# Effects of Increased Surface Area and Chemisorbed H$_2$O on the Relative Stability of Nanocrystalline γ-Al$_2$O$_3$ and α-Al$_2$O$_3$

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Corundum, α-Al$_2$O$_3$, appears to be the thermodynamically stable phase of aluminum oxide at all common pressure and temperature conditions, but attempted syntheses of nanocrystalline Al$_2$O$_3$ usually result in other polymorphs of the oxide (transition aluminas). Herein we explore the possibility that γ-Al$_2$O$_3$ becomes the thermodynamically stable polymorph when a critical surface area is exceeded. High-temperature solution calorimetry was performed on several samples of nanocrystalline γ-Al$_2$O$_3$ and α-Al$_2$O$_3$. The aluminas adsorbed atmospheric H$_2$O which could not be completely removed without coarsening (particularly for α-Al$_2$O$_3$). Samples of γ-Al$_2$O$_3$ with <21 mg/(100 m$^2$) and α-Al$_2$O$_3$ with <29 mg/(100 m$^2$) coverages of adsorbed H$_2$O lied at equal enthalpies with respect to corundum and H$_2$O(g, 298 K), independent of surface area. This result provides experimental verification for a direct dependence of the heat of adsorption on the surface energy of the adsorbent. Attempts at correcting the data for heat effects due to adsorbed H$_2$O revealed that increased surface area of nanocrystalline α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ significantly destabilized the materials with respect to coarse grained samples. However, down to the lowest attainable coverages of H$_2$O the experimental "surface energies" of the two phases were nearly equal. Our results cannot definitely rule out the assumption that γ-Al$_2$O$_3$ is surface energy stabilized with respect to α-Al$_2$O$_3$. However, if this is the case, the high-energy sites on the α-Al$_2$O$_3$ surface are relatively few, and effectively stabilized at low temperatures by adsorbed H$_2$O. The enthalpy of hypothetical coarse grained γ-Al$_2$O$_3$ was also explored and found to be +13.4 ± 2.0 kJ/mol relative to coarse grained α-Al$_2$O$_3$.

## I. Introduction

The synthesis of nanocrystalline metal oxides often yields material with a structure differing from the room-temperature thermodynamically stable modification for a particular stoichiometry.[1] Examples are the repeated syntheses of nanocrystalline cubic BaTiO$_3$,[2] tetragonal ZrO$_2$,[3] and monoclinic Y$_2$O$_3$.[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 metal oxide "surface energies" are available due to the difficulty inherent in such measurements.[5]

Corundum, α-Al$_2$O$_3$, appears to be the thermodynamically stable phase of aluminum oxide at all common pressure and temperature conditions, but attempted syntheses of nanocrystalline Al$_2$O$_3$ usually result in γ-Al$_2$O$_3$.[6] In addition, γ-Al$_2$O$_3$ can maintain surface areas of ~200 m$^2$/g at 1073 K, whereas nanophase α-Al$_2$O$_3$ will coarsen to <30 m$^2$/g at such temperatures. Recently, Blonski and Garofalini[7] performed molecular dynamics simulations of various α-Al$_2$O$_3$ and γ-Al$_2$O$_3$ surfaces and obtained estimates of the surface energies. They found that on the whole the surface energies of α-Al$_2$O$_3$ were significantly greater than those of γ-Al$_2$O$_3$ (for exposed surfaces of various orientations) and suggested that "this may explain the experimental difference in surface area between these two forms of alumina." Using their data, our calculations show that γ-Al$_2$O$_3$ may become the energetically stable polymorph as specific surface areas exceed ~175 m$^2$/g (see Figure 1).
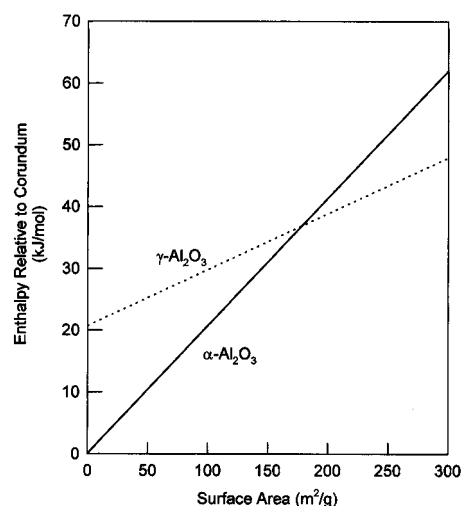


**Figure 1.** Calculated enthalpy of alumina polymorphs vs surface area based on molecular dynamics simulations and data for small surface area materials. Enthalpy of γ-Al$_2$O$_3$ at zero surface area taken from ref 12.

Although these simulations strongly suggest that γ-Al$_2$O$_3$ is a surface stabilized phase, the role of adsorbed species, and in particular adsorbed H$_2$O, on the relative stability of the polymorphs has not been addressed. Metal oxide crystallites are commonly terminated by a layer of hydroxyl ions, and in nanophase materials this can amount to a significant weight percentage of H$_2$O. The inherent high surface area of γ-Al$_2$O$_3$ results in the ubiquitous presence of H$_2$O on the material, which

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has led some to suggest that hydroxyl ions are a necessary component of the defect structure.[8] Earlier reports have postulated that $\gamma$-Al$_2$O$_3$ is actually a hydrogen spinel,[9] though this has recently been questioned.[10] As both nanophase $\alpha$-Al$_2$O$_3$ and nanophase $\gamma$-Al$_2$O$_3$ are synthesized by decomposition of hydrous materials, a discussion of the energetics of these aluminas in the absence of H$_2$O may not be relevant to any physically attainable situation. The experimentally relevant question may lie in the relative stability of the hydrated polymorphs with increasing surface area. We have used high-temperature solution calorimetry to study the energetics of nanophase aluminas as a function of surface area and coverage of adsorbed H$_2$O. Our results indicate that adsorbed H$_2$O stabilizes the surfaces of both polymorphs such that they have similar surface energies down to the lowest attainable H$_2$O coverages (before coarsening sets in). In addition, experimental verification is provided for a direct dependence of the heat of adsorption of H$_2$O on the surface energy of the adsorbent, and the enthalpy of the $\gamma$-Al$_2$O$_3 \rightarrow \alpha$-Al$_2$O$_3$ transition is discussed.

## II. Experimental Section

**A. Sample Preparation and Characterization.** Samples of nanocrystalline $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ were prepared (at Alcoa) through topotactic decompositions of diaspore, $\alpha$-AlOOH, and boehmite, $\gamma$-AlOOH, respectively. High-purity, coarse grained $\alpha$-Al$_2$O$_3$, $\alpha$-AlOOH, and $\gamma$-AlOOH were also prepared by Alcoa. Coarse grained $\gamma$-Al$_2$O$_3$ is not readily prepared, as temperatures where coarsening sets in also result in partial transformation to $\delta$- and $\theta$-Al$_2$O$_3$.[11] An approximation for thermodynamic data on coarse grained $\gamma$-Al$_2$O$_3$ can be taken from a previous high-temperature solution calorimetry study (at 978 K in 2PbO·B$_2$O$_3$) of the isostructural $(1 - x)$MgAl$_2$O$_4 -$ $x$Al$_{8/3}$O$_4$ defect spinel solid solution series.[12] As these alumina rich spinel samples were prepared at $\geq$1773 K, they were certainly of low surface area. The 77 m$^2$/g $\gamma$-Al$_2$O$_3$ studied in this work was a commercial $\gamma$-Al$_2$O$_3$ obtained from Alfa Products. It was the same batch on which enthalpy of solution measurements (in 2PbO·B$_2$O$_3$ at 978 K) were made by Navrotsky et al.[12] and was included in this work as a test for the validity of our H$_2$O correction and for comparison in discussing the energetics of the $\gamma$-Al$_2$O$_3 \rightarrow \alpha$-Al$_2$O$_3$ transition.

Powder X-ray diffraction (XRD) was used to determine the structure and phase purity of the aluminas with a Siemens D500 diffractometer using Cu K$\alpha_1$ radiation. Surface area of the powders was determined by BET adsorption on samples outgassed at 473 K for 2 h using N$_2$ as the adsorbed species. The adsorbed water content of the samples was determined via thermogravimetric analysis (TGA) using a Netzsch 409 TGA/DTA. Alternatively, the water content was evaluated by heating pellets of accurately known mass to 1773 K for 2 h and attributing any weight loss to H$_2$O.

**B. Calorimetry.** High-temperature drop solution calorimetry was performed in a Tian-Calvet twin microcalorimeter, which has been described in detail by Navrotsky,[13] operating at ~979 K with 2PbO·B$_2$O$_3$ as the solvent. Samples were pressed into pellets of ~10−20 mg and dropped, from room temperature, into the hot zone of the calorimeter. The measured heat effect was a combination of the heat content and heat of solution of the Al$_2$O$_3$. Due to their high surface area, the nanophase aluminas had significant amounts of adsorbed water which also contributed to the measured heat effect. All experiments were run under flowing Ar (90 mL/min) to flush evolved H$_2$O from the calorimeter and avoid base line shifts. It has been previously demonstrated that under these conditions the water does not remain in or interact energetically with the solvent and exits

the calorimeter as H$_2$O(g, 979 K).[14] Transposed temperature drop calorimetry, wherein the sample was dropped into empty (without solvent) platinum crucibles, was performed on some $\gamma$-Al$_2$O$_3$ samples. The measured heat effect was the heat content of the sample and the heat due to water removal.

**C. Correction for Adsorbed H$_2$O.** Although dry samples would have been preferable, these high-surface area aluminas could not be completely dried without coarsening. In fact, the samples contained adsorbed H$_2$O in their "as-prepared" state, as they were synthesized via low-temperature calcination (673− 1073 K) of aluminum oxyhydroxides. The extent of dehydroxylation of Al$_2$O$_3$ is mainly a function of drying temperature, and we were limited in choice of drying temperature by the calcination temperature used in preparation of the sample. Exceeding the calcination temperature resulted in coarsening, which was severe in the case of $\alpha$-Al$_2$O$_3$. Therefore, as in previous studies on AlPO$_4$ zeolites,[15] the samples were exposed to the air in the calorimetry laboratory, which has a precisely controlled environment (295 $\pm$ 1 K and 55 $\pm$ 2% relative humidity), for $\geq$7 days. This assured a stable, equilibrium water content in the samples. This equilibrium water content was then determined thermogravimetrically as described above. In general, a better reproducibility and lower standard deviation in the water content was obtained via calcining and weighing pellets than with TGA (Netzsch STA 409), presumably due to slight differences in the buoyancy correction necessary with this instrument. Therefore, the water contents reported below are from the pellet experiments and are the average value of at least three determinations. The Netzsch STA 409 was used to determine the residual water content on samples heated at, 573 K for 1 h, 979 K for 6 h, and samples heated at 398 K for 2 h.

To experimentally assess the energetic effects due to adsorbed H$_2$O, pellets (~15 mg) with equilibrium water content were accurately weighed and then heated in air at 398 K for ~1 h. They were then weighed again and immediately dropped into the calorimeter. The difference in mass between the first and second weighings was used to calculate a new water content on the basis of the equilibrium water content. This procedure gave calorimetric data on each sample with varying water content, and the enthalpy of drop solution calorimetry, $\Delta H_{ds}$, versus mole fraction H$_2$O was plotted for each sample. The best straight line was then fit by least squares. The slope of this line gave the enthalpy of dehydration in kilojoules per mole of H$_2$O (see Figure 4). The calcination temperature used in the preparation of some $\gamma$-Al$_2$O$_3$ samples exceeded the calorimeter temperature. On these samples, the enthalpy of dehydration was directly evaluated by transposed temperature drop calorimetry. To minimize the magnitude of the heat effect due to adsorbed H$_2$O, additional calorimetric experiments were performed wherein the sample was allowed to equilibrate and partially dehydrate at 573 K under flowing Ar in the calorimeter. The sample was then dropped into the solvent from 573 K yielding data for samples with only ~20% of the equilibrium adsorbed H$_2$O content.

## III. Results and Discussion

**C. Relative Stability of Hydrated Polymorphs.** Metal oxide crystallites are commonly terminated by a layer of hydroxyl ions. Direct information as to changes in the relative stability of these hydrated polymorphs with increasing surface area can be obtained by comparison of calorimetric data for hydrated samples of similar surface area. If the enthalpy difference between the $\alpha$ and $\gamma$ samples of similar surface area decreases with increasing surface area, this would imply a lower surface energy for $\gamma$ alumina. In Figure 2A, the raw $\Delta H_{ds}$
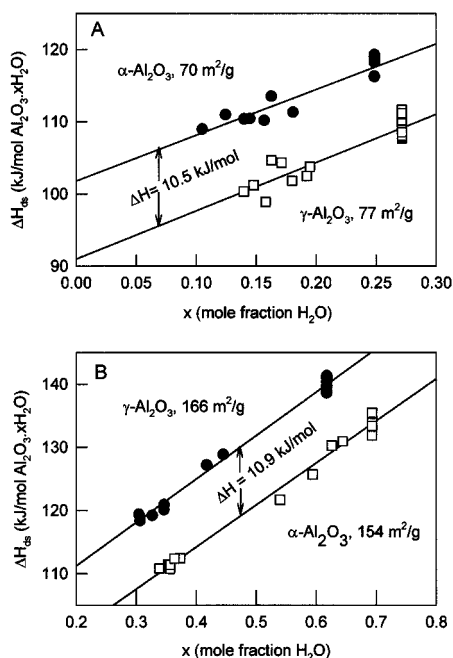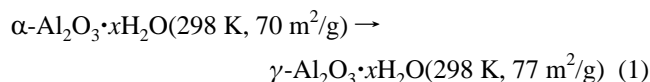
**Figure 2.** $\Delta H_{ds}$ values as a function of the mole fraction of H$_2$O for (A) 70 m$^2$/g $\alpha$-Al$_2$O$_3$ and 77 m$^2$/g $\gamma$-Al$_2$O$_3$ and (B) 154 m$^2$/g $\alpha$-Al$_2$O$_3$ and 166 m$^2$/g $\gamma$-Al$_2$O$_3$. The enthalpy difference between the hydrated polymorphs remains relatively constant with increasing surface area.

values are plotted versus mole fraction of H$_2$O for 70 m$^2$/g of $\alpha$-Al$_2$O$_3$ and 77 m$^2$/g of $\gamma$-Al$_2$O$_3$. The vertical distance between the least squares fitted straight lines yields $\Delta H$ for the reaction

$$\alpha\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(298\text{ K}, 70\text{ m}^2/\text{g}) \rightarrow$$
$$\gamma\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(298\text{ K}, 77\text{ m}^2/\text{g}) \quad (1)$$

of $+10.5 \pm 1.5$ kJ/mol from for $x = 0.1-0.3$ (mole fraction of H$_2$O). In Figure 2B, the same analysis is shown for samples of over twice the surface area, 154 m$^2$/g of $\alpha$-Al$_2$O$_3$ and 166 m$^2$/g of $\gamma$-Al$_2$O$_3$. The enthalpy difference between these samples is very close to that of the lower surface area materials, $+10.9 \pm 1.5$ kJ/mol from $x = 0.3$ to $x = 0.7$. Therefore we see no direct evidence for a significant difference in surface energy between the hydrated polymorphs. This is easily explained as adsorbed H$_2$O "cures" the surface defects by bonding to coordinatively unsaturated ions. Although the hydrated surfaces have nearly equal energies, the anhydrous surfaces may differ. Our attempts at correcting the data for heat effects due to H$_2$O desorption are discussed in the following section.

**B. Correction for Adsorbed H$_2$O.** The results of the sample characterization and calorimetric experiments are summarized in Table 1. The equilibrium H$_2$O content increased fairly regularly with increasing surface area (Figure 3). The least squares fitted straight lines in Figure 3 yield 66.9 and 61.4 mg of H$_2$O/(100 m$^2$) for $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, respectively. From examination of Table 1, it can be seen that H$_2$O removal for some samples accounts for as much as 60% of the total measured heat effect. A correction of this magnitude is obviously a critical parameter and warrants further discussion before the effect of nanosizing on the relative stability of anhydrous $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ is examined.

As desorption is generally an endothermic process, there is a lower limit to the possible value for our H$_2$O correction. Assuming no excess interaction between Al$_2$O$_3$ and H$_2$O (i.e. heat of adsorption equal to the heat of condensation of H$_2$O), the enthalpy change for the reaction which occurs to adsorbed

H$_2$O upon introduction to the calorimeter,

$$\text{H}_2\text{O}(\text{adsorbed on Al}_2\text{O}_3, 295\text{ K}) \rightarrow \text{H}_2\text{O}(\text{gas}, 979\text{ K}) \quad (2)$$
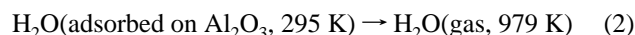
can be obtained from literature values for the heat content of H$_2$O(l), H$_2$O(g), and the enthalpy of vaporization of H$_2$O at 373.15 K. Between 298 and 979 K, eq 2 yields 70.09 kJ/mol of H$_2$O as the lower limit for our H$_2$O correction.

It is known that at least three types of H$_2$O adsorption occur on the surface of Al$_2$O$_3$.[16,17] The first type of water is tightly bound, chemisorbed H$_2$O, which exists as hydroxyl ions bonded to Al$^{3+}$ in various configurations (of which five to seven are normally distinguished by IR spectroscopy).[11,17-22] Chemisorbed (hydrogen bonded) molecular H$_2$O can also exist, and adsorption of H$_2$O on Al$_2$O$_3$ at room temperature has been shown to result in tightly bound molecular H$_2$O.[23] Finally, depending on the temperature and partial pressure of the H$_2$O, additional layers of physisorbed molecular H$_2$O can be present. The differential heat of adsorption for this physisorbed H$_2$O is on the order of the enthalpy of condensation of H$_2$O, but the differential heat of adsorption of the chemisorbed water can be significantly greater, and at low coverage it can even exceed the value for bulk hydroxylation (i.e. the enthalpy change per mole of water for the reaction Al$_2$O$_3$ + H$_2$O $\rightarrow$ 2AlOOH).[24] The average value we obtained for the enthalpy of dehydration from the slopes of $\Delta H_{ds}$ vs mole fraction of H$_2$O plots was 67.9 $\pm$ 5.4 kJ/mol (see Figure 4), which is very close to the enthalpy difference between liquid H$_2$O at 298 K and gaseous H$_2$O at 979 K (70.09 kJ/mol). These values are typical of physically adsorbed H$_2$O and are not valid for the more tightly bound chemisorbed H$_2$O which cannot be removed by heating at 398 K. Consequently, $\Delta H_{ds}$ vs mole fraction H$_2$O plots cannot be extrapolated to zero water content to obtain accurate values for anhydrous samples.

The differential heat of adsorption of H$_2$O on Al$_2$O$_3$ has been found to show Freundlich behavior (logarithmic dependence on coverage),[25] revealing that the surface of Al$_2$O$_3$ is highly heterogeneous. However, the integral heat of adsorption (or desorption) for the entire equilibrium coverage of H$_2$O can be fairly well-estimated by a constant. For our samples with equilibrium H$_2$O contents, the total or integral enthalpy of dehydration, $\Delta H_{\text{H}_2\text{O}}$, for a sample of mole fraction $x$ (i.e. Al$_2$O$_3 \cdot x$H$_2$O), can be represented as

$$\Delta H_{\text{H}_2\text{O}} = x_p(\Delta H_{\text{H}_2\text{O}})_p + x_c(\Delta H_{\text{H}_2\text{O}})_c \quad (3)$$

$$x_p + x_c = 1 \quad (4)$$

where $x_p$ is the mole fraction of physisorbed H$_2$O, $x_c$ the mole fraction of chemisorbed H$_2$O, $(\Delta H_{\text{H}_2\text{O}})_p$ is the enthalpy of desorption for the physisorbed H$_2$O, and $(\Delta H_{\text{H}_2\text{O}})_c$ is the enthalpy of desorption of the chemisorbed H$_2$O. The corrected enthalpy of drop solution calorimetry for the Al$_2$O$_3$ is then $\Delta H_{\text{Al}_2\text{O}_3}$, which is obtained from the equation

$$\Delta H_{\text{Al}_2\text{O}_3} = \Delta H_{ds} - x\Delta H_{\text{H}_2\text{O}} \quad (5)$$

Our $\Delta H_{ds}$ vs mole fraction H$_2$O plots support the use of 70.09 kJ/mol for $(\Delta H_{\text{H}_2\text{O}})_p$, but a value for $(\Delta H_{\text{H}_2\text{O}})_c$ is needed. Coster et al.[24] and Gervasini and Auroux[26] have shown that values for the initial heat of adsorption (at lowest attainable coverages of "preadsorbed" H$_2$O) can exceed 200 kJ/mol of H$_2$O. The differential heat of adsorption falls logarithmically with increasing coverage ($\Theta$), reaching the heat of condensation of H$_2$O ($\sim$44 kJ/mol) at coverages of $\sim$15 OH/nm$^2$ ($\sim$22.6 mg of H$_2$O/(100 m$^2$)). With our equilibrium H$_2$O contents averaging $\sim$63

**TABLE 1: Summary of Sample Characterization and Calorimetric Data[a]**

| phase (XRD) | surface area (m²/g) | wt % H₂O | $x$ Al₂O₃·$x$H₂O equilibrium | $x$ Al₂O₃·$x$H₂O chemisorbed[b] | $(\Delta H \text{H}_2\text{O})_p$[c] (kJ/mol of H₂O) | $\Delta H_{\text{H}_2\text{O}}$ total[d] (kJ/mol of H₂O) | $\Delta H_{\text{ds}}$[e] (kJ/mol of Al₂O₃·$x$H₂O) | $\Delta H_{\text{Al}_2\text{O}_3}$[f] (kJ/mol of Al₂O₃) |
|---|---|---|---|---|---|---|---|---|
| α-Al₂O₃ | 0.83 | 0.00 (1) | 0.00 | 0.00 | | | 106.35 | 106.35 ± 0.53 (8) |
| α-Al₂O₃ | 57 | 3.61 ± 0.13 (4) | 0.2101 | 0.0871 | 61.4 | 97.4 | 115.64 | 96.3 ± 1.4 (19) |
| α-Al₂O₃ | 70 | 4.24 ± 0.04 (3) | 0.2486 | 0.1074 | 63.3 | 98.5 | 117.70 | 93.4 ± 1.3 (14) |
| α-Al₂O₃ | 106 | 8.05 ± 0.05 (5) | 0.4917 | 0.1642 | 60.9 | 92.1 | 132.30 | 87.6 ± 1.9 (20) |
| α-Al₂O₃ | 154 | 9.91 ± 0.06 (5) | 0.6175 | 0.2417 | 68.7 | 95.9 | 139.35 | 80.9 ± 0.9 (15) |
| γ-Al₂O₃[g] | ~1 | | | | | | 86.0 | 86.0 ± 2.0 |
| γ-Al₂O₃ | 77 | 4.61 ± 0.11 (5) | 0.2714 | 0.1088 | 67.0 | 96.5 | 109.19 | 83.1 ± 1.6 (16) |
| γ-Al₂O₃ | 166 | 10.98 ± 0.05 (5) | 0.6926 | 0.2451 | 66.6 | 92.9 | 133.86 | 69.8 ± 1.2 (16) |
| γ-Al₂O₃ | 187 | 11.35 ± 0.12 (5) | 0.7189 | 0.2719 | 69.7 | 95.0 | 134.57 | 66.3 ± 1.5 (16) |
| γ-Al₂O₃ | 200 | 12.52 ± 0.16 (4) | 0.8036 | 0.2918 | 69.7 | 94.0 | 141.24 | 65.7 ± 1.2 (19) |
| γ-Al₂O₃ | 231 | 13.19 ± 0.07 (3) | 0.8529 | 0.3400 | 80.1 | 96.3 | 146.65 | 61.9 ± 1.4 (15) |
| γ-Al₂O₃ | 253 | 15.88 ± 0.06 (4) | 1.060 | 0.3743 | 73.8 | 93.4 | 158.88 | 59.1 ± 1.4 (15) |

[a] The uncertainty reported in weight percent of H₂O and corrected $\Delta H_{\text{ds}}$ are standard deviations. The numbers in parentheses are the numbers of experiments performed. [b] Mole percentage of chemisorbed H₂O calculated on the basis of 26.8 or 24.7 mg of chemisorbed H₂O per 100 m² for α and γ samples respectively. [c] Enthalpy of removal of physisorbed H₂O determined from $\Delta H_{\text{ds}}$ vs mole fraction of H₂O plots. Using gaseous H₂O at 979 K as the final state. [d] Total enthalpy of H₂O removal determined via eqs 3 and 4. [e] Enthalpy of drop solution for samples with equilibrium H₂O content. [f] Corrected enthalpy of drop solution, $\Delta H_{\text{Al}_2\text{O}_3} = \Delta H_{\text{ds}} - x(\Delta H_{\text{H}_2\text{O}})$. [g] Theoretical coarse grained γ-Al₂O₃ taken from a previous high-temperature solution calorimetric study of $(1 - x)\text{MgAl}_2\text{O}_4 - x\text{Al}_{8/3}\text{O}_4$ defect spinel solid solutions at 978 K in 2PbO·B₂O₃.[12]
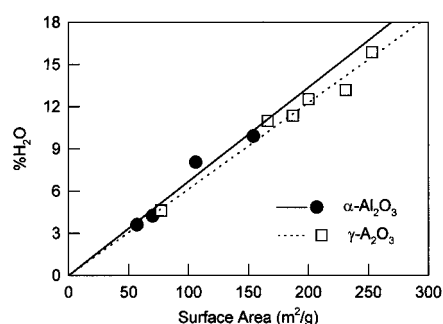


**Figure 3.** Equilibrium H₂O content for the nanophase aluminas as a function of surface area. The least squares fitted straight lines yield 66.9 and 61.4 mg of H₂O/(100 m²) for α-Al₂O₃ and γ-Al₂O₃, respectively.

mg/(100 m²), about two-thirds of the adsorbed H₂O on our samples is physisorbed H₂O. This is supported by our $\Delta H_{\text{ds}}$ vs mole fraction of H₂O plots (Figure 4). The remaining one-third of the adsorbed H₂O is chemisorbed. Coster et al.[24] fitted their adsorption data to Freundlich curves of the type

$$\Delta H = a - b \ln \Theta \tag{6}$$

where $a$ and $b$ were empirically determined coefficients and $\Theta$ was the fractional coverage defined such that $\Theta = 1$ corresponded to the quantity of irreversibly adsorbed H₂O. Our integration of their curves yields an average of 132.9 kJ/mol for the integral heat of chemisorption of H₂O for coverages of 5.4 OH/nm². However, they estimated that an additional ~5 OH/nm² was adsorbed on their Al₂O₃ before the start of the experiments. As no data exist for the heat of adsorption of these tightly bound hydroxyls, we assume that this average value found for coverages of 5 OH/nm² < $\Theta$ < 10 OH/nm² can be applied to the first 10 OH/nm². For coverages between ~10 OH/nm² and ~15 OH/nm², they found a nearly linear decrease from ~85 kJ/mol to the heat of condensation of H₂O (~44 kJ/mol), which yields an average value of ~65 kJ/mol. The integral heat of chemisorption for coverages below 15 OH/nm² is then

$$0.667(133 \text{ kJ/mol}) + 0.333(65 \text{ kJ/mol}) = 110 \text{ kJ/mol} \tag{7}$$

In our calorimetry, the final state of H₂O is H₂O(g, 979 K), and the heat content of gaseous H₂O between 298 and 979 K, 25.8 kJ/mol, needs to be added to this value to yield a value for $(\Delta H_{\text{H}_2\text{O}})_c$ of 136 kJ/mol.

We will accept the values of 70.1 kJ/mol for $(\Delta H_{\text{H}_2\text{O}})_p$ and 136 kJ/mol for $(\Delta H_{\text{H}_2\text{O}})_c$. TGA revealed that all of the nanophase aluminas adsorbed slightly different equilibrium coverages of H₂O. The amount of chemisorbed H₂O (per mole of Al₂O₃) should depend on the density of the polymorph as higher density phases should have a closer packing of coordinatively unsaturated ions per unit surface area. The density of γ-Al₂O₃ is 3.67 g·cm⁻¹, and the density of α-Al₂O₃ is 3.99 g·cm⁻¹.[11] The density ratio of the polymorphs is then $\rho_\gamma/\rho_\alpha = 0.92$, and the average surface density ratio should then be $(\rho_\gamma/\rho_\alpha)^{2/3} = 0.946$. We defined the chemisorbed H₂O as that remaining on the samples after a 2 h of heat treatment at 398 K and determined this value for each sample by TGA. The average amount of chemisorbed H₂O thus found for γ-Al₂O₃ was 24.7 mg/(100 m²), and that found for α-Al₂O₃ was 26.8 mg/(100 m²). This ratio is 0.92, which is in fair agreement with that expected on density considerations. The coverages are also very close to the amount of chemisorbed H₂O on transition aluminas given by Coster et al.[24] (i.e. 22.7 mg/(100 m²) or 15 OH/nm²). The amount of chemisorbed H₂O on γ-Al₂O₃ agreed well with a previous study by DeBoer et al.,[16] who empirically found that 24.8 ± 0.5 mg of H₂O/(100 m²) remained on transition aluminas after extensive heating at 393 K. This corresponds to ~17 OH/nm², which is very close to the maximum value for monolayer coverage of hydroxyls (based on the closest packing of O²⁻ ions) of 19 OH/nm².[27] These data seem to coincide well, and we have adopted 24.7 and 26.8 mg/(100 m²) as the amount of chemisorbed H₂O for γ-Al₂O₃ and α-Al₂O₃, respectively. Therefore $x_c$ was set as the percentage of the H₂O comprising the first 24.7 or 26.8 mg of H₂O/(100 m²) (~17 OH/nm²) and $x_p$ as the remainder. This resulted in slightly different values of $\Delta H_{\text{H}_2\text{O}}$ being used for each sample, averaging 94.7 ± 1.5 kJ/mol for γ-Al₂O₃ and 97.2 ± 2.9 kJ/mol for α-Al₂O₃ (see Table 1).

To assess the validity of this H₂O correction, transposed temperature drop calorimetry was performed on a γ-Al₂O₃ sample with a surface area of 166 m²/g. Although this sample has a high surface area and resulting high-equilibrium H₂O content, it was prepared by heating boehmite at 1073 K for 24 h. Therefore minimal grain growth and reduction in the surface area would be expected during the transposed temperature drop experiment which heats the sample to 979 K for ~1 h, and heat effects due to H₂O removal could be isolated. TGA showed that the 166 m²/g of γ-Al₂O₃, which initially contained 10.98 wt % H₂O, retained 0.53 wt % H₂O after 2 h at 979 K. Taking
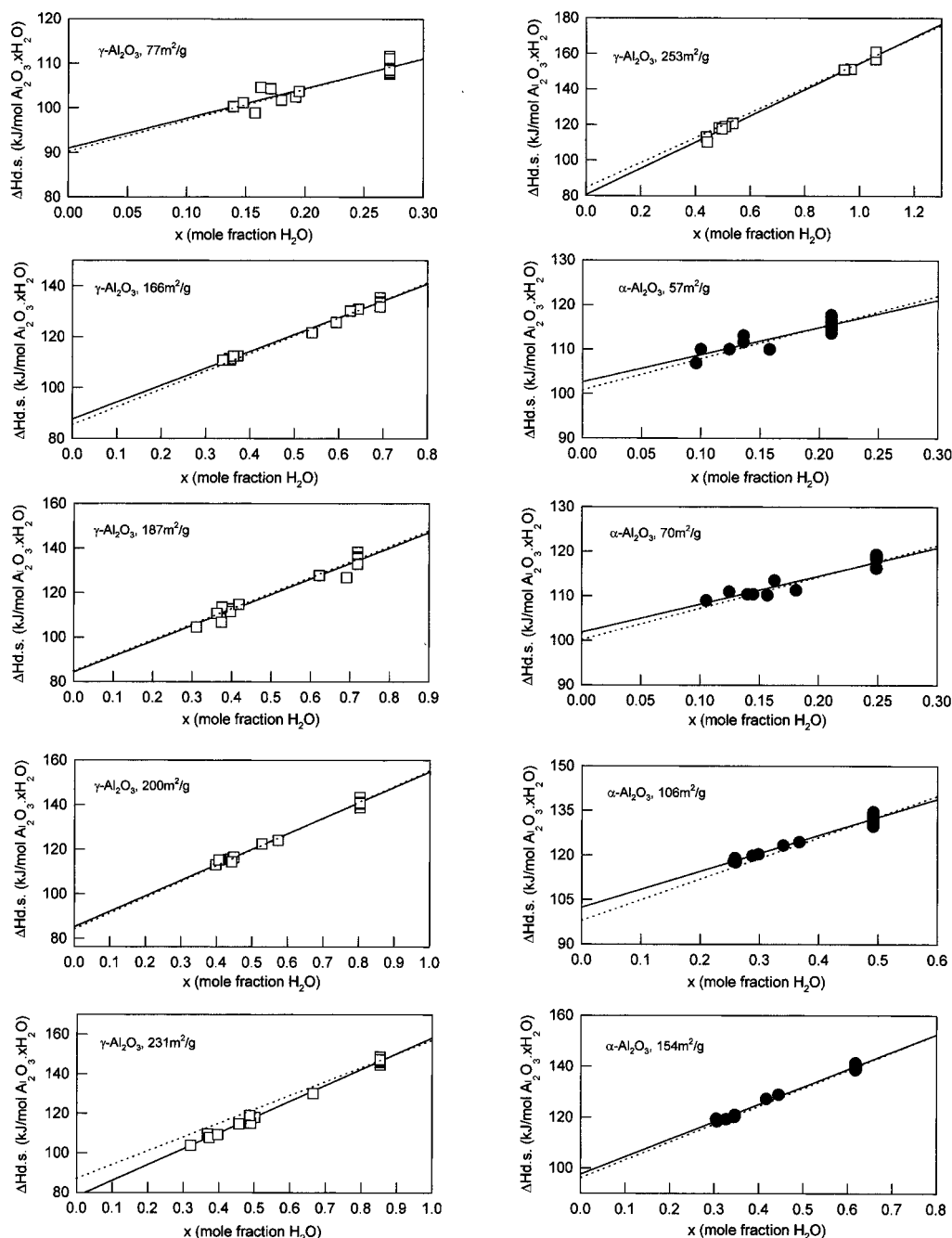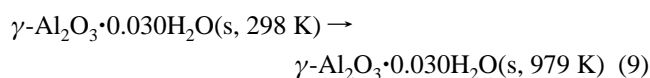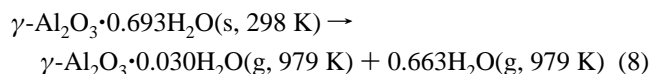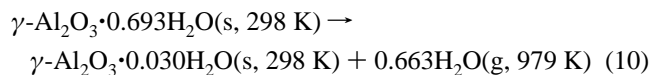
**Figure 4.** $\Delta H_{ds}$ values as a function of mole fraction H$_2$O ($x$) for the nanophase aluminas. The dotted lines represent the slope obtained assuming the heat content of liquid H$_2$O between 298 and 979 K, 70.09 kJ/mol of H$_2$O.

this result into consideration, the heat effect measured during the experiment was that of reaction 8, and $\Delta H_{H_2O}$ can be calculated via the following thermodynamic cycle:

$$\gamma\text{-Al}_2\text{O}_3\cdot 0.693\text{H}_2\text{O(s, 298 K)} \rightarrow$$
$$\gamma\text{-Al}_2\text{O}_3\cdot 0.030\text{H}_2\text{O(g, 979 K)} + 0.663\text{H}_2\text{O(g, 979 K)} \quad (8)$$

$$\gamma\text{-Al}_2\text{O}_3\cdot 0.030\text{H}_2\text{O(s, 298 K)} \rightarrow$$
$$\gamma\text{-Al}_2\text{O}_3\cdot 0.030\text{H}_2\text{O(s, 979 K)} \quad (9)$$

net:

$$\gamma\text{-Al}_2\text{O}_3\cdot 0.693\text{H}_2\text{O(s, 298 K)} \rightarrow$$
$$\gamma\text{-Al}_2\text{O}_3\cdot 0.030\text{H}_2\text{O(s, 298 K)} + 0.663\text{H}_2\text{O(g, 979 K)} \quad (10)$$

$$\Delta H_{10} = \Delta H_8 - \Delta H_9$$

From transposed temperature drop calorimetry we obtained $133.85 \pm 0.68$ kJ/mol for reaction 8. To complete the cycle, a value for reaction 9, the heat content of hydrated Al$_2$O$_3$ is needed. The tightly bound water is certainly in the form of surface hydroxyl groups bound to Al$_2$O$_3$. The vibrational frequencies of these isolated hydroxyls occur in the high-frequency range of the IR spectrum ($\nu \geq 3600$ cm$^{-1}$).[22] These frequencies correspond to characteristic temperatures of >5200 K, which is well out of our experimental temperature range. Therefore, OH vibrations should not contribute to the heat content of Al$_2$O$_3\cdot x$H$_2$O. However, additional Al$-$O vibrations should contribute. We therefore assume the heat content of Al$_2$O$_3\cdot x$H$_2$O to be the heat content of Al$_2$O$_3$ in the experimental temperature range multiplied by $(1 + x/5)$. For Al$_2$O$_3\cdot 0.030$H$_2$O, the heat content between 298 and 979 K is then (1.006)(75.5) kJ/mol = 75.9 kJ/mol. Using these values and the data in Table 1, the calculated enthalpy change for reaction 10 is then 57.2
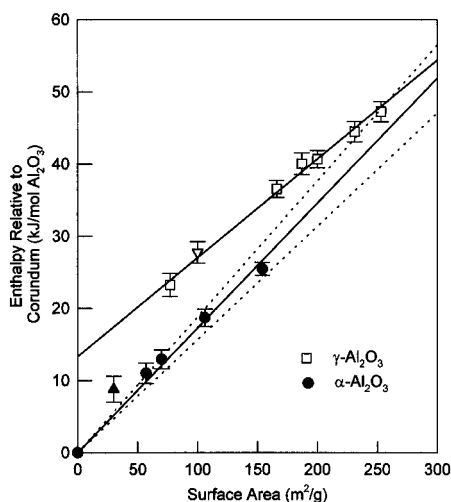
**Figure 5.** Enthalpy of alumina samples relative to coarse grained $\alpha$-Al$_2$O$_3$ as a function of surface area. The solid lines represent the data obtained using our best values for $\Delta H_{H_2O}$. The dotted lines show the variation in the result obtained for $\alpha$-Al$_2$O$_3$ after increasing the value of $(\Delta H_{H_2O})_c$ by 10 kJ/mol. The triangular points represent the data obtained from calorimetry on AlOOH samples (see text).

**TABLE 2: Surface Energies of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$**

| | surface energy (J/m$^2$) | |
|---|---|---|
| | from calorimetry | from molecular dynamics[a] |
| $\alpha$-Al$_2$O$_3$ | 1.69 | 2.0 to 8.4 |
| $\gamma$-Al$_2$O$_3$ | 1.34 | 0.8 to 2.5 |

[a] For relaxed surfaces, various orientations.
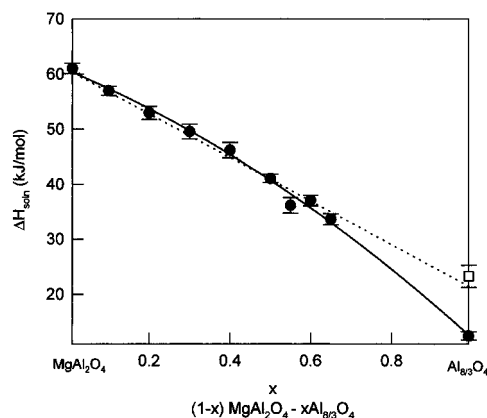


**Figure 6.** Solution calorimetry data from Navrotsky et al.[12] on the $(1 - x)$MgAl$_2$O$_4 - x$Al$_{8/3}$O$_4$ defect spinel solid solution series. Fitting the data to a second degree polynomial extrapolates to a value matching the $\Delta H_{soln}$ obtained from 77 m$^2$/g of $\gamma$-Al$_2$O$_3$ (filled circles, solid line). However, a simple linear interpretation extrapolates well to the value obtained in this work for hypothetical coarse grained $\gamma$-Al$_2$O$_3$ (open square, dotted line).
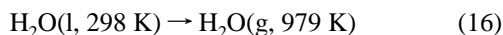
$\pm$ 1.6 kJ/(0.663 mol of H$_2$O), or 86.5 $\pm$ 2.4 kJ/mol of H$_2$O. However, the 0.03 mol % H$_2$O remaining adsorbed in the transposed temperature drop experiment is removed in drop solution calorimetry and contributes to the measured heat effect. Assuming 136 kJ/mol for removal of this last portion of chemisorbed H$_2$O yields 90.6 $\pm$ 3.0 kJ/mol. This is in agreement with the value we obtained for $\Delta H_{H_2O}$ on the basis of our $\Delta H_{ds}$ vs mol fraction H$_2$O plots and the data of Coster et al.[24] The same analysis was performed on a 77 m$^2$/g sample of $\gamma$-Al$_2$O$_3$. The value obtained for $\Delta H_{ttd}$ on this sample which initially had 0.270 mol % of adsorbed H$_2$O was 99.4 $\pm$ 1.1 kJ/mol. The difference between $\Delta H_{ds}$ and $\Delta H_{ttd}$ yields a value for the $\Delta H_{soln}$ of this 77 m$^2$/g $\gamma$-Al$_2$O$_3$ which agrees very well with the value of $\Delta H_{soln}$ obtained by Navrotsky et al.[12] on this same sample. Through a cycle analogous to that shown for the 166 m$^2$/g of $\gamma$-Al$_2$O$_3$ above, an enthalpy of dehydration of 93.6 $\pm$ 6.4 kJ/mol of H$_2$O was obtained. As this sample maintained 0.018 mol % H$_2$O after transposed temperature drop calorimetry, the final value for $\Delta H_{H_2O}$ was 96.4 $\pm$ 6.4 kJ/mol of H$_2$O. This number is again in agreement with our value of $\Delta H_{H_2O}$. The somewhat larger uncertainty is a result of the smaller H$_2$O content on this sample. Unfortunately, this method of checking the H$_2$O correction could not be used on any of the nanophase $\alpha$-Al$_2$O$_3$ samples as they were all prepared at temperatures below 923 K. At this point we can only assume that the value of $\Delta H_{H_2O}$ for $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ are similar.

**C. Relative Stability of Anhydrous Polymorphs.** The final state of the reaction which occurs upon dropping a pellet of Al$_2$O$_3 \cdot x$H$_2$O into the solvent in the calorimeter is the same for all samples; a dilute solution of Al$_2$O$_3$ in 2PbO$\cdot$B$_2$O$_3$ and gaseous H$_2$O at 979 K. Therefore, as long as the data are corrected for heat effects due to removal of H$_2$O, any differences in this corrected enthalpy of drop solution calorimetry, $\Delta H_{Al_2O_3}$, is directly related to enthalpy differences in anhydrous Al$_2$O$_3$ samples. In Figure 5, $\Delta H_{Al_2O_3}$ for all of the Al$_2$O$_3$ samples are plotted versus surface area. For clarity, the results are reported as enthalpy relative to coarse grained corundum by subtracting the corrected $\Delta H_{ds}$ from that obtained from a coarse grained (0.8 m$^2$/g) $\alpha$-Al$_2$O$_3$ (106.35 $\pm$ 0.53 kJ/mol). Unlike the molecular dynamics simulation of Blonski and Garafolini[7] (Figure 1), our calorimetric study shows nearly equal surface

energies for the two polymorphs (see Table 2). The experimental surface energy of $\alpha$-Al$_2$O$_3$ was 1.69 J/m$^2$. This was slightly higher than that of $\gamma$-Al$_2$O$_3$, 1.34 J/m$^2$, but the two polymorphs do not become energetically equivalent below surface areas of 300 m$^2$/g.

Extrapolation of the $\gamma$-Al$_2$O$_3$ line in Figure 5 to zero surface area suggests that coarse grained $\gamma$-Al$_2$O$_3$ should be +13.4 $\pm$ 2.0 kJ/mol less energetically stable than corundum. This does not agree with the value obtained from the aforementioned study of the isostructural $(1 - x)$MgAl$_2$O$_4 - x$Al$_{8/3}$O$_4$ defect spinel solid solution series, which placed $\gamma$-Al$_2$O$_3$ at +21.4 $\pm$ 2.0 kJ/mol relative to corundum.[12] However, we have gathered several pieces of data which support this less endothermic value for the enthalpy of the $\alpha$-Al$_2$O$_3 \rightarrow \gamma$-Al$_2$O$_3$ transition. The solution calorimetry data from the $(1 - x)$MgAl$_2$O$_4 - x$Al$_{8/3}$O$_4$ defect spinel solid solution series are shown as the filled circles in Figure 6. With our value for coarse $\gamma$-Al$_2$O$_3$ at +13.4 $\pm$ 2.0 kJ/mol relative to corundum, and the heat of solution of corundum as +30.9 $\pm$ 0.5 kJ/mol, the heat of solution of this material should be +17.5 $\pm$ 2.1 kJ/mol. As the data in Figure 6 are on a 4 oxygen per mole basis (for comparison with MgAl$_2$O$_4$), our value for coarse grained $\gamma$-Al$_2$O$_3$ must be multiplied by 1.33 to yield $\Delta H_{soln}$ = +23.3 $\pm$ 2.3 kJ/mol of Al$_{8/3}$/O$_4$. This point appears as the empty square or the right ordinate at $x = 1$. Navrotsky et al.[12] found that a second order polynomial could be extrapolated to match the $\Delta H_{soln}$ value obtained for a 77 m$^2$/g of $\gamma$-Al$_2$O$_3$ at $x = 1$ (solid line). However, a linear extrapolation of their data agrees well with the currently obtained value for coarse $\gamma$-Al$_2$O$_3$ (dotted line, $r^2$ = 0.987), which supports the less endothermic value for the transition between low-surface area materials. In addition, varying the value used for $(\Delta H_{H_2O})_c$ by as much as $\pm$ 30 kJ/mol does not significantly effect the value for coarse $\gamma$-Al$_2$O$_3$ obtained by extrapolation of the line through the $\gamma$-Al$_2$O$_3$ points to zero surface area in Figure 5. Likewise, in Figure 2, the two $\alpha$- and $\gamma$-aluminas of nearly equal surface areas and H$_2$O content lie $\sim$11.0 $\pm$ 1.5 kJ/mol apart, as do all of the hydrated
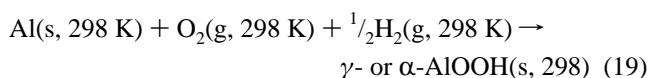
$\alpha$- and $\gamma$-alumina samples with monolayer H$_2$O coverage in Figure 8 (see below). The value listed in JANAF Tables[28] for $\Delta H_f^\circ$ of $\gamma$-Al$_2$O$_3$ is $-1656.9 \pm 6.3$ kJ/mol, which places it at $+18.8 \pm 6.4$ kJ/mol relative to corundum. Figure 5 predicts that the $\gamma$-Al$_2$O$_3$ on which this value was based had a surface area of $50 \pm 25$ m$^2$/g. In fact, the value of $\Delta H_f^\circ$ of $\gamma$-Al$_2$O$_3$ listed in JANAF Tables was based in part on the early high-temperature solution calorimetry work of Yokokawa and Kleppa,[29] who likewise found that the heat of solution of $\gamma$-Al$_2$O$_3$ can increase $\sim 20$ kJ/mol with increasing calcination temperature (i.e. coarsening). To determine $\Delta H$ for the $\alpha$- to $\gamma$-alumina transition, they chose the highest heat of solution for $\gamma$-Al$_2$O$_3$ attainable before the appearance of any higher transition aluminas (i.e. $\delta$ and $\theta$). The range of surface area between 50 and 100 m$^2$/g is precisely the area where partial transformation of $\gamma$-Al$_2$O$_3$ to $\delta$-Al$_2$O$_3$ would be expected. Therefore, our data for $\gamma$-Al$_2$O$_3$ agree with the published values when the latter are reinterpreted to include the effects of surface area on the energetics.

The uncertainty reported as error bars in Figure 5 is the standard deviation for the calorimetric experiments and does not take into account any uncertainty in the value of $(\Delta H_{H_2O})_c$. On the basis of the results of our transposed temperature drop experiments, we can be reasonably confident of the value of $(\Delta H_{H_2O})_c$ for $\gamma$-Al$_2$O$_3$, but we were unable to asses the energetics of removal of chemisorbed H$_2$O on $\alpha$-Al$_2$O$_3$. The dotted lines in Figure 5 demonstrate how changes of $\pm 10$ kJ/mol in $(\Delta H_{H_2O})_c$ will effect the results for $\alpha$-Al$_2$O$_3$. If the value of $(\Delta H_{H_2O})_c$ for $\alpha$-Al$_2$O$_3$ is 10 kJ/mol more endothermic, the enthalpy of $\gamma$-Al$_2$O$_3$ will fall below that of $\alpha$-Al$_2$O$_3$ at surface areas of $\sim 200$ m$^2$/g, which is in reasonable agreement with the molecular dynamics simulations.

**D. Energetics of Decomposition of Boehmite and Diaspore.** The uncertainty in $(\Delta H_{H_2O})_c$ for $\alpha$-Al$_2$O$_3$ must be more fully addressed. To check the validity of our correction for $\alpha$-alumina, we performed both drop solution calorimetry and transposed temperature drop calorimetry on the aluminum oxide hydroxides boehmite and diaspore. Through XRD and BET adsorption studies of the products, we have found that well-crystallized boehmite yields $\gamma$-Al$_2$O$_3$ with a surface area of 100 m$^2$/g and well-crystallized diaspore yields $\alpha$-Al$_2$O$_3$ with a surface area of 30 m$^2$/g after 1 h calcinations at 979 K (i.e. the final state of a transposed temperature drop experiment). If the relative energetic stability of the polymorphs at room temperature is known, the enthalpy difference between the 979 K calcination products can be obtained. The value we obtained from drop solution calorimetry ($\Delta H_{14}$) on diaspore was $+105.24 \pm 0.23$ kJ/mol. The $\Delta H_f^\circ$ of diaspore can be calculated from the drop solution data and the following thermodynamic cycle:

$$\alpha\text{-AlOOH (s, 298 K)} \rightarrow$$
$$\tfrac{1}{2}\text{Al}_2\text{O}_3(\text{soln, 979 K}) + \tfrac{1}{2}\text{H}_2\text{O (g, 979 K)} \quad (14)$$

$$\alpha\text{-Al}_2\text{O}_3\text{ (s, 298 K)} \rightarrow \text{Al}_2\text{O}_3\text{ (soln, 979 K)} \quad (15)$$

$$\text{H}_2\text{O(l, 298 K)} \rightarrow \text{H}_2\text{O(g, 979 K)} \quad (16)$$

$$2\text{Al(s, 298 K)} + \tfrac{3}{2}\text{O}_2(\text{g, 298 K}) \rightarrow \alpha\text{-Al}_2\text{O}_3(\text{s, 298 K}) \quad (17)$$

$$\text{H}_2(\text{g, 298}) + \tfrac{1}{2}\text{O}_2(\text{g, 298 K}) \rightarrow \text{H}_2\text{O(l, 298 K)} \quad (18)$$

net:

$$\text{Al(s, 298 K)} + \text{O}_2(\text{g, 298 K}) + \tfrac{1}{2}\text{H}_2(\text{g, 298 K}) \rightarrow$$
$$\gamma\text{- or } \alpha\text{-AlOOH(s, 298)} \quad (19)$$

$$\Delta H_f^\circ = \Delta H_{19} =$$
$$\Delta H_{14} + \tfrac{1}{2}\Delta H_{15} + \tfrac{1}{2}\Delta H_{16} + \tfrac{1}{2}\Delta H_{17} + \tfrac{1}{2}\Delta H_{18}$$
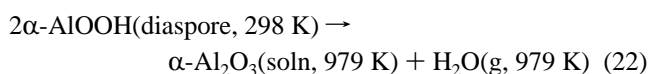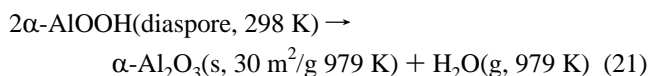
Using the data in Tables 3 and 4, we obtain $\Delta H_f^\circ = -997.78 \pm 1.37$ kJ/mol for diaspore, which is in fairly good agreement with the value given by Apps et al.,[30] of $-999.3$ kJ/mol. No uncertainty in this value was specified by Apps et al., but we must assume it is at least as large as the uncertainty on $\Delta H_f^\circ$ of $\alpha$-Al$_2$O$_3$, or $\pm 1.2$ kJ/mol.

The value of $\Delta H_{ds}$ obtained for boehmite was $102.90 \pm 0.42$ kJ/mol. As the end state of the reaction occurring during drop solution calorimetry is the same for boehmite and diaspore (a dilute solution of Al$_2$O$_3$ in 2PbO·B$_2$O$_3$ and gaseous H$_2$O at 979 K), the enthalpy difference between the polymorphs is obtained directly from the difference in $\Delta H_{ds}$ and the enthalpy change of the reaction
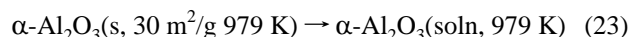
$$\gamma\text{-AlOOH(s, 298 K)} \rightarrow \alpha\text{-AlOOH(s, 298 K)} \quad (20)$$
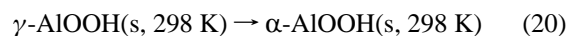
was determined to be $-2.34 \pm 0.53$ kJ/mol. The enthalpy of formation of boehmite is then $-995.44 \pm 1.43$ kJ/mol, which is in good agreement with the value given by Apps et al., $-995.31$ kJ/mol (see Tables 3 and 4).

The dehydration of diaspore was also studied by transposed temperature drop calorimetry. The measured heat effect, $\Delta H_{ttd}$, was a combination of the enthalpy of decomposition of $\alpha$-AlOOH and the heat content of the products (H$_2$O and $\alpha$-Al$_2$O$_3$) between 295 and 979 K. As BET and XRD studies showed that well-crystallized diaspore will dehydrate to a 30 m$^2$/g $\alpha$-Al$_2$O$_3$ at 979 K, the enthalpy change measured through transposed temperature drop calorimetry was that of reaction 23. The enthalpy of solution of this 30 m$^2$/g $\alpha$-Al$_2$O$_3$ can then be calculated from the thermodynamic cycle

$$2\alpha\text{-AlOOH(diaspore, 298 K)} \rightarrow$$
$$\alpha\text{-Al}_2\text{O}_3(\text{s, 30 m}^2/\text{g 979 K}) + \text{H}_2\text{O(g, 979 K)} \quad (21)$$

$$2\alpha\text{-AlOOH(diaspore, 298 K)} \rightarrow$$
$$\alpha\text{-Al}_2\text{O}_3(\text{soln, 979 K}) + \text{H}_2\text{O(g, 979 K)} \quad (22)$$

net:

$$\alpha\text{-Al}_2\text{O}_3(\text{s, 30 m}^2/\text{g 979 K}) \rightarrow \alpha\text{-Al}_2\text{O}_3(\text{soln, 979 K}) \quad (23)$$

$$\Delta H_{soln} = \Delta H_{23} = -\Delta H_{21} + \Delta H_{22}$$

We obtained $\Delta H_{soln} = +24.62 \pm 0.91$ kJ/mol. TGA showed 0.018 mol % H$_2$O still adsorbed on this 30 m$^2$/g of $\alpha$-Al$_2$O$_3$ after 1 h at 979 K. If we again assume 136 kJ/mol for desorption of this H$_2$O, it lowers the $\Delta H_{soln}$ to $+22.2 \pm 2.0$ kJ/mol, which places the sample at $+9.4 \pm 2.2$ kJ/mol relative to corundum. The same experiments were performed on boehmite, which dehydrated to a 100 m$^2$/g $\gamma$-Al$_2$O$_3$ and gave a $\Delta H_{ttd}$ of $+92.93 \pm 0.88$ kJ/mol. Through a cycle analogous to that above, and considering that TGA showed 0.030 mol % H$_2$O remained adsorbed after 1 h at 979 K, we calculated $\Delta H_{soln} = +3.2 \pm 1.5$ kJ/mol for this 100 m$^2$/g of $\gamma$-Al$_2$O$_3$. These data appear as the triangular points in Figure 5. The $\gamma$-Al$_2$O$_3$ sample appears to agree well with the other values, again suggesting that our $\Delta H_{H_2O}$ value is correct for $\gamma$-Al$_2$O$_3$. However, the 30 m$^2$/g $\alpha$-Al$_2$O$_3$ sample does not fall on the line through the other $\alpha$-Al$_2$O$_3$ samples. It does agree with the dotted line representing

**TABLE 3: Results of Drop Solution Calorimetry ($\Delta H_{ds}$), Transposed Temperature Drop Calorimetry ($\Delta H_{ttd}$), and the Corresponding Enthalpy of Formation for Boehmite and Diaspore**[a]

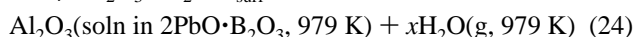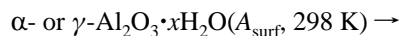| | $\Delta H_{ds}$ (kJ/mol of AlOOH) | $\Delta H_{ttd}$ (kJ/mol of AlOOH) | $\Delta H_f°$ (kJ/mol of AlOOH) |
|---|---|---|---|
| $\gamma$-AlOOH | 102.90 ± 0.42 (8) | 99.24 ± 0.31 (8) | -995.44 ± 1.55 |
| $\alpha$-AlOOH | 105.24 ± 0.23 (8) | 92.93 ± 0.88 (8) | -997.78 ± 1.37 |

[a] Numbers in parentheses are the numbers of experiments performed.

**TABLE 4: Thermodynamic Data (kJ/mol) from Literature Sources for Relevant Compounds in the Al−O−H System**[a]

| material | $\Delta H_f°$ | $\Delta H$(298K→979 K) |
|---|---|---|
| α-AlOOH | −999.3[a] | e |
| γ-AlOOH | −999.5[a] | e |
| α-Al$_2$O$_3$ | −1675.7 ± 1.2[b] | 75.5[c] |
| γ-Al$_2$O$_3$ | −1656.9 ± 6.3[b] | 75.5[c] |
| H$_2$O(l) | −285.83 ± 0.04[b] | 70.09[d] |
| H$_2$O(g) | −241.82 ± 0.04[b] | 25.85[d] |

[a] Apps et al.[30] [b] JANAF Thermochemical Tables.[11] [c] Robie et al.[31] [d] Knacke and Kubaschewski.[37] [e] Known only from 200 to 600 K.

a higher value of $(\Delta H_{H_2O})_c$ used for α-Al$_2$O$_3$ (146 kJ/mol of H$_2$O). As the initial and final states of the transposed temperature drop experiments on diaspore were both very well defined, the low value obtained for $\Delta H_{soln}$ of the 30 m$^2$/g α-Al$_2$O$_3$ suggests that $\Delta H_{H_2O}$ should be somewhat higher for α-Al$_2$O$_3$. A higher value of $\Delta H_{H_2O}$ (more endothermic heats of desorption) implies a higher anhydrous surface energy for α-Al$_2$O$_3$. This correlation is explored in the following section.
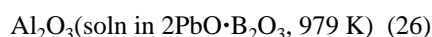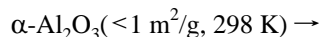
**E. Relation between Heat of Chemisorption and Surface Energy of Adsorbent.** The enthalpy change measured by drop solution calorimetry was that of the reaction
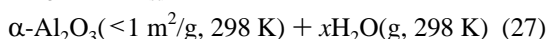
α- or γ-Al$_2$O$_3$·$x$H$_2$O($A_{surf}$, 298 K) →

$\quad$ Al$_2$O$_3$(soln in 2PbO·B$_2$O$_3$, 979 K) + $x$H$_2$O(g, 979 K) (24)

where $x$ is the mole fraction of adsorbed H$_2$O and $A_{surf}$ the specific surface area. As heats of adsorption of H$_2$O are usually reported with gaseous H$_2$O at 298 K as the reference state, it is convenient to add the heat content of H$_2$O between 979 K and room temperature (25.85 kJ/mol of H$_2$O)[31] to the above reaction, yielding

α- or γ-Al$_2$O$_3$·$x$H$_2$O($A_{surf}$, 298 K) →

$\quad$ Al$_2$O$_3$(soln in 2PbO·B$_2$O$_3$, 979 K) + $x$H$_2$O(g, 298 K) (25)
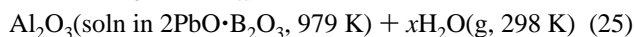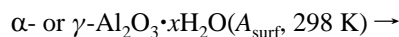
Furthermore, as the final state of the Al$_2$O$_3$ is the same for all samples, all of the data can be reported as excess enthalpy relative to corundum by subtracting the $\Delta H_{ds}$ value for coarse grained α-Al$_2$O$_3$:

α-Al$_2$O$_3$(<1 m$^2$/g, 298 K) →

$\quad\quad\quad\quad$ Al$_2$O$_3$(soln in 2PbO·B$_2$O$_3$, 979 K) (26)

which we measured as +106.35 ± 0.53 kJ/mol to reaction 26, yielding

α- or γ-Al$_2$O$_3$·$x$H$_2$O($A_{surf}$, 298 K) →

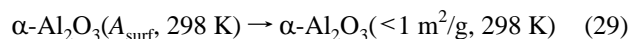$\quad\quad$ α-Al$_2$O$_3$(<1 m$^2$/g, 298 K) + $x$H$_2$O(g, 298 K) (27)

As enthalpy is a state function, we can divide the above reaction into two contributions for α-Al$_2$O$_3$ samples. (For γ-Al$_2$O$_3$, a third contribution, the enthalpy of the α to γ transition, also needs to be included.) The enthalpy change of the first is
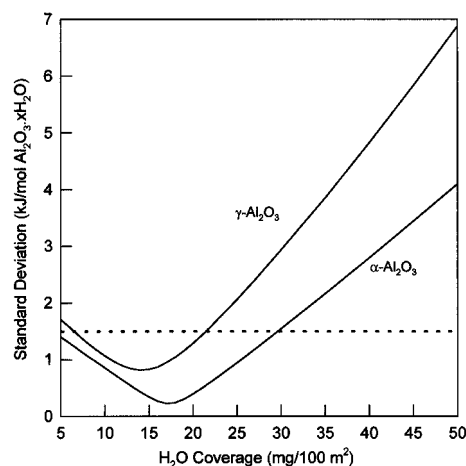


**Figure 7.** Standard deviation of the mean for $\Delta H_{ds}$ values extrapolated to varying coverage in mg/(100 m$^2$). The horizontal dotted line at 1.5 kJ/mol represents our average experimental standard deviation.
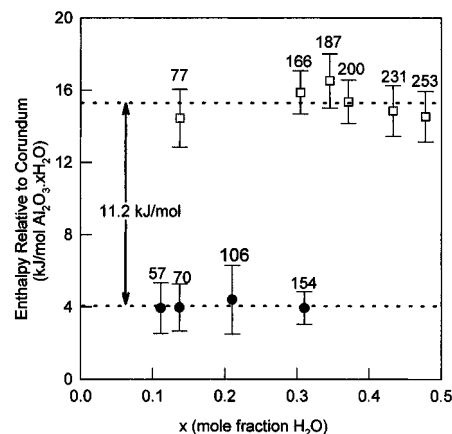


**Figure 8.** Enthalpies relative to corundum and H$_2$O(g, 298 K) for aluminas with H$_2$O coverages occurring at the minima in Figure 7 (17 mg/(100 m$^2$) for α-Al$_2$O$_3$ and 14 mg/(100 m$^2$) for γ-Al$_2$O$_3$) plotted versus mole fraction of H$_2$O. Although these samples contain different amounts of H$_2$O, they lie at equal enthalpies at these coverages (see text).
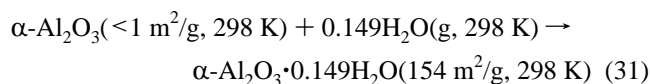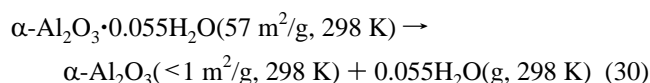
proportional to the heat of adsorption of H$_2$O

α-Al$_2$O$_3$·$x$H$_2$O($A_{surf}$, 298 K) →

$\quad\quad\quad\quad$ α-Al$_2$O$_3$($A_{surf}$, 298 K) + $x$H$_2$O(g, 298 K) (28)
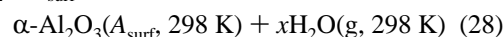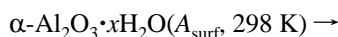
and the enthalpy change of the second contribution

$\quad$ α-Al$_2$O$_3$($A_{surf}$, 298 K) → α-Al$_2$O$_3$(<1 m$^2$/g, 298 K) (29)

is proportional to the excess enthalpy of the nanophase alumina due to surface energy. In Figure 7, the standard deviation of the mean $\Delta H_{ds}$ value (in the form of reaction 27) for the six γ-Al$_2$O$_3$ and four α-Al$_2$O$_3$ samples studied is plotted versus the coverage of H$_2$O. At coverages of <29 mg of H$_2$O/(100 m$^2$) for α-Al$_2$O$_3$ and <21 mg of H$_2$O/(100 m$^2$) for γ-Al$_2$O$_3$ the standard deviation falls below our average experimental accuracy of ±1.5 kJ/mol. At the minima in Figure 7 the average $\Delta H_{ds}$ values are +4.06 ± 0.23 and +15.26 ± 0.82 kJ/mol relative to corundum and H$_2$O(g, 298 K) for α-Al$_2$O$_3$·$x$H$_2$O and γ-Al$_2$O$_3$·$x$H$_2$O, respectively (see Figure 8). From these data, we obtain a $\Delta H$ for the α-Al$_2$O$_3$·$x$H$_2$O → γ-Al$_2$O$_3$·$x$H$_2$O transition of +11.2 ± 0.9 kJ/mol between samples with nearly equal surface area and water contents, which is in good agreement with the value obtained from comparison of raw $\Delta H_{ds}$ values from such samples (see Figure 2).

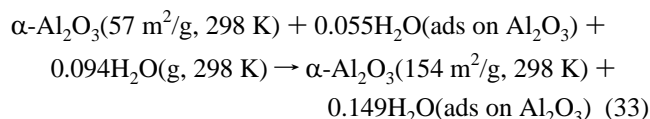The fact that all $\alpha$-Al$_2$O$_3\cdot x$H$_2$O samples lie at equal enthalpy at this particular coverage when in the form of reaction 27 indicates that the hypothetical reaction 32 obtained from the thermodynamic cycle
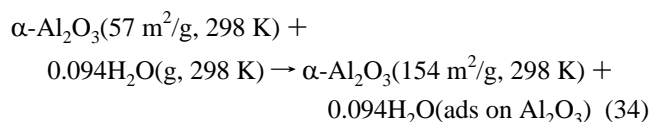
$$\alpha\text{-Al}_2\text{O}_3\cdot0.055\text{H}_2\text{O}(57\ \text{m}^2/\text{g},\ 298\ \text{K}) \rightarrow$$
$$\alpha\text{-Al}_2\text{O}_3(<1\ \text{m}^2/\text{g},\ 298\ \text{K}) + 0.055\text{H}_2\text{O}(\text{g},\ 298\ \text{K})\ \ (30)$$

$$\alpha\text{-Al}_2\text{O}_3(<1\ \text{m}^2/\text{g},\ 298\ \text{K}) + 0.149\text{H}_2\text{O}(\text{g},\ 298\ \text{K}) \rightarrow$$
$$\alpha\text{-Al}_2\text{O}_3\cdot0.149\text{H}_2\text{O}(154\ \text{m}^2/\text{g},\ 298\ \text{K})\ \ (31)$$

net:

$$\alpha\text{-Al}_2\text{O}_3\cdot0.055\text{H}_2\text{O}(57\ \text{m}^2/\text{g},\ 298\ \text{K}) + 0.094\text{H}_2\text{O}$$
$$(\text{g},\ 298\ \text{K}) \rightarrow \alpha\text{-Al}_2\text{O}_3\cdot0.149\text{H}_2\text{O}(154\ \text{m2/g},\ 298\ \text{K})\ \ (32)$$
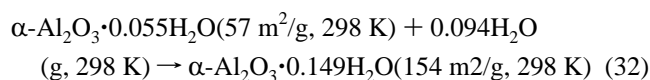
is accompanied by a zero enthalpy change. The same would be true for all analogous cycles linking other $\alpha$-alumina samples of different surface area with <29 mg/(100 m$^2$) of adsorbed H$_2$O.[32] Making the reasonable assumption that the integral heat of adsorption of H$_2$O for a particular coverage is independent of the specific surface area of the adsorbent, reaction 32 can be regarded as

$$\alpha\text{-Al}_2\text{O}_3(57\ \text{m}^2/\text{g},\ 298\ \text{K}) + 0.055\text{H}_2\text{O}(\text{ads on Al}_2\text{O}_3) +$$
$$0.094\text{H}_2\text{O}(\text{g},\ 298\ \text{K}) \rightarrow \alpha\text{-Al}_2\text{O}_3(154\ \text{m}^2/\text{g},\ 298\ \text{K}) +$$
$$0.149\text{H}_2\text{O}(\text{ads on Al}_2\text{O}_3)\ \ (33)$$

which reduces to

$$\alpha\text{-Al}_2\text{O}_3(57\ \text{m}^2/\text{g},\ 298\ \text{K}) +$$
$$0.094\text{H}_2\text{O}(\text{g},\ 298\ \text{K}) \rightarrow \alpha\text{-Al}_2\text{O}_3(154\ \text{m}^2/\text{g},\ 298\ \text{K}) +$$
$$0.094\text{H}_2\text{O}(\text{ads on Al}_2\text{O}_3)\ \ (34)$$

If we again divide reaction 34 into two contributions as in reactions 27–29 above, it can be seen that reaction 34 will have a zero enthalpy change only if the exothermic contribution due to adsorption of H$_2$O is exactly canceled by the endothermic effect of creating new surface. Therefore, the integral heat of adsorption for this coverage of H$_2$O, which may represent a monolayer (see below), is directly proportional to the surface energy of the anhydrous alumina. Such behavior was predicted by Cerofolini[33] and is easily rationalized by considering the following scenario. The surface of the alumina contains coordinatively unsaturated Al$^{3+}$ and O$^{2-}$ ions, which are destabilized with respect to the bulk and account for most of the excess surface energy. Adsorption of H$_2$O onto these sites completes the coordination and lowers the energy of the surface. From the analysis shown in Figure 2, it can be seen that the energy of the hydrated $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ surfaces are very similar. The enthalpy of the bond between the Al$^{3+}$ and OH$^-$ (or H$_2$O) should then depend upon the initial instability of the coordinatively unsaturated surface ions, or the surface energy of the anhydrous surface itself. Therefore, higher energy surfaces should bond H$_2$O more tightly and give more exothermic heats of adsorption. On the other hand, a surface with a relatively small surface energy makes smaller energetic gains by completing the coordination spheres of its surface atoms through adsorption. Hence it should give smaller heats of adsorption.

As pointed out in Figure 7 this equality in $\Delta H_{ds}$ values for samples of different surface area does not occur at every coverage. The minima in standard deviation of the mean

value from different surface area samples of each polymorph occur at coverages of ~14 mg/(100 m$^2$) for $\gamma$-Al$_2$O$_3$ and ~17 mg/(100 m$^2$) for $\alpha$-Al$_2$O$_3$. For $\gamma$-Al$_2$O$_3$, 14 mg H$_2$O/(100 m$^2$) would correspond to a surface density of 9.2 OH/nm$^2$, and for $\alpha$-Al$_2$O$_3$, 17 mg H$_2$O/(100 m$^2$) would correspond to a surface density of 11.4 OH/nm$^2$. Both of these values are well below the maximum monolayer hydroxyl coverage based on close packing of oxide ions (19 OH/nm$^2$) and are in fairly good agreement with the amount of H$_2$O irreversibly adsorbed on transition aluminas found recently by Coster et al.[24] of ~10.4 OH/nm$^2$. The minimum for $\alpha$-Al$_2$O$_3$ occurs at a higher coverage than $\gamma$-Al$_2$O$_3$, again indicating the higher density of surface ions and adsorption sites which would be expected on the basis of the bulk densities. This suggests that these coverages correspond to the adsorption of the quantity of H$_2$O needed to effectively cure all of the surface defects (i.e. a monolayer) yielding energetically equivalent hydrated surfaces. Comparison of the integral heat of adsorption for monolayer coverage of H$_2$O (or hydroxyls) should be a good means of determining the relative surface energies of polymorphs.

**F. Surface Energy of Partially Dehydrated Samples.** As the two phenomena are intimately related, anhydrous surface energies cannot be obtained from hydrated surfaces without accurate knowledge of the heats of chemisorption. We therefore attempted to dehydrate the samples as far as possible without coarsening. Samples were suspended on an Al$_2$O$_3$ rod at a height inside the calorimeter where the temperature was 573 K. They were maintained at this position and temperature for 1 h under flowing Ar. The extent of dehydration under such conditions was determined for each sample via TGA. After the 1 h drying period, the sample was dropped from 573 K into the solvent in the calorimeter. TGA revealed that ~80% of the adsorbed H$_2$O was removed by heating at 573 K. This corresponds to removal of all of the physisorbed H$_2$O and roughly half of the chemisorbed H$_2$O. For comparison with the data from samples dropped from room temperature, the heat content of Al$_2$O$_3\cdot x$H$_2$O (as defined above) between 298 and 573 K (see Table 5), was added to each $\Delta H_{ds}$ value. The data were then corrected for the remaining chemisorbed H$_2$O by again assuming 136 kJ/mol for each polymorph. This treatment yielded nearly equal surface energies of 1.69 J/m$^2$ for $\alpha$-Al$_2$O$_3$ and 1.68 J/m$^2$ for $\gamma$-Al$_2$O$_3$ (Figure 9). For anhydrous $\gamma$-Al$_2$O$_3$ to become energetically stable with respect to anhydrous $\alpha$-Al$_2$O$_3$ at a specific surface area of ~250 m$^2$/g, the value for $(\Delta H_{H_2O})_c$ would have to be at least 216 kJ/mol for $\alpha$-Al$_2$O$_3$ (see dotted line in Figure 9). Subtracting the heat content of gaseous H$_2$O between 979 and 298 K reveals that the integral heat of chemisorption at 298 K for $\alpha$-Al$_2$O$_3$ would have to be 190 kJ/mol for the ~9 OH/nm$^2$ coverage of H$_2$O which cannot be removed at 573 K. This is significantly higher than the 133 kJ/mol given by Coster et al.[24] for such coverages on transition aluminas. One might conclude that such a large difference in heats of adsorption between the polymorphs would be easily measurable, but the inability to remove this 9 OH/nm$^2$ without coarsening $\alpha$-Al$_2$O$_3$ complicates such experiments.

**G. General Discussion.** Although we could detect no great difference in surface energies, the universally observed difference in surface area of the polymorphs must have some driving force. There are several explanations for the rapid coarsening of $\alpha$-Al$_2$O$_3$ despite the apparently equal surface energies we have obtained. It is possible that the apparent high (nearly equal to that of $\alpha$) surface energy for $\gamma$-Al$_2$O$_3$ is due to changes in the bulk structure, such as variations in Al$^{3+}$ distribution in the defect spinel structure. However, John et al.,[34] performed $^{27}$Al

**TABLE 5: Summary of Sample Characterization and Calorimetric Data for Samples Partially Dehydrated at 573 K**

| phase | surface area $(m^2/g)$ | $x_{573}{}^a$ | $H(573\,K) - H(298\,K)^b$ $(kJ/mol\ of\ Al_2O_3 \cdot xH_2O)$ | $\Delta H_{ds}(573\,K)^c$ $(kJ/mol\ of\ Al_2O_3 \cdot xH_2O)$ | $\Delta H_{ds}\ (298\,K)^d$ $(kJ/mol\ of\ Al_2O_3 \cdot xH_2O)$ | $\Delta H_{Al_2O_3}{}^e$ $(kJ/mol\ of\ Al_2O_3)$ |
|---|---|---|---|---|---|---|
| $\alpha$-Al$_2$O$_3$ | 79 | 0.063 | 27.48 | 72.95 ± 0.71 | 100.43 ± 0.71 | 91.86 ± 0.71 |
| $\alpha$-Al$_2$O$_3$ | 156 | 0.114 | 27.75 | 67.64 ± 1.70 | 95.39 ± 1.70 | 79.89 ± 1.70 |
| $\gamma$-Al$_2$O$_3$ | 77 | 0.061 | 27.47 | 59.68 ± 0.55 | 87.15 ± 0.55 | 78.85 ± 0.55 |
| $\gamma$-Al$_2$O$_3$ | 173 | 0.131 | 27.85 | 53.08 ± 2.05 | 80.93 ± 2.05 | 63.11 ± 2.05 |
| $\gamma$-Al$_2$O$_3$ | 253 | 0.215 | 28.31 | 49.43 ± 1.55 | 77.80 ± 1.55 | 48.56 ± 1.55 |

$^a$ Mole percent of H$_2$O adsorbed after 1 h heat treatment at 573 K. Determined via TGA. $^b$ Heat content of Al$_2$O$_3\cdot x$H$_2$O determined as described in text. $^c$ Raw $\Delta H_{ds}$ data for samples dropped from 573 K. $^d$ $\Delta H_{ds}$ data adjusted to room temperature values. $^e$ Room temperature adjusted $\Delta H_{ds}$ values corrected for adsorbed H$_2$O using 136 kJ/mol of H$_2$O.
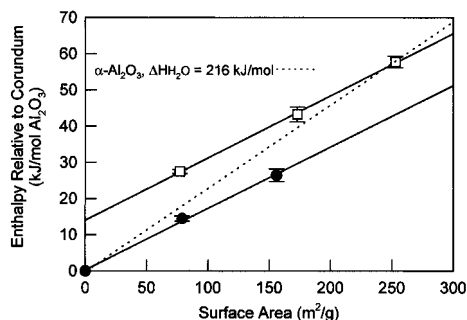


**Figure 9.** $\Delta H_{ds}$ values obtained from samples partially dried at 573 K corrected for remaining H$_2$O using 136 kJ/mol. The dotted line represents the data for $\alpha$-Al$_2$O$_3$ using 216 kJ/mol for $(\Delta H_{H_2O})_c$.

NMR on $\gamma$-Al$_2$O$_3$ and found a relatively constant 25 ± 4% of the Al$^{3+}$ in tetrahedral coordination after calcination at various temperatures between 773 and 1073 K. We measured an enthalpy difference of 24.0 ± 2.1 kJ/mol between $\gamma$-Al$_2$O$_3$ samples of 77 and 253 m$^2$/g. For even half of this value to be due to a variation in cation distribution of $\leq$8%, the interchange enthalpies for Al$^{3+}$ and vacancies in tetrahedral or octahedral coordination would have to be >150 kJ/mol. This seems very unlikely considering that the "site preference energy" for octahedral Al$^{3+}$ over tetrahedral Al$^{3+}$ in spinels appears to be ~40 kJ/mol.[35]

It may also be possible that the surfaces of these nanocrystals reconstruct to a similar surface phase independent of the bulk structure. However, the two polymorphs adsorbed different amounts of H$_2$O, with $\alpha$-Al$_2$O$_3$ consistently adsorbing a higher weight percentage than $\gamma$-Al$_2$O$_3$. The extent of adsorption should depend upon the number of coordinatively unsaturated surface sites, which in turn depends upon the density of the polymorph. The higher weight percentage of H$_2$O on the $\alpha$-Al$_2$O$_3$ samples is evidence that the surfaces of the nanocrystals do retain some of the character of the bulk polymorph and are not simply reconstructed to the same surface phase.

If there is a difference in surface energy between the polymorphs which destabilizes $\alpha$-Al$_2$O$_3$ at high specific surface areas, the majority of the excess energy is concentrated on a few surface sites. These unstable sites are effectively cured by adsorption of H$_2$O which accounts for the nearly equal surface energies we have repeatedly obtained. When these sites are exposed by desorption of H$_2$O, the material rapidly coarsens to lower its surface area and decrease its excess enthalpy. It is interesting to recall that nanophase $\alpha$-Al$_2$O$_3$ has only been prepared by decomposition of diaspore. Therefore, during and immediately after its synthesis it is continuously in the presence of H$_2$O. The 154 m$^2$/g of $\alpha$-Al$_2$O$_3$ was prepared at ~673 K, at which temperature significant quantities of H$_2$O could be chemisorbed to stabilize the high surface area. It is possible that such high-surface area $\alpha$-Al$_2$O$_3$ can not be synthesized in the absence of this surface stabilizing H$_2$O.

The coarsening behavior can also be rationalized if $\alpha$-alumina has a *lower* surface energy than $\gamma$-alumina. The adsorbed hydroxyls on $\alpha$-Al$_2$O$_3$ would then be more easily removed at lower temperatures and the exposed anhydrous surface would coarsen rapidly. Likewise, if $\gamma$-Al$_2$O$_3$ has a higher surface energy, the hydroxyls would require more thermal energy for removal, and $\gamma$-Al$_2$O$_3$ would maintain a coverage of hydroxyl ions at high temperatures. These hydroxyls could prevent the material from sintering, accounting for the ability of $\gamma$-Al$_2$O$_3$ to maintain high surface areas at high temperatures. It is actually quite logical to suspect that $\gamma$-Al$_2$O$_3$ has a higher anhydrous surface energy. About 25% of the Al$^{3+}$ ions in $\gamma$-Al$_2$O$_3$ are in tetrahedral coordination. A surface Al$^{3+}$ in a tetrahedral site would have only 3-fold coordination,[10] which is surely a highly unstable state for Al$^{3+}$. The situation can be thought of in terms of activation energies, with the anhydrous surface being the peak in the potential energy diagram. Higher surface energy materials have higher barriers to coarsening, as the exposure of anhydrous surface is a highly unstable intermediate. Clearly, the picture is much more complicated than many have thought, and an easily obtained high surface area does not necessarily correspond to a low surface energy for the anhydrous phase.

## IV. Conclusions

We found no direct evidence for surface energy stabilization of $\gamma$-Al$_2$O$_3$ with respect to $\alpha$-Al$_2$O$_3$. Both surfaces are stabilized by adsorbed H$_2$O, and the hydrated surfaces are energetically equivalent. If a difference in surface energy does exist between the anhydrous polymorphs, it would be evident as more exothermic heats of H$_2$O adsorption on the higher energy surface. However, the energetically significant adsorbed H$_2$O amounts to less that 9 OH/nm$^2$. By heating at temperatures >1000 K, it is possible to dehydroxylate $\alpha$-Al$_2$O$_3$ to coverages below 9 OH/nm$^2$, but surface areas of the resulting material will decrease to $\leq$40 m$^2$/g, which makes surface energies difficult to measure by calorimetry. Spectroscopic study (FTIR) of surface Al−O vibrational modes of highly dehydroxylated $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ may elucidate the relative Al−O bond energies of these surfaces. Such a study has already been conducted on $\gamma$-Al$_2$O$_3$.[36] The enthalpy of the $\alpha$-Al$_2$O$_3 \rightarrow \gamma$-Al$_2$O$_3$ transition in coarse grained materials is +13.4 ± 2.0 kJ/mol. This value is less endothermic than those previously reported but does not include contributions due the inherent high surface area of $\gamma$-Al$_2$O$_3$ as were contained in previous studies.[12,29] The enthalpies of formation of boehmite and diaspore are −995.44 ± 1.33 and −997.78 ±1.37 kJ/mol, respectively, which are consistent with recently published values.[30]

## References and Notes

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