**Impact of Nanoparticle-Support Interactions in Co3O4/Al2O3 Catalysts for the Preferential Oxidation of Carbon Monoxide**

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# **Abstract**

Different supporting procedures were followed to alter the nanoparticle-support interactions (NPSI) in two Co3O4/Al2O3 catalysts, prepared using the reverse micelle technique. The catalysts were tested in the dry preferential oxidation of carbon monoxide (CO-PrOx) while monitoring their phase stability using four complementary *in situ* techniques, *viz.,* magnet-based characterisation, PXRD, combined XAS/DRIFTS as well as *quasi in situ* XPS, respectively. The catalyst with weak NPSI achieved higher CO2 yields and selectivities at temperatures below 225 °C compared to the sample with strong NPSI. However, relatively high degrees of reduction of Co3O4 to metallic Co were reached between 250 and 350 °C for the same catalyst. The presence of metallic Co led to the undesired formation of CH4, reaching a yield of over 90% above 300 °C. The catalyst with strong NPSI formed very low amounts of metallic Co (less than 1%) and CH4 (yield of up to 20%) even at 350 °C. When the temperature was decreased from 350 to 50 °C under the reaction gas, both catalysts were slightly re-oxidised and gradually re-gained their CO oxidation activity while the formation of CH4 diminished. The present study, for the first time, shows a strong relationship between catalyst performance (*i.e.*, activity and selectivity) and phase stability, both of which are affected by the strength of the NPSI. When using a metal oxide as the active CO-PrOx catalyst, it is important for it to have significant reduction resistance to avoid the formation of undesired products, *e.g.*, CH4. However, the metal oxide should also be reducible (especially on the surface) to allow for a complete conversion of CO to CO2 *via* the Mars-van Krevelen mechanism.

**KEY WORDS:** *CO-PrOx, Co3O4/Al2O3, nanoparticle-support interactions, catalyst performance, phase stability, in situ characterisation*

# **Introduction**

Heterogeneous catalysts commonly comprise metal or metal oxide nanoparticles anchored on mechanically- and thermo-stable carriers referred to as supports.1 Most supports are either metal oxides (*e.g.*, SiO2 and Al2O3) or non-oxidic materials (*e.g.*, graphite and SiC) with high mass-specific surface areas. High surface area is preferred as it allows for the uniform distribution of nanoparticles on the support and the deposition of relatively high amounts of the nanoparticles (or metal loadings), respectively.1 The support material also helps prevent nanoparticle growth which may be induced by the high temperatures applied either during catalyst pre-treatment/activation (*e.g.*, calcination or reduction) and/or by the chemical environment of the reaction.2

As a result of nanoparticle anchoring, certain properties of the nanoparticles (adsorption and reduction/oxidation capabilities) may be affected compared to their unsupported counterpart.3 The method used to prepare the supported catalyst and the nature of the support material chosen also plays a significant role in controlling the final properties of the nanoparticles.4, 5 In general, very strong nanoparticle-support interactions (NPSI) between an oxidic support and oxide nanoparticles usually causes the reduction of the nanoparticles to be difficult.6-8 For example, the conventional impregnation of irreducible supports like SiO2 and Al2O3 with an aqueous solution of cobalt nitrate, results in Co3O4-based catalysts which are relatively hard to reduce to metallic Co in a H2 environment. On the other hand, on reducible supports like CeO2 and ZrO2, the reduction of Co3O4 is thermally less demanding but is still relatively difficult when compared to the reduction of unsupported Co3O4.6, 8

We have previously conducted an *in situ* study investigating the effect of the crystallite size of Al2O3-supported Co3O4 nanoparticles on the preferential oxidation of CO (CO-PrOx) in a H2-rich gas mixture.9 CO-PrOx is a promising final step for the removal of trace amounts of CO in H2-rich streams (*e.g.*, from the consecutive CH4 steam reforming and the water-gas shift processes) before being fed into proton exchange membrane fuel cells (PEMFC’s) for power generation as the CO poisons the Pt-based anode catalyst of PEMFC’s.10-12 We were able to show that Co3O4 reduces to CoO and ultimately to metallic Co at high reaction temperatures and that the reduction is influenced by crystallite size. This catalyst phase change proved to be unfavourable as less CO2 was formed and instead, CH4 was produced due to the presence of the metallic Co. Co3O4 or specifically the Co3+-Co2+ redox pair is believed to play an important role in the oxidation of CO.13-16

After observing the phase transformations, we speculated that introducing strong NPSI in the Co3O4/Al2O3 system would limit the reduction of Co3O4 and widen the temperature window for the CO-PrOx reaction. In our previous study,9 the reverse micelle technique was used to prepare unsupported Co3O4 nanoparticles of varying sizes. The Al2O3 support was only contacted with the Co3O4 nanoparticles after their calcination.9, 17 This way, the strength of the interaction between the support and the nanoparticles could be minimised to allow for the exclusive study of crystallite size effects. However, in the present study, two of the four different supporting methods detailed by Fischer *et al.*5 to alter the NPSI were explored. Their approach involved contacting the Al2O3 support with each of the cobalt species (*e.g.*, Co(NO3)2, Co(OH)x or Co3O4, respectively) formed during the different stages of the reverse micelle technique or during catalyst pre-treatment. Therefore, the uniqueness of our work is in how we have manipulated the interaction between the Co3O4 nanoparticles and the Al2O3 support to influence the activity and phase stability of Co3O4 during CO-PrOx. To the best of our knowledge, such a study has not been done before in the context of CO-PrOx.

The prepared Co3O4/Al2O3 catalysts were then tested under “dry” CO-PrOx conditions (*i.e.*, with no H2O and CO2 present in the feed) and characterised using four complementary *in situ* techniques *viz.*, Powder X-Ray Diffraction (PXRD), Magnetometry, and combined X-Ray Absorption Spectroscopy (XAS) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). PXRD, Magnetometry and XAS are bulk-sensitive techniques which were used to study the phase changes of the Co3O4/Al2O3 catalysts and DRIFTS is a surface-sensitive technique used for the detection of adsorbed reaction species as a function of temperature and time. Lastly, *quasi in situ* X-Ray Photoelectron Spectroscopy (XPS) was carried out to study the nature of the surface of each catalyst at selected reaction temperatures.

# **Method**

## **Catalyst preparation**

Two supported catalysts were prepared using the reverse micelle technique but the method of supporting the nanoparticles was varied in each case. Each of the two variations have been described in detail by Fischer *et al*.5 The catalysts were named CAT 1 and CAT 2 to distinguish between the variations made for the supporting. See Table 1 for the composition of the reverse micelle solutions.

To prepare CAT 1, an aqueous solution containing Co(NO3)2.6H2O (Sigma Aldrich, reagent grade 98% purity) was added to a stirring mixture of n-hexane (AR grade, Kimix) and the non-ionic surfactant pentaethylene glycol dodecylether (PEGDE) (Akzo Nobel) at room temperature and atmospheric pressure. Thereafter, aqueous NH3 (25 wt.-%, Kimix) at a 1:4 Co2+:NH3 molar ratio was added to the prepared reverse micelle solution to initiate the precipitation process, followed by the dropwise addition of acetone (AR grade, Kimix) to destabilise the reverse micelles and liberate the green precipitate (most likely Co(OH)x). Acetone was further used to wash the precipitate and rid it of excess surfactant. The precipitate was allowed to settle and then supernatant was decanted through siphoning. The precipitate was dried and calcined at 120 °C and 200 °C, respectively. The obtained Co3O4 powder was re-dispersed in distilled water under ultrasonication at room temperature and atmospheric pressure for 60 minutes and thereafter the suspension was transferred to a pre-weighed dry powder of Al2O3 (Puralox, SCCa 5-150, Sasol Germany: SBET = 162 m2/g, Vpore = 0.47 cm3/g, dpore = 11.5 nm, dparticle = 150 - 200 μm) in order to achieve a loading of 10 wt.-% Co3O4. The water was evaporated under reduced pressure in a rotary evaporator.

Unlike in the preparation of CAT 1, obtaining CAT 2 involved the addition of the Al2O3 support after the precipitation with NH3 (but before the addition of acetone). The slurry was stirred for 60 minutes. After extensive washing of the solid with acetone, a green (Co(OH)x) precipitate together with the reddish-pink impregnated Al2O3 support was obtained. The impregnated support was much denser than the precipitate and therefore, was separated using a separating funnel. The precipitate not taken up by the support was not re-dispersed and deposited onto the already impregnated support as this would have resulted in nanoparticles with different interactions with the support within the same sample. However, by not depositing the precipitate, the targeted 10 wt.-% Co3O4 loading was not achieved. Nonetheless, the impregnated support was dried and calcined at 120 °C and 400 °C, respectively. The composition of the reverse micelle solutions and the subsequent drying and calcination conditions used were to ensure that the Co3O4 crystallites in CAT 1 and CAT 2 have similar starting average sizes5 (see also section 3.1).

**Table 1:** Composition of the reverse micelle solutions prepared for obtaining CAT 1 and CAT 2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Sample Name** | **n-hexane (g)** | **PEGDE (g)** | **H2O (g)** | **o/s a (mol/mol)** | **w/s b (ω, mol/mol)** | **Co(NO3)2.6H2O (g)** |
| **CAT 1** | 875.0 | 161.0 | 12.0 | 25.6 | 1.7 | 1.3 |
| **CAT 2** | 500.0 | 68.4 | 26.4 | 34.5 | 8.7 | 2.6 |

a oil-to-surfactant molar ratio.

b water-to-surfactant molar ratio.

## **Catalyst characterisation**

Powder X-Ray Diffraction (PXRD) was performed in a Bruker D8 Advance X-ray diffractometer equipped with a cobalt source (λKα1 = 1.78897 Å) and a position sensitive detector (Bruker Vantec). For all samples, the optics were set to parallel beam geometry. A 2θ range of 20 – 120°, step size of 0.043° and a time per step of 0.75 sec was used, giving a scan time of 29 min 50 sec. All recorded diffraction patterns were compared to known diffraction patterns from the International Centre for Diffraction Data PDF-2 database18 to determine the species present. To further identify phases and obtain the average crystallite size, Rietveld refinement utilising the software package Topas 4.219 was carried out. As the alumina support material used in this study is known to be present as mixed phases of γ-Al2O3 and δ-Al2O3, and as the crystal structure of δ-Al2O3 is not known at this stage, an approach for Partial Or Not Known Crystal Structures (PONKCS), first described by Scarlett and Madsen,20 was used.

Transmission Electron Microscopy (TEM) was performed for each sample using a Tecnai F20 Transmission Electron Microscope operated at 200 kV with a field emission gun. The obtained micrographs were analysed using the freeware ImageJ21 in order to ultimately obtain average particle sizes and size distributions. The Co3O4 loading was determined by Energy-Dispersive X-Ray (EDX) spectroscopy using a LEO 1450 SEM/EDX instrument.

The reducibility of the individual catalysts was assessed by Hydrogen Temperature-Programmed Reduction (H2-TPR) performed in a Micromeritics AutoChem 2910 instrument equipped with a Thermal Conductivity Detector (TCD). 0.1 g freshly prepared supported catalyst was loaded in a U-tube quartz reactor and heated from 60 – 920 °C using a 10 °C/min ramp rate in a flow of 5 vol.-% H2 in Ar (50 ml (NTP)/min).

## ***In situ* catalyst characterisation and testing**

### *Quasi in situ X-ray Photoelectron Spectroscopy*

X-Ray Photoelectron Spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD photoelectron spectrometer utilising monochromatic Al radiation (1486.6 eV photon energy) at the Cardiff Catalysis Institute, UK. All data were acquired at a pass energy and step size of 40 eV and 0.1 eV, respectively, for high resolution spectra; and 160 eV and 1 eV, respectively, for survey scans. Charge compensation was achieved using the Kratos immersion lens system and all spectra subsequently calibrated to the C(1s) line taken to be 284.8 eV.

For the *quasi in situ* H2-TPR and CO-PrOx experiments, the samples were firstly pressed in to discs and placed in a gold-plated cup before placement into a Kratos catalysis cell and evacuated to a vacuum of *ca.* 10-7 mbar. Pure H2 or the CO-PrOx feed mixture (0.9% CO, 0.9% O2, 50% H2, 40% N2 and 8.2% Ar), respectively, was then flowed through the cell, controlled with a mass flow controller. The amount of CAT 1 and CAT 2 used was 0.5 g and the total gas flow was 50 and 30 ml(NTP)/min, respectively, to maintain a constant GHSV of 60000 ml/gCo3O4.hr. The samples were heated using a PBN heater under gas flow from 50 °C to the desired temperature which was held for an hour. Reaction quenching was achieved by swapping to Ar to purge the system and cooling down under this stream. Where there was a mixture of chemical phases after a heat treatment, their relative concentrations were calculated using CasaXPS (v2.3.17 PR1.1) after removal of a Shirley background and applying sensitivity factors from the manufacturer. Line shapes used for fitting the Co(2p3/2) region were derived from standard materials.

### *In situ Magnetometry and PXRD studies*

A low-frequency vibrating sample magnetometer22, 23 with a maximum field strength of 2 T (developed at the University of Cape Town (UCT) in collaboration with Sasol LTD, South Africa) and a UCT-developed PXRD capillary cell23-25 mounted on a Bruker D8 Advance Laboratory X-ray diffractometer equipped with a molybdenum source (λKα1 = 0.7093 Å) were used for the catalyst testing experiments. The optics of the diffractometer were set to parallel beam geometry to minimize possible peak shifts due to sample height difference (sample displacement). The magnetometer was specifically designed for the detection of ferromagnetic and superparamagnetic materials. In the present study, this is only metallic Co26 as Co3O427 and CoO28 are antiferromagnetic. (see Supporting Information for the definitions of ferromagnetism, superparamagnetism and antiferromagnetism). On the other hand, the PXRD can detect the crystalline phases Co3O4, CoO and Co up to the intrinsic instrument limitations regarding crystallite size and concentration.

During catalyst testing in the magnetometer, the temperature was held for 60 minutes at every 25 °C between 50 and 350 °C during heating and cooling at a rate of 1 °C/min, while magnetization measurements were taken at a field strength of 2 T every 10 minutes. The data from these measurements and those from a previously performed calibration of a 0.1 g freshly reduced metallic cobalt sample enabled the calculation of the degree of reduction, defined as the amount of metallic cobalt formed relative to the amount of cobalt in the starting material Co3O4 (see Figure S1 as well as Equations S1 and S2 in the Supporting Information). Similarly, PXRD patterns were also recorded during the 60-minute holding time every 10 minutes. A 2θ range of 15 – 30°, step size of 0.019° and a time per step of 0.2 sec (giving a scan time of 4 min 2 sec) was chosen for each scan.

Both instruments are based on a single fixed bed reactor and for the experiments performed in each instrument, the gas composition and the gas-hourly space velocity (60000 ml/gCo3O4.hr) were kept constant. The reaction mixture composed of 0.9% CO, 0.9% O2, 52.1% H2 and balance N2. We note that the amount of O2 added is in excess of the stoichiometric amount by a factor of 2 to ensure complete conversion of CO to CO2. The use of a stoichiometric amount of O2 and other O2:CO ratios will be of focus in a future publication. Also, the gases CO2 and H2O were not co-fed as the study aimed at investigating the sole effect of H2 on the catalytic performance and reduction of Co3O4. The presence of CO2 and H2O may mask this effect. However, the effect of both H2O and CO2 will also be a topic of a future publication. The amount of the supported catalyst loaded into the magnetometer reactor was 1.1 g for CAT 1 and 1.7 for CAT 2 to compensate for the slight differences in the Co3O4 loadings (see the EDX results in Table 2) and the gas flow rate was kept at 100 ml(NTP)/min. The mass of catalyst loaded into the PXRD capillary cell reactor was 0.015 g with the gas flow rate of 1.4 ml(NTP)/min for CAT 1 and 0.9 ml(NTP)/min for CAT 2.

The products were analysed using an Agilent Technologies 490 micro-GC fitted with three analysis modules equipped with thermal conductivity detectors for detecting CO, O2, H2, CO2, CH4 and N2. Two Molecular Sieve 5Å PLOT columns of 10 and 20 m lengths were employed to separate the gases. In the shorter column, Ar was chosen as the carrier gas to allow for the detection of H2 while H2 was chosen as the carriergas in the 20 m column separating O2, N2, CH4 and CO. The third column was a 10 m PoraPlot Q column with H2 as the carrier gas and was mainly used for the separation and detection of CO2. The reactor outlet gas was injected into the micro-GC every 5 minutes throughout the experiments. We note that the conversion of H2 was too low to be accurately measured because of the low amounts of O2 (for H2O formation) and CO (for CH4 and H2O formation) that were fed.



### *Combined in situ XAS/DRIFTS studies*

XAS measurements were performed at the Co K-edge (7709 eV) on the B18 beamline at Diamond Light Source (session: SP16006-1), Didcot, UK. Measurements were performed in transmission mode using a QEXAFS setup with fast-scanning Si (111) double crystal monochromators for the Co edge. The time resolution of the spectra reported herein was 95.53 secs/spectrum (kmax = 14.8). A DaVinci arm fitted with Praying Mantis Optics was used to refocus the IR beam outside the FTIR spectrometer so that the X-ray beam could be transmitted through the DRIFTS cell. The samples were placed in a previously reported Harrick X-ray transmission DRIFTS cell attached to the end of the DaVinci arm.29-31 The XAS/ DRIFTS cell has an X-ray path length of 3.17 mm placed 1.04 mm below the surface of the catalyst. DRIFTS spectra were collected with an Agilent Carey 680 FTIR spectrometer taking one scan every minute with a resolution of 4 cm−1 using the liquid nitrogen cooled MCT detector.

Each sample was heated from room temperature to 100 °C at a rate of 10 °C/min in helium which was then replaced with the reaction gas (0.9% CO, 0.9% O2, 52.1% H2 and balance N2) at a flow rate of 4.7 ml(NTP)/min for 0.05 g of CAT 1 and 2.9 ml(NTP)/min for 0.05 g of CAT 2. Upon reaching 100 °C, both XAS and DRIFTS spectra were recorded over a one-hour duration. Thereafter, the temperature was changed using a ramp rate of 1 °C/min and held every 25 °C for one hour until reaching a maximum temperature of 350 °C. The cell was cooled back down to 100 °C in a similar stepwise fashion under the reacting gas as in the heating ramp. XAS/DRIFTS measurements were taken continuously throughout each experiment.

EXAFS (Extended X-ray Absorption Fine Structure) Analysis: All spectra were acquired concurrently with the Co foil placed between It and Iref. The data processing was performed using IFEFFIT with the Horae package (Athena and Artemis).32, 33 The amplitude reduction factor, S02 was derived from EXAFS data analysis of the Co foil.

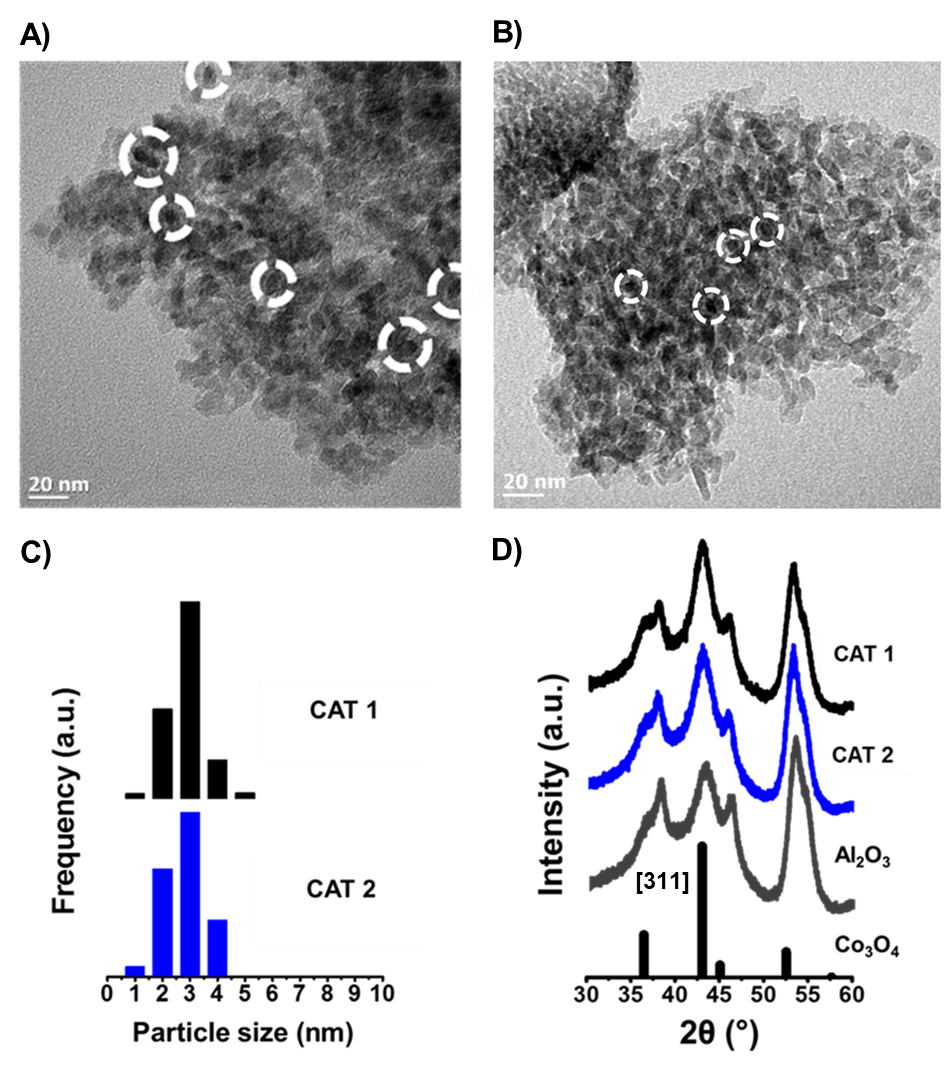
# **Results and Discussion**

## ***Ex situ* TEM, PXRD and EDX analysis**

For the various supporting procedures followed, it was important to keep the size of the cobalt oxide crystallites in the two catalysts within a similar narrow size range. This was to allow for the effect(s) of the NPSI during CO-PrOx to be studied excluding any size effects. Fischer *et al*.5 observed that the supporting procedure followed to obtain CAT 2 results in Co3O4 nanoparticles with a size between 3 and 4 nm even when the impregnated support was calcined at 400 °C. On the other hand, the method used to obtain CAT 1 allows for more flexibility as sizes larger than 4 nm can potentially be obtained. This is because the support is only contacted with the calcined Co3O4 nanoparticles at a later stage in the overall synthesis, and in doing so the crystallite size remains unchanged.9, 17 Furthermore, the size of the nanoparticles in CAT 1 is mostly determined by the composition of the reverse micelle solution *i.e.*, the oil/water-to-surfactant ratio and the amount of Co(NO3)2.6H2O used. Therefore, the average size of the Co3O4 nanoparticles was set to vary within the narrow range of 3 - 5 nm, which was achieved by applying a low water to surfactant ratio in the reverse micelle system, especially in the case of CAT 1 (Table 1).

TEM analysis was used to obtain size distributions and determine the average size of the Co3O4 particles. It should be noted that the images in Figure 1A and 1B give a relatively poor contrast between the Co3O4 particles and those of the Al2O3 support; however, number-based particle size distributions could still be derived and are shown in Figure 1C. The presence of Co3O4 in each catalyst was confirmed with PXRD (Figure 1D) which also yielded the average volume-based crystallite size. The 2θ range shown in Figure 1D highlights the differences between the two supported catalysts and the bare support. As the average crystallite sizes for each catalyst are below 5 nm, the reflections due to Co3O4 are low in intensity and are partially overlapping with those of the Al2O3, especially the [311] reflections at 43° of both phases. However, the presence of Co3O4 in CAT 1 and CAT 2 was ultimately confirmed by an increase in the intensity of the [311] reflection relative to the [400] reflection of Al2O3 at 53.7°.

Summarised in Table 2 are the PXRD- and TEM-derived volume- and number-based average crystallite sizes, respectively. The volume-based sizes from PXRD and TEM are in very good agreement and similar sizes for both catalysts were obtained even though different supporting procedures were followed. For the full recorded PXRD scans of the catalysts and the support, as well as the fits obtained after carrying out Rietveld refinement, see Figure S2. Table 2 also shows the EDX-derived Co3O4 loading for the different supported catalysts and Figure S3 shows the size of the different regions of each sample that were scanned for the detection of Co, O and Al. The loading targeted in each sample was 10 wt.-%. The method for preparing CAT 2 did not allow for the complete uptake of Co(OH)x by the Al2O3 support as already mentioned in section 2.1.

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**Figure 1:** TEM images of **A)** CAT 1 and **B)** CAT 2 as well as the derived **C)** particle size distributions. The white dashed circles show some of the identified Co3O4 particles. **D)** Recorded PXRD patterns of CAT 1, CAT 2 and the bare Al2O3 support (radiation source: Co kα1 = 1.78897 Å). Also included is the reference diffraction lines of Co3O4 (ICDD card no.: 01-073-1701).

**Table 2:** PXRD- and TEM-derived average Co3O4 crystallite sizes for CAT 1 and CAT 2 as well as the EDX-derived Co3O4 loadings.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample Name** | **PXRD sizea (nm)** | **TEM sizeb (nm)** | **TEM sizec (nm)** | **EDX Co3O4 loading (wt.-%)** |
| **CAT 1** | 4.5 | 3.3 ± 0.6 | 3.7 ± 0.7 | 9.4 |
| **CAT 2** | 3.8 | 3.2 ± 0.8 | 3.9 ± 0.9 | 5.9 |

a volume-based average crystallite size obtained by Rietveld refinement with Topas 4.2.

b TEM number-based average crystallite sizes and standard deviations calculated by: and.



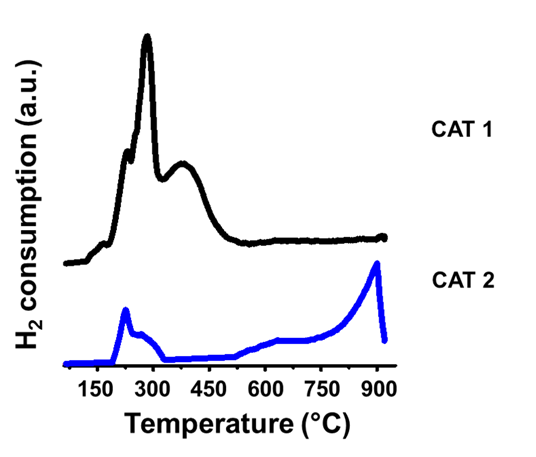
c TEM volume-based average crystallite sizes and standard deviations calculated by: and; whereis the total number of particles counted, is the length of particle and is the number of particles with the size.



## **H2-TPR and *quasi in situ* XPS studies**

The success of the different supporting methods in altering the strength of the NPSI was first assessed using H2-TPR. Figure 2 shows the H2-TPR profiles of CAT 1 and CAT 2. The Co3O4 particles in CAT 1 reduce below 500 °C in multiple reduction steps. The particles in CAT 2 display two reduction peaks in the temperature range of 180 - 350 °C and a separate peak above 750 °C. Others have also observed similar reduction behaviour for Al2O3-supported Co3O4 catalysts as that seen for CAT 2.5-7 The two low-temperature peaks are generally assigned to the reduction of weakly-bound Co3O4 possibly forming CoO and metallic Co. The high-temperature peak above 750 °C can be assigned to the reduction of strongly-bound CoOx species or cobalt aluminate-like species (CoxAlyOz).

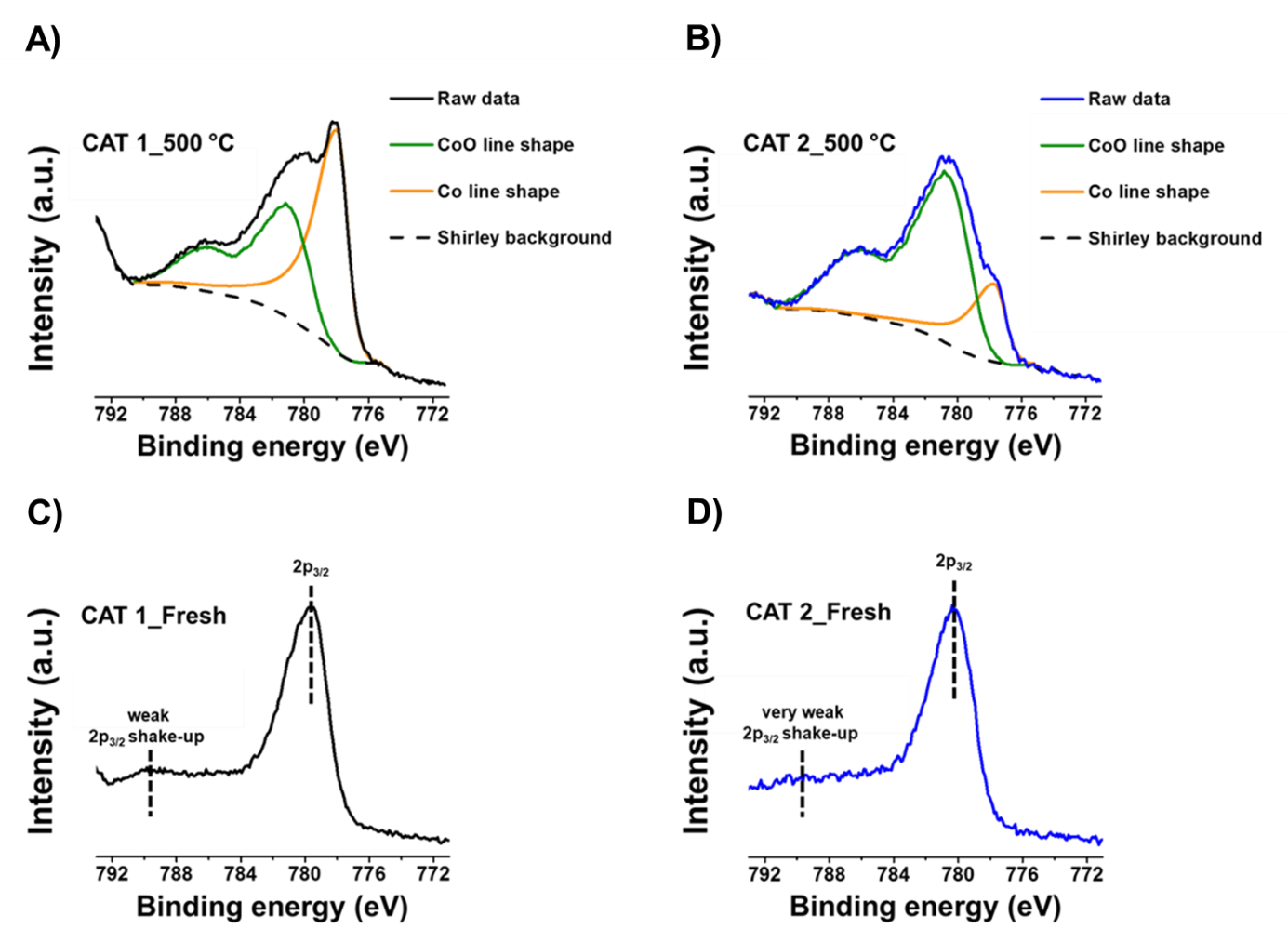
In the synthesis of CAT 2, some Co2+ ions of the precursor may have reacted with some of the Al2O3 support to form these hard-to-reduce species during calcination.5 Alternatively, these species could also be formed during the H2-TPR experiment due to the presence of the reduction product H2O.34 As the temperatures are increased, the Co3+ ions of Co3O4 are reduced to Co2+ ions and some of these ions could then react with the support. CAT 1 was prepared from contacting dispersed, pre-calcined Co3O4 particles with the Al2O3 support, which consequently minimised the interaction between the particles and the support.5



**Figure 2:** H2-TPR profiles of CAT 1 and CAT 2.

*Quasi in situ* XPS analysis was performed during H2-TPR studying the surface composition of each catalyst after their low-temperature reduction. As observed from the H2-TPR results (Figure 2), CAT 1 showed most of its reduction activity below 500 °C while CAT 2 displayed reduction behaviour below and above this temperature. Figure 3 shows the recorded Co 2p core-level spectra of CAT 1 and CAT 2 in their oxidic states and after exposure to H2 at 500 °C. The position of the main Co 2p3/2 peak in the spectra of the fresh CAT 1 and CAT 2 samples is at 779.7 and 780.4 eV, respectively, in excellent agreement with values reported in the literature for pure Co3O4.13, 16, 35, 36 After treatment in H2, CAT 1 shows the presence of Co2+ in the form of CoO (781.5 eV) and metallic Co (778.3 eV), respectively, at a ratio of 45:55 while CAT 2 had a CoO:Co0 ratio of 78:22.

The results obtained for both catalysts indicate that Co3O4 was not completely converted to metallic Co. In contrast, during H2-TPR, CAT 1 showed no (or little) reduction behaviour above 500 °C which implied almost complete reduction of this catalyst. However, it should be noted that the design of the cell used for the *quasi in situ* experiments is a “flow-over” system where the gas mostly passes over the pressed/pelleted sample and does not penetrate deep into it. On the other hand, the U-tube reactor used for conventional H2-TPR is a “flow-through” system where the gas does flow through the packed catalyst bed. These differences in hydrodynamics could explain the slight disagreement in the reduction results obtained (especially for CAT 1). Nevertheless, it is evident that CAT 2 possesses much stronger NPSI compared to CAT 1.



**Figure 3:** Recorded Co 2p core level spectra of CAT 1 and CAT 2, {**A)** and **B)**} after being treated at 500 °C in pure H2, together with spectra for their fresh unreduced state, {**C)** and **D)**} respectively.

## ***In situ* catalyst characterisation and testing**: *Magnetometry, PXRD, XPS and combined XAS/DRIFTS studies*

* + 1. *PXRD, Magnetometry and XPS*

Catalyst testing was performed in a fixed-bed reactor under dry CO-PrOx conditions (*i.e.*, in the absence of H2O and CO2) and coupled with *in situ* characterisation using the previously mentioned Magnetometer22, 23 and PXRD capillary cell.23-25 Figures 4 and 5 show the magnetometry and PXRD data as well as the calculated average outlet gas flow rates of CO, O2, CO2 and CH4 as a function of temperature for CAT 1 and CAT 2. We note that the chosen presentation of the catalytic data as shown in Figures 4 and 5 gives a clearer picture of the different reactions taking place (*viz.*, CO oxidation to CO2, H2 oxidation to H2O and CO hydrogenation to CH4) by showing the changing concentrations of all gases being detected at the reactor outlet. However, the CO2 yield, O2 selectivity to CO2 and CH4 yield are presented in Figures S4, S5 and S6, respectively, in the Supporting Information. The catalyst CAT 1 exhibits superior CO oxidation activity below 225 °C - reaching higher CO2 yields than CAT 2 at all temperatures and achieving the highest yield (98%) at a temperature of 175 °C. The weak NPSI in CAT 1 are thought to be advantageous in that a higher amount (or surface area) of the active Co3O4 sites is made available to the gas reactants instead of strongly interacting with the support. Also, according to most literature, CO oxidation over Co3O4 is believed to proceed *via* the Mars-van Krevelen (MvK) mechanism13-16, 37, 38 which requires the Co3O4 surface to be redox active. Therefore, the high activity of CAT 1 can also be attributed to the facile reducibility of the oxide phase.

The co-fed O2 is also consumed in each reaction, with CAT 1 reaching complete O2 conversion at 200 °C and CAT 2 achieving a similar conversion at 250 °C. Although complete O2 conversion is reached at these temperatures, the yields of CO2 are seen to decrease above 225 °C. This is an indication of a loss in CO2 selectivity because of the competing H2 oxidation reaction, which has also proven to be unavoidable even over other catalysts especially when O2 is fed in excess of the stoichiometric amount (see section 2.3.1.).8-13, 15, 16, 36, 39-41 In addition, CAT 1 reduces from Co3O4 to CoO at 225 °C according to PXRD and to metallic Co at 250 °C as measured in the magnetometer. Concurrent with the formation of metallic Co is the formation of CH4, which also competes with the CO oxidation reaction.8, 9, 36, 40, 41 We note that the metallic Co phase in CAT 1 is not observed in PXRD because of the overlap between the expected fcc Co reflection at 19.96° and the alumina reflection at 20.6°. We also note that at 350 °C, the calculated degree of reduction of Co3O4 to metallic Co from the magnetometry data is 22% which is equivalent to 1.6 wt.-% of metallic Co (and 7.4 wt.-% CoO) in the entire supported sample. This low weight fraction of the metal in conjunction with the expected small crystallite size is close to the detection limit of laboratory-based PXRD.

For CAT 2, neither CoO nor metallic Co are observed in PXRD but the decrease in the intensity of the Co3O4 [311] reflection between 250 and 275 °C suggests that this catalyst was also partially reduced. The magnetometer estimated a very low degree of reduction to metallic Co for CAT 2 (less than 1%), which further supports the previously observed and discussed low reducibility. Although a low degree of reduction and a low yield of CH4 (21%) is achieved by CAT 2, the amount of CO exiting the reactor increases with increasing temperature, which is undesired for H2 fuel cell applications. This increasing exit CO indicates that H2 oxidation is favoured over the CO oxidation pathway at elevated temperatures seeing that O2 is depleted above 250 °C.

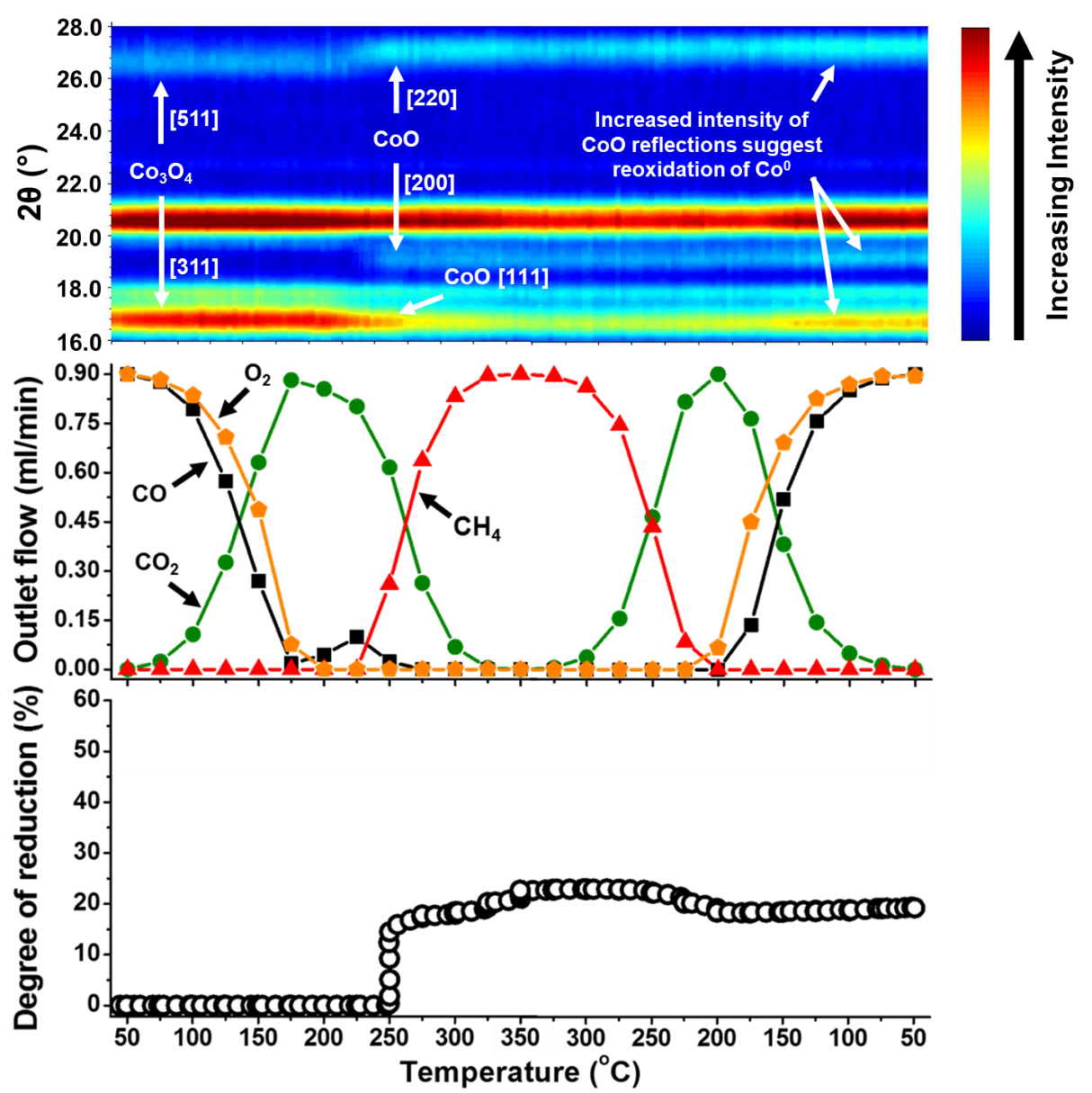
*Quasi in situ* XPS was performed after exposing each catalyst to dry CO-PrOx conditions at 350 °C in the previously described “flow-over” cell. Figure 6 shows the Co 2p core-level spectra of CAT 1 and CAT 2. At 350 °C CAT 1 contains both CoO and metallic Co at a ratio of 66:34, while in CAT 2 only the CoO phase is detected (see Figure 6). Despite the XPS estimating a slightly higher relative metallic Co content than the magnetometer (a result of the differences in their reactor and gas flow systems, as well as their depth profile *i.e.*, bulk (magnetometry) versus surface sensitivity (XPS)), the trends in the captured reduction behaviour remain highly comparable.

When cooling the reactor below 350 °C, both catalysts gradually recover their CO oxidation activity as CO hydrogenation and H2 oxidation diminish.9, 41 Surprisingly, the catalysts achieve higher CO2 yields (at 225 °C in case of CAT 2 and 200 °C in case of CAT 1), compared to the yields achieved during the heating steps. According to the magnetometry data, the amount of metallic Co eventually decreases which implies re-oxidation of the catalysts. In CAT 2, there is complete disappearance of the metallic phase at 225 °C while in CAT 1, the degree of reduction decreases from 22 to 19% at 200 °C and stays constant till 50 °C. We consider that complete re-oxidation of metallic Co was not achieved because of the high overall H2:O2 partial pressure ratio and perhaps also kinetically hindered due to the stepwise decrease in temperature from 350 to 50 °C.

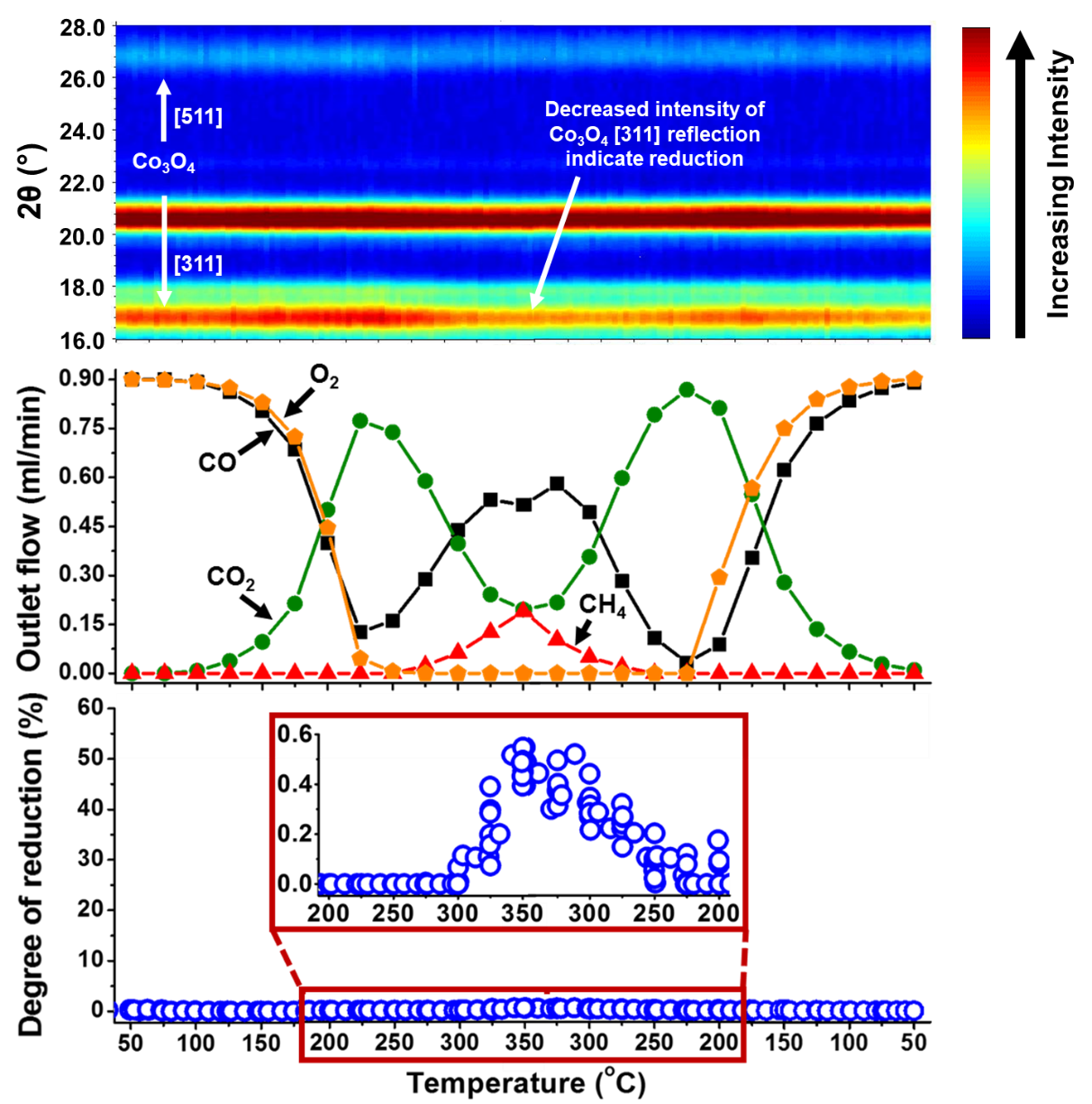
PXRD shows the presence of CoO during cooling in CAT 1 but no evidence of Co3O4 and remains inconclusive in terms of the presence of these oxides in CAT 2. Nonetheless, it is possible that the surfaces of these catalysts may contain the active Co3+-Co2+ redox pair required for the oxidation of CO which would explain the recovery of the activity upon cooling. In addition to surface and/or bulk re-oxidation, the decreasing temperature may be kinetically favouring the oxidation of CO over methanation and H2 oxidation.

From the PXRD, magnetometry and XPS studies, the effect of employing different supporting methods is shown as both catalysts display clear differences in terms of their CO oxidation activity and Co3O4 phase stability. The catalyst CAT 2, with very strong NPSI, exhibited higher resistance to reduction (as also observed during H­2-TPR) but was less active than CAT 1 before any detectable phase changes could occur. The low CO oxidation activity of CAT 2 is possibly a consequence of having low amounts of surface Co3O4 sites (or area) and very low (surface) reducibility because of the strong NPSI. Therefore, these studies have highlighted the advantages and disadvantages of either having a highly reducible catalyst or an almost irreducible one.

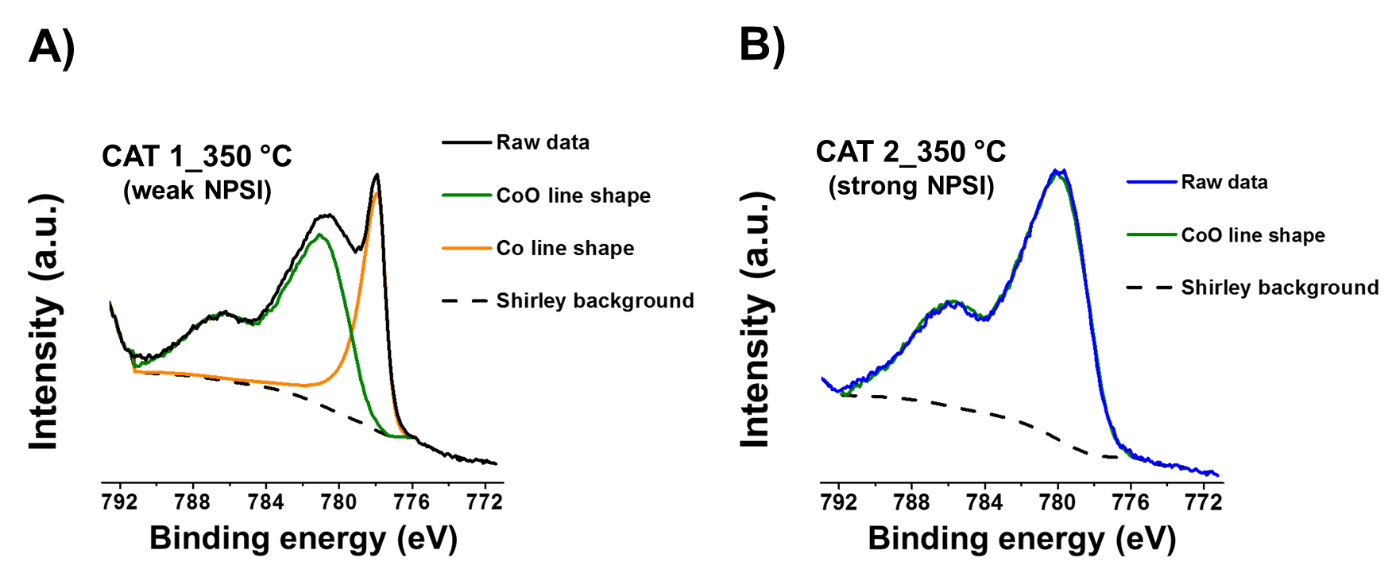
Due to the small crystallite sizes and low mass fractions of Co3O4 (especially in CAT 2), adequate characterisation of the catalysts was challenging. Furthermore, quantification of the oxide phases was not possible from the PXRD patterns. Therefore, X-ray Absorption Spectroscopy (XAS) was employed to further study the catalysts during dry CO-PrOx conditions. This technique enables the analysis of amorphous and crystalline bulk materials with different magnetic properties (*e.g.*, Co0, Co3O4). As PXRD, magnetometry and XAS are bulk techniques, and full *in situ* or *operando* XPS experiments could not be performed, the XAS studies were coupled with surface-sensitive Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). DRIFTS would reveal the different adsorbed surface and gas phase species present as a function of reaction conditions, which could in turn inform on the type of cobalt (oxide) surface formed.



**Figure 4:** (***top***) On-top view of the PXRD patterns recorded for CAT 1 (radiation source: Mo kα1 = 0.7093 Å), (***middle***) the measured outlet flow rates of CO, O2, CO2 and CH4, (***bottom***) as well the changes in the degree of reduction calculated from themagnetometer-derived data. The PXRD reflections for Co3O4 and CoO were assigned using the ICDD card nos.: 01-073-1701 and 00-043-1004, respectively.



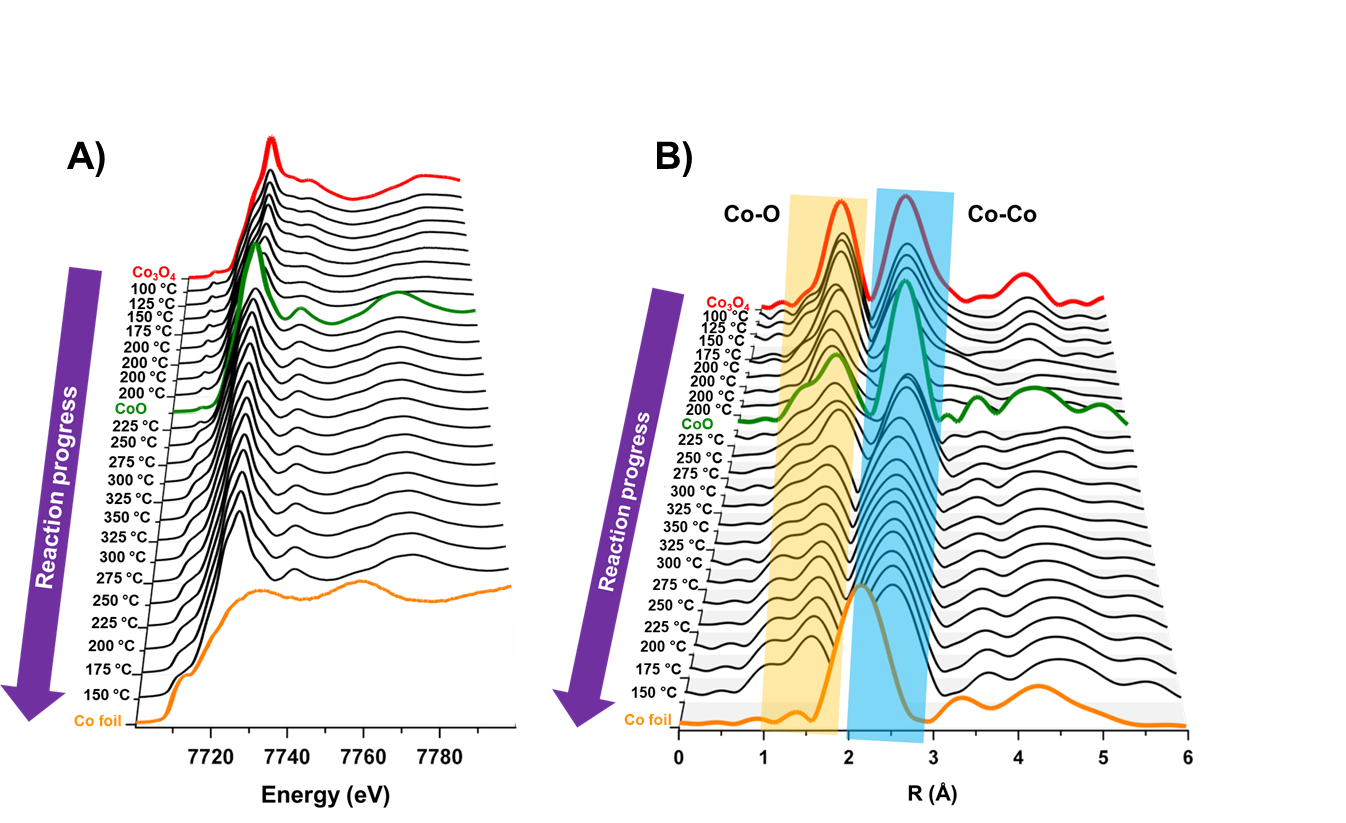
**Figure 5:** (***top***) On-top view of the PXRD patterns recorded for CAT 2 (radiation source: Mo kα1 = 0.7093 Å), (***middle***) the measured outlet flow rates of CO, O2, CO2 and CH4, (***bottom***) as well the changes in the degree of reduction calculated from themagnetometer-derived data. Also included is a magnified region of the degree of reduction plot (from 200 °C (heating) to 200 °C (cooling)).



**Figure 6:** Recorded Co 2p core level spectra of **A)** CAT 1 and **B)** CAT 2 after being exposed to dry CO-PrOx conditions at 350 °C.

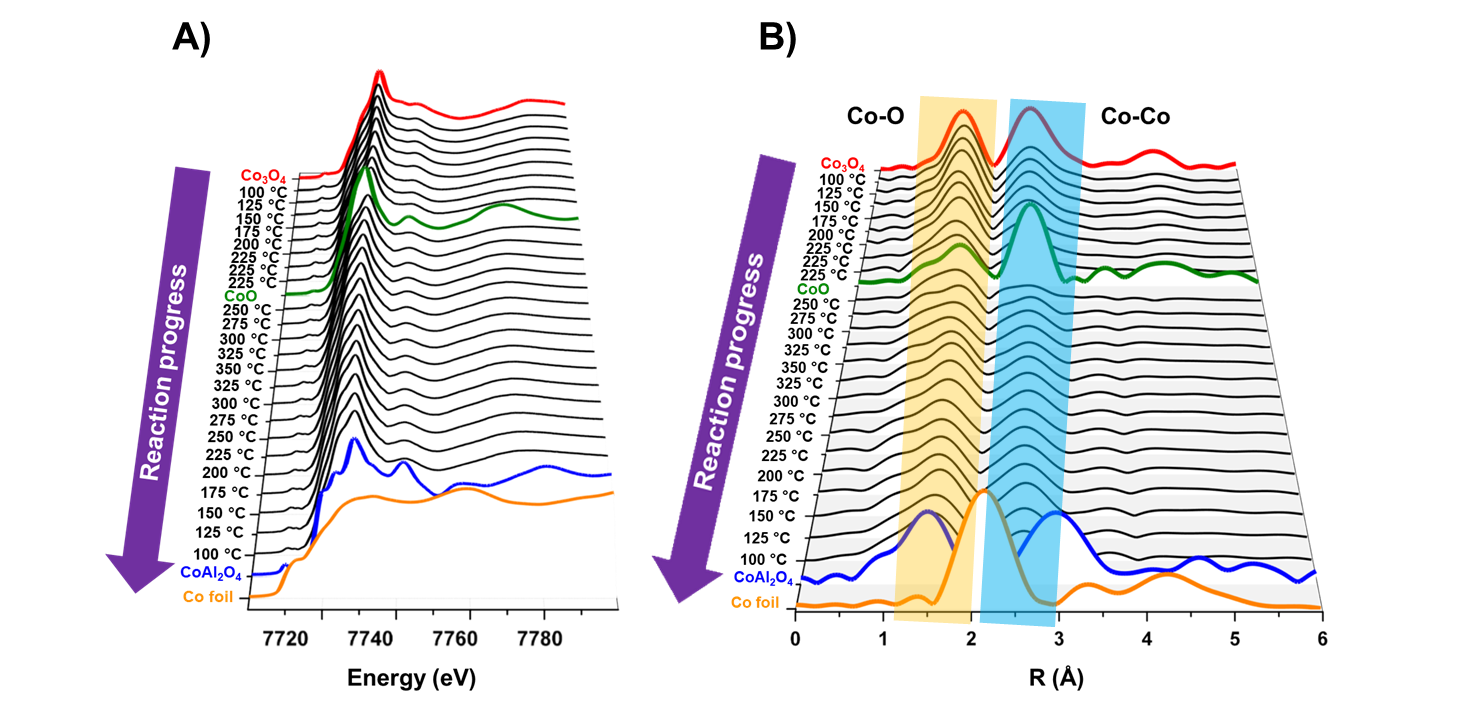
* + 1. *Combined XAS/DRIFTS*

Combined XAS/DRIFTS studies were performed on both catalysts, ramping under the CO-PrOx reaction gas in a stepwise manner similar to the PXRD and magnetometry studies. The X-ray Absorption Near Edge Structure (XANES) spectra of the fresh CAT 1 sample (*i.e.*, between 50 and 175 °C) are consistent with cobalt being predominantly in the form of Co3O4. From 200 °C the main edge shifts to lower energy with the spectra resembling a mixture of CoO and Co between 250 and 350 °C. The presence of CoO is observed from the main feature after the edge shifting from 7729 eV to 7726 eV42, 43 and the slight increase in the feature at 7709 eV is consistent with the formation of metallic Co42, 43 in Figure 7A. A linear combination fit of the XANES data (Figure S7A) suggests approximately 30% of the Co is present as Co0, consistent with the 34% and 22% Co0 estimated from the XPS and magnetometry results, respectively, with the remaining 70% cobalt in the form of CoO. Again, differences in the hydrodynamics of the utilized sample presentation devices are expected to result in minor differences. However, from the Fourier Transform of the EXAFS data in Figure 7B, there is no evidence of metallic features which, as with the PXRD, could be due to the presence of very small Co0 clusters and/or not bulk-like Co0.

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**Figure 7:** **A)** Normalized XANES spectra and **B)** the k2 weighted Fourier Transform of the EXAFS data of the CAT 1 sample during dry CO-PrOx. The reference spectra of Co3O4, CoO and Co foil are also included. Preparation method for Co3O4 and CoO can be found in ref. (44).

The fresh CAT 2 sample also resembles Co3O4 below 200 °C, similar to CAT 1. Above this temperature, the XANES spectra indicate a transformation to CoO, with a shift in the main edge towards lower energy and the main feature after the edge moving towards 7726 eV (Figure 8A). Unlike the CAT 1 sample, no evidence of Co0 is observed from the XANES spectra or from the k2 weighted Fourier Transform of the EXAFS data (Figure 8B), which agrees with the PXRD, and XPS studies as well as the catalytic performance where only limited amounts of CH4 (less than 20% yield) were formed. A linear combination fit of the XANES spectra (Figure S7B) suggests that at 350 °C the catalyst contains approximately 20% Co3O4 and 80% CoO. However, the magnetometer, the most sensitive technique for the detection of metallic cobalt under the given reaction conditions and sample presentation devices, detected small amounts of metallic Co, corresponding to a degree of reduction of under 1%.

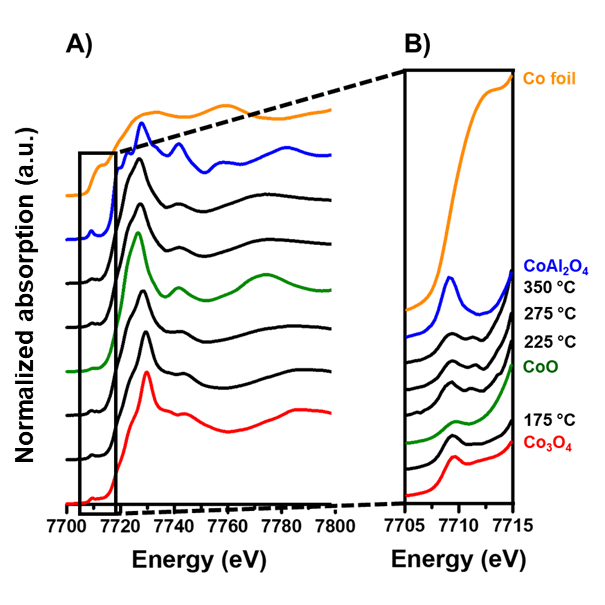


**Figure 8: A)** Normalized XANES spectra and **B)** the k2 weighted Fourier Transform of the EXAFS data of the CAT 2 sample during dry CO-PrOx. The reference spectra of Co3O4, CoO, CoAl2O4 and Co foil are also included. Preparation method for CoAl2O4 can be found in ref. (45).

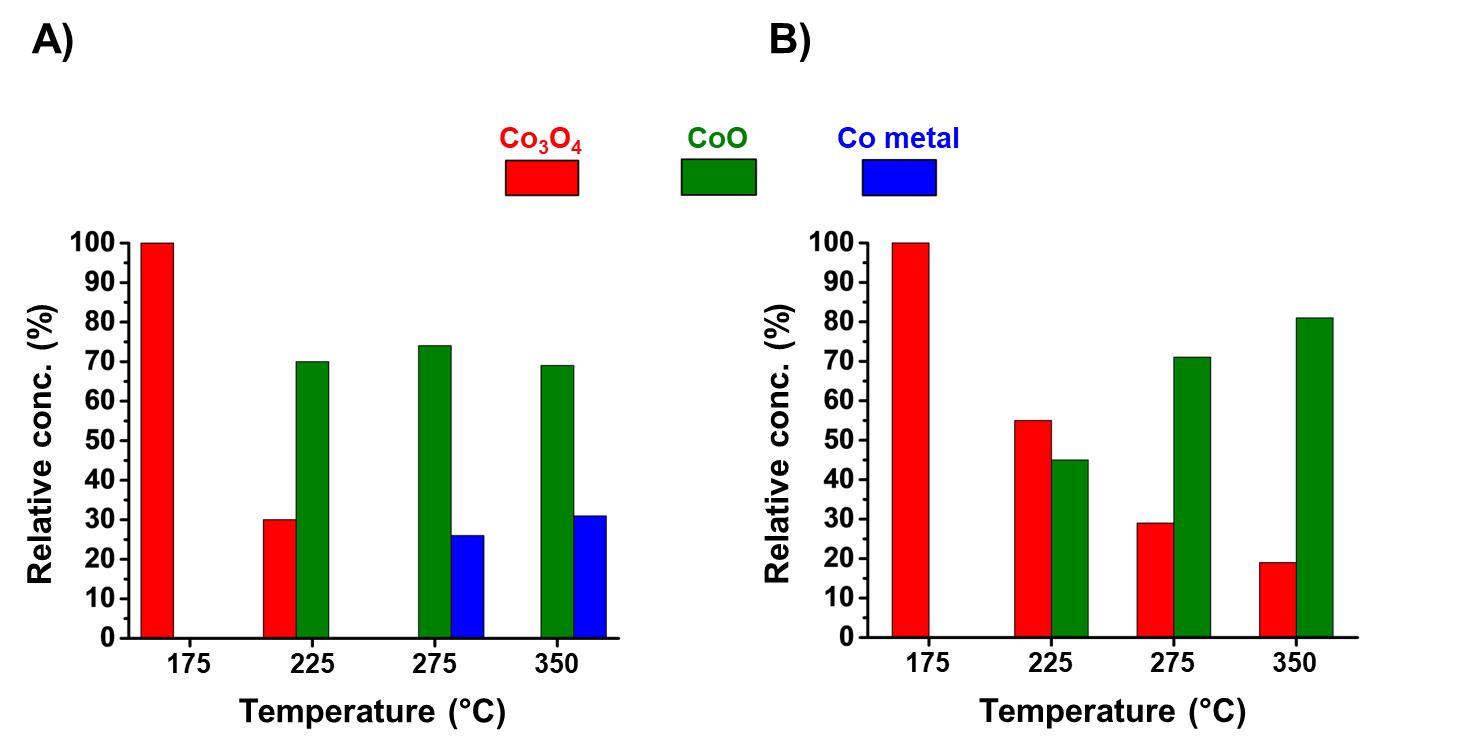
The XANES spectra of CAT 2 shown in Figure 8A from 225 °C to 350 °C and back to 100 °C exhibit a feature at 7711 eV (also see Figure 9 which highlights this feature at selected temperatures) not previously observed in the XANES spectra of CAT 1. This feature appears to closely coincide with the metallic Co pre-edge feature at 7709 eV. However, the assignment of this feature to Co0 may not be accurate as the magnetometry and gas chromatography results only show the formation of Co0 and CH4, respectively, at much higher reaction temperatures (above 225 °C). Referencing to the pre-edge of CoAl2O4 seems to also rule out the presence of this mixed metal oxide as being the feature at 7711 eV.

At this stage, without any evidence from the literature, it is thought that the feature at 7711 eV may be some other CoxAlyOz species which differs from the bulk CoAl2O4. From the H2-TPR results there are Co-based species (either formed during calcination or H2-TPR) in CAT 2 requiring temperatures above 750 °C to reduce and such reduction behaviour is commonly associated with cobalt aluminate-like species (CoxAlyOz) in Co3O4/Al2O3 (or Co/Al2O3).5-7, 34 Furthermore, Tsakoumi *et al*.46 proposed that Co particles smaller than 5.3 nm may form such species at the nanoparticle-support interface after reduction in H2. Therefore, it is possible that during CO-PrOx, CAT 2 forms small amounts of CoxAlyOz that remain stable above 225 °C and even upon cooling back to 100 °C.

Despite the presence of an unknown CoxAlyOz phase, Figure 10 shows the results from the LCF performed at selected temperatures during heating for both catalysts assuming the presence of Co3O4, CoO and metallic Co only. It can be seen that CAT 1 shows partial reduction to CoO and Co0, which is consistent with the XPS, magnetometry and PXRD studies. However, CAT 2 shows minimal reduction only forming CoO in the XAS studies with small amounts of Co0 only observed in the analysis of the magnetometry data.



**Figure 9: A)** Normalized XANES spectra at selected reaction temperatures upon heating and **B)** a magnified region of the XANES spectra (between 7705 and 7715 eV) recorded during CO-PrOx over CAT 2. The reference spectra of Co3O4, CoO, CoAl2O4 and Co foil and are also included.



**Figure 10:** Results from the linear combination fit of the XANES at selected temperatures during heating for **A)** CAT 1 and **B)** CAT 2.

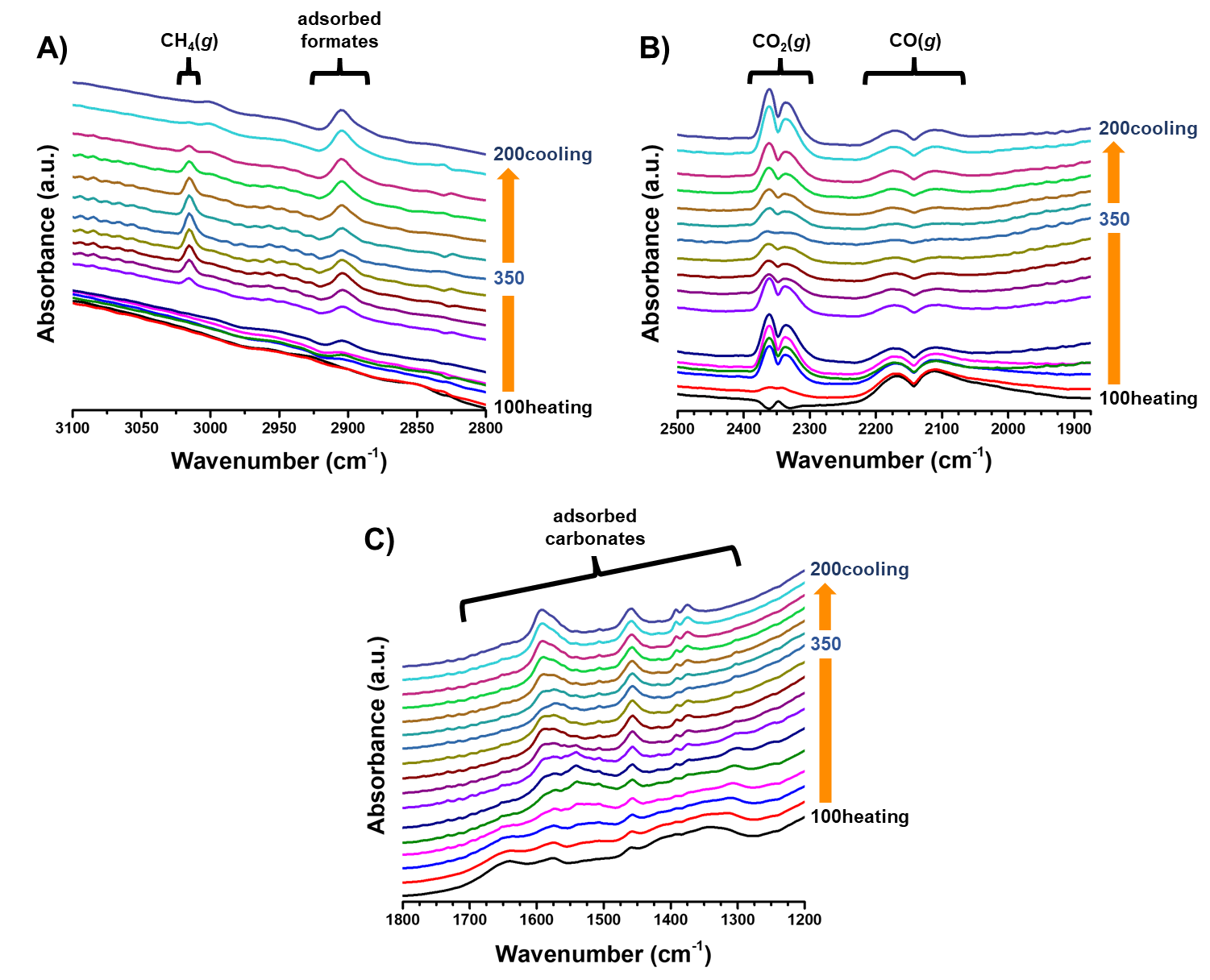
Both surface-adsorbed species and gas phase species were monitored using DRIFTS due to the geometry of the cell.29-31 The formation of gas phase CH4 and CO2 was monitored at temperatures consistent with the GC data shown in Figure 4 for CAT 1. The formation of CO2 from the gas phase bands at 2360 and 2335 cm-1 8, 40 in Figure 11B also follows the trend observed from the GC analysis during the *operando* magnetometry and PXRD experiments, reaching a maximum between 175 - 225 °C. The formation of CH4 in the DRIFTS spectra at 3020 cm-1 40 is recorded above 250 °C when heating and disappears below 250 °C when cooling (see Figure 11A), consistent with the formation and re-oxidation of Co0, respectively (see magnetometry and XAS results).

No adsorbed CO species were observed in the recorded spectra (even after subtracting the gas phase CO band, see Figure S9) as the stretching modes of CO adsorbed on Co0, Co2+ and Co3+ are expected at 2023 − 2025 cm-1, 2120 − 2170 cm-1 and 2178 − 2180 cm−1, respectively.14, 47 The absence of these bands agrees with previous studies, where only carbonate species (1700 – 1200 cm-1) or possibly formates (2905 cm-1) are reported during CO oxidation and CO-PrOx.8, 14, 16, 40, 48 It is possible that CO reacts rapidly on Co3O4 to form carbonates as has been suggested in the literature.16 The lack of CO adsorption bands on Co0 could be due to the limited stability of these species under flowing gases, as these bands are reported to be easily removed on evacuation.47

Carbonate species are however, observed under CO-PrOx conditions on CAT 1 as shown in Figure 11C. Monodentate carbonates are assigned to the bands at 1507, 1390 and 1375 cm-1,16, 48 which grow gradually during the reaction even upon cooling. This gradual growth in concentration is also observed for the formates at 2905 cm-1.16, 48 As these bands do not follow measured trends in the reactor outlet gas composition, we suggest they may be spectator species. Bidentate carbonates (1540, 1249 cm-1)16 are formed above 150 °C and increase in intensity up to 250 °C. This coincides with the temperature where CO2 production reaches a maximum, indicating that these species may possibly be involved in the oxidation reaction.

Similar carbonates were also present in CAT 2 as the temperature was increased (see Figure S10A). However, we note that it is difficult to elucidate the kind of cobalt surface (*i.e.*, if it is oxidic or metallic) onto which the carbonates are adsorbed as their stability could be temperature dependent and some may not necessarily partake in the reaction (*e.g.*, monodentates in the present case). Furthermore, carbonates were also observed on bare Al2O3 under CO-PrOx conditions (Figure S10B) which implies that the formation and/or adsorption of these species is not limited to the cobalt surfaces only.

Therefore, only the bands for the gas phase species and bidentate carbonates provide some information on the nature of the catalyst’s surface at the different reaction temperatures (together with the data from XPS, PXRD, magnetometry and XAS). However, the position at which the IR spectra were taken along the catalyst bed may have not been ideal as there could be different surfaces exposed and consequently, different species being adsorbed and detected. It may be helpful to perform spatially-resolved DRIFTS (combined with XAS),49 which might allow for the sample to be analysed at different reactor positions and discriminate between different catalyst surfaces and surface adsorbed species.



**Figure 11:** DRIFTS spectra collected during the CO-PrOx reaction over the CAT 1 sample showing the **A)** CH4(g) and formates, **B)** CO2(g) and CO(g), as well as the **C)** carbonates region.

# **Conclusions**

The present study has addressed the challenges faced when using the transition metal oxide Co3O4, regarding its catalytic performance and phase stability under the reducing environment of CO-PrOx. This was possible through the use of various *in situ* techniques which collectively provided very valuable insight into the effect of NPSI on the performance and phase stability of Co3O4. Depending on the method of preparing the supported catalyst, the strength of the nanoparticle-support interaction (NPSI) can be greatly affected. It was shown that by firstly preparing calcined Co3O4 nanoparticles and then physically mixing these with the Al2O3 support in a liquid medium (*i.e.*, CAT 1), results in weak NPSI; but contacting the support with Co(NO3)2.6H2O (*aq.*) within a reverse microemulsion (*i.e.*, CAT 2) gives a supported catalyst with much stronger NPSI. From the kinetic data obtained during the *operando* CO-PrOx experiments, weak NPSI favour high CO oxidation activity over unreduced Co3O4 while strong NPSI minimise Co3O4 reduction and the unwanted formation of CH4 at elevated reaction temperatures. The observations from the *in situ* analysis and kinetic data suggest that significant stability of the active oxide phase is desired, however, the catalyst (surface) needs to be reducible to some extent as this is a requirement for the oxidation of CO over metal oxides *via* the Mars-van Krevelen mechanism. Therefore, future work can focus on investigating either other support materials or (oxidation) promoters that can maximise both catalyst stability and activity.

# **Associated Content**

# **Supporting Information**

The concept of magnetism, magnetometer calibration, linear combinations of selected XANES spectra and other DRIFTS data can be found in the ESI which is available free of charge at https://pubs.acs.org. In addition, the raw data supporting this study are openly available from the University of Cape Town repository at DOI: 10.25375/uct.8332652.

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# **Notes**

The authors declare no competing financial interest.

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