Explanation of the Observed Dearth of Three-Coordinated Al on γ-Alumina Surfaces

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Abstract: NMR data have revealed that γ-alumina surfaces do not contain any three-coordinated Al atoms, despite the fact that their presence is expected on the basis of the bulk structure of the material. We report density-functional calculations of γ-alumina (110) surfaces that reveal a massive spontaneous reconstruction of the ideally terminated bulk. The three-coordinated Al atoms initially in the surface layer drop into vacant octahedral interstices in the second layer where they become six-coordinated. The predicted reconstruction is also fully consistent with IR studies of hydroxylated γ-alumina surfaces and reveals the physical origin of results obtained by earlier computational simulations.

1. Introduction

The aluminas are among the technologically most important catalytic materials, serving both as catalytic supports[1] and as catalysts in their own right.[2] They are employed in applications from petroleum refining[2] to automotive emissions control.[3] Accordingly, there has been prolonged widespread interest in the structure and function of alumina surfaces.[4] Of particular importance is the distribution of surface Al atoms and their coordination states, since coordinatively unsaturated surface Al atoms are the source of the surface Lewis acidity, which is central to catalysis.[5] One of the most powerful techniques for elucidating the distribution of Al atoms of various coordination on the surface is ^{27}Al cross-polarization NMR spectroscopy.[6] Meticulous studies of γ-alumina with this technique have produced a perplexing result.[5] No three-coordinated Al is observed, despite the fact that the presence of three-coordinated Al on the surface would be expected based on the bulk structure. This result is particularly important because the presence of three-coordinated Al has often been assumed for the purposes of assigning IR bands of the hydroxylated surface.[2,4,7,8] We have resolved this conundrum with density-functional-theory (DFT) calculations. We find that when the (110C) layer of γ-alumina is exposed, it undergoes a massive spontaneous reconstruction. The three-coordinated Al atoms, initially in the surface layer, drop from the surface layer into vacant octahedral interstices in the next lower layer.

2. Computational Method

The density functional theory[9] calculations employed the generalized gradient approximation (GGA) to the exchange-correlation energy,[10] as described in the review by Payne et al.[11] The electron−ion interactions were described with nonlocal reciprocal-space pseudopotentials[12] in the Kleinman-Bylander form.[13] A plane wave basis was used to describe the electronic density with a cutoff energy of 1000 eV as determined by convergence studies. Integrations over the Brillouin zone employed a grid of k points with a spacing of 0.1 Å^{-1} chosen according to the Monkhorst-Pack scheme.[14] The structural relaxation studies employed a 56-atom unit cell consisting of a slab of γ-alumina 4 layers thick. The atoms in the bottom layer were frozen, as were the dimensions (a, b, c, α, β, γ) of the unit cell. The system was infinitely periodic with a vacuum spacing between slabs of 10 Å. The starting structure from which the slab was generated was that of fully relaxed γ-alumina in its lowest energy form.[15]

3. Results

γ-Alumina is derived from the thermal dehydration of boehmite.[16] Its structure is very closely related to that of Mg-spinel,[17] which has the primitive unit cell $Mg_2 Al_4 O_8$. In Mg-spinel, the oxygen atoms are cubic close-packed, the Mg atoms are tetrahedrally (T_d) coordinated by oxygen, and the Al atoms

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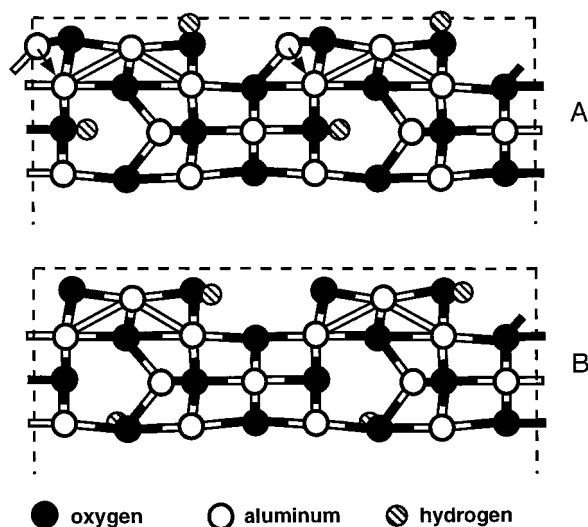(17) Wyckoff, R. W. G. *Crystal Structures*; Interscience Publishers: New York, NY, 1963.

Figure 1. Edge-on view of the top four layers of γ-alumina before (a) and after (b) relaxation. Note that the three-coordinated Al are absorbed into the first subsurface layer. The bottom layer of atoms was frozen during the calculation.

are octahedrally (O_h) coordinated by oxygen. Recently, we have shown that γ-alumina has a range of valid stoichiometries H_{3m} Al_{2-m} O_3, ($0 \leq m \leq 1/3$) but the lowest energy form has the stoichiometry of a hydrogen–aluminum spinel.[15] The primitive unit cell of the lowest energy form is HAl_5O_8, where the H atom and one Al atom occupy (nominally) the Mg sites in the spinel structure, and the remaining 4 Al atoms occupy the Al sites in the spinel structure. In HAl_5O_8, 20% of the Al atoms (1 in 5) are tetrahedrally coordinated by oxygen and 80% (4 in 5) of the Al atoms are octahedrally coordinated by oxygen. It is important to note, however, that throughout the range of valid stoichiometries ($0 \leq m \leq 1/3$), including the fully dehydrated limit ($m = 0$), the structure contains Al in both tetrahedral and octahedral coordination. In the present work, calculations were performed for the HAl_5O_8 stoichiometry. We will show, however, that our main results have general validity.

Although early surface studies focused on the (100) face,[18] it is now known that the (110) face of γ-alumina is preferentially exposed.[2] For example, Z-contrast scanning transmission electron microscopy (Z-STEM) images of γ-alumina, in application as an automotive catalytic support, showed the (110) surfaces to be exposed.[19] There are, however, two (110) layers in γ-alumina, denoted (110C) and (110D).[2] We carried out structural relaxations of these two surfaces and found that it is energetically preferred to expose the (110C) layer. Structural relaxation of the (110C) surface of γ-alumina also showed that it undergoes an interesting and important reconstruction. The unrelaxed (110C) layer exposes both three-coordinated Al atoms (Al in T_d coordination with one oxygen removed) and four-coordinated Al atoms (Al in O_h coordination with two oxygen atoms removed). When this structure is relaxed, the three-coordinated Al atoms drop from the surface layer into vacant octahedral interstices in the next lower layer. An edge-on view of this reconstruction is shown in Figure 1. In addition to the large physical displacement exhibited in Figure 1, the reconstruction entails a large energy gain, about 10 eV for the unit cell employed here, which translates into 2 J·m^{-2}.

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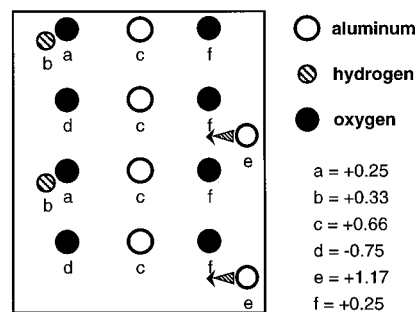(19) Nellist, P. D.; Pennycook, S. J. *Science* (Washington, D.C.) **1996**, *274*, 413.

Figure 2. Top-down view of the unrelaxed (110C) surface of γ-alumina. Note that the charge on the three-coordinated Al is +1.17 prior to reconstruction. After reconstruction the three-coordinated Al atoms drop from the surface layer into the first subsurface layer, after which their charge is zero. The observed reconstruction thereby eliminates the electrostatically most unstable species from the surface.

The reconstruction can be rationalized by observing the electrostatic distribution. We use the following definition of effective charge introduced by Knözinger and Ratnasamy,[2] based on the Pauling electrostatic valence rules:[20] (*atom charge*) = (*preferred valence of atom*) + (*sum of strengths of bonds to atom*). Here, (*bond strength*) = (*preferred charge of adjacent atom*)/ (*coordination of adjacent atom*). Figure 2 shows the unrelaxed (110C) surface of γ-alumina along with charges assigned as above. The arrows indicate the motion of the three-coordinated Al atoms upon structural relaxation. Note that, prior to relaxation, the three-coordinated Al atoms are assigned a charge of 1.17, the largest (in magnitude) of any surface atom. After relaxation, however, these Al atoms are six-coordinated by oxygen. Since every oxygen atom in the bulk is four-coordinated, the new charge on the Al atom after reconstruction is, by the above scheme, $(+3) + 6(-2/4) = 0$. The reconstruction therefore completely eliminates the electrostatically most unstable surface species, three-coordinated Al.

The predicted reconstruction is consistent with results obtained by earlier theoretical studies of γ-alumina surfaces. Alvarez et al.[21] carried out molecular dynamics (MD) studies of γ-alumina surfaces using empirical potentials. In MD simulations starting from truncated bulk surfaces, they reported the loss of Al from tetrahedral cation positions on the γ-alumina (110C) surface. More recently, similar behavior was reported by Gunji et al.[22] While no mechanism for the observed depletion was proposed, it is now clear that their observed result is a manifestation of the spontaneous reconstruction reported here.

4. Discussion

The surface reconstruction reported here provides a natural explanation for the perplexing experimental result[7] mentioned in the Introduction. As already noted, the (110C) layer contains both four-coordinated Al and six-coordinated Al. When exposed, one would therefore expect both three-coordinated and four-coordinated Al atoms on the surface as shown in Figure 3. Cross-polarizing ^{27} Al NMR studies,[6] however, found no observable three-coordinated Al.[5] This mystery is explained by our surface-reconstruction studies. The three-coordinated Al atoms drop from the surface layer into vacant octahedral interstices in the next lower layer.

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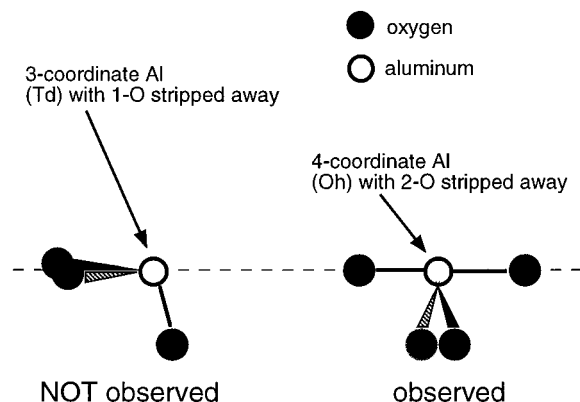
Figure 3. Two types of Al expected on the surface of γ-alumina when the (110C) layer is exposed. ^{27}NMR studies find four-coordinated Al, but not three-coordinated Al,[5] a quandary resolved by the reconstruction reported here.

Further confirmation of the surface reconstruction reported here comes from IR studies of hydroxylated γ-alumina surfaces. Dry γ-alumina is well-known to chemisorb water.[18] This chemisorption leads to the formation of surface hydroxyl groups that have been the subject of numerous studies by IR spectroscopy.[2,4,7,8,18,23] These studies clearly document that there are three prominent bands in the IR spectrum of surface OH groups of γ-alumina. Tsyganenko and Filimonov[8] appear to be the first to have proposed that these three bands arise from three basic types of chemisorbed OH. These three types, denoted I, II, and III, correspond to the O atom of the OH group in question being bound to one, two, or three surface Al atom(s), respectively. Later, Knözinger and Ratnasamy[2] subdivided types I and II into I_a, I_b, II_a, and II_b, where the subscript a denotes that (one of) the bonding Al atom(s) is itself in tetrahedral coordination, and the subscript b indicates that all of the bonding Al atoms are in octahedral coordination. More recently, Tsyganenko and Mardilovich[4] have replaced a and b with integer subscripts to indicate the exact coordination of each of the Al atoms that are bonding to the chemisorbed OH. Each digit of the integer subscript denotes the coordination of one of the Al atoms bonding to O of the chemisorbed OH. (O from the chemisorbed OH is included in this count.) Equating the designations of Knözinger and Ratnasamy with this most recent system we see that $I_a = I_4$, $I_b = I_6$, $II_a = II_{64}$, $II_b = II_{66}$, etc. Liu and Truitt[7] have added a few minor refinements to this model for the type III case and give a complete review of the incremental improvements of the model.

In the most modern assignment, the three major bands are assigned to I_6, II_{66}, and III, with two other minor bands being assigned to hydrogen-bonded OH and/or various type III groups.[7] Conspicuous by their absence are OH groups of type I_4. If the three-coordinated Al shown in Figure 3 were present on the γ-alumina surface, upon hydroxylation one would expect type I_4 groups to form. This is particularly true in light of recent ab initio results of Tachikawa and Tsuchida.[24] The ab initio

studies showed that surface Al in tetrahedral sites is a stronger Lewis acid than surface Al in octahedral sites. Type I_4 OH groups should therefore form even more easily than those of type I_6. The fact that the latter give rise to one of the three prominent bands in the IR spectrum of surface OH, and the former are not observed, is completely consistent with our surface-reconstruction studies, which find that three-coordinated Al atoms at the (110C) surface of truncated bulk γ-alumina are depleted by a spontaneous reconstruction.

Finally, we address stoichiometries other than HAl$_5$ O$_8$, namely H$_{3m}$ Al$_{2-m}$ O$_3$, with $m \neq 1/8$.[15] These materials also have a spinel structure. For $m < 1/8$, a fraction of the cation sites are vacant, thus a (110C) surface occasionally has a cation vacancy. The existence of such cation vacancies has no bearing on the mechanism we report. If a three-coordinated Al (see Figure 3) is absent, obviously there is no Al to reconstruct. If a four-coordinated Al (see Figure 3) is absent, it does not impact the reported reconstruction since three-coordinated Al and four-coordinated Al are not adjacent on γ-alumina (110C) surfaces. For $m > 1/8$, there is excess interstitial hydrogen in the bulk. Once more, this has no bearing on our results regarding the relaxation of surface Al atoms. These observations are consistent with those of Tsyganenko and Mardilovich,[4] who noted that different hydrogen contents do *not* lead to any new structures on the hydroxylated surface.

5. Conclusions

We have carried out DFT studies of the energetically preferred (110C) surface of γ-alumina. It is found that that when the (110C) layer is exposed, it undergoes a massive spontaneous reconstruction. The three-coordinated Al atoms initially in the surface layer drop into vacant octahedral interstices in the first subsurface layer. In addition to the large physical displacement of the initially three-coordinated Al, the reconstruction liberates an energy of 2 J·m^{-2}. This spontaneous reconstruction of the truncated bulk explains the perplexing experimental observation that no three-coordinated Al is observed on γ-alumina surfaces[5] despite the fact that their presence should be expected on the basis of simple truncation of the bulk at the (110C) surface, the preferentially observed surface. The predicted reconstruction is also fully consistent with IR studies of hydroxylated surfaces and gives new insight into earlier computational simulations.

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