

Transition metal atoms on different alumina phases: The role of subsurface sites on catalytic activity

S. N. Rashkeev,¹ K. Sohlberg,² M. V. Glazoff,^{3,1} J. Novak,⁴ S. J. Pennycook,⁵ and S. T. Pantelides^{1,5}

¹*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235*

²*Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104*

³*Alcoa Technical Center, Alcoa, Inc., Alcoa Center, Pennsylvania 15069-0001*

⁴*Alcoa World Alumina, Port Allen, Louisiana 70767*

⁵*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

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Transition metals (Pt, Pd, Rh, Cr, etc.) are widely used as catalysts on γ - and η -alumina, two phases of Al_2O_3 , but the catalytic activity of Cr on γ -alumina degrades rapidly. We report density-functional calculations that trace the origin of the effect to differences in surface reconstruction caused by different distributions of bulk cation vacancies. On η -alumina, Cr atoms remain on the surface, threefold-coordinated and reactive; on γ -alumina, they get trapped in subsurface octahedral sites and become inactive. Some metal atoms (e.g., Mn) also get trapped, but the other catalytic elements (Pt, Pd, Rh) do not. Steric constraints, size effects, or other qualitative considerations are not adequate to account for the results.

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γ - and η -alumina are widely used in catalysis. They have a high degree of porosity, i.e., a large surface area, and can serve both as a catalytic support¹ and as a catalyst.^{2,3} When γ - and η -aluminas are used as catalytic supports, they are coated with dispersed nanoparticles of transition metals, e.g., Pt, Pd, Rh, Cr, etc., that are the primary active catalysts.¹ Direct *Z*-contrast atomic-resolution imaging of individual dispersed catalyst atoms (Pt and Rh) on the insulating γ -alumina surface demonstrated that these atoms may exist on the surface as isolated atoms, in small clusters (dimers, trimers, etc.) or as more extended raftlike structures depending on the type of atoms.⁴ It has been shown that the catalytic activity of the clusters of metallic atoms on solid supports depends strongly on their size and shape,^{5,6} i.e., there exists a possibility of tailoring the catalytic behavior of metal clusters by controlling the cluster size.

Though both γ - and η -alumina are effective substrates for several transition-metal catalysts, Cr, which is widely used for dehydrogenation of alkanes,⁷⁻⁹ exhibits an unusual property. Though Cr/ η -alumina catalytic systems last up to two to three years without degradation, analogous systems based on γ -alumina degrade within weeks.^{10,11} It has been found that Cr atoms disappear from the surface and tend to form aluminum chromates.¹¹ This considerable difference between γ - and η -alumina is quite puzzling because both phases have the spinel crystal structure with roughly 11% of the cation sites being vacant to achieve stoichiometry. The two phases differ only in the bulk distribution of these vacancies.¹²

In this paper we report the results of first-principles density-functional calculations with which we probe the behavior of Cr and other similar transition metal elements on γ - and η -alumina surfaces. We find that differences in the reconstruction of γ - and η -alumina surfaces, which have been traced to the bulk distribution of cation vacancies,¹³ are ultimately responsible for the observations. In particular, the octahedral interstitial sites in the first two subsurface layers are different in the two phases because of the different reconstructions. The local topologies are so significantly distorted that simple steric arguments, preferred oxidation states, size

differences, or other qualitative considerations are not sufficient to allow a conclusion on whether Cr or any of the other transition-metal elements would stay on the surface or get trapped in the subsurface layer, where they might saturate their valencies and be catalytically inactive. The results of calculations demonstrate clearly that the bonding of Cr atoms on a γ -alumina surface in catalytically active positions is *metastable*; the lowest-energy configuration is in an octahedral interstitial site in the first subsurface layer. The reverse is true for Cr on an η -alumina surface, where it can bond metastably in an analogous interstitial octahedral site, but its lowest-energy configuration is on the surface where it is catalytically active. We checked the other catalytic elements (Pt, Pd, Rh) and found that all of them prefer the surface sites where they are catalytically active. One might attribute the effect to the fact that Cr atoms prefer octahedral coordination in Cr oxides, whereas the other catalytic elements do not form such oxides easily. Nevertheless, we also found that Mn, which has a mixed coordination preference in its oxides, also gets trapped in the γ -alumina octahedral sites, whereas Mo, which is isoelectronic to Cr and also forms oxides with octahedral coordination, is totally unstable in the octahedral sites and spontaneously pops out onto the surface. One might suggest that Mo, being a *5d* transition element, is physically larger, but its atomic radius actually differs from that of Mn by only 0.04 Å and both are smaller than the radius of Al, which sets the length scale in the crystal structure. Overall, the results demonstrate the power of the first-principles, parameter-free calculations to determine the energetically preferred configurations in complex materials. These configurations are achieved by nature through a subtle balancing of many competing effects.

The results of the present work complement earlier experimental and theoretical work on the surfaces of the alumina phases. Experiments found that the two surfaces differ greatly in surface reactivity.¹ Cross-polarizing ²⁷Al NMR spectroscopy¹⁴ found that there are no three-coordinated Al atoms on the preferentially exposed (110) surface of γ -alumina. The first-principles calculations reported in Ref.

15 confirmed that the three-coordinated Al atoms that are initially present on the surface of γ -alumina (i.e., upon simple termination of the bulk structure) drop from the surface layer into empty octahedral sites in the first subsurface layer. The cation vacancies are located predominantly on the tetrahedral cation sublattice in γ -alumina and on the octahedral cation sublattice in η -alumina,¹⁶ and this difference in the Al coordination in the two alumina polytypes explains the difference in their surface reconstruction and different levels of their Lewis acidity.¹³

The present calculations were based on density-functional theory, the generalized gradient approximation for exchange correlation, supercells, and plane waves.¹⁷ The ultrasoft pseudopotentials for O, H, and Cr, and norm-conserving pseudopotentials for Al, and the VASP codes¹⁸ were used. We thoroughly tested the bulk volume relaxation for totally ordered α -alumina (corundum) structure and found an excellent agreement of the calculated mass density (4.008 g/cm³) with experimental data (3.987 g/cm³).¹⁹ The energy cutoff for the basis set was set at 24 Ry, and all integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with four \mathbf{k} points in the relevant irreducible wedge.²⁰ Most of our calculations were non-spin-polarized. We checked their validity comparing the spin-polarized and non-spin-polarized calculations of the total-energy differences and energy barriers for some representative configurations and found no appreciated difference, i.e., the single Cr atom does not significantly polarize the electronic structure of the system.

The surfaces were modeled by infinitely repeating slabs with an interslab vacuum spacing of 10 Å. The structural relaxations were performed for supercells consisting of slabs five atomic layers thick (70 atoms for η -alumina and 72 atoms for γ -alumina) described in detail earlier.¹³ Previous studies demonstrated that five-layer slab models are sufficiently thick that the surface chemistry and surface reconstructions are converged with respect to increasing the thickness of the slab model.²¹ The starting structure for each slab was that of fully relaxed η - or γ -alumina as described in Ref. 13. The supercells expose the (110C) layer (and in the case of η -alumina, the three-coordinated Al atoms that are responsible for strong Lewis acidity) of either γ - or η -alumina at the surface (it was experimentally shown that the (110) face of γ -alumina is preferentially exposed,^{3,4} and it is energetically preferred to expose the (110C) layer rather than the (110D) layer¹⁵). The lowest layer of the slab is considered a “bulk layer,” and the coordinates of its atoms were frozen. We confirmed all the results on surface relaxations for γ - and η -alumina described in Ref. 13.

When adatoms were placed on one of the surfaces, several different sites were investigated and the minimum-energy positions and energy barriers for migration were calculated. For equilibrium configurations, the structures were relaxed until the total energy was minimized (the total-energy difference between the two last geometric iterations was no greater than a fixed tolerance, in this work, 10^{-3} eV; we also controlled that the largest force for the optimized structure did not exceed 0.02 eV/Å). All the calculations were performed at zero temperature since experimental evidence suggests the

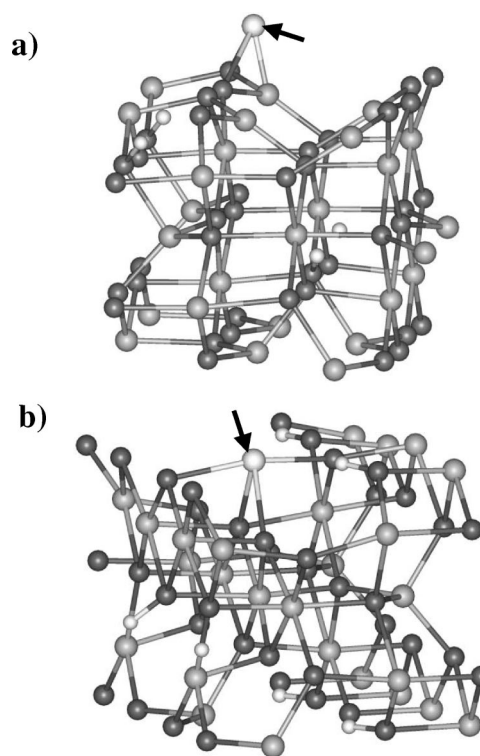


FIG. 1. A chromium atom at its lowest energy position at (a) η - and (b) γ -alumina surface. Aluminum atoms are shown in dark gray, oxygen in black, hydrogen in white, chromium in light gray (also indicated by arrows).

systems are stable to about 1000–1200 °C,²² which is higher than a typical operating temperature for catalytic processes. Diffusion barriers were calculated by successively fixing the position of the migrating atom at several points along a chosen diffusion path (we always check several different paths and take 5–10 points along each) and one of the atoms far away from it and relaxing all other atoms. (The second atom was chosen to be an atom that does not appreciably change its position in the initial and final intermediates. This prevents “sliding” of the entire unit cell.)

We will first describe the results of calculations for Cr as an adatom on the reconstructed surface of η - and γ -alumina. We examined a wide range of possible sites and found that, on η -alumina, the total energy is minimized when Cr is bonded one of the surface three-coordinated Al atoms and two neighboring surface oxygen atoms as shown in Fig. 1(a) (the bond to the Al atom is much stronger). Chromium atoms can diffuse along the surface, jumping from one three-coordinated Al to another (by moving along the zigzag-shaped “valley” located between the three-coordinated Al’s). The trajectory of such a motion also has a zigzag shape. The activation energy for this process is 2.5 eV, i.e., is much lower than any typical activation energy for moving an Al atom in the bulk of transition alumina. (For example, the activation energy to move Al atom into an interstitial, i.e., to form a vacancy-interstitial Frenkel pair, is of the order of 4–5 eV.²²) Cr atoms are chemically active anywhere on this migration path, including at the minimum-energy structure. For example, a very strong Cr-H bond (bond energy about

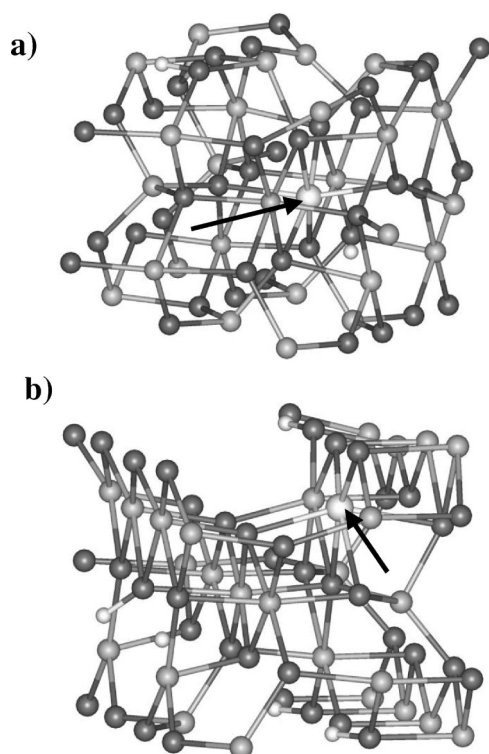


FIG. 2. A chromium atom at the nearest to interface six-coordinated positions at: (a) η - and (b) γ -alumina surface. The notation for different atoms is the same as in Fig. 1.

4.7 eV) is formed when a hydrogen atom is deposited on the top of chromium. Attachment of hydrogen to chromium is required in the catalytic dehydrogenation processes in which chromium facilitates abstracting one of the hydrogen atoms from hydrocarbon molecules (C_nH_{2n+2}). The energy gain of forming the new Cr-H bond is larger than the energy cost of breaking the C-H bond in a hydrocarbon molecule (a typical C-H bond has a bond energy of about 4.29 eV),²³ a fact that explains why the dehydrogenation process occurs.

On the reconstructed γ -alumina surface, the energy of the system is minimized when Cr attaches to four undercoordinated surface oxygen atoms. One of these four bonds is much longer and weaker than the other three. This result implies that Cr participates in the formation of three chemical bonds, just as it does on the η -alumina surface [Fig. 1(b)]. Chromium can also diffuse along the γ -alumina surface, with an activation barrier that is also about 2.5 eV. The motion of Cr is basically one dimensional, along the “trench” created by the undercoordinated surface oxygen atoms. In any of these positions Cr also can form a chemical bond with a hydrogen atom, similar to the case on the η -alumina surface, $E \sim 4.8$ eV. Therefore, in general, the catalytic system based on Cr on a γ -alumina support should be similar to that based on Cr on η -alumina.

While an adsorbed Cr atom forms similar structures on the surfaces of γ - and η -alumina, the difference between the two catalytic supports becomes essential when one examines the possibility of Cr occupying a site in the nearest *subsurface layer*. In γ -alumina, Cr can be accommodated in an interstitial position in the *first* subsurface layer where it cre-

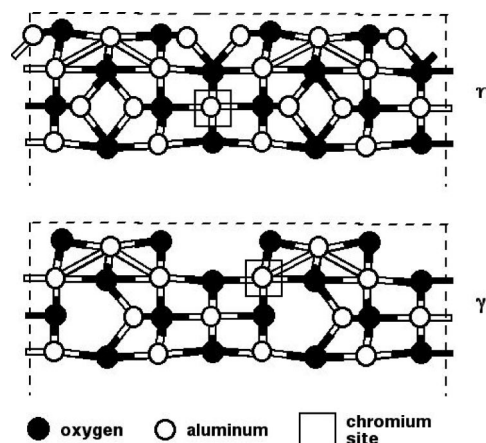


FIG. 3. Schematic edge on view of the position of Cr within the top four atomic layers of γ - and η -alumina. The box indicates the preferred Cr position. In η -alumina Cr occupies an octahedral vacancy in the third layer, directly below the trench. In γ -alumina, Cr occupies an octahedral interstitial in the second layer. Note the close proximity of a tetrahedral vacancy to the Cr position in the case of γ -alumina.

ates six bonds with surrounding atoms. When Cr moves to this position from the surface, the system gains about 1.5 eV in energy per unit cell. The activation barrier for Cr move from a surface site to the subsurface interstitial site is 2.2 eV what is comparable with the surface diffusion barrier. Therefore it is very probable that Cr atoms leave the surface and occupy these sites. This process is analogous to the relaxation of three-coordinated Al on the surface of unrelaxed γ -alumina into octahedral sites in the first subsurface layer.¹⁵ In fact, the six-coordinated Cr site is in close proximity to the six-coordinated Al atom that was originally three-coordinated on the surface and then relaxed to this position [Fig. 2(b)].

When Cr is placed in an analogous octahedral site in the first subsurface layer of η -alumina, the state is metastable with an energy that is 1.4 eV higher than that of the catalytically active surface adatom configuration. The large difference from the corresponding γ -alumina site can be attributed to different local distortions arising from the differences in the reconstructions of the two surfaces. In contrast, we found that a Cr atom can potentially be trapped in the *second subsurface layer* of η -alumina [Fig. 2(a)]. However, in order to get there, the Cr atom must overcome a potential energy barrier, which is on the order of the activation barrier for migration of an aluminum vacancy in a spinel structure. We have established this barrier to be in the range of 4.5–6 eV (the barrier depends on the cation site in the spinel structure and on the migration path). Therefore the event of Cr disappearing from the surface and moving into the bulk of η -alumina is very improbable except at very high temperatures. Instead, Cr remains on the surface and may participate repeatedly in dehydrogenation reactions. The preferred Cr positions in the subsurface layers of the two alumina polytypes are also schematically shown in Fig. 3. Cr is metastable in vacancies and interstitials with tetrahedral coordination in both the alumina polytypes.

The fact that Cr gets trapped in a subsurface octahedral interstitial site in γ -alumina might be attributed to the fact that it forms oxides in which it is octahedrally coordinated.²⁴ However, the same arguments would apply to η -alumina. Examination of the analogous sites in the two phases shows that the octahedrons formed by the Cr neighbors are distorted in different ways, suggesting that the total energy is affected by subtle phenomena. We explored this issue further by performing calculations for other transition-metal elements, namely, Mo, Pd, Rh, Pt, and Mn. The catalytic elements Pt, Pd, and Rh prefer the surface sites where they are catalytically active and do not diffuse into subsurface layers which is consistent with the fact that these elements do not easily form oxides with octahedral coordination. However, Mo which is isovalent to Cr (and one could expect that it would behave similarly to Cr), is not stable in the subsurface vacancy like Cr, but pops spontaneously to the surface if placed there. Furthermore, Mo does not occupy the same surface site as Cr either, preferring to coordinate to two Al and two O atoms, at the same time massively distorting the neighboring environment. Moreover, Mn, which is not isovalent to Cr is indeed stable in the subsurface site. These results cannot be explained by differences in atomic radii because the radius of Mo actually differs from that of Mn by only 0.04 Å and both are smaller than the radius of Al.

We conclude that a capture of surface adsorbed Cr atoms by the bulk is facile at much lower temperatures in γ -alumina than in η -alumina. On the γ -alumina surface Cr moves along the “trench” of surface atoms with an activation barrier of 2.5 eV. Along this migration path it remains catalytically active and can form strong bonds with hydrogen atoms of hydrocarbon molecules that come close to the surface. While moving along such trenches, Cr can get trapped

into an interstitial in the nearest subsurface layer where it becomes six-coordinated and therefore cannot exhibit any catalytic activity. The barrier to move into this trapped position is comparable to that for surface diffusion barrier, i.e., as long as the Cr has sufficient thermal energy for migration, the event of Cr trapping is quite probable. On the η -alumina surface the energy barrier to trapping is much higher and Cr remains on the surface with high probability, even at temperatures sufficient for surface diffusion. This result explains the disappearance of Cr atoms from the γ -alumina surface and the more rapid degradation of the γ -alumina supported catalysts. This picture is fully consistent with experimental and industrial observations.^{10,11}

In summary, we have studied interactions of Cr atoms with γ - and η -alumina surfaces. We found that at both surfaces Cr is highly active and can participate in catalytic reactions. In both cases it is energetically favorable for Cr to occupy a subsurface layer position where it becomes sixfold coordinated. The activation barrier for Cr to enter such positions, however, is *much higher in the case of η -alumina*. An important consequence of this result is that Cr can sustain its catalytic activity at the η -alumina surface for a very long time, while becoming completely deactivated on the γ -alumina surface within several weeks. In contrast, other catalytic elements (Pt, Pd, Rh) always prefer to stay in catalytically active sites on the surface of both phases.

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