

Atomically Dispersed Pt-group Catalysts: Reactivity, Uniformity, Structural Evolution, and Paths to Increased Functionality

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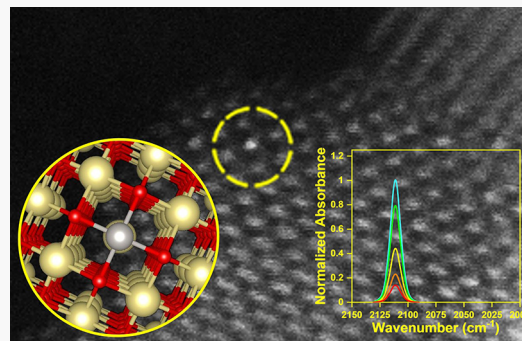
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ABSTRACT: The development of experimental and computational tools that give accurate and visual active site descriptions has renewed research interest in atomically dispersed metal catalysts. In this perspective, we describe our approach to synthesizing and understanding atomically dispersed Pt-group metals on oxide supports. Using site-specific characterization, we show that these metal species have distinct reactivity from metal clusters. We argue that producing materials where all metal sites have identical local coordination is key to both accurately assessing catalytic properties and achieving single-site behavior. Methods for assessing site uniformity are considered. We show that producing uniform metal species allows us to describe their structure at the atomic scale and understand how this structure evolves under different conditions. Finally, we suggest pathways to increased functionality for atomically dispersed catalysts, through control of their local coordination and steric environment and through cooperativity with different sites.



Over the past decade, interest in atomically dispersed Pt-group metal catalysts has grown tremendously. The term “single atom catalysts” has been widely adopted.¹ But studies on these materials date back much farther. Forty years ago, J. T. Yates recounted work published by his Ph.D. advisor in 1957: “For Al_2O_3 supported Rh, Yang and Garland first postulated that at low Rh concentrations, where sintering did not occur at reduction temperatures below 200 °C, Rh existed in a condition closely approaching *atomic* dispersion (i.e., isolated Rh atoms).”^{2,3} Hence, it is worth considering what has motivated the recent dramatic rise in interest in this area. The development of advanced structural characterization tools and quantum chemical calculations that enable accurate active site descriptions has played a major role. In particular, aberration-corrected scanning transmission electron microscopy (AC-STEM), which allows direct observation of atomically dispersed metal species, has been transformational.⁴ This renewed interest also stems from new demands for atom efficient and environmentally friendly chemical conversion processes.^{5–8} In this sense, atomically dispersed Pt-group metal catalysts provide perfect precious metal utilization and the potential to approach the catalytic specificity found in homogeneous organometallic catalysts and enzymes.

The catalytic specificity of organometallic complexes is enabled by their uniform and tunable local coordination environments. To achieve similar properties with supported atomically dispersed Pt-group metals, questions regarding active site uniformity and tunability of local coordination must be addressed. In the heterogeneous catalysis literature a

“single-site heterogeneous catalyst” implies a sample across which all sites look and act the same, analogous with the behavior of organometallic complexes.⁹ The idea of single-site behavior in heterogeneous catalysis is again one that has interested researchers for some time, with W. O. Haag concluding 25 years ago “The possibility to synthesize zeolite catalysts with a well-defined pre-determined number of active sites of uniform activity is certainly without parallel in heterogeneous catalysis”.^{10,11} Metal clusters and particles on oxide supports do not contain uniform active sites, as their terminations present metal sites with varying coordination numbers and their structures are fluxional under relevant conditions.^{12–14} In this Perspective, we argue that atomically dispersed Pt-group metals catalysts on oxide supports are in some cases approaching the active site uniformity implied in the definition of single-site catalysts. However, significant challenges remain before the catalytic specificity of these materials begins to rival that of organometallic complexes.

This Perspective starts by providing reactivity results that demonstrate atomically dispersed Pt-group metal catalysts exhibit reaction selectivity and kinetic behavior that is distinct

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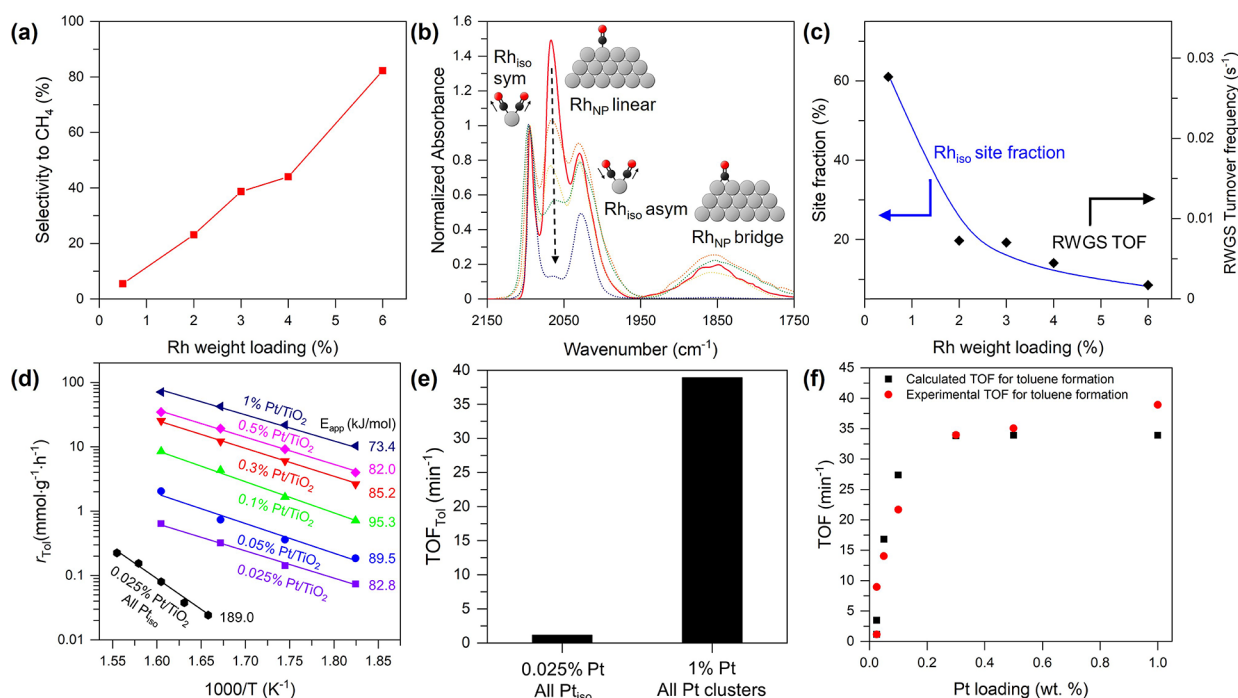


Figure 1. Quantifying site distributions to understand the reactivity of atomically dispersed species. (a) Selectivity of CO₂ reduction to CH₄ over Rh/TiO₂ catalysts as a function of metal loading. Measured at 200 °C in a 10:1 CO₂:H₂ feed ratio. (b) Infrared spectra of CO adsorbed at 25 °C on Rh/TiO₂ catalysts. Insets illustrate assignments of vibrational modes. 6% Rh/TiO₂ is shown as a solid trace; other weight loadings are shown as dotted lines. The arrow denotes decreasing Rh loading from 6 to 0.5%. (c) Correlation between Rh_{iso} site fraction quantified by CO IR and reverse water gas shift (RWGS) turnover frequency plotted as a function of wt % Rh. TOFs were measured at 200 °C at a 10:1 CO₂:H₂ feed ratio. (d) Arrhenius plots showing apparent activation barriers for HDO of *m*-cresol to toluene over Pt/TiO₂ catalysts. $T = 275\text{--}350$ °C for catalysts containing Pt_{NP}; $T = 330\text{--}370$ °C for the catalyst containing only Pt_{iso}; $P = 1$ atm H₂; Pt/TiO₂ catalysts containing any observable quantity of Pt_{NP} show similar barriers. (e) Turnover frequencies for HDO of *m*-cresol for Pt_{iso} and Pt_{NP}. Measured at 350 °C in 1 atm H₂. (f) Experimental and calculated TOF for HDO of *m*-cresol over Pt/TiO₂ catalysts at 350 °C. Calculated values obtained from a linear combination of TOF values for Pt_{iso} and Pt_{NP}, weighted by the relative site fractions of each. Reproduced with permission from refs 21 and 22. Copyrights 2015 and 2020 American Chemical Society.

from metal clusters. This difference in reactivity motivates the development of rigorous relationships between metal structure and function. We discuss the concept of active site uniformity, particularly the requirements to achieve it and how it can be assessed. Next, the structural evolution of active sites under varied environmental conditions is highlighted, with a focus on how *in situ* spectroscopy and microscopy combined with theoretical calculations provide important insights into oxide support dependent trends. Finally, we end with an outlook on pathways to increased complexity and functionality in atomically dispersed Pt-group metal active sites. We propose that modification of the binding site alone provides insufficient control over reactivity; the surrounding environment and its participation in catalysis is key.

Distinct Reactivity of Atomically Dispersed Metals. Early work revealed that precious metals dispersed as isolated atoms (or ions) had distinct reactivity from metal clusters for alkane hydrogenolysis, cyclotrimerization, water gas shift, and CO oxidation.^{15–18} Subsequently, extensive work was done to develop synthetic methods for producing atomically dispersed metals.¹⁹ In most studies, the existence of atomically dispersed species was evidenced via spectroscopic measurements or confirmed with AC-STEM. However, the most active catalytic sites are not always the most prevalent, leaving open the question of whether a subpopulation of metal clusters or oxidized metal clusters could be the active site.²⁰

To substantiate the distinct catalytic properties of atomically dispersed Pt-group metal species on oxide supports, we applied site-specific probe molecule vibrational spectroscopy. This approach allowed us to quantify relative fractions of exposed sites in materials with varying distributions of atomically dispersed species and metal clusters.^{21–23} Relating site fractions to measured turnover frequencies (TOF) for product formation allowed us to define self-consistent TOFs for each type of active site and provide rigorous structure–function relationships demonstrating the distinct catalytic properties of atomically dispersed Pt-group metals.

Panels a–c of Figure 1 show an example of Rh dispersed on TiO₂ for catalyzing the reduction of CO₂ by H₂.²¹ Figure 1a shows that selectivity to CH₄, with CO production via the reverse water gas shift (RWGS) reaction as the alternative pathway, increased with increasing Rh weight loading on TiO₂. This observation is consistent with previous studies on Ru/Al₂O₃ catalysts.²⁴ Using CO probe molecule IR spectroscopy, atomically dispersed Rh (Rh_{iso}) and metallic Rh cluster (Rh_{NP}) adsorption sites are distinguishable, as seen in Figure 1b. Rh_{iso} interacting with CO forms a *gem*-dicarbonyl structure, Rh(CO)₂, with symmetric and asymmetric stretching modes appearing at 2097 and 2028 cm⁻¹, respectively, although these band positions depend on support composition.^{2,3} CO adsorbed to Rh_{NP} show bands at ~2070 and 1860 cm⁻¹, associated with CO adsorbed in linear and bridge bound geometries, respectively.^{2,3} From the spectra in Figure 1b it is

clear that the fraction of exposed Rh sites existing as Rh_{iso} and Rh_{NP} varied with Rh weight loading on TiO_2 . Known extinction coefficients for these various CO stretches, and an assumption that all Rh sites accessible for catalysis are probed by CO, allowed for quantitative determination of the relative fraction of Rh sites existing as Rh_{iso} or Rh_{NP} in a catalyst.²⁵ Using this approach, CO_2 methanation TOF was observed to quantitatively correlate with the fraction of Rh_{NP} sites, while RWGS TOF correlated to the fraction of Rh_{iso} species, Figure 1c. This provided a clear demonstration that Rh_{iso} has distinct selectivity for this reaction and allowed the assignment of site-specific TOFs that were consistent across samples with varying distributions of sites.²¹

Using CO probe molecule IR spectroscopy to understand metal site partitioning allowed us to determine the unique catalytic properties of atomically dispersed species for several other reactions. For the hydrodeoxygenation of *m*-cresol, a phenolic representative of bio-oil compounds, atomically dispersed Pt (Pt_{iso}) and Pt clusters (Pt_{NP}) on TiO_2 showed distinct kinetic behavior.²² As seen in Figure 1d, the E_{app} for toluene formation was ~ 190 kJ/mol for a catalyst that exclusively showed features associated with Pt_{iso} in CO probe molecule IR characterization (band at ~ 2112 cm^{-1} , see below). By contrast, the E_{app} was ~ 85 kJ/mol for a catalyst that exclusively showed features associated with Pt_{NP} (band at ~ 2060 cm^{-1} , see below). At 350 °C, the Pt_{NP} catalyst showed 40× higher TOF for toluene formation than the Pt_{iso} catalyst did (Figure 1e).

The relative fractions of Pt_{iso} and Pt_{NP} varied with Pt weight loading on TiO_2 , as evidenced by changes in relative CO band intensities in IR.²² Assuming the values in Figure 1e provided independent TOFs for Pt_{iso} and Pt_{NP} , we developed a model that related the TOF for a given catalyst to the fraction of Pt_{iso} and Pt_{NP} multiplied by their site-specific TOFs. The fraction of each type of site was described by the corresponding CO IR stretching band intensity multiplied by its relative extinction coefficient. This analysis resulted in self-consistent estimates of the relative extinction coefficients for the two CO stretches and a predictive model for catalytic behavior, Figure 1f.

An important result of this analysis is that for samples containing $\sim 10\%$ of exposed Pt sites as Pt_{NP} and 90% as Pt_{iso} , the E_{app} was dominated by the behavior of Pt_{NP} (see the purple data in Figure 1d). This demonstrates how critical quantitative site distribution analysis is for assigning the reactivity of atomically dispersed Pt-group metal species. A similar analysis was recently reported for CO oxidation on supported Ir catalysts.²⁶

In analogous studies of Rh catalysts, we consistently observed distinct reactivity of Rh_{iso} species and Rh_{NP} . We found that Rh_{iso} species paired with support acid sites enabled selective methanol carbonylation to acetic acid under halide-free conditions, while Rh clusters catalyzed methanol decomposition to CO and CO_2 .²⁷ In the reduction of NO by CO under the wet environments prevalent in catalytic converters, we showed that Rh_{iso} species on Al_2O_3 and CeO_2 catalyze NH_3 formation with $\sim 100\%$ selectivity at low temperature.²³ By contrast, Rh_{NP} exhibited lower reactivity and were selective for N_2 production, suggesting that Rh_{iso} species may be responsible for low temperature NH_3 production in three-way catalysts.

These studies, using site-specific characterization to quantify active site distributions, substantiate the notion that atomically dispersed Pt-group metal species have distinctive, albeit not

always enhanced, reactivity compared with metal clusters. Results such as those shown in Figure 1f highlight the necessity of such an approach for accurately defining the reactivity of atomically dispersed Pt-group metal species. In samples containing mostly atomically dispersed species, a small subpopulation of metal clusters dominated observed kinetic behavior.

Thus far, we have considered all atomically dispersed metal species as a single active site type. Given the heterogeneity of the oxide support that coordinates these species, it is next worth considering whether all atomically dispersed Pt-group metal sites are structurally and chemically identical (i.e., single-site species).

Uniformity of Atomically Dispersed Metals. For atomically dispersed metals to approach single-site behavior, uniformity in active site structure across the support is key.²⁸ Consistent local coordination leads to identical adsorption and catalytic performance for each site and straightforward relationships between structure and properties. Producing uniform atomically dispersed Pt-group metal catalysts depends on the availability of regular and stable anchoring sites on the support. Ordered crystalline zeolites provide such anchoring sites and in the simplest cases provide singular adsorption sites. Consequently, a large body of work exists on producing atomically dispersed metals in zeolites with uniformity comparable to homogeneous metal complexes.²⁹ Similar active site uniformity has also been observed for atomically dispersed metal on single crystal oxide model systems.³⁰ Anchoring sites on conventional high surface area oxide supports are more heterogeneous.³¹ In the limit of amorphous oxides, such as SiO_2 , a near continuum of local coordination environments exists.³²

We were interested in developing approaches to synthesize atomically dispersed Pt-group metal species on conventional oxide supports (e.g., TiO_2 , CeO_2) with uniformity approaching that of zeolite supports and single crystal oxides.^{33–38} We began with the idea that at low metal loadings, the highest energy sites on the support would be selectively titrated, producing the thermodynamically most stable and thus uniform atomically dispersed species. To promote spatial separation of atomically dispersed species, electrostatic adsorption was used for metal deposition onto small particle size (~ 5 nm diameter) supports.³³ Before presenting results for atomically dispersed Pt on TiO_2 as an illustrative example, we first consider how uniformity can be assessed.

X-ray absorption spectroscopy (XAS) provides information on the chemical state and local coordination of a metal, but this information reflects the average of every atom of that metal in the material. Thus, uniformity cannot be addressed directly, and the value of structural fits for materials known from other techniques to have a distribution of structures is questionable. AC-STEM can probe individual metal atoms to understand their structure and chemical state. However, obtaining this level of detail is difficult and offers a statistically limited representation.³⁹

Chemical probes are a powerful tool to assess structural uniformity. For example, examining the IR spectra of probe molecules like CO or NO adsorbed to metal species can yield useful insights.^{40,41} This technique gives both statistically complete and site specific information. It can also assess adsorption site uniformity and communication between adsorption sites. Other techniques that probe the site-specific nature of adsorbed species, such as nuclear magnetic resonance

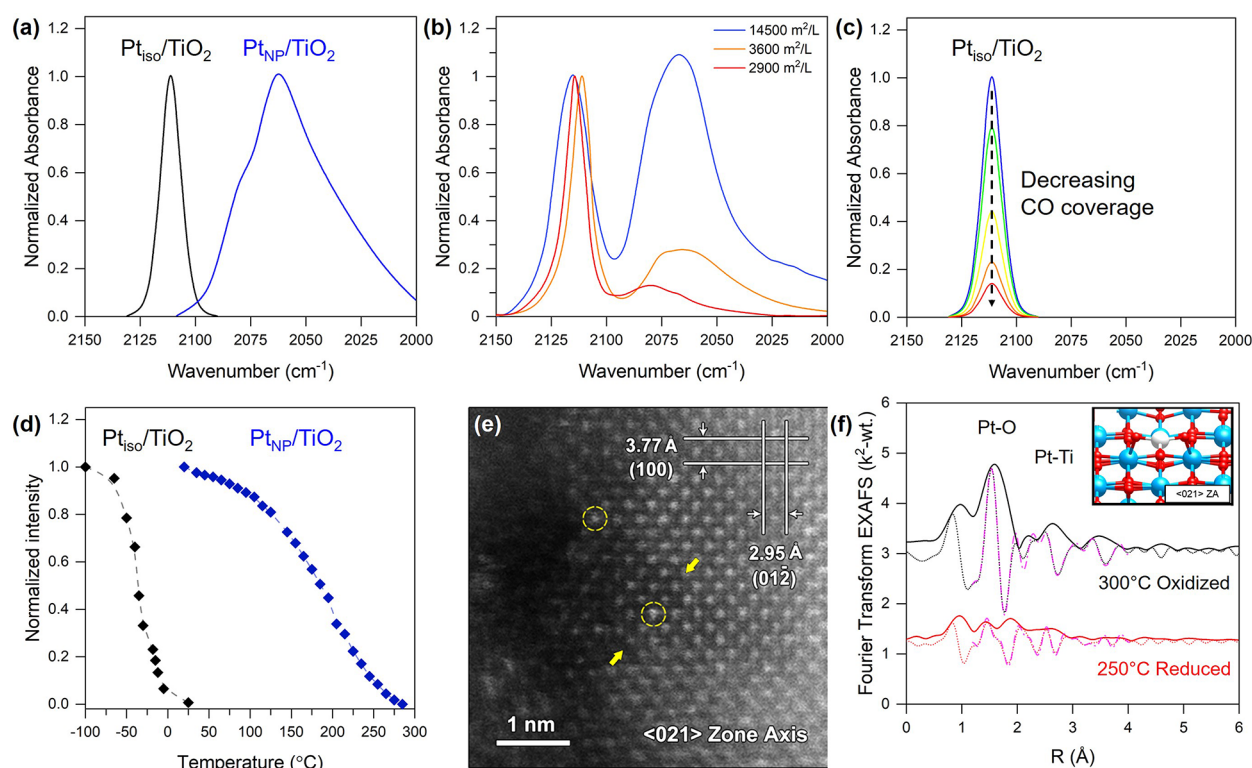


Figure 2. Assessing the uniformity of atomically dispersed Pt on TiO₂. (a) FTIR of CO adsorbed at 25 °C on Pt on TiO₂ prepared by electrostatic adsorption at 0.025 wt % and dry impregnation at 1 wt %. Catalysts were pretreated at 250 °C in H₂ for 1 h. (b) CO IR showing the effect of surface loading during synthesis on Pt structures formed on TiO₂. Catalysts were prepared by electrostatic adsorption at a weight loading of 0.05% Pt and pretreated at 250 °C in H₂ for 1 h. (c) CO IR for 0.025% Pt/TiO₂ during a TPD experiment. (a)–(c) are presented in normalized absorbance for comparison. (d) Integrated intensity of CO stretches bound to catalysts shown in (a) as a function of temperature in a TPD experiment at a ramp rate of 10 °C/min. (e) Aberration-corrected high angle annular dark field STEM imaging of Pt on TiO₂ imaged along the <021> zone axis. Isolated Pt atoms are identified with dotted yellow circles. (f) Fourier-transform magnitude EXAFS spectrum of 0.025% Pt/TiO₂ pretreated at 250 °C in H₂ for 1 h. The spectrum for the same catalyst pretreated in O₂ at 300 °C in O₂ for 1 h is shown for comparison. Approximate regions for Pt–O and Pt–Ti scattering are indicated. Dotted lines show the imaginary portion of spectra, fits are shown in magenta (fitting window of 1.2–4.0 Å). The inset shows the DFT calculated structure for reduced catalyst consistent with IR, STEM, and EXAFS characterization. Reproduced with permission for refs 22, 33, and 35. Copyrights 2020 and 2017 American Chemical Society and 2019 Springer Nature.

spectroscopy, also provide an assessment of adsorption site uniformity.⁴²

It has been proposed that the full width at half-maximum (fwhm) of adsorbed CO stretching bands on atomically dispersed metal sites can be used to assess the uniformity of the metal coordination environment.⁴³ Several factors contribute to the fwhm of adsorbed CO stretching modes.⁴⁴ Homogeneous broadening as a result of the finite lifetime of vibrationally excited species is given by $\Delta\nu = T/2\pi c$, where $\Delta\nu$ is the fwhm in cm⁻¹, c is the speed of light, and T is the lifetime of vibrationally excited CO. For CO on Pt (111), this lifetime is about a picosecond, giving a line width estimate of ~ 4 cm⁻¹, reasonably consistent with observations for homogeneous metal carbonyls.⁴³

For atomically dispersed species, vicinal support OH groups may influence the bound CO vibrational frequency, ν_{CO} . Localization of the atomically dispersed metal on terrace, step, or kink oxide support sites may also cause variations in ν_{CO} . DFT calculations considering Rh_{iso} and Pt_{iso} on anatase TiO₂ examined these effects.^{34,35,38} Vicinal OH species and adsorption site variation (step vs terrace) introduced 2–14 cm⁻¹ shifts in the calculated ν_{CO} for otherwise identical species (same metal oxidation state and coordination number to support oxygen). This change in ν_{CO} could be more significant

for supports such as Al₂O₃, which have a broad range of OH characteristics.⁴⁵ Thus, broad bands for adsorbed CO are likely due to metal atoms sitting in a range of environments on the support. Metal species in diverse environments will have varied structural bond distances, adsorbate binding energies, and catalytic properties. If the oxidation state of the atomically dispersed metal changes, shifts in ν_{CO} may be larger (>50 cm⁻¹), which would result in multiple bands for adsorbed CO.³⁴ We suggest that when CO IR is used to characterize atomically dispersed Pt-group sites, studies should demonstrate uniformity using this technique, with a fwhm of <15 cm⁻¹ and the presence of only a single CO stretching band, before employing structural analysis tools, such as STEM imaging or XAS, to propose or substantiate theoretical active site models.

To highlight the utility of CO probe molecule IR we focus on Pt/TiO₂. Figure 2a compares the CO IR spectra of 1.0 wt % Pt/TiO₂ prepared by dry impregnation to 0.025 wt % Pt/TiO₂ prepared by electrostatic adsorption.³³ These samples were reduced at 250 °C in H₂ prior to characterization, a critical consideration as CO bound to Pt_xO_y clusters have similar stretching frequencies as CO bound to Pt_{iso} but are easily reduced to metallic nanoparticles.³⁶ Pt/TiO₂ (1.0 wt %) showed a CO band centered at 2060 cm⁻¹ with fwhm of 48 cm⁻¹. This is consistent with CO bound to metallic Pt atoms

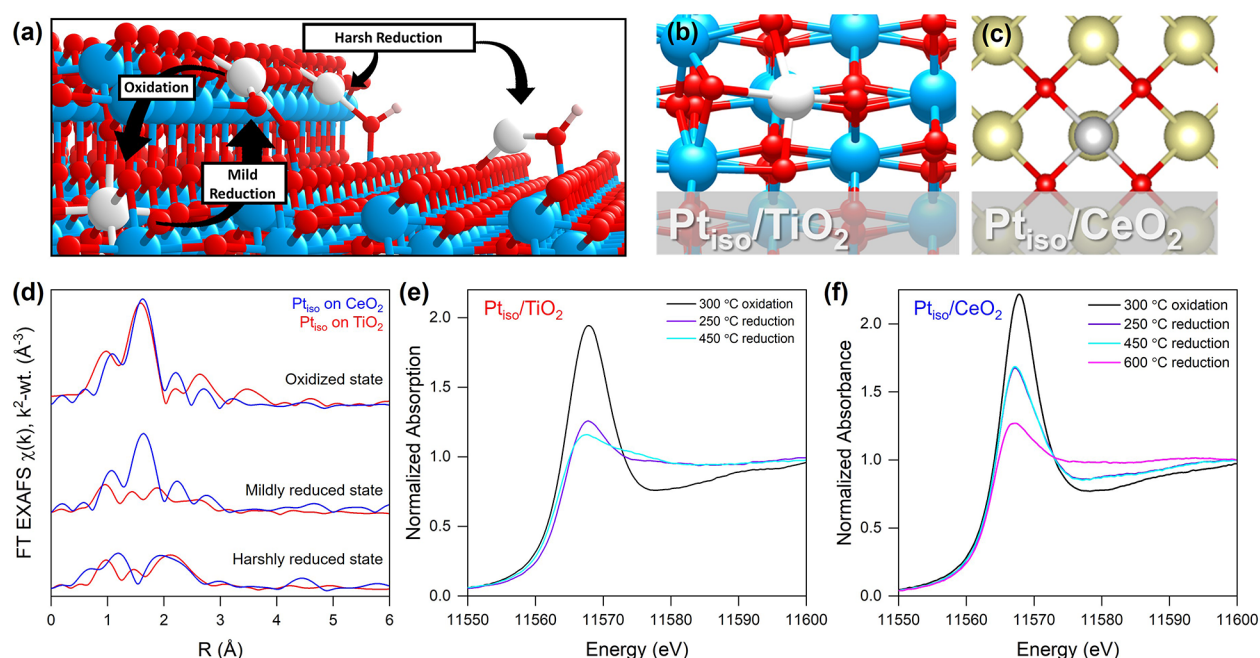


Figure 3. Dynamic evolution of atomically dispersed metal catalysts. (a) Schematic of the evolution of atomically dispersed Pt on TiO₂ under varying environmental conditions. (b, c) Comparison of the local structure of atomically dispersed Pt on TiO₂ and CeO₂ following mild reduction at 250 °C in H₂. Comparison of (d) Fourier-transformed magnitude EXAFS and XANES of the Pt L_{III} edge (e, f) of atomically dispersed Pt on TiO₂ and CeO₂. In (d) the oxidized state refers to catalysts pretreated at 300 °C in O₂, mildly reduced to catalysts pretreated at 250 °C in H₂, and harshly reduced to catalysts pretreated at 450 °C in H₂ and 600 °C in H₂ for Pt/TiO₂ and Pt/CeO₂, respectively. Reprinted with permission from refs 35 and 36. Copyrights 2019 and 2020 Springer Nature and American Chemical Society.

of varying coordination numbers.⁴⁶ This band position shifts with coverage, reflecting intermolecular dipole–dipole interactions on a supported nanoparticle. By contrast, 0.025 wt % Pt/TiO₂ showed a single band at 2112 cm^{−1} with a fwhm of ~8 cm^{−1}, similar to homogeneous carbonyl complexes and mononuclear Pt supported on zeolites.^{43,47} This indicates that CO is bound to Pt_{iso} with nearly identical coordination environments to the support.

This degree of structural uniformity was achieved by systematic optimization of synthetic conditions (pH, weight loading, and surface loading) with concomitant assessment by CO IR. For example, decreasing the surface loading (increasing dilution) during synthesis decreased the resulting production of Pt_{NP} and increased the uniformity of Pt_{iso} species, Figure 2b.³³

Support for the assignment of CO adsorbed to Pt_{iso}, in addition to further assessment of uniformity, can be provided by temperature-programmed desorption (TPD). Figure 2c shows that ν_{CO} and fwhm remained constant during TPD from Pt_{iso} on TiO₂.³³ This indicates there is no dipole–dipole interaction between neighboring CO molecules and supports the uniformity of the Pt_{iso} species.

In a CO TPD measurement, uniform atomically dispersed species should display one sharp desorption event. Figure 2d shows indeed that the temperature window over which desorption occurs from Pt_{iso} on TiO₂ is narrower than that of Pt_{NP} on TiO₂. In the TPD spectrum, which plots desorption rate versus temperature, the desorption peak for Pt_{iso} has a fwhm of ~40 °C, consistent with what is expected for a single adsorption energy without readsorption.^{48,49} By contrast, Pt_{NP} showed a fwhm of ~140 °C, similar to a nonuniform surface with a variation in adsorption energies of ~40 kJ/mol.^{48,49} Atomically dispersed metal species with varying oxidation state

and coordination to the oxide support can exhibit adsorption energy differences of this magnitude.³⁵ Similarly, proximity to support OH groups results in differences in an adsorption energy of ~20 kJ/mol for CO bound to Rh_{iso}.³⁸ Through these effects, TPD can identify differences even in materials with similar static CO IR spectra. We suggest then that CO TPD (or microcalorimetry) can provide useful insights on the uniformity of atomically dispersed metal sites.⁵⁰ We also note that care should be taken to avoid artifacts in TPD measurements on supported materials.^{51,52} In the measurements presented here, diffuse reflectance FTIR (DRIFTS) was used to assess CO coverage as a function of temperature. The probe volume in a DRIFTS measurement is extremely small. Most of the scattered IR light that is detected comes from the top surface of the catalyst bed, thus minimizing readsorption effects.

Having confirmed the homogeneity of metal species in a material, structural probes coupled with DFT calculations can help develop a consistent picture of their local structure. In Figure 2e,f we show aberration-corrected STEM imaging and EXAFS that were used to support a DFT based structural model for atomically dispersed Pt on TiO₂.³⁵ This model showed agreement in theory and experiment in coordination numbers (Pt–O, Pt–O–Ti), adsorption characteristics (adsorption energy and vibrational frequency of CO), and location along support (in line with Ti columns as confirmed by STEM). This level of agreement is only expected for cases in which a high degree of metal uniformity exists and should serve as a starting point for computational investigations of reactivity.

Although no consensus exists about methods that can be applied universally, we believe more careful assessment of uniformity will allow for more straightforward comparison

between atomically dispersed Pt-group metal catalysts, and the development of trends to understand their behavior. We suggest that chemical probes are perhaps the most powerful tools for assessing uniformity and provide metrics that should be used in this analysis. Probe catalytic reactions may also be useful as a test of uniformity. Useful probe reactions should be responsive to changes in metal electronic structure and not modify active site structure. Reactivity of different sites must also be known *a priori*. The response of reactivity to chemical titrants may also be useful in identifying site uniformity but has not been widely applied to this class of catalysts.

To this point, our assessment of the uniformity of atomically dispersed species and determination of their local structure has been based on a fixed environmental condition. However, considering that the structure and composition of both atomically dispersed metals and the support may change in response to their environment, *in situ* analysis is needed.

Structural Evolution of Atomically Dispersed Metal Coordination Environments. Supported nanoparticles change their structure in response to their surrounding environment.^{12,13} They do so to minimize surface free energies in the presence of adsorbates. Organometallic complexes similarly adjust their oxidation state and coordination sphere to their chemical potential landscape.⁵³ It is unsurprising then that the physical and electronic structure of atomically dispersed metals adapts to changes in environment. To understand this dynamic behavior, materials that have structurally uniform active sites are key. Diversity in metal structure precludes the use of sample-averaged techniques to describe the behavior of atomically dispersed species. Heterogeneity can also alter the dynamics of the atomically dispersed species. Metal clusters can reduce the stability of atomically dispersed species in the presence of hydrogen by facilitating H₂ dissociation. Hydrogen atoms can spill over from the metal surface onto the support and destabilize nearby cationic isolated metal atoms.⁵⁴ Developing synthetic methods for producing uniform atomically dispersed metals on oxide supports enabled us to describe their structural dynamics.

We analyzed the structural evolution of Rh_{iso} and Pt_{iso} on reducible oxide supports (CeO₂ and TiO₂) under varying environmental conditions.^{35–37} Figure 3a depicts the evolution in coordination environment under oxidizing and reducing environments for Pt_{iso} on TiO₂. This picture is inferred from experimental characterization correlated with theoretical calculations. Under oxidizing conditions, Pt_{iso} prefers to dope into the oxide lattice. Pt_{iso} sits in cation replaced positions, with saturated M–O bonding and an oxidation state of 4+. EXAFS measurements of Pt_{iso} on TiO₂ and CeO₂ were well fit with a Pt–O coordination number of ~6 and a Pt–O bond length of ~2.0 Å.^{35,36} EXAFS spectra, shown in Figure 3d, show a similar scattering pattern for Pt_{iso} on the two supports following oxidation pretreatment. As the gas phase environment becomes reducing (H₂ or CO at mild temperature) Pt_{iso} and Rh_{iso} lose coordination to support oxygens and concomitantly reduce their oxidation state. Although Pt_{iso} shows a coordination number to oxygen of ~4 on CeO₂ and TiO₂ following exposure to H₂ at 250 °C, the geometry Pt adopts differs. On CeO₂, Pt forms four symmetric bonds to oxygen in a square planar geometry expected for Pt²⁺.⁵⁵ TiO₂ lacks this symmetric site, resulting in Pt adopting a distorted square planar structure with two distinct Pt–O bond lengths (Figure 3b,c).³⁵ The difference in Pt_{iso}–O coordination following 250 °C reduction in H₂ is clear in the EXAFS spectra of Pt_{iso} on

TiO₂ and CeO₂, Figure 3d. Under more aggressively reducing conditions, the square planar cationic state is destabilized, and the metal atom adopts a near neutral oxidation state. The weak coordination to the oxide support renders the metal atom mobile. These mobile metal atoms are likely precursors to cluster formation.³⁵

The chemical potential windows at which these transitions occur depend on the nature of the metal and the support. Oxophilic atomically dispersed metals seek to maximize M–O bonding and are more difficult to displace from cation replaced positions. For example, Pd and Ni are more stable doped in CeO₂ than Pt.⁵⁶ Support composition also plays a role, with more reducible oxides stabilizing cationic Pt_{iso} and Rh_{iso} species. For example, as shown in Figure 3e,f Pt_{iso} shows higher stability in the +2 square planar environment on CeO₂ than on TiO₂. Reduction temperatures of ~600 °C are needed to destabilize this structure and form a mobile reduced Pt species on CeO₂, whereas this occurs at ~450 °C on TiO₂. Beyond oxide support reducibility, the geometry of the metal adsorption site may also play a role in stability.

The mechanism by which this evolution occurs is likely to involve energetics of the support as well as the atomically dispersed metal. We have observed that mobile, near-neutral atomically dispersed metals are produced concurrently with support reduction and hydroxylation. Thus, mobile atomically dispersed species likely form both because of the preference of the metal to reduce its oxidation state, but also because of the destabilization of the binding site in the support (i.e., the support surface begins to reconstruct). Consistent with this, recent surface science studies show Pd atoms become mobile on Fe₃O₄ single crystals after the support is hydroxylated and begins to reconstruct.⁵⁷

These changes in the local coordination of Pt_{iso} and Rh_{iso} impact their reactivity. We expect that a bond-order conservation relationship should exist for atomically dispersed species. Pt_{iso} and Rh_{iso} more strongly coordinated to support oxygens should have a lower propensity to form additional bonds with adsorbates. Conversely, Pt_{iso} and Rh_{iso} with fewer bonds to the support should coordinate strongly to gas phase molecules. We observed this for Pt_{iso} on TiO₂ supports, with the adsorption of CO becoming stronger as the structure evolved from a cation substituted species to a near-neutral surface species.³⁵

This bond order conservation relationship should be maintained with changes to support composition. Supports with more reactive surface oxygen should bind metal atoms more strongly. This imparts the metal with high stability against sintering, but weak interaction with adsorbates. We find that Pt_{iso} on CeO₂ is more stable as a cation and binds CO weaker than Pt_{iso} on TiO₂.^{33–36} We speculate that for a nonreducible support, such as Al₂O₃, the stability of Pt_{iso} would be lower and the adsorption energy of small molecules on Pt_{iso} would be stronger. Recent simulations that studied the most stable states of Pd atoms on Al₂O₃ are consistent with this proposal, with Pd forming neutral species by ~100 °C with CO as a reducing agent.⁵⁸ A similar bond-order conservation argument has been made for metal clusters on well-defined oxide supports.^{59,60} These studies highlight the need for systematic analysis of the evolution of atomically dispersed metal catalyst structure with varying metal and support. Establishing these trends from computational work alone may be challenging as identifying the most realistic structures is not trivial.

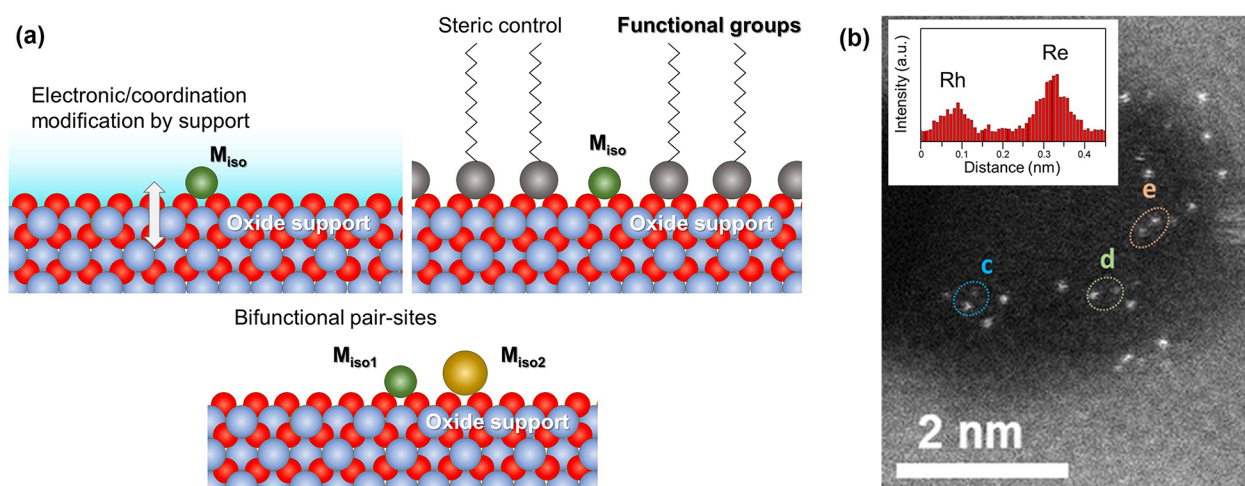


Figure 4. Pathways to increased functionality for atomically dispersed catalysts. (a) Illustration of ways that the catalytic behavior may be controlled. (Clockwise from top left) The support can influence metal reactivity by tuning its electronic structure or local coordination. Support functionalization can change the steric environment surrounding the metal site. Colocalizing two atomically dispersed metals can enable bifunctional reactivity. (b) Aberration-corrected high angle annular dark field STEM imaging of Rh–Re pair sites. Rh–Re pairs are shown in dotted circles. The inset shows an intensity line scan for the pair labeled “e”. Reprinted with permission from ref 86. Copyright 2019 American Chemical Society.

Rationalizing Controversies in Atomically Dispersed Metal Catalysis. Synthesizing the concepts discussed in this perspective allows us to clarify why discrepancies in reports about the structure, properties, and characterization signatures of single atom catalysts are so common. For instance, reports continue to appear describing the properties of isolated Pt atoms on CeO_2 supports, with vastly different conclusions.^{36,55,61–66} We believe many of these discrepancies can be attributed to a lack of uniformity in the metal sites in these materials, and specifically the coexistence of both isolated Pt species and Pt clusters. We advocate that performing control experiments using Pt clusters, particularly in their oxidized state, is critical for correctly identifying the properties of atomically dispersed metals.

Lack of these control experiments can lead to misallocation of the properties of clusters to those of single atoms. It is common to suggest that only atomically dispersed species are present if no Pt–O–Pt, or Pt–Pt, scattering (depending on oxidizing or reducing pretreatment) is observed in EXAFS measurements. However, this has little value without demonstrating with a control sample whether this scattering would be observed for small (<2 nm) oxidized metal clusters. In fact, previous studies have shown that oxidized Pt clusters do not show clear Pt–O–Pt scattering.^{67–69} Cluster control samples are also critical for probe molecule spectroscopic band assignments. For example, on the basis of their high stretching frequency, bands at 2095 cm^{-1} have been attributed to isolated Pt atoms on CeO_2 .^{61,62} However, oxidized Pt clusters show identical features in CO-IR, calling this spectroscopic assignment into question.^{36,70,71} In some cases, this can be addressed by considering both CO stretching frequencies and adsorption energies of bound CO from experimental and theoretical analyses to substantiate band assignments.^{33,34,38,72} Finally, cluster control samples (in the oxidized and reduced states) are critical to put the catalytic activity of atomically dispersed species in perspective.^{36,63}

Another issue that has clouded understanding of the properties of atomically dispersed species is insufficient consideration of structural changes that occur to active sites

under reaction conditions. Recent work has highlighted the dynamics of atomically dispersed species and small metal clusters and demonstrated how these dynamics can affect interpretation of catalytic performance.^{20,73–76} Finally, we note that more attention should be paid to surface species present on oxide supports (e.g., hydroxyls, adsorbed water).^{31,37,45} These species can coordinate to atomically dispersed metals species and thereby affect their stability and properties and play an important role in catalytic processes.

Outlook—Pathways to Increased Functionality. In this Perspective, we have highlighted the importance of assessing active site uniformity and understanding active site structural evolution for developing rigorous structure–function relationships for atomically dispersed metal catalysts. Detailed studies that have addressed the ideas mentioned above show that the local coordination of atomically dispersed Pt sites plays a key role in determining their reactivity. Supports can also participate with metal sites in reaction mechanisms either indirectly by dictating M–O coordination number and charge state (illustrated in Figure 4a)^{77–80} or directly through Mars van Krevelen processes,^{18,35} H-spillover,⁵⁷ and vicinal acid site participation.^{27,81} Developing mechanistic insights will continue to be important as catalysts with increased functionality and complexity are designed. Below, we suggest some pathways to increasing the functionality and performance of atomically dispersed metal catalysts.

The largest use of Pt-group metals in catalysis is for automotive emission control. Consequently, intense focus has gone toward studying atomically dispersed metals for reactions associated with this application.^{82–84} The design of atomically dispersed Pt-group metal catalysts for processes that currently use homogeneous catalysts, due to their superior selectivity, is another area for potential impact. But producing heterogeneous catalysts with active site tunability and uniformity that rivals homogeneous catalysts will require pushing the boundaries of current synthesis and characterization approaches. For example, to manipulate the enthalpy and entropy of elementary reaction steps, homogeneous catalysts control both active site electronic structure and steric

environment. Achieving a similar level of control with atomically dispersed heterogeneous catalysts would need to involve controlling the three-dimensional space around active sites,⁸⁵ in addition to their coordination to the support (Figure 4a).

Another intriguing concept is localizing two different atomically dispersed metal active sites with distinct properties in close enough proximity to enable bifunctional reactivity. This is analogous to demonstrations of cooperative catalysis by organic acids and bases on SiO₂ supports.⁸⁷ Structures are beginning to be synthesized that have potential for such behavior.^{86,88,89} For example, we recently reported the targeted synthesis of atomically dispersed Rh–Re site pairs, Figure 4b.⁸⁶ In this case, our results using ethylene hydroformylation as a model reaction suggested that Re simply acted to modify the properties of Rh, which carried out all reaction elementary steps. But one could also imagine a situation in which both sites simultaneously act to stabilize reactants and kinetically relevant transition states.

For atomically dispersed metal active sites with higher levels of complexity, untangling catalytic mechanisms and forming clear structure–function relationships becomes increasingly difficult. Thus, assessing site uniformity and structural evolution under reaction environments becomes even more critical. Our example for Rh–Re site pairs highlights this challenge. The *ex-situ* image shown in Figure 4b clearly shows the coexistence of dispersed Re species and Rh–Re site pairs, raising questions about the nature of the active site under reaction conditions. Further, when multiple species influence the active site, there are more functionalities that could be modified by exposure to reaction conditions. Thus, to realize the promise of atomically dispersed metal catalysts as selective and tunable materials we believe it is essential to focus on fundamental questions like those discussed in this perspective, in addition to exploratory discovery.

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Notes

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