Evidence of High-Pressure Rhodium Sesquioxide in the Rhodium/γ-Alumina Catalytic System

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We report an investigation of Rh-containing nanostructures dispersed on γ-alumina. This system is representative of many common heterogeneous catalysts that consist of transition metals dispersed on a high surface area support. Previous atomic-resolution *Z*-contrast STEM observations have shown the Rh particles to exist as thin "rafts" on the (100) surface of γ-alumina. This finding is intriguing given that the preferred surface exposure of γ-alumina is (110). Here we present first-principles density functional studies and simulated *Z*-STEM imaging suggesting that these Rh-containing structures consist of the high-pressure rhodium sesquioxide (II) phase growing on the surface.

Introduction

Energy costs and environmental concerns are driving today's search for improved heterogeneous catalysts that can deliver precise reactivity with great durability. Improved catalysts would have a major impact because heterogeneous catalysis is the enabling technology for petroleum refining, for control of the final gaseous emissions from petroleum combustion, and for industrial chemical production. In principle, tremendous advances in catalyst design could result from predictive atomic-scale design, (i.e., design based on theoretical calculations that predict the reactions on a catalyst given its atomic-scale structure). In practice, while there are volumes of experimental results relating catalytic activity to composition and morphology, information about the atomic-scale surface structure of real heterogeneous catalysts is much more sparse.

One technique that can give direct atomic-scale structural information about catalytic surfaces is electron microscopy.[1–3] Nearly three decades ago it was suggested that Rh forms raft-like structures when dispersed on an alumina surface.[4] The interpretation was, however, based on assuming simple mass thickness contrast applied to a bright field image. As subsequently pointed out, this ignores the likelihood that the observed raft-like features could be caused by diffraction contrast in the crystalline support.[5] In more recent work,[6] (two of us) reported atomic-resolution *Z*-contrast scanning transmission electron microscopy (*Z*-STEM) images of a 1.2 weight % Rh-on-alumina catalyst. As *Z*-contrast imaging can be interpreted in terms of mass thickness, these observations provided definitive evidence for rafts. Very thin rafts of Rh atoms, a few square nanometers in area, were observed with spacing of the atomic rows suggesting an underlying oxygen sublattice corresponding to a γ-alumina (100) surface. This finding is remarkable because γ-alumina is thought to preferentially expose the (110) surface,[7] and other metal/γ-alumina catalysts such as Pt/γ-alumina[8] are based on the (110) surface of γ-alumina. The presence of the (100) exposure is not unprecedented though. The La/γ-alumina system exhibits both the (110) and (100) surfaces of γ-alumina.[9] In that case, the energy cost of exposing the less favorable (100) face is lowered by the fact that the binding of La to the γ-alumina (100) surface is very strong (ca. 8.6 eV/La atom).

TABLE 1: Energy of Association of a Single Isolated Rh atom onto Each of Five Positions (Denoted A, B, C, D and E) on the γ-Alumina Surface and a Sixth Site Partially Buried in the Surface (Denoted "in")[a]

reaction	stoichiometry	ΔE (eV)
γ-alumina(100) + $Rh_{(s)}$ → $Rh^{(A)}$/γ-alumina(100)	$RhH_8Al_{40}O_{64}$	4.8
γ-alumina(100) + $Rh_{(s)}$ → $Rh^{(B)}$/γ-alumina(100)	$RhH_8Al_{40}O_{64}$	4.7
γ-alumina(100) + $Rh_{(s)}$ → $Rh^{(C)}$/γ-alumina(100)	$RhH_8Al_{40}O_{64}$	"B" site
γ-alumina(110) + $Rh_{(s)}$ → $Rh^{(D)}$/γ-alumina(110)	$RhH_4Al_{26}O_{44}$	−2.0
γ-alumina(110) + $Rh_{(s)}$ → $Rh^{(E)}$/γ-alumina(110)	$RhH_4Al_{26}O_{44}$	−1.2
γ-alumina(110) + $Rh_{(s)}$ → $Rh^{(in)}$/γ-alumina(110)	$RhH_4Al_{26}O_{44}$	−4.2
γ-alumina(110) + $2Rh_{(s)}$ → Rh_2/γ-alumina(110)	$Rh_2H_4Al_{26}O_{44}$	0.56

[a] The (100) surface is modeled as a 5-layer thick slab of stoichiometry $H_8Al_{40}O_{64}$. The (110) surface is modeled as a 5-layer thick slab of stoichiometry $H_4Al_{26}O_{44}$. The total energy of one atom of $Rh_{(s)}$ is taken as that of a single unit cell of Rh metal containing one atom.

To better understand the Rh/γ-alumina catalytic system, in particular the interesting "raft" structures, we have combined first-principles calculations with simulated *Z*-contrast imaging of Rh/γ-alumina. Since alumina-supported Rh is a prototypical catalytic system similar to those used in automotive emissions control, petroleum refining and chemical production, this investigation will also contribute to the knowledge base required for the predictive atomic-scale design of heterogeneous catalysts. The results give strong evidence that the Rh structures are in fact regions of the high-pressure phase Rh_2O_3−II.

Methods

Theory. Atomic-scale bulk and surface structures were modeled with infinitely repeating supercells. The electronic

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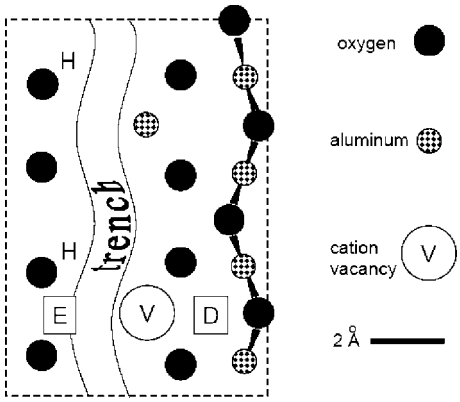

Figure 1. Schematic top-down view of oxygen-terminated γ-alumna (110C) surface. The flying wedges indicate the elevation of the terminating oxygen atoms above the nominal plane of the surface. The orientation of the "trench" in the surface and positions of surface H atoms are also noted. "D" and "E" indicate possible sites for Rh binding.

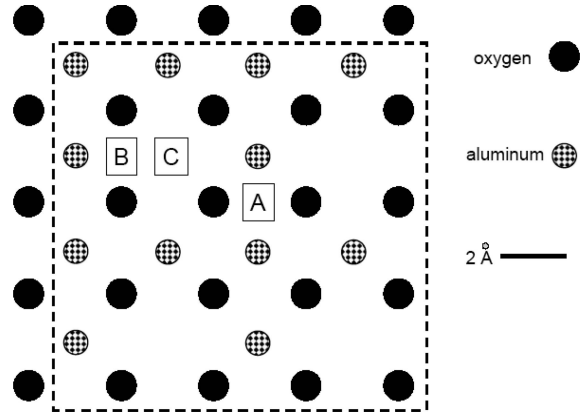

Figure 2. Schematic top-down view of oxygen-terminated γ-alumna (100) surface. "A", "B", and "C" indicate possible sites for Rh binding.

structure was then calculated with density functional theory[10] (DFT) using the generalized gradient approximation[11,12] (GGA) to the exchange-correlation energy as coded in CASTEP.[13] Pseudopotentials[14] were used to represent the interactions of the valence electrons with the atomic cores and the valence electron density was expanded in a plane wave basis, truncated according to a cutoff energy of 380 eV. Within this set of approximations, the total energy is given as a functional of the electron density, which is in-turn dependent on the atomic coordinates. Structural optimization is achieved by seeking structures that are local minima in the total energy surface. Using this methodology, optimization of the structure of Rh metal (fcc) produces a lattice constant of $a = b = c = 2.776$ Å, ($\alpha = \beta = \gamma = 60°$), which compares to the experimental value of 2.69 Å.[15]

The catalyst surface was modeled by placing one or more atoms of Rh, or units of rhodium oxide, onto an optimized slab of fully hydrogenated γ-alumina[16] 5 layers thick. Previous studies of the γ-alumina surface demonstrated that at 5 layers, the surface structure is converged with respect to increasing the slab thickness.[17,18] (For computational efficiency, some preliminary screening calculations, used to eliminate unlikely structures, were carried out using 4-layer slabs.) Two surface models were employed. The (110C) surface was modeled with a (10.65 × 7.47 Å) surface cell of stoichiometry $H_4Al_{26}O_{44}$, shown in top-down view in Figure 1. Because the surface is preferentially oxygen terminated,[7,8] a terminating row of oxygen atoms was added to bridge adjacent 4-coordinated Al atoms on the surface with Al−O−Al structures, thereby completing their octahedral coordination. The terminating row of oxygen atoms is shown with flying wedges in Figure 1 to denote its elevation above the nominal surface plane. The position of the well-known "trench" in the (110C) surface is also noted. This (110C) surface structure was described in detail previously.[8] The (100) surface of γ-alumina was modeled with a (10.65 × 10.20 Å) surface cell of stoichiometry $H_8Al_{40}O_{64}$, shown in top-down view in Figure 2. In both cases the vacuum spacing between slabs was set to 10 Å. During structural optimization, the atoms in the bottom layer and the unit cell parameters (a, b, c, α, β, γ) were frozen. Optimizations were taken to be converged when the change between iterations was less than the following values: total energy 2.0×10^{-5} eV/atom, rms displacement of atoms 1.0×10^{-3} Å, rms force on atoms 5.0×10^{-2} eV Å^{-1}, and (for unit cell optimizations) the rms of the stress tensor 1.0×10^{-1} GPa. This theoretical model was previously used successfully to investigate the Pt/alumina[8], La/alumina,[9] and Cr/alumina[19] systems.

Microscopy. High-angle annular dark field scanning transmission electron microscope (HAADF-STEM, aka *Z*-STEM) images of Rh/γ-alumina were obtained with a VG Microscopes HB603U operated at 300kV accelerating voltage. In *Z*-contrast STEM, the microscope probe beam is focused to a tiny spot on a thin slab of material. The transmitted electrons are collected with an annular detector, which collects the electrons scattered to high angles. High-angle scattering is predominantly Rutherford scattering, roughly proportional in intensity to the square of the nuclear charge *Z*. Scanning the probe beam across the material therefore yields a spatial mapping of the atoms, with an image intensity that is sensitive to the nuclear charge. Consequently, heavy Rh atoms show up as bright spots on the dark background due to the relatively light alumina support material. The spatial resolution is ca. 1.3 Å.

Z-STEM images were simulated from the optimized theoretical structures by convolution simulation, which is an excellent approximation in the case of thin Rh raft structures.[20] The substrate was deleted to match the experiment where it was tilted slightly off axis and therefore only the Rh atoms were showing resolution.

Results and Discussion

The *Z*-STEM image in Figure 3a shows a "raft" of Rh on the alumina surface. Note that the rows of Rh are resolved in one direction, showing a separation of about 2.8 Å, but are not resolved in the perpendicular direction, (along the rows) indicating that their projected separation within the rows is less than 1.3 Å.

Pure Rh Surface Structures. In order to investigate the Rh/γ-alumina structures, we modeled the interaction of one (or more) Rh atom(s) with γ-alumina. Table 1 shows the association energy for a single Rh atom onto each of five selected surface sites. The results show clearly that binding to the (100) surface is endothermic. In addition, Rh atoms placed at "C" sites spontaneously relax to "B sites on the (100) surface. (See Figure 2.) Even if every such site held a Rh atom, it could not explain the "raft" structures seen in the *Z*-STEM images. By contrast, binding of Rh to the (110C) surface is exothermic in multiple locations. We found, however, that if a single Rh atom is placed in one of the empty octahedral interstitial sites in the first subsurface layer of γ-alumina (110), upon structural relaxation it relaxes back toward the surface resulting in considerable

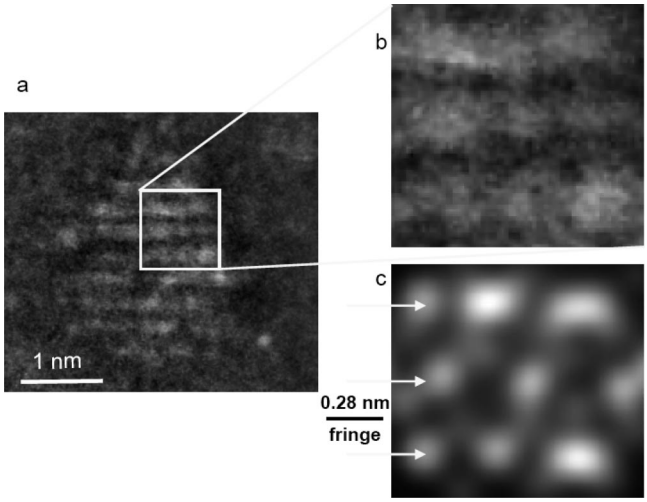

Figure 3. (a) *Z*-STEM image of Rh on γ-alumina (from ref 6). (b) Exploded view ca. 1.0 × 1.0 nm. (c) Simulated image based on optimized Rh_2O_3−II structure on γ-alumina (100) showing same area as part b.

distortion of the local surface structure. This latter case represents the most favorable binding site, although there is presumably an energy barrier involved in the process of moving the Rh atom into this site.

Insight into the preference of Rh for subsurface sites is revealed by considering the degree of valance saturation of the Rh atom. As a metric of degree of valance saturation we use the Pauling electrostatic valance rules,[7] which give an estimate of the charge on a selected atom. Application of the rules gives the charge on Rh at a "D" site on the (110) surface as +1.2, i.e. it possesses a significant degree of valance unsaturation. By similar analysis, a Rh atom at a "B" site on the (100) surface has a Pauling charge of +1.8, which is even more valance unsaturated and hence energetically less favorable, in agreement with the computed association energies. By contrast, when incorporated into an interstitial site in the first subsurface layer, Rh has a Pauling charge of −0.1, i.e. it is nearly valance neutral. This suggests that incorporation of the Rh into a subsurface interstitial site is energetically favorable because it completes the Rh valance and brings the Rh to near electrostatic neutrality. It seems likely that this could in fact be the driving force behind the process by which a small number of Rh cations are incorporated into γ-alumina, leading to acceleration of its transformation to α-alumina.[21]

On the basis of the supposition that the observed structure consists of a thin raft of Rh on the γ-alumina surface,[6] and the finding that, when isolated, Rh atoms bind preferentially to the (110) surface, and the preference of γ-alumina to expose the (110) surface,[7] we placed a close-packed cluster of Rh atoms on γ-alumina (110C) and performed first-principles structural optimization. The Rh−Rh distance was initially set to 2.5 Å, between the typical Rh−Rh distance seen in molecular systems[22] of about 2.4 Å and that seen in Rh metal[15] of 2.69 Å. We found that upon structural optimization, the structure underwent massive distortion including the ejection of one or more Rh atoms from the surface, indicating an unphysical structure.

Next we tried to leverage the *Z*-STEM result that the Rh atoms appear to be arranged in rows that are separated by about 2.8 Å. On the assumption that Rh will prefer to bind to oxygen over Al we looked for an exposure of γ-alumina that might support rows of Rh atoms separated by about 2.8 Å. A strong candidate appeared to be the preferentially exposed (110) surface

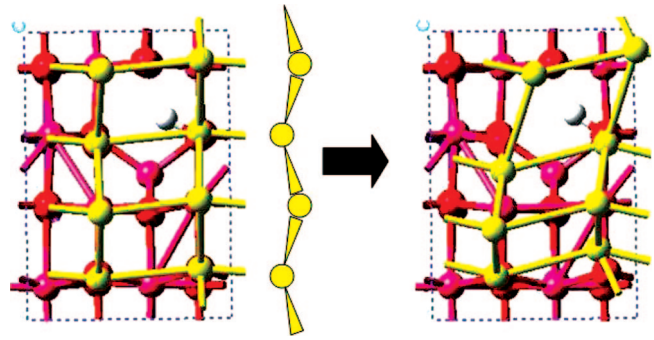

Figure 4. Optimization of corrugated rows of Rh atoms (shown in yellow) on γ-alumina (110C). The corrugation of the Rh rows in the direction normal to the surface is shown schematically in the middle insert. Note that the optimization destroys the linearity of the Rows of Rh, which is inconsistent with *Z*-STEM images.

of γ-alumina, which contains rows of oxygen atoms separated by about 2.7 Å. (Aside: It is plausible that if the preferred separation of the rows of Rh atoms is 2.8 Å but the rows of oxygen in the underlying support are separated by about 2.7 Å, this could effectively limit the width of a Rh cluster by setting a maximum number of rows that can be grown without introducing a lattice-mismatch defect. This would be consistent with the small size of Rh rafts observed.) We therefore constructed a structure with rows of Rh atoms directly above the oxygen rows on the γ-alumina surface but simultaneously corrugated in the direction normal to the surface. This corrugation is designed to lead to a projected Rh−Rh separation along a row of less than 1.3 Å. In other words, we attempted to deliberately construct a structure like the one in the *Z*-STEM image. Again we found that, upon structural relaxation, the structure underwent massive distortion destroying the linearity of the Rh rows, in disagreement with the *Z*-STEM result. The initial and final structures are shown in Figure 4. No other low-index surface of γ-alumina appeared to offer the possibility to construct properly spaced Rh rows.

To test whether multiple Rh atoms have any tendency to cluster at all, we started with the optimized structure for a single Rh atom on γ-alumina (110C) and placed an adjacent Rh atom 2.5 Å distant. After structural optimization the structure is 0.56 eV higher in energy than the undoped slab plus 2 atoms of Rh metal. In other words, it is energetically preferred for the second Rh atom to be either ejected from the surface, or bonded to a distant surface site. These results suggest that clustering of pure Rh atoms is not favored. A similar result was seen in investigations of La atoms on the γ-alumina surface, where it was found that two La atoms do not show any preference for association[9]. Additionally, it was found that displacement of two surface hydrogen atoms by Rh and the formation of hydrogen gas ($H_4Al_{20}O_{32} + 2Rh_{(s)} \rightarrow Rh_2H_2Al_{20}O_{32} + H_{2(g)}$) is energetically very unfavorable, even at 300 K when the entropic factor due to the formation of H_2 gas is included.

In brief, we did not find any stable structures of pure Rh on γ-alumina that were even remotely reminiscent of that seen in the *Z*-STEM image and, in fact, saw that Rh atoms prefer to be incorporated into a subsurface interstitial site.

Oxide Surface Structures. While pure Rh clusters on alumina do not appear to be physical, there are some hints that the Rh may be oxidized. (At the time the Rh/alumina image was taken, the instrument was not sufficiently sensitive to image oxygen so its presence or absence within the Rh raft is unknown. In addition it would be difficult to distinguish oxygen in the raft from oxygen in the support.) First, our earlier studies of

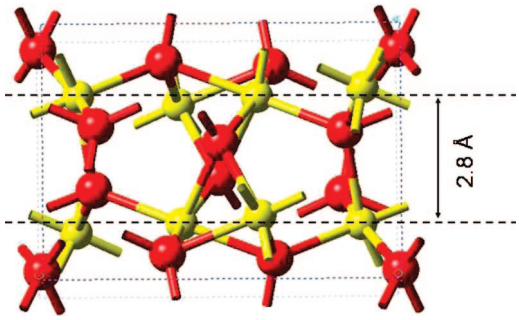

Figure 5. Structure of Rh_2O_3−II. Note that in the orientation displayed, the separation of the rows of Rh atoms is ca. 2.8 Å, but the projected separation of the Rh atoms within the rows is much shorter.

the related Pt/alumina catalytic system found that small Pt clusters are stabilized by partial oxidation in the form of a capping OH group[8]. *Z*-contrast STEM images of Pt on γ-alumina showed Pt trimers with anomalously long Pt−Pt distances. Instead of the typical Pt−Pt separation of 2.7 Å, the images showed the Pt−Pt distances to be about 3.0 Å. First-principles calculations showed that by capping the trimer with an OH group, charge density was depleted from the Pt−Pt bonds, lengthening them. Second, Campbell[23] has shown that transition metal oxides can actually have enhanced stability as a thin film. In other words, under some conditions a thin oxide film on a metal surface is not only more stable than the pure metal plus oxygen gas, but also more stable than the bulk oxide.

To investigate the possibility that an oxide of Rh is forming the observed "raft" on the alumina surface, we considered the oxides of Rh. There are three known sesquioxides of Rh, denoted with Roman numerals I, II, and III.[24] Phase I is the "regular" phase and it has the corundum structure. Phase II has higher material density and is the high pressure (HT-HP) phase. Phase III is intermediate between I and II. It has an interesting layered structure and is entropically stabilized,[24] thereby stable at high temperatures and low pressures (HT-LP). For the present investigation, phase II is perhaps the most interesting because, in certain projections, as shown schematically in Figure 5, it exhibits rows of Rh atoms (shown in yellow) separated by about 2.8 Å. We placed a thin "chunk" of Rh II sesquioxide on a γ-alumina (100) surface and carried out first-principles structural optimization. Upon optimization, we found that not only is the structure stable but, as shown in Figure 3c, it produces a simulated image very similar to the one observed experimentally (Figure 3b). Note that in both the experimental and simulated images, there are rows of Rh atoms separated by 2.8 Å, but the atoms are essentially unresolved along the rows. The presence of Rh_2O_3−II is consistent with earlier TEM studies of γ-alumina-supported Rh catalysts where the formation of particles of the HT-HP Rh_2O_3 phase was observed after aging in air at high temperatures.[21]

The fact that the high-pressure phase of Rh sesquioxide is stable on the alumina surface is quite interesting and presumably arises from the difference in atomic radius between Al and Rh. Rh is a larger atom than Al. In order obtain a good "fit" between Rh oxide and Al oxide, the Rh oxide lattice needs to be squeezed slightly. That is exactly the case in a high pressure phase.

Conclusions

We have combined first-principles calculations with simulated *Z*-contrast imaging to investigate the raft-like structures observed on Rh/γ-alumina, a prototypical catalytic system. The following points have been observed: (1) When isolated, Rh atoms prefer to bind to the (110) surface of γ-alumina, interactions with the (100) surface being exothermic, but binding at a surface site is less favorable than incorporation of the Rh into an octahedral interstitial site in the first subsurface layer. (2) Clustering of Rh atoms on the γ-alumina surface is not energetically favored, i.e. two widely separated Rh adatoms represents a lower energy state than an Rh_2 structure. (3) The "rafts" of Rh observed by *Z*-STEM consist of regions of high-pressure Rh_2O_3−II phase.

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