

Surface Reconstruction and the Difference in Surface Acidity between γ - and η -Alumina

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Abstract: The surfaces of the γ and η forms of alumina are well known to differ significantly in Lewis acidity. Surface reconstructions observed on γ - and η -alumina are also qualitatively different, despite the close similarity of the bulk structures. Here we demonstrate through first-principles calculations that subtle differences in the bulk point defect distribution between these two forms of alumina give rise to the major differences in the mode of surface reconstruction and correlate with the different levels of Lewis acidity.

Introduction

The surface structures of γ - and η -alumina are of significant technological importance, owing to the wide-spread use of these materials in heterogeneous catalysis systems,¹ such as those employed in petroleum refining,² in the production of bulk and fine chemicals,³ and in automotive catalytic converters.⁴ The coordination of Al atoms on γ - and η -alumina surfaces is of particular interest because valence-unsaturated surface Al atoms are a source of surface Lewis acidity, which is central to catalysis.⁵ A detailed description of the η -alumina surface structure could also be of considerable value in assigning atomic-scale mechanisms to its dehydration, rehydration, and hydroxylation,^{6–10} critical issues in catalytic systems.¹¹

Dramatically different surface structures involving valence-unsaturated Al atoms have been reported on γ - and η -alumina surfaces.^{5,12} This is remarkable because the two materials have very similar bulk structures. In fact, the bulk structures of γ - and η -alumina are so closely related that in some historical instances they have been considered to be identical.^{13,14}

Previously, we suggested that γ - and η -alumina nominally

represent two extremes of the possible distribution of point defects (vacancies or H atoms) in cubic alumina, which depends on the precursor material.¹⁵ Here we report first-principles calculations of η -alumina bulk and surfaces and compare the results with our earlier results for γ -alumina bulk¹⁵ and surfaces.¹⁶ We are able to elucidate the origin of the different structures involving valence-unsaturated Al found on γ - and η -alumina surfaces. The results are in excellent agreement with experimental work employing ²⁷Al NMR,⁵ and X-ray and neutron scattering¹² and provide an explanation for the well-known greater acidity of η -alumina over γ -alumina.^{1,17,18}

Computational Method

The structural relaxation studies employed two models: a 56-atom unit cell consisting of a slab of η -alumina four layers thick and a 72-atom unit cell consisting of a slab five layers thick. 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 interslab vacuum spacing of 10 Å. The starting structure from which each slab was generated was that of fully relaxed η -alumina. Similar four-layer calculations were previously carried out for γ -alumina.¹⁶ A new five-layer calculation has been carried out as a check. As indicated in Table 1, the results of the structural relaxations in the four-layer

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(1) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980; Section 4.5.

(2) Knözinger, H.; Ratnasamy, P. *Catal. Rev.—Sci. Eng.* **1978**, *17*, 31.

(3) Shi, B.; Davis, B. H. *J. Catal.* **1995**, *157*, 359.

(4) Taylor, K. C. *Catal. Rev.—Sci. Eng.* **1993**, *35*, 457.

(5) Coster, D.; Blumenfeld, A. L.; Fripiat, J. J. *J. Phys. Chem.* **1994**, *98*, 6201.

(6) Borello, E.; Della Gatta, G.; Fubini, B.; Morterra, C.; Venturello, G. *J. Catal.* **1973**, *35*, 1.

(7) Della Gatta, G.; Fubini, B.; Stradella, L. *J. Chem. Soc., Faraday Trans. 2*, **1977**, *73*, 1040.

(8) Fubini, B.; Giannello, E.; Della Gatta, G. *J. Chim. Phys.* **1978**, *75*, 578.

(9) Breyse, M.; Coudurier, G.; Claudel, B.; Faure, L. *J. Lumin.* **1982**, *26*, 239.

(10) Chen, Y.; Hyldtoft, J.; Jacobsen, C. J. H.; Nielsen, O. F. *Spectrochim. Acta A* **1995**, *51*, 2161.

(11) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, *27*, 497.

(12) Zhou, R.-S.; Snyder, R. L. *Acta Crystallogr.* **1991**, *B47*, 617.

(13) Dragoo, A. L.; Diamond, J. J. *J. Am. Ceram. Soc.* **1967**, *50*, 568.

(14) Thornton, J. A.; Chin, J. *Am. Ceram. Soc. Bull.* **1977**, *56*, 504.

(15) Sohlberg, K.; Pennycook, S. J.; Pantelides, S. T. *J. Am. Chem. Soc.* **1999**, *121*, 7493.

(16) Sohlberg, K.; Pennycook, S. J.; Pantelides, S. T. *J. Am. Chem. Soc.* **1999**, *121*, 10999.

(17) MacIver, D. S.; Tobin, H. H.; Barth, R. T. *J. Catal.* **1963**, *2*, 485.

(18) Léonard, A. J.; Semaille, P. N.; Fripiat, J. J. *Proc. Br. Ceram. Soc.* **1969**, *103*, 103.

(19) Liu, X.; Truitt, R. E. *J. Am. Chem. Soc.* **1997**, *119*, 9856.

(20) Alvarez, L. J.; Sanz, J. F.; Capitán, M. J.; Centeno, M. A.; Odrizola, J. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3623.

(21) Alvarez, L. J.; Blumenfeld, A. L.; Fripiat, J. J. *J. Chem. Phys.* **1998**, *108*, 1724.

(22) Gunji, I.; Teraishi, K.; Endou, A.; Miura, R.; Yin, X. L.; Yamauchi, R.; Kubo, M.; Chatterjee, A.; Miyamoto, A. *Appl. Surf. Sci.* **1998**, *132*, 549.

(23) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140A*, 1133.

(24) Perdew, J. P.; *Phys. Rev. B* **1986**, *33*, 8822.

(25) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.

(26) Al pseudopotential: Winkler, B.; Milman, V.; Hennion, B.; Payne, M. C.; Lee, M. H.; Lin, J. S. *Phys. Chem. Miner.* **1995**, *22*, 461. H pseudopotential: CASTEP default reciprocal-space; O pseudopotential: Winkler, B.; Milman, V.; Hennion, B.; Payne, M. C.; Lee, M. H.; Lin, J. S. *Phys. Chem. Miner.* **1995**, *22*, 461.

(27) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425.

Table 1. Comparison of the Computed and Experimental Position of Quasi-Trihedral and Quasi-Octahedral Al on η - and γ -Alumina Surfaces, Respectively^a

method	quasi-trihedral (on η)	quasi-octahedral (on γ)
theor 4-layer (this work)	0.17	0.86
theor 5-layer (this work)	0.17	0.74
expt ¹²	0.162	0.748

^a Distances are given from the nearest (111) oxygen plane in angstroms.

and five-layer models were quantitatively very similar for both η - and γ -alumina. Further validation of the model comes from our earlier study of the reconstruction and hydroxylation of γ -alumina surfaces.¹⁶ As reported therein, the results are in excellent agreement with cross-polarizing ²⁷Al NMR studies of γ -alumina surfaces,⁵ with FTIR studies of surface hydroxylation,¹⁹ and with empirical potential-based molecular dynamics simulations.^{20–22}

The calculations employed density functional theory²³ with the generalized gradient approximation (GGA) to the exchange–correlation energy,²⁴ as described in the review by Payne et al.²⁵ The electron–ion interactions were described with nonlocal reciprocal-space pseudo-potentials²⁶ in the Kleinman–Bylander form.²⁷ The electronic density was expanded in a plane wave basis with a cutoff energy (determined by convergence studies) of 1000 eV. The hydrogen and oxygen atoms present introduce localized regions of high electron density into the structure. This “lumpiness” in the electron density implies that there is a high-frequency component in the electron density, which favors gradient-corrected exchange–correlation (GGA) and a large plane wave basis. 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.²⁸

Results

Both γ - and η -alumina are known as “spinel aluminas” because their structures are very closely related to that of Mg-spinel. η -Alumina is a dehydration product of bayerite, also found naturally in bauxite,²⁹ and γ -alumina is a dehydration product of boehmite.³⁰ In the related material Mg-spinel, the oxygen atoms are cubic close packed. The Mg atoms fill the 8(a) positions of the $Fd\bar{3}m$ space group and are therefore tetrahedrally coordinated by oxygen. (The tetrahedrally coordinated Mg occupy the T_d sublattice). The Al atoms fill the 16(d) positions of $Fd\bar{3}m$ and are therefore octahedrally coordinated by oxygen. (The octahedrally coordinated Al occupy the O_h sublattice). Both γ - and η -alumina have bulk structures also based on cubic close-packed oxygen with Al atoms (and under some conditions, H atoms) occupying some or all of the cation sites in the two spinel cation sublattices. Since the stoichiometry of aluminum oxide is Al₂O₃, neither cation sublattice in the Mg-spinel structure is adequate to accommodate all of the Al atoms necessary to produce the proper 2:3 ratio of Al:O. Complete occupation of *both* cation sublattices would result in an Al:O ratio of 3:4 (Al₃O₄), an excess of Al. In both γ - and η -alumina, some of the possible cation sites must be vacant for proper stoichiometry. The principle difference in bulk structure between γ - and η -alumina lies in the distribution of the cations over the two sublattices.^{12,31} The most complete and detailed experimental report of the structures of γ - and η -alumina, including the distribution of vacancies over the two cation sublattices, correlation lengths, and disorder, has been presented by Zhou and Snyder.¹²

In general, the fraction of the Al that is octahedrally coordinated (x_{O_h}) in any spinel alumina must fall within the range [62.5% \leq x_{O_h} \leq 75%]. The stoichiometry demands one cation vacancy out of nine spinel cation sites. To demonstrate the range of possible distributions for the cation vacancies, we start from the Mg-spinel primitive cell (Mg₂Al₄O₈), and multiply by 1.5 to achieve a formula with exactly nine cations, (Mg₃,Al₆O₁₂). (Here the comma separates the T_d and O_h cation species.) Replacing all Mg atoms with Al and introducing one cation vacancy, two limiting structures can be produced: (□Al₂-Al₆O₁₂) in which case all of the vacancies occupy tetrahedral (T_d) sites and 75% of the cations are octahedrally (O_h) coordinated, or (Al₃,□Al₅O₁₂) in which case all of the vacancies occupy octahedral sites and only 62.5% of the cations are octahedrally coordinated.

The above cation distributions over the two spinel cation sublattices are limiting cases, restricted by the spinel lattice and the Al₂O₃ stoichiometry. They may be nominally assigned to fully dehydrated γ - and η -alumina.¹⁵ ²⁷Al NMR studies by John et al.³² found 75 \pm 4% Al-coordinated O_h in γ -alumina and 65 \pm 4% Al-coordinated O_h in η -alumina. These results are supported by the ²⁷Al NMR studies of Lee et al.,³³ who reported quantitatively comparable results for γ -alumina, (η -alumina was not considered in ref 33) and by detailed X-ray and neutron scattering studies of Zhou and Snyder,¹² who reported a preference for vacancies at tetrahedral sites in γ -alumina and at octahedral sites in η -alumina.¹²

Of course, in a real material, there is some degree of disorder in the occupation of cation lattice sites. For example, it is not necessary for a real sample to exist at one extreme or the other of the physically allowed range (62.5% \leq x_{O_h} \leq 75%). Additionally, some cations may occupy sites other than 8(a) and 16(d) of $Fd\bar{3}m$. Indeed, in the case of η -alumina, Ernst et al.³¹ reported that a fraction of the Al atoms occupies the 16(c) and 48(f) sites. Furthermore, for these very high surface area materials, sufficiently many cations reside on surfaces that a significant fraction of them may be found in coordination environments not readily accessible to cations within the bulk.¹² For example, a three-coordinated Al would arise from a tetrahedrally coordinated Al being exposed at the surface. When at the surface layer, one of the four oxygens coordinating the Al in a tetrahedral site would be stripped away, leaving a three-coordinated Al. If the Al cation relaxes somewhat toward the remaining three oxygens (these lie in a (111) oxygen plane), its environment is termed “quasi-trihedral” and such species comprise 13% of all Al in η -alumina.¹² By way of contrast, quasi-trihedral Al are not seen in γ -alumina, but “quasi-octahedral” Al are.¹² A quasi-octahedral results when an Al resides much farther from the adjacent oxygen (111) plane, in a position where it is essentially six-coordinated.¹²

Three-coordinated Al will nominally be exposed when the (110C) layer of either γ - or η -alumina is exposed at the surface. We have carried out surface relaxation studies of γ -alumina surfaces using first-principles calculations and found that reconstruction of these surfaces accounts for the observed dearth of three-coordinated Al on γ -alumina (110) surfaces.¹⁶ The nominally three-coordinated Al at the (110C) surface relax into the first subsurface layer to become quasi-octahedral. We have also carried out calculations of the relaxation of η -alumina surfaces and found the nominally three-coordinated Al relax only until they become quasi-trihedral. This remarkable differ-

(28) Monkhorst, H. J.; Pack, J. D. *Phys. Rev.* **1976**, *B13*, 5188.

(29) Tilley, D. B.; Eggleton, R. A. *Clays Clay Miner.* **1996**, *44*, 658.

(30) Hill, R. J. *Clays Clay Miner.* **1981**, *29*, 435.

(31) Ernst, F.; Pirouz, P.; Heuer, A. H. *Philos. Mag. A* **1991**, *63*, 259.

(32) John, C. S.; Alma, N. C. M.; Hays, G. R. *Appl. Catal.* **1983**, *6*, 341.

(33) Lee, M.-H.; C–F. Cheng, Heine, V.; Klinowski, J. *Chem. Phys. Lett.* **1997**, *265*, 673.

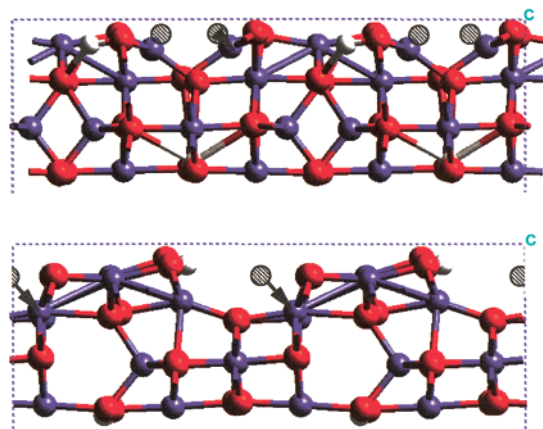


Figure 1. Comparison of the relaxation of γ - and η -alumina (110C) surfaces. (η top, γ bottom) Oxygen atoms are shown in red and aluminum atoms in blue. The shaded circles represent the approximate initial position of the surface three-coordinated Al atoms prior to relaxation. The arrows indicate the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

ence in the way γ - and η -alumina surfaces relax is depicted in Figure 1. The degree of surface relaxation between γ -alumina and η -alumina is in quantitative agreement with experiments, as shown in Table 1. Note the profoundly different degree of relaxation between γ - or η -alumina. Zhou and Snyder¹² used X-ray and neutron diffraction to determine that, in η -alumina, the quasi-trihedral Al lie 0.162 Å from the nearest (111) oxygen plane. The calculation yields 0.17 Å. For γ -alumina, Zhou and Snyder¹² reported that the quasi-octahedral Al lie 0.748 Å from the nearest (111) oxygen plane. The calculation yields 0.74 Å. The agreement between theory and experiment is excellent, confirming our conclusions. Because the relaxation processes are exothermic, the reverse processes are facilitated by elevated temperatures. At finite temperature, one would expect a fraction of the three-coordinated Al to remain on the γ -alumina surface, in higher energy positions. This is consistent with the molecular dynamics simulations of Alvarez et al.²⁰

Discussion

Since the chemical environment due to the first coordination shell is identical for the nominally three-coordinated Al on γ -alumina (110C) and η -alumina (110C), the difference in the degree of relaxation must result from the second coordination shell, where the closest differences appear. The first and second coordination shells of the nominally three-coordinated surface Al atoms in γ - and η -alumina are shown schematically in Figure 2. Note that some of the octahedrally coordinated Al atoms in the second coordination shell in γ -alumina are replaced by a vacancy (or H atom) in η -alumina. This means that, in η -alumina, some of the oxygen atoms that are directly coordinating the three-coordinated Al are themselves less fully coordinated than they would be in γ -alumina. With less complete coordination, it follows that these oxygen atoms are better Lewis bases and hence provide a more favorable bonding site for the three-coordinated Al. In short, the three-coordinated Al on η -alumina surfaces do not relax into quasi-octahedral coordination because they do not *need* to fully relax into octahedral coordination to achieve a satisfactory bonding arrangement.

The above explanation suggesting that the three-coordinated Al on η -alumina surfaces are more nearly valence satisfied than their counterparts on γ -alumina surfaces can be made more quantitative by application of the definition of effective charge introduced by Knözinger and Ratnasamy,² based on the Pauling

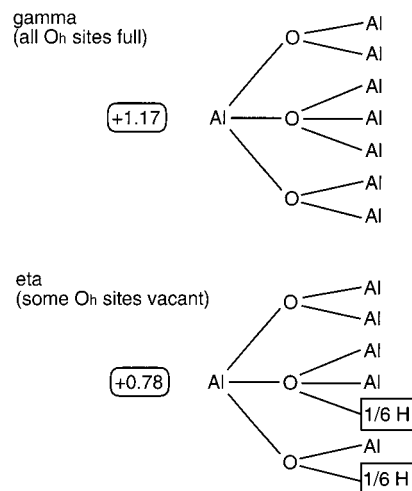


Figure 2. Schematic of the first and second coordination shells of nominally three-coordinated Al exposed at unreconstructed γ - and η -alumina (110C) surfaces. Note that in the case of γ -alumina the second coordination shell is complete, whereas in the case of η -alumina some of the Al atoms are replaced by vacancies or (1/6)H. This results in a higher effective charge on the surface Al in the case of γ -alumina.

electrostatic valence rules:³⁴ (*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*). Applying these rules, we see that when an Al atom in a tetrahedral site is exposed at the surface in γ -alumina, it becomes nominally three-coordinated and the effective charge is +1.17. Clearly this is electrostatically a highly unstable species. If an Al atom in a tetrahedral site is exposed at the surface in η -alumina, however, the effective charge is only +0.78. This lower effective charge arises from differences in the second coordination shell. In γ -alumina, *all* of the sites in the octahedral cation sublattice are occupied by Al atoms, so the oxygen atoms directly coordinating the nominally three-coordinated Al have their full complement of coordinating Al cations. In η -alumina, however, two of the aluminum atoms in the second coordination shell of the nominally three-coordinated Al are replaced by (1/6) hydrogen atoms; i.e., each H is shared among six oxygen atoms, only one of which is an oxygen directly coordinating the nominally three-coordinated Al. This loss of coordination to the oxygens is a benefit to the nominally three-coordinated Al; it is more nearly valence satisfied than its counterpart in γ -alumina. It is worth noting that we are describing the situation for the HAl_5O_8 perfect spinel composition of alumina.¹⁵ When an H atom resides in a tetrahedral site, there are four energetically degenerate positions that it may occupy (forming an O–H bond with any of the four nearest-neighbor O atoms). When treating a slab, or a system with defects, this degeneracy is slightly broken and consequently one position may be slightly favored over the others. These different choices of the H distribution are essentially insignificant.³⁵ In the fully dehydrated limit, the H atoms are replaced by vacancies. This does not qualitatively change the Pauling effective charges, which become +1.17 for γ -alumina and +0.86 for η -alumina in the dehydrated limit. Details of the dehydration process can be found in refs 16 and 36.

In addition to the fact that the three-coordinated Al in η -alumina is more nearly valence satisfied than its counterpart

(34) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(35) Sohlberg, K.; Pennycook, S. J.; Pantelides, S. T. The bulk and surface structure of γ -alumina. *Chem. Eng. Commun.*, in press.

(36) Wilson, S. J. *J. Solid State Chem.* **1979**, *30*, 247.

in γ -alumina, there is also less potential benefit to its full relaxation into quasi-octahedral coordination. In the case of γ -alumina, when the nominally three-coordinated Al relaxes into an empty octahedral interstice in the first subsurface layer, its effective charge becomes 0.0. In the case of η -alumina, however, if the nominally three-coordinated Al relaxed into an empty octahedral interstice in the first subsurface layer, its effective charge would become -0.2 , indicating an electrostatically less satisfactory position.

The result reported here, that three-coordinated Al appear on η -alumina surfaces as quasi-triangular Al, but relax to become quasi-octahedral Al on γ -alumina surfaces, also correlates to the relative acidity of η -alumina versus γ -alumina.^{1,17,18} It is known from semiempirical³⁷ and ab initio³⁸ cluster model calculations that Al atoms in T_d 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. Detailed studies of this inverse correlation between LUMO energy and Lewis acidity may be found in ref 39. Other relevant studies of solid acidity include refs 40 and 41. Since the three-coordinated Al are depleted from the γ -alumina surfaces by their spontaneous relaxation into six-coordinated sites in the first subsurface layer, but remain in three-coordination on the surface of η -alumina, it is expected that η -alumina surfaces should exhibit the greater Lewis acidity of the three-coordinated Al, in agreement with the well-known properties of these transition aluminas.^{1,17,18}

(37) Fleisher, M. B.; Golender, L. O.; Shimanskaya, M. V. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 745.

(38) Tachikawa, H.; Tsuchida, T. *J. Mol. Struct.* **1995**, 96, 277.

(39) Kawakami, H.; Yoshida, S. *J. Chem. Soc., Faraday Trans. 2* **1985**, 81, 1129.

(40) Nicholas, J. B.; Xu, T.; Haw, J. F. *Top. Catal.* **1998**, 6, 141; Nicholas, J. B.; Hess, A. C. *J. Am. Chem. Soc.* **1994**, 116, 5428.

(41) Brandle, M.; Sauer, J. *J. Am. Chem. Soc.* **1998**, 120, 1556.

Conclusions

We have applied density functional theory calculations to study the relaxation of γ -alumina surfaces and found that reconstruction of these surfaces accounts for the differences in surface Al coordination observed for γ - and η -alumina. Our surface reconstruction studies are based on models derived from limiting cases, founded on the observation that the fundamental distinction between γ - and η -alumina reduces to a difference in the distribution of Al atoms and vacancies over the two cation sublattices in the spinel structure. The calculations predict differences in the degree of surface relaxation between γ -alumina and η -alumina that are in excellent quantitative agreement with experiments. We have further demonstrated that these significantly different surface structures observed on γ - and η -alumina arise from subtle differences in the bulk point defect distribution, giving rise to qualitatively different effective charges for the Al atoms at the surface. The results provide insight into the well-known greater Lewis acidity of the η -alumina form.

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