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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b07093 • Publication Date (Web): 13 Sep 2017 Downloaded from http://pubs.acs.org on September 14, 2017

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Catalyst architecture for stable single atom dispersion enables site-specific spectroscopic and reactivity measurements of CO adsorbed to Pt atoms, oxidized Pt clusters and metallic Pt clusters on TiO₂

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Keywords: Single Atom Catalysts, Isolated Site Catalysts, Pt, CO oxidation, IR Spectroscopy

ABSTRACT: Oxide-supported precious metal nanoparticles are widely used industrial catalysts. Due to expense and rarity, developing synthetic protocols that reduce precious metal nanoparticle size and stabilize dispersed species is essential. Supported atomically dispersed, single precious metal atoms represents the most efficient metal utilization geometry, although debate regarding the catalytic activity of supported single precious atom species has arisen from difficulty in synthesizing homogeneous and stable single atom dispersions and a lack of sitespecific characterization approaches. We propose a catalyst architecture and characterization approach to overcome these limitations, by depositing ~1 precious metal atom per support particle and characterizing structures by correlating Scanning Transmission Electron Microscopy imaging and CO probe molecule infrared spectroscopy. This is demonstrated for Pt supported on anatase TiO2. In these structures isolated Pt atoms, Pt_{iso}, remain stable through various conditions and spectroscopic evidence suggests Pt_{iso} species exist in homogeneous local environments. Comparing Pt_{iso} to ~1 nm pre-oxidized (Pt_{ox}) and pre-reduced (Pt_{metal}) Pt clusters on TiO₂, we identify unique spectroscopic signatures of CO bound to each site, and find CO adsorption energy is in the order: Pt_{iso} << Pt_{metal} <Pt_{ox}. Pt_{iso} species exhibited a 2-fold greater turnover frequency for CO oxidation than 1 nm Pt_{metal} clusters, but share an identical reaction mechanism. We propose the active catalytic sites are cationic interfacial Pt atoms bonded to TiO_2 and that Pt_{iso} exhibits optimal reactivity because every atom is exposed for catalysis and forms an interfacial site with TiO₂. This approach should be generally useful for studying the behavior of supported precious metal atoms.

1. Introduction

Supported Pt-group metal catalysts are of critical importance due to their use in a broad range of chemical conversion technologies,^{1,2} with the highest demand in terms of metal mass coming from automotive three-way catalytic convertors.^{3,4} Due to a naturally low abundance of Pt-group metals in the earth's crust,^{5,6} significant efforts have been devoted to developing approaches that maximize metal utilization efficiency thereby reducing costs and promoting sustainability.⁷ The primary approach to maximize metal utilization efficiency is increasing the metal surface area to volume ratio by decreasing the size of nanometer scale particles, leaving a greater fraction of the total metal atoms in the catalyst available to drive chemistry.8 At the ultimate limit, this corresponds to single metal atoms deposited on supports, a class of materials called single atom, atomically dispersed, or isolated site catalysts, which exhibit perfect metal utilization, where all atoms are exposed to reactants and available for driving catalytic reactions.9 The critical consideration in motivating the development of isolated site Pt-group metal catalysts is whether these materials will maintain, or enhance, the inherent reactivity of small nanoparticles to enable improvements in

specific activity and reduced catalyst costs.^{10,11} Additional interest in isolated site Pt-group metal catalysts has been fueled by the idea that these materials could bridge the gap between heterogeneous and homogeneous catalysis, potentially providing unique opportunities to tune selectivity in difficult chemical conversions.^{12–15}

Research into isolated Pt-group, and more broadly precious, metal atoms on oxide supports has spanned decades with initial focus on providing spectroscopic evidence of their existence. For example, following the assignment of the Rh gem dicarbonyl species, $Rh(CO)_2$, to CO bound to isolated Rh atoms on oxides using infrared (IR) spectroscopy, efforts were devoted to identifying the structure, formation mechanism, and local geometry of these species.¹⁶ While initial research focused on the spectroscopic identification of isolated precious metal atoms on oxide supports, the ability to directly observe single heteroatoms on supports by aberration corrected scanning transmission electron microscopy (STEM) has sparked renewed interest into the synthesis, characterization, and potentially unique reactivity of isolated site precious metal catalysts.¹⁷ There is a growing body of literature reporting the reactivity of isolated site precious metal catalysts for reactions including water gas shift,¹⁸⁻²¹ CO₂ hydrogenation,²² ethylene dimerization,²³ ACS Paragon Plus Environment

butadiene hydrogenation,¹³ and NO reduction,²⁴ suggesting a broad and exciting range of potential applications. One system that has received significant attention is the adsorption and oxidation of CO on oxide supported isolated Pt atoms (Ptiso). Attention stems from the apparent simplicity of the reaction, but more relevantly from the potential to use Pt_{iso} species to reduce the massive demand of Pt for use in automotive (mostly in diesel engines) CO oxidation catalysis.^{25,26} Interestingly, significant variations exist in the reported strength of interaction between CO and oxide supported Pt_{iso}, and the reactivity of these species in CO oxidation. For example, there are theoretical and experimental reports that CO binds weaker^{8,27-31} and stronger^{32,33} to Pt_{iso} species compared to metallic Pt cluster (Pt_{metal}) surfaces, with binding energies on Pt_{iso} ranging from 20 to >200 kJ/mol depending on support and analysis approach. Similarly, there are variations in reports regarding the comparative reactivity of Pt_{iso} and Pt_{metal} clusters for CO oxidation, where Pt_{iso} species have been identified as the more and less reactive active site.^{27,32–35}

Variations in the strength of interaction and reactivity of CO on oxide supported Ptiso species are certainly related to the specific metal oxide support composition, which acts as a ligand modifying Ptiso species reactivity. However, given the range of conclusions with inconsistency across similar classes of supports (i.e. reducible, such as CeO₂, FeO_x, TiO₂) it is likely that variations in reported activity and strength of interaction between CO and Ptiso are also related to challenges associated with the synthesis of stable Pt_{iso} species on oxide supports and the unambiguous identification of these species. While different approaches have been used to deposit Ptiso species on oxide supports, it has been consistently reported that agglomeration into small Pt clusters occurs during high temperature oxidation (calcination),³⁵ reduction,³⁶ or exposure to reaction conditions.³⁷ The lack of Pt_{iso} stability in response to standard treatments used in the activation of Pt catalysts makes the rigorous identification of Ptiso reactivity difficult. For example, a lack of stability in high temperature calcination conditions necessitates mild oxidation treatments, which results in retained existence of ligands or counter ions on the catalyst that could influence reactivity and mobility of the Pt complex.^{31,35,38,39} Furthermore, if Pt_{iso} species cannot be exposed to H2 at elevated temperature, there exists the possibility that small, oxidized Pt (Ptox) clusters co-exist on the support,⁴⁰ which are difficult to differentiate from Pt_{iso} species given the similar cationic charge and local bonding environment of Pt in these structures. Finally, a lack of stability under reaction conditions makes it difficult to separate the reactivity of Pt_{iso} species from Ptmetal clusters. For rigorous analyses of the reactivity of supported Pt_{iso} species it is critical to develop strategies to maintain their structure under standard pretreatments used for supported Pt catalysts.

In addition to the synthesis of stable Pt_{iso} species, rigorous sampleaveraged and site-specific characterization approaches are needed to differentiate Pt_{iso} , Pt_{metal} clusters and Pt_{ox} clusters. While STEM imaging provides visual evidence of the presence of single atoms, the statistically limited nature of the technique coupled with the inability to provide 3-D representations of a support surface at atomic resolutions from the 2-D projections that makeup images suggest that STEM should be coupled with complimentary characterization techniques. Photon-based spectroscopies, such as X-ray absorption (XAS) and X-ray photoelectron spectroscopy (XPS), have been widely used to identify the charge state and local coordination of supported metal catalysts.⁴¹ The utility of these techniques to differentiate characteristics of Pt_{iso} species, such as a cationic charge or coordination only to oxygen atoms is hindered because these are also signatures of small supported Pt_{ox} clusters. Because of these similarities, differentiation of Pt_{iso} and Pt_{ox} by XPS or XAS requires maintained cationic charge and lack of Pt-Pt coordination in conditions where Pt_{ox} clusters reduce to Pt_{metal} clusters. Furthermore, the existence of even a few Pt clusters in a sample can lead to inconclusive results as the signal of all Pt species are averaged in the calculation of coordination numbers in XAS.

Probe molecule infrared (IR) spectroscopy with CO is a widely used characterization technique that allows probing of the local structure, oxidation state, and coordination environment of supported precious metals.⁴² CO probe molecule IR is a sampleaveraged technique that also is site-specific due to the varying vibrational frequency of CO when adsorbed to different types of supported metal sites, and it can be operated in a temperature programmed manner to extract information about the chemical reactivity of distinct precious metal sites.²² Similar to issues with XAS or XPS, distinguishing vibrational bands of CO when adsorbed to Ptiso and Ptox clusters requires consideration, as previous reports on these species identify their stretching frequencies both existing in the range ~2080-2130 cm⁻¹. $^{40,43-45}$ The similar vibrational frequency of CO when adsorbed to Ptiso and Ptox, which is blueshifted (higher frequency) from the stretching frequency of CO on Pt_{metal} (2030-2100 cm⁻¹), arises from the similar cationic charge of Pt in both structures.

It is consistently seen across all characterization approaches that the development of synthetic approaches to create stable Pt_{iso} species on oxide supports that survive through calcination, reduction, and reaction conditions is required to unambiguously distinguish Pt_{iso} , Pt_{ox} clusters and Pt_{metal} clusters. The importance of distinguishing these species is substantiated by reports showing that Pt_{ox} species ranging from small clusters containing a few Pt atoms to extended single crystal surfaces exhibit strong interactions with CO and minimal CO oxidation reactivity,⁴⁶⁻⁴⁸ potentially obfuscating measurements of Pt_{iso} reactivity if these species are not differentiated and distinctly compared.⁴⁹

Here we introduce a general approach to synthesize stable $\ensuremath{\text{Pt}_{\text{iso}}}$ catalysts by using ~5 nanometer (nm) diameter oxide nanoparticles (TiO₂ in this case) as supports and controlling Pt weight loading and synthesis conditions to deposit ~1 Pt atom per support particle. Using a correlated STEM and CO probe molecule IR characterization approach it was shown that Pt remains site isolated on TiO₂ particles through high temperature (450 °C) calcination, reduction in H₂ (300 °C), exposure to CO oxidation reaction conditions for ~3 days, and when aged on the shelf for ~1 month. CO adsorption on Pt_{iso} is characterized by a sharp (6-8 cm⁻¹ full with at half maximum, FWHM) IR band centered at 2112 cm⁻¹ that does not change frequency, width, or symmetry with coverage, while CO adsorption on 1 nm diameter Pt_{metal} (2040-2100 cm⁻¹) and Pt_{ox} (2100-2125 cm⁻¹) clusters is characterized by broader bands that shift in frequency and shape with coverage. Temperature programmed analysis showed that the interaction strength between CO and Pt species is in the order Pt_{iso} << Pt_{metal} < Pt_{ox}. The reactivity of Pt_{iso} and Pt_{metal} was compared in steady-state CO oxidation measurements void of heat and mass transfer effects, which showed that Pt_{iso} exhibited a 2-fold higher turnover frequency (TOF) compared to 1 nm Pt_{metal} clusters at 200 °C, but an identical reaction mechanism. We interpret the results in terms of the active site for CO oxidation on TiO₂ supported Pt being interfacial cationic Pt atoms, demonstrating that when supported on TiO₂, Pt_{iso} species exhibit optimal reactivity on a per mass and site basis because every

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atom is exposed for catalysis and creates an interfacial site with the support. It is expected that the approach demonstrated here would be generally useful for making rigorous assignments of spectroscopic and reactivity behavior of isolated precious metals on various oxides.

2. Experimental Methods

2.1 Materials

High purity (99.995%) Tetraammineplatinum(II) nitrate (TAPN) was purchased from Sigma-Aldrich (#482293) and used as the Pt precursor. 5 nanometer diameter anatase TiO₂ (99.5%) crystals with high surface area (290 m²/g) were purchased from US Research Nanomaterials (Stock # US3838) and used as the support in this study. Reagent grade NH₄OH (28-30% concentration) used in catalyst synthesis was obtained from Acros Organics (#423300250). SiO₂ gel (Davisil Grade 62, pore size 150 Å, 60-200 mesh, Part #243981, Sigma Aldrich) and acid purified SiO₂ (Sigma Aldrich, #84880) were used for catalyst co-impregnation and catalyst dilution, respectively. For the IR and steady-state reactivity experiments, the following gases were used: 10% H₂/Ar ($\pm 2\%$, Airgas), He (UHP, 99.999%, Airgas), 10% O₂/He ($\pm 2\%$, Airgas), and 10% CO/He ($\pm 2\%$, Airgas) in an Al tank to prevent metal carbonyls from entering reactant streams.

2.2 Catalyst Synthesis

The synthesis of catalysts containing a predominance of Ptiso species was achieved by a wet impregnation technique called strong electrostatic adsorption (SEA)50 using low Pt weight loadings (0.025-0.15 wt%), large synthesis volumes to promote homogeneous deposition of Pt on the support, and controlled solution pH (8-12.5). In a typical synthesis of 0.025 wt% catalyst containing exclusively Pt_{iso} species, 1 g of TiO₂ was crushed, sieved to a powder finer than 75 µm, and dried in a vacuum oven at 120 °C overnight prior to synthesis. 25 mL of deionized water was mixed with 75 mL of NH4OH to dissolve the TiO2 support, resulting in a solution pH of 12.2. Separately, 10 mg of TAPN was dissolved in 5 mL of deionized water from which 300 µL were taken and added to 25 mL of NH₄OH to create a precursor solution with a pH of 12.2. The 25 mL TAPN solution was injected over 12.5 hours into the support solution while constantly stirring to achieve a final total solution volume of 125 mL with a surface loading (see equation 1) of 2900 m²/L. Following the slow precursor addition, the final solution was heated to 70 °C until completely dried.

1) Surface Loading =
$$\frac{Mass_{support} * Surface Area_{support}}{Volume_{solution}}$$

For the synthesis of 1 wt% Pt catalysts containing Pt clusters and no Pt_{iso} species, an incipient wetness (dry) impregnation (DI) procedure was used. In a typical synthesis of 1 g of catalyst, 20 mg of TAPN was dissolved in 1200 μ L of deionized water and the solution was added to 990 mg of TiO₂ (dried and sieved as mentioned above), forming a paste. The paste was heated to 70 °C until completely dried. The dried catalysts were placed in a vacuum oven at 120 °C overnight and sieved to 75 μ m.

All catalysts were calcined in a tube furnace at 450 $^{\circ}$ C for 4 hours in flowing air after ramping up to temperature at a rate of 10 $^{\circ}$ C/min.

The high temperature and extended duration of the calcination ensures removal of all remaining amine or nitrate ligands from the TAPN precursor which are completely decomposed under these conditions.⁵¹

2.3 STEM Imaging

STEM imaging was performed on a JEOL JEM-ARM300F Grand ARM transmission electron microscope equipped with two spherical aberration correctors and a 300 kV cold field emission gun. High-angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 22 mrad and inner and outer collection angles of 83 and 165 mrad, respectively. 20-30 images were collected of each sample to observe at least 100 Pt species and enable convincing structural assignments of the CO IR spectra. STEM imaging conditions were set to minimize the electron beam effect. A relatively small probe current 20 pA was used for imaging. Meanwhile, the magnification was always kept below 8,000,000 and the acquisition time was less than 16 seconds. Single Pt atoms were observed to be stable under these conditions.

2.4 IR Characterization

Prior to collecting CO probe molecule IR spectra, catalysts were loaded into a Harrick High Temperature Reaction chamber (ZnSe windows) mounted inside a ThermoScientific Praying Mantis diffuse reflectance adapter set in a Nicolet iS10 FTIR spectrometer with a Mercury Cadmium Telluride (MCT) detector cooled by liquid nitrogen. Mass flow controllers (Teledyne Hastings) were used to control the gas flow rates across the reactor bed and all gases were first passed across both an isopropyl alcohol-liquid nitrogen cold trap held at -80 °C and a glass trap filled with Drierite desiccant to remove trace moisture. The surface temperature in the catalyst bed was calibrated using an optical pyrometer due to the known gradient in the bed of the Harrick reactor.^{52,53}

CO probe molecule IR spectroscopy was used to identify unique vibrational signatures of CO adsorbed to various Pt structures. To examine the spectral features of CO on each structure, as well as the stability of CO and reactivity in an O2 flow, the following protocol was used. First, an in-situ oxidation (300 °C for 30 min in a 10% O_2 /He mixture at 50 sccm) or reduction (240 °C for 1 hour in pure H₂, 50 sccm) pre-treatment was performed to allow differentiation of Ptox clusters from Ptmetal clusters and Ptiso species. Next, catalysts were cooled to room temperature in He flowing at 100 sccm. Once at room temperature, CO was adsorbed until saturation coverage by flowing 10% CO/He at 50 sccm for 10 minutes, where it was observed that bands associated with CO adsorption on Pt no longer changed. The system was flushed for 2 minutes in He at 100 sccm to remove any gas phase CO, which has vibrational bands that overlap with bands associated with CO adsorbed on cationic Pt species. Next, the stability of remaining chemisorbed CO was probed either in a temperature programmed desorption (TPD) experiment or in a temperature programmed oxidation (TPO) experiment. In the TPD experiment, the temperature was ramped from room temperature to 500 °C at a rate of ~7 °C/min in 100 sccm of He flow. Alternatively in the TPO experiment, oxygen was introduced (50 sccm of 10% O₂/He) to



Figure 1. Synthesis Approaches for producing site-isolated Pt and Pt clusters on TiO₂. (**A**). Schematic of the strong electrostatic adsorption based synthetic protocol used to deposit 1 Pt atom per 5 nm diameter TiO₂ particle through controlling weight loading, solution volume, and solution pH. By tuning the solution pH, a Coulombic attraction between the surface oxygen anion (O⁻) and the cationic precursor $[(NH_3)_4Pt]^{+2}$ promotes the deposition of 1 Pt atom per TiO₂ particle. (**B**). A schematic of the dry impregnation approach for producing exclusively Pt clusters, where higher weight loadings, no control of pH and smaller solution volumes are used to deposit the Pt precursor onto TiO₂ particles.

the chemisorbed CO still held at room temperature and a temperature ramp to 500 °C at a ramp rate of 10 °C/min followed. Spectra were recorded throughout the entirety of experiments in Kubelka Munk (KM) units with 32 scans and 0.482 cm⁻¹ data spacing being averaged into a spectrum, allowing half-minute increments between each measurement.

2.5 Steady State CO Oxidation Kinetics

Differential reactor measurements were made in a glass tubular packed-bed reactor to directly measure and compare the steady state CO oxidation reactivity of the various prepared catalysts. In all cases, a half-inch glass tube was used with a 4:1 length to diameter ratio of the catalyst bed to minimize the possibility of channeling. Calcined Pt/TiO₂ catalysts were sieved to < 75 μ m and coimpregnated with inert SiO₂ gel at a 1:4 ratio of catalyst to SiO₂. The mixture was sonicated for 30 minutes in a round bottom flask with water and stirred overnight. The flask was then transferred to a rotary evaporator and vacuum dried over a 30 minute period at 110 rpm. The entire batch of co-impregnated catalyst was then further diluted 5:1 by an acid purified SiO₂ (Sigma Aldrich, #84880) and loaded into the packed bed reactor. The dilution and coimpregnation steps were used to minimize (1) the pressure drop that would occur with gas flow through a packed bed of 5 nm diameter TiO₂ particles, (2) the size of domains containing 5 nm TiO₂ particles, which would introduce mass transfer and diffusion effects on the kinetic rates, and (3) hot-spot formation that is associated with this highly exothermic reaction. No pressure drop across the catalyst bed was observed following the co-impregnation of the catalyst and across all flow rates of interest the reaction rate stayed constant (Figure S1) suggesting no mass transfer limitations (i.e. kinetic measurements were made in a reaction limited regime).

For steady-state CO oxidation measurements, 50 mg of catalysts were loaded into the reactor and pre-treated with a 2 hour reduction in pure H₂ at 20 sccm and 300 °C. The catalyst was cooled to 200 °C in 160 sccm He and then exposed to reaction conditions (1% CO, 1% O₂, 98% He at 200 sccm total flowrate) for 10 hours to allow steady state to be reached; during the 10 hour period reaction rates varied by less than 5%. Following the activation period, the reactor was cooled to 140 °C in the same composition and activation barrier measurements were made using 10 °C temperature increment steps over a period of 2 minutes, followed by holding at a given temperature for 2 hours to ensure steady state signals were reached in the mass spectrometer (MS). Partial pressure dependent measurements were made utilizing a home-built programmable Arduino controller that automated a solenoid valve control that allowed the reactants to bypass the reactor for baseline measurements in the MS before and after every change in pressure. An identical pretreatment to the activation barrier measurements preceded the partial pressure dependent measurements including the 10 hours on stream at 200 °C. Following the activation period, instead of cooling, the partial pressure dependent measurements were executed at 200 °C. The total flowrate for all partial pressure measurements was 200 sccm in a balance of He. The CO partial pressure dependence was run first, beginning with the highest CO feed ratio of 1.5% CO to 0.5% O2 and ending with the lowest CO feed ratio of 0.25% CO to 0.5% O2. At the start and end of each feed ratio, the reactants were flowed for 20 min bypassing the reactor to get a baseline signal in the MS. In between baseline measurements, the reactants were flowed across the catalyst bed for a period of 2 hours to obtain a steady state signal. Immediately following the lowest CO feed composition, while still at 200 $^{\circ}\text{C}\textsc{,}$ the O_2 partial pressure dependent measurements began with the highest O2 feed ratio (0.5% CO to 1.5% O₂) following a 40 min bypass period. The alternating bypass/reactor cycle continued for 7 steady state measurements with sequentially decreasing O2 feed composition and constant CO pressure, ending with a feed ratio of 0.5% CO to 0.25% O2. For both sets of reaction experiments and for all catalysts, the reported kinetic measurements are an average of at least 3 unique measurements (i.e. new catalyst preparations were loaded into the reactor) to ensure repeatability and consistency. Temperature was controlled in the home-built furnaces using programmable PID controllers (Omega CN7800). Flowrates were controlled by calibrated mass flow controllers (Teledyne Hastings). Gas streams were cleaned of humidity prior to the reactor using a Drierite bed (tests with the addition of an isopropyl alcohol-liquid nitrogen trap showed no effect on rate), and Al-lined CO tanks were purchased to prevent metal carbonyl formation and ensure clean CO streams. All effluent gases were measured using calibrated online mass spectrometry (Halo 201, Hiden Analytical).

3. Results

3.1 Synthesis and vibrational band assignments of CO adsorbed to Pt_{iso}



Figure 2. Surface loading and pH optimization for producing Pt_{iso} . (A). IR spectra of CO adsorbed at saturation coverage and room temperature to 0.05 wt% Pt/TiO₂ SEA catalysts prepared at a pH of 12 and precursor solution addition rate of 2 mL/hr and varying surface loadings. (B). IR spectra of CO adsorbed at saturation coverage and room temperature to 0.05 wt% Pt/TiO₂ SEA catalysts prepared a 3,600 m²/L surface loading, precursor solution addition rate of 2 mL/hr, and varying solution pH's. All catalysts were reduced at 240 °C in H₂ prior to CO adsorption. The spectra were normalized to the intensity of the band at 2112 cm⁻¹, assigned to CO adsorbed to Pt_{iso}, to enable direct comparison of the influence of synthetic conditions on the relative proportion of CO adsorption sites. Catalysts were pretreated in flowing H₂ for 1 hour at 240 °C.

It was hypothesized that the preparation of exclusively Pt_{iso} species with high stability could be achieved by using small oxide nanoparticles as supports and depositing ~1 Pt atom per support particle. In this geometry, the required migration between support particles should minimize agglomeration to form Pt multimers, even if Pt atoms were mobile on the oxide surface. To synthesize this structure we used ~5 nanometer diameter anatase TiO₂ particles (surface area 290 m^2/g), and low Pt weight loadings that correspond to less than 1 Pt atom per TiO₂ particle (0.025-0.05 wt% corresponding to 0.2-0.4 Pt atoms/TiO₂ particle). If a stochastic distribution of Pt atoms were deposited onto TiO₂ particles, there would be a significant fraction of TiO2 particles containing >1 Pt atom, see Figure 1(A). To mitigate the clustering of Pt atoms that would be expected on a stochastic basis and promote a homogeneous deposition of the Pt atoms across the support particles, large synthesis volumes were coupled with Pt precursor addition over long time periods, creating an evenly mixed and dilute slurry. Principles from the strong electrostatic adsorption (SEA) wet impregnation technique were used to promote repulsive interactions between Pt ions in solution and attractive interactions between Pt ions and the TiO₂ surface.^{50,54-56} By modifying the TiO₂ support surface through pH adjustment by the addition of NH4OH, hydroxyls were deprotonated to form O- anions at the TiO₂ surface that Coulombically attract $[(NH_3)_4Pt]^{+2}$, as shown in Figure 1(A). Through a combination of small TiO2 particles, low Pt weight loadings, homogeneously mixed solutions and controlled TiO₂-Pt cation interactions, it was expected that there was a high probability to produce stable Pt_{iso} species.

As a comparison for the designed synthesis of Pt_{iso} catalysts, a 1 wt% Pt/TiO_2 catalyst was prepared by incipient wetness (dry) impregnation (DI) with the goal of exclusively producing Pt clusters, Figure 1(B). The 1 wt% loading dictates that on average ~8.4 Pt atoms would be deposited per TiO₂ particle, with low solution volume and lack of pH modification eliminating the expected driving force for Pt_{iso} formation. Even with the lack of specific efforts to control Pt particle size in this synthesis, nanometer and sub-nanometer diameter particles were expected to form due to the required migration between TiO₂ particles for particle sintering and the relatively small number of Pt atoms deposited per TiO₂ particle.

Due to its high sensitivity to local bonding environment, CO probe molecule IR spectroscopy was utilized to analyze how synthesis parameters influenced the resulting Pt structure. Characterization of structural properties and charge of supported Pt catalysts using CO as a probe molecule with IR is abundant in literature.^{42,57} For supported Pt_{metal} particles there are well-established values for vibrational frequency of adsorbed CO.58 When CO is adsorbed to Pt_{metal} sites the vibrational frequency increases from 2040 to 2100 cm⁻¹ as Pt-Pt coordination number increases from ~5 (characteristic of corners or defect sites on Pt particles) to 9 (characteristic of extended (111) surfaces on Pt particles).⁵⁸ In contrast, when CO is adsorbed to oxide supported cationic Pt species (Ptox clusters, Ptiso species, or Pt coordinated with oxidizing ligands) the CO vibrational frequency is blueshifted from the Pt_{metal} adsorption sites, typically to >2100 cm^{-1.59} The blueshifted frequency for CO adsorbed to cationic Pt sites compared to Pt_{metal} sites derives from the decreased charge transfer to CO and CO bond distance being closer to the gas phase CO distance.⁶⁰ We hypothesized that for catalysts synthesized using the SEA approach described above, which were pretreated through harsh calcination (4 hours at 450 °C in air) and in-situ reduction (1 hour at 240 °C in H₂), any remaining IR bands of CO adsorbed to Pt sites with stretching frequencies > 2100 cm⁻¹ must be due to the presence of Pt_{iso} species, as all oxidizing ligands from synthesis would be removed by the calcination and any Ptox clusters would be reduced to Ptmetal clusters during the reduction.

Figure 2(A) shows the IR spectra of CO adsorbed at saturation coverage and room temperature to 0.05 wt% SEA catalysts synthesized at a pH of 12, Pt precursor addition rate of 0.025 mg of Pt per hour, and varying surface loading (inversely proportional to synthesis solution volume, or qualitatively dilution). The spectra were normalized to the intensity of the CO stretching band at 2112 cm⁻¹ to compare the relative amount of CO adsorbed to Pt_{metal} sites (2040-2090 cm⁻¹). It can be seen that as the surface loading was decreased (more dilute synthesis condition), the intensity of the band associated with CO adsorption at a cationic Pt site (2112 cm⁻¹) increases relative to the intensity of the broad band associated with CO adsorption on Pt_{metal} sites.

Figure 2(B) shows the spectra of CO adsorbed at saturation coverage to 0.05 wt% SEA catalysts synthesized at a Pt precursor addition rate of 0.025 mg of Pt per hour, surface loading of 3,600 m²/L and varying pH between 8 and 12.5.



Figure 3. Correlative IR and STEM for CO vibrational band assignments on Pt_{iso} and Pt_{metal} . (A-C) IR spectra of CO adsorbed at saturation coverage and room temperature to 0.05 wt% Pt/TiO₂ SEA, 0.15 wt% Pt/TiO₂ SEA and 1 wt% Pt/TiO₂ DI catalysts, respectively, that had been reduced at 240 °C in H₂ prior to CO adsorption. (D-F) Representative STEM images of the same 3 catalysts after reduction ex-situ, where IR spectra in (A-C) correlate to STEM images of the same catalyst in (D-F). In the STEM images, Pt_{iso} species with diameter of ~175 pm are circled in yellow, while clusters with diameter ~ 1 nm are circled in red.

It was observed that as the synthesis pH was increased the catalysts trended toward containing a single CO adsorption site with a symmetric CO stretching band at a frequency of 2112 cm⁻¹ and a FWHM of < 10 cm⁻¹, with optimized synthetic conditions consistently producing FWHM of 6-8 cm⁻¹. Catalysts synthesized at closer to neutral pH contained Pt_{metal} CO adsorption sites and broadened asymmetric bands centered at 2112 cm⁻¹, as seen in Figure 2B.

A series of Pt/TiO₂ catalysts were prepared with the optimized conditions of Pt precursor addition rate of 0.025 mg of Pt per hour, surface loading of 3,600 m²/L, pH of 12.2 and varying Pt loading from 0.025 – 0.5 wt%. The IR spectra of CO adsorbed at saturation coverage to this series of catalysts are shown in Figure S2. It can be seen that when there was nominally less than 1 Pt atom/TiO₂ particle during the synthesis (0.025-0.05 wt%) a single, sharp CO band with a frequency at 2112 cm⁻¹ was observed. When the Pt weight loading was increased above 1 Pt atom/TiO₂ particle (> 0.1 wt%) a second broad CO band formed with a frequency of 2040-2090 cm⁻¹, signifying CO adsorbed to Pt_{metal} sites. The ratio of the band intensity at 2040-2090 cm⁻¹ increased relative to the 2112 cm⁻¹ band as the Pt weight loading was increased.

To summarize the influence of synthetic protocol on the CO probe molecule IR spectra, it was found that when Pt was deposited onto 5 nm anatase TiO₂ particles under highly dilute conditions, at high pH, and with weight loadings lower than 1 Pt atom/TiO₂ particle, a single CO stretching band with frequency 2112 cm⁻¹ and FWHM of 6-10 cm⁻¹ was observed. Given that in all cases the catalysts were pre-treated by H₂ under conditions known to reduce Pt_{ox} clusters into Pt_{metal} clusters, the retained existence of a CO adsorption site with a stretching frequency characteristic of adsorption on cationic Pt atoms, and the sharpness of the CO band, suggest an assignment of the 2112 cm⁻¹ vibrational mode to CO adsorbed to Pt_{iso} species on the anatase TiO₂ support.

To support the IR assignment of CO adsorbed to Pt_{iso} on anatase TiO₂, a correlated IR-STEM analysis was executed. We focused on 3 samples: (1) 0.05 wt% catalyst synthesized by the optimized SEA protocol, (2) 0.15 wt% catalyst synthesized by the identical SEA protocol, and (3) 1 wt% catalyst synthetized by the DI approach. Both SEA catalysts were prepared using pH of 12.2, surface loading of 2900 m²/L and Pt precursor addition rate of 0.025 mg of Pt per hour. For these samples we collected CO probe molecule IR spectra at saturation coverage, see Figures 3(A-C), and 20-30 STEM images of the same materials, examples of which are shown in Figures 3(D-F), after they had been calcined and reduced through identical protocols prior to both characterizations. In ~30 STEM images of the 0.05 wt% SEA catalyst, Ptiso species were the predominantly observed Pt species with only ~3 Pt clusters with diameter <1 nm observed, Figure 3(D). An average diameter of 0.176 nm was observed for the Ptiso species, see Figure S3. The measured diameter of the Pt_{iso} species cannot be directly related to the Pt atomic radius, but instead shows that the measured size of Pt_{iso}

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59 60 species is larger than the resolution of the instrument and thus, Pt_{iso} species can be distinguished from dimers or trimers of Pt. The STEM images identifying Pt_{iso} species are in excellent agreement with the IR spectra of the same CO saturated sample, Figure 3(A), where the intensity of the band at 2112 cm⁻¹ was ~180-times more intense than the broad band observed between 2040-2090 cm⁻¹. For the 0.15 wt% SEA catalyst, STEM imaging showed a significant increase in the number of Pt clusters (0.84 nm average diameter) compared to the 0.05 wt% SEA catalyst and the maintained existence of Pt_{iso} species, Figure 3(E), in good agreement with the IR spectra of the CO saturated catalyst, Figure 3(B), which showed an increased relative intensity of the CO stretching band at 2040-2090 cm⁻¹ compared to the 0.05 wt% SEA catalyst. Finally, STEM images of the 1 wt% DI catalyst showed the existence of predominantly clusters with an average diameter of 1.1 nm and a few larger particles with an average diameter of 4.3 nm, Figure 3(F), corroborating the IR of the CO saturated catalyst in Figure 3(C), which showed almost exclusively CO stretching band intensity between 2040-2090 cm⁻¹.

STEM imaging showed conclusive evidence of the retained existence of predominantly Pt_{iso} species on the 0.05 wt% SEA catalyst following calcination and reduction, as hypothesized in the design of the synthesis approach. Furthermore, the correlated STEM-IR analysis provides convincing evidence that the sharp CO stretching band at 2112 cm⁻¹ can be assigned to CO adsorbed on Pt_{iso} on anatase TiO₂.

3.2 Site-specific signatures of CO adsorbed to Pt_{isor} , Pt_{metal} and Pt_{ox}



Figure 4. Differentiating CO adsorbed to Pt_{iso} , Pt_{metal} and Pt_{ox} . (A) CO adsorbed at room temperature and saturation coverage to a 1 wt% Pt/TiO₂ DI catalyst that had been pre-reduced (red), and pre-oxidized (black), sequentially. (B) CO adsorbed at room temperature and saturation coverage to a 0.05 wt% Pt/TiO₂ SEA catalyst that had been pre-reduced (red), and pre-oxidized (black), sequentially. The intensity of the spectrum collected from CO on the pre-oxidized catalyst was multiplied by 100 to allow comparison.

With the demonstrated stability of Pt_{iso} species on 5 nm TiO₂ particles following reductive treatment, we chose the 1 wt% DI (containing predominantly Pt clusters) and 0.05 wt% SEA (containing predominately Pt_{iso} species) catalysts to identify spectroscopic signatures that differentiate CO adsorbed to Pt_{iso} and Pt_{ox} clusters, which both contain cationic Pt atoms. To achieve this, both catalysts were first pre-treated for 1 hour at 240 °C in flowing H₂, then exposed to CO at room temperature to saturation coverage and characterized by IR. The catalysts were then oxidized to remove adsorbed CO and oxidize the Pt structures (280 °C, 30 min in 10%)

 $O_2),$ cooled to room temperature, and exposed to CO again for characterization by IR. By performing the experiments sequentially on the same catalysts, spectra of CO adsorbed to Pt_{metal} and Pt_{ox} clusters could be compared to CO adsorbed to Pt_{iso} species that have been pre-oxidized or pre-reduced.

In Figure 4(A) it is seen that following reduction, the spectrum of CO adsorbed at saturation coverage to the 1 wt% DI catalyst shows two predominant CO stretching bands overlapping in the region associated with CO adsorbed to Pt_{metal} sites centered at 2077 cm⁻¹, assigned to well-coordinated (WC) Pt sites, and 2058 cm⁻¹, assigned to under-coordinated (UC) Pt sites.^{61,62} The spectrum showed almost no intensity in the frequency range associated with CO adsorbed to cationic Pt sites (>2100 cm⁻¹), suggesting fully reduced Pt clusters.

Following oxidation of the 1 wt% DI catalyst, the spectrum of adsorbed CO showed a decrease in the intensity of bands associated with CO bound to Pt_{metal} sites (2040-2090 cm⁻¹) as compared to the reduced catalyst, and the appearance of a broad band associated with CO adsorbed to cationic Pt sites (>2100 cm⁻¹), see Figure 4(A). Peak deconvolution using a least-squares fit of multiple Gaussian peaks showed that the CO stretching band associated with adsorption on cationic Pt sites was centered at ~2118 cm⁻¹ and had a FWHM of 25-30 cm⁻¹, Figure S4. STEM imaging of the 1% DI catalyst following the reductive and oxidative treatment showed essentially identical Pt structure geometries, containing predominantly Pt clusters with an average of ~1 nm diameter and a few larger Pt particles with an average ~4 nm diameter, Figure S5. Given the lack of structural change in Pt particles following oxidative and reductive treatment, the broad CO stretching band between ~2090-2140 cm⁻¹ in Figure 4A is assigned to CO adsorption on Pt_{ox} clusters, consistent with previous reports.^{45,63} The CO stretching bands at frequencies below 2090 cm⁻¹ observed in Figure 4(A) following oxidative treatment are assigned to Pt structures (or portions of Pt structures) that were reduced by the flowing CO, as previously observed for Pt/TiO₂ catalysts.⁶⁴ However, from the combined IR and STEM data, which showed no significant structural changes of Pt following oxidative and reductive treatment,³⁶ it is clear that CO only partially reduced the Ptox clusters. This is an important point that will be addressed in the discussion section, as the only partial reduction of oxidized Pt clusters by CO suggests the possible existence of Pt structures containing reduced Pt metal species in addition to retained oxygen and is supported by the observation of CO stretching bands at frequencies associated with both adsorption on metallic and cationic Pt atoms.

In contrast to the behavior of Pt clusters seen in Figure 4(A), where the CO stretching bands assigned to adsorption on cationic Pt sites only appeared following oxidation pre-treatments, for the 0.05 wt% SEA catalyst it was observed that the predominant CO stretching band at 2112 cm⁻¹, which we assigned to CO adsorbed to Pt_{iso}, is present following pre-treatment in a reducing atmosphere, see Figure 4(B). However, following pre-oxidation of the catalyst and CO adsorption the overall intensity of the CO stretching bands in the IR spectrum significantly decreased (100-fold), resulting in bands at 2040-2090 cm⁻¹ and 2090-2130 cm⁻¹, which appear similar to the spectrum of pre-oxidized 1 wt% DI shown in Figure 4(A). It is proposed that Pt_{iso} species either exhibit preferential adsorption of O₂ compared to CO or that vacancies in the TiO₂ lattice induce migration that poisons the Pt_{iso} species.^{34,65} Thus, following the oxidative treatment, Pt_{iso} species are poisoned and do not allow CO to ad-



Figure 5. Site-specific signatures of CO adsorbed to Pt_{iso} , Pt_{metal} and Pt_{ox} . (A). IR spectra of CO adsorbed at room temperature and saturation coverage on a pre-reduced 0.05 wt% SEA catalyst during He flushing. (B). CO adsorbed to a reduced 1 wt% DI catalyst during a He and O₂ flush at room temperature and a TPO ramp. (C). CO adsorbed to an oxidized 1 wt% DI catalyst during the identical protocol as (B).

sorb, while the few Pt clusters in this catalyst exist in a combination of reduced and cationic atoms, similar to the 1 wt% DI catalyst.

To briefly summarize, through the use of the 1 wt% DI and 0.05 wt% SEA catalysts, which contain Pt clusters and Pt_{iso} species, respectively, and controlling oxidative or reductive pretreatments, we can differentiate the IR spectra of CO adsorbed to Pt_{iso}, Pt_{ox} clusters, and Pt_{metal} clusters. This is critical, as CO adsorption on both cationic Pt species shows bands with similar stretching frequencies (2112 cm⁻¹ on Pt_{iso} and 2118 cm⁻¹ on Pt_{ox} clusters), with the main difference being the width of the band (<10 cm⁻¹ on Pt_{iso} and 25-30 cm⁻¹ on Pt_{ox}), making them otherwise difficult to differentiate. The rigorous assignment of vibrational bands associated with CO adsorption on Pt_{iso}, Pt_{ox} and Pt_{metal} sites enables comparison of the CO adsorption strength and characteristics of the CO desorption process on each adsorption site through TPD experiments in the IR.

Figure S6(A) and S6(B) show the IR spectra associated with various temperatures recorded during TPD experiments ($\beta = 7$ °C/min) performed on 1 wt% DI catalysts that had been prereduced and pre-oxidized, respectively. On the pre-reduced catalysts, desorption of CO was observed to initiate from Pt_{metal} sites at ~50 °C and be mostly completed by 300 °C, Figure S6(A). The desorption temperature was higher than traditionally seen in TPD experiments of CO from Pt clusters. We attribute this discrepancy to the time needed to average data collected in a given spectrum, causing each spectrum to represent a range of temperatures.⁶² With increasing temperature, a characteristic redshift in CO stretching frequency occurred as the band intensity decreased due to the decreased dipole-dipole interactions of neighboring CO molecules on the Pt_{metal} surface. For the pre-oxidized 1 wt% DI catalyst, it was observed that CO was bound more strongly to cationic Ptox sites $(>2100 \text{ cm}^{-1})$ as compared to Pt_{metal} sites $(<2100 \text{ cm}^{-1})$, with significant desorption from Ptox sites occurring only above 200 °C and incomplete even at 350 °C, Figure S6(B). The stronger adsorption of CO to Ptox clusters, compared to Ptmetal clusters, is consistent with previous results on Pt single crystals and supported Pt.^{45,47,48,66} During CO desorption from Ptox sites various shifts in the CO band frequency and width were observed, suggestive of evolving oxidation states and structure of adsorption sites during the temperature ramp.

In contrast to the stability of CO exhibited on Pt clusters, Figure 5(A) shows IR spectra collected following saturation of Ptiso sites by CO on a reduced 0.05 wt% SEA catalyst under flowing He at room temperature. It was observed that all CO desorbed from Pt_{iso} sites within 30 minutes following first order unimolecular desorption kinetics as shown in Figure S7, thus no temperature ramp was executed. It is obvious that CO binds more weakly to the Pt_{iso} sites compared to Pt_{metal} or Pt_{ox} sites. In addition to the low stability of CO observed on Pt_{iso} sites, throughout desorption the CO stretching band remained symmetric and the FWHM stayed constant at ~8 cm⁻¹. Furthermore, as CO desorbed, the vibrational frequency was constant. The absence of a coverage dependent shift in the stretching frequency of CO on Ptiso sites shows there is no interaction between adsorbed CO molecules and CO must therefore be spatially isolated on atomically dispersed Pt atoms, in contrast to the behavior observed on Pt_{metal} and Pt_{ox} sites in Figure S6.⁶⁷ Lastly, the retained symmetry and FHWM of the vibrational band of CO on Pt_{iso} during desorption is strong evidence that the Pt-CO species are homogeneous in nature, likely all located at a common adsorption site on the TiO2 support.68

With an understanding of the comparative strength of interaction of CO with the various adsorption sites, we also wanted to analyze the relative reactivity of CO bound to these sites in transient experiments. We focused on CO bound to Pt_{metal} and Pt_{ox} sites, because CO binds too weakly to Pt_{iso} sites to analyze reactivity in transient experiments. Figure 5(B) and (C) show IR spectra collected on respectively reduced and oxidized 1 wt% DI catalysts, during the following experimental protocol: CO adsorption to saturation at room temperature, He exposure at room temperature for 10 minutes, a 10% O₂/ He mixture for 10 minutes, and a temperature programmed oxidation (TPO) ramp ($\beta = 10 \text{ °C/min}$) to 500 °C in the 10% O_2 mixture. It is seen in Figure 5(B) that CO adsorbed to Pt_{metal} sites is stable in the presence of He at room temperature, consistent with Figure S6(A). Upon exposure to the 10% O₂/He mixture at room temperature, CO reacts to produce CO₂.³³ During the TPO, the remaining CO is converted to CO₂ almost completely by 120 °C, with only a small amount of CO adsorbed to Ptox sites (formed during the oxidation ramp) remaining intact until above 300 °C. This shows the high reactivity of CO on Pt_{metal} sites for oxidation by O2, as is well known.

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Conversely, in Figure 5(C) it was observed that CO bound to Pt_{ox} sites on the pre-oxidized 1 wt% DI catalyst is significantly less reactive than CO bound to Pt_{metal} sites observed in Figure 5(B), with minimal reactivity until > 160 °C. As in Figure 4(A), initially the pre-oxidized catalyst has some metallic character due to reduction of Pt_{ox} clusters by CO, as evidenced by the CO stretching frequencies characteristic of adsorption on Pt_{metal} sites (2040-2090 cm⁻¹). The difference in reactivity of CO bound to Pt_{ox} and Pt_{metal} sites is highlighted in Figure 5(C) by the almost complete loss in CO bound to Pt_{metal} sites following O_2 introduction at room temperature, with the retained existence of CO bound to Pt_{ox} sites until much higher temperature.

The TPD and TPO experiments on Pt_{iso} , Pt_{metal} and Pt_{ox} sites highlight several unique characteristics distinguishing site-specific spectroscopic and reactive characteristics of adsorbed CO. First, CO adsorption strength is in the order $Pt_{iso} << Pt_{metal} < Pt_{ox}$. Second, CO adsorbed to the Pt_{iso} species exhibit constant FWHM, band position, and band symmetry with changing coverage, which is in stark contrast to observations on Pt_{ox} and Pt_{metal} sites, demonstrating the homogeneity of the produced Pt_{iso} species and further substantiating the IR assignment.⁶⁸ Third, CO adsorbed to Pt_{ox} sites is significantly less reactive in O₂ than CO adsorbed to Pt_{metal} sites, suggesting Pt_{ox} sites play no role in steady state CO oxidation reactivity measurements on Pt/TiO_2 catalysts.

3.3 Steady-state CO oxidation reactivity of Pt_{iso} and Pt_{metal}

To directly compare the reactivity of Pt_{iso} and Pt_{metal} sites for the CO oxidation reaction, steady state measurements were executed under strict kinetic control as a function of temperature and reactant partial pressure. 1 wt% DI and 0.025 wt% SEA catalysts were used to compare the reactivity of these sites, as the 1 wt% DI material contains almost exclusively 1 nm Pt clusters, while the 0.025 wt% SEA material contained almost exclusively Pt_{iso} species. To minimize the partial pressure drop across the catalyst bed, hot spot formation, and mass transfer limitations, the catalysts were co-impregnated onto a SiO₂ gel support and further diluted in SiO₂, as described in the methods section. Flow rate dependent kinetic measurements provide evidence of kinetic control in the rate measurements, see Figure S1.



Figure 6. CO oxidation Kinetics. (A). Arrhenius plots showing temperature dependence of the per-gram Pt rate $(mol \cdot s^{-1} \cdot g_{Pt}^{-1})$ of CO oxidation on each catalyst from 160-200 °C in a 200 sccm flow of 1% CO, 1% O₂, balance He. (**B**) Linearized per-gram Pt rates $(mol \cdot s^{-1} \cdot g_{Pt}^{-1})$ as a function of CO and O₂ pressure. The reported data is an average of three unique sets of measurements on freshly loaded catalysts into the reactor, ensuring reproducibility.

The catalysts were reduced for 2 hours in 20 sccm of pure H₂ at 300 °C to ensure all clusters were Pt_{metal} and then were exposed to 1% CO, 1% O₂, 98% He at 200 °C for 10 hours to reach steady state reactivity. Figure 6(A) shows the rate of CO oxidation as a function of temperature over the two catalysts, where it was observed that the apparent activation energy (E_{app}) on the Pt_{iso} species is higher than on the 1 nm Pt_{metal} clusters (69 kJ/mol on Pt_{iso} versus 53 kJ/mol on Pt_{metal} sites). The measured E_{app} for both catalysts are consistent with previous measurements for CO oxidation over Pt on reducible supports, which range from 40-70 kJ/mol on CeO2⁶⁹ and 50-60 kJ/mol on TiO₂.⁷⁰ Higher barriers around 85 kJ/mol are typically observed when Pt is supported on non-reducible supports like Al₂O₃.^{52,71} Pt_{iso} species exhibited enhanced CO oxidation rates on a per gram Pt basis as compared to 1 nm Pt_{metal} clusters, ranging from 4x greater at 140 °C to 6x greater at 200 °C. Following CO chemisorption measurements for the 1 wt% DI catalyst to determine the number of available Pt sites, and assuming 100% dispersion for the 0.025 wt% SEA catalyst, rates were converted to turn over frequencies (TOF), see Figure S8. At 140 °C, the TOF on Pt_{iso} sites is ~12% higher than on 1 nm Pt_{metal} clusters, while at 200 $^{\circ}\text{C}$ the TOF is ~2x greater on Pt_{iso} compared to 1 nm Pt_{metal} clusters.



Figure 7. Catalyst stability under reaction conditions and in-situ analysis. IR spectrum of CO adsorbed at room temperature and saturation coverage to the 0.025 wt% Pt/TiO₂ SEA catalyst during a He flush prior to reaction, (**A**), and after 64 hours on stream, (**B**). (**C**) Insitu IR spectrum collected at 200 °C after 2hr of CO Oxidation (1% CO, 1% O₂, balance He) from the 0.025 wt% Pt/TiO₂ SEA catalyst. IR spectrum of CO adsorbed at room temperature and saturation coverage to the 1 wt% DI catalyst during a He flush prior to reaction, (**D**), and after 64 hours on stream, (**E**). The band centered at 2080 cm⁻¹ is assigned to CO on well-coordinated Pt_{metal} sites, CO-Pt_{metal,WC}, while the band centered at 2060 cm⁻¹ is assigned to CO on under_coordinated Pt_{metal} sites, CO-Pt_{metal,UC}. (**F**) In-situ IR spectrum collected at 200 °C after 2hr of CO Oxidation (1% CO, 1% O₂, balance He) from the 1 wt% Pt/TiO₂ SEA catalyst.

Partial pressure dependence measurements were made on the two catalysts at 200 °C, as shown in Figure 6(B). From the slopes of the linearized plots in Figure 6(B), we found that the reaction rate was not dependent on CO partial pressure and dependent on O2 partial pressure with a 1/2 order dependence, and thus we derived a consistent rate law on both catalysts of, Rate $\propto P_{o_2}^{1/2}$.^{69,72} The difference in rates between the 1 nm Pt_{metal} clusters and Pt_{iso} species in the partial pressure dependent measurements was comparable to the difference measured at 200 °C in the temperature dependent studies (Figure 6(A)), with Pt_{iso} species being 6-8x more reactive on a per g Pt basis. To ensure that the Pt_{iso} and 1 nm Pt_{metal} clusters retained their structures following the ~64 hours on stream under CO oxidation conditions that was required to obtain kinetic data, the two catalysts were characterized by CO probe molecule IR preand post-reaction. In Figure 7(A) and 7(B), the IR spectra associated with CO adsorbed to the 0.025 wt% SEA catalyst pre- and post-reaction is shown as a function of time in a He flow at room temperature. The pre- and post-reaction catalysts show almost identical spectra, with an 8 cm⁻¹ FWHM for CO adsorbed to Pt_{iso} at 2112 cm⁻¹ that displays a constant frequency and FWHM as CO

readily desorbs at room temperature. This is convincing evidence that the predominant Pt_{iso} structure is retained even after ${\sim}64$ hours on stream under CO oxidation conditions. Furthermore, to substantiate that kinetic measurements were not skewed by structural changes to the catalyst as it aged on the shelf between repetitive measurements, the 0.025 wt% SEA catalyst was characterized by CO probe molecule IR one month after initial synthesis and showed no change in the reported signatures CO on Pt_{iso} sites, see Figure S9, further substantiating the excellent stability of Pt_{iso} species in the catalyst architectures used in this study.

In Figure 7(D) and (F), the IR spectra of CO adsorbed to the reduced pre- and post-reaction 1% DI catalyst at saturation coverage and room temperature are shown. Some small changes in the shape of the CO IR spectrum in the post-reaction catalyst is evident, suggesting some restructuring of the Pt catalyst due to exposure to CO oxidation conditions, which has been reported previously.^{52,73} However, the reconstruction of Pt particles induced by CO oxidation conditions is minimal and known to occur on very rapid time scales prior to steady-state reactivity being reached, thus reconstruction did not influence the kinetic comparison. To obtain insights into the operating state of Pt_{iso} and Pt_{metal} clusters under CO oxidation conditions, in-situ IR spectra were taken at reaction conditions (1% CO, 1% O₂, 98% He at 200 °C) over a 2 hour period at which point subsequent spectra were identical, indicating steady state CO oxidation had been achieved. In Figure 7(C), a representative *in-situ* IR spectrum collected from the 0.025 wt% SEA catalyst spanning the CO and CO2 IR stretching frequencies is shown. Bands in the range of 2250-2400 cm⁻¹ shows that CO2 production is occurring, while the bands between 2150-2200 cm⁻¹ and 2050-2150 cm⁻¹ are associated with gas phase CO vibrations. Interestingly, there is no visible stretch associated with CO adsorbed to Ptiso sites under steady state reaction conditions. A small shoulder around 2060 cm⁻¹ is present, which is likely due to CO adsorbed to the minority of sub-nm Pt clusters present on the 0.025% SEA catalysts. The in-situ spectrum collected from the 1 wt% DI catalyst shows the presence of gas phase CO2 and CO, consistent with the 0.025 wt% catalyst, but two bands at 2080 and 2060 cm⁻¹ are also present, suggesting CO is adsorbed to Pt_{metal} sites at significant coverage under reaction conditions. Overlapping with the gas phase CO is a broad band associated with CO adsorbed to a cationic Pt site at 2120 cm⁻¹. The in-situ IR spectra provide an interesting insight that while the Pt_{iso} and 1 nm Pt_{metal} cluster active sites exhibit very similar rate laws, the coverage of CO on these sites under reaction conditions is quite different. The mechanistic implications of this result will be discussed below.

4. Discussion

Compared to previous reports where Pt_{iso} species were observed to form Pt clusters under oxidative conditions, reductive conditions, reaction conditions, or under an electron beam in a TEM, the Pt_{iso} species reported here on TiO₂ nanoparticles retained their structure and homogeneous distribution under all considered conditions.^{33,34,37} The lack of stability for most Pt_{iso} species under various conditions is not surprising, given the known mechanism of Pt sintering through Pt atom emission and migration on supports.⁷⁴ One approach to overcome the low stability of Pt_{iso} species is to provide anchoring sites, for example coordinatively unsaturated Al^{3+} sites or square planar binding pockets on CeO₂, where Pt_{iso} species bind particularly strongly.^{8,32,75,76} However, even in these cases there is no evidence that Pt_{iso} species remain stable under reduction conditions, which are required to differentiate the reactivity of Pt_{iso} species and Pt_{ox} clusters.

An alternative approach, which was proposed here, is to isolate a single Pt atom on a single support particle – effectively marooning Pt_{iso} species on TiO₂ islands – such that Pt aggregation would require an energetically unfavorable hop between support particles.⁷⁷ This idea has been proposed recently, where phosphotungstic or phosphomolybdic acids have been used to host single Pt or Rh atoms.^{78,79} These small acidic clusters are interesting supports for single metal atoms because they are well defined and small. However, the stability of these catalysts is limited by the low stability of the supports, which degrade below 200 °C, thus limiting their applicability.

The evident stability of the Pt_{iso} species reported here under a wide range of conditions, with no specific anchoring sites on the support, is suggestive that our synthesis strategy was successful in primarily depositing a single Pt atom per TiO₂ particle. In an analysis of the STEM imaging of the 0.05% SEA catalysts shown in Figure 3D, only 2 of the 30 images containing Pt_{iso} species showed evidence of multiple Pt_{iso} species per TiO₂ particle, see Figure S10 for examples. Even in these cases, overlapping TiO_2 particles in the images could not be ruled out as a source of close Pt_{iso} species proximity. Thus, the STEM imaging supported the hypothesis that primarily 1 Pt atom was deposited per TiO_2 particle.

This conclusion agrees with the observed trends in the influence of synthetic conditions on the production of Pt_{iso} species versus Pt clusters support this conclusion. For example, for catalysts synthesized at weight loadings consistent with having less than 1 Pt atom per TiO₂ particle (< 0.1 wt%), the IR signature of CO on Pt_{iso} species dominated, provided that the synthesis was executed under extremely dilute and homogeneously mixed conditions where the interaction between Pt ions and TiO2 particles in solution would be rare and thus the deposition of a single Pt ion per TiO₂ particle would be favored. Furthermore, weight loading dependent measurements shown in Figure S2 indicate that even when using optimized synthetic conditions, if the Pt weight loading dictated that on average there should be greater than 1 Pt atom per TiO2 particle then Pt cluster formation occurred. Together these considerations provide strong evidence that our synthetic strategy induced the deposition of ~1 Pt atom per TiO₂ particle when operating at sufficiently low weight loadings and that this architecture was the primary reason the Ptiso species exhibited excellent stability. The high stability was critical to differentiate the spectroscopic signatures and reactivity of the $Pt_{\mbox{\tiny iso}}$ species from $Pt_{\mbox{\tiny metal}}$ and $Pt_{\mbox{\tiny ox}}$ clusters.

We next focus on the IR spectra and adsorption energy of CO on the various Pt sites. CO adsorption on Pt surfaces, nanoparticles, and clusters has been studied in great detail using IR and TPD and our results on Pt_{metal} and Pt_{ox} clusters agree well with previous reports. CO adsorbed to 1 nm Ptmetal clusters on the 1 wt% DI catalyst exhibited two distinct bands centered at 2077 cm⁻¹ and 2058 cm⁻¹ respectively assigned to CO adsorbed to WC and UC Pt atoms on the clusters.^{52,58,61,62} Greater intensity was observed for the band associated with CO adsorption on UC sites, which is consistent with the expected higher concentration of UC sites compared to WC sites given the distribution of Pt cluster and particle sizes observed by STEM (1 nm diameter clusters with some 4 nm particles). On the pre-oxidized 1 wt% DI catalyst, the IR spectrum of adsorbed CO exhibited a broad band at 2118 cm⁻¹ that was assigned to CO adsorption on Ptox clusters.⁶⁴ This assignment has been made previously and was substantiated here by STEM analysis showing constant Pt particle size regardless of reduction or oxidation pretreatment, Figure S5. The blueshifted stretching frequency of CO adsorbed to Pt_{ox} clusters, compared to Pt_{metal} clusters of the same size, derives from the decreased charge transfer to CO, due to the cationic oxidation state of Pt in Pt_{ox} clusters. All of the IR analysis is consistent with previous results.^{40,45,64}

The adsorption energy of CO was observed by TPD to be stronger on Pt_{ox} clusters than on Pt_{metal} clusters, indicated by the higher desorption temperature. This is in line with previous results where the maximum rate of CO desorption from Pt_{ox} was observed to occur at temperatures 100 °C higher than on Pt_{metal} (280 °C for Pt_{ox} versus 180 °C for Pt_{metal}) during TPD experiments from reduced and oxidized Pt single crystals.^{47,48} The stronger adsorption energy of CO on Pt_{ox} clusters explains why these sites exhibit extremely low reactivity for CO oxidation – CO poisons the catalytic surface. This also highlights the importance of differentiating Pt_{iso} and Pt_{ox} species in analysis of reactivity, because without differentiation the large adsorption energy of CO and low CO oxidation reactivity on Pt_{ox} could confuse the inherent reactivity of Pt_{iso} sites. While IR spectroscopic analysis of CO bound to Pt_{metal} and Pt_{ox} clusters is abundant in literature, there are far fewer rigorous analyses of CO bound to oxide supported Ptiso species. Previous reports of the vibrational frequency for assigned bands associated with CO bound to Ptiso species vary with changes in the support (Ptiso/H-Mordenite,⁴⁰ 2123 cm⁻¹; Pt_{iso}/H-ZSM-5,³³ 2115 cm⁻¹; Pt_{iso}/CeO₂, 2095 cm⁻¹;³² Pt_{iso}/FeO_x,²⁷ 2080 cm⁻¹), but are generally comparable to 2112 cm⁻¹ reported here for Pt_{iso}/TiO₂. The variation in band position of CO bound to Ptiso species is likely caused by varying interactions of the Pt_{iso} species with the support, where previous studies have found that the stretching frequency of CO bound to supported metals redshifts when going from more acidic to more basic supports.⁶⁸ Consistent in all reports is the ~40 cm⁻¹ blueshift of the frequency of the CO stretch when bound to Ptiso species compared to Pt_{metal} clusters. The common blueshifted CO stretching frequency on Pt_{iso} species derives from the cationic oxidation state (likely 2+), which stems from direct coordination of Ptiso with oxygen atoms on the oxide support. Additionally, similar to a few of the previous reports, the band associated with CO stretching when adsorbed to Ptiso/TiO2 was observed to exhibit a constant frequency as a function of CO coverage, which occurs due to the lack of dipole-dipole coupling of adjacent CO ligands on dispersed adsorption sites, and is a critical spectroscopic signature of CO bound to isolated metal sites.^{27,40,44}

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59 60 Two emerging and important questions associated with single metal atom catalysts on oxide supports are: (1) Are these single site catalysts, meaning all metal atoms sit on the same site on the support, or are metal atoms distributed over many types of sites on the support? (2) Where on the support the precious metal atoms sit?

It has been proposed that the FWHM of the adsorbed CO stretching band can be used to qualitatively address the question of how homogeneously the metal atoms are distributed on a support, with the idea that a broader CO band FWHM is suggestive of isolated metal atoms sitting in a variety of local environments, which creates a range of varying interactions between the metal atom and CO.68 Previous reports of IR spectra for CO adsorbed to Ptiso species have shown relatively broad FWHM, ranging from 15 to > 30 cm⁻¹ (Pt_i- $_{so}/H$ -Mordenite,⁴⁰ ~18 cm⁻¹; Pt_{iso}/H-ZSM-5,³³ ~25 cm⁻¹; Pt_i- $_{so}/CeO_2$, ³² 30 cm⁻¹; Pt_{iso}/FeO_x, ²⁷ >30 cm⁻¹), signifying that Pt_{iso} species are adsorbed to a range of different sites on the support. In comparison, we report much tighter FWHM between 6-10 cm⁻¹ for the CO stretching band when adsorbed to Ptiso/TiO2, which is indicative that the Ptiso species are homogeneously distributed at a single, or a few very similar, adsorption site on the TiO2 support. A recent analysis of Ir single atoms on carefully prepared zeolite supports reported a ~5 cm⁻¹ FWHM, which compared well to a 4 cm⁻¹ FWHM for a homogeneous organometallic Ir carbonyl complex in solution, revealing that the zeolite supported single Ir atoms is likely a single site material. Comparing the Ir case to the 6 cm⁻¹ FWHM observed for the CO stretch when adsorbed to Pt_{iso}/TiO₂ observed here, it seems that our synthetic approach is able to localize the Pt_{iso} species at a single adsorption site on TiO2, although we do not have a homogeneous Pt-CO analogue for direct comparison to prove this. Interestingly, it can be seen in Figure 2B that when catalysts were synthesized with lower pH the CO band broadens (for example to a FWHM of 22 cm⁻¹ at a synthesis pH of 8) and loses symmetry, suggesting the existence of Ptiso species at multiple adsorption sites on the TiO2 support. It seems that careful control of synthetic conditions are required to deposit Ptiso species at consistent sites on the support.

While we cannot comment directly on the structure of the TiO₂ site where Pt_{iso} predominantly adsorbed, we can use the observed CO adsorption strength to infer some characteristics of the site. A very weak adsorption energy of CO on Pt_{iso}/TiO_2 can be inferred from the observed facile desorption of CO at room temperature in an inert atmosphere. This is similar to the predicted weak adsorption on CO on Ptiso species adsorbed in square planar configurations to CeO2 surfaces, where the Pt_{iso} species is calculated to be adsorbed very strongly to CeO2.^{8,29} Thus, it is hypothesized that Pt_{iso} species reported here are bound to a location (or a few similar locations) on the TiO₂ support with a very strong adsorption energy, such that their strong coordination to the support reduces the binding energy of CO. The weak Pt-CO interaction for Pt_{iso}/TiO₂ reported here suggests that CO does not render the Pt atom mobile as has previously been observed,⁸⁰ which is in agreement with the tight FHWM of the CO stretching frequency that indicates Pt is primarily located at a single location on the support.

A previous report examined the adsorption location of Pt_{iso} species on rutile TiO₂, which suggest O-vacancies are the most stable sites, although this information cannot be directly related to our work because the TiO₂ support nanoparticles were 100% anatase.⁸¹ However, given the small size and high density of defects that are expected to exist on 5 nm diameter anatase crystals used as supports in this study, it would not be surprising if the predominant adsorption site for Pt_{iso} species was a defect or step site on TiO₂. It should be noted that it is possible that impurities in the TiO₂ could provide an anchoring site for Ptiso species, although the quantity of any single impurity in the TiO2 used here is smaller than the amount of Pt, suggesting impurities did not provide a stable binding site. Our results are suggestive that the Ptiso species analyzed here are essentially single site materials, and that Ptiso is adsorbed strongly enough to the TiO₂ support to minimize metal atom mobility, creating a weak interaction with CO.

An interesting apparent paradox that emerges from our results is the significant difference in CO adsorption energy on Pt_{iso} species and Pt_{ox} clusters. The Pt_{ox} clusters form from partial CO reduction of pre-oxidized Pt_{metal} clusters, and contain CO adsorption sites that are characteristic of Pt^{2+} and Pt^{0} , Figure 4 and 5. We propose that on these partially oxidized Pt clusters, some Pt^{2+} species remain in under-coordinated geometries, perhaps bound locally to only 2 oxygen atoms, enabling strong binding to CO. Conversely, the weak binding between Pt_{iso} species and CO suggests that these Pt^{2+} species are strongly locally coordinated to oxygen atoms in TiO₂. We propose that the two Pt species with apparently similar oxidation state (likely Pt^{2+}) exhibit strong differences in interaction strength with CO due to differences in their local coordination.⁸² These details will be explored more in the future.

Next we discuss the steady-state CO oxidation reactivity of Pt_{i-so}/TiO₂, and comparative reactivity of 1 nm Pt_{metal} clusters on TiO₂, in the context of previous reports for Pt_{iso} on other supports. A previous report of CO oxidation over Pt/FeO_x catalysts showed a ~2-fold increase in CO oxidation TOF for Pt_{iso} sites compared to Pt_{metal} sites on 1 nm Pt clusters, which is in excellent agreement with our results for similar Pt species on TiO₂.²⁷ However, the Pt_{iso}/FeO_x catalyst exhibited significantly higher CO oxidation TOF as compared to our reported Pt_{iso}/TiO₂ catalyst, where the same TOF (~0.1 s⁻¹) observed on Pt_{iso}/TiO₂ at 200 °C was observed at room temperature for Pt_{iso}/FeO_x. More recently, it was reported that Fe₂O₃ supported Pt_{iso}/TiO₂ reported when correcting for differences in

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 O_2 partial pressure.⁸³ ZnO supported Pt_{iso} was also examined in the same report showing almost identical TOFs (when corrected for differences in O_2 partial pressure) as observed here for TiO₂. We attribute reactivity differences for Pt_{iso} on these reducible supports to differences in the activation energy for oxygen abstraction from the supports, as discussed below.⁸⁴

In contrast to the comparison with Ptiso reducible supports, Ptiso/TiO2 exhibited significantly higher reactivity for CO oxidation as compared to Pt_{iso}/Θ -Al₂O₃³⁴ and Pt_{iso}/γ -Al₂O₃.⁸³ Pt_{iso}/TiO_2 showed ~10x higher TOF compared to Pt_{iso}/Θ -Al₂O₃ at 200°C (0.013 s⁻¹ vs $.11 \text{ s}^{-1}$) despite the 3.7x higher oxygen partial pressure in the experiments on Pt_{iso}/Θ -Al₂O₃, which given our deduced rate law suggest a 20x higher inherent TOF for CO oxidation on Pt_{iso}/TiO₂. Similarly, ~4x higher TOF was observed compared to Pt_{iso}/γ -Al₂O₃ despite 4x higher oxygen partial pressure, suggesting roughly 8x higher inherent TOF for CO oxidation on Pt_{iso}/TiO₂. A comparison of CO oxidation on Pt_{iso}/Θ -Al₂O₃ and 1 nm Pt_{metal} clusters on Θ -Al₂O₃ showed a 5x higher reactivity for Pt_{metal} clusters. This can be understood by the required activation of oxygen from Θ -Al₂O₃ in the catalytic cycle on Ptiso, which is energetically difficult, compared to the known CO oxidation mechanism on Al₂O₃ supported Pt clusters where the entire reaction cycle occurs on Pt.52,71

Pt_{iso} species in a KLTL zeolite were reported to achieve TOFs of 0.0038 s⁻¹ prior to oxidation of tetraamine Pt complexes, and 0.012 s⁻¹ following oxidation of the catalysts when operating at 150 °C in 1% CO, 5% O₂, 94% He at atmospheric pressure.³⁵ On Pt_{iso}/TiO₂ at 150 °C and 5x lower O₂ partial pressure a TOF of 0.015 s⁻¹ was measured, which suggests that at the same O₂ partial pressure the Pt_{iso}/TiO₂ catalyst would be ~3x more active than the Pt_{iso}/KLTL catalyst. In this case no direct comparison to the reactivity of Pt clusters was made. We find that the reactivity of Pt_{iso} is highly dependent on the support, and that only for reducible oxide supported Pt_{iso} species is the CO oxidation reactivity of Pt_{iso} enhanced compared to Pt_{metal} clusters.

To interpret the support dependent reactivity of Pt_{iso} apparent from literature and the site dependent reactivity of Pt_{iso} versus 1 nm Pt_{metal} species we observed, we consider the observed CO oxidation rate law and activation barriers. Both the Ptiso and the 1 nm Ptmetal containing catalysts on TiO22 exhibited identical rate laws with half order dependence in O2 partial pressure and zero order dependence in CO partial pressure. This is consistent with CO oxidation measurements made under similar conditions on CeO2 supported Rh, Pt, Pd and Ni particles.^{69,72} We observed via *in-situ* IR that the Ptiso species had low steady state coverage of CO, while the Ptmetal sites have significant coverage of CO under reaction conditions. However, the observation of CO coverage on Pt_{metal} sites under reaction conditions does not mean that there is a significant coverage of CO on sites at the interface between Pt_{metal} clusters and the TiO2 surface, where direct bonding between Pt and oxygen on TiO2 renders Pt atoms cationic.

These results suggest that the reaction proceeds via a Mars van Krevlen mechanism on both TiO_2 supported Pt structures, where the rate-limiting step involves the migration of atomic oxygen from TiO_2 onto Pt_{iso} or interfacial Pt atoms on Pt_{metal} clusters, which is known as reverse oxygen spillover.^{29,69,85} The half order reaction dependence in O_2 partial pressure demonstrates that O_2 dissociation is an unlikely rate limiting step, as this would produce a first order O_2 dependence.^{69,72} The hypothesis of reverse oxygen spillover from TiO_2 to interfacial Pt atoms occurring in the catalytic cycle and being the rate-limiting step is consistent with well-known behavior of late transition metals promoting the reducibility of oxides.⁸² For example, it was inferred from microkinetic modeling that under water gas shift reaction conditions on Pt/TiO₂ catalysts, a non-negligible concentration of oxygen vacancies at the Pt/TiO₂ interface could be stable. This is in contrast to the low vacancy concentration on bare TiO₂ under the same conditions.^{82,86} Experimental studies using isotopic labeling of oxygen have also implicated oxygen atoms in TiO₂ as active species in the water gas shift reaction on Pt/TiO₂ catalysts.⁸⁷

In addition to evidence that Pt can promote the reducibility of TiO₂, there is strong evidence of relatively facile reverse oxygen spillover from oxides to small metal clusters and single atoms. For example, it has been demonstrated via experiments and theoretical calculations that reverse oxygen spillover from CeO₂ to Pt (or Rh) is an exothermic process and can occur under mild conditions.^{88,89} Furthermore, it has been shown via theoretical calculations that for small Ru and Ni clusters on TiO₂, reverse oxygen spillover is energetically thermoneutral or exothermic and it was further postulated that this process would be more exothermic on nanoparticles of TiO₂, as were used in our experiments, compared to extended TiO₂ surfaces used in the models. Thus, we conclude that oxygen migration from TiO₂ to interfacial Pt species could be both energetically feasible and the rate limiting step under the explored CO oxidation conditions consistent with our partial pressure dependent measurements and with precedent from previous analyses of reverse oxygen spillover and the known ability of metals to promote oxide reducibility.90,91

In addition to addressing the half order dependence of rate on O2 partial pressure, it is important to understand mechanistically how there could be a lack of dependence on CO partial pressure. The lack of CO partial pressure dependence requires that neither gas phase CO nor adsorbed CO be involved in the rate-limiting step and further that the coverage of CO on the active site is essentially zero. For the case of Ptiso active sites, in-situ IR analysis showed no measurable coverage of CO on Ptiso species, which is consistent with kinetic assessments based on the observed partial pressure dependences. However, on the 1 nm Pt_{metal} clusters, significant CO coverage was observed under reaction conditions. It is proposed that interfacial Pt atoms, which are cationic due to coordination with oxygen atoms at the TiO2 surface, exhibit reduced CO binding energies compared to metallic Pt atoms that exist on the clusters away from the interface.^{46,83,87,92-94} The reduced CO binding energy at interfacial Pt atoms, which are coordinated to both the Pt cluster and the support, minimizes CO coverage under reaction conditions, enabling a mechanism and rate law that is consistent with observations on Pt_{iso} species.

The involvement of support oxygen in the CO oxidation catalytic cycles on $P_{t_{iso}}$ species suggests the support dependent TOF measured for CO oxidation on $P_{t_{iso}}$ (inferred from comparison to literature) likely stems from the differing activation energy associated with abstraction of atomic oxygen from the oxide support. This can be further understood by considering the measured CO oxidation E_{app} and rate law compared to previous measurements. CO oxidation by Pt_{metal} clusters supported on Al_2O_3 under similar conditions as reported here shows an E_{app} of ~85 kJ/mol, a rate law that is first order in O_2 and negative first order in CO, and further shows significantly lower TOF than reported here for Pt/TiO_2 . These differences provide evidence that the entire reaction cycle occurs on WC sites on the Pt_{metal} clusters and that the Pt_{metal} surface is saturated by CO.^{52,71} Comparison to the Pt/TiO_2 results for both Pt_{iso} and Pt_{metal}

sites (where a different rate law and decreased E_{app} were observed) strongly suggests that the CO oxidation mechanism is different under identical conditions for reducible and non-reducible oxide supported Pt structures, and that the difference stems from the participation of the support in the catalytic cycle on reducible oxides. It is hypothesized that the lower E_{app} observed for 1 nm Pt_{metal} clusters compared to Pt_{iso} on TiO₂ (53 versus 68 kJ/mol) is due to the weaker influence of Pt_{iso} species on the reducibility of TiO₂ and as a result the increased barrier for oxygen migration onto Pt sites. Even with the increased barrier on Pt_{iso}, the TOF for CO oxidation is greater than on 1 nm Pt_{metal} clusters, which indicates that more of the total exposed sites in the Pt_{iso}/TiO₂ catalyst are active sites for CO oxidation as compared to on 1 nm Pt_{metal} clusters.



Figure 8. Proposed scheme of the active site of Pt_{iso} and Pt_{metal} clusters. The scheme highlights the proposed active sites (green) for Pt_{iso} and Pt_{metal} species in CO oxidation. All Pt_{iso} sites are active, while on 1 nm Pt_{metal} clusters, only 33% of total atoms (or about 60% of exposed surface atoms) are active interfacial sites. The blue Pt atoms are non-active sites, which are saturated with CO under reaction conditions but are proposed not to participate in the reaction.

Based on the above analysis we propose that the catalytic CO oxidation cycle for both 1 nm Pt_{metal} clusters and Pt_{iso} species involves reverse oxygen spillover from TiO2 to interfacial Pt atoms in the rate-limiting step. The interfacial Pt atoms in these structures are suggested to be well-coordinated to their local environment and cationic, causing the CO adsorption energy to be relatively weakened mitigating CO poisoning that is well known for metallic Pt atoms under similar conditions. It is important to point out that if cationic Pt atoms exist in an under-coordinated local environment and thus bind CO more strongly, as seen for our Ptox case, these sites will be poisoned by CO until the oxygen is abstracted to form metallic sites. Thus, a careful balance between charge on the Pt atom and coordination to local environment, in addition to existence at an interface with a reducible oxide that enables reverse oxygen spillover, is requisite for forming the most active sites on reducible oxide supported Pt structures.

This hypothesis is consistent with recent work analyzing 2 to 20 nm Pt, Pd and Ni particles on CeO_2 where a model was developed that related the concentration of interfacial metal atoms to the CO oxidation TOF, but extends this trend down to the limit of a single metal atom active site. As the fraction of total metal atoms existing at the interface increases 10x when shrinking clusters from 2 nm down to a single atom, this significantly benefits metal utilization efficiency. A comparison of the CO oxidation rate per-gram Pt and TOF on the Pt_{iso} and 1 nm Pt_{metal} clusters on TiO2 support this conclusion, where a proposed 1 nm Pt cluster structure is shown in Figure 8. Assuming interfacial Pt atoms are the only active site,

catalysts containing exclusively Ptiso species are predicted to be 3x more active on a per-gram Pt basis compared to 1 nm Pt_{metal} clusters, whereas a 4-6x difference was measured; similarly Pt_{iso} are predicted to have a 1.75x greater TOF than the 1 nm Pt_{metal} clusters, whereas a ~1.12-2x difference was measured. The agreement between the relative measured rates and model predicted values is quite good considering the calculated rates and TOFs assumed a 1 nm Pt cluster structure while STEM analysis confirmed a few larger Pt particles existed in the 1 wt% DI catalyst and that there was a small difference in the activation barrier of the two sites (Pt_{iso} vs Pt_{metal}) stemming from their differing ability to induce support reduction. Therefore, it is concluded that Ptiso/TiO2 catalysts are the most efficient utilization of Pt in CO oxidation when supported on TiO₂, because every atom is exposed for catalysis and interfaces with support which provides relatively mobile O atoms for the catalytic cycle via reverse oxygen spillover and weakens the CO binding energy.

Conclusions

In conclusion, we demonstrated a synthetic approach and catalyst architecture where Pt_{iso} species were dispersed on 5 nm diameter TiO₂ particles at a ratio of < 1 Pt atom per TiO₂ particle, creating Ptiso species that were stable through a wide range of conditions. Using a correlated STEM imaging and CO probe molecule IR characterization approach, distinguishing IR signatures of CO bound to Ptiso, Ptox clusters and Ptmetal clusters on TiO2 were identified that allow rapid identification and characterization of each type of site. It was found that the Pt_{iso} species produced through the SEA synthesis approach were essentially single-site species, inferred from the tight ~6-8 cm⁻¹ FWHM of the adsorbed CO stretching band. Using the inferred spectroscopic signatures, the order of CO adsorption energy on these sites was identified to be Ptiso<< Ptmetal < Ptox, where adsorbed CO on Ptox was essentially inactive for oxidation of CO below ~200 °C. Rigorous kinetic measurements for steady state CO oxidation on Ptiso and 1 nm Ptmetal clusters showed that the Pt_{iso} sites are inherently more reactive because every Pt atom on the catalyst interfaces with the support where the reaction takes place and is exposed to reactants. This work demonstrates that Pt_{iso} on certain reducible supports provide the most efficient metal utilization for CO oxidation and further that the architecture and synthetic approach proposed here could be generally useful for probing spectroscopic signatures and reactivity of isolated previous metal atom catalysts.

ASSOCIATED CONTENT

Supporting Information. Figures S1-10 and associated discussion are provided in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

P.C. acknowledges funding from University of California, Riverside, and National Science Foundation (NSF) CAREER grant number

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59 60 CBET-1554112. XP and GWG acknowledge NSF Grant CBET-1159240 for partial support. STEM Imaging was performed at the Irvine Materials Research Institute (IMRI).

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