Surface Energies and Thermodynamic Phase Stability in Nanocrystalline Alumina

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Corundum, α-Al₂O₃, is the thermodynamically stable phase of coarsely crystalline aluminum oxide, but syntheses of nanocrystalline Al₂O₃ usually result in γ-Al₂O₃. Adsorption microcalorimetry, thermogravimetric analyses, and Brunauer-Emmett-Teller adsorption experiments, coupled with recently reported high-temperature solution calorimetry data, prove that γ-Al₂O₃ has a lower surface energy than α-Al₂O₃ and becomes energetically stable at surface areas greater than 125 square meters per gram and thermodynamically stable at even smaller surface areas (for example, 75 square meters per gram at 800 kelvin). The results are in agreement with recent molecular dynamics simulations and provide conclusive experimental evidence that differences in surface energy can favor the formation of a particular polymorph.

Syntheses of nanocrystalline metal oxides often yield materials structurally different from the thermodynamically stable phase (1). Examples are nanocrystalline cubic BaTiO₃ (2), tetragonal ZrO₂ (3), and monoclinic Y₂O₃ (4). It is commonly assumed that these metastable structures are adopted in order to lower the total energy of the material through a decrease in surface energy. However, little experimental data on oxide surface energies are available (5).

Corundum, α-Al₂O₃, is the thermodynamically stable phase of coarsely crystalline aluminum oxide at standard temperature and pressure conditions, but syntheses of nanocrystalline Al₂O₃ usually result in γ-Al₂O₃ (6). In addition, γ-Al₂O₃ can maintain surface areas of ~150 m² g⁻¹ at 1073 K (7), whereas nanophase α-Al₂O₃ coarsens to values ~50 m² g⁻¹ at such temperatures. Recently, Blondi and Cerofolini (8) performed molecular dynamics simulations of various α-Al₂O₃ and γ-Al₂O₃ surfaces. The surface energies for α-Al₂O₃ (9) were significantly higher than those of γ-Al₂O₃. According to their data, assuming preferential exposure of the surfaces with lowest energy, γ-Al₂O₃ should become the energetically stable polymorph as specific surface areas exceed ~125 m² g⁻¹ (Fig. 1). The thermodynamic stability of γ-Al₂O₃ should be even greater than implied by this energy. As a result of the presence of tetrahedral and octahedral sites in its spinel-type structure, and the fairly random distribution of Al³⁺ and vacancies over these sites, γ-Al₂O₃ has a greater entropy than α-Al₂O₃. The entropy change of the α-Al₂O₃ to γ-Al₂O₃ transition, ΔSₐ→γ, is about 5.7 J K⁻¹ mol⁻¹ (10). Therefore, at room temperature, γ-Al₂O₃ could become thermodynamically stable with respect to α-Al₂O₃ at specific surface areas greater than 100 m² g⁻¹, and at 800 K (a temperature typical of a hydroxide decomposition), γ-Al₂O₃ might become thermodynamically stable at specific surface areas greater than only 75 m² g⁻¹ (dotted line, Fig. 1).

We have recently explored this possibility by high-temperature solution calorimetry on several samples of nanocrystalline α-Al₂O₃ and γ-Al₂O₃ (11). However, the surfaces of the Al₂O₃ were modified by adsorbed H₂O, which could not be completely removed without severe coarsening (especially for α-Al₂O₃). The surface energies of the hydrated polymorphs were nearly equal, indicating that the heat of chemisorption of H₂O is directly proportional to the surface energy of the anhydrous phase [a relation predicted by Cerofolini (12)]. Consequently, we could not determine the anhydrous surface energies without accurate knowledge of the heats of chemisorption of H₂O. Herein we report these crucial data.

The heats of chemisorption of H₂O on two samples of γ-Al₂O₃ and two samples of α-Al₂O₃ [prepared according to the methods of Perrotta et al. (13)] were measured with a Calvet-type microcalorimeter. About 100 mg of alumina was thermally activated under vacuum. The temperature was increased at 2 K min⁻¹ to 1023 K, held at 1023 K for 2 hours, and cooled to the adsorption temperature, 303 K. The sample was then exposed to successive small doses of H₂O vapor (0.3 to 3.0 cm³ per gram of alumina). The residual pressure was increased from 6.67 mPa to 66.7 Pa in 15 to 20 steps. The heat released and volume of H₂O adsorbed were measured at each step.

The specific surface areas [measured by means of N₂ adsorption at 77 K by the Brunauer-Emmett-Teller (BET) method], residual H₂O contents [as judged by thermogravimetric analysis (TGA)], and phase purity [measured by powder x-ray diffraction (7, 14)] were determined after the powders were subjected to the outgassing procedure described above.

The TGA revealed that an average 2.6 OH nm⁻² were not removed under the outgassing conditions. The adsorption data in Fig. 2 are therefore shown as starting at this coverage to account for the presence of these “preadsorbed” hydroxyls. The differential heat of H₂O adsorption on γ-Al₂O₃ (Fig. 2) decreases logarithmically with increasing coverage (Freundlich behavior), which is consistent with previous studies of this material (15, 16). In contrast, the differential heat of H₂O adsorption on α-Al₂O₃ does not show regular logarithmic decay and decreases far less rapidly with increasing coverage. The first 10 OH nm⁻² adsorbed to the α-Al₂O₃ surface give heats of adsorption that are in excess of ~150 kJ mol⁻¹, whereas only the first 5 OH nm⁻² exceed this value on γ-Al₂O₃. This imbalance indicates a greater number of high-energy sites on α-Al₂O₃ per unit surface area, which are relaxed by the most strongly chemisorbed hydroxyls. This observation is strong evidence that the surface energy of α-Al₂O₃
Fig. 4. Differential (A) and integral (B) heats of chemisorption of H2O on γ-Al2O3 [36 m2 g⁻¹ (●), 61 m2 g⁻¹ (■) and γ-Al2O3 [72 m2 g⁻¹ (▲), 161 m2 g⁻¹ (▼)] as a function of hydroxyl coverage.

is higher than that of γ-Al2O3.

Assuming that the heat of desorption is the negative of the heat of adsorption (17), these data can be used to correct our previously reported calorimetry data on hydrated samples for heat effects due to H2O desorption. High-temperature drop solution calorimetry had been performed in a Tian-Calvet twin microcalorimeter (18) operating at ~979 K, with 2PbO·B2O3 as the solvent. The measured heat effect was a combination of the heat content of H2O vapor between 298 K and 979 K, the heat of solution of the Al2O3. This is represented by reaction 1, where x is the mole fraction of adsorbed H2O and Asurf is the specific surface area. The room-temperature enthalpy difference between the anhydrous nanophasie aluminas and coarse corundum can then be obtained through the following thermochemical cycle

\[
\begin{align*}
\text{α or γ-Al2O3 (Asurf 298 K)} & + x\text{H}_2\text{O (adsorbed on Al2O3, 298 K)} \rightarrow \\
\text{Al2O3 (dissolved in 2PbO·B2O3, 979 K)} & + x\text{H}_2\text{O (gas, 979K)} \\
\text{H2O (adsorbed on Al2O3, 298 K)} & \rightarrow \\
\text{H2O (gas, 979 K)} & \rightarrow \\
\text{α-Al2O3 (corundum, 298 K) → Al2O3} & \text{(dissolved in 2PbO·B2O3, 979 K)}
\end{align*}
\]  

Equation 2 and ΔH2 represent the correction for heat effects due to adsorbed H2O. The integral heat of desorption of for all of the adsorbed H2O and the heat content of H2O vapor between 298 and 979 K.

Before the high-temperature solution calorimetry, the samples were allowed to equilibrate at H2O partial pressure and temperature (heating rate = 5 K min⁻¹) to each measured data point, so that the extrapolated line intersected the origin (Fig. 2B). The average integral heat of H2O chemisorption for these coverages can be obtained from the data in Fig. 2B and Table 2. To account for the "preadsorbed" 2.6 OH nm⁻², we extrapolated the data below 6 OH nm⁻² linearly to zero OH nm⁻² and adjusted by adding 0.490 J m⁻² to each measured data point, so that the extrapolated line intersected the origin (Fig. 2B). The average integral heat of H2O chemisorption for these coverages is then ~163.7 ± 8.8 kJ (mol H2O)⁻¹ for γ-Al2O3 and ~122.5 ± 4.5 kJ (mol H2O)⁻¹ on α-Al2O3. This value for γ-Al2O3 is in good agreement with previous work (15, 16), but no previous data are available for fine-grained α-Al2O3. So that we could use these data in our H2O correction (ΔH4), the heat content of H2O vapor between 298 and 979 K, 25.8 kJ mol⁻¹, was added to the negative of these values. For the remaining physisorbed H2O, the heat of adsorption is (by definition) equal to the heat of condensation of the adsorbate. With our final state as H2O vapor at 979 K, it contributes 70.1 kJ per mole of physisorbed H2O to ΔH2 (19). The value of ΔHf then is calculated as a weighted average of the contributions from chemisorbed and physisorbed H2O, yielding ΔHf = 118.0 ± 3.5 kJ (mol H2O)⁻¹ for α-Al2O3 and 101.5 ± 1.8 kJ (mol H2O)⁻¹ for γ-Al2O3.

Through the cycle shown in Eqs. 1 through 5, the enthalpies of the nanophasie aluminas relative to coarse grained corundum can now be obtained (Table 1 and Fig. 3). At specific surface areas greater than 125 m² g⁻¹, γ-Al2O3 lies at lower enthalpy (is more energetically stable) than α-Al2O3. The surface energies obtained from the slopes of the least squares fitted lines in Fig. 3 are 2.64 J m⁻² for α-Al2O3 and 1.67 J m⁻² for γ-Al2O3. These values are in agreement with those obtained by computer simulations (8, 9). For example, Blonski and Garofalini (8) obtained surface energies (for various exposed surface planes after relaxation) ranging from 2.0 to 8.4 J m⁻² for α-Al2O3 and 0.8 to 2.5 J m⁻² for γ-

Fig. 3. Enthalpy H of alumina samples relative to coarse-grained α-Al2O3 as a function of surface area. The γ-Al2O3 (□) lies at lower enthalpy than α-Al2O3 (○) when specific surface areas exceed ~125 m² g⁻¹. (●) Data for a 30 m² g⁻¹ sample of α-Al2O3 obtained from solution calorimetry obtained from drop solution and transposed temperature drop calorimetry on diasporite [see (17) for details]. The dotted line represents the free energy G of γ-Al2O3 relative to corundum at 800 K.

Fig. 2. Differential (A) and integral (B) heats of adsorption of H2O on α-Al2O3 [36 m² g⁻¹ (●), 61 m² g⁻¹ (■) and γ-Al2O3 [72 m² g⁻¹ (▲), 161 m² g⁻¹ (▼)] as a function of hydroxyl coverage.
The excellent agreement between our calorimetric study and the simulations (8, 9) is evident upon comparison of Figs. 1 and 3, which both show γ-Al2O3 becoming energetically stable with respect to α-Al2O3 at surface areas >125 ± 10 m2 g−1. Furthermore, as discussed above, the greater entropy of γ-Al2O3 makes this polymorph truly thermodynamically stable with respect to α-Al2O3 at surface areas greater than 100 m2 g−1 at room temperature, and greater than only 75 m2 g−1 at 800 K.

To further explore the difference in surface energies and coarsening behavior of the polymorphs, a dynamic study of hydroxyl coverage as a function of temperature was performed on two samples of nearly equal surface area (156 m2 g−1 α-Al2O3 and 166 m2 g−1 γ-Al2O3). To determine the weight percentage of adsorbed H2O with increasing temperature, TGA was performed in static air at a heating rate of 5 K min−1 to 1773 K. The BET surface area of the aluminas as a function of temperature was determined from samples heated in Pt crucibles in open air at 5 K min−1 to 573, 673, 773, 873, 973, 1073, 1173, 1273, and 1373 K and immediately quenched to room temperature by quick removal from the furnace.

Thermogravimetric analysis of the 166 m2 g−1 γ-Al2O3 and 156 m2 g−1 α-Al2O3 revealed slight differences in dehydration behavior (Fig. 4A). The loss of H2O from γ-Al2O3 followed a smooth, featureless curve, whereas that of α-Al2O3 showed small fluctuations between 673 and 873 K. The coarsening, however, was drastically different for the two polymorphs (Fig. 4B). The α-Al2O3 began to coarsen rapidly above 773 K, whereas the γ-Al2O3 did not coarsen until above 1173 K. By comparing these two curves, we obtain the coverage of hydroxyl groups on the alumina surfaces as a function of temperature (Fig. 4C). At low temperatures (<773 K), the coverages are fairly similar for both polymorphs. Above 773 K, however, there is a plateau in the coverage of hydroxyl groups on α-Al2O3. The α-Al2O3 is both rapidly losing H2O and rapidly coarsening between 773 and 1173 K while apparently maintaining a fairly constant coverage of ~9 OH nm−2. Above 1073 K, the coverage on α-Al2O3 gradually decreases. The similarities between the hydroxyl coverages with increasing temperature (Fig. 4C) and differential heats of adsorption (Fig. 2A) are striking. Both sets of data provide a type of energy "spectrum" of the available surface sites and indicate a higher density of high-energy sites on the α-Al2O3 surface.

The results reported here explain the relative ease of synthesis of nanocrystalline γ-Al2O3 as opposed to nanocrystalline α-Al2O3 and have far-reaching implications from phase development in oxide systems to the synthesis and potential application of nanocrystalline materials. As we have shown that surface-energy differences thermodynamically stabilize γ-Al2O3 over α-Al2O3, the same may indeed be true for cubic BaTiO3 (20) and other technologically important materials for which a nanocrystalline morphology would be potentially beneficial in device fabrication. The nanocrystalline tetragonal modification of ZrO2 results in a significantly lower exothermic heat of immersion in H2O compared to that of coarse monoclinic ZrO2, which suggests surface-energy destabilization of monoclinic ZrO2 as well (21). However, a desired phase being metastable as a nanophas with respect to a less desirable polymorph does not preclude its synthesis, as is evidenced by the 154 m2 g−1 γ-Al2O3 studied in this work and in (11). Such materials can still be obtained by well-designed synthetic routes.

### Table 1
Summary of sample characterization and high-temperature solution calorimetry data from (11). The corrected integral heat has been adjusted for chemisorbed H2O (see Eq. 1).

<table>
<thead>
<tr>
<th>Phase (XRD)</th>
<th>Surface area (m2 g−1)</th>
<th>x in Al2O3·yH2O (equilibrium)</th>
<th>ΔH1 (kJ mol−1 Al2O3·yH2O)</th>
<th>ΔH2 (kJ mol−1 Al2O3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al2O3</td>
<td>0.83</td>
<td>0.00</td>
<td>106.4 ± 0.5</td>
<td>0.00</td>
</tr>
<tr>
<td>α-Al2O3</td>
<td>57</td>
<td>0.210</td>
<td>115.6 ± 1.4</td>
<td>15.6 ± 1.6</td>
</tr>
<tr>
<td>α-Al2O3</td>
<td>70</td>
<td>0.249</td>
<td>117.7 ± 1.3</td>
<td>18.0 ± 1.7</td>
</tr>
<tr>
<td>α-Al2O3</td>
<td>106</td>
<td>0.493</td>
<td>132.3 ± 1.9</td>
<td>32.1 ± 2.8</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>77</td>
<td>0.271</td>
<td>139.4 ± 0.9</td>
<td>39.9 ± 2.7</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>166</td>
<td>0.693</td>
<td>133.9 ± 1.2</td>
<td>42.8 ± 1.9</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>187</td>
<td>0.719</td>
<td>136.4 ± 1.5</td>
<td>44.8 ± 2.1</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>200</td>
<td>0.804</td>
<td>141.2 ± 1.2</td>
<td>46.7 ± 2.1</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>253</td>
<td>1.060</td>
<td>158.9 ± 1.4</td>
<td>54.5 ± 2.6</td>
</tr>
</tbody>
</table>

*Enthalpy of drop solution of coarse-grained corundum (ΔH2); see Eq. 3.

### Table 2
Results of sample characterization and heat of adsorption experiments. The analysis was done after outgassing in a vacuum at 1023 K for 2 hours. The amount of chemisorbed H2O is defined as 1.79 OH nm−2 for α-Al2O3 and 16.5 OH nm−2 for γ-Al2O3. The corrected integral heat has been adjusted for average residual hydroxyl coverage (2.6 OH nm−2).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Surface area (m2 g−1)</th>
<th>Residual H2O (weight %)</th>
<th>Residual coverage (OH nm−2)</th>
<th>Integral heat for chemisorbed H2O (J m−2)</th>
<th>Corrected integral heat for chemisorbed H2O (J m−2)</th>
<th>Integral heat for chemisorbed H2O (kJ mol−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al2O3</td>
<td>61</td>
<td>0.15</td>
<td>1.6</td>
<td>−1.849</td>
<td>−2.339</td>
<td>−157.4</td>
</tr>
<tr>
<td>α-Al2O3</td>
<td>36</td>
<td>0.19</td>
<td>3.5</td>
<td>−2.036</td>
<td>−2.526</td>
<td>−169.9</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>161</td>
<td>0.48</td>
<td>2.0</td>
<td>−1.149</td>
<td>−1.639</td>
<td>−119.4</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>72</td>
<td>0.36</td>
<td>3.3</td>
<td>−1.232</td>
<td>−1.722</td>
<td>−125.7</td>
</tr>
</tbody>
</table>

Avg = −163.7 ± 8.8

At high temperatures, the TDS term in the free energy may dominate, and a transition from coarse α-Al2O3 to γ-Al2O3 can be expected at a high enough temperature. No such transition has been detected up to the melting point of α-Al2O3, 2327 K (S. Schneider, Pure Appl. Chem. 21, 115 [1970]), but the liquid structure of alumina has been shown to have γ-Al2O3 character (that is, tetrahedrally coordinated Al3+) seen by S. Ansell et al. (Phys. Rev. Lett. 78, 464 [1997]). The lowest temperature at which the
α-Al2O3 to γ-Al2O3 transition could occur when then be the melting point, so the change in Gibbs free energy ΔG of the α-Al2O3 to γ-Al2O3 transition would be zero at 2327 K. Taking the enthalpy of the α-Al2O3 to γ-Al2O3 transition as 13.4 kJ mol⁻¹ (17), ΔH°_f (Al2O3) = 10.7 kJ mol⁻¹ (17).

17. Hysteresis in adsorption isotherms, which implies a difference between the heats of adsorption and desorption, has been observed [see, for example, A. Bailey et al., Trans. Faraday Soc. 67, 231 (1971)]. However, these phenomena are usually associated with porous adsorbates, where irreversible changes in the pore structure occur upon desorption. For the relatively nonporous aluminas considered here, the assumption that the heat of adsorption is the negative of the heat of desorption should be valid.

The Effect of Pressure on Deuterium-Hydrogen Fractionation in High-Temperature Water

T. Driesner

The pressure dependence of deuterium-hydrogen (D–H) fractionation in water to 500°C and 200 megapascals has been calculated from high-temperature, high-pressure spectroscopic data. Pressure effects have a maximum at the critical temperature of water (20 per mil between 22 and 200 megapascals). Even larger effects are predicted for vaporlike densities from molecular dynamic simulations and molecular orbital calculations. Pressure effects explain many of the large discrepancies in published mineral–water D–H fractionation curves. Possible applications to natural examples include mineral–water isotope geobarometry.

The stable isotopes of oxygen and hydrogen have been the most commonly used geochemical tracers in the study of both fossil and modern fluid-rock interaction processes for more than 30 years (1). The most fundamental prerequisite for a successful application of D/H and 18O/16O ratios to the reconstruction of fluid sources, fluid quantities, flow directions, or stable-isotope geothermometry is the experimental or theoretical determination of accurate mineral-fluid isotope fractionation factors (2).

From statistical mechanical expressions that were derived in the 1940s to calculate equilibrium constants for isotope-exchange reactions between molecular species (3), it appeared that the equilibrium constants (and hence, fractionation factors) are a function of temperature only, because for free molecules and solid phases (that is, the favorite objects of theoretical studies and isotope geothermometry, respectively), the vibrational frequencies do not change significantly with pressure. Only for large pressure differences of several gigapascals, shifts of the vibrational frequencies of solids may lead to measurable effects on isotope fractionation (4).

However, unlike the case of solids, the vibrational frequencies of water undergo significant changes even at low to moderate pressures at temperatures of interest to many fields of stable-isotope geochemistry (5–9). Hence, at any given temperature, the fractionation of hydrogen (and oxygen) stable isotopes in systems involving water must be pressure dependent. Here, I quantify the pressure dependence and demonstrate its geochemical importance.

The practical usage of Fig. 1B is that to calculate the pressure effect Γ_p, is (10)

\[
\Gamma_p = \left( \frac{Q_{D/H}}{Q_{H}} \right)_{\text{total}} \times \left( \frac{Q_{D/H}}{Q_{H}} \right)_{\text{ref}} (2)
\]

with subscript P(ref) denoting a reference pressure and P the pressure of interest. Then, substitution of Eqs. 1 and 2 into Eq. 3 shows that the contributions of all frequency bands that do not shift with pressure can cancel out in the calculation of Γ_p. Hence, only a single spectral model rather than a full model of the vibrational density of states is required to calculate the pressure effect (11).

Using Eq. 3, I calculated the pressure effect to 500°C and 200 MPa. The results indicate a significant pressure effect at all temperatures. The curves in Fig. 1A are smoothed to remove undulations on the order of 1 unit in 1000 ln Γ_p (that is, 1 per mil in δD) resulting from the limited precision of the spectroscopic data. The strongest effects are observed near-critical temperatures and pressures below about 100 MPa (12). This becomes more obvious when the results are plotted as contour lines of equal pressure effect in a P-T diagram (Fig. 1B). Whereas the variations are rather small below 350°C, steep gradients can be seen between 350° and 450°C. This result is not surprising, because most physical properties of water show small gradients in the low-temperature region and steep gradients near the critical point that are reduced at higher temperatures (13).

The practical usage of Fig. 1B is that to determine the effect of pressure on a mineral–water equilibrium fractionation factor at a given temperature, the difference between the contour lines at any two pressures has to be added to the fractionation factor when going up in pressure, or subtracted when going down.

To estimate the effect of pressure on the fractionation of the other important pair of stable isotopes in fluid-rock interaction studies (13O/18O), I carried out similar calculations using the data of Frantz et al. (5), and assuming that the O–H stretching fre-