

Effects of Increased Surface Area and Chemisorbed H₂O on the Relative Stability of Nanocrystalline γ -Al₂O₃ and α -Al₂O₃

J. M. McHale and A. Navrotsky*

Princeton Materials Institute and Department of Geosciences, Princeton University,
Princeton, New Jersey 08544

A. J. Perrotta

ALCOA Technical Center, Aluminum Company of America, Alcoa Center, Pennsylvania 15069

Received: September 9, 1996; In Final Form: November 6, 1996[®]

Corundum, α -Al₂O₃, appears to be the thermodynamically stable phase of aluminum oxide at all common pressure and temperature conditions, but attempted syntheses of nanocrystalline Al₂O₃ usually result in other polymorphs of the oxide (transition aluminas). Herein we explore the possibility that γ -Al₂O₃ becomes the thermodynamically stable polymorph when a critical surface area is exceeded. High-temperature solution calorimetry was performed on several samples of nanocrystalline γ -Al₂O₃ and α -Al₂O₃. The aluminas adsorbed atmospheric H₂O which could not be completely removed without coarsening (particularly for α -Al₂O₃). Samples of γ -Al₂O₃ with <21 mg/(100 m²) and α -Al₂O₃ with <29 mg/(100 m²) coverages of adsorbed H₂O lied at equal enthalpies with respect to corundum and H₂O(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 H₂O revealed that increased surface area of nanocrystalline α -Al₂O₃ and γ -Al₂O₃ significantly destabilized the materials with respect to coarse grained samples. However, down to the lowest attainable coverages of H₂O the experimental "surface energies" of the two phases were nearly equal. Our results cannot definitely rule out the assumption that γ -Al₂O₃ is surface energy stabilized with respect to α -Al₂O₃. However, if this is the case, the high-energy sites on the α -Al₂O₃ surface are relatively few, and effectively stabilized at low temperatures by adsorbed H₂O. The enthalpy of hypothetical coarse grained γ -Al₂O₃ was also explored and found to be +13.4 ± 2.0 kJ/mol relative to coarse grained α -Al₂O₃.

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 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 metal oxide "surface energies" are available due to the difficulty inherent in such measurements.⁵

Corundum, α -Al₂O₃, appears to be the thermodynamically stable phase of aluminum oxide at all common pressure and temperature conditions, but attempted syntheses of nanocrystalline Al₂O₃ usually result in γ -Al₂O₃.⁶ In addition, γ -Al₂O₃ can maintain surface areas of ~200 m²/g at 1073 K, whereas nanophase α -Al₂O₃ will coarsen to <30 m²/g at such temperatures. Recently, Blonski and Garofalini⁷ performed molecular dynamics simulations of various α -Al₂O₃ and γ -Al₂O₃ surfaces and obtained estimates of the surface energies. They found that on the whole the surface energies of α -Al₂O₃ were significantly greater than those of γ -Al₂O₃ (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 -Al₂O₃ may become the energetically stable polymorph as specific surface areas exceed ~175 m²/g (see Figure 1).

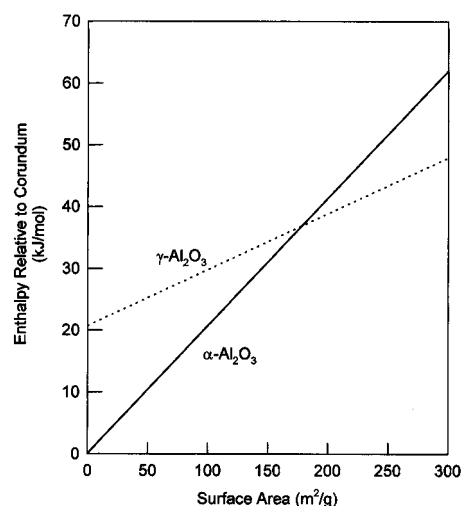


Figure 1. Calculated enthalpy of alumina polymorphs vs surface area based on molecular dynamics simulations and data for small surface area materials. Enthalpy of γ -Al₂O₃ at zero surface area taken from ref 12.

Although these simulations strongly suggest that γ -Al₂O₃ is a surface stabilized phase, the role of adsorbed species, and in particular adsorbed H₂O, 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 H₂O. The inherent high surface area of γ -Al₂O₃ results in the ubiquitous presence of H₂O on the material, which

[®] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

has led some to suggest that hydroxyl ions are a necessary component of the defect structure.⁸ Earlier reports have postulated that γ - Al_2O_3 is actually a hydrogen spinel,⁹ though this has recently been questioned.¹⁰ As both nanophase α - Al_2O_3 and nanophase γ - Al_2O_3 are synthesized by decomposition of hydrous materials, a discussion of the energetics of these aluminas in the absence of H_2O 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_2O . Our results indicate that adsorbed H_2O stabilizes the surfaces of both polymorphs such that they have similar surface energies down to the lowest attainable H_2O coverages (before coarsening sets in). In addition, experimental verification is provided for a direct dependence of the heat of adsorption of H_2O on the surface energy of the adsorbent, and the enthalpy of the γ - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_3 transition is discussed.

II. Experimental Section

A. Sample Preparation and Characterization. Samples of nanocrystalline α - Al_2O_3 and γ - Al_2O_3 were prepared (at Alcoa) through topotactic decompositions of diaspor, α - AlOOH , and boehmite, γ - AlOOH , respectively. High-purity, coarse grained α - Al_2O_3 , α - AlOOH , and γ - AlOOH were also prepared by Alcoa. Coarse grained γ - Al_2O_3 is not readily prepared, as temperatures where coarsening sets in also result in partial transformation to δ - and θ - Al_2O_3 .¹¹ An approximation for thermodynamic data on coarse grained γ - Al_2O_3 can be taken from a previous high-temperature solution calorimetry study (at 978 K in $2\text{PbO} \cdot \text{B}_2\text{O}_3$) of the isostructural $(1-x)\text{MgAl}_2\text{O}_4 - x\text{Al}_{8/3}\text{O}_4$ defect spinel solid solution series.¹² As these alumina rich spinel samples were prepared at ≥ 1773 K, they were certainly of low surface area. The $77 \text{ m}^2/\text{g}$ γ - Al_2O_3 studied in this work was a commercial γ - Al_2O_3 obtained from Alfa Products. It was the same batch on which enthalpy of solution measurements (in $2\text{PbO} \cdot \text{B}_2\text{O}_3$ 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_2O correction and for comparison in discussing the energetics of the γ - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_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 $\text{Cu K}\alpha_1$ 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_2O .

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 $2\text{PbO} \cdot \text{B}_2\text{O}_3$ 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_2O_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_2O 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 $\text{H}_2\text{O}(\text{g}, 979 \text{ K})$.¹⁴ Transposed temperature drop calorimetry, wherein the sample was dropped into empty (without solvent) platinum crucibles, was performed on some γ - Al_2O_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_2O . 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_2O 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_2O_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 α - Al_2O_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 ± 1 K and $55 \pm 2\%$ relative humidity), for ≥ 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_2O , 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, ΔH_{ds} , versus mole fraction H_2O 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_2O (see Figure 4). The calcination temperature used in the preparation of some γ - Al_2O_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_2O , 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 $\sim 20\%$ of the equilibrium adsorbed H_2O 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 α and γ samples of similar surface area decreases with increasing surface area, this would imply a lower surface energy for γ alumina. In Figure 2A, the raw ΔH_{ds}

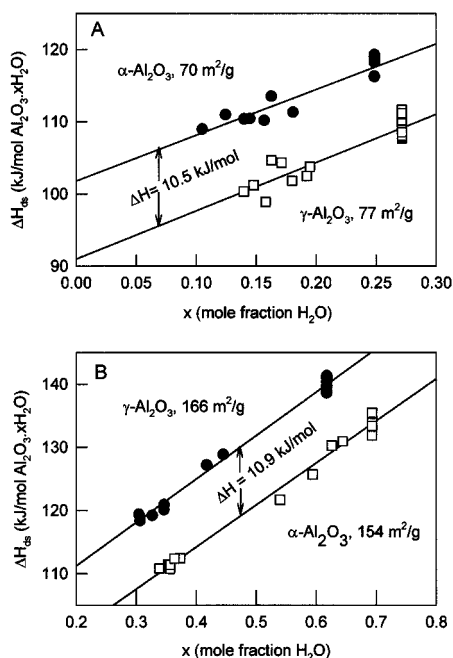
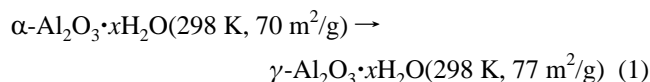


Figure 2. ΔH_{ds} values as a function of the mole fraction of H₂O for (A) 70 m²/g α -Al₂O₃ and 77 m²/g γ -Al₂O₃ and (B) 154 m²/g α -Al₂O₃ and 166 m²/g γ -Al₂O₃. The enthalpy difference between the hydrated polymorphs remains relatively constant with increasing surface area.

values are plotted versus mole fraction of H₂O for 70 m²/g of α -Al₂O₃ and 77 m²/g of γ -Al₂O₃. The vertical distance between the least squares fitted straight lines yields ΔH for the reaction

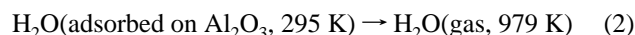


of $+10.5 \pm 1.5$ kJ/mol from for $x = 0.1$ – 0.3 (mole fraction of H₂O). In Figure 2B, the same analysis is shown for samples of over twice the surface area, 154 m²/g of α -Al₂O₃ and 166 m²/g of γ -Al₂O₃. The enthalpy difference between these samples is very close to that of the lower surface area 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 H₂O “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 H₂O desorption are discussed in the following section.

B. Correction for Adsorbed H₂O. The results of the sample characterization and calorimetric experiments are summarized in Table 1. The equilibrium H₂O 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 H₂O/(100 m²) for α -Al₂O₃ and γ -Al₂O₃, respectively. From examination of Table 1, it can be seen that H₂O 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 α -Al₂O₃ and γ -Al₂O₃ is examined.

As desorption is generally an endothermic process, there is a lower limit to the possible value for our H₂O correction. Assuming no excess interaction between Al₂O₃ and H₂O (i.e. heat of adsorption equal to the heat of condensation of H₂O), the enthalpy change for the reaction which occurs to adsorbed

H₂O upon introduction to the calorimeter,



can be obtained from literature values for the heat content of H₂O(l), H₂O(g), and the enthalpy of vaporization of H₂O at 373.15 K. Between 298 and 979 K, eq 2 yields 70.09 kJ/mol of H₂O as the lower limit for our H₂O correction.

It is known that at least three types of H₂O adsorption occur on the surface of Al₂O₃.^{16,17} The first type of water is tightly bound, chemisorbed H₂O, which exists as hydroxyl ions bonded to Al³⁺ in various configurations (of which five to seven are normally distinguished by IR spectroscopy).^{11,17–22} Chemisorbed (hydrogen bonded) molecular H₂O can also exist, and adsorption of H₂O on Al₂O₃ at room temperature has been shown to result in tightly bound molecular H₂O.²³ Finally, depending on the temperature and partial pressure of the H₂O, additional layers of physisorbed molecular H₂O can be present. The differential heat of adsorption for this physisorbed H₂O is on the order of the enthalpy of condensation of H₂O, 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 $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlOOH}$).²⁴ The average value we obtained for the enthalpy of dehydration from the slopes of ΔH_{ds} vs mole fraction of H₂O plots was 67.9 ± 5.4 kJ/mol (see Figure 4), which is very close to the enthalpy difference between liquid H₂O at 298 K and gaseous H₂O at 979 K (70.09 kJ/mol). These values are typical of physically adsorbed H₂O and are not valid for the more tightly bound chemisorbed H₂O which cannot be removed by heating at 398 K. Consequently, ΔH_{ds} vs mole fraction H₂O plots cannot be extrapolated to zero water content to obtain accurate values for anhydrous samples.

The differential heat of adsorption of H₂O on Al₂O₃ has been found to show Freundlich behavior (logarithmic dependence on coverage),²⁵ revealing that the surface of Al₂O₃ is highly heterogeneous. However, the integral heat of adsorption (or desorption) for the entire equilibrium coverage of H₂O can be fairly well-estimated by a constant. For our samples with equilibrium H₂O contents, the total or integral enthalpy of dehydration, ΔH_{H_2O} , for a sample of mole fraction x (i.e. $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), can be represented as

$$\Delta H_{H_2O} = x_p(\Delta H_{H_2O})_p + x_c(\Delta H_{H_2O})_c \quad (3)$$

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

where x_p is the mole fraction of physisorbed H₂O, x_c the mole fraction of chemisorbed H₂O, $(\Delta H_{H_2O})_p$ is the enthalpy of desorption for the physisorbed H₂O, and $(\Delta H_{H_2O})_c$ is the enthalpy of desorption of the chemisorbed H₂O. The corrected enthalpy of drop solution calorimetry for the Al₂O₃ is then $\Delta H_{Al_2O_3}$, which is obtained from the equation

$$\Delta H_{Al_2O_3} = \Delta H_{ds} - x\Delta H_{H_2O} \quad (5)$$

Our ΔH_{ds} vs mole fraction H₂O plots support the use of 70.09 kJ/mol for $(\Delta H_{H_2O})_p$, but a value for $(\Delta H_{H_2O})_c$ is needed. Coster et al.²⁴ and Gervasini and Auroux²⁶ have shown that values for the initial heat of adsorption (at lowest attainable coverages of “preadsorbed” H₂O) can exceed 200 kJ/mol of H₂O. The differential heat of adsorption falls logarithmically with increasing coverage (Θ), reaching the heat of condensation of H₂O (~ 44 kJ/mol) at coverages of ~ 15 OH/nm² (~ 22.6 mg of H₂O/(100 m²)). With our equilibrium H₂O contents averaging ~ 63

TABLE 1: Summary of Sample Characterization and Calorimetric Data^a

phase (XRD)	surface area (m ² /g)	wt % H ₂ O	x Al ₂ O ₃ ·xH ₂ O		(ΔH _{H₂O}) _p ^c (kJ/mol of H ₂ O)	ΔH _{H₂O} total ^d (kJ/mol of H ₂ O)	ΔH _{ds} ^e (kJ/mol of Al ₂ O ₃ ·xH ₂ O)	ΔH _{Al₂O₃} ^f (kJ/mol of Al ₂ O ₃)
			equilibrium	chemisorbed ^b				
α-Al ₂ O ₃	0.83	0.00 (1)	0.00	0.00			106.35	106.35 ± 0.53 (8)
α-Al ₂ O ₃	57	3.61 ± 0.13 (4)	0.2101	0.0871	61.4	97.4	115.64	96.3 ± 1.4 (19)
α-Al ₂ O ₃	70	4.24 ± 0.04 (3)	0.2486	0.1074	63.3	98.5	117.70	93.4 ± 1.3 (14)
α-Al ₂ O ₃	106	8.05 ± 0.05 (5)	0.4917	0.1642	60.9	92.1	132.30	87.6 ± 1.9 (20)
α-Al ₂ O ₃	154	9.91 ± 0.06 (5)	0.6175	0.2417	68.7	95.9	139.35	80.9 ± 0.9 (15)
γ-Al ₂ O ₃ ^g	~1						86.0	86.0 ± 2.0
γ-Al ₂ O ₃	77	4.61 ± 0.11 (5)	0.2714	0.1088	67.0	96.5	109.19	83.1 ± 1.6 (16)
γ-Al ₂ O ₃	166	10.98 ± 0.05 (5)	0.6926	0.2451	66.6	92.9	133.86	69.8 ± 1.2 (16)
γ-Al ₂ O ₃	187	11.35 ± 0.12 (5)	0.7189	0.2719	69.7	95.0	134.57	66.3 ± 1.5 (16)
γ-Al ₂ O ₃	200	12.52 ± 0.16 (4)	0.8036	0.2918	69.7	94.0	141.24	65.7 ± 1.2 (19)
γ-Al ₂ O ₃	231	13.19 ± 0.07 (3)	0.8529	0.3400	80.1	96.3	146.65	61.9 ± 1.4 (15)
γ-Al ₂ O ₃	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 ΔH_{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 ΔH_{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, ΔH_{Al₂O₃} = ΔH_{ds} - x(ΔH_{H₂O}). ^g Theoretical coarse grained γ-Al₂O₃ taken from a previous high-temperature solution calorimetric study of (1 - x)MgAl₂O₄ - xAl_{8/3}O₄ defect spinel solid solutions at 978 K in 2PbO·B₂O₃.¹²

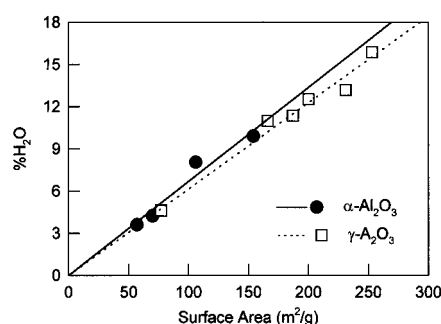


Figure 3. Equilibrium H₂O content for the nanophase aluminas as a function of surface area. The least squares fitted straight lines yield 66.9 and 61.4 mg of H₂O/(100 m²) for α-Al₂O₃ and γ-Al₂O₃, respectively.

mg/(100 m²), about two-thirds of the adsorbed H₂O on our samples is physisorbed H₂O. This is supported by our ΔH_{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

$$\Delta H = a - b \ln \Theta \quad (6)$$

where a and b were empirically determined coefficients and Θ 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 < Θ < 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

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

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 (ΔH_{H₂O})_c of 136 kJ/mol.

We will accept the values of 70.1 kJ/mol for (ΔH_{H₂O})_p and 136 kJ/mol for (ΔH_{H₂O})_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⁻³, and the density of α-Al₂O₃ is 3.99 g·cm⁻³.¹¹ 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 ΔH_{H₂O} 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

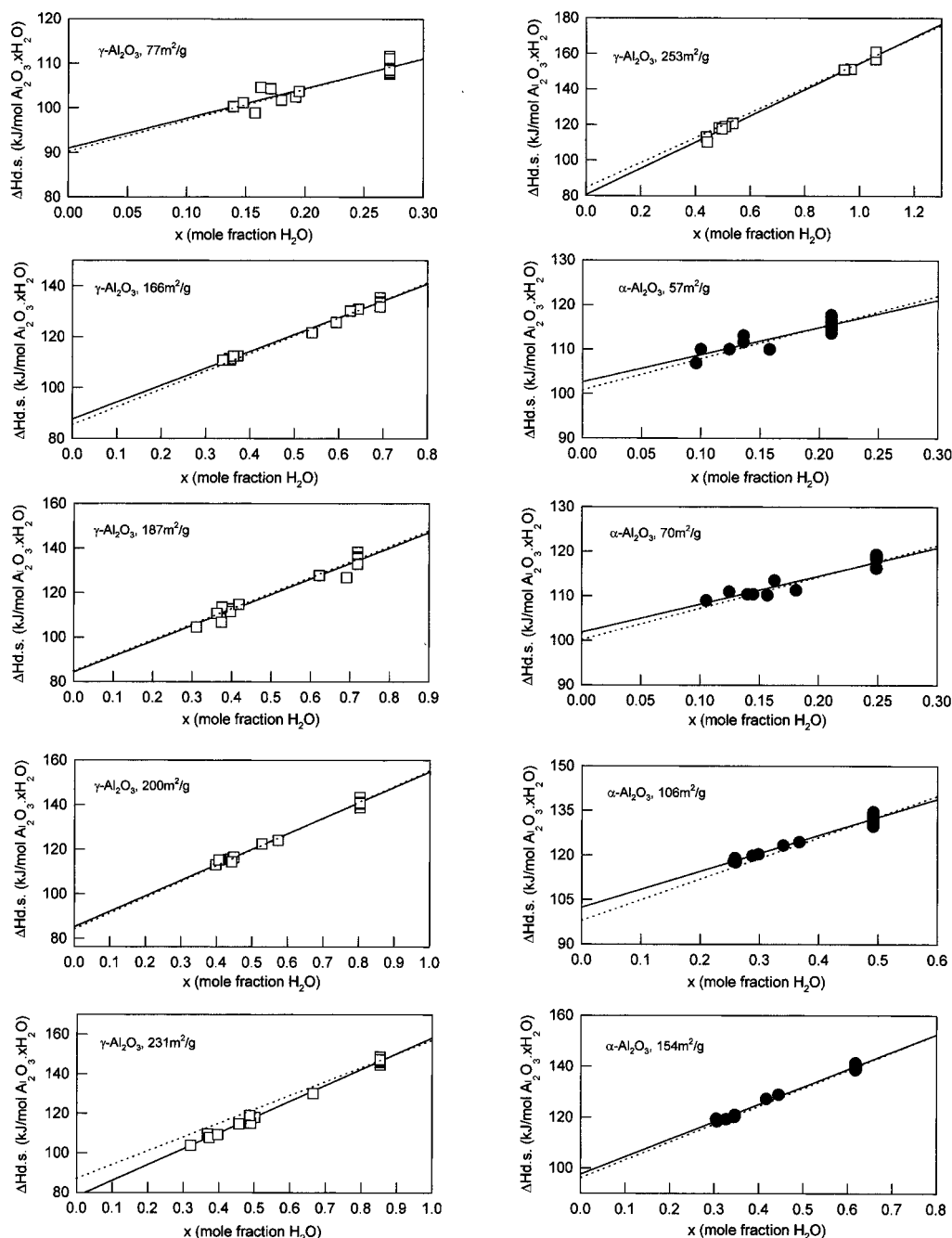
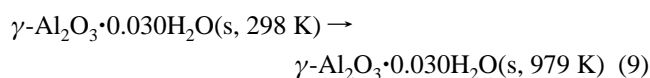
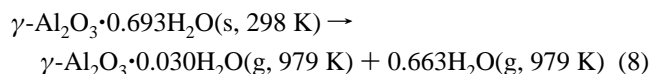
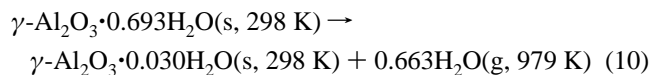


Figure 4. $\Delta H_{d.s.}$ values as a function of mole fraction H_2O (x) for the nanophase aluminas. The dotted lines represent the slope obtained assuming the heat content of liquid H_2O between 298 and 979 K, 70.09 kJ/mol of H_2O .

this result into consideration, the heat effect measured during the experiment was that of reaction 8, and $\Delta H_{\text{H}_2\text{O}}$ can be calculated via the following thermodynamic cycle:



net:



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

From transposed temperature drop calorimetry we obtained 133.85 ± 0.68 kJ/mol for reaction 8. To complete the cycle, a value for reaction 9, the heat content of hydrated Al_2O_3 is needed. The tightly bound water is certainly in the form of surface hydroxyl groups bound to Al_2O_3 . The vibrational frequencies of these isolated hydroxyls occur in the high-frequency range of the IR spectrum ($\nu \geq 3600 \text{ cm}^{-1}$).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 $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. However, additional Al—O vibrations should contribute. We therefore assume the heat content of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ to be the heat content of Al_2O_3 in the experimental temperature range multiplied by $(1 + x/5)$. For $\text{Al}_2\text{O}_3 \cdot 0.030\text{H}_2\text{O}$, 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

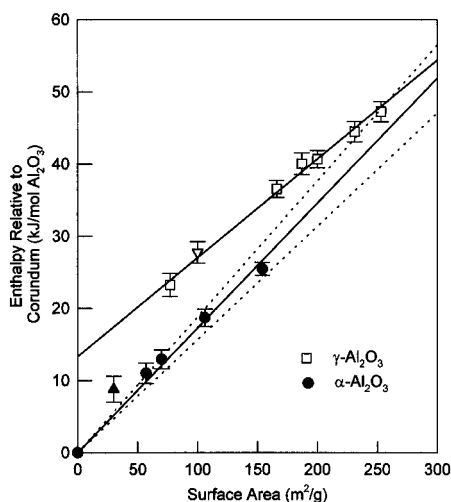


Figure 5. Enthalpy of alumina samples relative to coarse grained α - Al_2O_3 as a function of surface area. The solid lines represent the data obtained using our best values for $\Delta H_{\text{H}_2\text{O}}$. The dotted lines show the variation in the result obtained for α - Al_2O_3 after increasing the value of $(\Delta H_{\text{H}_2\text{O}})_c$ by 10 kJ/mol. The triangular points represent the data obtained from calorimetry on AlOOH samples (see text).

± 1.6 kJ/(0.663 mol of H_2O), or 86.5 ± 2.4 kJ/mol of H_2O . However, the 0.03 mol % H_2O 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_2O yields 90.6 ± 3.0 kJ/mol. This is in agreement with the value we obtained for $\Delta H_{\text{H}_2\text{O}}$ on the basis of our ΔH_{ds} vs mol fraction H_2O plots and the data of Coster et al.²⁴ The same analysis was performed on a 77 m^2/g sample of γ - Al_2O_3 . The value obtained for ΔH_{td} on this sample which initially had 0.270 mol % of adsorbed H_2O was 99.4 ± 1.1 kJ/mol. The difference between ΔH_{ds} and ΔH_{td} yields a value for the ΔH_{soln} of this 77 m^2/g γ - Al_2O_3 which agrees very well with the value of ΔH_{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 γ - Al_2O_3 above, an enthalpy of dehydration of 93.6 ± 6.4 kJ/mol of H_2O was obtained. As this sample maintained 0.018 mol % H_2O after transposed temperature drop calorimetry, the final value for $\Delta H_{\text{H}_2\text{O}}$ was 96.4 ± 6.4 kJ/mol of H_2O . This number is again in agreement with our value of $\Delta H_{\text{H}_2\text{O}}$. The somewhat larger uncertainty is a result of the smaller H_2O content on this sample. Unfortunately, this method of checking the H_2O correction could not be used on any of the nanophase α - Al_2O_3 samples as they were all prepared at temperatures below 923 K. At this point we can only assume that the value of $\Delta H_{\text{H}_2\text{O}}$ for γ - Al_2O_3 and α - Al_2O_3 are similar.

C. Relative Stability of Anhydrous Polymorphs. The final state of the reaction which occurs upon dropping a pellet of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ into the solvent in the calorimeter is the same for all samples; a dilute solution of Al_2O_3 in $2\text{PbO} \cdot \text{B}_2\text{O}_3$ and gaseous H_2O at 979 K. Therefore, as long as the data are corrected for heat effects due to removal of H_2O , any differences in this corrected enthalpy of drop solution calorimetry, $\Delta H_{\text{Al}_2\text{O}_3}$, is directly related to enthalpy differences in anhydrous Al_2O_3 samples. In Figure 5, $\Delta H_{\text{Al}_2\text{O}_3}$ for all of the Al_2O_3 samples are plotted versus surface area. For clarity, the results are reported as enthalpy relative to coarse grained corundum by subtracting the corrected ΔH_{ds} from that obtained from a coarse grained (0.8 m^2/g) α - Al_2O_3 (106.35 ± 0.53 kJ/mol). Unlike the molecular dynamics simulation of Blonski and Garafolini⁷ (Figure 1), our calorimetric study shows nearly equal surface

TABLE 2: Surface Energies of α - Al_2O_3 and γ - Al_2O_3

	surface energy (J/m ²)	
	from calorimetry	from molecular dynamics ^a
α - Al_2O_3	1.69	2.0 to 8.4
γ - Al_2O_3	1.34	0.8 to 2.5

^a For relaxed surfaces, various orientations.

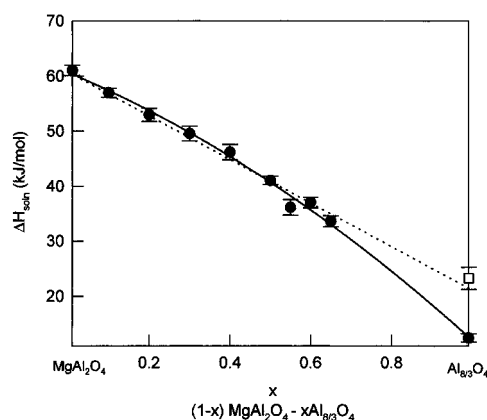


Figure 6. Solution calorimetry data from Navrotsky et al.¹² on the $(1-x)\text{MgAl}_2\text{O}_4 - x\text{Al}_{8/3}\text{O}_4$ defect spinel solid solution series. Fitting the data to a second degree polynomial extrapolates to a value matching the ΔH_{soln} obtained from 77 m^2/g of γ - Al_2O_3 (filled circles, solid line). However, a simple linear interpretation extrapolates well to the value obtained in this work for hypothetical coarse grained γ - Al_2O_3 (open square, dotted line).

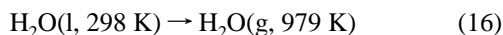
energies for the two polymorphs (see Table 2). The experimental surface energy of α - Al_2O_3 was 1.69 J/m². This was slightly higher than that of γ - Al_2O_3 , 1.34 J/m², but the two polymorphs do not become energetically equivalent below surface areas of 300 m^2/g .

Extrapolation of the γ - Al_2O_3 line in Figure 5 to zero surface area suggests that coarse grained γ - Al_2O_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 $(1-x)\text{MgAl}_2\text{O}_4 - x\text{Al}_{8/3}\text{O}_4$ defect spinel solid solution series, which placed γ - Al_2O_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 α - $\text{Al}_2\text{O}_3 \rightarrow \gamma$ - Al_2O_3 transition. The solution calorimetry data from the $(1-x)\text{MgAl}_2\text{O}_4 - x\text{Al}_{8/3}\text{O}_4$ defect spinel solid solution series are shown as the filled circles in Figure 6. With our value for coarse γ - Al_2O_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_2O_4), our value for coarse grained γ - Al_2O_3 must be multiplied by 1.33 to yield $\Delta H_{\text{soln}} = +23.3 \pm 2.3$ kJ/mol of $\text{Al}_{8/3}\text{O}_4$. 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 ΔH_{soln} value obtained for a 77 m^2/g of γ - Al_2O_3 at $x = 1$ (solid line). However, a linear extrapolation of their data agrees well with the currently obtained value for coarse γ - Al_2O_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 $(\Delta H_{\text{H}_2\text{O}})_c$ by as much as ± 30 kJ/mol does not significantly effect the value for coarse γ - Al_2O_3 obtained by extrapolation of the line through the γ - Al_2O_3 points to zero surface area in Figure 5. Likewise, in Figure 2, the two α - and γ -aluminas of nearly equal surface areas and H_2O content lie $\sim 11.0 \pm 1.5$ kJ/mol apart, as do all of the hydrated

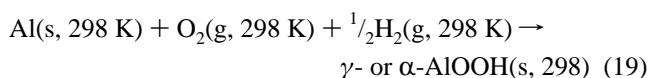
α - and γ -alumina samples with monolayer H₂O coverage in Figure 8 (see below). The value listed in JANAF Tables²⁸ for ΔH_f° of γ -Al₂O₃ is -1656.9 ± 6.3 kJ/mol, which places it at $+18.8 \pm 6.4$ kJ/mol relative to corundum. Figure 5 predicts that the γ -Al₂O₃ on which this value was based had a surface area of 50 ± 25 m²/g. In fact, the value of ΔH_f° of γ -Al₂O₃ 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 γ -Al₂O₃ can increase ~ 20 kJ/mol with increasing calcination temperature (i.e. coarsening). To determine ΔH for the α - to γ -alumina transition, they chose the highest heat of solution for γ -Al₂O₃ attainable before the appearance of any higher transition aluminas (i.e. δ and θ). The range of surface area between 50 and 100 m²/g is precisely the area where partial transformation of γ -Al₂O₃ to δ -Al₂O₃ would be expected. Therefore, our data for γ -Al₂O₃ 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 γ -Al₂O₃, but we were unable to assess the energetics of removal of chemisorbed H₂O on α -Al₂O₃. The dotted lines in Figure 5 demonstrate how changes of ± 10 kJ/mol in $(\Delta H_{H_2O})_c$ will effect the results for α -Al₂O₃. If the value of $(\Delta H_{H_2O})_c$ for α -Al₂O₃ is 10 kJ/mol more endothermic, the enthalpy of γ -Al₂O₃ will fall below that of α -Al₂O₃ at surface areas of ~ 200 m²/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 α -Al₂O₃ must be more fully addressed. To check the validity of our correction for α -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 γ -Al₂O₃ with a surface area of 100 m²/g and well-crystallized diaspore yields α -Al₂O₃ with a surface area of 30 m²/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 (ΔH_{14}) on diaspore was $+105.24 \pm 0.23$ kJ/mol. The ΔH_f° of diaspore can be calculated from the drop solution data and the following thermodynamic cycle:



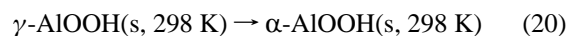
net:



$$\Delta H_f^\circ = \Delta H_{19} = \Delta H_{14} + \frac{1}{2}\Delta H_{15} + \frac{1}{2}\Delta H_{16} + \frac{1}{2}\Delta H_{17} + \frac{1}{2}\Delta H_{18}$$

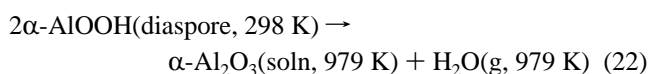
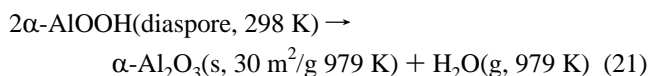
Using the data in Tables 3 and 4, we obtain $\Delta H_f^\circ = -997.78 \pm 1.37$ kJ/mol for diaspore, which is in fairly good agreement with the value given by Apps et al.,³⁰ of -999.3 kJ/mol. No uncertainty in this value was specified by Apps et al., but we must assume it is at least as large as the uncertainty on ΔH_f° of α -Al₂O₃, or ± 1.2 kJ/mol.

The value of ΔH_{ds} obtained for boehmite was 102.90 ± 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 Al₂O₃ in 2PbO·B₂O₃ and gaseous H₂O at 979 K), the enthalpy difference between the polymorphs is obtained directly from the difference in ΔH_{ds} and the enthalpy change of the reaction

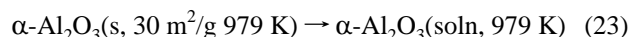


was determined to be -2.34 ± 0.53 kJ/mol. The enthalpy of formation of boehmite is then -995.44 ± 1.43 kJ/mol, which is in good agreement with the value given by Apps et al., -995.31 kJ/mol (see Tables 3 and 4).

The dehydration of diaspore was also studied by transposed temperature drop calorimetry. The measured heat effect, ΔH_{td} , was a combination of the enthalpy of decomposition of α -AlOOH and the heat content of the products (H₂O and α -Al₂O₃) between 295 and 979 K. As BET and XRD studies showed that well-crystallized diaspore will dehydrate to a 30 m²/g α -Al₂O₃ at 979 K, the enthalpy change measured through transposed temperature drop calorimetry was that of reaction 23. The enthalpy of solution of this 30 m²/g α -Al₂O₃ can then be calculated from the thermodynamic cycle



net:



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

We obtained $\Delta H_{\text{soln}} = +24.62 \pm 0.91$ kJ/mol. TGA showed 0.018 mol % H₂O still adsorbed on this 30 m²/g of α -Al₂O₃ after 1 h at 979 K. If we again assume 136 kJ/mol for desorption of this H₂O, it lowers the ΔH_{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 m²/g γ -Al₂O₃ and gave a ΔH_{td} of $+92.93 \pm 0.88$ kJ/mol. Through a cycle analogous to that above, and considering that TGA showed 0.030 mol % H₂O remained adsorbed after 1 h at 979 K, we calculated $\Delta H_{\text{soln}} = +3.2 \pm 1.5$ kJ/mol for this 100 m²/g of γ -Al₂O₃. These data appear as the triangular points in Figure 5. The γ -Al₂O₃ sample appears to agree well with the other values, again suggesting that our ΔH_{H_2O} value is correct for γ -Al₂O₃. However, the 30 m²/g α -Al₂O₃ sample does not fall on the line through the other α -Al₂O₃ samples. It does agree with the dotted line representing

TABLE 3: Results of Drop Solution Calorimetry (ΔH_{ds}), Transposed Temperature Drop Calorimetry (ΔH_{td}), and the Corresponding Enthalpy of Formation for Boehmite and Diaspore^a

	ΔH_{ds} (kJ/mol of AlOOH)	ΔH_{td} (kJ/mol of AlOOH)	ΔH_f° (kJ/mol of AlOOH)
γ -AlOOH	102.90 \pm 0.42 (8)	99.24 \pm 0.31 (8)	-995.44 \pm 1.55
α -AlOOH	105.24 \pm 0.23 (8)	92.93 \pm 0.88 (8)	-997.78 \pm 1.37

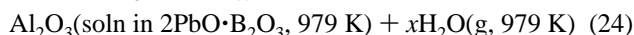
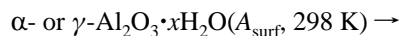
^a Numbers in parentheses are the numbers of experiments performed.**TABLE 4: Thermodynamic Data (kJ/mol) from Literature Sources for Relevant Compounds in the Al–O–H System^a**

material	ΔH_f°	$\Delta H(298\text{K} \rightarrow 979\text{K})$
α -AlOOH	-999.3 ^a	e
γ -AlOOH	-999.5 ^a	e
α -Al ₂ O ₃	-1675.7 \pm 1.2 ^b	75.5 ^c
γ -Al ₂ O ₃	-1656.9 \pm 6.3 ^b	75.5 ^c
H ₂ O(l)	-285.83 \pm 0.04 ^b	70.09 ^d
H ₂ O(g)	-241.82 \pm 0.04 ^b	25.85 ^d

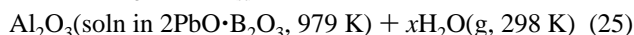
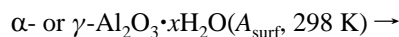
^a Apps et al.³⁰ ^b JANAF Thermochemical Tables.¹¹ ^c Robie et al.³¹^d Knacke and Kubaschewski.³⁷ ^e Known only from 200 to 600 K.

a higher value of (ΔH_{H_2O})_c used for α -Al₂O₃ (146 kJ/mol of H₂O). As the initial and final states of the transposed temperature drop experiments on diaspore were both very well defined, the low value obtained for ΔH_{soln} of the 30 m²/g α -Al₂O₃ suggests that ΔH_{H_2O} should be somewhat higher for α -Al₂O₃. A higher value of ΔH_{H_2O} (more endothermic heats of desorption) implies a higher anhydrous surface energy for α -Al₂O₃. This correlation is explored in the following section.

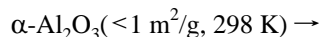
E. Relation between Heat of Chemisorption and Surface Energy of Adsorbent. The enthalpy change measured by drop solution calorimetry was that of the reaction



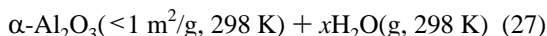
where x is the mole fraction of adsorbed H₂O and A_{surf} the specific surface area. As heats of adsorption of H₂O are usually reported with gaseous H₂O at 298 K as the reference state, it is convenient to add the heat content of H₂O between 979 K and room temperature (25.85 kJ/mol of H₂O)³¹ to the above reaction, yielding



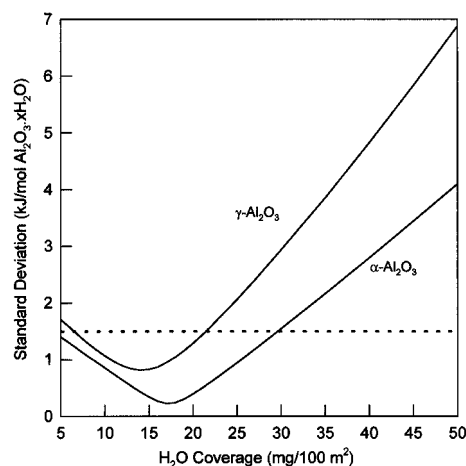
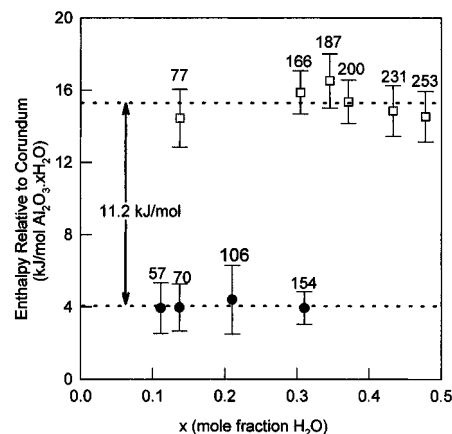
Furthermore, as the final state of the Al₂O₃ is the same for all samples, all of the data can be reported as excess enthalpy relative to corundum by subtracting the ΔH_{ds} value for coarse grained α -Al₂O₃:



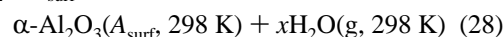
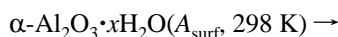
which we measured as +106.35 \pm 0.53 kJ/mol to reaction 26, yielding



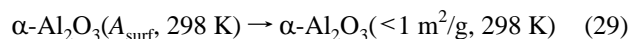
As enthalpy is a state function, we can divide the above reaction into two contributions for α -Al₂O₃ samples. (For γ -Al₂O₃, a third contribution, the enthalpy of the α to γ transition, also needs to be included.) The enthalpy change of the first is

**Figure 7.** Standard deviation of the mean for ΔH_{ds} values extrapolated to varying coverage in mg/(100 m²). The horizontal dotted line at 1.5 kJ/mol represents our average experimental standard deviation.**Figure 8.** Enthalpies relative to corundum and H₂O(g, 298 K) for aluminas with H₂O coverages occurring at the minima in Figure 7 (17 mg/(100 m²) for α -Al₂O₃ and 14 mg/(100 m²) for γ -Al₂O₃) plotted versus mole fraction of H₂O. Although these samples contain different amounts of H₂O, they lie at equal enthalpies at these coverages (see text).

proportional to the heat of adsorption of H₂O

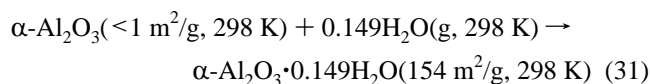
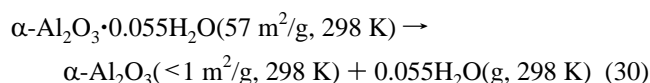


and the enthalpy change of the second contribution

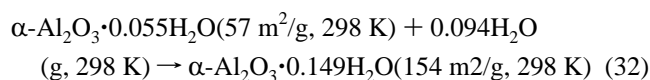


is proportional to the excess enthalpy of the nanophase alumina due to surface energy. In Figure 7, the standard deviation of the mean ΔH_{ds} value (in the form of reaction 27) for the six γ -Al₂O₃ and four α -Al₂O₃ samples studied is plotted versus the coverage of H₂O. At coverages of <29 mg of H₂O/(100 m²) for α -Al₂O₃ and <21 mg of H₂O/(100 m²) for γ -Al₂O₃ the standard deviation falls below our average experimental accuracy of ± 1.5 kJ/mol. At the minima in Figure 7 the average ΔH_{ds} values are +4.06 \pm 0.23 and +15.26 \pm 0.82 kJ/mol relative to corundum and H₂O(g, 298 K) for α -Al₂O₃·xH₂O and γ -Al₂O₃·xH₂O, respectively (see Figure 8). From these data, we obtain a ΔH for the α -Al₂O₃·xH₂O \rightarrow γ -Al₂O₃·xH₂O transition of +11.2 \pm 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 ΔH_{ds} values from such samples (see Figure 2).

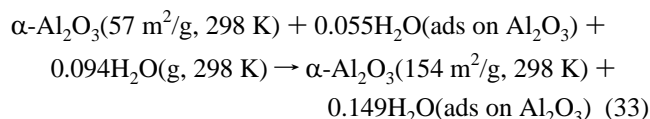
The fact that all α -Al₂O₃·*x*H₂O samples lie at equal enthalpy at this particular coverage when in the form of reaction 27 indicates that the hypothetical reaction 32 obtained from the thermodynamic cycle



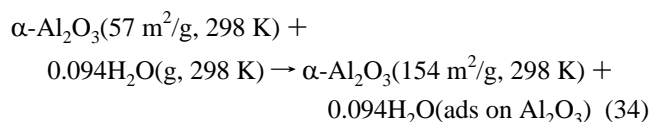
net:



is accompanied by a zero enthalpy change. The same would be true for all analogous cycles linking other α -alumina samples of different surface area with $<29 \text{ mg}/(100 \text{ m}^2)$ of adsorbed H₂O.³² Making the reasonable assumption that the integral heat of adsorption of H₂O for a particular coverage is independent of the specific surface area of the adsorbent, reaction 32 can be regarded as



which reduces to



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 H₂O is exactly canceled by the endothermic effect of creating new surface. Therefore, the integral heat of adsorption for this coverage of H₂O, which may represent a monolayer (see below), is directly proportional to the surface energy of the anhydrous alumina. Such behavior was predicted by Cerofolini³³ and is easily rationalized by considering the following scenario. The surface of the alumina contains coordinatively unsaturated Al³⁺ and O²⁻ ions, which are destabilized with respect to the bulk and account for most of the excess surface energy. Adsorption of H₂O 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 α -Al₂O₃ and γ -Al₂O₃ surfaces are very similar. The enthalpy of the bond between the Al³⁺ and OH⁻ (or H₂O) 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 H₂O 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 ΔH_{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 $\sim 14 \text{ mg}/(100 \text{ m}^2)$ for γ -Al₂O₃ and $\sim 17 \text{ mg}/(100 \text{ m}^2)$ for α -Al₂O₃. For γ -Al₂O₃, $14 \text{ mg H}_2\text{O}/(100 \text{ m}^2)$ would correspond to a surface density of $9.2 \text{ OH}/\text{nm}^2$, and for α -Al₂O₃, $17 \text{ mg H}_2\text{O}/(100 \text{ m}^2)$ would correspond to a surface density of $11.4 \text{ OH}/\text{nm}^2$. Both of these values are well below the maximum monolayer hydroxyl coverage based on close packing of oxide ions ($19 \text{ OH}/\text{nm}^2$) and are in fairly good agreement with the amount of H₂O irreversibly adsorbed on transition aluminas found recently by Coster et al.²⁴ of $\sim 10.4 \text{ OH}/\text{nm}^2$. The minimum for α -Al₂O₃ occurs at a higher coverage than γ -Al₂O₃, 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 H₂O 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 H₂O (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 Al₂O₃ 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 $\sim 80\%$ of the adsorbed H₂O was removed by heating at 573 K. This corresponds to removal of all of the physisorbed H₂O and roughly half of the chemisorbed H₂O. For comparison with the data from samples dropped from room temperature, the heat content of Al₂O₃·*x*H₂O (as defined above) between 298 and 573 K (see Table 5), was added to each ΔH_{ds} value. The data were then corrected for the remaining chemisorbed H₂O by again assuming 136 kJ/mol for each polymorph. This treatment yielded nearly equal surface energies of 1.69 J/m^2 for α -Al₂O₃ and 1.68 J/m^2 for γ -Al₂O₃ (Figure 9). For anhydrous γ -Al₂O₃ to become energetically stable with respect to anhydrous α -Al₂O₃ at a specific surface area of $\sim 250 \text{ m}^2/\text{g}$, the value for $(\Delta H_{\text{H}_2\text{O}})_c$ would have to be at least 216 kJ/mol for α -Al₂O₃ (see dotted line in Figure 9). Subtracting the heat content of gaseous H₂O between 979 and 298 K reveals that the integral heat of chemisorption at 298 K for α -Al₂O₃ would have to be 190 kJ/mol for the $\sim 9 \text{ OH}/\text{nm}^2$ coverage of H₂O 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 $9 \text{ OH}/\text{nm}^2$ without coarsening α -Al₂O₃ 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 α -Al₂O₃ despite the apparently equal surface energies we have obtained. It is possible that the apparent high (nearly equal to that of α) surface energy for γ -Al₂O₃ is due to changes in the bulk structure, such as variations in Al³⁺ distribution in the defect spinel structure. However, John et al.,³⁴ performed ²⁷Al

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	$H(573\text{ K}) - H(298\text{ K})^b$ (kJ/mol of Al ₂ O ₃ ·xH ₂ O)	$\Delta H_{\text{ds}}(573\text{ K})^c$ (kJ/mol of Al ₂ O ₃ ·xH ₂ O)	$\Delta H_{\text{ds}}(298\text{ K})^d$ (kJ/mol of Al ₂ O ₃ ·xH ₂ O)	$\Delta H_{\text{Al}_2\text{O}_3}^e$ (kJ/mol of Al ₂ O ₃)
α -Al ₂ O ₃	79	0.063	27.48	72.95 ± 0.71	100.43 ± 0.71	91.86 ± 0.71
α -Al ₂ O ₃	156	0.114	27.75	67.64 ± 1.70	95.39 ± 1.70	79.89 ± 1.70
γ -Al ₂ O ₃	77	0.061	27.47	59.68 ± 0.55	87.15 ± 0.55	78.85 ± 0.55
γ -Al ₂ O ₃	173	0.131	27.85	53.08 ± 2.05	80.93 ± 2.05	63.11 ± 2.05
γ -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 H₂O adsorbed after 1 h heat treatment at 573 K. Determined via TGA. ^b Heat content of Al₂O₃·xH₂O determined as described in text. ^c Raw ΔH_{ds} data for samples dropped from 573 K. ^d ΔH_{ds} data adjusted to room temperature values. ^e Room temperature adjusted ΔH_{ds} values corrected for adsorbed H₂O using 136 kJ/mol of H₂O.

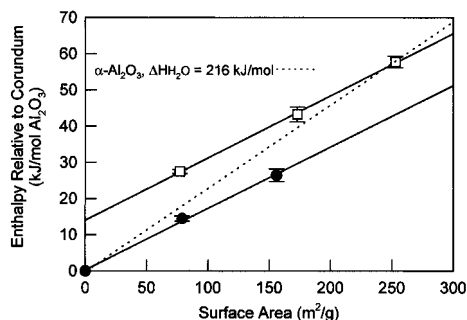


Figure 9. ΔH_{ds} values obtained from samples partially dried at 573 K corrected for remaining H₂O using 136 kJ/mol. The dotted line represents the data for α -Al₂O₃ using 216 kJ/mol for $(\Delta H_{\text{H}_2\text{O}})_c$.

NMR on γ -Al₂O₃ and found a relatively constant $25 \pm 4\%$ of the Al³⁺ 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 γ -Al₂O₃ samples of 77 and 253 m²/g. For even half of this value to be due to a variation in cation distribution of $\leq 8\%$, the interchange enthalpies for Al³⁺ 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 Al³⁺ over tetrahedral Al³⁺ 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 H₂O, with α -Al₂O₃ consistently adsorbing a higher weight percentage than γ -Al₂O₃. 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 H₂O on the α -Al₂O₃ 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 α -Al₂O₃ 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 H₂O which accounts for the nearly equal surface energies we have repeatedly obtained. When these sites are exposed by desorption of H₂O, the material rapidly coarsens to lower its surface area and decrease its excess enthalpy. It is interesting to recall that nanophase α -Al₂O₃ has only been prepared by decomposition of diaspor. Therefore, during and immediately after its synthesis it is continuously in the presence of H₂O. The 154 m²/g of α -Al₂O₃ was prepared at ~ 673 K, at which temperature significant quantities of H₂O could be chemisorbed to stabilize the high surface area. It is possible that such high-surface area α -Al₂O₃ can not be synthesized in the absence of this surface stabilizing H₂O.

The coarsening behavior can also be rationalized if α -alumina has a lower surface energy than γ -alumina. The adsorbed hydroxyls on α -Al₂O₃ would then be more easily removed at lower temperatures and the exposed anhydrous surface would coarsen rapidly. Likewise, if γ -Al₂O₃ has a higher surface energy, the hydroxyls would require more thermal energy for removal, and γ -Al₂O₃ would maintain a coverage of hydroxyl ions at high temperatures. These hydroxyls could prevent the material from sintering, accounting for the ability of γ -Al₂O₃ to maintain high surface areas at high temperatures. It is actually quite logical to suspect that γ -Al₂O₃ has a higher anhydrous surface energy. About 25% of the Al³⁺ ions in γ -Al₂O₃ are in tetrahedral coordination. A surface Al³⁺ in a tetrahedral site would have only 3-fold coordination,¹⁰ which is surely a highly unstable state for Al³⁺. 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 γ -Al₂O₃ with respect to α -Al₂O₃. Both surfaces are stabilized by adsorbed H₂O, 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 H₂O adsorption on the higher energy surface. However, the energetically significant adsorbed H₂O amounts to less than 9 OH/nm². By heating at temperatures > 1000 K, it is possible to dehydroxylate α -Al₂O₃ to coverages below 9 OH/nm², but surface areas of the resulting material will decrease to ≤ 40 m²/g, which makes surface energies difficult to measure by calorimetry. Spectroscopic study (FTIR) of surface Al–O vibrational modes of highly dehydroxylated α -Al₂O₃ and γ -Al₂O₃ may elucidate the relative Al–O bond energies of these surfaces. Such a study has already been conducted on γ -Al₂O₃.³⁶ The enthalpy of the α -Al₂O₃ \rightarrow γ -Al₂O₃ transition in coarse grained materials is $+13.4 \pm 2.0$ kJ/mol. This value is less endothermic than those previously reported but does not include contributions due the inherent high surface area of γ -Al₂O₃ as were contained in previous studies.^{12,29} The enthalpies of formation of boehmite and diaspor are -995.44 ± 1.33 and -997.78 ± 1.37 kJ/mol, respectively, which are consistent with recently published values.³⁰

Acknowledgment. This work was supported by The Aluminum Co. of America and by NSF Grant DMR 95-00812.

References and Notes

- (1) For reviews see: (a) Gleiter, H. *Nanostruct. Mater.* **1995**, 6, 3. (b) Seigel, R. W. *Nanostruct. Mater.* **1994**, 4, 121. (c) Gleiter, H. *Prog. Mater. Sci.* **1989**, 33, 223. (d) Freer, R., Ed. *Nanoceramics, British Ceramic Proceedings No. 51*; The Institute of Materials: London, 1993. (e) Siegel, R. W. *MRS Bull.* **1990**, 5, 60.
- (2) Flaschen, S. S. *J. Am. Ceram. Soc.* **1955**, 77, 6194.
- (3) Garvie, R. C. *J. Phys. Chem.* **1978**, 82, 218.
- (4) Skandan, G.; Foster, C. M.; Frase, H.; Ali, M. N.; Parker, J. C.; Hahn, H. *Nanostruct. Mater.* **1992**, 1, 313.
- (5) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1990; pp 313–318.
- (6) See for example: (a) Johnston, G. P.; Muenchausen, R.; Smith, D. M.; Fahrenholtz, W.; Foltyn, S. *J. Am. Ceram. Soc.* **1992**, 75, 3293. (b) Kumar, P. M.; Borse, P.; Rohatgi, V. K.; Bhoraskar, S. V.; Singh, P.; Sastry, M. *Mater. Chem. Phys.* **1994**, 36, 354.
- (7) Blonski, S.; Garofalini, S. H. *Surf. Sci.* **1993**, 295, 263.
- (8) Soled, S. J. *Catal.* **1983**, 81, 252.
- (9) DeBoer, J. H.; Houben, G. M. M. *Proceedings of the International Symposium on the Reactivity of Solids, Part I*; Elanders Boktryckeri Aktiebolag: Gothenburg, Sweden, 1955; pp 237–244.
- (10) Zhou, R.-S.; Snyder, R. L. *Acta Crystallogr.* **1991**, B47, 617.
- (11) Wefers, K.; Misra, C. *Oxides and Hydroxides of Aluminum*; Alcoa Technical Paper No. 19; Revised; Aluminum Co. of America: Alcoa Center, PA, 1987.
- (12) Navrotsky, A.; Wechsler, B. A.; Geisinger, K.; Seifert, F. *J. Am. Ceram. Soc.* **1986**, 69, 418.
- (13) Navrotsky, A. *Phys. Chem. Miner.* **1977**, 2, 89.
- (14) Navrotsky, A.; Rapp, R. P.; Smelik, E.; Burnley, P.; Circone, S.; Chai, L.; Bose, K.; Westrich, H. R. *Am. Miner.* **1994**, 79, 1099.
- (15) Hu, Y.; Navrotsky, A.; Chen, C.-Y.; Davis, M. E. *Chem. Mater.* **1995**, 7, 1816.
- (16) DeBoer, J. H.; Fortuin, J. M. H.; Lippens, B. C.; Meijs, W. H. *J. Catal.* **1963**, 2, 1.
- (17) Knozinger, H.; Ratnasamy, P. *Catal. Rev.—Sci. Eng.* **1978**, 17, 31.
- (18) Peri, J. B. *J. Phys. Chem.* **1965**, 69, 220.
- (19) Tsyganenko, A. A.; Filimonov, V. N. *Spectrosc. Lett.* **1972**, 5, 477.
- (20) Busca, G.; Lorenzelli, V.; Sanchez Escribano, V.; Guidetti, R. *J. Catal.* **1991**, 131, 167.
- (21) Huggins, B. A.; Ellis, P. D. *J. Am. Chem. Soc.* **1992**, 114, 2098.
- (22) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, 27, 497.
- (23) Peri, J. B.; Hannan, R. B. *J. Phys. Chem.* **1960**, 64, 1526.
- (24) Coster, D. J.; Fripiat, J. J.; Mucsas, M.; Auroux, A. *Langmuir* **1995**, 11, 2615.
- (25) See ref 5, p 693.
- (26) Gervasini, A.; Auroux, A. *J. Phys. Chem.* **1993**, 97, 2628.
- (27) Wade, W. H.; Hackerman, N. *J. Phys. Chem.* **1960**, 64, 1196.
- (28) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, 11, Suppl. 2.
- (29) Yokokawa, T.; Kleppa, O. J. *J. Phys. Chem.* **1964**, 68, 3246.
- (30) Apps, J. A.; Neil, J. M.; Jun, C.-H. *Thermochemical Properties of Gibbsite, Bayerite, Boehmite, Diaspore, and the Aluminate Ion between 0 and 350 °C*; U.S. Nuclear Regulatory Commission Report; NUREG/CR-5271, LBL-21482, RW; U.S. Nuclear Regulatory Commission: Washington, D.C., 1989.
- (31) Robie, R. A.; Hemmingway, B. S.; Fisher, J. R. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures*; Geological Survey Bulletin 1452; U.S. Geological Survey: Washington, D.C., 1979.
- (32) Again, for γ -Al₂O₃, a third contribution, the ΔH of the α to γ transition need also be included.
- (33) Cerofolini, G. F. *Surf. Sci.* **1975**, 51, 333.
- (34) John, C. S.; Alma, N. C. M.; Hays, G. R. *Appl. Catal.* **1983**, 6, 341.
- (35) Navrotsky, A.; Kleppa, O. J. *J. Inorg. Nucl. Chem.* **1967**, 29, 2701.
- (36) Lavalley, J.-C.; Benaissa, M. *J. Chem. Soc., Chem. Commun.* **1984**, 13, 908.
- (37) Knacke, O.; Kabschewski, O.; Hesselmann, K., Eds. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag: New York, 1991.