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Heats of Adsorption of Water on α- and γ-Alumina

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Heats of immersion of α- and γ-alumina in water have been determined for samples outgassed at temperatures up to 600°C. The results are combined with values of the residual surface-water content, determined by deuterium exchange, to give heats of adsorption of water as a function of uptake. The results are discussed and compared with similar data obtained, or calculated, from the published literature.

INTRODUCTION

The adsorption of water on alumina merits detailed investigation, since alumina is an important catalyst in which the activity is greatly influenced by the presence of adsorbed water. Under atmospheric conditions the surface of alumina is hydrated, and is effectively saturated with both molecularly adsorbed water (*1*, *2*) and dissociatively chemisorbed water present as hydroxyl groups (*3*, *4*). On vacuum outgassing at elevated temperatures, this water is progressively removed, although hydroxyl groups are not completely eliminated even at 1000°C (*3*, *4*). Residual surface-water content can be determined by both physical and chemical methods (*2*, *4–6*), and the results can be expressed as fractional surface coverages if the structure of the alumina is known, and appropriate assumptions are made concerning the number of adsorption sites in unit surface area. When outgassed alumina is immersed in water at 25°C, both physical and chemical adsorption occur, and the surface returns to a hydrated state. This results in high, values for the heats of immersion, which increase in magnitude with the extent of surface dehydration (*2*, *7*, *8*). If $q_{i(S\alpha L)}$ and $q_{i(S\beta L)}$ are the heats of immersion expressed in erg cm^{-2}, for two samples of the same alumina with residual-water contents of n_α and n molecules cm^{-2}, respectively, the integral heat of adsorption of liquid water over the coverage range $(n_\alpha - n_\beta)$ is given by

$$Q = k(q_{i(S\alpha L)} - q_{i(S\beta L)})/(n_\alpha - n_\beta).$$

In this expression k is a constant converting erg molecule^{-1} into the more familiar units of kcal mole^{-1}. In the limit $n_\beta \rightarrow n_\alpha$, the integral heat of adsorption tends to the differential value at n_α. It follows that differential heats of adsorption q are easily obtained from the slope of plots of $q_{i(SL)}$ against n. Heats of adsorption determined in this way are numerically less than those for adsorption from the vapor phase by the molar heat of vaporization.

The determination of heats of adsorption by immersion calorimetry has advantages over gas-adsorption calorimetry and the isosteric method, in that nonselective adsorption is avoided and in that adsorption takes place at a single temperature (*9*). The method is not satisfactory, however, if the surface anneals during outgassing, since this may prevent rehydration to the same final state on immersion. Furthermore, if rehydration is an activated process, heat liberation may be too slow for accurate measurement in conventional immersion calorimeters.

It is the purpose of the present communication to report heats of adsorption of water on α- and γ-alumina determined by immersion calorimetry and to compare the results with values which can be directly obtained, or calculated, from the published literature.

EXPERIMENTAL

Heats of immersion were determined at 25°C using a differential microcalorimeter, which has been described (*10, 11*). Residual surface hydrogen was determined by deuterium exchange (*5, 8*), and surface areas were determined by the BET method using nitrogen at 77°K ($\sigma_{N_2} = 16.2$ Å^2).

The α- and γ-Al_2O_3 used were from the identical preparation used in previous investigations (*8, 11*), and had been prepared by heating trihydrate to 1200 and 600°C, respectively. The total impurities in each alumina amounted to ~500 ppm. Prior to the determination of heats of immersion, residual hydrogen, or surface area, samples were outgassed in thin glass bulbs at a selected temperature in the range 100–600°C for 72 hr at $<10^{-6}$ Torr. Liquid-nitrogen traps protected the samples from contamination by water, mercury, or stopcock grease, and after outgassing, the bulbs were sealed off and removed from the vacuum system. The specific surface area of the α-Al_2O_3 was 13.4 m^2 g^{-1} and X-ray diffraction confirmed the α-structure. The specific surface area of the γ-Al_2O_3 was 103 m^2 g^{-1}, and was found to be independent of outgassing temperature up to 600°C. X-Ray diffraction confirmed the γ-structure, and showed a small amount of χ-Al_2O_3 to be present.

The water used in immersion calorimetry was purified by double distillation after passage through ion-exchange resin.

RESULTS AND DISCUSSION

Values obtained for the heats of immersion and residual surface hydrogen after outgassing at various temperatures are given in Table 1. In the calorimetric experiments, there was no evidence for the slow heat evolution observed by Guderjahn *et al.* (*12*); in all cases, heat evolution was rapid and complete in 5–10 min.

Figures 1 and 2 show plots of the residual surface hydrogen on α- and γ-Al_2O_3, expressed as percentage coverages of an OH monolayer, as a function of outgassing temperature. In constructing these figures, the published estimates of the monolayer capacities of hydroxyl groups have been used: 1.9×10^{15} OH cm^{-2} for α-Al_2O_3 (*7*) and 1.25×10^{15} OH cm^{-2} γ-Al_2O_3 (*4*). Such a plot has previously been given by Peri (*4*) for γ-Al_2O_3, and we now extend this by presenting further data for γ-Al_2O_3 and for α-Al_2O_3, both from our own work and from the literature (*2, 4, 13–18*). The findings support the view expressed by Peri (*4*), that a reasonable estimate for surface hydroxyl coverage can be made from a knowledge of the outgassing temperature alone, if the alumina is outgassed under conditions of a reasonably good vacuum. Although a coverage in excess of a full monolayer of hydroxyl groups indicates the presence of molecularly adsorbed water, a nominal 100% coverage does not necessarily mean the absence of molecular water. This arises from the possibility that the most weakly bound hydroxyl groups may be desorbed before the most strongly bound water molecules.

TABLE 1

HEATS OF IMMERSION AND RESIDUAL SURFACE HYDROGEN ON α- AND γ-Al_2O_3

	α-Al_2O_3		γ-Al_2O_3	
Outgassing temperature (°C)	$q_{i(SL)}$ (erg cm^{-2})	Surface hydrogen (atom cm^{-2})	$q_{i(SL)}$ (erg cm^{-2})	Surface hydrogen (atom cm^{-2})
100	399	4.13×10^{15}	430	1.67×10^{15}
200	584	2.18×10^{15}	518	1.07×10^{15}
300	773	1.30×10^{15}	648	7.68×10^{14}
400	800	5.40×10^{14}	762	4.27×10^{14}
500	964	2.97×10^{14}	835	2.62×10^{14}
600	1065	8.37×10^{13}	994	1.83×10^{14}

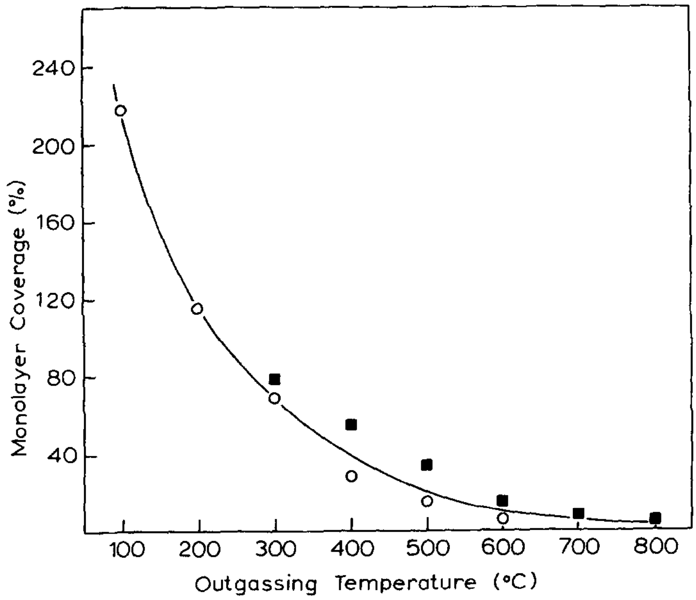

FIG. 1. Residual hydrogen on α-Al_2O_3, expressed as hydroxyl group coverage: ○—present work; ■—Ref. (*13*).

Heats of adsorption of water on α- and γ-Al_2O_3 expressed as a function of uptake, are given in Table 2. The values were determined by the graphical differentiation of plots of $q_{i(SL)}$ against n, and were subsequently corrected for adsorption from the gas phase by addition of the molar heat of vaporization at 25°C, 10.51 kcal $mole^{-1}$.

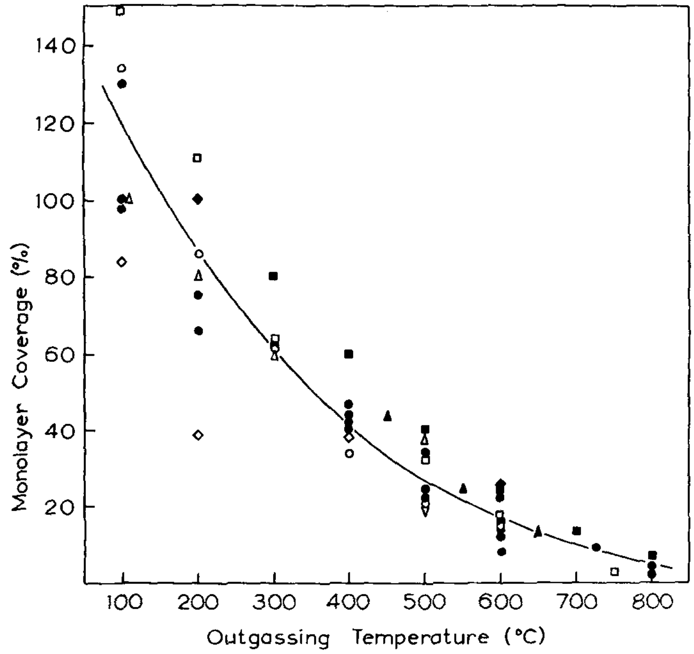

FIG. 2. Residual hydrogen on γ-Al_2O_3, expressed as hydroxyl group coverage: ○—present work; □—Ref. (*2*); ●—Ref. (*4*); ■—Ref. (*13*); ◇—Ref. (*14*); ◆—Ref. (*15*); △—Ref. (*16*); ▲—Ref. (*17*); ▽—Ref. (*18*.)

TABLE 2
HEATS OF ADSORPTION AS A FUNCTION OF UPTAKE

Uptake (molecules $cm^{-2} \times 10^{-14}$)	Heat of adsorption (kcal $mole^{-1}$)	
	α-Al_2O_3	γ-Al_2O_3
1.0	26.1	45.4
2.0	21.0	26.6
3.0	18.7	22.0
4.0	17.3	19.3
5.0	16.2	17.9
6.0	15.4	16.7
7.0	14.8	16.2
8.0	14.3	15.8
10.0	13.6	—
12.0	13.1	—
16.0	12.4	—
20.0	12.2	—

In the evaluation of *n*, it was assumed that two residual hydrogen atoms were equivalent to one water molecule either dissociatively, or undissociatively, adsorbed. It is apparent that heats of adsorption on γ-Al_2O_3 are consistently higher than those on α-Al_2O_3 at corresponding uptakes, and this is further emphasised if the uptakes are expressed as fractional coverages for dissociative chemisorption to form hydroxyl groups. The present values of the heats of adsorption, together with values from the literature, are plotted as a function of uptake in Figs. 3 and 4.

The values for α-Al_2O_3 are closer to those of Yao (*19*), determined by vapor adsorption calorimetry, than to those of Venable, Wade, and Hackerman (*20*), determined by immersion calorimetry of surfaces possessing known amounts of presorbed water. The present results do not exhibit plateaux in the plot of heat of adsorption against uptake as observed by Yao (*19*), and thus do not support his suggestion that water is adsorbed as molecules and is associated with a higher heat on cations than on anions. The differences between the published values (*19*, *20*) lie in the degree of surface dehydration prior to adsorption, rather than in the method of measurement. This is supported by the reduced values for the heat of adsorption obtained after presorbing water and subsequently outgassing at 22°C (*19*). It follows that the published data should be corrected for the surface water remaining after outgassing, if they

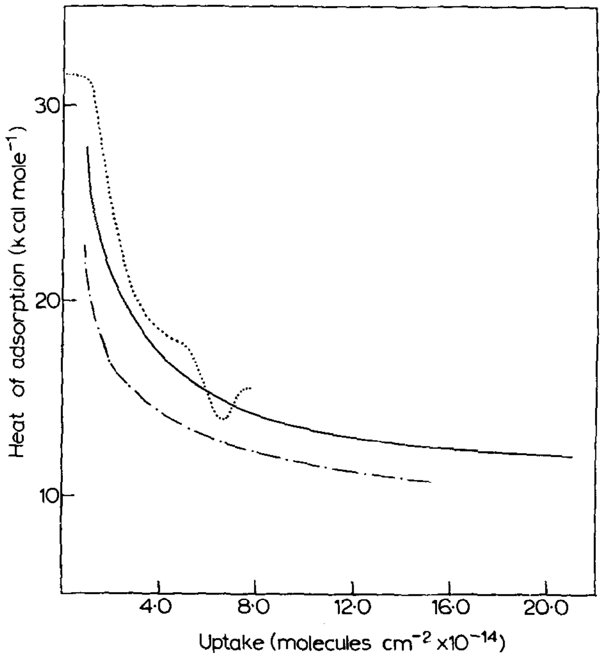

FIG. 3. Heat of adsorption of water on α-Al_2O_3: —, present work; ··, Ref. (*19*); – · –, Ref. (*20*).

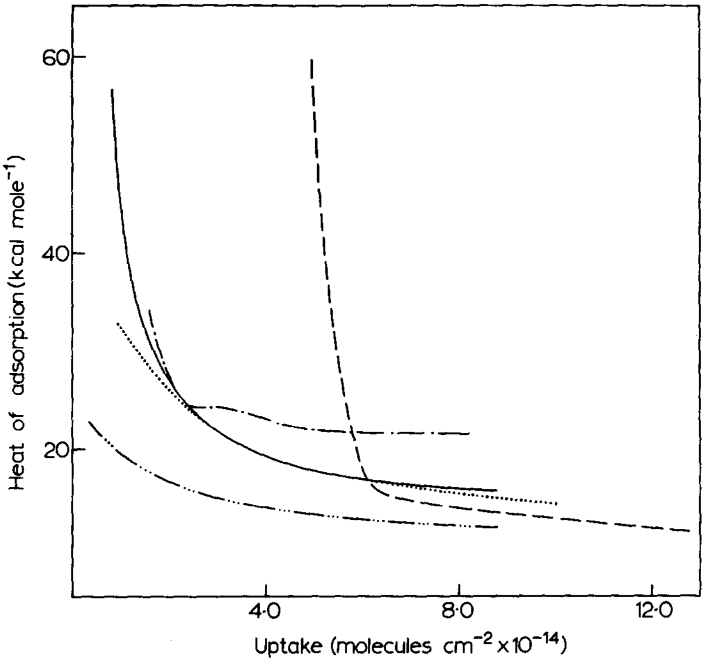

FIG. 4. Heat of adsorption of water on γ-Al_2O_3: —, present work; ···, calculated from reference *(2)*; –··· –··· –, Ref. *(20)*; – – –, Ref. *(21)*; –· –· –, Ref. *(22)*.

are to be strictly comparable with the present results. Figure 1 suggests that Yao's α-Al_2O_3 possessed $<4\%$ of a monolayer of OH groups after outgassing at 900°C, whereas Venable *et al.* worked with samples possessing water in excess of a full monolayer of OH groups after outgassing at 160°C. Although such a correction makes little difference to Yao's data, the heats of adsorption of Venable *et al.* become considerably higher than those of Yao and of ourselves at corresponding uptakes. We conclude that the α-Al_2O_3 used by Venable *et al.* was more extensively dehydrated than Fig. 1 would suggest, and that rehydration was not restricted to molecular adsorption on a fully hydroxylated surface.

More data are available for heats of adsorption of water on γ-Al_2O_3 than on α-Al_2O_3, although no determinations by vapor-adsorption calorimetry are known to have been made. MacIver, Tobin, and Barth *(2)* determined heats of immersion as a function of outgassing temperature, and we have calculated heats of adsorption from their data, assuming complete surface dehydration after outgassing at 900°C. This assumption permits an independent check of our results, and is justifiable both in terms of Fig. 2 and experimental observations of MacIver *et al.* The results are in good agreement with our own, and are identical over the coverage range 2.4×10^{14}–6.8×10^{14} molecules cm^{-2}. As was found for α-Al_2O_3, the values obtained by Venable *et al.* *(20)* are lower than those presently obtained at corresponding uptakes, and correction for the degree of surface hydration after outgassing at 160°C yields values higher than ours.

Two sets of values of isosteric heats of adsorption on γ-Al_2O_3 as a function of uptake are available. Cornelius *et al.* *(21)* determined isotherms gravimetrically at temperatures between 33 and 536°C, whereas Spannheimer and Knözinger *(22)* determined isotherms by a chromatographic technique at temperatures between 76 and 453°C. Figure 4 shows that the agreement between the two investigations is poor, and both sets of values vary from those presently obtained by considerably more than the difference expected between differential and isosteric heats of adsorption. One source of these discrepancies may be the different criteria of a fully dehydrated surface used in the published work, and for which corrections using Fig. 2 are inapplicable. Cornelius *et al.* (*21*) accepted that γ-Al_2O_3 calcined in air at 1250°C possessed a surface free from water, whereas Spannheimer and Knözinger (*22*) dehydrated their γ-Al_2O_3 in a flow of helium at 800°C. To determine heats over an appreciable coverage range, both sets of authors found it necessary to measure isotherms over a wide temperature range. The heats of adsorption so obtained do not relate to a single temperature, so that variations with temperature, as well as with coverage, might be contained within the results. This effect is unlikely, however, to account for the existing discrepancies.

Morimoto *et al.* (*13*) obtained heats of immersion of both α- and γ-Al_2O_3 in water which passed through a maximum value as the outgassing temperature was raised, indicating that the aluminas annealed and prevented rehydration to the same final state. Heats of adsorption calculated from their data are anomalous in that they increase with coverage. We have reported a similar increase in the heat of adsorption with coverage (*8*), which arose from a lack of values of $q_{i(SL)}$ for samples outgassed above 400°C and a subsequent undue dependence on the value of $q_{i(SL)}$ at that temperature. The present work corrects this error, and supports the view that alumina surfaces rehydrate to the same final state when immersed in water at 25°C.

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