Dual role of CO in the stability of subnano Pt clusters at the Fe₃O₄(001) surface

Roland Bliemᵃ, Jessi E. S. van der Hoevenᵇ, Jan Hulvaᵃ, Jiri Pavelec³, Oscar Gamba⁴, Petra E. de Jonghᵇ, Michael Schmid⁴, Peter Blaha⁴, Ulrike Diebold⁴, and Gareth S. Parkinsonᵃᵇ

ᵃInstitute of Applied Physics, TU Wien, 1050 Vienna, Austria; ⁣ᵇInorganic Chemistry and Catalysis, Debye Institute for Nanomaterials, Utrecht University, NL-3584 CG Utrecht, The Netherlands; and ⁣ᶜInstitute of Materials Chemistry, TU Wien, 1040 Vienna, Austria

Edited by Thomas E. Mallouk, The Pennsylvania State University, University Park, PA, and approved June 17, 2016 (received for review April 7, 2016)

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Significance

The catalytic activity of metal particles is highly size-dependent in the subnanometer regime, which makes understanding how and why particle sizes change in reactive atmospheres particularly important. Here, we show that carbon monoxide plays a dual role in the coarsening of otherwise highly stable Pt atoms on an Fe₃O₄(001) support: CO adsorption weakens the adatom–support interaction inducing mobility, and stabilizes the Pt dimers against decay into two adatoms. Our results illustrate how molecules modify the clustering dynamics on surfaces, provide much-needed insight into how deactivation and redispersion can occur in single-atom catalyst systems, and demonstrate an approach to prepare size-distinguished clusters for studies of the size effect.


The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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¹To whom correspondence should be addressed. Email: parkinson@ip.tuwien.ac.at.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1605649113/-/DCSupplemental.

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process at room temperature (of the order of $10^{-3} \text{ s}^{-1}$ for an excitation frequency of $10^{13} \text{ s}^{-1}$). Annealing to 280 °C in UHV reduces the coverage of Pt adatoms drastically, allowing the conclusion that the transition is thermally induced and the remaining Pt features are likely stabilized by surface defects.

In Fig. 2, we show that CO adsorption on Pt adatoms presents a clear signature in STM that can be interpreted with the aid of DFT+U calculations. Fig. 2A–D shows a sequence of STM images acquired while exposing 0.15 ML Pt adatoms to $2 \times 10^{-10}$ mbar CO. The Pt adatoms are labeled before CO exposure ($P < 10^{-10}$ mbar), contains several Pt and Pt adatoms and a bright, double-lobed feature in the center of the scanning area. Increasing the CO pressure to $2 \times 10^{-10}$ mbar (Fig. 2B) results in a second double-lobed feature at the former position of a Pt adatom (labeled Pt–CO), and a new, single-lobed feature at the former position of a Pt adatom (labeled Pt–CO). Between Fig. 2B and D, transitions between the Pt–CO and Pt–CO state occur. Likely, both entities are chemically identical, i.e., they consist of one Pt atom and one CO molecule. The only difference between these species would be their adsorption geometry. To check whether adsorption of another molecule from the residual gas could be responsible for the observed features, we also exposed the as-deposited Pt adatoms to the most common components of the residual gas as measured by a quadrupole mass spectrometer: H, CO, CO, CH, H, and O. The presence of trace amounts of O in our vacuum system is linked to the use of this gas during sample preparation.) No bond formation or other interactions with the Pt adatoms were observed for any gas molecule other than CO at room temperature.

DFT+U calculations for CO adsorption on Pt adatoms are consistent with strong Pt–CO binding. The configuration of Pt–CO shown in Fig. 2E is favored by 5.53 eV compared with a free

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**Fig. 1.** (A) STM image of 0.2 ML Pt/Fe$_3$O$_4$ (001). The surface Fe$_{oct}$ atoms are imaged as rows along the [110] direction (illustrated by the parallel blue lines). The bright features on the rows of Fe (example highlighted by cyan arrow) are due to surface OH groups (37, 38). The red and yellow frames highlight Pt adatoms in two different geometries: bridging surface O atoms in between (Pt$_1$) and parallel to (Pt$_1^*$) the Fe$_{oct}$ rows. (B and C) DFT+U-based force-relaxed structural models of the two adsorption configurations.

**Fig. 2.** CO adsorption and Pt site interchange. (A–D) STM image sequence (same place) acquired during exposure to $2 \times 10^{-10}$ mbar CO. (A) Pt adatoms in two configurations (Pt$_1$, Pt$_1^*$) and bright, double-lobed features are observed. (B) CO adsorption on Pt$_1$ and Pt$_1^*$ adatoms results in bright, double-lobed and oval features, respectively. (C) The Pt$_1^*$–CO labeled in red in B changes site, transforming into a Pt$_1$–CO feature. (D) The Pt$_1$–CO formed and labeled in cyan in B transforms into a Pt$_1^*$–CO feature. (E) Structural model of Pt$_1$–CO/Fe$_3$O$_4$(001). Upon adsorption of CO, the Pt adatom is lifted up and shifts perpendicular to the Fe rows to an off-centered position. (F) Simulated STM images at +2 V sample bias: Pt adatom, Pt$_1^*$ adatom, Pt$_1$–CO, mirrored Pt$_1$–CO. The latter is an overlay image of Pt$_1$–CO in the two equivalent off-centered positions to simulate switching during the scan, induced thermally or by the STM tip.
Pt atom and a free CO molecule in vacuum. The Pt$_1$ adatom is lifted up by $\sim$1.3 Å away from the surface plane, and shifted perpendicular to the surface Fe-row direction. In this asymmetric geometry, one Pt–O bond is stretched to $\sim$2.98 Å, which compares to $\sim$2.03 Å for the second Pt–O bond and $\sim$1.98 Å for both Pt–O bonds before CO adsorption. In STM images at 78 K (Fig. S2) and in simulated STM images (Fig. 2F) the Pt$_1$ carbonyl is imaged as a single, bright, oval protrusion, offset from the center of the Pt adsorption site. This resembles one of the two lobes observed in experiment. When this feature is scanned with a sample bias of +2 V (Fig. S2C), the protrusion switches repeatedly from one side of the unit cell to the other, suggesting that the STM tip can move the Pt–CO between two nearby sites that are energetically and symmetrically equivalent. Similar tip-induced switching behavior has been observed for dangling bond pairs on hydrogenated semiconductor surfaces (41, 42). To estimate the switching barrier we calculated the DFT energy of the likely transition state, a Pt$_1$–CO species centered between the Fe$_{oct}$ rows. We found this energy to be only $\sim$0.25 eV higher than the minima, suggesting that the double-lobed feature observed at room temperature is a time average of thermally activated switching. The Pt$_1$*-adatom is also lifted up from the surface (by $\sim$0.7 Å) by CO adsorption, but remains in the same location laterally. We considered the possibility that the double-lobed feature could be a Pt$_1$–(CO)$_2$ species. However, we never observed a different type of CO adsorption event, which would lead to Pt$_1$–CO in this case, although it should be clearly visible in STM. Moreover, the observed switching between the Pt$_1$*-CO and Pt$_1$–CO states agrees well with the energies derived from the DFT+U calculations.

Fig. 3 shows STM images of Pt/Fe$_2$O$_4$(001) in a constant CO pressure of $2 \times 10^{-10}$ mbar, selected from a 55-frame movie acquired over approximately 3 h. The CO induces mobility, and Pt clusters are formed over time. The sizes of the individual clusters are determined by tracking each individual Pt atom. Fig. 3A shows a large-area image of the surface after 10 min of CO exposure. The yellow frame highlights a smaller region selected for detailed analysis in Fig. 3B–G. In Fig. 3B–D, Pt adatoms are observed, two in Pt$_1$, configuration and two in Pt$_{2+}$ configuration. Going through the panels from left to right we find that CO adsorbs initially on one Pt$_1$ and one Pt$_{1+}$ (Fig. 3C), and that the CO feature then coalesces with the remaining Pt$_1$*-adatom to form a Pt dimer in Fig. 3D. The Pt$_1$*-CO subsequently joins the dimer to form a trimer in Fig. 3E. Finally, the remaining Pt$_1$ adatom adsorbs a CO molecule in Fig. 3F, and coalesces with the trimer to form a Pt tetramer in Fig. 3G. It should be emphasized that, because of tip convolution effects, the identification of cluster sizes by their appearance is very hard if not impossible with STM (43). With our approach, the STM signature of the different cluster sizes can be ascertained, which allows determining the exact number of Pt atoms contained within each cluster in the larger scanned area (Fig. 3F). In Fig. 3 the largest clusters contain four atoms. The cluster size distribution in areas scanned with the STM during the CO exposure is comparable to those in areas located further away. Thus, the Pt$_1$–CO mobility and sintering is not induced by the STM tip.

It is important to note that the Pt carbonyl is the only diffusing species observed in the STM movies. Dimers, trimers, and larger clusters are immobile, even in CO pressures up to $10^{-6}$ mbar. Fig. 4A shows an STM image of 0.15 ML Pt/Fe$_2$O$_4$(001) acquired as part of a different STM movie starting from adatoms where the CO pressure was increased up to $10^{-6}$ mbar in a stepwise manner. As in Fig. 3, we determine the number of Pt atoms in each cluster by watching its assembly. The resulting size distribution is narrow, ranging from one to five atoms. The majority of clusters contain two or three atoms. The bar graph illustrates the number density of Pt clusters (blue, 71.5 ± 4.7% of all features, $5.69 \times 10^{16}$ clusters per m$^2$) versus the adatom phase (yellow, $2.27 \times 10^{16}$ adatoms per m$^2$). The graph represents the average from two experiments in which 0.15 ML Pt adatoms were sintered in different amounts of CO. In both cases the remaining adatom density was between 0.01 and 0.02 ML. The shaded area corresponds to the respective standard deviation.

To investigate the stability of the subnano clusters formed by CO-induced sintering at reaction temperatures, we heated the surface to 520 K in UHV. The average coverage of Pt adatoms increased by almost 130%, and the number of clusters decreased by more than 60%. The remaining clusters were larger, with an average size of $\sim$7.6 atoms ($\sim$3.3 atoms before annealing). This trend is again illustrated by the bar graph beneath the STM image in Fig. 4B, which clearly shows that adatoms are the dominant Pt-related feature after annealing (71.2 ± 8.9%). The complete absence of small clusters suggests that these species are unstable without CO, and that CO desorption drives the breakup. In a control experiment, the
adatoms were heated in UHV without prior exposure to CO. This treatment leads to a small decrease in the adatom density, but no discernible change in the cluster density. This suggests that the adatoms become mobile at 520 K and can incorporate within existing clusters. Crucially, the constant cluster density highlights the importance of CO for new cluster nucleation. The crucial role of CO for the stability of the clusters is supported by the XPS measurements in Fig. 5, which show that CO was adsorbed on the clusters following room-temperature exposure, but desorbs after heating to 520 K. Before CO exposure (blue curves) the Pt 4f\textsubscript{7/2} peak at 71.4 eV resembles that of metallic Pt, consistent with the very small electron transfer predicted by DFT\textsuperscript{+U}. Following 120 L CO exposure (red) a peak appears in the C 1s region at 287.7 eV, which is higher than CO adsorbed in an atop site on Pt(111) (286.8 eV). The adsorption of the CO causes the Pt 4f to shift up in binding energy to 72.4 eV, which is also higher than when CO is adsorbed atop on Pt(111). Finally, heating above the desorption temperature of CO on Pt (∼500 K), the peak in C 1s is gone and the Pt 4f peak shifts back to the metallic position. Note that CO does not adsorb on the pristine Fe\textsubscript{3}O\textsubscript{4}(001) surface at room temperature, where all experiments were performed.

The assertion that Pt cluster stability is linked to adsorbed CO is supported by DFT\textsuperscript{+U} calculations. In the absence of CO, two Pt\textsubscript{1} isolated adatoms are preferred to a Pt dimer (two adatoms: 7.78 eV, one Pt dimer: 6.35 eV with respect to Pt in the gas phase). A Pt\textsubscript{2}(CO)\textsubscript{1} species is also unfavorable with respect to one Pt\textsubscript{1} carbonyl and one adatom (E[Pt\textsubscript{2}(CO)] = 8.44 eV and E[Pt\textsubscript{1} + Pt\textsubscript{1}CO] = 3.89 eV + 5.53 eV = 9.42 eV). Crucially, a Pt dimer with two adsorbed CO molecules is slightly more stable than two Pt\textsubscript{1}–CO species (11.16 eV compared with 11.06 eV). Thus, the formation of dimers can only proceed in the presence of (at least) two adsorbed CO molecules. When CO is desorbed, the strong Pt\textsubscript{1}/Fe\textsubscript{3}O\textsubscript{4} interaction leads to a redispersion of Pt, and a partial recovery of the adatom phase.

Discussion

The agglomeration phenomena described here are a clear case of gas-induced coarsening, a well-known process that causes
catalyst deactivation. Nevertheless, unequivocal identification of the mobile species is rare, and through our combined use of STM, XPS, and DFT, we clearly demonstrate that a Pt–CO species drives the coalescence of single Pt atoms into clusters. Moreover, we demonstrate this occurs because the adsorption of the CO molecule weakens the Pt–O bonds, facilitating diffusion. Adsorption of one CO (which, as argued above, appears as a double-lobed feature in STM) is sufficient to allow the Pt to move across the surface.

In recent years knowledge of the size effect in subnano catalysis has been revolutionized by the ability to deposit size-selected clusters on model support surfaces (6, 44–47). Our approach to monitor cluster formation in an atom-by-atom fashion produces a model system where the cluster size and distribution is accurately known. Following the behavior of such “size-distinguished” ensembles in reactive atmospheres could provide valuable insights into catalytic reactions in the nonscalable cluster regime. Indeed, we recently demonstrated that subnano Pt clusters grown by the CO-induced sintering approach are active for CO and H₂ oxidation via a Mars–van Krevelen-type mechanism (32). Surprisingly, we find that the CO also stabilizes dimers against decay. Thus, in addition to providing mobility, CO plays a crucial role in the growth kinetics by providing stability to the smallest clusters that act as further nucleation sites. In the UHV environment, the binding of the metal adatoms to the substrate is sufficiently strong that spontaneous formation of a Pt dimer is energetically unfavorable. Similar behavior was observed previously for Ag on the same surface, and extremely high adatom coverages were achieved because the nucleation of stable clusters was suppressed (35, 36). Here, this limitation is bypassed when two Pt−CO species meet, because their merger produces a Pt₂(2CO)₂ dimer that is stable and can function as a seed for further growth. When the sample is heated, the CO desorbs, and the small clusters break up into single Pt atoms.

The results described here contain several important lessons for the rapidly emerging, yet controversial field of single-atom catalysis. Here, the goal is to use single atoms as active sites for catalytic reactions to maximize the efficient use of noble metals such as Pt. Sintering clearly runs counter to this objective, and the ability to rapidly recover the adatom phase is considered vital to economic viability. In our work, the strong CO–Pt interaction is clearly detrimental as it accelerates the sintering process. The problem of the strong CO–Pt bond has been recognized before, and has been proposed to poison low-temperature oxidation reactions on a variety of substrates (48). Based on our results, it seems plausible that the catalytic activity reported for single-atom catalysis based on Pt could result from subnano particles formed under reaction conditions, which subsequently redissipate after the fact. In this light, although Pt is clearly an excellent catalyst as a nanoparticle, a less reactive (cheaper) metal would almost certainly yield a better and more stable single-atom catalyst. It would be fascinating indeed if, in an attempt to reduce the amount of Pt, it becomes possible to circumvent its use entirely.

In summary, we have analyzed the interaction of CO with Pt adatoms and clusters in detail. CO-induced mobility leads to the agglomeration of Pt into subnano clusters, and the presence of the CO stabilizes the smallest clusters against decay. Our results provide insights into coarsening processes at surfaces, which should be applicable to established catalysts based on oxide-supported metal clusters. CO-induced adatom sintering provides a well-defined initial state for experiments into the size-dependent properties of small Pt clusters.

Experimental Methods

The STM experiments were performed in a two-vessel UHV system. It consists of a preparation chamber and an analysis chamber. The latter is equipped with an Omicron p-STM, which was operated in constant current mode. The substrate material was a synthetic Fe₃O₄(001) crystal grown using the floating zone method (49). The crystal was prepared by cycles of sputtering with Ar⁺ ions (E₀ = 1 keV, Jₘₐₓₛₚₗ = 6.5 μA/cm², 10 min) followed by annealing at 870 K in 6.6 × 10⁻⁷ mbar O₂ (15 min). Temperatures were measured with a K-type thermocouple attached to the sample holder. The systematic error of the measurement is estimated as ±20 K (at 520 K). At high temperatures, the uncertainty of the temperature readout increases (±50 K at 900 K) because the thermocouple is not calibrated directly to the sample. The XPS data were acquired in a second UHV chamber equipped with a He₂ flow cryostat, a twin-anode X-ray source (Al, Ag), a Focus 500 monochromator, and a SPECS Phoibos 150 analyzer. In this system, the sample is prepared by cycles of sputtering with Ne⁺ ions (E₀ = 1 keV, Jₘₐₓₛₚₗ = 2.3 μA/cm²) and annealing in O₂ using a directional douser creating a local pressure of P = 10⁻⁵ mbar at the sample. In both chambers Pt was deposited using a modified Omicron single-particle electron-beam evaporator. The deposition rate (0.3 ML/min, 1 ML = 1 atom per reconstructed unit cell = 1.2 × 10⁻¹⁸ m⁻²) was calibrated using a water-cooled quartz-crystal microbalance. The DFT calculations are based on the augmented plane wave + local orbital method as implemented in Wien2K (50). We used the generalized gradient approximation with a Hubbard U (U_eff = 3.8 eV) to treat the strongly correlated Fe 3d electrons. The adsorption of Pt adatoms was modeled on a 17-layer 2×2 supercell of the ½(2×2)-reconstructed Fe₃O₄(001) surface with inversion symmetry and a vacuum layer of ~13 Å. In total, the slab contains 244 atoms plus 2 or 4 Pt atoms and 2 or 4 C and O atoms in the calculations including CO molecules. The atomic sizes used for Fe, O, and Pt were 0.98, 0.79, and 1.11 Å, respectively. A plane-wave cutoff of Rₑₘₐₓₛₚₗ = 7.0 corresponding to 296.6 eV was used, and the Brillouin zones of the surface models were sampled with a 3 × 3 × 1-k mesh. The surface models were relaxed until all forces were below 1 mRy/bohr (26 meV/Å). A Fermi broadening of 0.08 eV was used. The charge transfer from Pt adatoms to the slab was estimated from the change in the partial charge distribution in the Pt atom and the change in the magnetic moment of the total slab, the Pt adatom, and the adjacent O atoms.

ACKNOWLEDGMENTS.

G.S.P., R.B., O.G., J.H., and J.P. acknowledge funding from the Austrian Science Fund (FWF) START Prize Y 847-N20 and Project P24925-N20. R.B. and O.G. acknowledge a stipend from the Vienna University of Technology and the FWF as part of the doctoral college SOLID54FUN (W1243). P.2.d.e. acknowledges support from NWO-Vici 724.012.001. U.D. and J.P. acknowledge support by the European Research Council (H2020) “OxideSurfaces.” M.S. was supported by the FWF within SFB F45 “FOXL,” P.B. was supported by the FWF (Projects SFB F41 “ViCoM” and the doctoral college W1243 “Solids4Fun”).


