JOURNAL OF CATALYSIS 2, 1–7 (1963)

Study of the Nature of Surfaces with Polar Molecules II. The Adsorption of Water on Aluminas

J. H. DE BOER, J. M. H. FORTUIN,[*] B. C. LIPPENS,[†] AND W. H. MEIJS[‡]

From the Department of Chemical Technology, Technological University, Delft, The Netherlands

Received January 8, 1962

Aluminas adsorb a large amount of water from a humid atmosphere. Only part of the water thus adsorbed can be expelled by drying at 120°C. The remaining water content (referred to as "chemisorbed" water) is proportional to the specific surface area of the sample and amounts to 24.8 mg $H_2O/100\ m^2$. This amount points to a binding of one water molecule to two oxygen atoms in the surface.

The surface covered with "chemisorbed" water adsorbs another quantity of water by physisorption. From the adsorption isotherms the monolayer capacity V_m can be calculated with the BET equation; V_m is also approximately proportional to the specific surface area of the sample and amounts to about 33 mg $H_2O/100\ m^2$.

At relative water vapor pressures above about 0.4 capillary condensation in the pores of the aluminas of these experiments occurs.

Lauric acid can be adsorbed on the water layer adsorbed on the alumina surface. Up to a certain "critical" water content the lauric acid adsorption decreases with increasing amount of adsorbed water. Above this "critical" value the lauric acid adsorption remains constant, water being displaced from the surface by lauric acid. The "critical" water content is proportional to the specific surface area and amounts to about 50 mg $H_2O/100\ m^2$. So for each "chemisorbed" water molecule another water molecule can be bound by a strong physisorption.

From the relation between lauric acid adsorption and specific surface area of rehydrated samples it appears that water molecules "chemisorbed" under the conditions studied probably do not react with oxygen atoms in the surface forming OH groups but rather are bound to the surface oxygen ions by very strong hydrogen bonds.

INTRODUCTION

Aluminas are capable of adsorbing a considerable quantity of water from a humid atmosphere at room temperature. Various authors (*1–10*) who studied these phenomena, concluded that part of the water adsorbed is weakly bound to the alumina and can be expelled by evacuation or heating at temperatures of 100–120°C. The rest of the adsorbed water is often supposed to have reacted with the oxygen atoms in the surface forming OH groups. Some authors (*3, 6*) even assumed that part of this residual water is taken up in the lattice of the aluminas. Peri and Hannan (*10*) concluded from infrared studies that, on a γ-alumina surface, water is adsorbed at room temperature as water molecules, whereas only by heating at temperatures above 300°C are OH groups formed.

---

[*] Present address: Central Laboratory Staatsmijnen in Limburg, P.O. Box 18, Geleen (The Netherlands).

[†] Present address: Laboratory for Inorganic Chemistry, Technological University, Eindhoven (The Netherlands).

[‡] Chemical Laboratory of the National Defence Research Council T.N.O., Rijswijk, Z. H. (The Netherlands).

In the present study this very strongly bound water will be defined as "chemisorbed" water, though it is not certain that a real chemisorption has occurred. The more loosely bound water which can be expelled by heating at 120°C, will be defined as "physisorbed" water.

STARTING MATERIALS

P.S.H.: commercial gibbsite type H manufactured by Peter Spence & Co.

H.W.: commercial aluminum oxide for chromatographic purposes obtained from Hopkins and William Ltd., consisting of a mixture of χ- and γ-alumina and some boehmite.

M.B.: commercial aluminum oxide standardized according to Brockmann obtained from Merck, Darmstadt, consisting of a mixture of χ-, γ- and κ-alumina.

H.S.: gelatinous boehmite prepared from aluminum tri-isopropoxide by hydrolysis with steam at 120°C.

The aluminas used were prepared from the starting materials by heating in air during 6 hr; they are indicated by adding a suffix giving the heating temperature in °C. Hence an alumina obtained by heating the starting material H.S. at 520°C is indicated as H.S. 520, etc.

PROCEDURES

a. Total amount of adsorbed water. The adsorption of water was performed by placing some grams of the aluminas in evacuated desiccators having a constant water vapor pressure (effected by means of saturated salt solutions or of sulfuric acid solutions of known concentration). The temperature was kept constant at 20°C; equilibrium was usually obtained within a week. The total water content was determined by the increase of weight of the sample and checked by the loss on ignition at 1200°C.

b. "Chemisorbed" water. The heated aluminas were rehydrated by placing them in water vapor of a relative pressure of 0.12. After drying at 120°C during 24 hr in air the amount of chemisorbed water was determined by the loss on ignition at 1200°C. A relative pressure of 0.12 was chosen to obtain a fast adsorption of water; the same results for the amount of chemisorbed water could be obtained by rehydrating at relative pressures at 10^{-2} or lower, but it took a long time then to reach equilibrium. With the rather arbitrarily chosen temperature of 120°C reproducible values were obtained; a slight deviation of this temperature did not noticeably influence the results.

c. Specific surface area and lauric acid adsorption. These quantities were determined as described in Part I of this series *(11)*.

CHEMISORPTION OF WATER ON H.S. ALUMINAS

Table 1 gives the results of the determination of chemisorbed water on H.S. aluminas. The meaning of the symbols is as follows:

W_t, the water content of the alumina after heating at t°C;

W_R, the chemisorbed water, determined as described above;

S_t and S_R, the specific surface area of the alumina after heating at t°C, and after rehydrating in water vapor and drying at 120°C, respectively.

It appears from this table that the chemisorption of water causes the specific BET surface area, as measured by low-temperature adsorption of nitrogen, to decrease somewhat. In order to correlate the water adsorption with the specific surface area we have to estimate the specific surface area at zero water content $S_{w=0}$ by extrapolation, assuming (a) that the total amount of residual water after heating (W_t) is present in the surface layer and (b) that a linear relationship between the specific surface area and the amount of chemisorbed water exists. In the last two columns of Table 1, $S_{w=0}$ and the amount of chemisorbed water per unit of surface area $W_R/S_{w=0}$ are given. A mean value for $W_R/S_{w=0}$ of 24.8 ± 0.5 mg H_2O/100 m^2 can be calculated.

TABLE 1

CHEMISORPTION OF WATER ON H.S. ALUMINAS[a]

Sample	W_t[b]	S_t[c]	W_R[b]	S_R[c]	$S_{W=0}$[c]	$W_R/S_{W=0}$[d]
H.S. 520	25.5	285	77.8	252	301	25.8
H.S. 600	13.4	249	64.0	233	253	25.3
H.S. 620	13	246	59.3	224	252	23.5
H.S. 750	6	191	47.4	183	192	24.7
H.S. 800	5	182	44.5	175	183	24.3
H.S. 890	5	140	34.6	139	140	24.7
H.S. 900	3	141	33.4	138	141	23.7

[a] See ref. (*12*).

[b] mg $H_2O/g\ Al_2O_3$.

[c] $m^2/g\ Al_2O_3$.

[d] mg $H_2O/100\ m^2$.

PHYSISORPTION OF WATER ON H.S. ALUMINAS

The total amount of adsorbed water W_x depends on the relative water vapor pressure x used for the conditioning of the alumina. Table 2 gives the results for four different values of x. Part of W_x is chemisorbed water W_R. Subtracting W_R from W_x we obtain the amount of physisorbed water W_p.

Taking the surface area after rehydration (S_R) and drying at 120°C as reference area we obtain the degree of coverage of the physisorbed water as W_p/S_R. The monolayer capacity of this physisorbed water V_m (mg H_2O per gram Al_2O) s calculated with the aid of the BET equation and with it V_m/S_R (mg H_2O per 100 m^2 surface area, S_R). A mean value of 33 mg $H_2O/100\ m^2$ is found. For the higher relative pressures about the same values of W_p/S_R are found for the different samples; at lower pressures where the degree of coverage is only 50 to 70% of the monolayer capacity, more variation in the results occur. We may consequently conclude that the surface covering of the physisorbed water is only little dependent on the heating temperature of the alumina except for coverings appreciably lower than the monolayer capacity.

TABLE 2

PHYSISORPTION OF WATER ON H.S. ALUMINAS

		$x = 0.075$			$x = 0.12$			$x = 0.23$			$x = 0.32$				
Sample	S_R[a]	W_x[b]	W_p[b]	W_p/S_R[c]	W_x[b]	W_p[b]	W_p/S_R[e]	W_x[b]	W_p[b]	W_p/S_R[c]	W_x[b]	W_p[b]	W_p/S_R[c]	V_m[b]	V_m/S_R[e]
H.S. 520	252	117	39	15.7	128	50	19.8	—	—	—	180	102	40.6	87	34.4
H.S. 620	224	98	39	17.4	112	53	23.6	135	76	33.9	152	93	41.6	75	33.5
H.S. 750	183	82	35	19.0	88	41	22.4	109	62	33.9	120	73	40.0	58	31.7
H.S. 890	139	61	26	18.7	67	32	23.0	81	46	33.1	91	56	40.4	44	31.7

[a] $m^2/g\ Al_2O_3$.

[b] mg $H_2O/g\ Al_2O_3$.

[c] mg $H_2O/100\ m^2$.

At relative pressures above about 0.4 the total amount of water adsorbed varies greatly for the different samples (Fig. 1). This has to be attributed to capillary condensation in excess over the multimolecular adsorption in pores of different shapes and dimensions.

LAURIC ACID ADSORPTION ON HYDRATED SAMPLES

Figure 2 gives the results of lauric acid adsorption (LA_{ads}) on some alumina samples previously conditioned in water vapor (*13*). It appears that the lauric acid adsorption decreases with increasing water

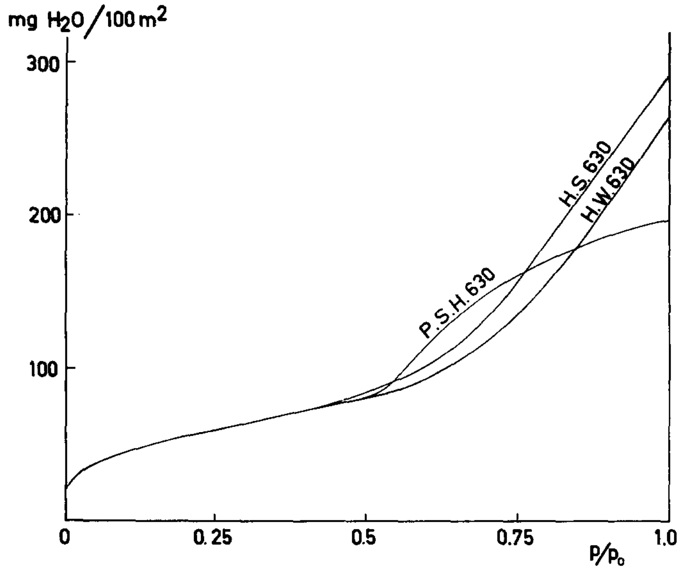


FIG. 1. Adsorption isotherms of water on some aluminas.

content of the samples up to a certain "critical" value and then, abruptly, becomes constant. This "critical" water content W_c is apparently proportional to the specific surface area of the alumina at zero water content ($S_{w=0}$, Table 3) giving a mean value of 50 mg H_2O/100 m^2.

The decrease of the lauric acid adsorption (the first part of the curves in Fig. 2) is attended by a change in the shape of the isotherm (Fig. 3): The lauric acid is less strongly adsorbed on the hydrated aluminas than on the waterfree aluminas. If the water content of the samples is above the

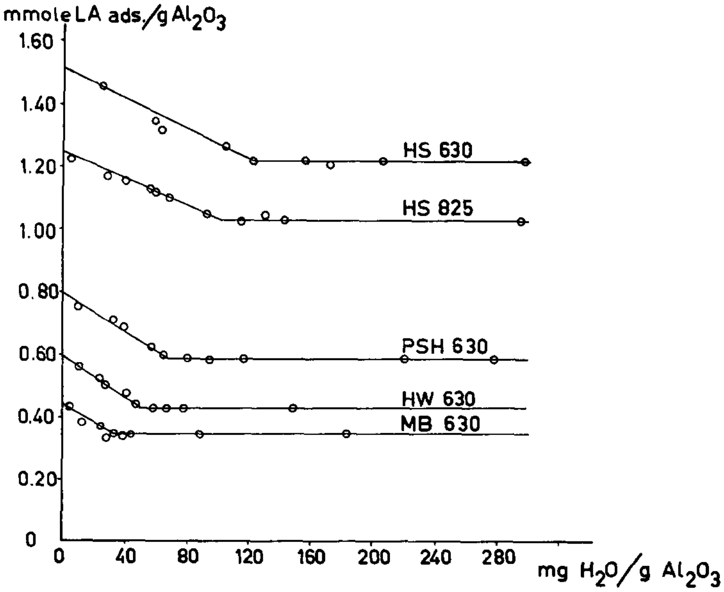


FIG. 2. Lauric acid adsorption on rehydrated aluminas as a function of total water content.

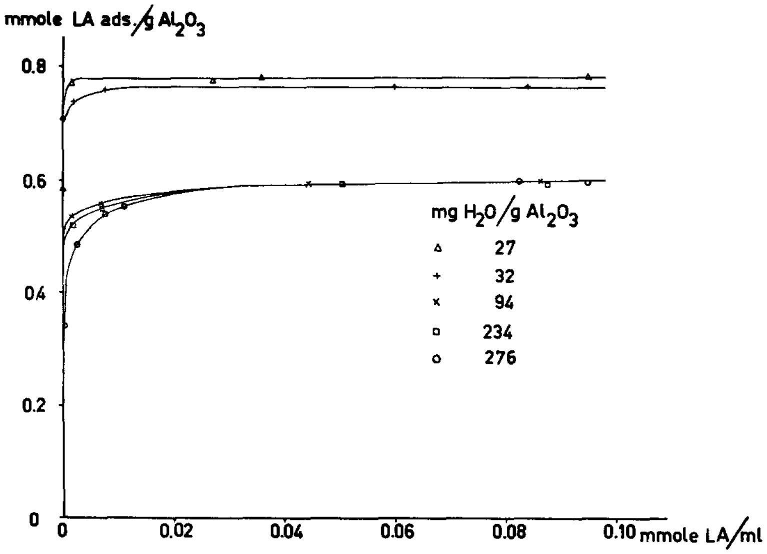


FIG. 3. Influence of adsorbed water on the shape of lauric acid adsorption isotherms.

critical value (the horizontal part of the curves in Fig. 2) the separation of drops of liquid water is sometimes observed after lauric acid adsorption, showing that some of the water adsorbed is displaced by the lauric acid.

TABLE 3
CRITICAL WATER CONTENT OF ALUMINAS FOR LAURIC ACID ADSORPTION

Sample	W_c[a]	S_{w-0}[b]	W_c/S_{w-0}[c]
H.S. 630	119	244	49
H.S. 825	102	201	51
P.S.H. 630	69	132	52
H.W. 630	50	96	52
M.B. 630	34	72	48

[a] mg H_2O/g Al_2O_3.
[b] m^2/g Al_2O_3.
[c] mg H_2O/100 m^2.

If we plot the lauric acid adsorption as a function of the relative water vapor pressure at which the aluminas were conditioned (Fig. 4) it appears that about half of the "critical" water content is adsorbed at very low relative pressures (below 10^{-3}) and has to be considered "chemisorbed" water. The other half of the critical water content has to be considered strongly bound physisorbed water.

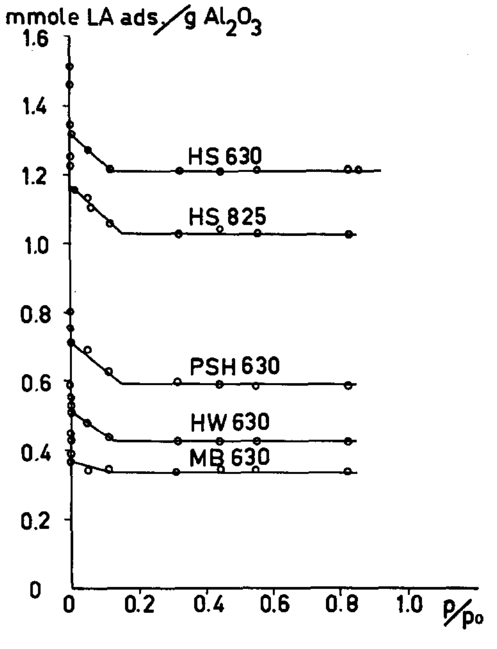


FIG. 4. Lauric acid adsorption on rehydrated aluminas as a function of the relative water vapor pressure during rehydration.

THE SURFACE COVERING OF ALUMINAS BY WATER

Chemisorption of water proceeds to the extent of 24.8 mg H_2O/100 m^2. As none of the samples investigated showed an appreciable deviation from this value, we may conclude that all the water is present in the surface layer, only negligible amounts being in the lattice.

One molecule of this water occupies a surface area of $(10^{22} \times 18)/24.8 \times 6 \times 10^{20}) = 12.1$ Å². In part I of this series we made clear that the most probable lattice plane in the surface will be the 111 plane of the spinel lattice, in which each oxygen atom takes in a surface area of 6.74 Å². Consequently each water molecule chemisorbed is bound to approximately two oxygen atoms in the surface.

In Part I we found that the specific lauric acid adsorption, *f*, amounts to 0.617 mmole of lauric acid per 100 m² for the aluminum oxide surface and to 0.43 mmole/100 m² for the aluminum hydroxide surface.

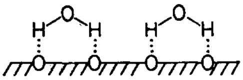
For some samples we compared the BET surface area with lauric acid adsorption before and after the chemisorption of water (Table 4).

TABLE 4
INFLUENCE OF REHYDRATION ON LAURIC ACID ADSORPTION

Sample	Before rehydration			After rehydration and drying at 120°C		
	S_t[a]	LA_t[b]	f_t[c]	S_R[a]	LA_R[b]	f_R[c]
H.S. 800	182	1.117	0.613	175	1.046	0.598
H.S. 900	141	0.886	0.628	138	0.826	0.599

[a] m²/g Al_2O_3.
[b] mmole/g Al_2O_3.
[c] mmole/100 m².

It appears that the presence of chemisorbed water on the surface hardly influences the specific lauric acid adsorption. The great difference in *f* for a hydroxide surface and for a surface covered with chemisorbed water molecules forces us to suppose that under the conditions studied, no OH groups are formed by this type of chemisorption of water, but that the oxygen atoms of the water molecules form the outside of the adsorbed layer. Such a water molecule then will be bound to two surface oxygen ions by very strong hydrogen bonds as:



This agrees with the results of the infrared studies by Peri and Hannan (7) that OH groups are only formed at higher temperatures.

In addition to the chemisorbed water mentioned above water can be physisorbed. From the critical water content it follows that about 25 mg H_2O/100 m² is strongly physisorbed. Apparently this type of adsorption follows the periodicity of the chemisorbed water: one molecule of water being strongly physisorbed per molecule of chemisorbed water. Still more water can be bound by physisorption, forming a multimolecular adsorption layer and possibly a capillary condensate. Taking it together with the strongly physisorbed water it shows a monolayer capacity of 33 mg H_2O/100 m².

Consequently we find the following types of water sorption on the aluminas:

a. Water, which cannot be expelled by heating at 120°C and which is bound by very strong hydrogen bonds to the surface oxygen ions; it is often referred to as "chemisorbed" water. A complete monolayer of this type contains about 25 mg H_2O/100 m².

b. Water, which cannot be displaced from the surface layer by lauric acid, but is expelled by heating at 120°C. One molecule of this strongly physisorbed water is bound per water molecule of type *a* "chemisorbed" on the alumina surface.

c. The rest of the water adsorbed on the surface gives, together with water of type *b*., an apparently normal type of multimolecular adsorption with a V_m value of 33 mg H_2O/100 m². If this figure has a physical meaning it points to a rearrangement of the strongly physisorbed water of type *b* when, at higher relative pressures, more water is physisorbed. The monolayer capacity of 33 mg H_2O/100 m² S_R means a surface area of 9.1 Å² per water molecule in the statistical monolayer.

d. In pores of suitable shape and dimensions water can be taken up in excess over the multimolecular adsorption by capillary condensation.

REFERENCES

1. IMELIK, B., *Compt. rend.* **233**, 1284 (1951).
2. PAPÉE, D., *Compt. rend.* **234**, 234, 952, 2536 (1952).
3. DE BOER, J. H., AND HOUBEN, G. M. M., *Proc. Intern. Symp. Reactivity of Solids, Gothenburg, 1952.*
4. KIPLING, J. J., AND PEAKALL, D. B., *Research (London)* **8**, 31 (1955).
5. KIPLING, J. J., AND PEAKALL, D. B., *in* "Chemisorption" (W. E. Garner, ed.), p. 59. Butterworth's, London, 1957.
6. GLEMSER, O., AND RIECK, G., *Z. Angew. Chem.* **67**, 652 (1955); **68**, 182 (1956).
7. DE BOER, J. H., *Proc. 2nd Intern. Congress Surface Activity,* p. 93. Butterworth's, London, 1957.
8. DE BOER, J. H., *Z. Angew. Chem.* **70**, 383 (1958).
9. DE BOER, J. H., *Svensk Kemisk Tidskrift* **72**, 9 (1960).
10. PERI, J. B., AND HANNAN, R. B., *J. Phys. Chem.* **64**, 1526 (1960).
11. DE BOER, J. H., HOUBEN, G. M. M., LIPPENS, B. C., MEIJS, W. H., AND WALRAVE, W., *J. Catalysis* **1**, 1 (1962).
12. MEIJS, W. H., Thesis, Delft, 1961, p. 60.
13. FORTUIN, J. M. H., Thesis, Delft, 1959, Chapter VI.