Redox aluminophosphates: applying fundamental undergraduate theory to solve global challenges in the chemical industry

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Abstract

As global resources are pressed by the demands of the modern lifestyle, acquainting students with Sustainable Chemistry will be crucial in educating responsible chemists of the future. For this undertaking, we present *Redox Aluminophosphates*; a laboratory-based practical with targeted resources that has been designed to relate fundamental catalytic theory to core concepts in Green Chemistry. As part of this assignment, students are directed in the preparation of aluminophosphate materials using distinctive synthetic protocols (hydrothermal synthesis, calcination), and are required to apply their knowledge of analytical techniques to solid-state characterisation. Students then use their heterogeneous redox catalysts in the oxidation of cyclohexane to K A oil (the industrial feedstock of adipic acid, a precursor to nylons), with gas chromatography-mass spectrometry (GC-MS) analyses providing an opportunity to introduce Green Chemistry metrics. With supporting resources, oral presentation, and student-led discussions, this practical aims to equip the undergraduate student with the tools needed to rationalise structure-activity relationships in porous heterogeneous catalysts. Using a systems thinking approach, *Redox Aluminophosphates* is a holistic practical, combining empiricism with critical analysis, self-study, and group work to relate undergraduate theory to real-world problems, whilst demonstrating how laboratory-scale procedures can be extrapolated to the industrial setting.

Keywords: Upper-Division Undergraduate, Analytical Chemistry, Inorganic Chemistry, Polymer Chemistry, Laboratory Instruction, Transfer, Applications of Chemistry, Catalysis, Green Chemistry, Industrial Chemistry, Sustainability, Systems Thinking.

Introduction

Motivation

Many developments that are now considered an integral part of our modern society have been supported by developments in the chemical industry. However, in continuing to meet a growing consumer demand in sectors such as healthcare, technology and energy, our global resources have been depleted and the environment is at risk of irrevocable damage. With onus on the Chemical (and wider global) communities to adopt sustainable practices, educating a new generation of responsible scientists will be crucial in maintaining a society that is equipped to confront future challenges.

In 1998, Anastas and Warner presented the 12 Principles of Green Chemistry[1] that have since become the precepts of Sustainable Chemistry (Figure 1).[2] Within these guidelines, catalysis has been designated a 'Foundational Pillar',[3] recognising its significance in the development of environmentally-friendly chemical processes.[4]

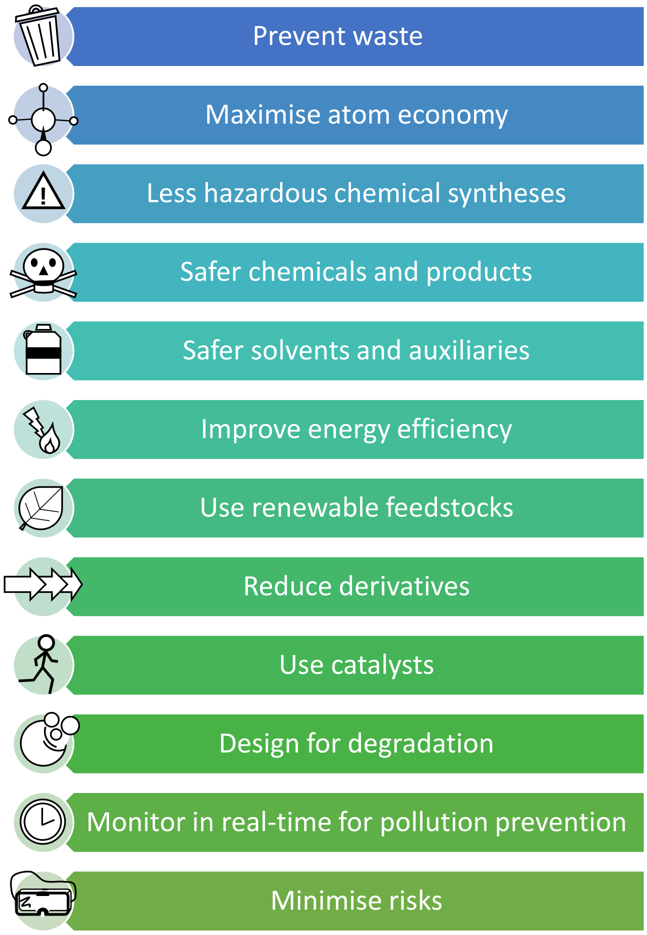


Figure 1: The 12 principles of green chemistry.

Whilst catalysis is an established topic in the undergraduate Chemistry course, its practical implementation can sometimes become obscured in dissecting the underlying theory. Therefore, to demonstrate the broader impact of catalysis to the undergraduate student, we conceived the *Redox Aluminophosphates* (RAP) experiment and supporting content, which seeks to develop the academic-level understanding of catalysis into a greater appreciation for its practical application within the chemical industry. Using case studies from polymer manufacture to contextualise the practical component, undergraduate lecture material is extrapolated to cutting-edge chemical research. Over several years of implementation, the *Redox Aluminophosphates* experiment has been optimised to foster academic and personal development, including transferable and employability-relevant skills such as the critical evaluation of current affairs; incorporating a systems thinking[5] mind-set by examining some aspects of nylons from cradle to grave: from processes involved in their synthesis, their uses and finally their recycling or fate of waste products. Importantly, *Redox Aluminophosphates* realises important targets in sustainability education practice,[6] delivering the fundamentals of Green Chemistry in a manner that encourages introspection, and fosters an awareness of an individual's impact on global sustainability.

Systems thinking

Systems thinking has been defined as linking chemistry teaching and learning with educational research and theories and with earth and societal systems.[5] It seeks to reorient chemistry education and its attributed power to drive curricular development[7] as well as a high impact teaching tool for teaching valuable and transferable skills to students also in a classroom setting by Hutchison.[8] *Redox* *aluminophosphates* ties practical experiments and a subsequent chemistry sustainability lecture course to a real-world scenario and allows the participants to extrapolate the impact of energy-use, waste production and greener processes, and thus joins chemistry teaching to societal and earth systems. It is a setting that deliberately avoids calculation of yields but asks students to deliberate other green metrics as has been suggested by Anastas *et al.*[9] and it fits in a wider context of laboratory class teaching similar to the approach described by Dicks *et al*..[10]

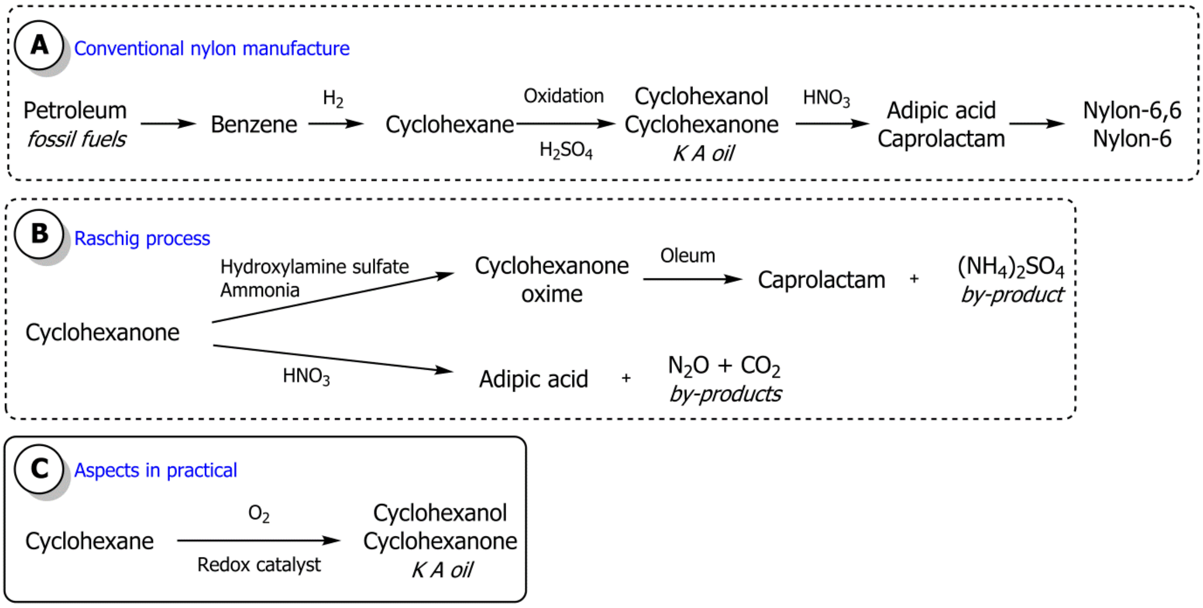


Figure 2: Redox aluminophosphates catalyst (solid box) in the wider context of systems thinking aspects: Overview of industrial pathways (A: conventional nylon synthesis, B: aspects of the Raschig process) and (C) use of student-synthesised redox catalyst in the practical to produce K A oil

The activities in *Redox aluminophosphates* are constructively aligned[11] and have been improved over the course of several years through reflection and annual student feedback. While the educational theory combines systems thinking in practical chemistry education, the influence of the link between research and laboratory teaching has additionally proven beneficial. Students are provided an overview of conventional nylon manufacture (Figure 2A) and engage in aspects of chemical systems thinking[12] like mechanistic reasoning (cyclohexanone to adipic acid and ε-caprolactam, Figure 2B) and study a context-based scenario (synthesis of K A oil, Figure 2C) and think about a sustainable perspective that is aligned with the 12 Principles of Green Chemistry (Figure 1).

Systems thinking includes features of a life-cycle analysis (LCA) which considers aspects like resources, environmental issues of an industrial process and the fate of the waste and product after use. This holistic approach is also referred to as cradle-to-grave assessment. This is a powerful accounting and management tool, albeit it is very specific to a process and product.[13-15] For this reason *Redox aluminophosphates* is limited to a qualitative analysis of the LCA of nylon syntheses comparing conventional routes and an alternative (RAP) that is still actively pursued.[16]

Molecular sieves and heterogeneous catalysis

It is estimated that 90 % of industrial-scale chemical syntheses employ catalysis at some point in the manufacturing process,[17] whether this is to enhance productivity, improve reaction efficiency, or to mitigate the use of hazardous reagents. Heterogeneous catalysts (characterised by their interfacial separation from the reaction medium) are particularly sought in this sector due to the relative ease with which they can be recycled, and their typically high physicochemical stability. Porous, crystalline aluminosilicates (zeolites)[18] have made a significant impact in the chemical industry,[19] finding extensive application not only in catalysis, but also in technologies that exploit their unique uptake and release properties. As a result, zeolite science has burgeoned,[20] and synthetic developments[21] have led to new 'zeotype' frameworks with varied elemental compositions.[22] The aluminophosphates (AlPOs)[23] are exemplar:[24-25] these porous oxide materials comprise an ordered assembly of alternating [AlO_4] and [PO_4] units and, akin to zeolites, are created by hydrothermal synthesis in the presence of a structure-directing agent (SDA) (SI for additional details). For AlPOs, the SDA is typically an organic amine that templates the three-dimensional framework, before being eliminated by heating in air at high temperature to remove the organic SDA. By appropriately selecting the reaction conditions and SDA, AlPOs can be prepared in a range of structures - many of which are isostructural with zeolites. The resultant solids contain ordered pores and cavities of molecular dimensions and, as a result, exhibit molecular sieving capabilities. This is an important property of zeotype materials, and it is regularly exploited in catalysis to effect selective transformations by the regulation of species that enter, leave, or form within the framework (reactant and product shape-selectivity). In addition, AlPOs can undergo isomorphous substitution (*Figure 3*), a substitution of heteroatoms into the framework, to modify its reactive properties.[26] When the heteroatom is a metal (M) which possesses multiple, stable oxidation states (*e.g.* Co, Fe and Mn), it is possible to catalyse redox reactions at the metal centre. Catalytic redox activity in MAlPOs has been exploited in many processes, including the oxidation of hydrocarbons and olefins,[27] and the ammoximation of ketones.[28]

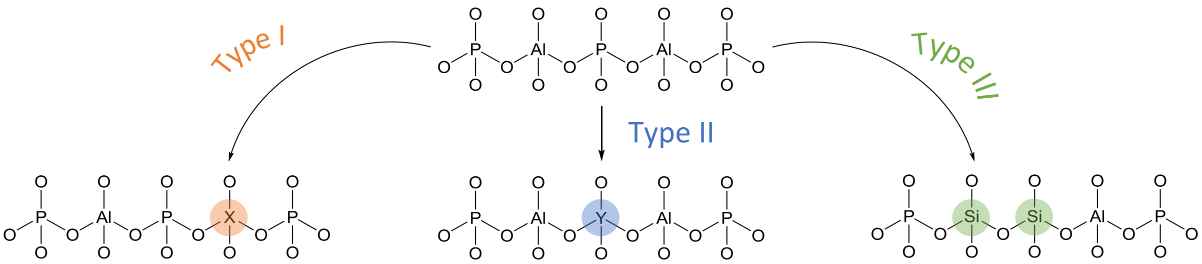


Figure 3: The reactive properties of aluminophosphates can be modified by isomorphous substitution of heteroatoms into the framework. Type I substitution involves replacing Al with a heteroatom (X), in Type II substitution P is replaced by a heteroatom (Y) and in Type III substitution, both Al and P are substituted by Si.

Industrial context: nylon production

Given the huge demand for oxy-functionalised chemicals, the oxidation of abundant hydrocarbon feedstocks is immensely important in the chemical industry. Whilst executing targeted oxidations to form useful compounds is often challenging, the development of selective redox catalysts has led to considerable progress in this field.[29]

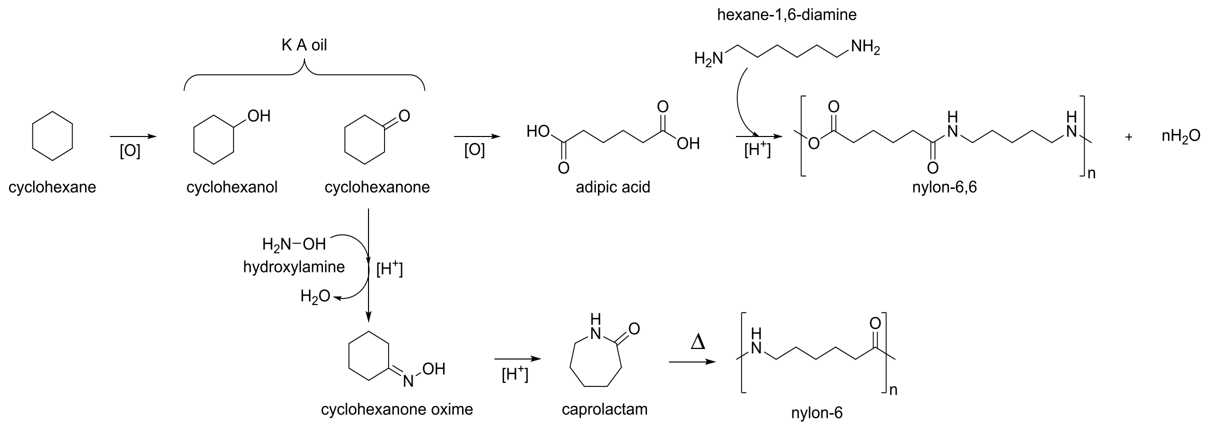


Figure 4: Schemes for the synthesis of nylon-6 and nylon-6,6 polymers.

K A oil, the mixture of cyclohexanone (K) and cyclohexanol (A) produced by the oxidation of cyclohexane, is an important intermediate in the production of the nylon-6 and nylon-6,6 polymers (Figure 4).

Conventionally, large-scale cyclohexane oxidation has employed a homogeneous Co or Mn catalyst that only maintains a high selectivity for (the more reactive) K A oil when conversions are low.[30] Also, where these catalysts (and the more benign alternative previously reported for an educational practical)[31] occupy the same phase as the reaction mixture, catalyst isolation can be challenging, and incur additional separation steps that are detrimental to the overall sustainability of the process.

The development of heterogeneous redox catalysts has led to vast improvements in K A oil yield, and, in some cases, these systems can even facilitate the direct oxidation of cyclohexane to adipic acid (a fundamental building block of polyamide fibres and polyurethanes). Moreover, as solid-phase catalysts can be readily removed from the fluid-phase reaction, elaborate, costly and wasteful separation steps can be eliminated. The metal-doped aluminophosphates have shown particular aptitude in the oxidation of cyclohexane, as both the nature of the metal dopant[32] and the framework structure[33] can be used to control product output. For example, FeAlPO-31 (5.4 Å pores) and FeAlPO-5 (7.3 Å pores), whilst having identical active sites, produce very different product mixtures in the oxidation of cyclohexane (Figure 5).[34] Whilst FeAlPO-5 produces predominantly cyclohexanol and cyclohexanone, the size constraints imposed by FeAlPO-31 hinder the diffusion of cyclic species, favouring multiple reactions to the linear product (adipic acid) that can more readily escape the pores. The same rationale can be used to evaluate the activity of the numerous redox-active AlPO catalysts, providing students with an opportunity to consider the mechanistic implications associated with the framework structure and hence justify the catalysis.

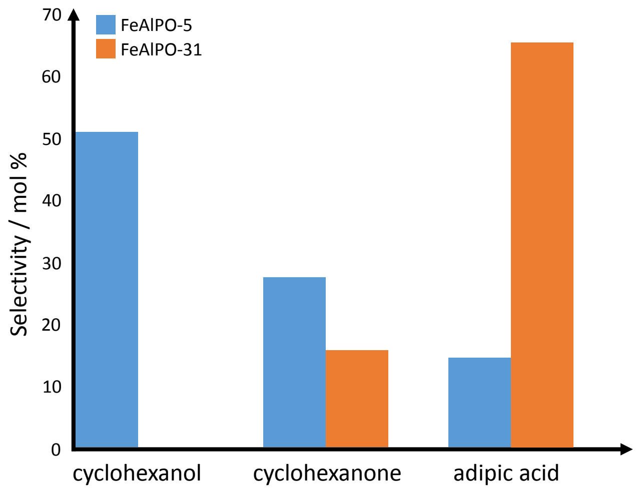


Figure 5: The product selectivity of FeAlPO-31 and FeAlPO-5 (at similar levels of conversion) in the aerial oxidation of cyclohexane (24 hours, 373 K).[34]

Whilst nylon-6,6 production continues to support the adipic acid market, there is increasing demand for the chemical intermediates used in the production of nylon-6, its recyclable analogue. As part of the practical, students are required to evaluate the multi-step processes for the production of nylon-6 and nylon-6,6 and consider the impact of the material lifecycle 'from cradle to grave'. As part of this, students discuss the advantages and limitations to the AlPO-catalysed process over conventional industrial routes, and consider the mechanistic implications of the choice of framework topology and dopant species.

Learning Objectives

Whilst zeolite chemistry has previously been used for pedagogic purposes, many examples focus on solid-state and materials chemistry, and use structural characterisation as the principal tool for materials evaluation.[35-40] Where others have presented experiments to illustrate the real-world application of zeolites (exploiting their transport, sorptive, and ion-exchange properties),[41-44] those focussing on the catalytic properties of these materials deal exclusively with acid-catalysed transformations,[45-48] and the discussion of concepts in catalysis, sustainability, and green chemistry metrics are limited. To the best of our knowledge, this practical is unique in its use of a heteroatom-doped *zeotype* framework for a catalytic *redox* reaction, and in its particular emphasis on using a heterogeneous catalyst to discuss Green Chemistry concepts.

In the practical component, students first synthesise Co-substituted AlPO-5, and then use this redox catalyst to facilitate the oxidation of cyclohexane to K A oil. Students use X-ray power diffraction and colour changes to characterise their catalyst, and gas chromatography with mass spectrometry (GC-MS) to determine the efficiency of their catalysis. At the end of this practical students will be able to:

- safely operate an autoclave and perform a hydrothermal synthesis at high temperature and pressure;
- set up a calcination involving pressurised air cylinders and a tube furnace;
- prepare and submit samples to the open-access mass spectrometry suite and then retrieve, process, and interpret gas chromatographic and mass spectrometric data;
- evaluate the efficiency of a catalytic process on the basis of key, quantitative metrics;
- formulate mechanistic arguments to predict the outcome of aluminophosphate-mediated industrial processes and consider their Green Chemistry potential;

- evaluate longevity and recyclability of different polyamides by specifically appraising nylon-6 and nylon-6,6;
- calculate channel dimensions and pore sizes of specified inorganic frameworks;
- exploit X-ray diffraction analysis to determine unit cell dimensions;
- relate catalytic outcomes directly to the redox behaviour of elements in a solid-state framework;
- relate the sustainable credentials of the RAP process, with respect to the 12 Principles of Green Chemistry, and comment on real-world aspects of the life cycle of the two principal nylon products;
- present and defend data and results in front of a critical audience.

Pre-laboratory material

To present the rationale for this practical, the laboratory script commences with an overview of AlPO chemistry, from basic structure and synthesis, to characterisation and application in heterogeneous catalysis. Mindful that at this stage in their undergraduate course, many students will have had little exposure to zeolite science, the preamble is supplemented by a narrated presentation that develops the underlying concepts, and expands the scope of inorganic framework materials. For more comprehensive insights, a selection of relevant literature is highlighted[25, 28, 49-50] and students are encouraged to engage with the available resources for the benefit of later assignments. The resources that accompany this practical, as well as the experiment itself, reiterate the real-world application of catalysis in the polymer industry, whilst making connections to fundamental chemical theory (further details in SI).

Managing hazards

The lab-based component of this practical requires students to follow a number of procedures, each of which presents its own hazards. Whilst some aspects, such as the oxidation reaction assembly, will be familiar to a second-year undergraduate, others are more specific to this experiment and require detailed instruction. Therefore, to prepare students for the practical component, hazards are stated explicitly in the instruction booklet, and restated in the personal laboratory notebook. Furthermore, to ensure that students have understood the hazards, safety aspects are incorporated into the compulsory, online, pre-lab quiz.

To control exposure to chemical hazards (table 7/SI), students are expected to exercise good laboratory practice at all times, working in a fume hood as much as feasibly possible, and wearing lab coat, goggles and gloves. Of particular note are the hazards associated with of cobalt (II) acetate; airborne particulates are minimised by weighing the solid in a well-ventilated fume hood and immediately dissolving to form an aqueous solution, reducing risk of inhalation.

Arguably, the step posing greatest physical risk (table 8/SI) to the student is the hydrothermal synthesis, as this requires both high temperature and pressure to crystallise the CoAlPO-5 catalyst. Whilst the hydrothermal synthesis is carried out in a PTFE-lined, stainless steel autoclave that is engineered to withstand high pressure (or otherwise rupture in a controlled manner), the multi-component autoclave must be assembled correctly in order to maintain pressure in a safe and effective manner. To minimise risks, students are notified of the potential hazards of the hot, pressurized autoclaves, and provided with detailed rules for safe operation. Moreover, a video showing step-by-step assembly of the autoclave is provided as part of the pre-lab material, and laboratory staff observe the set-up during the practical. The other potentially hazardous step is the operation of the high-temperature tube furnace and associated pressurised air cylinder but this is undertaken by trained teaching staff, once the students have transferred their samples to the room-temperature furnace.

Experimental

Redox Aluminophosphates offers a comprehensive practical experience, incorporating synthetic inorganic chemistry, organic transformation, and spectrometric analysis, underpinned by physical chemistry concepts. An overview of the laboratory practical is depicted in Figure 6 and details to all practical aspects can be found in the supporting information.

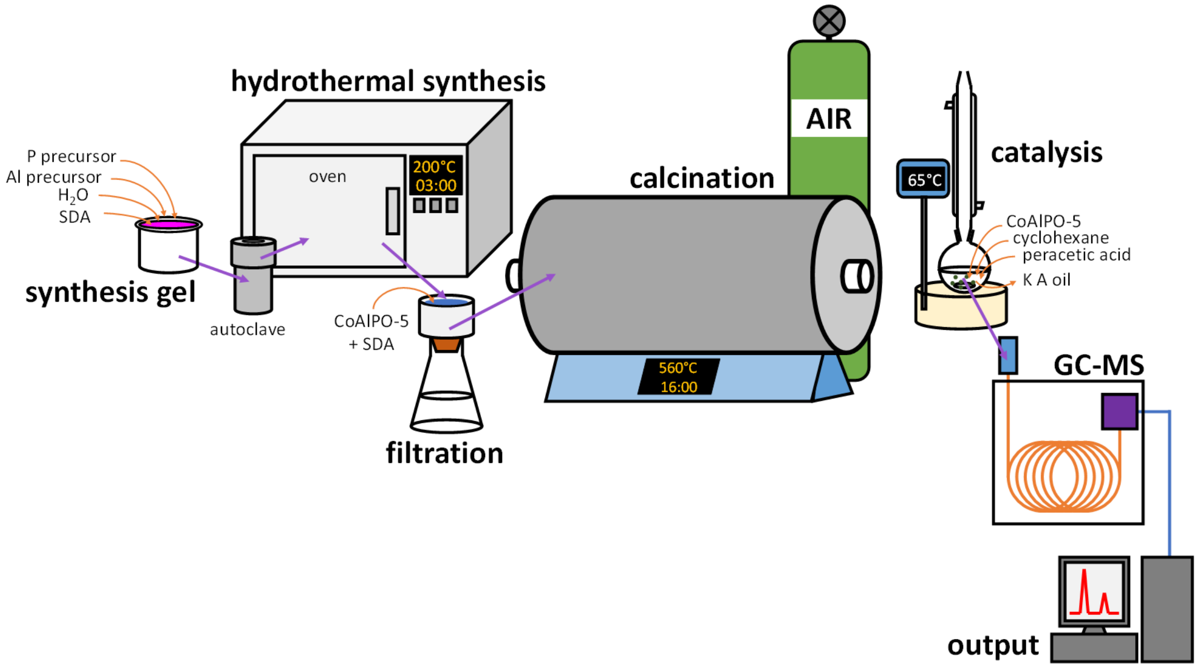


Figure 6: The redox aluminophosphate practical incorporates a variety of laboratory techniques. CoAlPO-5 is first crystallised from the synthesis gel by hydrothermal synthesis. The solid catalyst is collected by vacuum filtration, and calcined prior to its catalytic application. Finally, the activity of the CoAlPO-5 material is assessed by GC-MS analysis of the catalytic oxidation of cyclohexane.

Synthesis of CoAlPO-5

The practical begins with preparation of the CoAlPO-5 synthesis gel following an established and reliable protocol. Students calculate reagents quantities in advance, and prepare a gel of composition 0.96Al : 1.5P : 0.04Co : 0.8SDA : 40H_2O following set instructions that are detailed in the supporting information. The CoAlPO crystallisation is achieved within a reasonable timescale by hydrothermal synthesis and the gel composition is determined purely by the ratio of starting materials and reagents. The synthesis of the CoAlPO-5 catalyst is completed by calcination in a tube furnace under a flow of air.

Catalysis: Cyclohexane oxidation to K A oil

Students assemble a glass apparatus and perform the catalytic oxidation of cyclohexane to K A oil using their CoAlPO-5 catalyst. The oxidant used in the laboratory is peracetic acid (30-45 % in acetic acid), that is slowly added to the stirred reaction, which is then brought to reflux for 2 hours. After a quick work-up, the reaction mixture is ready for GC-MS analysis.

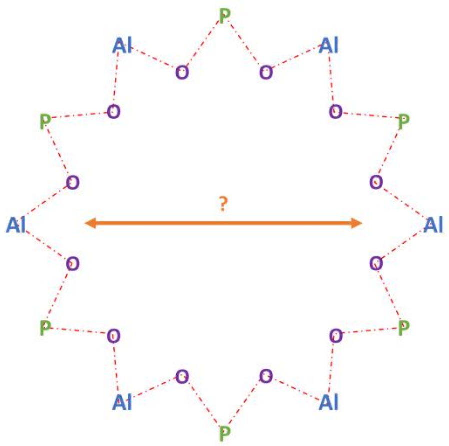
GC-MS Analysis

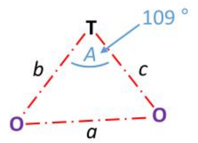
Students are guided in the preparation of samples for GC-MS analysis which comprises submission of a barcode-labelled and sealed vial with a crimped metal cap *via* an online open access system. Students place their sample in the GC autosampler, automated analysis and data processing follows and the resultant data accessed and analysed online.

Results and Assessment

Whilst the synthesis of the CoAlPO-5 catalyst is relatively straightforward, it provides a foundation to elaborate a range of chemical concepts. To ensure that students actively engage with the underlying theory, they are presented with a set of questions that use undergraduate theory to rationalise observations in the lab, and extrapolate these to the wider, industrial context. For example, AlPOs are typically highly-crystalline materials, and thus routinely characterised using powder X-ray diffraction techniques. Students index the powder pattern of the CoAlPO-5 catalyst, and calculation of hexagonal unit cell parameters is used to reinforce their understanding of Bragg's Law.

Students also use fundamental mathematics to estimate the pore dimensions of select AlPO frameworks (Figure *7*) before discussing the mechanistic implications of steric restriction on key catalytic transformations in nylon production. Further to this, students assess the advantages and limitations of AlPO-catalysis over conventional industrial routes, and apply Green Chemistry principles for the life cycle analysis of the nylon-6 and nylon-6,6 polymers.





Cosine Rule: $a^2 = b^2 + c^2 - 2bc\cos(A)$

Bond	Bond length / Å
Al-O	1.72
P-O	1.54

Ionic Radius of O^{2-} = 1.40 Å

Figure 7: Using the tetrahedral angle, relevant bond lengths and atomic radii, it is possible to estimate the pore size of AlPO-5 using the cosine rule.

The *Redox Aluminophosphates* practical also applies undergraduate theory to topics beyond catalytic theory. For example, the choice of doping cobalt into the AlPO-5 also provides an opportunity for students to apply their synoptic knowledge of crystal field theory to rationalise the observed colour changes that accompany the individual synthetic steps of both experiments. These relate to the relocation of Co(II) from the discrete precursor compound (pink, octahedral, d^7) into the crystalline framework (blue tetrahedral, d^7), and subsequent oxidation to the redox-active catalyst, which then contains Co(III) species (green, tetrahedral, d^6) (see SI).

Students are principally assessed on these topics through a group presentation, which they prepare in advance of the laboratory session. The presentation is delivered to a member of staff who encourages discussions that develop the underlying theory, thus providing students with experience of answering questions *viva voce*. Moreover, the small-group setting creates a constructive environment to provide feedback on their chemical knowledge and oral presentation skills. Finally, this format provides a fertile ground for open-ended discussions of their life-cycle analysis of the synthetic aspect and the two different nylons. Encouragingly, student have endorsed the presentation component of this practical as beneficial to the development of their team-work and organisational skills. They equally value the nature of the discussion that strengthens their appraisal of real-life scenarios.

Additionally, students are expected to summarise the key results and observations as part of a single-page, experimental report. Accompanying the report, students analyse and assign their own gas chromatographic data based on the fragmentation and isotope patterns observed in their mass spectra. This provides experience of evaluating their catalytic reaction in a quantitative manner, *via* the conversion of starting material and selectivity towards the desired reaction products. By calculating the turnover number of their reaction, students are also introduced to important catalytic metrics. Sample data from student practicals and presentations are collated in the supporting information.

Student Feedback

An important aspect of enhancing the student experience is to develop a laboratory practical that invokes synoptic knowledge and aligns with the lecture course. Additionally, in a research-led teaching environment it can be edifying to connect the educational laboratory experiment with topical research activities. Herein, *Redox aluminophosphates* benefits from its foundations in in-house catalysis research. Informal student feedback from the undergraduate class has recognised the research-teaching link, and students have championed the opportunity to "be part of" a research task, handling "research-grade equipment" as they feel that they can "learn and achieve a lot more when the practical/theory is related to real-world applications".

Undoubtedly, enhancing the student experience has been a key incentive in developing *Redox Aluminophosphates*. As such, to establish whether the objectives of the practical are effectively conveyed to the students, their experience was assessed *via* questionnaires. Initially, *Redox aluminophosphates* was conceived with a focus on the affective and psychomotor learning domain, with assessment after the laboratory activity through a summative report. However, on soliciting feedback from the students, the assessment component has evolved, with aspects of the original summative assessment being reformed as a *viva voce*-style presentation that allows for tailored and immediate feedback. In addition, student counsel has led to development in the wider curriculum, with redevelopment of the Level 3 *Sustainable Chemistry* course to improve alignment with the learning outcomes of the practical activity.

Free text student feedback (table 9/SI) confirms the challenging yet rewarding nature of both the practical activity and the group presentation aspect, and recognises its real-world applicability. As part of the 2016-2017 questionnaire, students (19 members) were asked to rate different aspects of the learning process on a Likert scale ranging from *complete disagreement* to *complete agreement* (table 10/SI). All students found the laboratory class to be an *active process* that *made them think* (> 50 % completely agree). Everyone *learned from this lab class* (half of the students mostly agrees, whereas the other half completely agrees), while 89 % were stimulated to *ask questions* on the topics covered in the activity. The presentation aspect, including its summative nature, was somewhat controversial, with ~ 16 % not in favour and 11% slightly disagreeing with its learning benefit (Figure 8 and Figure 9).

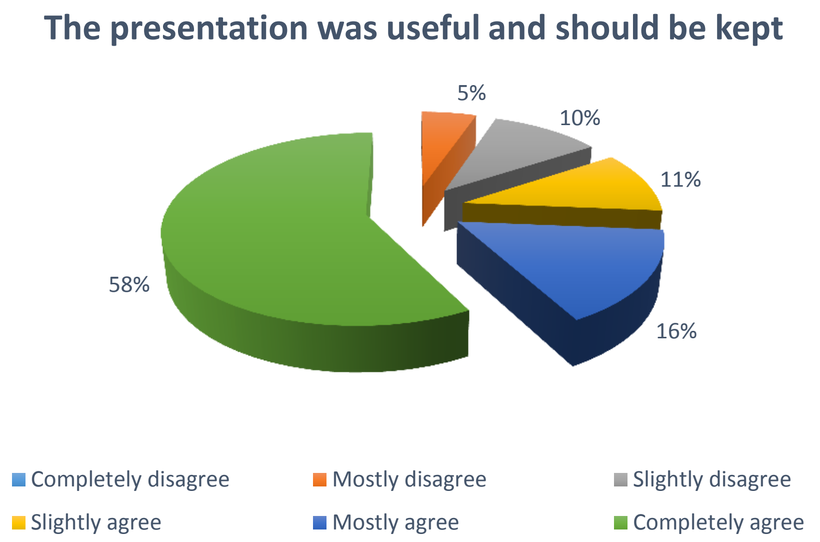


Figure 8: Student opinion of the usefulness and future of the presentation component of the *Redox Aluminophosphate* practical.

Nonetheless, the majority of the students supported the changes following constructive alignment of the learning outcomes, teaching activities, and assessment tasks. Almost half of the students completely agreed that they learned from the *viva voce*-style questions and the feedback during *Redox Aluminophosphates*, and recommended that this summative assessment be kept (16 % mostly and 58 % completely agree).

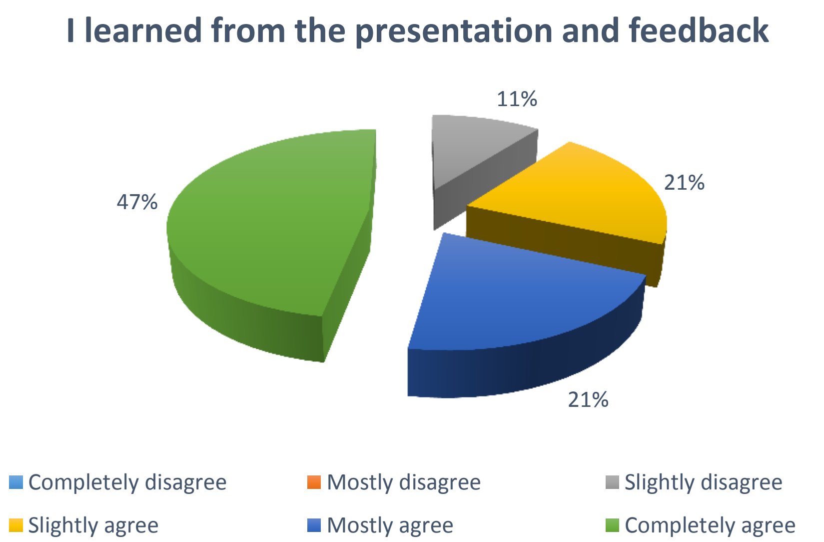


Figure 9: The student learning curve for the presentation component of the *Redox Aluminophosphates* practical.

In a more recent questionnaire (2017-2018), students were asked to rate their exposure to a range of relevant topics and skills, before and after undertaking the practical. Each student provided a score on a linear scale from 1 (no experience) to 5 (very competent), and a paired t-test was performed on the data. In all cases, there was a statistically significant ($p < 0.001$) improvement in the mean score awarded by the 2017-2018 students (74 members) after undertaking the RAP practical (Table 1 below and table 11/SI).

Table 1: Comparative Mean Scores Awarded by Students in a Skill Self-Assessment before and after the RAP Practical

Topic or Skill addressed in the Questionnaire Items about the RAP Practical	**Mean scores,[a] *N* = 74**	
	Before Practical	**After Practical**
Catalysis theory (how catalysts work, why they are used in reactions)	2.76	4.01
Catalysis metrics (conversion, selectivity, turnover number)	1.87	3.63
Analysing my own data	3.30	3.83
Framework materials (zeolites, AlPOs – their structure and reactivity)	1.77	3.94
Indexing powder patterns	3.45	4.11
Techniques to characterise solid materials	2.49	3.39
The concept of green chemistry and sustainability	2.68	3.89
Presenting work in the form of an oral presentation	2.97	3.75
Group work	2.49	3.39
Organisational skills and time management	3.69	3.96

[a] *Scores based on a scale of 1-5, with 1 indicating "No Experience" and 5, "Very Competent"*

The students were also asked to identify topics that they felt were supported by the RAP practical (Table *2*). Of the suggested areas, a large proportion of the student body identified X-ray diffraction as being reinforced by the practical, and this was often reiterated in the written feedback.

Table 2: Percentage of Students Who Related Fundamental Concepts Addressed in the RAP Practical to Material in Their Lecture Courses.

Topic	**% of Students (*N* = 74)**
X-ray diffraction	85
Mass spectrometry	53
Solid-state chemistry (zeotype materials)	76
Crystal field theory	60
Redox reactions	72

In the development of practical skills, the preparation and submission of GC-MS samples, hydrothermal synthesis and calcination, were frequently identified in written responses. Encouragingly, > 70 % of the student group acknowledged the wider applicability of the RAP to their academic course and also to real-world applications (Table *3*).

Table 3: Student Feedback on the Wider Benefits of the RAP Practical

Statements for Response	**Students Who Agree or Strongly Agree, % (*N* = 74)**
The theory accompanying this practical supported the content from my undergraduate lecture course.	72
The practical gave me practical experience of laboratory techniques that I had not previously encountered.	71
The practical demonstrates the application of chemistry to solve 'real-world' problems.	73
The RAP practical has increased my interest in studying the CHEM 3044/6103 Sustainable Chemistry module	53

It is also encouraging that over half of the undergraduate class expressed an increased interest in studying the Sustainable Chemistry module after undertaking *Redox Aluminophosphates*,[51] given the large number of optional module that are available to the students - both within the Chemistry Department and also the wider university. Several free text feedback comments linked sustainability of important industrial catalytic processes plus other issues related to green chemistry and product lifecycle to *Redox Aluminophosphates* and how principles experienced therein can solve current challenges.

Redox Aluminophosphates provides quality practical education and fulfils the UN Sustainable Development Goal 4.[52] Importantly, three more sustainability goals are associated with RAP and its application to the real world, predominantly "Clean water" (goal 6) and "Climate action" (goal 13) can be addressed by the students as the industrial production of nylon-6 and its precursors using RAP catalysis allows for improved freshwater ecosystem management through reduction of salt loads in aqueous waste streams, while a much better atom economy and more energy-efficient processes are identified as desirable factors helping to avoid climate change. The students also linked goal 12 "responsible consumption and production" to this project and specifically relate the recyclability of nylon-6 vs nylon-6,6 to better consumer behaviour. In systems-thinking style, students finally identified the need for a renewable feedstock that should replace cyclohexane as starting material.

Moreover, the holistic approach comprises new drivers for a sustainable mind-set as the open market demands more greener, natural products in the face of increasing cost of key commodity chemicals. Equally, ever stricter legislation regarding hazardous substances (REACH, ROHS, COMAH) drives the development of more sustainable processes and generates a mandate for adequately educated chemists. The *Redox Aluminophosphates* experimental suite addresses all these in systems thinking mode.

Redox Aluminophosphates as a laboratory experiment and as a concept includes elements featuring prominently in the biogeochemical flows (P, N) of the planetary boundaries framework.[53] Bearing these and the UN Sustainable Development Goals (SDG) in mind, a logical evolution then includes using a systems thinking visualisation tool, namely a system- oriented concept map extension (SOCME), in future and expanding to a more detailed systems thinking approach at various stages (*e.g.* SOCME for Al or freshwater, broadening societal impact side).

Conclusions

Whilst catalysis is a familiar topic in the undergraduate Chemistry course, the importance of its real-world application can be eclipsed by the underlying physical concepts. We therefore present the *Redox Aluminophosphates* practical as a means of discussing fundamental undergraduate theory in the context of Industrial catalysis. In the constructively-aligned practical component, students undertake hydrothermal synthesis and calcination to prepare a redox-active aluminophosphate catalyst. This material is then directly applied to the oxidation of cyclohexane to K A oil; an industrially-relevant transformation in the polymer industry. Quantitative assessment (achieved *via* GC-MS analyses) exposes students to catalytic metrics and green chemistry concepts and sustainability goals, whilst the use of AlPO materials provides immense scope to evaluate catalytic mechanism. Within a laboratory setting, *Redox Aluminophosphates* demonstrates how catalysts can effect a real enhancement in chemical synthesis and, through the supporting literature, demonstrates how this can be realistically scaled to the industrial setting. By implementing systems thinking aspects to a laboratory class, *Redox Aluminophosphates* connects Earth and Societal Systems through laboratory experiments, retrospection and prediction with Chemistry Teaching & Learning and associated Educational Research & Theories.

Associated content

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.]

Hazard information, experimental procedures, feedback data and statistical analysis.

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Notes

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