Design of Highly Selective Pt Nanoparticle Catalysts for Aerobic Oxidation of KA-Oil using Continuous-Flow Chemistry


Abstract: Highly active and selective aerobic oxidative catalysts, alkoxyl (precursor for adipic acid and ε-caprolactam) has been achieved in high yields using continuous electron microscopy by utilizing uncapped noble metal nanoparticles (Au, Pt & Pd) catalysts. These are designed by a one-step in situ methodology, within three-dimensional porous molecular architectures, to afford robust heterogeneous catalysts. Detailed spectroscopic characterization of the nature of the active sites at the molecular level, coupled with aberration-corrected scanning transmission electron microscopy, reveals that the synthetic methodology and associated activation procedures play a vital role in regulating the morphology, shape and size of the metal nanoparticles. These discrete, isolated active centers have a profound influence on the activation of molecular oxygen, for selective catalytic oxidations.

Cyclohexanone is an important commodity chemical used in the production of adipic acid and ε-caprolactam, which are important precursors used in the industrial manufacture of nylon 6, 6 and nylon 6 respectively.[1] The selective hydrogenation of phenol,[2] direct oxidation of cyclohexanol[3] and dehydrogenation of cyclohexanol[4] are commonly used for the production of cyclohexanone, either in its pure form or as KA-oil (a mixture of cyclohexanol and cyclohexanone). Given the challenges associated with the aerobic oxidation of hydrocarbons employing heterogeneous catalysts, dehydrogenation of cyclohexanol or KA-oil has proved commercially attractive. In this Communication, we explore the prospects for the aerobic oxidation of KA-oil using heterogenized metal nanoparticle (NP) catalysts (Figure 1). In particular, we have focused on developing a continuous-flow system[5] that would enhance the current yields obtained by the dehydrogenation route, whilst at the same time maximizing the overall selectivities (>99%) to the desired cyclohexanone product.

Noble metal NPs, including Pt, Pd and Au, have demonstrated a precedent for exceptional activity in a number of selective oxidation and hydrogenation processes.[7] Interestingly, the use of metal NPs in the oxidation of cyclohexanol (and KA-oil in particular) under continuous-flow conditions is somewhat limited (see Table SI2a). Au/Cu-fiber NP catalysts[8] produce modest cyclohexanone yields (≤75%), but require a complex and intensive catalyst synthesis procedure. A range of Cu-based catalysts,[9] and other transition-metal variants employing Ti, Co and Mn[10] active centers have been investigated, notwithstanding the fact that a large proportion of these catalysts require high concentrations of corrosive initiators, co-solvents and stoichiometric oxidants. Table SI2a highlights some relevant examples of cyclohexanol oxidation and dehydrogenation. It further demonstrates the limited use of continuous-flow methods, with a large majority of catalytic processes utilizing a batch setup. Developing low-temperature, selective oxidation of KA-oil could therefore be potentially attractive if cyclohexanone selectivities and yields can rival traditional cyclohexanol oxidation and dehydrogenation pathways.[4]

In this study we capitalize[11] on exploiting the synergistic potential of microporous copper chlorophosphate (CuClP) frameworks bearing flexible anion exchange properties, and devising new synthetic strategies for generating (see SI1) in situ, isolated and well-defined NPs of Pt, Pd and Au (2-5 nm), as embodied in Figure 1. In particular, changes in the local structural environment of the NPs were monitored over a range of activation temperatures using x-ray absorption spectroscopy (XAS). The shape- and size-distribution of the active sites within the microporous support architecture were probed using aberration-corrected scanning transmission electron microscopy (AC-STEM) and the compositional integrity of the NPs was ascertained using complementary energy-dispersive x-ray spectroscopy (STEM-EDXS). The findings from here have been rationalized with a view to evaluating structure-property relationships in catalytic studies involving the activation of molecular oxygen. The stability of these solid NPs and versatility of this approach has been investigated in the aerobic oxidation of KA-oil, under continuous-flow conditions thereby affording potential scope for the industrial applicability of these catalysts.[6]
X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

Figure 2. 2a depicts the XPS spectra and 2b the magnitude and imaginary component of the k^2 weighted Fourier transform for the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

Figure 2. 2a depicts the XPS spectra and 2b the magnitude and imaginary component of the k^2 weighted Fourier transform for the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

Figure 2. 2a depicts the XPS spectra and 2b the magnitude and imaginary component of the k^2 weighted Fourier transform for the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.

X-ray photoelectron spectroscopy (XPS) was employed to probe the nature of noble metal species adjacent to the surface of the microporous framework, with respect to different activation temperatures. A clear trend was observed for the Pt/CuClP catalyst, which showed a transition from a mixture of Pt(II) and Pt(0) with 4f_{7/2} peaks at 72.4 eV and 70.8 eV respectively, to purely Pt(0) species, as the activation temperature was progressively increased from 150 to 200 °C: (Figure 2a). Furthermore, it was established that an activation temperature of 200 °C was sufficient for the complete reduction of the Pt precursors to form NPs under these activation conditions.

XAS was used to probe the coordination geometry and local structural environment of the active sites with a view to gaining a better understanding on NP formation and extrusion, with progressive increase in activation temperatures. Concurrent trends with the XPS are exhibited in both the EXAFS data of the three Pt/CuClP species reduced under different activation temperatures. Both techniques demonstrate the progressive reduction of the [PtCl_4]^2- precursor towards the metallic Pt(0) species with increase in temperature. Figure 2a is plotted with reference samples in Figure S13a. For Figure 2b the associated scattering paths are included for the imaginary component and the fitting parameters are displayed in Table SI4a.
The catalytic results for the aerobic oxidation of KA-oil with the Pt, Pd and Au catalysts, activated at different temperatures, is
Figure 3a contrasts the aerobic production of cyclohexanone with supported NP/CuClP catalysts. Showing the superior activity of Pt/CuClP for this process and the ability to optimize this reaction with adroit catalyst design. 3b highlights the exceptional catalytic lifetime of the Pt/CuClP catalyst, displaying consistent cyclohexanol conversion and cyclohexanone selectivity profiles over a 10 hr period. Full tabulated data is presented in Tables SI7a and b respectively.

Reaction temperature: 200 °C, air flow: 25 mLmin⁻¹, substrate flow: 15 µLmin⁻¹, WHSV: 1.8 hr⁻¹.

presented in Figure 3 (for further details see SI7). Figure 3a highlights the superior performance of the Pt catalyst over that of its corresponding Pd and Au analogues, and it is remarkably noteworthy that the selectivity for the desired cyclohexanone was in excess of 99+% for the Pt catalyst (reaction mixtures were analyzed for dibasic acids (including adipic acid) and we did not observe any evidence for their formation). Not only is the Pt/CuClP a highly effective and selective aerobic oxidation catalyst (the undoped framework is inert (SI6)), but the robust nature of this material is evidenced by both its ability to maintain high levels of activity and selectivity over extended periods on stream, as displayed in Figure 3b (see also Figure SI7a). More importantly, the material retains its structural integrity post-catalysis evidenced by both its sustained phase purity (Figures SI5b) and consistent NP size distribution (Figure SI8d), where no agglomeration or restructuring is observed thus, demonstrating the recyclablility and stability (Table SI7d) of the catalyst. These findings support the hypothesis that the catalytic activity of these materials can be intrinsically linked to the degree of NP formation: the [PtCl₄]²⁻ precursor has a greater propensity for NP formation over a range of activation temperatures and this, in concert with the surrounding microporous architecture, bestows superior catalytic performance for the aerobic oxidation of KA-oil. In order to further understand this behavior, all three catalysts were examined using high-resolution STEM, in order to probe the shape- and size-distribution of the NPs and, in particular, their precise location with respect to the crystalline structure of the microporous framework.

High-resolution studies, using AC-STEM, have shown in detail the abundant formation of nanocrystalline Pt NPs (2-5 nm in diameter), which are well-dispersed on the CuClP framework, whose crystalline integrity could also be visualized directly (Figures 4a, b and SI8a). In this regard it is apparent that the atomic number contrast and often “direct interpretability” of annular dark-field (ADF) STEM imaging, combined with the high-spatial resolution enabled by AC optics, can yield significant insight into the crystallographic structures of both the extruded NPs and the microporous framework. Hence ADF AC-STEM can be a particularly powerful approach for the elucidation structure-property relationships in these materials. The much more limited NP formation in the Pd/CuClP system is also readily apparent from AC-STEM, as exemplified in Figures 4c, d and SI8b. Complementary compositional studies using STEM-EDXS also confirmed the well-defined nature of the Pt/CuClP and Pd/CuClP systems, with abundance and paucity of NPs, respectively (Figures SI9a and b).

The potentially more complex phenomena in the Au/CuClP system (as seen from the EXAFS) was also systematically

Figure 4. ADF AC-STEM images of the respective NP/CuClP materials activated at 200 °C. The crystalline structure of the framework is rendered visible via the lattice planes containing heavy atoms. (a, b) showing...
abundance of Pt NPs; (c, d) limited Pd NP formation; (e, f) prevalence of Au NPs within the CuClP framework. Extended figures and further details are provided in SI8.

investigated in AC-STEM and STEM-EDXS studies, including samples activated at different temperatures. As shown in Figures 4e, f, Si8c and Si8c, regions of extensive well-defined small NP formation could be observed for the Au/CuClP system, even when the sample was activated at 200 °C (analogous to the Pt/CuClP).

Consistent with the XPS studies, these would appear to predominate at thin or surface regions of the framework. Further, STEM and spatially resolved STEM-EDXS elemental mapping on Au/CuClP samples activated at higher temperatures indicate an increased extrusion of both Au and Cu, with some degree of intermixing. It therefore appears that the Au samples have the potential to possess a range of active species, including small extruded Au NPs on the surface as well as larger Au, Cu or Au–Cu NPs. These preliminary findings therefore indicate the potential for tailored Au/Cu alloying or combined extrusion, which enhances the prospects for exploiting bifunctional (bimetallic) catalysis in the future74–6 (these aspects will be reported in detail in a future publication).

By employing a combination of complimentary structural, spectroscopic and high-resolution microscopy techniques, we have contrasted the varying degrees of NP formation and the superior properties of the [PCL]5 precursor to yield well-defined, isolated NPs (predominantly 2.3 nm) within microporous framework architectures. The local structural environment, and the precise nature and location of these active sites, is exigent for their superior performance (approaching unrivaled yields of >90% by adapting a ‘closed-loop’ system (Table SI9)) in the aerobic oxidation of KA-oil, under continuous-flow conditions. This design strategy further offers adequate scope for the creation of multimetallic (e.g. Au–Pt) and multifunctional heterogeneous catalysts, in our continued quest for the activation of molecular oxygen in sustainable catalytic processes.17

Experimental Section

Details on catalyst synthesis, activation, characterization and catalysis are provided in the Supporting Information. Briefly, the CuClP framework doped with gold, platinum or palladium tetrachloride precursors were hydrothermally synthesized at 448 K for 48 hr.11[4] Materials were post-synthetically activated under reduction for 2 hr at specified temperatures (423 – 523 K) under a 150 mL min−1 flow of 5% hydrogen in nitrogen. The aerobic oxidation of KA-oil was studied under continuous-flow conditions under atmospheric pressure employing a custom-made fixed-bed reactor (Cambridge Reactor Design). A typical reaction setup consisted of 240 mg of catalyst with a substrate flow rate of 15 μL min−1 and an air flow rate of 25 mL min−1 at 473 K. Products were analyzed and quantified by gas chromatography using appropriate calibrations using a 2 M triethyleneglycol dimethyl ether in acetone external standard.

Acknowledgements

We thank Diamond Light Source, the National EPSRC XPS User’s Service (NEXUS), A*STAR (AMG & CSH), Clare College Cambridge (RKL), EPSRC UK Catalysis Hub (EP/K014706/1, EP/K014686/1, EP/K014854/1 & EP/K014714/1), EU 7th Framework Program (FP7/2007-2013, ESTEEM2, #312483 (PAM), ERC #291522-3DIMAGE (RKL & PAM) are also thanked for financial assistance.

Keywords: Nanoparticle Catalysis • Aerobic Oxidation • Flow-Chemistry • KA-Oil Oxidation • High Selectivity


Pt, Pd & Au nanoparticles were generated \textit{in situ} by anion extrusion from porous framework architectures. Spectroscopic and aberration-corrected scanning transmission electron microscopy reveal that activation conditions are crucial for the generation of isolated active centres. The design strategy affords highly active and selective catalysts, for the industrially-significant aerobic oxidation of KA-oil, under continuous-flow conditions.