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Adsorption of Bases on γ-Al_2O_3

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The irreversible adsorption of several bases on γ-Al_2O_3 has been measured. The γ-Al_2O_3 was dried at 800°C, rewetted, and before measurement pretreated at temperatures between 200 and 800°C. The adsorption of ammonia was measured between 25 and 400°C with a microbalance. Infrared spectra of NH_3 adsorbed on alumina at 25 and 150°C were also recorded.

The adsorption of organic bases was measured by a gas-chromatographic technique. From the results it is concluded that: (a) the amount adsorbed depends on the cross-sectional area of the molecule and not on its basic strength; (b) γ-Al_2O_3 preheated above 400°C is a pure Lewis acid.

INTRODUCTION

Adsorption of bases, sometimes studied in connection with spectroscopic methods, is often used for the determination of acid properties of the γ-Al_2O_3 surface (*1–5*). Most of these investigations are carried out with one type of base, for example ammonia (*6*), pyridine (*7*), or aldehyde (*8*). Only in a few cases has a comparison been made between the adsorption characteristics of different bases (*9*). From these studies it is concluded that different types of acid centers occur on γ-Al_2O_3, some with a Lewis acid and others with a Brönsted acid nature. In addition, it is assumed that all types have a certain acid strength distribution.

The number and strength of the acid sites are measured in two ways. In the first place, changes in infrared spectra of adsorbed molecules are attributed to differences in strength of acid sites or in the number of sites of different acidity. In the second place, the amount of strongly bonded base is measured as a function of temperature. This method gives, in fact, an exact figure for the number of sites, but it yields only an arbitrary measure for the acidity.

The acid strength distribution can, however, be derived in principle from a study of the adsorption of bases with different basic strengths. One may expect that under identical circumstances the amount of adsorbed base decreases with decreasing basic strength. In this paper we report studies of the adsorption of nine different bases on γ-Al_2O_3. We have also studied the adsorption of water, benzene, and thiophene. It is well known that the acid properties of γ-Al_2O_3 change as a function of water content and pretreatment. Therefore alumina samples pretreated at different temperatures have been used.

METHODS

Adsorbent

The alumina used was γ-Al_2O_3 Type C, a commercial alumina obtained from Degussa, Frankfurt. The surface area was 114 m^2/g. The alumina was pressed into self-supporting disks of about 100 mg and heated to 800°C, after which the disks were contacted with humid air for at least 24 hr. Finally the samples were preheated *in situ* at temperatures between 100 and 800°C. An X-ray diffractogram revealed that after this pretreatment the γ-Al_2O_3 contained some δ-Al_2O_3 as well.

Adsorbates

Reagent grade chemicals were used without further purification. Except for allylamine, no indication was found for the presence of large amounts ($>1\%$) of impurities.

Apparatus

The adsorption of ammonia and water was determined gravimetrically in a Cahn electrobalance. The pyrex housing was evacuated conventionally by a mercury diffusion pump and a rotary pump. The samples were placed in a quartz "hangdown tube," which could be heated to 900°C by means of an oven.

Infrared spectra were recorded on a Cary White 90 double beam spectrometer. Use of a reference cell, identical to the sample cell, allowed spectra to be recorded down to 1000 cm^{-1}. The cell permitted *in situ* treatment of the alumina disks. The spectrometer was connected to a computer, which enabled us to compensate for differences in disk thickness.

The adsorption of the amines, benzene, and thiophene was studied by means of a pulse-flow technique. The apparatus can be compared with a conventional gas chromatograph in which the column is replaced by a quartz U-tube filled with about 500 mg of alumina. After passing the U-tube, the carrier gas is led through a cooling trap filled with liquid nitrogen. That part of the pulse which does not adsorb on the alumina sample condenses completely in this trap. When the liquid nitrogen is replaced by water, the condensed product reevaporates and is led to a thermal conductivity detector.

Procedure

The adsorption experiments with ammonia were carried out as follows. In the evacuated balance chamber an alumina disk was preheated to a temperature between 300 and 800°C. NH_3 was admitted at room temperature. After a few hours the establishment of equilibrium was checked by evacuating the system and readmitting ammonia. This procedure had to be repeated several times before the catalyst was saturated with ammonia. The temperature was then raised to 400–500°C in steps of 75–100°C.

The adsorption of water was investigated in the same way.

Since the adsorption of ammonia at room temperature appeared to be a very slow process, the amount of irreversibly bonded NH_3 was also measured by admitting the gas at 400°C and subsequently evacuating. The sample was then cooled stepwise to room temperature, ammonia being admitted after each temperature decrease of 75–100°C. After a few hours, the reversibly bonded ammonia was evacuated.

The alumina disks used for the infrared investigation of NH_3 adsorption were preheated *in vacuo* at 330°C for several hours. Ammonia was admitted at 25 or 150°C. Spectra were recorded after the disk in the sample cell had been evacuated at room temperature.

The adsorption of the other adsorbates was investigated by sending five 10 μl pulses over 500 mg γ-Al_2O_3 preheated at a temperature between 300 and 800°C. Ten minutes after each pulse, the nonadsorbed quantity was measured. Physically bonded molecules were desorbed at room temperature by passing helium for 17 hr. This amount was also measured. Finally the sample was heated at 100°C and again the desorbed quantity was measured.

RESULTS AND DISCUSSION

Figure 1 shows the coverage of alumina with irreversibly bonded water as a function of temperature. The molecular area of water was taken as 12.1 Å^2 as is given by De Boer *et al.* (*10*) for chemisorbed water on alumina. The absence of a band at 1630 cm^{-1} in the infrared spectra indicates that all the chemisorbed water is present as hydroxyl groups. It appears that at room temperature a quantity of water equal to the weight of about one layer chemisorbs on the alumina surface. At 500°C the surface is covered less than 10% with chemisorbed water (hydroxyl groups). The total quantity of water lost by heating the

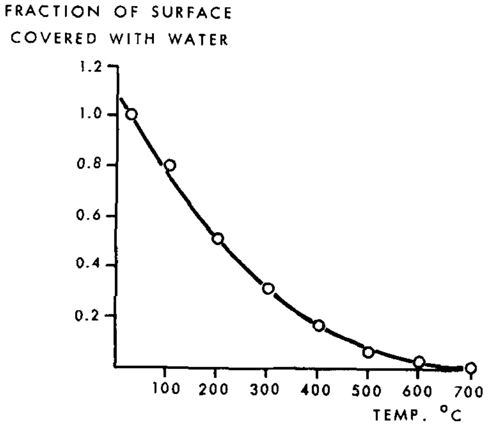

FIG. 1. Surface coverage of alumina with irreversibly bonded water as a function of temperature.

sample from 25 to 800°C amounted to 28 mg/g Al_2O_3.

Figure 2 shows the amount of irreversibly bonded ammonia at different temperatures as a function of preheating temperature. These results correspond with those of MacIver *et al.* (*6*), although the quantity of ammonia which adsorbs on alumina preheated at 600°C differs from that given by MacIver *et al.* The agreement in the total adsorbed quantities is remarkable because MacIver's starting material was aluminium hydroxide while in these investigations rewetted γ-Al_2O_3, already preheated at 800°C, was used. This agreement indicates that the adsorption centers on both types of surface are identical.

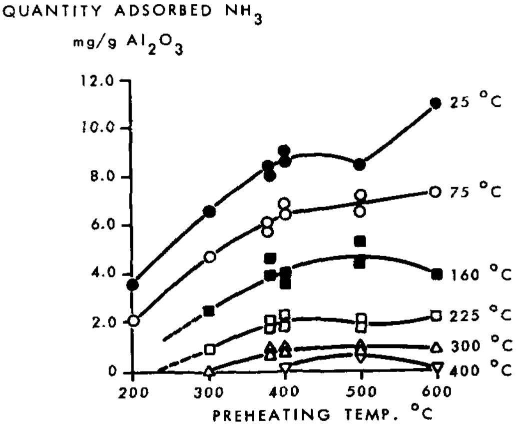

FIG. 2. NH_3 adsorption on γ-Al_2O_3 at different temperatures.

When ammonia is adsorbed at room temperature on an alumina disk preheated at 330°C *in vacuo*, the infrared spectrum shown in Fig. 3 is obtained. The bands at 1610 and 1230 cm^{-1} correspond to the δ_d and δ_s of ammonia coordinatively bonded to surface Al^{3+}-ions (*2, 12, 13*). A small part of ammonia is adsorbed as NH_4^+ bonded via hydrogen bridges. In the spectrum this is reflected by the adsorptions at 1450 and 1470 cm^{-1} (δ_a) which are usually found when ammonia is adsorbed on alumina predried at relatively low temperatures (*12*). The small band at 1700 cm^{-1} may be the corresponding symmetrical deformation vibration (δ_s).

No bands are observed at 1410, 1510, or 1560 cm^{-1} as should have resulted from formation of NH_4^+ on Brönsted sites, NH_2^-, or another form of chemisorbed NH_3, respectively (*2*). This is in agreement with Peri's study of ammonia adsorption on alumina predried at 400°C and with Dunken and Fink, who also did not find evidence for dissociative adsorption under these conditions (*12*).

Figure 3 also shows the infrared spectrum of NH_3 adsorbed at 150°C. As compared to the room temperature adsorption the most remarkable difference is the appearance of a band at 1560 cm^{-1}. Dunken and Fink attributed this absorption to a dissociative chemisorption (NH_2^-). However, they only observed this 1560 cm^{-1} band when ammonia was adsorbed on alumina predried at a temperature above 500°C. According to Peri (*2*) this band has to be ascribed to another nondissociative form of chemisorbed ammonia. Besides this form of adsorption the coordinatively bonded NH_3, already found at room temperature, occurs (absorption at 1610 and 1230 cm^{-1}).

Because of the relatively low pretreatment temperature (330°C) the N–H and O–H stretchings in the region 3800–3000 cm^{-1} are not very well resolved. Anyhow, all the spectra show after NH_3 adsorption a decrease of absorbancy at 3700 cm^{-1}, indicating that the number of isolated hydroxyl groups is decreased. This phenomenon is always observed upon ammonia adsorption on alumina (*2, 12*).

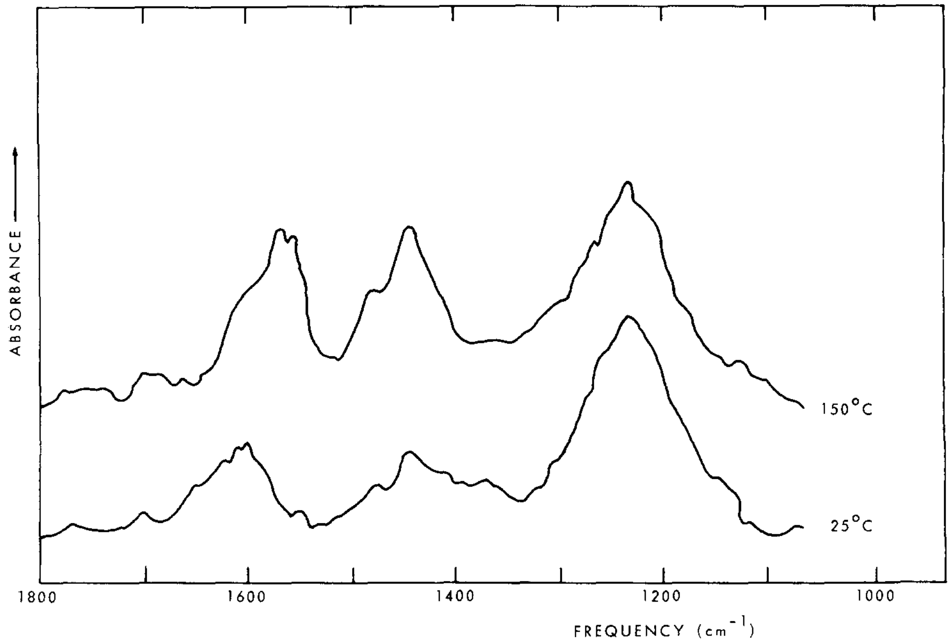

FIG. 3. Infrared spectrum of NH_3 adsorbed on alumina: adsorbed at 25°C and evacuated (10^{-4} Torr); adsorbed at 150°C, cooled down to 25°C and evacuated (10^{-4} Torr).

Figure 4 shows the results of dynamical adsorption experiments with γ-Al_2O_3 preheated at 400°C. The amount adsorbed has been plotted as a function of the reciprocal value of the molecular area of the adsorbate ($1/\sigma$). Values for σ were obtained from the work of McClellan and Harnsberger (*14*). In fact $1/\sigma$ is a measure of the maximum quantity that can be adsorbed in a monolayer. It appears that the degree of coverage is equal for all adsorbates and is less than one (~0.4 at room temperature). This means that only a definite fraction of the alumina surface is capable of adsorbing bases. Moreover, the acid sites must be closely spaced on this particular fraction of the surface. The same conclusion was drawn by Hirschler (*9*) from titration with amines of varying steric demand.

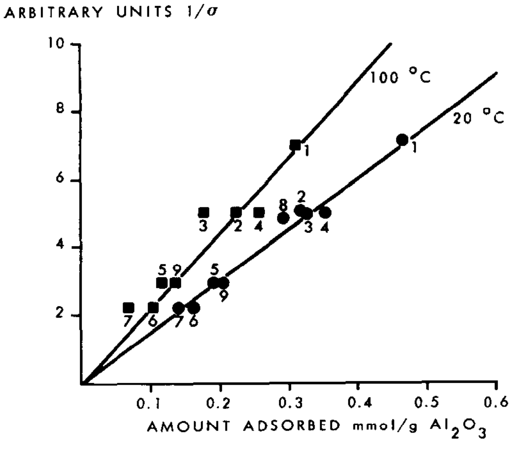

FIG. 4. Correlation between the reciprocal molecular area ($1/\sigma$) and the quantity of adsorbed base. 1. NH_3; 2. allylamine; 3. butylamine; 4. propylamine; 5. diethylamine; 6. triethylamine; 7. diisopropylamine; 8. acetone; 9. diethyl ether.

The results for benzene and thiophene have not been included because these compounds are not bonded irreversibly. Differences in basic strength (see Table 1) appear to have no measurable influence on the degree of coverage. At higher temperatures, however, the adsorbed quantities are less. This indicates the existence of an acid strength distribution among the adsorption centers. At first sight these two conclusions are inconsistent; on the one hand the acid strength appears to have influence on the adsorbed quantity, whereas, on the other hand, the base strength seems to have no

TABLE 1
pK VALUE AT 25°C OF CONJUGATE ACIDS USED IN DYNAMIC ADSORPTION EXPERIMENTS[a]

Bases	pK	Bases	pK
ammonia	9.3	triethylamine	10.9
allylamine	9.7	diisopropylamine	10.9
n-propylamine	10.5	acetone	−7.2
n-butylamine	10.6	diethyl ether	−3.6
diethylamine	10.6		

[a] See ref 15.

influence at all. This contradiction can be explained when one considers the energies involved in the adsorption process. Thus it has been found that the heat of adsorption of NH_3 on Al_2O_3 at 300°C decreases from 45 to 15 kcal/mol when the surface coverage increases from 0 to 25% (*4*). From the p*K* values given in Table 1 it appears that the difference in free energy between the amines and ammonia in the case of proton addition is at most 2 kcal/mol. Unfortunately exact energy figures in the case of electron pair donation–acceptance are not known. However, it seems reasonable to state that the differences in acid–base formation of the bases used are less than 5 kcal/mol. These relatively small differences have only a small influence on the adsorption characteristics, mainly because there exists a broad distribution in acid strength (*4*). In fact this influence is so small that it is obscured by the experimental error.

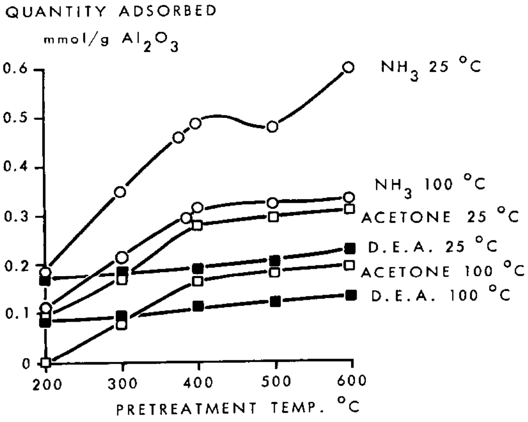

FIG. 5. Quantity of adsorbed base at 25 and 100°C as a function of pretreatment temperature of the alumina.

From the fact that the relation given in Fig. 4 holds for ammonia, amines, acetone, and ether, and not for benzene and thiophene, it may be concluded that the adsorption centers are electron pair acceptors, i.e., Lewis acids.

Aluminas preheated at temperatures higher than 400°C show the same behavior, whereas samples preheated at lower temperatures behave differently. In the last case the adsorbed quantities are no longer related to their molecular areas; besides, acetone is no longer irreversibly bonded. This is confirmed by the results given in Fig. 5. In this figure the quantities of adsorbed ammonia, amine, and acetone are compared at different preheating temperatures.

Alumina preheated at 400°C has a 15% higher coverage of irreversibly adsorbed acetone at 100°C than alumina preheated at 300°C. In this temperature range the surface coverage of the alumina with water decreases about 15%. This suggests that stronger Lewis acids are formed during dehydration between 300 and 400°C.

The mechanism of the adsorption of ammonia, diethylamine, and acetone on alumina, predried below 400°C, obviously differs from that occurring on samples pretreated at higher temperatures (Fig. 5). At a surface coverage over 20% of a chemisorbed monolayer of water it is very probable that hydroxyl groups (Brönsted sites) are involved in the adsorption mechanism.

The behavior of diethylamine is quite remarkable; the adsorption seems unaffected by the pretreatment temperature. We have noticed a similar phenomenon in studying the adsorption of benzaldehyde on rewetted γ-alumina by infrared spectroscopy. The spectra showed that benzaldehyde was still adsorbed on Lewis sites, as was found for the adsorption on alumina predried at 400°C. This indicates that hydroxyl groups must have been driven away from surface aluminium ions. A mechanism similar to this might apply for diethylamine.

TABLE 2
DYNAMIC ADSORPTION EXPERIMENTS CARRIED OUT WITH DIETHYLAMINE AT DIFFERENT TEMPERATURES

Temperature of injection (°C)	Quantity still adsorbed (mmol/g Al_2O_3) at			
	−25°C	20°C	50°C	100°C
−25	0.25	0.08	—	0.00
−25	0.25	0.09	—	0.00
20	—	0.19	—	0.11
20	—	0.19	—	0.12
50	—	—	0.16	0.11

The adsorption of ammonia on alumina at room temperature is a very slow process. It takes at least 24 hr before equilibrium is established. This could be ascribed to: 1. physically adsorbed molecules blocking the sites for chemisorption *(11)*; 2. the existence of an activation energy for chemisorption; 3. diffusion.

By means of dynamic adsorption experiments carried out at different temperatures, it is possible to discern between the three possibilities. In these experiments the alumina was kept at −25°C, +20°C, and +50°C during the injection of amine. For the injections at 20 and 50°C the quantities still adsorbed at 100°C are equal, but when the injections were done at −25°C the adsorbed quantity at 100°C is zero. Similar phenomena are observed for the adsorbed quantity at room temperature (see Table 2). These experiments point to the conclusion that there is an activation energy for adsorption. The infrared spectra preclude the possibility that for ammonia the activation energy is caused by a dissociative adsorption. From the results given in Table 2 it may also be concluded that the activation energy for adsorption increases with increasing strength of the surface bond. This is confirmed by ammonia adsorption experiments in which the ammonia was admitted at 400°C, followed by evacuting, cooling, and again admitting of ammonia at a lower temperature. In these experiments equilibrium was always rapidly established.

CONCLUSIONS

a. The adsorption centers on samples preheated above 400°C are of a Lewis acid nature. The Lewis acid sites are likely to be formed from hydroxyl groups during dehydration between 300 and 400°C.

b. The acid strength of the hydroxyl groups is less than the acid strength of the Lewis acid sites.

c. The coverage of Lewis acid sites by bases is proportional to the reciprocal value of molecular area of the adsorbates. This can only be explained if it is assumed that the Lewis acid sites are regularly distributed over definite fractions of the surface.

d. The adsorption of bases on alumina is an activated process. The activation energy for adsorption increases with increasing bond strength between surface and adsorbates.

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