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Joaquin Resasco, Feifei Yang, Tong Mou, Bin Wang, Phillip Christopher, and Daniel E. Resasco ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.9b04330 • Publication Date (Web): 03 Dec 2019 Downloaded from pubs.acs.org on December 4, 2019

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Relationship between Atomic Scale Structure and Reactivity of Pt catalysts: Hydrodeoxygenation of m-cresol over Isolated Pt Cations and Clusters

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Abstract

Atomically dispersed late transition metal cations have attracted significant attention as next generation heterogenous catalysts. However, relationships between the catalytic behavior of atomically dispersed metal cations and active sites on metal nanoparticles have been difficult to establish, due in large part to the difficulty in characterizing the local atomic structure of these metal species. Here, we use the hydrodeoxygenation (HDO) of m-cresol, a model bio-oil compound, to understand relationships between metal structure and reactivity down to the limit of atomically dispersed active sites. Through a combination of kinetic studies, spectroscopic characterization, and density functional theory calculations, we find that isolated Pt cations supported on TiO_2 are significantly less active than small Pt clusters for m-cresol HDO due to their lower activity for hydrogen dissociation and their weaker interaction with m-cresol. We demonstrate that m-cresol HDO reaction kinetics are particularly sensitive to the active Pt structure, suggesting that catalytic reactivity can be a more reliable indicator of catalyst structure than commonly used characterization approaches. These findings provide insights into the ability of isolated Pt cations to catalyze elementary processes critical for hydrogenation catalysis.

Keywords: Atomically dispersed catalysts, single atom catalysis, m-cresol, hydrodeoxygenation, Pt

Introduction

Since the proposal that catalytic surfaces contain active sites with differing reactivity, there has been ongoing interest in understanding the link between the structure of these sites and their properties.¹ For instance, many studies have explored the relationship between the size of supported metal particles and their reactivity.²⁻⁶ Recently, there has been significant interest in extending these relationships to the limit of atomically dispersed late-transition metal cations.⁷⁻⁹ However, it has proven experimentally difficult to devise synthetic methods for producing exclusively atomically dispersed species with uniform structures and properties.¹⁰ Instead, many

synthetic methods produce a distribution of metal structures including atomically dispersed species with varying coordination to the oxide support, and small metal particles.¹⁰⁻¹¹
Furthermore, recent studies have demonstrated the difficulty in differentiating these atomic scale structures using common characterization techniques.¹²⁻¹³ These challenges preclude the understanding of the catalytic behavior of atomically dispersed metal cations and the relationships between their properties and those of extended metal surfaces.

While common characterization tools are often insensitive to subtle changes in molecular level structure of these materials, reaction kinetics are not. Therefore, it is possible that catalytic reactivity itself can be used as a probe of the structures present in a catalyst material. This is most practical for reactions in which the kinetics are known to be strongly dependent on active site structure. One such class of reactions is the hydrodeoxygenation (HDO) of biomass derived molecules. These reactions are used to remove excess oxygen content from biomass for potential use as fuels or fuel additives.¹⁴⁻¹⁵ Typically, these reactions require the ability of the catalyst to facilitate hydrogenation and dehydrogenation steps, as carbon-oxygen bond cleavage steps. This required multifunctionality could exist at metal-oxide catalyst interfaces, or over catalysts in which one site can enable both chemistries.¹⁶⁻²¹

In previous studies, we explored the mechanistic routes for HDO of cresol and related molecules on extended metal surfaces.²²⁻²⁶ We have shown that while oxophilic metals are able to catalyze HDO directly on the metal surface, the reactivity of noble metals, such as Pt and Pd, are promoted by the existence of exposed oxophilic cations on reducible oxide supports.²² On catalysts such as Pt and Pd on TiO₂ or ZrO₂ supports, HDO occurs at the metal-support interface with O in cresol binding to exposed Ti or Zr cations and the metal catalyzing H₂ activation and hydrogenation.²⁷ This reaction is therefore of particular interest to understand the ability of isolated metal catalyst resides at the metal-support interface, this reaction allows us to understand whether isolated Pt cations (Pt_{iso}) mimic the ability of perimeter sites on Pt nanoparticles supported on TiO₂, or whether the cationic nature of Pt_{iso} and lack of metal ensembles imparts fundamentally different reactivity.

Here, we evaluate the ability of Pt_{iso} species to catalyze HDO of m-cresol, a molecule representative of phenolic compounds in bio-oil and widely used as a model compound to understand the reactivity of families of biomass-derived species. We find that Pt_{iso} on TiO₂ is a poor catalyst for HDO of m-cresol compared to Pt clusters largely due to the unfavorable energetics of H₂ dissociation over Pt_{iso} species. Further, the strong coordination of the Pt_{iso} to oxygen atoms from the support imparts stability to the isolated metal cation under reductive environments but may reduce its propensity to bind cresol and activate carbon oxygen bonds. We also synthesize materials containing a mixture of Pt_{iso} and small Pt clusters to show that clusters dominate their catalytic behavior. Therefore, reactions themselves can be used as a sensitive probe of atomic scale active site structure. These findings demonstrate the limitations of isolated Pt cations in catalyzing hydrogenation reactions, and the relationships between their reactivity and their stabilizing coordination to the oxide support.

Results and discussion

Understanding the mechanism of HDO of m-cresol on Pt clusters

To begin to understand the relationship between atomic scale Pt structure and reactivity for HDO of m-cresol, we first demonstrate the influence of reaction temperature and support composition on m-cresol conversion over Pt clusters. Catalysts containing 1% weight (wt.) loading of Pt on TiO₂ and SiO₂ supports comprised of small Pt clusters (dispersion of 29 % and 49 % respectively, measured by CO pulse chemisorption) were synthesized by incipient wetness impregnation and used for comparison to catalysts containing Pt_{iso} species. While SiO₂ was chosen as an inert support where HDO is expected to occur solely over the metal surface,²⁴ TiO₂ was chosen as an active support where Ti cations at the metal-support interface can participate in the reaction.²⁸ Specific characteristics of these oxides are detailed in the methods section. The gas phase conversion of m-cresol was studied in a fixed bed reactor at atmospheric pressure, and care was taken to ensure all measurements were taken under strict kinetic control.²⁹ At low temperatures (<250 °C) over Pt clusters, ring hydrogenation occurs preferentially over deoxygenation (Fig 1a). In previous studies we showed that at these low temperatures, hydrogenation is thermodynamically favorable, while the barrier for cleavage of the C-O bond is prohibitively high to produce significant amounts of the deoxygenation product toluene (Fig 1a).^{24, 26} At high enough temperatures (>300 °C), kinetic barriers for deoxygenation can be overcome and toluene is produced with high selectivity. We will focus this study on the influence of Pt structure on HDO reactivity at 350 °C. However, comparisons of reactivity for ring hydrogenation at lower temperature are also discussed below.

Pt clusters (1 wt. %) on TiO₂ showed higher reactivity towards deoxygenation to toluene than Pt on SiO₂ (Fig 1b). This result was confirmed on lower weight loading materials (0.1 wt. %) as shown in Table S1. Previous studies have shown that this trend in activity is the result of active sites at the perimeter of Pt particles and the oxophilic TiO₂ support.^{17, 30} With this in mind, we were interested in understanding whether a catalyst composed of all Pt_{iso} species on TiO₂, in which every site interfaces with the support, would be equally active for this reaction, or whether Pt_{iso} species have different reactivity than perimeter sites on Pt clusters for this reaction.



Fig 1. Understanding HDO of m-cresol over Pt clusters. a) Yield to major products over 1 wt. % Pt/TiO₂ catalysts at low and high temperatures. Reaction conditions: W/F=0.05h; P=1atm H₂; TOS=20min. b) Comparison of toluene turnover frequency for Pt on different supports. Turnover frequency values (+/- 1min⁻¹) are based on number of surface sites counted by CO chemisorption. Reaction conditions: T=350°C; P=1atm H₂; TOS=20min; Conversion was maintained below 15% by adjusting W/F.

*Comparison of HDO activity of Pt*_{iso} and Pt clusters

To produce Pt_{iso} catalysts, synthesis was conducted via strong electrostatic adsorption.³¹ We have previously demonstrated that by using this synthetic technique and a support comprised of 5 nm diameter anatase TiO_2 nanocrystals at a weight loading of 0.025%, which correlates to nominally one Pt atom for every two TiO₂ particles, we can produce exclusively Pt_{iso} species.^{10, 32-33} Prior to analysis, the catalyst was calcined in air at 450 °C to remove remaining ligands from synthesis.³⁴ We then characterized the structure and local environment of Pt_{iso} species using CO probe molecule Fourier transform infrared (FTIR) spectroscopy following *in-situ* pretreatment of the catalyst in H₂ for 1 hour at 250 °C. No significant difference was observed in IR characteristics after pretreatment at 250 °C and 350 °C in H₂. After a saturating dose of CO at 25 °C and subsequent purging, a band centered at 2112 cm⁻¹ with a full-width at half maximum of 11 cm⁻¹ was observed (Fig 2a). During desorption of CO from the 0.025 % Pt/TiO₂ catalyst, the vibrational frequency did not change, indicating that Pt species were isolated and uniform in their local environment (Fig S1). This IR signature is consistent with our previous work on Pt_{iso} on TiO₂.^{10,} 32-33 Previously, through a combination of atomic resolution imaging, x-ray absorption spectroscopy, and density functional theory (DFT) calculations, we conclusively demonstrated that Pt_{iso} species under these conditions exist as PtO₂ structures bound to step or terrace sites on the anatase TiO₂ (101) surface.³²⁻³³ In contrast, after CO adsorption on the 1% Pt/TiO₂, a broad band centered at 2060 cm⁻¹ was observed, consistent with adsorption of CO on metallic Pt clusters.³² Having produced a uniform and well-defined Pt_{iso}/TiO₂ catalyst, as well as a comparative sample with only Pt clusters and a dispersion of 49% (which suggests a cluster size of ~ 2 nm), we then compared their performance for HDO of m-cresol.



Figure 2: Activity of isolated Pt cations and Pt clusters for HDO of m-cresol. a) CO probe molecule infrared spectroscopy of 0.025% and 1% Pt on TiO₂. The sharp band centered at 2112 cm⁻¹ is characteristic of isolated Pt cations. The broad band centered at 2060 cm⁻¹ is characteristic of Pt clusters. b) Comparison of TOF for toluene formation for 0.025% Pt and 1% Pt on TiO₂. Turnover frequency (+/-1 min⁻¹) for 1% Pt is based on number of surface sites counted by CO chemisorption; a dispersion of 100% is assumed for 0.025% Pt. Reaction conditions T=350°C; P=1atm H₂; TOS=20min. Conversion was maintained below 15% by adjusting W/F. c) CO probe molecule infrared spectroscopy of 0.025% Pt on TiO₂ before and after reaction testing. Identical spectra indicate isolated Pt cations are stable under reaction conditions.

As shown in Fig 2b, we find that the activity of Pt_{iso} for deoxygenation of m-cresol to produce toluene is ~40x lower on a per-site basis than it is over Pt clusters. Comparison of reactivity of 0.025% Pt/TiO₂ with TiO₂ supports not loaded with Pt demonstrates Pt_{iso} does have catalytic activity for HDO (Fig S2). To confirm that Pt_{iso} catalysts were stable under HDO reaction conditions, CO probe molecule IR was conducted before and after reactivity testing. After mild oxidation to remove carbonaceous deposits and reduction (300 °C in O₂ for 30 min, 250 °C in H₂ for 30 min), a nearly identical IR signature was observed, indicating that Pt_{iso} species are stable and that we can accurately assess their reactivity for HDO (Fig 2c). The stability of these Pt_{iso} species throughout pretreatment and reaction testing under reducing conditions contrasts with commonly reported behavior for atomically dispersed catalysts. We hypothesize that the unusual stability stems from the low Pt loading, which allows us to probe Pt cations that only occupy their most thermodynamically stable sites on the support.³⁵

To further demonstrate the sensitivity of HDO reactivity to Pt structure, a set of catalysts were synthesized using electrostatic adsorption with increasing weight loading to vary the ratio of Pt_{iso} species and Pt clusters. To ensure that samples included both Pt_{iso} species and Pt clusters, a higher Pt surface loading was used by choosing a lower surface area TiO_2 support (BET surface area 35-65 m²/g for the low surface area support, 290 m²/g for the high surface area support). This same low surface area support was used above for the 1% Pt/TiO₂ material. We have previously shown that at a fixed weight loading, a higher surface loading results in increased formation of Pt clusters.¹⁰ Examining the reactivity of lower surface area TiO₂ samples containing Pt loadings of 0.025-1 wt.% we see that the turnover frequency (TOF) for forming toluene increases with increasing Pt weight loading, until it saturates at ~0.3% Pt (Fig 3a). Further increases in weight loading up to 1.0% Pt resulted in minimal changes in per site activity. Furthermore, the TOF at a fixed weight loading of 0.025% Pt is ~5x higher in this case than for the sample containing exclusively Pt_{iso}.

To understand these trends in reactivity, we examined the structure of these different catalysts through CO probe molecule IR. For the 0.025% Pt sample deposited on the lower surface area support, we see a clear feature associated with Pt_{iso}, as before, with the band centered at 2112 cm⁻ ¹ and a tight FWHM of 12 cm⁻¹ indicating that these species coordinated to oxygen at uniform positions on the support. This further confirms that the local coordination for Pt_{iso} species are similar and uniform on the two TiO₂ supports with different surface areas. However, unlike the sample synthesized at lower Pt surface loading, here a weak, broad band centered at 2060 cm⁻¹ was also observed, indicating the presence of CO bound to metallic Pt clusters.³² As seen in Fig 3b, IR indicates the fraction of Pt existing in the form of clusters rather than Pt_{iso} increases with weight loading, as expected. To understand the relative contributions of these sites to measured activity, the IR and reactivity data were used together to extract estimates of relative extinction coefficients of CO bound to Ptiso and Pt clusters (Fig S3). This analysis allows conversion of IR intensities into estimates of the fractions of Pt atoms exposed as Pt_{iso} species or at the surface of Pt clusters (see methods for more details). Using this methodology, we find the extinction coefficient CO bound to Ptiso is ~5x larger than that of CO on metallic Pt clusters, consistent with previous measurements on isolated Rh cations and Rh clusters.³⁶ This implies that while Pt_{iso}. species have a small contribution to measured reactivity in samples containing a mixture of Pt structures, their contribution to measured CO IR spectra is much larger. Using this procedure, we predict that less than 10% of Pt existed in the form of Pt clusters for the 0.025% sample on the lower surface area TiO₂, however the TOF for toluene formation was $\sim 8x$ larger than the sample containing exclusively Pt_{iso}. Therefore, while Pt_{iso} species may have a larger contribution to signals observed in IR, the catalytic activity measured for this sample is dominated by the presence of the Pt clusters. Thus, reactivity for m-cresol HDO is a much more sensitive probe of the existence of Pt clusters in a given catalyst than CO IR analysis. However, IR is quite effective at identifying the presence of Pt_{iso} species. This analysis suggests that the activity trends observed with weight loading can be described by normalization of the activity to different fractions of active Pt cluster sites and minimally active Pt_{iso} sites. Rather than a higher weight loading catalyst possessing intrinsically higher activity sites, it simply contains a smaller fraction of inactive sites that reduce the calculated TOF. To more conclusively substantiate this point, temperature dependent reactivity measurements were

To more conclusively substantiate this point, temperature dependent reactivity measurements were taken to obtain apparent activation barriers. Comparing the samples synthesized at higher surface loading, which contain both Pt clusters and Pt_{iso} , very little change in barrier is observed with all catalysts showing a barrier of ~85 kJ/mol. This supports the idea that the same type of site, an interfacial site on a Pt cluster, is responsible for the observed activity of all of these Pt catalysts. In stark contrast, the barrier over the 0.025% Pt catalyst which contained exclusively Pt_{iso} species, showed a significantly higher apparent activation energy of 189 kJ/mol. Again, we note that the sample produced at a weight loading of 0.025% Pt on the lower surface area support, while showing only a weak feature for Pt clusters in IR, shows a barrier consistent with the behavior of Pt clusters, rather than Pt_{iso} .



Figure 3: Activity of catalysts containing both Pt_{iso} and Pt clusters for HDO of m-cresol. a) Turnover frequency values (+/- 1min⁻¹) for deoxygenation of m-cresol to toluene at 350 °C for samples of different weight loadings from 0.025-1.0 wt.%. Turnover frequency for higher Pt loadings is based on number of surface sites counted by CO chemisorption; a dispersion of 100% is assumed for lower weight loadings (<0.10% Pt). TOF of catalyst synthesized on higher surface area support containing exclusively Pt_{iso} shown for comparison. Reaction conditions T=350°C; P=1atm H₂; TOS=20min. Conversion was maintained below 15% by adjusting W/F. b) CO probe molecule infrared spectroscopy of the same catalysts. Data normalized to maximum peak intensity and offset for clarity. Dotted lines added to make weak features more easily visible. c) Arrhenius plots showing apparent activation barriers for the same catalysts. Reaction conditions: T=275-350 °C for catalysts containing Pt clusters; T=330-370 °C for the catalyst containing only Pt_{iso} ; P=1atm H₂; TOS=20 min. Conversion was maintained below 15% by adjusting W/F.

Understanding reactivity of Pt_{iso}

Having observed that Pt_{iso} species have low reactivity for HDO of m-cresol, we set out to understand why this is the case, and what fundamental differences exist between Pt_{iso} species and the perimeter site of a Pt cluster. We hypothesized that two limiting factors in the HDO of cresol could be responsible for the low Pt_{iso} reactivity: the difficulty of dissociating hydrogen over Pt_{iso} species, or the weak interaction between Pt_{iso} and cresol rendering it unable to effectively cleave the C-O bond.

To test the first possibility, we used cyclohexene hydrogenation as a probe reaction (Fig 4a).³⁷⁻³⁸ Comparing the 0.025% Pt catalysts composed of only Pt_{iso} with the catalysts containing both Pt_{iso} and Pt clusters, a significant difference in activity is observed. The catalyst composed of exclusively Pt_{iso} again shows significantly lower activity at a fixed temperature of 120 °C, and a temperature difference of 40°C (120°C vs 80°C) is needed to obtain similar cyclohexene conversion over both catalysts. This again suggests Pt_{iso} species have low activity for cyclohexene hydrogenation and the reactivity of the higher surface loading sample is dominated by Pt clusters. This is further supported by cyclohexene hydrogenation reactivity measured over a 1% Pt on TiO₂ sample, which quantitatively converts cyclohexene under the same conditions. This probe reaction indicates that hydrogen dissociation and alkene hydrogenation is not facile over Pt_{iso} . This is consistent with recent comparative studies of alkene hydrogenation over isolated Pt and Pd cations and small clusters.³⁹⁻⁴¹

Further insight into the hydrogenation activity of Pt_{iso} could be obtained by examining the trend in m-cresol conversion rates at a lower temperature of 220 °C, where HDO no longer occurs (Fig 4b). Turnover rates to hydrogenation products (methylcyclohexanone, methylcyclohexanol, and

methylcyclohexane) increased with Pt weight loading before saturating at the same loading that CO-IR showed Pt existed exclusively as Pt clusters. The catalyst material that IR indicated was composed of all Pt_{iso} had no measurable reactivity under these conditions. This further demonstrates that Pt_{iso} sites had no measurable activity for m-cresol conversion, and that turnover rates for all catalysts were dominated by the amount of Pt in the form of clusters. We previously showed a similar relationship between the relative fractions of isolated and clustered Rh species and the selectivity for CO₂ reduction.³⁶

Thermogravimetric analysis was performed of spent catalysts after HDO of m-cresol (T = 350 °C, TOS = 3.5 h) to understand differences in coke formation and their relation to hydrogenation activity. As shown in Fig S4, negligible coke formation was observed on the 1% Pt/TiO₂ sample containing a high density of Pt clusters. For the samples previously determined to contain a small fraction of Pt clusters (0.025% - 0.1% Pt) increasing amounts of coke were observed with decreasing Pt loading. At the lowest weight loading where Pt existed predominantly in the form of Pt_{iso}, similar amounts of coke were observed as a pure TiO₂ support indicating that the metal was unable to effectively clear coke from the oxide support. Similarly, significantly higher (~3x) amounts of coke were found on the sample containing exclusively Pt_{iso} species after reaction due to the higher surface area of this TiO₂ support (support surface area is 4-8x larger). These results taken together suggest that Pt clusters that are able to effectively dissociate hydrogen, allowing for spillover onto TiO₂ and hydrogenation of carbonaceous species on the oxide support, cleaning the surface from coking. Pt_{iso} species that are unable to effectively dissociate hydrogen are not able to clear the surface from coke.

DFT calculations were performed to examine the dissociative adsorption of H₂ over Pt_{iso} in order to corroborate these experimental measurements. To model the Pt_{iso} structure on TiO₂, we used a structure comprised of an adsorbed PtO_2 moiety at an anatase TiO_2 (101) terrace (Fig 5a). This structure was previously found to match experimental measurements for Pt_{iso} on TiO₂.³² To understand the effect of Pt local coordination, we also considered hydrogen dissociation on a Pt atom coordinated to two lattice-oxygen at a bridging position on the TiO_2 (101) surface (Fig 5b). We find that the dissociative adsorption of H_2 on the PtO₂ structure is highly exothermic (-282 kJ/mol). However, the most favorable adsorption sites are support oxygens adjacent to the Pt atom (forming a surface hydroxyl group). We expect that hydrogen atoms strongly bound to these support oxygens are not active for hydrogenation. In contrast, hydrogen adsorption on Pt atoms coordinated to two support oxygens is exothermic by only 20 kJ/mol using gas-phase H_2 as the reference (Fig 5a) indicating H_2 dissociation is not facile. The most favorable adsorption sites of two H atoms are found to be on the Pt atom and on the support oxygen adjacent to the Pt atom. Over a Pt (111) surface, the adsorption process has a higher exothermicity (-101 kJ/mol). H atoms dissociatively adsorb on the fcc sites of the Pt (111) surface (Fig 5c). Hydrogen dissociation barriers over the Pt (111) surface are known to be negligible, as contiguous metal sites provide favorable sites for dissociated hydrogen atoms to adsorb.⁴² Unlike a hydrogen atom bound to Pt, the surface hydroxyls formed after H₂ dissociation on Pt_{iso} is unreactive for hydrogenating unsaturated bonds. Interestingly, recent surface science studies for Pd atoms on Fe_3O_4 supports have experimentally shown a H₂ dissociation mechanism consistent with the picture our DFT calculations provide for H_2 dissociation over Pt_{iso} .⁴³ We note the contrast here between Pt_{iso} on an oxide support and isolated Pt atoms in a metal lattice studied for so called single atom alloys. The ability of these single atom alloys to dissociate hydrogen onto nearby metal sites allows them to be efficient catalysts for hydrogenation chemistry.^{42, 44} These experimental and computational

results together suggest that difficult dissociation of hydrogen is to a large extent responsible for the low activity of Pt_{iso} for HDO of cresol.

We also considered the possibility that HDO of m-cresol over Pt_{iso} could be hindered by the difficulty in performing C-O bond scission over these sites. In previous studies we have shown that the oxygen binding energy of the metal is an important descriptor for the barrier for the kinetically relevant C-O scission step in HDO.²³ Therefore, weaker interaction between Pt_{iso} and cresol could render it inactive for catalyzing this reaction step. We have previously shown that the binding energy of small adsorbates over stable Pt_{iso} sites is significantly lower than it is over extended Pt surfaces.^{10, 32} This can be intuitively described by a compromise between stability of a metal ion garnered from strong coordination to oxygens from the support, and a propensity of this ion to form additional bonds to adsorbates. Similar tradeoffs have been demonstrated for more extended metal particles on well-defined oxide supports through calorimetry studies.⁴⁵⁻⁴⁸ We expected therefore that weakened binding of cresol to Ptiso species would also result in an increased barrier for C-O bond scission, reducing activity for HDO. We expect that the binding energy of cresol through carbon should scale with the binding energy of CO, supporting weakened binding relative to an extended metal surface.⁴⁹ Furthermore, adsorption of cresol and phenolics is known to be enhanced by π interactions between the aromatic ring and metal terraces, which would not be possible over an isolated metal atom.⁵⁰ To substantiate this further, DFT calculations of cresol adsorption were done over the two Ptiso structures (Fig S5). Adsorption energies of -206 and -104 kJ/mol were found over the PtO₂ structure and the Pt_{iso} coordinating to two support oxygen ligands, respectively. We find the adsorption of cresol over Pt (111) to be exothermic with an adsorption energy of -229 kJ/mol. We note, however, that cresol adsorbed at the metal-support interface is likely the more kinetically relevant species than cresol adsorbed to Pt terraces, and that the presence of coadsorbates could influence binding energies. Thus, the relevant adsorption energy over Pt clusters is likely intermediate between that of Pt_{iso} and Pt (111).⁵¹ Taken together, these results show that the lower reactivity of Ptiso for HDO of m-cresol is mainly related to the difficulty in dissociating hydrogen over an isolated metal cation, while weak interactions between Pt_{iso} and cresol could potentially contribute to reactivity to a lesser extent.



Figure 4: Understanding activity of isolated Pt cations a) Activity of samples containing Pt_{iso} and Pt clusters for a probe hydrogenation reaction (cyclohexene hydrogenation). Reaction conditions: P=1 atm H_2 ; W/F=0.007h; TOS=3min. (b) Turnover frequency (+/- 0.1 min⁻¹) for ring hydrogenation of m-cresol to hydrogenation products (methylcyclohexanone, methylcyclohexanol, methylcyclohexane) at 250 °C for samples of different weight loadings from 0.025-1.0 wt.%. Reaction conditions: T=220 °C; P=1atm H₂; W/F=0.652h, TOS=20min. Note that the sample containing exclusively Pt_{iso} had no measurable activity under these conditions.



Figure 5: Adsorption of hydrogen on Pt structures. DFT optimized adsorbed structures with calculated heats of adsorption for (a,b) dissociative adsorption of H₂ over Pt_{iso} and (c) Pt (111). Pt_{iso} in (a) is modeled by a PtO₂ structure described previously.³² Pt_{iso} in (b) is modeled by a Pt atom coordinating to two oxygen ligands from the support on the anatase (101) surface. The balls refer to the atoms of H (white), O (red), C (grey), Pt (blue) and Ti (green), respectively.

Conclusions

In this study, we sought to understand the influence of Pt structure (down to the limit of single Pt cations) on reactivity for the upgrading of bio-oil derived molecules, specifically the HDO of mcresol. In doing so, we showed that the catalytic reactivity of different types of Pt species is extremely sensitive to their structure. Combining these results with our previous work showing the difficulty in accurately differentiating sub-nanometer Pt species from Pt_{iso} species, we argue that often catalytic reactivity is the most accurate probe of atomic scale structure.^{12, 36} We find that Pt_{iso} species show low HDO activity (~40x lower TOF to toluene than Pt clusters) due to their inability to effectively dissociate hydrogen and hydrogenate unsaturated bonds. We further synthesized materials in which Pt_{iso} and Pt clusters coexist and show that while Pt_{iso} species can have a large contribution to spectroscopic measurements, the catalytic activity is dominated by the clusters. This suggests that the sites most easily visible using characterization tools are not always those that most significantly govern measured catalytic properties.

These reactivity studies give some general insights about the propensity of isolated metal cations (particularly Pt) for catalyzing specific reaction steps. Results are beginning to emerge that show isolated cations in their thermodynamically most stable site on oxides often coordinate strongly to supports, but weakly to adsorbates in comparison to metal clusters. This suggests that their inherent ability to break bonds may be less than clusters, but also may be highly tunable based on modifying their adsorption site on the support or the support composition. Therefore, it can be concluded that

atomically dispersed catalysts, while not a panacea for catalysis, may provide well-defined and tunable catalytic sites for some reaction chemistries.

Methods:

Materials

The following materials were purchased from Sigma-Aldrich: Tetraammineplatinum nitrate (99.995%) (TAPN) with SKU no. 482293, SiO₂ (99.8%) with SKU no. 381276, reagent grade NH₄OH (> 25%) with SKU no. 17093, m-Cresol (99%) with SKU no. C85727, cyclohexene (\geq 99.0%) with SKU no. of 29240. Cyclohexene was purified by distillation before use.

For TiO₂ supported catalysts, two different materials were used as supports. To promote the formation of Pt clusters, lower surface area TiO₂ (99.5%) was purchased from Sigma-Aldrich with SKU no. 718467. To promote formation of exclusively atomically dispersed Pt species, a higher surface area TiO₂ composed of 5 nm anatase crystals was purchased from US Research Nanomaterials (Stock no. US3838). The quoted surface areas of the two supports were 35-65 m²/g and 290 m²/g, respectively.

Catalyst preparation

1 wt.% Pt/TiO₂ and 1 wt.% Pt/SiO₂ catalysts were prepared by an incipient wetness impregnation method. In a typical synthesis, 60.15 mg TAPN was dissolved in H₂O (4 ml for TiO₂, 10 ml for SiO₂), and dropwise added to 3 g pre-dried TiO₂ or SiO₂ support. After impregnation, the catalysts were dried at room temperature overnight.

Lower weight loading catalysts (0.025-0.5 wt.%) were prepared by strong electrostatic adsorption. For the synthesis of 0.025 wt.%Pt/TiO₂, 10 mg TAPN was dissolved in 5 ml H₂O, from which 1.5 ml was taken and mixed with 8.5 ml NH₄OH to prepare the precursor solution. 3 g TiO₂ support powder was dried in a vacuum oven at 120 °C for 12 h, and then dissolved to a mixture solution of 200 ml NH₄OH and 50 ml H₂O. The TAPN precursor solution was injected by a syringe pump at a rate of 0.5 ml/h to the support solution under constantly stirring. The final solution was heated to 70 °C until completely dried. The synthesis of Pt/TiO₂ catalysts with different Pt loading catalysts (0.05-0.5 wt.%) follows the same procedure as above, but with different concentration of precursor solutions.

All dried catalysts were placed in a vacuum oven at 120 °C for 12 h, and further calcined at 450 °C for 4 h in flowing air, at a ramping rate of 2 °C/min. Before reactivity testing, the catalyst powders were pressed, crushed, and sieved to 40-60 mesh.

Catalytic activity

Catalytic conversion of m-cresol or cyclohexene was carried out in a fixed-bed stainless-steel tube (6 mm o.d.) reactor at atmospheric pressure. The catalyst was pelletized between 40 and 60 mesh, mixed with inert silica beans as a diluent (40-60 mesh, 100 mg), and packed between two layers of quartz wool on top of a thermocouple placed inside the reactor tube. The catalyst sample was reduced in flowing H₂ at 350 °C for 1 h after heating at a rate of 10 °C/min. After reduction, the reaction was conducted at 80-370 °C depending on the measurement of interest. The m-cresol or cyclohexene was fed using a syringe pump (kd scientific) and vaporized (180 °C for m-cresol, 60 °C for cyclohexene) before entering the reactor. The reactor gas lines were heated at 250 °C to avoid any condensation. The products were analyzed and quantified online by a gas chromatograph (HP 5890), equipped with an HP-Innowax column (30 m × 0.5 mm ID × 0.25 µm) and a flame ionization detector. The effluent was trapped by methanol in an ice-water

bath and its components were identified by a gas chromatography-mass spectrometer (Shimadzu QP2010s). Fresh catalyst was used for each reactivity measurement at each space time (W/F, $g_{cat}g_{reactant}$ ¹h). The conversion and yield are reported in mol_{carbon}%.

Chemisorption Measurements

CO pulse chemisorption dispersion measurements were performed using a Micromeritics Autochem II 2920 gas analyzer. In a typical measurement, approximately 500 mg of calcined catalyst was loaded into a U-shaped sample tube and reduced at 623 K for 1 h in 10% H₂/Ar (Airgas). The catalyst was then flushed with He (99.999%, Airgas) while ramping to 798 K, and held at that temperature for 30 min. After the sample cooled to ambient conditions, pulse chemisorption measurements were performed with 10% CO/He (Airgas), while monitoring the effluent with a thermal conductivity detector. The total flow rate for each experiment was 50 sccm. Dispersion was calculated assuming hemispherical clusters and a Pt:CO ratio of 1:1. The volume of active gas adsorbed on the surface of each catalyst per gram of material was used in calculation of turnover frequencies (TOFs). Dispersions of 81, 64, and 49% were measured for 0.3, 0.5, and 1.0 wt. % Pt/TiO₂ respectively. A dispersion of 29% was measured for Pt/SiO₂. Dispersions of 100% were assumed for lower weight loadings (0.025-0.1%) due to the observation of significant amounts of Pt_{iso} species and the weak adsorption of CO at room temperature over Pt_{iso} sites on TiO₂.

Thermogravimetric Analysis of spent catalysts

Coke formation on spent catalysts were analyzed by Thermo Gravimetric Analysis (TGA). To compare coke formation, the catalysts were subjected to HDO reactivity testing at identical reaction conditions (Catalyst mass: 100 mg, T = 350 °C, m-Cresol = 0.1 ml/h, TOS = 3.5 h, H₂ = 58 ml/min). After reaction, the catalyst was cooled to room temperature in flowing H₂.

TGA analysis was carried out using a TGA Q500 instrument in flowing air. Approximately 30 mg of spent catalyst was loaded into the instrument. The temperature was initially rapidly increased to 150 °C and kept isothermal for 15 min. After this period the temperature was increased from 150 °C to 850 °C at a heating rate of 10 °C/min.

Infrared spectroscopy

FTIR experiments were carried out in a diffuse reflectance reaction chamber (Harrick Scientific) equipped with ZnSe windows, mounted inside a Praying Mantis diffuse reflectance adapter (Harrick Scientific), and coupled to a Thermo Scientific Nicolet iS10 FTIR spectrometer with a liquid-nitrogencooled HgCdTe (MCT-A) detector. During measurements, the FTIR and Praying Mantis diffuse reflection accessory were purged with dry N₂. In a typical experiment, the reactor was loaded with ~80 mg of pure Al_2O_3 support, followed by 25 mg of calcined catalyst packed on top of the inert support. The catalyst was pretreated in-situ in 50 sccm of a 10% H₂/Ar or 100% O₂ at various pretreatment temperatures for 1 hour prior to analysis. All feed gases were passed through a desiccant and liquid nitrogen cold trap to remove any humidity prior to the reaction chamber. Upon completion of the pretreatment, the catalyst was cooled to room temperature. All FTIR spectra were collected in difference mode. A background spectrum was then collected before introducing a flow of 10% CO in Ar for 10 minutes. CO was subsequently purged out by Ar flow.

Site fraction quantification

To estimate the relative fractions of Pt_{iso} and Pt clusters in samples containing a distribution of both species, infrared measurements were correlated to experimental reactivity data. For each material, the area of the infrared feature associated with CO adsorbed to Pt_{iso} or Pt clusters was integrated numerically. The

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site fraction can be obtained by weighting of the integrated area with the extinction coefficient for the site:

$$X_{i} = \frac{A_{i}/(\varepsilon_{i} \times N_{i})}{\sum_{i=1}^{n} [A_{i}/(\varepsilon_{i} \times N_{i})]}$$

where X_i is the fraction of total adsorbed molecules bound to each type of site; A_i is the absorption peak area associated with each type of site; ε_i is the relative extinction coefficient for each type of site; and N_i is number of metal atoms coordinated to the adsorbate, for n different types of sites. In this case we consider two types of sites (Pt_{iso} and Pt clusters) and the CO:Pt stoichiometry is taken as 1:1. The expected turnover frequency can then be obtained from a linear combination of the TOF of a material containing exclusively Pt_{iso} and one containing exclusively Pt clusters:

$$TOF_{calc} = X_{iso}TOF_{iso} + X_{cluster}TOF_{cluster}$$

As the extinction coefficient of Pt_{iso} is not known, this methodology was employed to obtain relative extinction coefficients by allowing them to vary such that the error between calculated and experimental turnover frequencies were minimized. This procedure was applied to reactivity data obtained at both 220 °C and 350 °C to obtain consistent extinction coefficients. TOF_{iso} values were obtained from data on 0.025% Pt samples on high surface area TiO₂ supports while $TOF_{cluster}$ values were obtained from 0.3% Pt samples.

Density Functional Theory Calculations

All first-principles calculations were performed with the Vienna Ab initio Simulation Package $(VASP^{52})$ with the projector-augmented wave method.⁵³ The electronic exchange-correlation energy was described using the Perdew-Burke-Ernzerhof (PBE) functional generalized gradient approximation.⁵⁴ Considering the self-interaction problem in the standard DFT formulation, the DFT + U method was used by introducing a Hubbard U correction with a value of 3 eV acting on 3d electrons of Ti.⁵⁵ The van der Waals interaction was included through Grimme's DFT-D3 semi-empirical method.⁵⁶ A kinetic cutoff energy of 400 eV was used in all the calculations. The energy and force convergence criteria were set to 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. A vacuum region of at least 15 Å was placed to eliminate interactions between the top and bottom of the slab model.

To model the Pt_{iso} structure on TiO_2 , we used a structural model comprised of an adsorbed Pt atom coordinated to two lattice-oxygen at a bridging position on the TiO_2 (101) surface. We included five TiO_2 (101) atomic layers with all the atoms being fully relaxed. In comparison, to model the Pt clusters, Pt (111) was chosen to represent the energetically most stable facet. The close-packed Pt (111) slab was modeled with a (4 × 4) supercell composed of four atomic layers. The bottom two layers were fixed to reflect the bulk, while the top two layers and molecules were allowed to relax. We used the Gamma point and a (3 × 3 × 1) k-mesh for calculations of the Pt_{iso} structure and the Pt(111) surface, respectively. The heats of dissociative adsorption of H₂ and adsorption of m-cresol were calculated according to the following equations:

 $\Delta E_{diss}(H_2) = E(2H^*/Pt\text{-slab}) - [E(Pt\text{-slab}) + E(H_2)]$ $\Delta E(m\text{-cresol}^*) = E(m\text{-cresol}^*/Pt\text{-slab}) - [E(Pt\text{-slab}) + E(m\text{-cresol})]$

Supporting Information

CO IR spectroscopy of Pt_{iso} during CO desorption, comparison of activity for Pt/TiO_2 catalysts and pure TiO_2 supports, extinction coefficient analysis, thermogravimetric analysis, DFT calculations for m-cresol adsorption on Pt clusters and Pt_{iso} .

Acknowledgements

PC acknowledges funding from the National Science Foundation (NSF) CAREER grant number CBET-1554112 and UCSB. DER and BW acknowledge support from the US Department of Energy, Office of Science BES grant number DE-SC0018284. FY is thankful for the support of the China Scholarship Council in the funding the exchange program to study at the University of Oklahoma.

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