Structure and Energetics of (111) Surface of γ-Al₂O₃: Insights from DFT Including Periodic Boundary Approach

Jiande Gu, Jing Wang, and Jerzy Leszczynski

ABSTRACT: The (111) surface of γ-alumina has been reexamined, and a new (111) surface model has been suggested. The local structure of this new surface of γ-alumina, (111)_n, has been optimized by the density functionals along with the full electron basis sets by using periodic boundary condition. This newly modeled (111)_n surface is characterized by the same stability as that of the (110) surface, and its surface energy amounts to 2.561 J/m², only about 0.002 J/m² larger than that of (110). Three different types of the tricoordinated Al centers have been identified on (111)_n. Molecular orbital (MO) analysis and the population analysis demonstrate that one type of Al, Al(I), is a nonpaired electron center. The singly occupied MO on Al(I) center is expected to play an important role in the catalytic activities of the γ-alumina. Moreover, the neighboring Al (Al(III)) on the (111)_n surface provides suitable acceptance position for the electron donating groups. The defected surfaces of (111)_n are found to be having a similar stability. The detachment of Al(I) from the (111)_n surface results in disappearance of the nonpaired electron centers. Meanwhile, the attachment of Al(I) on (111)_n surface will produce rich nonpaired electron centers on this new surface. Therefore, this newly defined surface is expected to attract the research interests in the catalytic activities of γ-alumina.

INTRODUCTION

One of the important forms of alumina phases determined by experimental investigations on deposited Al/Al₂O₃ multilayers is the so-called γ-alumina (γ-Al₂O₃). Although this form of alumina phase is widely used in industry, its accurate structure is still controversial. Understanding its structure and the corresponding properties inspires a large number of experimental and theoretical studies. Experimental and theoretical modeling on a low-index surface suggest the presence of pentacoordinated Al sites at the surface that might play a key role in the physicochemical properties of γ-Al₂O₃ surfaces. However, other studies indicated that the surface with tricoordinated centers is particularly important in the formation of active centers of dissociation of C–H bond in methane. Recent studies of the activation of methane on the γ-Al₂O₃ surfaces suggest that the highly reactive acid–base pairs created at the tricoordinated Al (Al(III)) enable low-energy pathways for the heterolytic splitting of C–H bond of methane.

The precise structure of γ-alumina is still undetermined though it has been modeled by different groups using theoretical approaches. Amongst these models, the model constructed by Digne et al. has been widely accepted for the investigations of the crystal facets in γ-alumina. On the basis of this model, most studies have been focused on the (100) and (110) surfaces. It is important to note that the highly reactive acid–base pair center, Al(III), exists only on the surface (110). On the other hand, the (111) surface of the γ-alumina has been reported to be much less stable and less important due to its high surface energy (as compared to that of (100) and (110) surfaces).

On examining Digne’s model of the γ-alumina, we noticed that there could exist a different form of (111) surface of the γ-alumina. Here, we report the local structure and the energy properties of this altered surface of γ-alumina (see Figure 2 below, denoted as (111)_n to differentiate the (111) surface model proposed by Digne et al.). Our studies demonstrate that this (111)_n surface has lower surface energy as compared to that of (110). Moreover, this new surface includes more tricoordinated Al centers, as compared to that of (110). Therefore, this newly reported findings should attract the
research interests, especially from a community interested in the catalytic activities of γ-alumina.

**METHODS AND MODEL**

**Selection of the (111)_n Surface.** The unit cell of the γ-alumina bulk was constructed according to the well-documented crystallographic data by Digne et al. (Figure 1).³⁴ Although this model cannot reproduce the intricacy of the γ-alumina entirely,³ it provides a good compromise between the structure reliability and the sizes compatible with quantum chemical calculations. On examination of the (111) surface of the γ-alumina proposed in ref 3 (see Scheme 1 for the corresponding surface selections of the γ-alumina and Figure 2, the light blue framed area that depicts (111) surface), we noticed that there is a similar surface that should be more stable. This is because less Al−O bond breaking is needed to form it (the black line indicated in Figure 2). The surface density of broken Al−O bonds is as low as 12.2 bonds/nm². As comparison, the surface density of broken Al−O bonds is 27.0 bonds/nm² for the surface (111) and 20.7 bonds/nm² for the surface (110).³ However, one should realize that surface energy does not depend entirely on the number of broken Al−O bonds. The bond energy also depends on the types of the Al−O bond. On the basis of this new (111)_n surface, a hexagonal lattice form of γ-Al₂O₃ unit cell was constructed, as shown in Figure 3. The construction of this new hexagonal lattice form does not alter the model of the γ-alumina. However, it provides an easy way to examine the (111)_n surface because in the hexagonal lattice form, (111)_n is on the surface of the unit cell, as can be seen from Figure 3. Similar to the rectangular form of the unit cell, this hexagonal form of cell also contains 40 atoms and 400 electrons. To ensure that there is sufficient bulk environment underneath the investigated surface, a supercell model consisting of two units along the (111)_n surface direction has been adapted (see Figure 4). Thus, a model of the supercell system that contains 80 atoms and 800 electrons has been used in the present computational study.

**Method of Computations.** The calculations are based on density functional theory (DFT). The spin-polarized density functional and the generalized gradient approximation by Perdew, Burke, and Ernzerhof (PBE/PBE)¹⁷,¹⁸ and the newly developed functional by Peverati and Truhlar (M11-L and MN12-L)¹⁹ have been used in the calculations. Instead of using the plane wave basis, such as in Vienna ab initio simulation package (VASP),²⁰−²² the localized basis set, the standard valence double ζ basis set, 6-31G,²³,²⁴ was applied. Also, the smaller basis set 3-21G²⁵ was tested for comparison. Periodic boundary conditions were applied for the description of the bulk phase. The total k-point number amounts to 76 for the two-unit cell system, and the corresponding repeated cell number reaches 1829 in the calculations for the bulk phase. For the computations of the surfaces, two-dimensional periodic boundary conditions were applied for the model systems. The total k-point number amounts to 52 in the surface phase studies. During the computations of the bulk phase, both atoms and the cell parameters were fully optimized. One should note that using a two-dimensional periodic boundary condition implies infinite vacuum above the studied surface. Therefore, the possible long-range interactions between the surfaces are not taken into consideration in this method. For the study of the surface, the positions of all of the atoms were fully optimized while the corresponding lattice vectors were kept fully optimized.

---

**Figure 1.** Unit cell of the γ-alumina bulk. Build according to ref 3. Color legends: red for O and light pink for Al.

**Figure 2.** Selections of the surface (111) and (111)_n of the γ-alumina. The blue line is the selection of the surface (111), and inside the light blue frame is the corresponding bulk (see Figure 4c of ref 3). The black line is the selection of the surface (111)_n, and inside the gray frame is the corresponding bulk. For color legends see Figure 1.

**Figure 3.** Two different views of the unit cell of the γ-alumina bulk in the hexagonal lattice form. This unit is a variation of the rectangular form of the unit cell build according to ref 3. Color legends: red for O and light pink for Al.

---

**Scheme 1. Selection of the Surfaces Corresponding to the Modeled γ-Alumina³**

---

**Figure 4.** Selection of the (111) surface. Build according to ref 3. Color legends: red for O and light pink for Al.
agreement compared to the experimental values of 46.39 Å³/Al₂O₃. However, the PBEPBE functional has a strong basis set smaller than that determined experimentally. Increasing 21G level of theory is 43.90 Å³ for each Al₂O₃, about 2.49 Å³/Al₂O₃. The cell volume calculated at the M11-L/3-21G level of theory is 45.65 Å³/Al₂O₃, still significantly overestimating the cell volume by about 0.74 Å³/Al₂O₃. This underestimates experimental data by about 0.74 Å³/Al₂O₃. The newly developed functional MN12-L type of basis set TZV slightly reduces the cell volume to 48.96 Å³/Al₂O₃, still significantly overestimating the cell volume as compared with the experimental value. Therefore, the following discussions will mainly be based on the results obtained using the PBEPBE functional with 6-31G and 3-21G basis sets.

### RESULTS AND DISCUSSION

The unit cell of the rectangular form of the model was optimized by DFT approach using the functional PBEPBE, M11-L, and MN12-L, with the all-electron basis set 6-31G (and also 3-21G), respectively. Table 1 summarizes the computed structural parameters of the cell unit, optimized by different methods.

| methods                  | PBEPBE    | M11-L     | MN12-L     | PW91⁴  |
|--------------------------|-----------|-----------|------------|--------|
| a (Å)                    | 5.648(5.510) | 5.491(5.417) | 5.559     | 5.587  |
| b (Å)                    | 8.528(8.320) | 8.285(8.172) | 8.364     | 8.413  |
| c (Å)                    | 8.241(8.067) | 8.029(7.936) | 8.097     | 8.068  |
| β (deg)                  | 91.00(91.14) | 91.24(91.26) | 91.28     | 90.59  |
| cell volume (Å³/Al₂O₃)   | 49.61(46.21) | 45.65(43.90) | 47.05     | 47.40  |
| space group              | P₆₃/m     |           |            |        |

⁴VASP calculations, using the plane wave basis ref 3. ⁵Experimental results ref 27. The cell unit optimized at the PBEPBE with the triple ζ basis set TZV.

Bulk structural parameters. The calculations using M11-L functional predict the most tightened cell parameters for the considered model. The cell volume calculated at the M11-L/3-21G level of theory is 43.90 Å³ for each Al₂O₃, about 2.49 Å³/Al₂O₃ smaller than that determined experimentally. Increasing the basis set to 6-31G improves the cell volume estimation. The cell volume calculated at M11-L/6-31G level amounts to 45.65 Å³/Al₂O₃. This underestimates experimental data by about 0.74 Å³/Al₂O₃. The newly developed functional MN12-L overestimates the cell volume by 0.66 Å³/Al₂O₃ when 6-31G basis set is used. With the 3-21G basis set, the functional PBEPBE predicts the cell volume of 46.21 Å³/Al₂O₃ best agreement compared to the experimental values of 46.39 Å³/Al₂O₃. However, the PBEPBE functional has a strong basis set dependency. The cell volume predicted at the PBEPBE/6-31G level of theory is 49.60 Å³/Al₂O₃, about 3.21 Å³/Al₂O₃ larger than that of the experimental value. Increasing to the triple-ζ type of basis set TZV 28,29 slightly reduces the cell volume to 48.96 Å³/Al₂O₃, still significantly overestimating the cell volume as compared with the experimental value. Therefore, the following discussions will mainly be based on the results obtained using the PBEPBE functional with 6-31G and 3-21G basis sets.

The fully optimized supercell unit in the hexagonal form in bulk is depicted in Figure 4. The space group is found to be P2₁/m for the fully optimized cell. Also, the fully optimized (111)ₙ surface model is given for comparison. As mentioned above, two slabs of the unit have been adapted to ensure inclusion of sufficient bulk environment underneath the considered surface. During the optimization process of the surface (111)ₙ, the periodic boundary conditions were applied only for the b and c directions of the unit cell. Also, the cell lengths of b and c in the surface unit were kept as the same as those of the optimized unit in bulk. The optimized structural parameters of the cell unit are summarized in Table 2, and the corresponding coordinates of the atoms in the cells are given in the Supporting Information. As expected, the cell volume in the hexagonal form of the model is virtually the same as that in its rectangular form. This indicates that the model selection and the computation method applied are reasonable and are suitable in the present study.

On the basis of the supercell (two-unit cell) model (in which the film consists of eight atomic layers, see Figure 4) the surface energy of the nonoptimized (111)ₙ surface is calculated to be 2.946 J/m² at the PBEPBE/6-31G level of theory. The corresponding surface energy is 3.091 J/m² at the PBEPBE/6-31G//3-21G level of theory. Optimization leads to the decrease in the surface energy by about 0.624 J/m². The surface energy of the optimized (111)ₙ surface amounts to 2.322 J/m² by the PBEPBE/6-31G//3-21G level of theory. Using the PBEPBE/6-31G//3-21G approach, this surface energy is 2.561 J/m². The surface energy difference resulted from the basis-set-induced geometric variation is around 0.24 J/m², as revealed by the PBEPBE method. This difference is smaller than that obtained by applying different functionals. The surface energy of (111)ₙ surface is computed to be 3.087 J/m² at the MN12-L/6-31G level of theory (3.781 J/m² for the nonoptimized surface).

For comparison, the surface energy of the (110) surface was calculated at the PBEPBE/6-31G//3-21G level of theory on the basis of the supercell of the rectangular form (Figure 5). The surface energy of the nonoptimized (110) surface is
calculated to be 3.355 J/m², about 0.264 J/m² larger than that of (111)_n surface. Furthermore, on the basis of the optimized structures, the surface energy of (110) surface is evaluated to be 2.559 J/m², about 0.002 J/m² smaller than that of (111)_n surface. Therefore, the formation of this novel (111)_n surface is expected to be as feasible as the case of (110) surface under the dehydrated conditions.

It is important to note that the surface energies calculated by using the localized basis sets (3-21G and 6-31G) are significantly larger than those computed by using the plane wave basis (using the VASP program).^{20−22} With the nonlocalized plane wave basis, the PBEPBE method predicts that the surface energy of the (111)_n surface amounts to 1.772 J/m², whereas that of the (110) surface is 1.760 J/m² at the same level of theory (supercell model, eight atomic layers, with a vacuum thickness of 40 Å between the periodically repeated slabs). For comparison, the relaxed surface energy of the (110) surface is reported to be 1.540 J/m² with PW91 functional (slab with eight atomic layers, with a vacuum thickness of 12 Å between the periodically repeated slabs, see ref 3).

It is clear that the surface energy predicted by using the localized basis sets is significantly larger than that by using the plane wave basis set. This surface energy difference can be attributed to the valence electrons only description of the Al−O bonding by the plane wave approaches. The larger surface energies predicted using the localized basis sets suggest that Al−O bonding may be included in the inner-shell electron configurations contribution.

The results of band gap predictions are found to be strongly related to the functional used. For the bulk phase, the band gap is 7.64 eV by the MN12-L/6-31G approach, whereas it is 5.86 eV by the PBEPBE/6-31G method. For comparison, the electron gap is 3.9−4.9 eV with the functional PW91 by using the plane wave basis set in the VASP calculations.\(^3,5\) For the (111)_n phase, the band gap predicted in the present study is reduced to 3.21 eV at the MN12-L/6-31G level of theory and to 3.25 eV at the PBEPBE/6-31G level of theory. This reduced electron gap implies existence of active sites on the surface.

**Local Structure of (111)_n Surface.** Only three-coordinated Al atoms are found in this (111)_n surface. One of them comes from the six-coordinated Al (marked I in Figure 4) in bulk phase and the other two are derived from the four-coordinated Al (marked II and III in Figure 4). The top view of

### Table 3. Geometries of the Local Structure of the Surface (111)_n Optimized by PBEPBE Functional with Basis Sets 6-31G and 3-21G\(^a\)

|                      | 3-21G  | 6-31G  | 3-21G  | 6-31G  |
|----------------------|--------|--------|--------|--------|
|                      | surface | bulk   | surface | bulk   |
| R_{iR}               | 1.878  | 1.963  | 1.921  | 2.006  |
| R_{iD}               | 1.878  | 1.960  | 1.920  | 2.002  |
| R_{ii}               | 1.896  | 1.888  | 1.907  | 1.921  |
| R_{iD}               | 1.800  | 1.836  | 1.821  | 1.873  |
| R_{ii}               | 1.738  | 1.788  | 1.765  | 1.818  |
| R_{iD}               | 1.738  | 1.788  | 1.765  | 1.818  |
| R_{ii}               | 1.730  | 1.837  | 1.746  | 1.873  |
| R_{iD}               | 1.748  | 1.777  | 1.766  | 1.805  |
| R_{ii}               | 1.748  | 1.777  | 1.766  | 1.805  |
| D_{ii}               | 57.06  | 59.21  | 57.65  | 59.91  |
| D_{ii}               | 3.36   | 33.26  | 0.09   | 32.64  |
| D_{iD}               | 19.24  | 33.61  | 17.20  | 33.85  |

\(^a\)R_{ij}: Al−O atomic distance in Å; D_{ij}: dihedral angle in (deg); for labels see Figure 6.
surface (111)$_n$ is about 3°. It seems that by sharing the coordinating atom O(3), the presence of Al(I) in the neighbor position strongly influences the bonding pattern of Al(II). This phenomenon will be discussed again in the next section.

Molecular orbital (MO) analysis demonstrates that one of the sp$^3$ type of MOs of Al(I) is singly occupied (Figure 7, highest occupied molecular orbital, HOMO $- 2$ of $\alpha$ MO and lowest unoccupied molecular orbital (LUMO) of $\beta$ MO). Consistent with the MO analysis, the population analysis based on the electron density (Table 4) reveals that the spin density of Al(I) amounts to 0.74 and that of Al(III) to 0.00. This single occupancy of Al(I) is further confirmed by the projected density of states (PDOS) analysis of the surface phase. The weak peak around $-0.4$ eV in Figure 8 is mainly attributed to the singly occupied HOMO $- 2$ of $\alpha$ MO, whereas the weak peak at around 3.4 eV is assigned to the corresponding LUMO of $\beta$ MO. This singly occupied MO of Al(I) is expected to play an important role in the catalytic activities of the $\gamma$-alumina. On the other hand, the unoccupied sp$^3$ MO of Al(III) (Figure 7) on the (111)$_n$ surface provides good acceptance location for the electron donating groups. Figure 9 displays the PDOS of the Al and O on the (111)$_n$ surface phase. As expected, the occupied lower energy bands are mainly contributed by the electrons from O, indicating the coordination bonding between the anionic O and the positively charged Al. On the other hand, the notable contributions from O to the first unoccupied bands suggest that the electrons of the O are more attracted toward the Al on the surface phase, as compared with on the bulk phase. This is consistent with the spin density analysis (Table 4) on the (111)$_n$ surface. Also, this indicates a stronger Al–O bond on the surface phase, agreeing with the short Al–O bond length, as revealed in the last section.

### (111)$_n$ Surface with Defects

As mentioned above, the bonding between O and Al(I) is weakened on the (111)$_n$ surface of the $\gamma$-alumina. Therefore, Al(I) might be detached from the (111)$_n$ surface during the surface creation. This Al(I) detached surface of the $\gamma$-alumina will be labeled here as (111)$_{nd}$. Meanwhile, this detached Al(I) is more likely to be retained on the other side of the surface during the crystal splitting process (see Figure 10), forming Al(I)-attached surface (111)$_{na}$. The surface energy of the nonoptimized (111)$_{nd}$ and (111)$_{na}$ surface is calculated to be 3.091 J/m$^2$ at the PBEPBE/6-31G//3-21G level of theory. Optimization leads to the surface energy of 2.556 J/m$^2$. Thus, the stability of the defected (111)$_n$ surface is nearly the same as that of the (110) surface. The local geometric parameters of the optimized (111)$_{nd}$ surface are listed in Table 5. Only Al(III) type of Al exists on this surface (see Figure 11). The detachment of Al(I) from the (111)$_n$ surface eliminates the planar form Al–O coordinating bonding. The dihedral angle of O(3)–O(4)–O(5)–Al(II) on the surface (111)$_{nd}$ is about 25°, roughly close to that of O(6)–O(7)–O(8)–Al(III) on the (111)$_n$ surface. Both MO analysis and the population analysis (Table 6) indicate that the Al atoms on this defected surface are close-shelled. The detachment of Al(I) from the (111)$_n$ surface removes the nonpaired

![Figure 7. HOMO $- 2$ of $\alpha$ orbital (upper, left) and LUMO of $\beta$ orbital (upper, right); LUMO $+ 3$ of $\alpha$ and $\beta$ orbital (bottom).](image-url)

**Table 4. Mulliken Charge and Spin Density of the Local Structure of the Surface (111)$_n$**

|        | charge | spin   |
|--------|--------|--------|
| Al(I)  | 0.923  | 0.737  |
| Al(II) | 1.037  | $-0.014$ |
| Al(III)| 1.088  | $0.001$ |
| O(1)   | $-0.994$ | $0.021$ |
| O(2)   | $-0.994$ | $0.021$ |
| O(3)   | $-1.010$ | $0.021$ |
| O(4)   | $-0.951$ | $0.005$ |
| O(5)   | $-0.951$ | $0.005$ |
| O(6)   | $-0.943$ | $0.002$ |
| O(7)   | $-0.961$ | $0.000$ |
| O(8)   | $-0.961$ | $0.000$ |

*Analysis based on the density by PBEPBE functional with basis sets 6-31G. For labels, see Figure 6.*

![Figure 8. PDOS of Al(I) on the (111)$_n$ surface phase.](image-url)
electron centers. Two types of Al are found on the surface (111)$_{na}$: Al(I) and Al(II). Similar to that on the (111)$_{n}$ surface, one nonpaired electron locates on Al(I), as shown by the population analysis (Table 6). As expected, the geometry of Al(I) on the surface (111)$_{na}$ resembles that on (111)$_{n}$ surface. The dihedral angle of O(1)–O(3)–O(2)–Al(I) on the surface (111)$_{na}$ is 56.77°. Meanwhile, Al(II) on the surface virtually lies in the plane formed by the three coordinating O atoms. This is evidenced by the value of 4° of the dihedral angle O(3)–O(4)–O(5)–Al(II) on the (111)$_{na}$ surface.

Figure 9. PDOS of Al and O on the (111)$_{n}$ surface phase. The total number of Al is 3 and that of O is 12 on the modeled surface.

Figure 10. Creation of the defected surfaces (111)$_{nd}$ and (111)$_{na}$.

Table 5. Geometries of the Local Structure of the Defected Surface (111)$_{na}$ and (111)$_{nd}$, Optimized by PBEPBE Functional with Basis Sets 3-21G

|                  | (111)$_{na}$ | (111)$_{nd}$ |
|------------------|--------------|--------------|
| $R_{1}$          | 1.903        |              |
| $R_{2}$          | 1.902        |              |
| $R_{3}$          | 1.880        |              |
| $R_{III,III}$    | 1.808        | 1.735        |
| $R_{III,IV}$     | 1.756        | 1.739        |
| $D_{132}$        | 56.77        |              |
| $D_{345,III}$    | 4.03         | 24.99        |

$R_{i,j}$: Al–O atomic distance in Å; $D_{ijk}$: dihedral angle in (deg), labels see Figure 9. II in (111)$_{na}$ and III in (111)$_{nd}$.

Figure 11. Top view of the defected surfaces (111)$_{nd}$ (left) and (111)$_{na}$ (right). Atoms underneath the surface have been deleted for clarity.

Table 6. Mulliken Charge and Spin Density of the Local Structure of the Surface (111)$_{na}$ and (111)$_{nd}$

|                  | (111)$_{na}$ | (111)$_{nd}$ |
|------------------|--------------|--------------|
| charge           | spin         | charge       | spin         |
| Al(I)            | 0.829        | 0.884        | 1.182        | 0.000        |
| Al(II, III)$^b$  | 0.898        | −0.014       | −0.945       | −0.008       |
| O(1)             | −0.973       | 0.027        | −0.982       | 0.013        |
| O(2)             | −0.972       | 0.027        | −0.982       | 0.013        |
| O(3)             | −1.019       | 0.025        | −0.945       | −0.008       |
| O(4)             | −0.950       | −0.000       | −0.982       | −0.013       |
| O(5)             | −0.950       | −0.000       | −0.982       | −0.013       |

$^a$Analysis based on the density by PBEPBE functional with basis sets 6-31G. For labels see Figure 9. $^b$Al(II) in (111)$_{na}$ and Al(III) in (111)$_{nd}$.
CONCLUDING REMARKS

The local structure of the newly revealed surface of γ-alumina, (111)γ, has been optimized by density functional methods along with the localized full electron basis sets using periodic boundary conditions. Our studies demonstrate that the (111)γ surface has lower surface energy as compared to that of (111) and similar surface energy as compared to that of (110). The surface energy of the optimized (111)γ surface of 2.561 J/m² is only 0.002 J/m² larger than that of (110), suggesting a higher degree of order in our laboratories. Our studies demonstrate that the (111)γ surface is of importance. Studies of these properties can provide information about the Lewis acidity of the Al(1) component for the catalytic activities of the γ-alumina. Moreover, the neighboring Al (Al(III)) on the (111)γ surface provides a suitable location for the electron donating groups. Therefore, this could be vital for the catalytic activities of γ-alumina.

The defected surfaces of (111)γ are found to have a similar stability. The detachment of Al(I) from the (111)γ surface results in disappearance of the nonpaired electron centers. Meanwhile, the attachment of Al(I) on (111)γ surface will produce rich nonpaired electron centers on this new surface. The study of the hydration properties and the corresponding thermal stability is of importance for the understanding of the catalysis procedures of the new surface. Also, the study of the adsorption properties of suitable probe molecules (e.g., CO) that can provide information about the Lewis acidity of the γ-alumina surface sites is of importance. Studies of these properties are underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01921. Coordinates of the studied models in the present report, including optimized structure of (111)γ surface of γ-alumina, optimized structure of bulk phase of γ-alumina, optimized structure of (111)γ surface of γ-alumina, and optimized structure of bulk phase of γ-alumina (PDF).

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jiande@icnanotox.org (J.G.).
*E-mail: jerzy@icnanotox.org (J.L.).

ORCID

Jerzy Leszczynski: 0000-0001-5290-6136

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Work in the USA was supported by the ONR grant N00014171306. The computation time was provided by the Extreme Science and Engineering Discovery Environment (XSEDE) by National Science Foundation Grant Number OCI-1053575 and XSEDE award allocation number DMR110088 and by the Mississippi Center for Supercomputer Research. The authors thank Dr. Pabitra Samanta for reading this manuscript and constructive comments.

REFERENCES

(1) Goswami, R.; Pande, C. S.; Bernstein, N.; Johannes, M. D.; Baker, C.; Villalobos, G. A high degree of enhancement of strength of sputter deposited Al/Al2O3 multilayers upon post annealing. Acta Mater. 2015, 95, 378–385.
(2) Wischert, R.; Copéret, C.; Delbecq, F.; Sautet, P. Optimal Water Coverage on Alumina: A Key to Generate Lewis Acid–Base Pairs that are Reactive Towards the C–H Bond Activation of Methane. Angew. Chem., Int. Ed. 2011, 50, 3202–3205.
(3) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Touilhoat, H. Use of DFT to achieve a rational understanding of acid–base properties of γ-alumina surfaces. J. Catal. 2004, 226, 54–68.
(4) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Touilhoat, H. Hydroxyl Groups on γ-Alumina Surfaces: A DFT Study. J. Catal. 2002, 211, 1–5.
(5) Pinto, H. P.; Nieminen, R. M.; Elliott, S. D. Ab initio study of γ-Al2O3 surfaces. Phys. Rev. B 2004, 70, No. 125402.
(6) Lodziana, Z.; Topsoe, N.; Norskov, J. K. A negative surface energy for alumina. Nat. Mater. 2004, 3, 289–293.
(7) Louwerse, M. J.; Rothenberg, G. Modeling Catalyst Preparation: The Structure of Impregnated-Dried Copper Chloride on γ-Alumina at Low Loadings. ACS Catal. 2013, 3, 1545–1554.
(8) Kovarik, L.; Genc, A.; Wang, C.; Qiu, A.; Peden, C. H. F.; Stanyi, J.; Kwak, J. H. Tomography and High-Resolution Electron Microscopy Study of Surfaces and Porosity in a Plate-like γ-Al2O3, J. Phys. Chem. C 2013, 117, 179–186.
(9) Larson, J. G.; Hall, W. K. Studies of the Hydrogen Held by Solids. VII. The Exchange of the Hydroxyl Groups of Alumina and Silica-Alumina Catalysts with Deuterated Methane. J. Phys. Chem. 1965, 69, 3080–3089.
(10) Robertson, P. J.; Scurrell, M. S.; Kemball, C. Exchange of alkanes with deuterium over γ-alumina. A Bronsted linear free energy relationship. J. Chem. Soc., Faraday Trans. 1 1975, 71, 903–912.
(11) Hargreaves, J. S. J.; Hutchings, G. J.; Joyner, R. W.; Taylor, S. H. A study of the methane-deuterium exchange reaction over a range of metal oxides. Appl. Catal., A 2002, 227, 191–200.
(12) Quanzhi, L.; Amenomiya, Y. Exchange reaction of methane on some oxide catalysts. Appl. Catal. 1986, 23, 173–182.
(13) Knözinger, H.; Ratnasamy, P. Catalytic Aluminas: Surface Models and Characterization of Surface Sites. Catal. Rev.: Sci. Eng. 1978, 17, 31–70.
(14) Joubert, J.; Salameh, A.; Krakoviack, V.; Delbecq, F.; Sautet, P.; Copéret, C.; Basset, J.-M. Heterolytic Splitting of H2 and CH4 on γ-Alumina as a Structural Probe for Defect Sites. J. Phys. Chem. B 2006, 110, 23944–23950.
(15) Krokidis, X.; Raybaud, P.; Gebichon, A. E.; Rebour, B.; Euzen, P.; Touilhoat, H. Theoretical Study of the Dehydration Process of Boehmite to γ-Alumina. J. Phys. Chem. B 2001, 105, 5211–5310.
(16) Paglia, G.; Rohl, A. L.; Buckley, C. E.; Gale, J. D. Determination of the structure of γ-alumina from interatomic potential and first-principles calculations: The requirement of significant numbers of nonspinel positions to achieve an accurate structural model. Phys. Rev. B 2005, 71, No. 224119.
(17) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(18) Perdew, J. P.; Burke, K.; Ernzerhof, M. Errata: Generalized gradient approximation made simple. Phys. Rev. Lett. 1997, 78, No. 1396.
(19) (a) Peverati, R.; Trulhar, D. G. M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. J. Phys. Chem. Lett. 2012, 3, 117–124. (b) Peverati, R.; Trulhar, D. G. An improved and broadly accurate local approximation to the exchange-correlation density functional: The MN12-L functional for electronic structure calculations in chemistry and physics. Phys. Chem. Phys. Chem. Phys. 2012, 14, 13171–13174.
(20) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758–1775.
(21) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, No. 11169.

(22) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6, 15—50.

(23) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 12. Further extensions of Gaussian-type basis sets for use in molecular-orbital studies of organic-molecules. *J. Chem. Phys.* 1972, 56, 2257.

(24) Binning, R. C., Jr.; Curtiss, L. A. Compact contracted basis-sets for 3rd-row atoms-GA-KR. *J. Comput. Chem.* 1990, 11, 1206—1216.

(25) Dobbs, K. D.; Hehre, W. J. Molecular-orbital theory of the properties of inorganic and organometallic compounds. 6. Extended basis-sets for 2nd-row transition-metals. *J. Comput. Chem.* 1987, 8, 880—893.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, M. A.; Robb, J. R.; Cheeseman, G.; Scalmani, V.; Barone, B.; Mennucci, G. A.; Petersson, G. E. et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

(27) Wilson, S. J. The dehydration of boehmite, γ-AlOOH, to γ-Al2O3. *J. Solid State Chem.* 1979, 30, 247—255.

(28) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian-basis sets for atoms Li to Kr. *J. Chem. Phys.* 1992, 97, 2571—2577.

(29) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian-basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* 1994, 100, 5829—5835.