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Theoretical proposal: a tunable heterogeneous catalyst

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Abstract

First principle calculations predict that the massive surface reconstruction of cubic alumina can be switched on or off by controlling the bulk H content and temperature. In one state the surface contains highly valence unsaturated Al atoms, the source of surface acidity central to catalysis. In the other state, these Al atoms bury themselves below the surface, giving a weaker surface acidity and a softer catalyst. These results evince a surface catalytic activity of alumina that can be tuned by switching between these two modes, opening the way for tunable heterogeneous catalysis. © 2000 Elsevier Science B.V. All rights reserved.

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Cubic alumina has a defective spinel structure. In the spinel structure ($MgAl_2O_4$), the Mg atoms are tetrahedrally coordinated and the Al atoms are octahedrally coordinated. The ratio of cation to anion sites is 3:4. In pure stoichiometric Al_2O_3, the ratio of cations to anions is 2:3. Consequently, in cubic forms of stoichiometric alumina, only eight of every nine cation sites are occupied by Al atoms. The empirical formula is $\square Al_8O_{12}$ (where $\square$ = vacancy), though one usually sees the unwieldy formula, $\square_{2\frac{2}{3}}Al_{21\frac{1}{3}}O_{32}$, which is based on a full spinel cubic cell [1–3].

Experiments [4,5] and theoretical calculations [6] have demonstrated that cubic alumina may exist over a range of hydrogen content. This range of H-content is captured by the formula $H_{3m}Al_{2-m}O_3$, which maintains valence neutrality. The value $m = 1/8$ corresponds to the ideal hydrogen–aluminum-spinel formula HAl_5O_8 where all the cation sites and all the anion sites are occupied. The H atoms may occupy either tetrahedral or octahedral sites. The value $m = 0$ corresponds to the hydrogen-free form where the empirical formula, including vacancies, is $\square Al_8O_{12}$. Here the vacancies may reside on either the tetrahedral or octahedral sublattice. The two extremes are denoted $(\square Al_2, Al_6)O_{12}$ and $(Al_3, \square Al_5)O_{12}$, where the comma separates the tetrahedrally coordinated species from those octahedrally coordinated. These two possibilities nominally correspond to the γ- and η-forms of cubic alumina [6], which are derived from different starting materials and exhibit minor differences in their X-ray diffraction patterns but significant differences in their catalytic activities.

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The surface of cubic alumina has been studied both by theoretical [7–11] and experimental [12,13] methods. In the present work we performed calculations (see Appendix A) to check the sensitivity of the reconstruction to the distribution of point defects (H or vacancies). We found that the mode of reconstruction is very different when the point defects are segregated to the tetrahedral or octahedral sublattices. First we note that, independent of the distribution of point defects, both the tetrahedral and octahedral cation sublattices are at least partially occupied by Al atoms, since neither sublattice is sufficient to hold all Al necessary to satisfy the stoichiometry. The preferentially exposed (1 1 0) surface [2,14] displays both tetrahedral and octahedral sites. One would, therefore, expect three-coordinated Al to arise when one of its four oxygen neighbors at a tetrahedral site is stripped away, and four-coordinated Al to arise when two of its six oxygen at an octahedral site are stripped away. When the defects reside on the tetrahedral cation sublattice, however, a massive spontaneous surface reconstruction occurs, the nominally three-coordinated Al drop from the surface layer into empty octahedral sites in the first subsurface layer, thereby depleting the three-coordinated Al from the surface. In contrast, when the point defects reside at sites in the octahedral cation sublattice, no such qualitative rebonding of surface Al occurs; the surface relaxes only slightly, exposing both three- and four-coordinated Al. This result is depicted in Fig. 1.

It has been shown that Al atoms at tetrahedral sites, when exposed at the surface (three-coordinated Al), have a lower energy acceptor orbital and therefore serve as stronger Lewis acids than Al atoms in O_h sites exposed at the surface [15, 16]. We are now able to conclude that the presence of these stronger Lewis acid sites is controlled by the surface reconstruction which in turn is controlled by the distribution of bulk point defects. Differences in Lewis acidity are a well documented property of the transition aluminas [17–19].

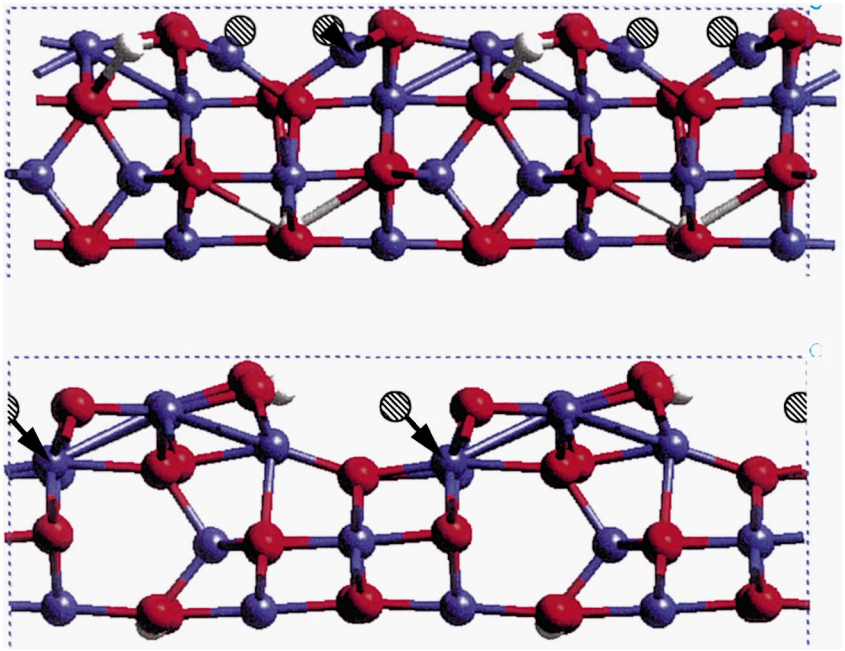

Fig. 1. Comparison of the relaxation of γ- and η-alumina (110C) surfaces. (η: top, γ: bottom) Oxygen atoms are shown in red and aluminum atoms in blue. The shaded circles represent the approximate initial positions of the surface three-coordinated Al atoms prior to relaxation. The arrows indicate the direction of movement.

In view of the above, we investigated the relative stability of the different distributions of point defects. Our total energy calculations show that the energetically preferred distribution of the point defects depends on whether the defect is H or □. In the case of HAl_5O_8, we have found that it is energetically preferred to have H nominally on the tetrahedral cation sublattice (each H actually occupies a site near one of the four oxygen neighbors). Normalizing the chemical potential to $Al_2O_3 + H_2O$, we find,

$$E\left[\tfrac{2}{5}HAl_5O_8(O_h) + \tfrac{4}{5}(H_2O)\right] - E\left[\tfrac{2}{5}HAl_5O_8(T_d) + \tfrac{4}{5}(H_2O)\right] = 0.06\ \text{eV}. \quad (1)$$

In the hydrogen-free form, however, the point defects (vacancies) prefer to occupy the octahedral cation sublattice.

$$E\left[\tfrac{1}{4}(\square Al_2, Al_6O_{12}) + H_2O\right] - E\left[\tfrac{1}{4}(Al_3, \square Al_5O_{12}) + H_2O\right] = 0.2\ \text{eV}. \quad (2)$$

From this total-energy perspective, H atoms prefer tetrahedral cation sites, whereas vacancies prefer octahedral cation sites. From an entropic perspective, there are twice as many octahedral cation sites as tetrahedral cation sites in the spinel structure. Theory, therefore, predicts that at high temperatures, when there is sufficient thermal energy to populate either site, entropy will favor point defects at the octahedral sites. At low temperatures where energetics prevail, H would prefer the tetrahedral sublattice. While the energy difference in the H-containing case is smaller than the expected accuracy of the calculations, the prediction is borne out by infrared spectroscopy, which finds H predominantly at the tetrahedral sites at low temperatures ($\leqslant 303$ K) and a preponderance of H on octahedral sites at elevated temperatures ($\geqslant 573$ K) [20]. [1] In principle, it should be possible to switch between these two defect distributions by capitalizing on these competing energetic and entropic effects through control of the temperature and H-content.

The above results lay a framework which may predicate the design of a novel tunable heterogeneous catalyst. We have seen that the catalytic activity of the surface is accentuated by the presence of three-coordinated Al on the surface. The presence of surface three-coordinated Al is in turn controlled by the distribution of point defects within the alumina bulk. It is therefore possible to tune the catalytic properties by adjusting the distribution of point defects. We recently demonstrated that H can be incorporated in or effused from bulk alumina by a "reactive sponge" process that entails the break up or reconstitution of H_2O molecules at the surface and the counterpropagation of Al atoms [6]. We now propose that incorporation of H to drive the low-temperature H-induced mode of reconstruction can be accomplished by pressurized steam. By raising the temperature, and if necessary pumping the steam out, the other reconstruction mode can be switched on. The fact that the high-temperature mode is catalytically more active holds promise for real applications in which catalysis needs to be done at high temperatures. The net conclusion is that atomic-scale knowledge can lead to the realization of a tunable catalyst controlled by macroscopic means, temperature and bulk H-content.

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[1] See also the discussion in Ref. [6].

Appendix A

The structural relaxation studies employed a 56-atom unit cell consisting of a slab of alumina four atomic layers thick. Calculations with five layer slabs (72-atom unit cell) were also carried out to check the sensitivity of the reconstructions to the thickness of the slab model. For the different slab thickness, the surface reconstructions were substantially identical. Only very minor differences in atomic positions were found, (on the order of 0.1 Å or less) suggesting that the slab models, while consisting of just four or five atomic layers, are sufficiently thick to capture the essential details of the surface reconstructions. The atoms in the bottom layer, and the dimensions (a, b, c, α, β, γ) of the unit cell were frozen. The system was modeled by infinitely repeating slabs with an inter-slab vacuum spacing of 10 Å. The starting structure from which each slab was generated was that of fully relaxed cubic alumina. The calculations employed density functional theory [21] with the generalized gradient approximation (GGA) to the exchange-correlation energy [22], as described in the review by Payne et al. [23]. The electron-ion interactions were described with non-local reciprocal-space pseudopotentials [24] in the Kleinman–Bylander form [25]. The electronic density was expanded in a plane wave basis with a cutoff energy (determined by convergence studies) of 1000 eV. 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 [26].

The computational results are supported by experimental work employing ^{27}Al NMR [12], which finds three-coordinated Al absent from γ-alumina surfaces, despite their expected presence based on a simple termination of the bulk [7]. (γ is a cubic form of alumina where the H dopants reside preferentially on the tetrahedral cation sublattice [6].) The qualitatively different relaxations of cubic alumina depending on the point-defect distribution are also supported by experiments employing X-ray and neutron scattering [13] on γ- and η-alumina. (η is a cubic form of alumina where the point defects reside preferentially on the tetrahedral cation sublattice [6].) The X-ray and neutron studies find that in γ-alumina, where the point defects are predominantly on tetrahedral cation sites, the surface relaxes dramatically and the abnormally coordinated surface Al reside 0.748 Å from the nearest oxygen plane. By contrast, in η-alumina where the point defects are predominantly on octahedral cation sites, the relaxation is minor and the abnormally coordinated surface Al are found just 0.162 Å from the nearest oxygen plane. Our calculations find 0.74 and 0.17 Å in the γ- and η-cases respectively, in excellent agreement with the experimental results.

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