Ptfeancr4 electrode, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The potential of CV (a) is from –0.65 V to 0 V, and that of CV (b) is from –0.65 V to 0.5 V. The black line represents the 15Ptfeancr4 catalyst. The red line represents the 15Ptfeancr3 catalyst.
Comparison of the CV’s for the same Pt loading prepared by the various deposition methods lends weight to this argument. As shown in fig. 4.17, the H adsorption and desorption is the most well resolved for the 15Ptfeancr4 sample. These results indicate that the use of the Fe to block the zeolite small cages can effectively improve the active Pt hydrogen adsorption surface area, as Pt may be forced to remain in the zeolite supercages.

![Cyclic Voltammogram](image)

Figure 4.17: the Comparison of steady state cyclic voltammogram of catalysts affected by different Pt loading and deposition method. Black line=15Ptfeancr4, red line=15impgancr4, Dash blue line =15anxcr4.

The detailed metal-metal interface within the zeolite may be characterised by the use of the in-situ EXAFS technique. The data was collected at −0.65 V, and the EXAFS data at the Pt L\textsubscript{III} edge was recorded for both samples. The resulting Chi data and the Fourier Transforms are displayed in figure 4.18. As reported by Sachtler, Fe\textsuperscript{2+} cations, which are incorporated into zeolite by ion exchange, are initially oxidized to Fe\textsuperscript{3+} during the calcination step. Since the Fe\textsuperscript{3+} ions have a high charge density, they are most favorably located in small cages, especially in hexagonal prisms due to the high negative charge of the prism. Nevertheless, Fe\textsuperscript{2+} can be obtained by following a reduction step at 350 °C or above according to the literature given by Park and Sachtler, who said that Pt might catalyze the reduction of Fe\textsuperscript{3+} to Fe\textsuperscript{2+} [22].
The data were fitted in r-space and a k$^3$ weighting was used as described previously. All Fourier transforms were Pt-Pt phase-corrected. The two samples were fitted with one Pt shell and one Fe ion shell, as these were found to be the major contributors to the EXAFS.

The Chi data obtained for the 15Ptfeacr3 catalyst exhibits a poorer data quality than that collected for the 15Ptfeacr4 sample, and this is reflected in the goodness fit value (R$_\text{exafs}$=55.46 for the 15Ptfeacr3; R$_\text{exaf}$=39.87 for the 15Ptfeacr4). The fit parameters in table 4.7 reveal that the Pt coordination number in the Pt-Pt first shell for the 15Ptfeacr3 catalyst is approximately 4.87, whilst the Pt coordination number for the 15Ptfeacr4 catalyst is 5.07. The Fe coordination number in the Pt-Fe shell for the 15Ptfeacr3 is 1.96 and 1.37 for the 15Ptfeacr4. Within the error of the fits these values are the same and a first shell metal coordination number of ~6.6 is obtained.

Table 4.7: Results of the fits of Pt shells

(a) The result of fit for the 15Ptfeacr3 sample. The data was collected at −0.65 V at room temperature.

<table>
<thead>
<tr>
<th>15Ptfeacr3</th>
<th>N</th>
<th>2σ$^2$/Å$^2$</th>
<th>R/Å</th>
<th>E$_\text{exf}$/eV</th>
<th>R$_\text{exafs}$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>4.87±0.57</td>
<td>0.0145±0.0011</td>
<td>2.72±0.011</td>
<td>-4.04±2.54</td>
<td>55.46</td>
</tr>
<tr>
<td>Shell 2 Fe</td>
<td>1.96±0.76</td>
<td>0.0320±0.0076</td>
<td>2.53±0.032</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit for the 15Ptfeacr4 sample. The data was collected at −0.65 V at room temperature

<table>
<thead>
<tr>
<th>15Ptfeacr4</th>
<th>N</th>
<th>2σ$^2$/Å$^2$</th>
<th>R/Å</th>
<th>E$_\text{exf}$/eV</th>
<th>R$_\text{exafs}$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pt</td>
<td>5.03±0.33</td>
<td>0.0134±0.0005</td>
<td>2.72±0.006</td>
<td>-3.93±1.67</td>
<td>39.87</td>
</tr>
<tr>
<td>Shell 2 Fe</td>
<td>1.37±0.40</td>
<td>0.0259±0.0049</td>
<td>2.51±0.019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.18: Chi data of fit for the 15 wt.% Pt/Fe/Y zeolite catalysts, phase corrected. The data were collected at -0.65 V vs. MMS reference electrodes in 1.0 mol dm$^{-3}$ H$_2$SO$_4$. (a)=15Ptfeancr3, (b)=15Ptfeanxcr4. The solid line represents the experimental row data, and dot line represents the fitted data.

The electrochemically active Pt surface area for the two samples was determined by the use of CO electroxidation. Figure 4.19 shows the cyclic voltammogram of CO oxidation - stripping and after stripping on the Pt surface. For the 15Ptfeancr3 sample the CO stripping peak is not well resolved from the Fe$^{2+}$/Fe$^{3+}$ couple, thus the active area could not be reliably determined for this sample from the CO peak. For the 15Ptfeanxcr4 sample the CO stripping peak is shifted to more positive potentials and an area was determined as shown in table 4.8.
Figure 4.19: the CVs of CO stripping and after stripping for the 15 wt.% Pt/Fe/zeolite electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ $\text{H}_2\text{SO}_4$. The red line represents the CV of CO oxidation and stripping from Pt surface, and the black line represents the CV after CO stripping. (a)=15Ptfeanxcr3 catalyst, (b)=15Ptfeanxcr4 catalyst.
Table 4.8: The active Pt surface area as determined by CO under potential deposition at −0.55 V in 2.5 mole dm⁻³ H₂SO₄ electrolyte solution at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under CO peak / C</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Ptfeancr3</td>
<td>0.707×10⁻²</td>
<td>0.133</td>
<td>1.49</td>
<td>2.80</td>
</tr>
<tr>
<td>15Ptfeancr4</td>
<td>4.493×10⁻²</td>
<td>0.137</td>
<td>1.54</td>
<td>110.96</td>
</tr>
</tbody>
</table>

The table 4.8 shows the active surface areas for the 15Ptfeancr3 and 15Ptfeancr4. The value of CO adsorption and oxidation area for the 15Ptfeancr4 electrode, around 110.96 m²/g, is greater than the value of 2.8 m²/g for the 15Ptfeancr3 electrode, and is larger than that for the 15anxcr4 electrode indicated in the section of 4.3.3 (c).

The hydrogen adsorption peaks were also used to calculate the active Pt surface area and the results are presented in Table 4.9.

Table 4.9. Active Pt surface area of hydrogen adsorption peak

(a) The potential was cycled from −0.65 V to 0 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak / C</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Ptfeancr3</td>
<td>1.168×10⁻²</td>
<td>0.133</td>
<td>1.49</td>
<td>48.95</td>
</tr>
<tr>
<td>15Ptfeancr4</td>
<td>1.732×10⁻²</td>
<td>0.137</td>
<td>1.54</td>
<td>70.46</td>
</tr>
</tbody>
</table>

(b) The potential was cycled from −0.65 V to 0.5 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak / C</th>
<th>mass of catalyst on electrode</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>15Ptfeancr3</td>
<td>1.334×10⁻²</td>
<td>0.133</td>
<td>1.49</td>
<td>55.90</td>
</tr>
<tr>
<td>15Ptfeancr4</td>
<td>2.089×10⁻²</td>
<td>0.137</td>
<td>1.54</td>
<td>84.98</td>
</tr>
</tbody>
</table>
The table 4.9 shows the active hydrogen adsorption surface area determined for the 15PtfeanCr3 and 15PtfeanCr4 electrodes. It is apparent that the value of active hydrogen adsorption Pt surface area for the 15PtfeanCr4 electrode is larger than that for the 15PtfeanCr3 electrode as electrodes are cycled between two potential regions, -0.65 V to 0 V and -0.65 V to 0.5 V, and the value of surface areas are for both electrodes are increased with the increase of positive potential limit from 0 V to 0.5 V.

The results indicate that Pt electrochemical active performance on the hydride region may be enhanced following the increase of pretreatment temperature.

4.4 Discussion

From the results obtained above, it is clear that the deposition method has a significant effect on the performance of the catalyst, as evidenced by the activity of catalyst in the hydride region during the electrochemical measurement with the use of cyclic voltammetry. The comparison of the active Pt hydrogen and CO adsorption area for each group of samples prepared by the different deposition methods has already been presented in the section above. However, overall comparisons of hydride regions and the area under CO oxidation and stripping peak for all samples are illustrated in figure 4.20 and figure 4.21.
Figure 4.20: the Comparison of active hydrogen adsorption area for all samples. The potential was cycled between -0.65 V to 0.5 V.

Figure 4.21: the Comparison of Pt surface area determined by CO for all samples. (The results for the PtFe/zeolite catalysts have not been included due to the Fe$^{2+}$/Fe$^{3+}$ couple.) The potential was cycled between -0.65 V to 0.5 V.

The electrochemically active surface areas (EASA) may be compared to the BET surface areas described in chapter 3. For the 1.5 wt.% loading Pt catalysts, the surface areas, as determined by the hydrogen adsorption peak areas (fig 4.20), are decrease in the order 15anxcr4 > 15impgancr4 > 5anxcr4 > 1anxcr4. This order is the same as that obtained in the BET measurement. The EASA's for the 5 wt.% catalysts, using the hydrogen adsorption, are all much smaller than those for the 1.5 wt.% catalyst. This may be attributed to the increase in the particle size on increasing the loading, i.e. the fraction of the Pt atoms on the surface of the Pt particles decreases as the particle size increases. This is confirmed by the fact that the 5andr4 catalyst, which had the largest particle size (55 atoms in the cluster), has the smallest EASA. The effect of Fe addition is to decrease the EASA, but not significantly.

Comparing the EASAs obtained using CO oxidation to those obtained with hydrogen adsorption a similar trend is observed. However, all of the EASAs obtained with CO are smaller than those obtained from the hydrogen adsorption. This difference may be
related the difficulty of CO diffusion through the zeolite pores to reach all of the Pt surface sites. Only CO adsorbed on the Pt surface can be oxidised. Therefore, the hydrogen adsorption EASA is probably more accurate.

As discussed in chapter 3, the deposition method has an effect on the distribution of the Pt on and in the zeolite support. A 1.0 wt.% Pt/Al₂O₃ sample was also studied as a reference material. This sample was supplied by Johnson Matthey. The Pt on the Al₂O₃ support is known to be restricted to the exterior surface due to the lack of a pore structure. The EASAs determined using hydrogen adsorption and CO oxidation for this sample are shown in tables 4.10 and 4.11 and the results have been included in figures 4.20 and 4.21. The values obtained are in the same range as those obtained for the 1.5 wt.% loading Pt catalyst prepared in this project.

Table 4.10: the active hydrogen adsorption area of Pt for the 1 wt.% Pt/Al₂O₃. The potential was cycled between −0.65 V to 0.5 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under H peak / C</th>
<th>mass of catalyst on electrode / g</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt.%Pt/Al₂O₃</td>
<td>1.087 x 10⁻²</td>
<td>0.009</td>
<td>1.00</td>
<td>60.59</td>
</tr>
</tbody>
</table>

Table 4.11: the active CO adsorption area of Pt for the 1 wt.% Pt/Al₂O₃. The potential was cycled between −0.65 V to 0.5 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge under CO peak / C</th>
<th>mass of catalyst on electrode / g</th>
<th>wt. % Pt</th>
<th>Pt active area Area/m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt.%Pt/Al₂O₃</td>
<td>2.385 x 10⁻²</td>
<td>0.009</td>
<td>1.00</td>
<td>87.06</td>
</tr>
</tbody>
</table>

As discussed above, zeolites are electronic insulators. Carbon was added in preparing the electrodes from the catalyst samples to provide electronic conductivity. The electrochemical measurements indicate that much of the Pt is electrochemically accessible. However, the electrochemical measurements alone cannot quantify the fraction of the Pt particles that are electrochemically accessible. In situ
(electrochemical) EXAFS measurements obtained under potential control in the hydrogen adsorption region (electrochemical reduction) can assist in quantifying this fraction. This is accomplished by comparing the EXAFS results obtained with hydrogen chemical reduction and those obtained with electrochemical reduction. The results of the fits are compared in table 4.12.

Table 4.12 Comparison of EXAFS fit parameters for Pt/zeolite catalysts after chemical and electrochemical reduction. Data collected at Pt L\_III edge.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Actual Loading/ wt.%</th>
<th>Chemical reduction</th>
<th>Electrochemical reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O present</td>
<td>N(_1)(Pt)</td>
<td>R(_1)(Pt) / Å</td>
</tr>
<tr>
<td>15ancr4</td>
<td>1.52</td>
<td>No</td>
<td>6.33</td>
</tr>
<tr>
<td>15anxcr4</td>
<td>0.77</td>
<td>No</td>
<td>6.00</td>
</tr>
<tr>
<td>5ancr4</td>
<td>7.76</td>
<td>No</td>
<td>7.47</td>
</tr>
<tr>
<td>5anxcr4</td>
<td>4.71</td>
<td>Yes 0.56</td>
<td>6.02</td>
</tr>
<tr>
<td>5andr4</td>
<td>7.40</td>
<td>No</td>
<td>8.31</td>
</tr>
<tr>
<td>15Ptfeancr3</td>
<td>1.49</td>
<td>No</td>
<td>3.82</td>
</tr>
<tr>
<td>15Ptfeancr4</td>
<td>1.54</td>
<td>No</td>
<td>3.82</td>
</tr>
</tbody>
</table>

As seen in table 4.12 the results from the EXAFS data analysis for the chemical and electrochemical reductions are quite similar for each of the catalysts. However some differences are noted. Oxygen neighbours are observed for the electrochemical reduction of 15ancr4 catalyst, but are not for the chemical reduction, and the opposite is observed for the 5anxcr4 catalyst. The number of Pt neighbours in the first shell is larger for the electrochemical reduction of PtFe/zeolite catalysts.

The absence or presence of oxygen neighbours indicates the extent to which the Pt particles are fully reduced by the reduction method. For the case of 5anxcr4 reduced chemically the incomplete reduction may be attributed to a leak in the gas treatment cell. The samples were treated in a fume cupboard in the preparation laboratory and then brought to the beamline under a hydrogen atmosphere. The cell was sealed with
epoxy, which needed repair from time to time. Due to time constraints and a shut down of the synchrotron ring, we were unable to repeat this measurement. For the 15ancr4 electrochemically reduced sample, examination of the cyclic voltammogram, figure 4.7, shows that the potential, -0.6 V vs. MMS, was not negative of the hydrogen adsorption peak for this sample. This result indicates that the mechanism of electrochemical reduction of the Pt particles on the zeolite support is related to the presence of adsorbed hydrogen species.

The mobility of hydrogen and protons on and in the zeolite structure has been studied extensively in the heterogeneous catalysis literature. Currently the most common explanation available is hydrogen spillover, with the spillover hydrogen having a strong effect on the catalytic reactions occurring in solid acidic catalysts. Many reports have described the nature of spillover hydrogen. \( \text{H}^+ \) has been regarded as one of the most important species in this process [23, 24]. The spillover \( \text{H}^+ \) ions can be transmitted along the surface of the zeolite support this increases the surface conductivity of the support [25, 26, 27, 28]. The zeolite acts as an electron bank to donate or receive electrons during catalytic reactions. This is possible due to the availability of the acidic sites, e.g. the Brønsted or Lewis acid sites. In the chemical reduction process, hydrogen is dissociatively adsorbed on the Pt particles. Excess \( \text{H}_{\text{ads}} \) can spill over on to the zeolite support. This starts a flow of protons along the acidic sites and can transport hydrogen species to other Pt particles on the zeolite.

To interpret the electrochemical reduction, reference may be made to the chemical reduction process and hydrogen spillover. In the electrochemical reduction the process may begin by reduction of \( \text{H}^+ \) to form adsorbed hydrogen, \( \text{H}_{\text{ads}} \). As in the case of the chemical reduction, a flow of hydrogen species across the zeolite surface may be triggered. Thus, Pt particles located within the zeolite structure, which is electronically insulating, can be electrochemically reduced. This theory is supported by the cyclic voltammetric data. The most well resolved hydrogen adsorption and desorption features for the 1.5 wt.% loading Pt catalysts is found for the 15ancr4 catalyst electrode. The addition of excess \( \text{NH}_4\text{NO}_3 \) during the ion exchange process provides more \( \text{H}^+ \) species on the zeolite structure in the final catalyst.
The cyclic voltammetric results for the 5 wt.% loading catalysts, however, appear to disagree with the idea that extra H⁺ species on the zeolite surface are needed to fully reduce the Pt particles. As seen in figure 4.13 the hydrogen adsorption and desorption features are clearly resolved for all of the 5 wt.% loading catalysts. With the increase in the loading two phenomena may become important. First, the Pt particles may not be as well distributed through the zeolite structure. More of the Pt particles may be located on the exterior surface of the zeolite. Only very high resolution TEM would be able to determine if this was the case. Secondly, the Pt salt used in the ion exchange was Pt(NH₃)₄(NO₃)₂. The NH₃ ligands decompose at temperatures greater than 250 °C, i.e. during the calcination process. Thus, the NH₃ ligands also contribute to the neutralization of additional H⁺ species on the zeolite structure. In the 5 wt.% loading case, the number of NH₃ ligands is three times greater than in the 1.5 wt.% loading case, and thus conversion of the NH₃ ligands may be more important. Therefore, the 5 wt.% loading voltammetric data is not in disagreement with the hydrogen spillover theory proposed above.

Examination of the CO oxidation data also supports the hydrogen spillover theory in the electrochemical reduction of the Pt particles. As described above, the CO is unable to diffuse through the zeolite pores, especially the small cages, to reach the entire Pt surface. Unlike the hydrogen species, there is no corresponding transport mechanism for CO to travel across the zeolite surface. Thus, the CO surface areas are not a good measure of the total surface area of the Pt particles. However, the CO surface areas may provide an indication of the fraction of the Pt particles that are located on the exterior surface or in the supercages of the zeolite support. For most of the catalysts the CO surface areas are only slightly smaller than the hydrogen surface areas, see tables 4.20 and 4.21. However, for the 15imp gan cr4 and 5andr4 catalysts significant differences are observed. The average particle size for the 15imp gan cr4 catalyst determined from the EXAFS data, is very small, only 13 atoms in the cluster. These particles are small enough to enter the sodalite cages and hexagonal prisms, which are likely to be inaccessible to the CO molecules. The particle size for the 5andr4 catalyst, however, was found to be very large, 55 atoms in the cluster. These particles are so large that they would block the pore openings of the zeolite and prevent CO from entering the internal structure.
The influence of the location of the Pt particles in the zeolite structure on the electrochemical response was investigated by comparing the 1.5 wt.% loading Pt/zeolite catalysts with PtFe/zeolite catalysts. As described in the results section above and in chapter 3, the effect of ion exchange with iron prior to ion exchange with platinum is to fix the location of the Pt particles. For the 15Ptfeancr3 catalyst the calcination step and reduction step were both carried out at 300 °C. This temperature is not high enough during the calcination step to oxidise the Fe^{2+} to Fe^{3+}. Thus, the smaller cages are not fully blocked to the Pt particles in this catalyst. However, for the 15Ptfeancr4 the calcination step was carried out at 350 °C and the reduction step at 400 °C. This temperature is sufficient to ensure that the Fe^{3+} ions block the smaller cages. Thus, the Pt particles should be forced to stay in the supercages.

The voltammetric data, see figure 4.16, shows that the hydrogen adsorption and desorption features are more well resolved for the 15Ptfeancr4 catalyst electrode compared to the 15Ptfeancr3 catalyst electrode. The corresponding EASA is also greater for the 15Ptfeancr4 catalyst electrode, see figure 4.20. The EASAs determined using CO oxidation were complicated by the presence of the Fe^{2+}/Fe^{3+} redox couple in the cyclic voltammogram at -0.05 V vs. MMS. However, a qualitative comparison of the CO stripping features in the cyclic voltammograms shown in figure 4.19 clearly shows that a much greater EASA is obtained for the 15Ptfeancr4 catalyst. In fact, this area, 110.96 m² g⁻¹, is the largest obtained for any of the zeolite-supported catalysts prepared in this project. This finding supports the concept that CO is usually unable to reach the all of Pt in particular the Pt particles located in the small cages, but is able to reach the Pt located in the supercages.

In summary, the results presented in this chapter demonstrate that even though the zeolite support is an electronic insulator, the Pt particles located inside the zeolite as well as those located on the exterior can be electrochemically accessible. A theory of hydrogen spillover was proposed to explain the complete reduction of the Pt particles on and in the zeolite support, regardless of their location (exterior, supercages, sodalite cages or hexagonal prisms). No such transport mechanism exists, however, for other chemical species, such as CO. The CO oxidation can only take place on the Pt particles located on the exterior surface or in the supercages of the zeolite support. This finding
was supported by comparison to two PtFe/zeolite catalysts, where the location of the Pt particles is more well defined.
4.5 References


Chapter 5: The Characteristics of Palladium Particles Supported on Y Zeolite

5.1 Introduction

The zeolite has the unique properties of high ion exchange capability and a crystalline structure with uniform pore size, which allows preparation of highly dispersed metals with a small particle size distribution [1]. The locations and sizes of metal clusters in zeolites are controlled by the preparation method. The focus of this chapter is zeolite supported Pd catalysts, as the location and particle size of Pd is strongly dependent on the calcination and reduction temperature. The detailed temperature effect on the Pd migration throughout zeolite cages has been described in section 1.2 of chapter 1. Scheme 1 illustrates the Pd location on the zeolite structure following different calcination and reduction temperatures [2].

Scheme 1: The location of Pd after different calcination and reduction treatment [2]
It can be seen from the scheme 1 that Pd(NH$_4$)$_4^{4+}$ ions are primarily exchanged onto the external surface of zeolite but that some of them are located in the zeolite supercages. The subsequent oxidation of the Pd salt depends on the calcination temperature. The Pd(NH$_4$)$_4^{4+}$ ions may be decomposed to Pd(NH$_4$)$_2^{2+}$ at temperatures $\leq$ 250 °C, and remain in the zeolite supercages. However, Pd$^{2+}$ ions are obtained when the calcination temperature is raised to 300 °C or 400 °C. These Pd$^{2+}$ ions have a higher mobility, they will migrate from the zeolite external surface and supercages into the small cages, such as the sodalite cages and hexagonal prisms. During the reduction step, the Pd species may once again become mobile. If the reduction temperature is restricted to 300 °C, the Pd species are not mobile and the species remain in either the sodalite cages or the supercages depending on the calcination temperature. However, when the reduction temperature is at 360 °C, or above, the Pd species become mobile and move from the zeolite small cages to supercages, independent of the calcination temperature.

As introduced in chapter 1, Pd has the capabilities of bulk incorporation of hydrogen. This leads to the high solubility and mobility of hydrogen in Pd. Consequently palladium is widely used in gas sensors as a hydrogen storage material [3]. Generally, hydrogen adsorption on Pd can be divided into two phases, $\alpha$ and $\beta$ Pd hydride phases ($\alpha$-PdH and $\beta$-PdH). In the electrochemical circumstance, $\beta$-PdH is associated with a direct hydrogen absorption reaction between electrode surface and sub-surface. Subsequently, $\alpha$-PdH may be formed by H migration from a near surface hydride phase to the deeper bulk of the metal, and a solution of H in Pd is formed via diffusion. The hydrogen diffusion into the Pd may be achieved by up-hill diffusion from decomposition of $\beta$-PdH layer into $\alpha$-PdH region, whereas hydrogen in the $\alpha$-PdH layer is decomposed and transferred into the Pd [4]. The process is reversible.

However, the electrochemical activity of Pd is great influenced by the electronic structure of the Pd cluster and its particle size. Consequently, the detailed local structural characterization of Pd particles has been probed by the use of in-situ X-ray adsorption spectroscopy (XAS) and in particular the fine structure known as Extended X-ray Absorption Fine Structure (EXAFS). The experiments were carried out using the synchrotron radiation source based at Daresbury National Laboratory.
5.2 Experimental

Preparation of the palladium microstructure in Y zeolite was carried out following the procedure that was employed for the preparation of 1.5 wt.% Pt/zeolite catalysts described in detail in chapter 2. The 1.5 wt.% Pd/zeolite catalysts were prepared by using Pd(NH₄)₄Cl₂ salt ion-exchanged with the zeolite, and then, the sample was washed with purified water. The filtered water for each wash was examined by the addition silver nitrate salt solution (AgNO₃) until no white precipitate occurred. This procedure is to ensure that the chloride ion is removed from the ion exchange solution completely, as it is regarded as a potential poisoning species for many reactions. Subsequently, the sample was dried at 120 °C in an oven, and then was calcined at 250 °C, 350 °C or 400 °C prior to being reduced at 360 °C or 400 °C in a fluidised bed reactor. The procedure and materials used to make Nafion-bound electrodes were identical for all types of Pd zeolite catalysts, and were the same as those used for the preparation of Pt/zeolite electrodes, which were depicted in chapter 4.

The electrodes were cut from the compressed sheet to the required size, 1 cm² for cyclic voltammetry measurements.

The electrodes used for the in-situ EXAFS measurement were fabricated by using Nafion® as binder as well. The quantity of catalyst in the electrode (1.8 cm² area) was dependent on the type of EXAFS measurement.

The electrochemical experiments were carried out in a glass cell shown in figure 2.9 in section 2.3.3 of chapter 2, which is fitted with three electrodes: reference electrode, counter electrode and working electrode. The procedure is the same as those described in the section 4.2.3 of chapter 4. The counter electrode (CE) was high surface area platinum gauze, and the reference electrode (RE) was an Hg/Hg₂SO₄ (MMS) electrode. The working electrode sealed in a PTFE ring was positioned as close as possible to the luggin capillary of the reference electrode. 2.5 mol dm⁻³ H₂SO₄ made with purified water from a Barnstead system (18 MΩ/cm), either 150 cm³ or 180 cm³, was used to fill the electrochemical cell. Subsequently, an inert gas, N₂ was introduced to purge the electrolyte solution thoroughly during the course of experiment. Cyclic voltammograms were recorded between −0.685 V to 0.5 V using a computer-
controlled potentiostat (Autolab PGSTAT20). All potentials quoted were with respect to the MMS reference electrode, and CVs were recorded at 1 mV/s.

5.3 Results

5.3.1 The Results of 40 wt.% Pd/C Electrode

A study for a 40 wt.% Pd/XC-72R electrode was undertaken to be able to compare the features of 1.5 wt.% Pd/zeolite electrodes. The typical features of a cyclic voltammogram (CV) for a 40 wt.%Pd/XC-72R electrode prepared by mixing 100 mg 40 wt.% Pd with 100 mg plain carbon powder and 1.5 wt.% Pd/XC-72R electrode can be distinguished in figure 5.1 and figure 5.2, overleaf.

A set of cyclic voltammograms with the scan rates at 20 mV/s employed for the 40 wt.% Pd/XC-72R electrode and 1 mV/s for the 1.5 wt/% Pd/XC-72R electrode were recorded in order to determine the electrochemical phenomena occurring on the electrode with different sweep rates. A sweep rate of 20 mV/s (fig.5.1) gives a clear separation of the peaks in the hydrogen absorption and desorption regions, as verified by the two, separated, quasi-reversible peaks at negative potentials that represent hydrogen adsorption and desorption on Pd surface. On the cathodic sweep, a peak observed at -0.47 V presents a strongly hydrogen adsorption site, and a small peak observed -0.53 V is a weakly hydrogen adsorption site (figure5.1 a and b). The additional peaks at -0.55 V (figure 5.1 a) and -0.569 V (figure 5.1 b) observed in the anodic sweep are attributed to the re-oxidation of H₂ formed during the cathodic sweep and trapped within the porous electrode structure following hydrogen evolution at -0.647 V (figure 5.1 a) and -0.633 V (figure 5.1 b) on the cathodic sweep and a second peak obtained at -0.382 V and -0.389 V (figure 5.1 a and figure 5.1 b) due to strongly bond H desorption. A small peak observed at -0.473 V on the positive going sweep (figure 5.1 a and b) is due to weakly bound H desorption. When the potential was further swept to 0.4 V or 0.5 V (figure 5.1) respectively, an oxidation current between 0.113 V and 0.4 V was obtained. A larger peak is observed either at 0.052 V (figure 5.1 a) or at 0.058 V (figure 5.1 b) on the cathodic sweep. This peak is attributed to removal of the Pd oxides formed on the anodic sweep. On a further sweep of potential from
0.4 V to 0.5 V, the oxidation current increases and oxygen evolution may be observed at the more positive potential region.

The sweep rate of 1 mV/s (fig.5.2) used for the 1.5 wt.% Pd/XC-72R electrode gives a clear separation of the peak at the hydrogen desorption region as well as that of the oxidation region. On the cathodic sweep a small peak at −0.586 V corresponding to the hydrogen adsorption is observed, and the peak observed at −0.68 V is related to hydrogen evolution. Subsequently, on the anodic sweep a peak observed at −0.612 V is due to the re-oxidation of hydrogen, and the second peak is attributed to hydrogen desorption. In contrast to the 40 wt.% Pd/XC-72R electrode, only one pair of hydrogen adsorption and desorption peaks are observed in the hydride region for the 1.5 wt.% Pd/XC-72R electrode. When the potential was further swept to 0.5 V, current attributed to oxide formation was observed at 0.195 V to 0.5 V. The peak current obtained at 0.0156 V on the negative sweep is due to stripping off of the Pd oxide formed on the anodic sweep.

Figure 5.1: The steady state cyclic voltammogram of 40 wt.% Pd on XC-72R electrode, scan rate of 20 mV/s in 2.5 mol dm⁻³ H₂SO₄. The potential in figure 5.1 (a) is scanned between −0.65 V to 0.5 V. The potential in figure 5.1 (b) is scanned between −0.65 V to 0.4 V.
Figure 5.2: the Steady state cyclic voltammogram of 1.5 wt.% Pd on XC-72R electrode, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$.

**5.3.2 The Electrochemical Characterization of 1.5 wt.% Pd/Y Zeolite**

The catalyst powders used during the EXAFS measurements are 1.5 wt.% Pd / zeolite catalysts, Pd(NH$_4$)$_4$Cl$_4$ salts ion-exchanged, calcined at 250 °C, 350 °C or, 400 °C and reduced at 360 °C or, 400 °C, respectively, and each sample is given an acronym 15Pdanc25r36, 15Pdancr35r36, 15Pdancr4. The electrodes of 1.5 wt.% Pd/zeolite were prepared by the mixture of catalyst powder with untreated XC-72R plain carbon powder and 15 wt.% Nafion.

The cyclic voltammogram (CV) in figure 5.3 was recorded by using an electrode fabricated with the 15Pdanc25r36 catalyst powder. The catalyst was prepared by Pd(NH$_4$)$_4$Cl$_4$ salt ion-exchanged with Na Y zeolite, calcined at 250 °C and reduced at 360 °C. The negative potential was limited to −0.675 V prior to the hydrogen evolution,
and the potential was extended to 0.4 V in the positive direction. The scan rate chosen was 1 mV/s. Thus, the study is focused on whole potential region, hydride and oxide formation regions, between $-0.675$ V to 0.4 V.

![Graph](image)

**Figure 5.3**: the Steady state cyclic voltammogram of a 1.5 wt.% Pd/Y zeolite electrode (15Pdanc25r36) in 2.5 mol dm$^{-3}$ H$_2$SO$_4$, scan rate of 1 mV/s from $-0.675$ V to 0.4 V.

It can be seen from the CV that two significant features are observed between $-0.55$ V and at $-0.675$ V, hydrogen absorption and desorption peaks. On the negative going sweep, there is one peak at $-0.645$ V due to hydrogen adsorption. A second peak observed at $-0.607$ V on the anodic sweep is associated with hydrogen desorption following hydrogen evolution at $-0.675$ V. Nevertheless, no separated hydrogen re-oxidation peak is observed at the negative potential limit. It may be that the energy for the re-oxidation of H$_2$ is very close to the energy required for the hydrogen desorption.

An oxidation current was obtained between $-0.11$ V to 0.4 V when the potential was swept in the positive direction. A small peak is observed at $-0.025$ V on the cathodic sweep is attributed to removal of the Pd oxides formed on the anodic sweep. Compared to the 40 wt.% Pd/XC-72R electrode, the relative currents for the H$_{ads}$ and oxide stripping are very different. This difference as well as the lack of a second H
adsorption peak may be related to the much smaller Pd particle size on the zeolite than on the carbon support.

Figure 5.4 displays a comparison of the CVs obtained for the 15Pdanc25r36 electrode and 15Pdanc35r36 electrode. The catalyst used for the preparation of 15Pdanc35r36 electrode is calcined at 350 °C and reduced 360 °C. The basic cyclic voltammograms recorded for the two catalysts comprise both Pd features (hydride + oxide regions).

![Cyclic Voltammogram](image)

**Figure 5.4: Comparison of the steady state cyclic voltammograms for the 15 wt.\%Pd/Y zeolite electrodes, scan rate of 1 mV/s in 2.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\). The solid line represents the CV for the 15Pdanc35r36 catalyst calcined at 350 °C and reduced at 360 °C. The dotted dashed line shows the CV for the 15Pdanc25r36 catalyst calcined at 250 °C and reduced at 360 °C.

The figure shows that the peak position of hydrogen adsorption observed for the 15Pdanc35r36 electrode is consistent with that obtained for the 15Pdanc25r36 electrode, and the hydrogen desorption potential at -0.608 V for the 15Pdanc35r36 electrode is almost identical to that observed for the 15Pdanc25r36 electrode. Moreover, the peak current of hydride region for the 15Pdanc35r36 electrode is a slightly increased when compared to that for the 15Pdanc25r36 electrode, this is also seen in the oxidation region, where a slightly increase of oxidation and reduction
current is observed. Neither catalyst shows a clearly resolved H re-oxidation peak in the anodic scan.

The 1.5 wt.% Pd/zeolite electrode prepared by the catalyst calcined and reduced at 400 °C was also employed to determine the temperature effect on the catalytic activity of the catalyst in the electrochemical environment. Figure 5.5 shows a comparison of CVs indicating the difference in the hydride region for all three electrodes (15Pdanc25r36, 15Pdanc35r36 and 15Pdancr4 catalysts). The cyclic voltammograms indicate that there is a slight shift of the hydrogen adsorption peak potential for the 15Pdancr4 electrode. The peak potential for H adsorption is negatively shifted to −0.656 V in comparison to the rest of electrodes during cycles from −0.675V to 0.4 V. An increased current of hydrogen adsorption and evolution is also observed on the cathodic sweep. H₂ re-oxidation is more evident with this catalyst and is seen as a shoulder at −0.656 V on the anodic sweep, whilst the larger increase of hydrogen desorption current is observed at −0.611 V on the anodic going sweep. The peak potential of hydrogen desorption for the 15Pdancr4 is slightly negative shifted as compared to those observed for the 15Pdanc35r36 and 15Pdanc25r36 electrodes. A slight increase in current is also displayed on the oxidation region, and is evidenced by the peak at 0.025 V where the removal of oxidation species formed on the anodic going sweep was observed.
Figure 5.5: the comparison of steady state cyclic voltammograms for the 1.5 wt.%Pd/Y zeolite electrodes, scan rate of 1 mV/s in 2.5 mol dm$^{-3}$ H$_2$SO$_4$. The red dash line represents the CV for the 15Pdanc35r36 catalyst calcined at 350 °C and reduced at 360 °C. The blue solid line shows the CV for the 15Pdanc25r36 catalyst calcined at 250 °C and reduced at 360 °C, and the black solid lines represents the CV for the 15Pdancr4 catalyst calcined and reduced at 400 °C.

5.3.3 The Results of Extended X-Ray Adsorption Fine Structure (EXAFS)

The X-ray absorption data discussed in this chapter was collected using station 9.2 of the Synchrotron Radiation Source (SRS) at Daresbury, UK. The transmission mode was used during the data collection. The details have been described in section 2.5 of chapter 2.

The catalyst powders used during the EXAFS measurements are 1.5 wt.% Pd / zeolite catalysts prepared with Pd(NH$_4$)$_4$Cl$_4$ salts and ion exchange. The catalysts are calcined
at 250 °C and reduced at 360 °C, calcined at 350 °C and reduced 360 °C or calcined and reduced at 400 °C, respectively.

Primarily, catalyst powders were ground with polyethylene or boron nitride powder and pressed to produce a pellet, and then, placed between two pieces of plastic as described in section 2.5.2 of chapter 2. The EXAFS data was recorded in air.

The EXAFS spectrum of each sample was recorded at the Pd K edge, and the data were analysed as described in chapter 2, section 2.5.3. All data shown below are $k^2$ weighted to emphasize the data quality.

The results of the analysis of the ex-situ EXAFS data obtained for the 1.5 wt. % Pd/zeolite catalyst powders are presented in table 5.1. The raw EXAFS data and their Fourier transforms are shown in figure 5.6. The data were useful out to $k=18$ Å$^{-1}$ for the 15Pdanc25r36 and 15Pdancr4 catalysts, 17 Å$^{-1}$ for the 15Pdanc35r36 catalyst, and were fitted in r-space. The $k^2$ weighting was used in each fitting as described above.

Table 5.1: The results of fit for each Pd shell

(a) The result of fit of the Pd K EXAFS data for the 15Pdanc25r36 catalyst in air

<table>
<thead>
<tr>
<th>15Pdanc25r36</th>
<th>N</th>
<th>2σ$^2$/Å$^2$</th>
<th>R/Å</th>
<th>E$_{eff}$/eV</th>
<th>R$_{exaf}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>0.95±0.09</td>
<td>0.0049±0.0012</td>
<td>2.02±0.006</td>
<td>-0.92±0.62</td>
<td>40.81</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>5.2±0.62</td>
<td>0.0141±0.0003</td>
<td>2.74±0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pd</td>
<td>2.05±0.54</td>
<td>0.0125±0.0032</td>
<td>3.41±0.017</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of the Pd K EXAFS data for the 15Pdanc35r36 catalyst in air

<table>
<thead>
<tr>
<th>15Pdanc35r36</th>
<th>N</th>
<th>2σ$^2$/Å$^2$</th>
<th>R/Å</th>
<th>E$_{eff}$/eV</th>
<th>R$_{exaf}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.45±0.25</td>
<td>0.0063±0.0023</td>
<td>2.01±0.012</td>
<td>0.90±1.12</td>
<td>41.84</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>4.25±0.28</td>
<td>0.0135±0.0006</td>
<td>2.74±0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pd</td>
<td>3.22±0.57</td>
<td>0.0147±0.0016</td>
<td>3.42±0.010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The result of fit of the Pd K EXAFS data for the 15Pdancr4 catalyst in air

<table>
<thead>
<tr>
<th>15Pdancr4</th>
<th>N</th>
<th>2σ²/Å²</th>
<th>R/Å</th>
<th>E_{ef}/eV</th>
<th>R_{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 O</td>
<td>1.10±0.30</td>
<td>0.0072±0.0038</td>
<td>2.01±0.018</td>
<td>-0.49±1.13</td>
<td>36.32</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>5.77±0.33</td>
<td>0.0141±0.0006</td>
<td>2.74±0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pd</td>
<td>2.22±1.01</td>
<td>0.0200±0.0053</td>
<td>3.39±0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.6: Chi data and Fourier transforms for the 1.5 wt.%Pd/Y zeolite catalysts, phase corrected. The data were collected at room temperature in air. The solid line represents the experimental data, and dashed represents the fitted data. (a)=15Pdanc25r36 catalyst (b)=15Pdanc35r36 catalyst (c)=15Pdancr4 catalyst
As can be seen in the panel in the left hand column of figure 5.6 (the $\chi(k)$ plots), the period of the EXAFS oscillations for the three samples are almost identical. Some differences are observed in the Fourier transforms. In particular the amplitude of the main peak at 2.74 Å is slightly greater for the 15Pdancr4 catalyst.

The dashed lines in figure 5.6 are the fits to the data. These lines follow the data very well, reflecting the goodness of the fit. Pd neighbours were obtained in fitting the EXAFS data for each of the samples. The distance of Pd-Pd in the first shell for the 15Pdanc25r36, approximately 2.74 Å, is consistent with those observed for the 15Pdanc35r36 and 15Pdancr4 samples. The distance of Pd-Pd in the second shell is slightly lengthened to 3.42 Å, as compared to the distance of 3.39 Å for the 15Pdancr4 sample, and is close to the distance of 3.41 Å for the 15Pdanc35r36 sample.

Only one Pt-O shell is observed for all three catalysts during the data fit. The distance of Pd-O for the 15Pdanc35r36 catalyst, approximately 2.01 Å, is consistent to that for the 15Pdancr4 catalyst, and is close to the value of 2.02 Å for the 15Pdanc25r36 catalyst. The presence of oxygen neighbours indicates that the as prepared samples were oxidised.

The results indicate that the Pd particle size of the 15Pdancr4 catalyst may be slightly larger than those for the 15Pdanc35r36 catalysts, and the Pd particle size of 15Pdanc35r36 catalyst is the smallest if one presumes that the geometries of Pd structure for these two catalysts follow the model discussed in chapter three.

### 5.3.4 The Results of in situ Extended X-Ray Adsorption Fine Structure (EXAFS)

The in-situ EXAFS data illustrated in this section for the 15Pdanc35r36 catalyst was collected at the Pd K edge under potential control. The in situ EXAFS data was collected at -0.68 V, -0.63 V, -0.5 V and +0.5 V. The reference electrode was MMS for all measurements. The EXAFS data was analysed according to the procedure described in section 2.5.3. The resulting CHI-data and their Fourier transforms obtained for the
15Pdanc35r36 sample at the different potentials are displayed in figure 5.7(a), 5.7(b), 5.7(c) and 5.7(d), respectively.

Fluorescence mode was used during the data collection, as the quantity of Pd loading on the zeolite support is very low. The raw EXAFS (Chi) data is shown in figure 5.7. The Chi data is useful out to k=15 Å⁻¹ for the potential at -0.68 V, 13 Å⁻¹ for the potential at -0.63 V, 14.0 Å⁻¹ for the potential at -0.5 V and 13.5 Å⁻¹ for the potential at 0.5 V. The data were fitted in r-space, and k² weighting was used. The fits are shown as the dashed lines in the diagrams and the fit parameters are summarized in table 5.2 (a), 5.2 (b), 5.2 (c) and 5.2 (d).

Table 5.2: The results of fit for each Pt shell

(a) The result of fit of the Pd K EXAFS data for the 15Pdanc35r36 catalyst, which data was collected at -0.68 V vs. MMS

<table>
<thead>
<tr>
<th>15Pdanc35r36</th>
<th>N</th>
<th>2σ² / Å²</th>
<th>R/Å</th>
<th>E_{ef} /eV</th>
<th>R_{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pd</td>
<td>7.86±0.46</td>
<td>0.0168±0.0007</td>
<td>2.83±0.005</td>
<td>-0.74±0.02</td>
<td>39.35</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>0.58±0.25</td>
<td>0.0061±0.0031</td>
<td>3.46±0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pd</td>
<td>4.74±2.60</td>
<td>0.0268±0.0080</td>
<td>4.00±0.036</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) The result of fit of the Pd K EXAFS data for the 15Pdanc35r36 catalyst, which data was collected at -0.63 V vs. MMS

<table>
<thead>
<tr>
<th>15Pdanc35r36</th>
<th>N</th>
<th>2σ² / Å²</th>
<th>R/Å</th>
<th>E_{ef} /eV</th>
<th>R_{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pd</td>
<td>7.09±0.31</td>
<td>0.0151±0.0005</td>
<td>2.80±0.004</td>
<td>1.91±0.81</td>
<td>26.00</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>1.11±0.22</td>
<td>0.0049±0.0017</td>
<td>3.47±0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 Pd</td>
<td>2.73±0.69</td>
<td>0.0127±0.0025</td>
<td>3.96±0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) The result of fit of the Pd K EXAFS data for the 15Pdanc35r36 catalyst, which data was collected at -0.5 V vs. MMS

<table>
<thead>
<tr>
<th>15Pdanc35r36</th>
<th>N</th>
<th>2σ² / Å²</th>
<th>R/Å</th>
<th>E_{ef} /eV</th>
<th>R_{exafs} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pd</td>
<td>5.65±0.61</td>
<td>0.0088±0.0005</td>
<td>2.74±0.005</td>
<td>1.08±1.55</td>
<td>34.72</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>2.42±0.54</td>
<td>0.0059±0.0036</td>
<td>3.80±0.024</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(d) The result of fit of the Pd K EXAFS data for the 15Pdanc35r36 catalyst, which data was collected at +0.5 V vs. MMS

<table>
<thead>
<tr>
<th>15Pdanc35r36</th>
<th>N</th>
<th>$2\sigma^2/\text{Å}^2$</th>
<th>R/Å</th>
<th>$E_{	ext{cf}}$/eV</th>
<th>$R_{\text{exafs}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1 Pd</td>
<td>6.18±0.52</td>
<td>0.0162±0.0009</td>
<td>2.73±0.008</td>
<td>1.07±1.64</td>
<td>46.30</td>
</tr>
<tr>
<td>Shell 2 Pd</td>
<td>4.68±3.06</td>
<td>0.0419±0.0363</td>
<td>3.33±0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shell 3 O</td>
<td>0.64±0.31</td>
<td>0.0272±0.0099</td>
<td>2.00±0.133</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.7: Chi data and Fourier transforms for the 1.5Pdnc35r36 catalyst, phase corrected. The data were collected at room temperature. The solid line represents the experimental data, and dashed represents the fitted data. (a) at −0.68 V (b) at −0.63 V (c) at −0.5 V (d) at +0.5 V.
The EXAFS fit parameters in table 5.2 reveal that the value of Pd-Pd distance in the Pd-Pd first shell for the 15Pdanc35r36 catalyst, approximately 2.83 Å at −0.68 V and 2.80 Å at −0.63 V, is slightly longer than the value of 2.75 Å observed for the bulk of Pd, whereas the value of Pd distance for the same catalyst, around 2.74 Å at −0.5 V and 2.73 Å at +0.5 V, is almost identical to that obtained from the bulk. The increase of Pd-Pd bond distance observed at −0.63 V or −0.68 V may be attributed to the fact that hydrogen ions are not only absorbed on the Pd surface but also are absorbed forming the hydride, PdH. An O coordination number, approximately 0.64, is observed for the 15Pdanc35r36 catalyst when the potential was set at +0.5 V. The value of Pd-O distance, around 2.00 Å is consistent with that obtained for the metal oxides.

The Pd coordination number is dependent on the applied potential. The largest coordination numbers are observed at -0.68 V and -0.63 V. At these potentials hydrogen is adsorbed on the Pd surface. As the potential is made more positive the hydrogen is desorbed. It is well known that hydrogen may also be absorbed by Pd forming the palladium hydride. When the hydrogen is desorbed the absorbed hydrogen leaves the metal particle. This may cause the particle surface to become rough, which would be evident as a lower coordination number as is observed at -0.5 V. When the potential is swept further positive to +0.5 V, in the oxide formation region, the coordination number also drops, now to 6.18 rather than the 7.0 – 7.8 observed at the most negative potentials. This drop is accompanied by the presence of oxygen in the first coordination shell. The oxygen atoms replace some of the Pd atoms in the first coordination shell. Thus, the decrease in the Pd-Pd coordination number may be fully explained by the formation of the oxide and we do not have to attribute this effect to a change in the particle size or morphology.

5.4 Discussion and conclusion

The experiments conducted in this chapter serve two purposes. First, by repeating the experiments with a different metal, Pd rather than Pt, it may be confirmed that the electrochemical activity of small metal particles supported on zeolites is general. In other words that the results obtained for Pt are not unique. Secondly, in the previous chapter the results for the electrochemical activity of the Pt/Y zeolite were interpreted
in terms of the location of the Pt particles on the zeolite support (external surface, supercages, sodalite cages or hexagonal prisms). Pd is more mobile than Pt in the zeolite structure due to their different d electron configuration [2]. The valence electrons on Pd are in the 4d orbitals, whilst on Pt they are in the 5d. So, as in the case of Fe$^{3+}$ presented in the previous chapter, Pd$^{4+}$ has a greater charge density than Pt$^{2+}$ and is, therefore more mobile. By controlling the calcination and reduction temperature the location of the Pd particles can be influenced.

The cyclic voltammogram results obtained for the 1.5wt% Pd/Y zeolite catalysts show the same basic features as those observed for the 40wt% Pd/C in the negative potential region (compare figures 5.5 and 5.1). These features are attributed to hydrogen adsorption and evolution, desorption and re-oxidation. In the positive potential region the cyclic voltammograms for the zeolite and carbon supported catalyst are not as similar. For the Pd/C electrode features are observed corresponding to the oxide formation and oxygen evolution. There is some evidence for a small oxide formation peak for the Pd/Y catalysts at 0.2 V and an oxide-stripping feature at 0.0 V. However, the relative currents observed for the oxide vs. the hydride features are much smaller for the Pd/Y catalyst compared to the Pd/C. This is in agreement with the results obtained for Pt/Y catalysts and may be attributed to the very small particle size of the zeolite supported metal particles. The EXAFS results obtained in the electrochemical cell confirm that the Pd particles on the zeolite support are very small. Using the Benfield model [5] the number of atoms ($N_1=5.65$) in the particle is approximately 12.

The influence of the location of the metal particles on the electrochemical activity may be estimated by comparing the hydride features in the cyclic voltammograms shown in figure 5.5. As the calcination and reduction temperatures are increased the charge associated with hydrogen adsorption is seen to increase.

From the literature [6] the various calcination and reduction temperatures used will determine the position of the Pd particles. As discussed in chapter 1, the research work done by Homeyer and Sachtler [2, 6] shows that the migration of the Pd ions, which are coordinated to one or two ammonia ligands into the sodalite cages, occurs after calcination at a temperature at 300 °C or above. They also found that the majority of Pd was released from sodalite cages to supercages following hydrogen reduction at
350 °C. Higher reduction temperatures (greater than 350 °C) were required to enable the Pd to migrate from the hexagonal prisms to back to the supercages. For the calcination at 250 °C and reduction at 360 °C, the particles will be located in the supercages. For calcination at 350 °C and reduction at 360 °C, the particles are located mostly in the sodalite cages and hexagonal prisms, with some remaining in the supercages. Finally, for calcination at 400 °C and reduction at 400 °C the particles will move to the supercages and the external surface of the zeolite structure. However, proper interpretation of the electrochemical results must also consider the particle size.

The EXAFS results show that the Pd particle size changes with the calcination and reduction temperature. The particle size estimate is complicated by the fact that the EXAFS was only obtained for the as prepared samples in air. The EXAFS fits all have oxygen neighbours as well as Pd neighbours in the first coordination shell. As a rough estimate of the particle size the Pd-O and Pd-Pd coordination numbers can be added together. For the catalysts calcined at 250 °C and reduced at 360 °C (15Pdanc25r36) this gives a first shell coordination of 6.15. For the 15Pdanc35r36 catalyst the first shell coordination number is 5.70, and for the 15Pdancr4 it is 6.87. Thus, the 15Pdanc35r36 catalyst exhibits the smallest particle size, with the 15Pdanc25r36 having a slightly larger size and the 15Pdancr4 having the largest particle size.

A larger particle size corresponds to a smaller surface area per gram of metal in the catalyst electrode. Thus, if the effect of calcination and reduction temperature was only a particle size effect the expected ordering of the hydride charge would be 15Pdancr4 < 15Pdanc25r36 < 15Pdanc35r36. However, this is not the trend observed. Therefore, the location of the metal particle must be taken into consideration.

The electrochemical results (figure 5.5) may therefore be more fully interpreted using the information obtained from the EXAFS and the predictions of the particle location based on the literature [6]. The 15Pdancr4 catalyst has the largest electrochemically active surface area, whilst having the largest particle size. The enhanced electrochemical area is attributed to the fact that the particles are located on the external surface and in the supercages of the zeolite support. Particles in these locations are more accessible to the protons in the solution. In addition the particles on the external surface may be in better electronic contact with the carbon support.
Comparing the particle sizes of the 15Pdanc35r36 and 15Pdanc25r36, the 15Pdanc35r36 is slightly smaller. Thus, the 15Pdanc35r36 should have a larger electrochemically active surface area (greater charge under the hydride features in the CV). This agrees well with the cyclic voltammograms shown in figure 5.5. However, the 15Pdanc25r36 particles are predicted to be in the supercages and should, therefore, be more easily accessible by the protons in solution. If the particles were the same size, the 15Pdanc25r36 should have the larger electrochemically active surface area. The areas under the hydride peaks for the 15Pdanc35r36 and 15Pdanc25r36 catalysts are very similar. Therefore, the combination of the two effects, particle size and location, must be in balance to give the same result.

The results for the Pd/Y zeolite system presented in this chapter confirm the conclusions obtained from the Pt/Y zeolite study. The electrochemical activity of the metal particles supported on the zeolite depends both on the location and size of the particles. The most electrochemically accessible particles are located on the external surface and in the supercages of the zeolite. For the purposes of catalysis enhanced by the structure of the zeolite the particles located in the supercages are more interesting. However, if using a zeolite support can stabilise particles smaller than those obtained on a carbon support, then the particles located on the external surface of the zeolite may prove interesting.
5.5 References


Chapter 6: Conclusions

As stated in the introduction to this thesis, the aim of the work presented here was to investigate the electron transfer process at Pt and Pd particles supported on Y zeolite using electrochemical and X-ray absorption spectroscopic techniques. It was hoped that the studies presented in this thesis would contribute to the understanding of how electron transfer can occur at the supported metal particles, even though the zeolite itself is a dc insulator. In this conclusions chapter several questions regarding the electron transfer process will be addressed and a preliminary study of the electrocatalytic technique of Pt/Y zeolite materials will be presented.

6.1 Utilization of zeolite supported metal particles

As seen in table 4.12 in chapter 4 the results obtained from the EXAFS data analysis for the chemical and electrochemical reductions are quite similar for most of the catalysts. Both the Pt-Pt coordination number in the Pt first shell and the Pt-Pt distances are in very good agreement. The small differences observed may be attributed to the errors in the data analysis itself. The presence of oxygen neighbours for the 5anxcr4 catalyst under chemical reduction control was attributed to a leak in the gas treatment cell. The oxygen neighbours observed for the 15anr4 catalyst under electrochemical reduction control was accounted for by fact that the reduction potential was not negative of the hydrogen adsorption peak. Accordingly, the results predict that the mechanism of electrochemical reduction of the Pt particles on the zeolite support is related to the presence of adsorbed hydrogen species. This mechanism is the same in the case of chemical reduction.

The EXAFS experiment is a steady state measurement. It is not clear, however, if the electrochemical reduction of the Pt particles occurs by a direct electron transfer or by mobile H_{ads}/H^+ species on the zeolite. A comparison of the surface areas of the Pt particles obtained from the EXAFS data analysis and the H adsorption peaks in the CVs may make the situation clearer.

The surface area of the catalysts may be expressed as the dispersion. Dispersion is the percentage of the Pt (~ Pd) atoms that are on the surface of the particles, i.e. \( \left( \frac{N_{\text{Surface}}}{N_{\text{Total}}} \right) \times 100\% \).
The theoretical dispersion can be calculated from the particle size predicted by the EXAFS data analysis. As seen in chapter 3 the first shell coordination number is related to the particle size. An analytical formula has been derived by Benfield [1]. Once the length of the side of the icosahedron or cuboctahedron is chosen the relative number of surface atoms can be calculated using Benfield formulas.

Table 6.1 displays the value of $N_S$ corresponding total number of surface atoms in the cluster for the catalysts following H$_2$ chemical reduction according to the model given by Benfield [1]. The reduced data were chosen, as there is less interference from the presence of oxygen neighbours in the first coordination shell. This has been discussed in chapter 3. The predicted particle size is very small and, therefore, a very high level of dispersion is expected.

Table 6.1: the values of Pt surface atoms in the particles on zeolite

<table>
<thead>
<tr>
<th>Acronym Name</th>
<th>$N_i$ from refinement</th>
<th>$N_S$ from Benfield’s formula ($Total$ $number$ $of$ $surface$ $atom$ $in$ $a$ $cluster$)</th>
<th>$N_T$ total atoms in cluster</th>
<th>Dispersion $N_S/N_T$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>6.33</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>15anxcr4$^b$</td>
<td>6.00</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>15impgancr4</td>
<td>4.28</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>15feancr3</td>
<td>5.17$^a$</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>15feance4</td>
<td>5.33$^a$</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>5ancr4</td>
<td>7.47</td>
<td>42</td>
<td>55</td>
<td>76</td>
</tr>
<tr>
<td>5anxcr4$^b$</td>
<td>6.02</td>
<td>12</td>
<td>13</td>
<td>92</td>
</tr>
<tr>
<td>5andr4</td>
<td>8.31</td>
<td>42</td>
<td>55</td>
<td>76</td>
</tr>
</tbody>
</table>

b. Oxygen neighbours present in the first coordination shell.

The electrochemical dispersion can be calculated from the hydrogen adsorption area (~charge) and the known mass of Pt on the electrode.

Table 6.2 shows the parameters used in calculating the dispersion from the electrochemical results. As seen in this table the dispersion values range from 3.46 ~ 29.4%. These values are much lower than the theoretical, EXAFS derived values, 76 ~ 92%.
The origins of the difference in the dispersions obtained from the EXAFS and the electrochemical methods probably reflected the different time scales of the measurements. As stated above, the EXAFS measurements were steady state measurements, taking ~ 45 minutes per scan and 2 ~ 3 scans were averaged. The electrochemical measurements are dynamic measurements. The scan rate was 1 mV s\(^{-1}\). The hydrogen adsorption peaks are spread over ~ 50 mV, which corresponds to ~ 50 seconds.

The different time scales of the two methods of the dispersion determined allow discrimination between the two possible mechanisms of electrochemical reduction. If the direct electron transfer mechanism was correct then the same dispersion should be obtained. This is not the case here. The dispersion from the electrochemical measurement is much smaller than that predicted by the EXAFS. Thus, it may be concluded that spill over from the electrochemically accessible Pt particles onto the zeolite and then to the other Pt particles.

Table 6.2: the values of Pt targets in the per cm\(^2\) electrode area

<table>
<thead>
<tr>
<th>Acronym Name</th>
<th>Calculated mass quantity in wt. percentage/(%)</th>
<th>(N_T) Pt atoms cm(^2)/10(^{17})</th>
<th>(N_S) Pt surface atoms per cm(^2)/10(^{16})</th>
<th>Dispersion (N_S/N_T/) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15ancr4</td>
<td>1.52</td>
<td>5.21</td>
<td>7.64</td>
<td>14.66</td>
</tr>
<tr>
<td>15anxcr4(^b)</td>
<td>0.77</td>
<td>2.64</td>
<td>7.77</td>
<td>29.44</td>
</tr>
<tr>
<td>15impanc4</td>
<td>1.68</td>
<td>5.77</td>
<td>13.90</td>
<td>24.09</td>
</tr>
<tr>
<td>15feanrcr3</td>
<td>1.49</td>
<td>5.11</td>
<td>8.33</td>
<td>16.30</td>
</tr>
<tr>
<td>15feancr4</td>
<td>1.54</td>
<td>5.28</td>
<td>13.04</td>
<td>24.70</td>
</tr>
<tr>
<td>5ancr4</td>
<td>7.76</td>
<td>26.62</td>
<td>13.11</td>
<td>4.93</td>
</tr>
<tr>
<td>5anxcr4(^b)</td>
<td>4.71</td>
<td>16.16</td>
<td>15.11</td>
<td>9.35</td>
</tr>
<tr>
<td>5andr4</td>
<td>7.40</td>
<td>25.38</td>
<td>8.79</td>
<td>3.46</td>
</tr>
</tbody>
</table>
6.2 Hydrogen/Proton transport

As seen in chapter 3 and chapter 4, the results obtained in the electrochemical and chemical reduction environments both predict that the 15anxcr4 sample, prepared with excess NH₄NO₃ salt, has the smallest Pt particle size and bigger H_ads area as compared to the results obtained for the catalysts, prepared with the same Pt salt without excess NH₄NO₃ salt. The results obtained for the electrochemical hydrogen reduction indicates that the mechanism of electrochemical reduction of the Pt particles on the zeolite support is related to the presence of adsorbed hydrogen species. The mobility of hydrogen and protons on and in the zeolite structure contribute to electrochemical reduction occurring much more easily. As discussed in chapter 4, the most common explanation available is hydrogen spillover theory, which is applied in solid acidic catalyst study. The spillover hydrogen offers a strong effect on the catalytic reactions occurring in solid acidic catalysts. In this theory, H⁺ has been regarded as one of the most important species in this process [2]. The spillover H⁺ ions can be transmitted along the surface of the zeolite support. This increases the surface conductivity of the support [3, 4, 5]. Excess H_ads can spill over on to the zeolite support due to the availability of the acidic sites, e.g. the Brønsted or Lewis acid sites. This leads to a flow of protons along the acidic sites and can transport hydrogen species to other Pt particles on zeolite.

According to reference made to the chemical reduction process and hydrogen spillover, in the electrochemical reduction H⁺ may be primarily reduced to form adsorbed hydrogen, H_ads. Then, a flow of hydrogen species across the zeolite surface may begin. Consequently, Pt particles located within the zeolite structure, which is electronically insulating, can be electrochemically reduced. This theory is supported by the electrochemical results, such as cyclic voltammetry, which was presented in chapter 4. The most well resolved hydrogen adsorption and desorption features for the 1.5 wt.% loading Pt catalysts are found for the 15anxcr4 catalyst electrode. The result predicts that the addition of excess NH₄NO₃ during the ion exchange process provides more H⁺ species on the zeolite structure in the final catalyst.

Currently, it is not known how these catalysts participate in the electrochemical oxidation process, as there is lack of ionic species that are easily identifiable. It is
noticed that the oxidation formation and stripping peaks are always very small compared to the H features. The evidence obtained from the CO oxidation for the catalysts discussed in the previous chapters show that most of the Pt can be oxidised as the areas of CO adsorption and stripping are equivalent to the hydrogen adsorption areas, but this could be that the CO itself is mobile. However, the oxidation behaviours of Pt/zeolite catalysts were tested by examining electrooxidation of some small organic species.

6.3 Electrooxidation of Small Organic Spices

The electrocatalytic oxidation of small organic molecules, such as methanol and formic acid, has been extensively investigated and the key aspects of the oxidation mechanism of such simple organic molecules on the Pt electrodes has been reviewed by Parsons and VanderNoot [6]. These organic molecules have simple structures. Accordingly, they perhaps have the simplest and most straightforward reaction mechanisms of all organic compounds, which are able to react on the Pt electrodes.

The overall reaction for methanol oxidation is presented as follows:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^- \quad (1)
\]

The reaction is thought to involve several adsorbed intermediates, such as CO, CHO, and COH species.

The overall reaction for the formic acid is presented as follows:

\[
\text{HCOOH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}^+ + \text{OH}^- + 4\text{e}^- \quad (2)
\]

Here, the intermediates are thought to be HCO and CO species.

The electrocatalytic oxidation of these small organic molecules is highly sensitive to the surface structure of the electrode material. The adsorption steps and adsorbed intermediates occurring in the reactions depend on the local symmetry of the electrode
surface. In general Pt is considered to be the most suitable catalyst for the electooxidation of these small organic molecules in acid electrolyte [7]. The product obtained from the complete oxidation of these small organic molecules is regarded as CO₂. Nevertheless, during the course of the reaction the Pt electrode is frequently deactivated with the coverage of a poison. Many research studies have suggested that CO is the main poison species involved in the oxidation of methanol and formic acid, and that CHO or COH are the intermediates [8, 9]. The CO is commonly regarded as occupying Pt sites and suppressing the overall decomposition reaction [10]. In contrast to methanol decomposition, the CO₂ formation pathway for formic acid oxidation is much more efficient than that of CO formation [6, 11, 12] so that the CO₂ formation process occurs at higher yield. Some authors have assumed that the surface oxides were simply acting as sources of oxygen [9, 13] for the oxidation of CO. However, others report that the solution phase OH⁻ is available for the source of the required oxygen as well [6, 14].

6.3.1 Oxidation of Methanol

The catalysts investigated during the course of experiments were those discussed in chapter three and chapter four. The electrodes were fabricated by using Nafton® as the binder. The details can be seen in section 4.2.2 of chapter 4 and chapter 2. The experiments for methanol and formic acid were carried out in a three-electrode glass cell described in section 2.3.3 of chapter 2. The base electrolyte solution was 2.5 mol dm⁻³ H₂SO₄ made with triply distilled water. The potentials were recorded with respect to the Hg/Hg₂SO₄ (MMS) reference electrode.

Firstly, the CV was cycled in 2.5 mol dm⁻³ sulphuric acid from −0.65 V to 0.5 V with the scan rate of 0.001 V s⁻¹ until a clean stable CV was obtained. Then, methanol or formic acid was added into the solution. The concentration of methanol or formic acid in the base electrolyte was kept at 1.0 mol dm⁻³. The potential was cycled between −0.65 V to 0.5 V until a stable CV was obtained. The positive potential was always limited to 0.5 V in order to avoid significant coverage of the electrode surface by adsorbed oxygen.
Figure 6.1 displays the CVs of methanol oxidation on the Pt/zeolite electrodes prepared with 1.5 wt.% Pt loading catalysts. The CVs show that the hydride region was suppressed by the presence of methanol in comparison to the normal CV obtained in the sulphuric acid. The peak current for methanol oxidation for the 15anr4 electrode is slightly greater than those obtained for the 15anxcr4 and 15impGANcr4 electrodes. In addition, the peak potential at 0.25 V for methanol oxidation on the 15anr4 electrodes is consistent with that obtained on the 15anxcr4 electrode. Current recorded in the oxidation region for the 15impGANcr4 catalyst is lower than those for 15anxcr4 and 15anr4 catalysts.

Differences are also observed on the hydrogen desorption regions. Hydrogen desorption on the Pt electrodes prepared by 15anxcr4 and 15impGANcr4 catalysts are not
completely blocked by methanol as was previously not observed for the catalyst prepared without excess nitrate (15ancr4 catalyst).

Figure 6.2 displays the CVs of methanol oxidation on the Pt/zeolite electrodes prepared by 5 wt.% Pt loading catalysts.

Figure 6.2: Effect of methanol oxidation for 5 wt.% Pt loading Pt/Zeolite catalysts in 2.5 mol dm⁻³ with 1 mol dm⁻³ methanol, scan rate of 1 mV s⁻¹. The black line presents a clean Pt/Zeolite CV. The red line shows the CV of methanol oxidation. (a)=5ancr4 catalyst, (b)=5anxcr4 catalyst, (c)=5andr4 catalyst

The features show that the hydride region is suppressed by presence of the methanol as was previously observed for the 15ancr4 and 15anxcr4 catalysts. The methanol oxidation CV for the 5anxcr4 catalyst is remarkably different from the CVs obtained for the 5ancr4 and 5andr4 catalysts and the CVs obtained for the 1.5 wt.% Pt catalysts.
Comparing the CVs of methanol oxidation for the 5 wt.% Pt loading catalysts to the CVs obtained for the 1.5 wt.% Pt loading catalysts, an abrupt increase of current is observed from −0.15 V to 0.2 V on the positive going sweep, and then, a stable current was maintained. Nevertheless, a current density of 0.001 A cm\(^{-2}\) is kept constantly from 0.4 V to 0.1 V on the negative going sweep. A great decrease of current is observed in the potential region from 0.2 V to −0.15 V.

The electrochemical activity towards methanol oxidation for the direct reduced catalyst (5andr4), has not been found as the current density \(i\) vs. potential \(E\) curves corresponding to the methanol oxidation are consistent to the clean CV obtained in the plain sulphuric acid. No current change is observed in the oxidation region. However, the hydride region is suppressed.

Comparing the CVs of methanol oxidation for the 5 wt.% Pt loading/zeolite catalysts to the CVs obtained for the 1.5 wt.% Pt loading/zeolite catalysts, most activity towards methanol oxidation is found for the 5anxcr4 catalyst as evidenced by the highest oxidation current presented in figure 6.2 (b). The least activity of methanol oxidation is thought to be the direct reduced 5andr4 catalyst (5 wt.% Pt loading on zeolite), as Pt particle sizes on zeolite for the direct reduced catalyst (5andr4) are big to block the zeolite pores and channels. This prohibits methanol from entering the cages and accessing the Pt electro-active surface area. The particle size for the 5 wt.% Pt loading/zeolite catalyst prepared with excess ammonia nitrate salt is smaller than those for the 5 wt.% Pt loading/zeolite catalysts prepared without excess ammonia nitrate salt (5anxcr4 and 5andr4 catalysts). Nevertheless, the particle size (5anxcr4) is still bigger than that for the 1.5 wt.% Pt loading/zeolite catalysts. The results indicate that the particle size is important for methanol oxidation, and a minimum particle size may be needed to obtain the better oxidation results. Also the results predict that some of the Pt active particles are on the zeolite external surface, while most of them remain in the zeolite supercages.

However, the electrocatalytic activity of methanol oxidation for the Pt/zeolite catalysts is not as high as that obtain from Pt/C catalyst.
6.3.2 Oxidation of Formic Acid

The electrocatalytic performances of formic oxidation for the 1.5 wt.% Pt/Y zeolite catalysts are examined and displayed in figure 6.3. The CVs show the profiles with peak current at 0.2 V for the 15ancr4 and 15impgancr4 catalysts and 0.25 V for the 15anxcr4 catalyst in the anodic going sweep. The oxidation starts immediately after the hydrogen desorption region, and the maximum oxidative current associated with the oxidation of formic acid is extended to 0.5 V for three catalysts, respectively. On the reverse scan, the oxidation starts at the reduction potential region of Pt oxide, but current is lower than that obtained in the forward scan at same potential region. Hydrogen adsorption regions for three catalysts are suppressed by the coverage of formic acid on the Pt surface.

![Graphs showing oxidation of formic acid](image)

Figure 6.3: Effect of HCOOH oxidation for the 1.5 wt.% Pt/zeolite electrodes in 2.5 mol dm\(^{-3}\) sulphuric acid with 1.0 mol dm\(^{-3}\) HCOOH, scan rate of 1 mV s\(^{-1}\). The black line presents a clean Pt/zeolite CV. The red line shows the CV of HCOOH oxidation. (a)=15ancr4 catalyst, (b) =15anxcr4 catalyst, (c) =15impgancr4 catalyst
Nevertheless, differences are observed in the hydrogen desorption region. The hydrogen desorption peak for the \textit{15\textsuperscript{imp}gan\textsuperscript{cr}4} catalyst, prepared with Pt nitrate salt and impregnation method, is not fully suppressed.

The cyclic voltammograms of HCOOH oxidation on Pt for the 5 wt.% Pt loading zeolite catalysts are given in figure 6.4

![Cyclic voltammograms](image)

Figure 6.4: Effect of HCOOH oxidation for the 5 wt.% Pt/zeolite electrodes in 2.5 mol dm\textsuperscript{-3} sulphuric acid with 1.0 mol dm\textsuperscript{-3} HCOOH, scan rate of 1 mV s\textsuperscript{-1}. The black line presents a clean Pt/zeolite CV. The red line shows the CV of HCOOH oxidation. (a)=\textit{5ancr4} catalyst, (b)=\textit{5anxcr4} catalyst, (c)=\textit{5andr4} catalyst

The CVs show that the current due to the oxidation of HCOOH is remarkably increased for the \textit{5ancr4} and \textit{5anxcr4} catalysts prepared with or without excess nitrate. A maximum peak current corresponding to the oxidation of HCOOH acid is observed at 0.2 V for the \textit{5ancr4} catalyst on the positive going sweep. On the reverse scan the peak current for the HCOOH acid oxidation occurs at 0.05 V.
The remarkably increase of current is also observed for the 5anxcr4 catalyst, prepared with excess nitrate, and the maximum current is observed at 0.5 V on the positive going sweep. The oxidation current on the cathodic sweep is primarily kept at 0.0024 A cm\(^{-2}\) until to 0.1 V, and then, an abrupt decrease of current is observed.

The cyclic voltammogram of HCOOH oxidation for the 5andr4 catalyst, prepared with Pt nitrate salt and direct reduction method, has not shown any change at the oxidation region on the positive going sweep and its reverse sweep.

Nevertheless, the CVs show that the hydrogen adsorption peaks for three catalysts are completely suppressed by the coverage of HCOOH on the Pt surface. This is in accordance to the phenomena observed for all catalysts during the methanol oxidative reaction.

Differences are also observed in the hydrogen desorption region for three catalysts. The hydrogen desorption peak obtained in the base electrolyte for the 5anxcr4 catalyst is consistent to the peak observed for the same catalyst upon the addition of HCOOH. A slight decrease of hydrogen desorption peak is obtained in the anodic sweep for the 5anxcr4 catalyst upon the addition of HCOOH acid, whilst the hydrogen desorption peak for the 5anxcr4 catalyst is completely suppressed.

Comparing the CVs of HCOOH oxidation for the 5 wt.% Pt loading/zeolite catalysts to the CVs obtained for the 1.5 wt.% Pt loading/zeolite catalysts, the most activity of HCOOH oxidation is found for the 5anxcr4 catalyst as evidenced by the highest oxidation current presented in the figure 6.4 (b). The least activity of HCOOH oxidation is observed for the direct reduced 5andr4 catalyst (5 wt.% Pt loading on zeolite), as Pt particle sizes on zeolite for the direct reduced catalyst (5andr4) are bigger than others. This leads to block the zeolite pores and channels. The results obtained for the oxidation of HCOOH acid are consistent with those obtained for the methanol oxidation. Once again this implies that the particle size is important for the methanol or HCOOH oxidation. A certain particle size may be needed to maintain the oxidation result. However, the kinetic process may also play an important role as the oxidation results may be depended on the proportion of H\(^+\) and small organic molecules occupying the electro-active Pt surface.
6.4 Conclusion and Future Directions

The results indicate that the Pt particles for the 15anxcr4 and 5anxcr4 catalysts, prepared with \([\text{Pt(}\text{NH}_3\text{)}_4]^{2+}/\text{NH}_4^+\), is most likely located on the supercages assisted by the presence of the \(\text{H}^+\) ions, which help to anchor the Pt particles to the zeolite cage walls. Thus, the catalyst is not mobile in the zeolite channel as compared to the 15anxcr4, 5anxcr4 and 5andr4 catalysts prepared with \([\text{Pt(}\text{NH}_3\text{)}_4]^{2+}\). The particle size of the catalyst with excess protons is thought to be small and highly dispersed on the zeolite structure. Moreover, the Pt particles for the 15Ptfecr3 and 15Ptfecr4 catalysts prepared with \([\text{Pt(}\text{NH}_3\text{)}_4]^{2+}/\text{Fe}^{2+}\) are immobile and remain in the zeolite supercages. The particle size for this type of catalyst is very small. The effect of ion exchange with \(\text{Fe}^{2+}\) ions prior to ion exchange with \(\text{Pt}^{2+}\) is similar to that in the presence of excess \(\text{H}^+\) ions. The \(\text{Fe}^{2+}\) ions anchor the Pt particle to the cage walls, restricting the mobility of the Pt during the reduction process.

As compared to the Pt particle size, Pd particle size is significantly larger than the Pt particle size prepared by the same way as for the Pd catalysts. This may be attributed to the mobility of Pd particles inside the zeolite structure. The Pd particle size and the location on the zeolite are strongly dependent on the calcination and reduction temperature. The results obtained for the Pd/zeolite or Pt/zeolite catalysts indicate that the metal particles on the external surface or inside zeolite cages are electrochemical accessible, and the particle can be electrochemically reduced as demonstrated by the different shape of cyclic voltammograms observed for these two elements.

However, this investigation of the Na Y zeolite supported Pt catalyst is only the beginning of such investigations. The various electrochemical reaction results indicate that metals inside zeolite cages are electrocatalytic active, but further studies still need to be carried out. This might lead to improve the electrocatalytic activity of these catalysts. However, the improvement in the electrochemical activity may be found with the use of other zeolite materials, such as L zeolite, which is the material with rich electron density. The electrode should be tested with the use of other electrochemical techniques. Consequently, the assessment may be addressed if zeolite supported metal catalysts, as the electrochemical catalysts, are useful in electrochemical catalysis.
6.5 References


