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Characterization of the Surface Basicity of Oxides by Means of Microcalorimetry and Fourier Transform Infrared Spectroscopy of Adsorbed Hexafluoroisopropanol

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The adsorption of hexafluoroisopropanol on alumina, silica, titania, thoria, magnesia, and iron oxide has been studied by gravimetry, volumetric analysis, microcalorimetry, and Fourier transform infrared spectroscopy. On all ionic oxides the adsorption is completely dissociative up to near the saturation range, where small amounts of undissociated adsorbed species are formed. Coadsorption experiments indicate that adsorption is selective on basic sites. The heats released during adsorption on the predominant surface sites are different on the different oxides, and allow the following surface basic strength scale to be proposed: $ThO_2 \geq MgO > Fe_2O_3 > TiO_2 > Al_2O_3$ (973 K) $> Al_2O_3$ (773 K). On silica the adsorption mechanism is completely different because of the lack of basicity. The main adsorbed species is liquid-like, with a small amount of alkoxy species. The method seems reliable for characterization of the basicity of catalyst surfaces.

INTRODUCTION

Different methods have been developed and widely applied to evaluate the strength and the amount of surface acid sites on catalysts (*1–3*). By contrast, no satisfactory methods have been proposed for the characterization of surface basicity, in spite of the increasing interest devoted to solid basic catalysts and basic sites on polyfunctional catalysts (*4*).

Pyrrole (*5*) and chloroform (*6*) have been proposed as specific probe molecules with which to evaluate spectroscopically the strength of surface basic sites; however, we have observed that both molecules easily transform on several surfaces, leading for instance to pyrrolate and formate species, respectively. In a previous paper (*7*) it was shown that the acidic halogenoalcohols such as fluoroalcohols adsorb selectively on alumina cation–anion couples having a predominant basic character (*7, 8*). As the oxygen atom of these molecules is almost nonbasic, as indicated by their small tendency to self-associate (*9, 10*), they show only a Brønsted acidic functional group that may interact with surface active sites. This is unlike the case of carboxylic acids, whose adsorption is much less specific (*7*). It has also been shown that the joint use of heat-flow microcalorimetry, which allows energetic characterization of the adsorption phenomena, and Fourier transform infrared (FT-IR) spectroscopy, which gives data on the nature of adsorption bonding, is very useful for the investigation of the interaction of alcohols with oxide surfaces (*8, 11*).

We have therefore thought that an acidic alcohol such as hexafluoroisopropanol, $(CF_3)_2CHOH$ ($pK_a = 9.3$), might be used as a microcalorimetric probe for the study of the surface basic strength of oxides, provided IR spectroscopy indicates that the adsorption mechanism is the same on all the oxides under study.

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EXPERIMENTAL

Some data on the oxide powders used are summarized in Table 1. The temperature of activation *in vacuo* was chosen so as to give a clean surface (from the IR point of view) on all oxides before adsorption. On alumina two different pretreatments were carried out to investigate their effect on surface basicity. The same activation procedure was performed before gravimetric, volumetric/calorimetric and IR measurements in the respective apparatus. Hexafluoroisopropanol was produced by Merck.

Gravimetric experiments were carried out on a McBain microbalance at room temperature. The irreversibly adsorbed amount has been defined as that remaining on the surface after dynamic evacuation at room temperature for 12 h.

Microcalorimetric experiments were carried out at room temperature with a Tian–Calvet heat-flow microcalorimeter, equipped with a Setaram NV 724 amplifier nanovoltmeter and a Servotrace Sefram recorder. The sample weight was usually between 0.3 and 0.8 g.

FT-IR spectra were recorded with Nicolet MX1 spectrometers, using self-supporting pressed disks of the pure oxide powders. The gas-phase spectra were automatically subtracted.

RESULTS

Volumetric and Gravimetric Measurements

In Table 1 some characteristic data for the oxide samples are reported together with the equilibrium pressures and total adsorbed amounts of hexafluoroisopropanol adsorption, as measured with the volumetric apparatus connected to the calorimetric cell (A), and the McBain thermobalance (B). Only slight differences are observed between the values for alcohol pressure P_{max} at saturation equilibrium measured by the two methods; however, more important differences can be noted in the total adsorbed amounts. In all cases the value measured by method A is lower than that measured by method B, and is more similar to that of the irreversible adsorbed amount measured by method B. These differences may arise from the different criteria used to estimate the completeness of the adsorp-

TABLE 1

Characteristics of the Oxide Samples and Adsorbed Amounts of Hexafluoroisopropanol

Oxide sample	Origin	Surface (m^2/g)	Main impurities before activation (wt%)	T_{act} (K)	P_{max} (Torr)		n_a (μmol/m^2)		
					A	B	Total		irrev
							A	B	B
SiO_2[a]	Carlo Erba	296	HCl 0.02	723	10.9	10.6	3.4	6.3	1.3
Al_2O_3[b]	Degussa C	96	HCl 0.5, Fe 0.16	773	3.2	3.6	3.2	3.9	2.6
Al_2O_3[b]	Degussa C	96	HCl 0.5, Fe 0.16	973	4.1	3.7	2.9	4.1	3.3
TiO_2[c]	Degussa P25	49	HCl 0.3, Al 0.15	673	3.1	2.8	3.2	3.6	2.8
Fe_2O_3[d]	FeOOH	14	SO_3 1.0, Al 0.2	673	2.1	2.5	2.3	4.4	2.7
MgO	Carlo Erba	31	CO_3^{2-} 0.5, Na 0.2	773	2.3	1.7	2.2	3.1	2.57
ThO_2	Rhone Poulenc	111	CO_3^{2-}, NO_3^- < 0.1	873	0.9	1.0	2.3	2.8	2.6

Note. T_{act} = activation temperature; P_{max} = equilibrium pressure at saturation; n_a = number of adsorbed molecules; A = volumetric data; B = gravimetric data.

[a] Gel.

[b] $\gamma + \delta$.

[c] Anatase 90%.

[d] Hematite (decomposition carried out at 973 K).

tion process. In the first case the experiment was ended when the released molar heat was comparable to the condensation heat of the alcohol, while in the second case the end was taken as the point where there was no further weight increase of the sample.

In Fig. 1 the adsorption isotherms of hexafluoroisopropanol measured with the volumetric apparatus are compared. Except in the case of silica, they present a similar shape, typical of a predominant strong irreversible adsorption followed by a narrow range of pressure-dependent adsorption, as already discussed in the case of adsorption on titania (*11*). The isotherm observed for adsorption on silica, on the other hand, shows a general trend typical of pressure-dependent adsorption, although a small amount of chemisorption may be observable at very low coverages.

Calorimetric Measurements

The differential heats for the adsorption of the alcohol on the different samples are compared in Fig. 2. They correspond to the heats released during each vapor admission in the calorimetric cell, relative to the volumetrically measured adsorbed amounts (*12*). Hence, these values may be used to compare the strength of the adsorption sites, supposing the adsorption mechanism is the same. We present the experimental data calculated directly from the measured heat flows (*12*) without interpolation, to illustrate the reliability of the measurements.

As will be discussed below, these curves are similar in shape except for silica. In the case of ionic oxides, plateaux or regions of slight decrease in q_{diff} are observed in the medium-coverage ranges, while at very low coverages much higher heats are released,

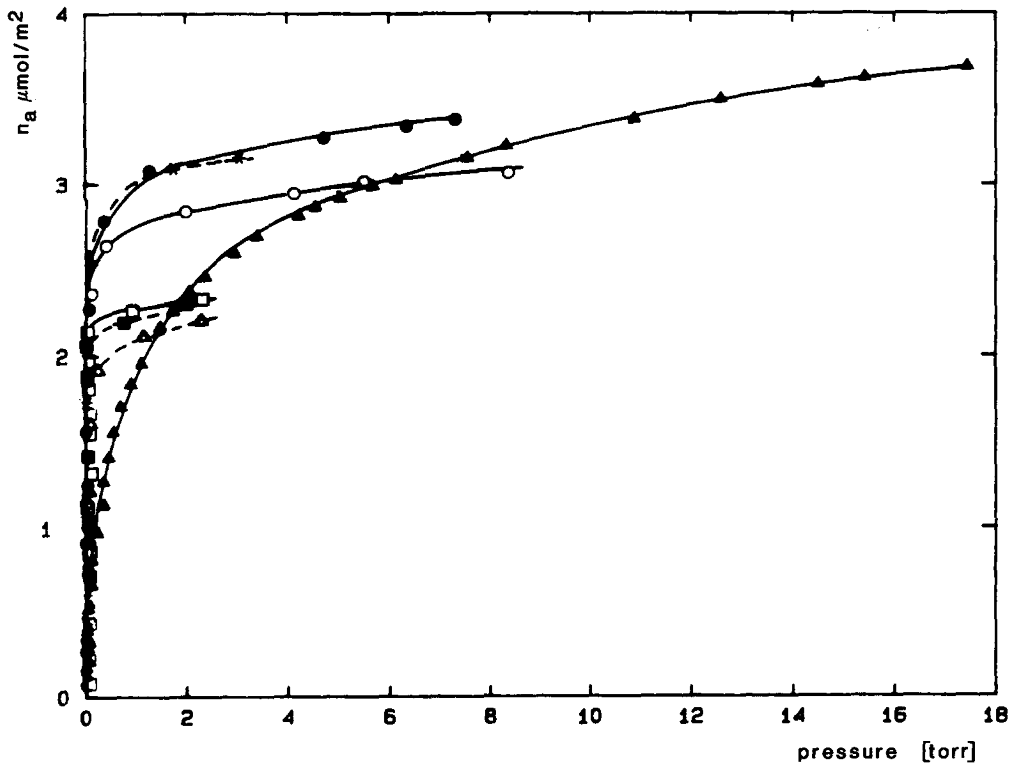


FIG. 1. Adsorption isotherms of hexafluoroisopropanol on (▲) silica, (●) alumina activated at 723 K, (○) alumina activated at 973 K, (*) titania, (□) thoria, (■) hematite, and (△) magnesia.

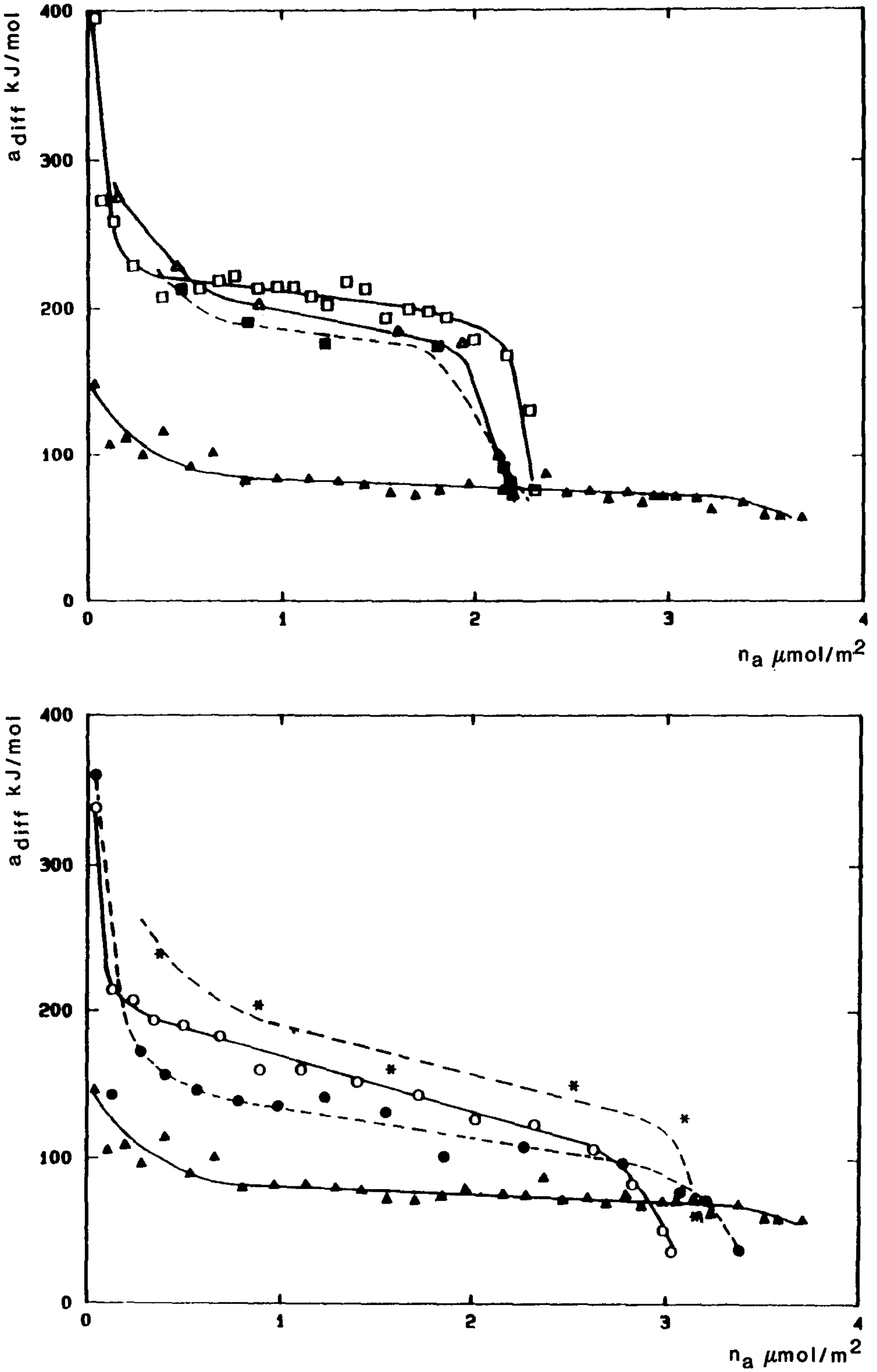


FIG. 2. Differential adsorption heats of hexafluoroisopropanol on (▲) silica, (●) alumina activated at 723 K, (○) alumina activated at 973 K, (*) titania, (□) thoria, (■) hematite, and (△) magnesia.

and at higher coverages the curve falls to values similar to that for the condensation of the alcohol. In the case of silica, on the other hand, the released heat is low in the overall range, except perhaps at the very first stage.

FT-IR Results

IR studies of the adsorption of hexafluoroisopropanol on alumina (*7*) and titania (*11*) have already been reported. They have shown that in both cases the chemisorption is completely dissociative up to near the saturation coverage. In this range small amounts of physisorbed molecules are observed. The dissociation is confirmed by the similarity of the spectra of the species arising from $(CF_3)_2CHOH$ and $(CF_3)_2CHOD$ as well as by the difference from the spectrum of the free compound, in the region 1400–1000 cm^{-1}. In particular, the δOH band, observed as a sharp band at 1308 cm^{-1} in CCl_4 dilute solution and near 1430 cm^{-1} (broad) in the pure liquid, is completely absent upon adsorption. This behavior is confirmed in all the present cases, except silica. This is shown in Fig. 3, for instance, where the spectrum of the species adsorbed on thoria is compared with that of $(CF_3)_2CHOH$ in CCl_4.

The dissociative adsorption leads to a new surface hydroxy group, characterized on alumina and titania by a sharp νOH band near 3635 cm^{-1} (*7, 11*). A similar band appears also on thoria (Fig. 4), and could correspond to the type II hydroxy groups typical of the ⟨211⟩ face, as previously discussed (*13*); however, on thoria another band, a little broader, also appears at 3550 cm^{-1}, and does not correspond to other "normal" free OH groups. It is therefore concluded that on these oxides the new OH groups are free or quasi-free, and differ from those produced by dissociation of less acidic alcohols such as methanol (*7, 13, 14*) which are hydrogen bonded. In the case of iron and magnesium oxide the new νOH band is broad and situated between 3400 and 3600 cm^{-1}.

Concerning the νCH band, we note that it is very weak in the pure compound, and is formed by two components due to two conformers (*10, 15*). The main band is located at 2930 cm^{-1} and is assigned to the C_1 conformer. In general, one weak band is observed in the case of the adsorbed species, and its frequency falls from 2935 cm^{-1} on TiO_2 to 2920 cm^{-1} on Al_2O_3 and 2880 cm^{-1} on both ThO_2 and MgO. Its intensity seems also to increase slightly in the same order.

The IR results confirm that the case of silica is different from the other oxides. The first species formed, which corresponds to

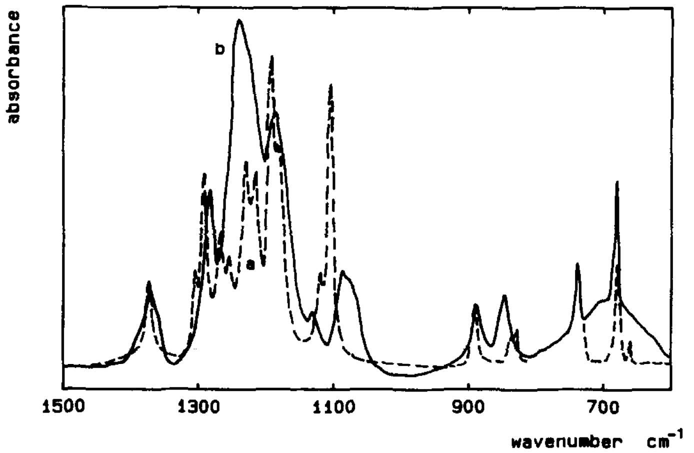


FIG. 3. FT-IR spectra of hexafluoroisopropanol in (a) dilute CCl_4 solution and (b) absorbed on thoria.

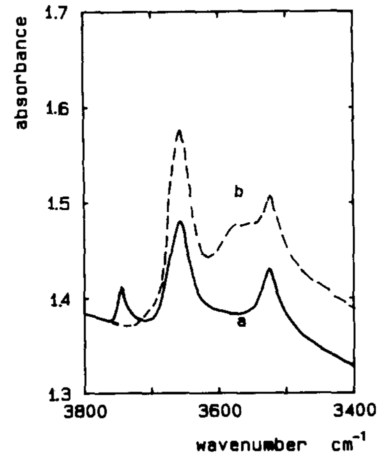


FIG. 4. FT-IR spectra of thoria (a) after activation and (b) after successive contact with hexafluoroisopropanol.

the more strongly adsorbed one as it is not desorbed after evacuation at room temperature for 4 h, is due to a reaction with surface hydroxy groups; the intensity of the νOH band of free silanol groups, in fact, decreases without formation of other νOH bands (Fig. 5). Simultaneously, $\nu \mathrm{CF}_3$ (1382, 1315 cm^{-1}) and νCH bands (2945 cm^{-1}) are formed, while the δOH band is not apparent. It is then concluded that this species is an ether-like one, formed by condensation of the alcohol with a few silanol groups.

Further alcohol introduction does not cause further decrease of the νOH band intensity of free silanol groups, thereby indicating that they are not involved. On the other hand, a broad νOH band appears at 3440 cm^{-1}, together with a δOH band at 1435 cm^{-1} and $\nu \mathrm{CF}_3$ at 1380 and 1300 cm^{-1}. All these bands are similar to those of the pure liquid (*10*). Therefore, it is possible to propose that the main product of the adsorption of hexafluoroisopropanol on silica is a liquid-like phase.

We must remark that on some other oxides (alumina, thoria and titania), some OH groups, those characterized by the higher frequency νOH bands [Fig. 5 and Refs. (*7, 11*)], are also involved in alcohol irreversible adsorption. It is therefore possible that a small amount of ether-like species is also formed in these cases.

DISCUSSION

Volumetric, gravimetric, calorimetric, and spectroscopic results agree that the mechanism of adsorption of hexafluoroiso-

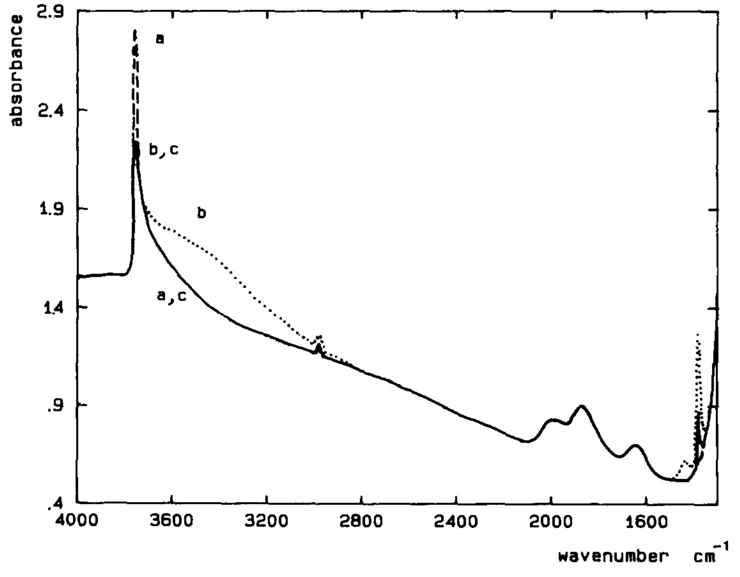
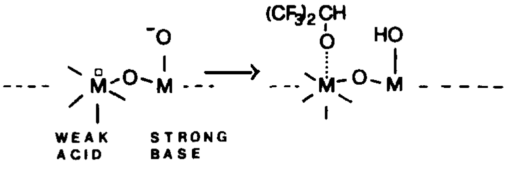


FIG. 5. FT-IR spectra of silica (a) after activation, (b) after successive contact with hexafluoroisopropanol, and (c) after successive overnight evacuation at room temperature.

propanol on covalent oxide silica is quite different from that on other more ionic oxides. On silica, in fact, all the data indicate that a limited amount of irreversible adsorption takes place, probably because of a reaction with silanol groups giving an ether-like species. It has already been reported that other alcohols such as methanol also give a similar reaction producing a surface ether-like species (*16*). At higher coverages weaker adsorption producing a liquid-like phase is observed. This agrees with the very high value for equilibrium pressure at saturation ($P_{\max}$ in Table 1) as well as the large reversibility of the process. In agreement, the measured q_{diff} is consistently small and close to the estimated condensation heat of the alcohol (about 75 kJ/mol).

In all other cases, IR spectroscopy indicates that the adsorption is completely dissociative up to near the saturation range. Previous studies on alumina (*7*) indicated that adsorption of $(CF_3)_2CHOH$ leaves the predominant stronger acidic sites free. This is in contrast with what we found for the less acidic "normal" alcohols, such as methanol (*7, 11*), which instead adsorb both on basic and on acidic sites. We have therefore concluded that on alumina there are cation–anion couples having either a strong acid or a strong basic character. Only the latter would act as adsorption sites for $(CF_3)_2CHOH$, because of the negligible basicity of its oxygen atom (Scheme 1). This result has been confirmed on TiO_2, since the saturation with $(CF_3)_2CHOH$ does not hinder the coordination of CO (*17*). This conclusion could be extended to the other ionic oxides. Therefore, if the adsorption mechanisms are assumed to be the same, the released heats are taken as a measure of the relative strength of the basic sites on ionic oxides. Small amounts of ether-like species could also be formed, but the heat released must be very low as on silica, and therefore negligible.



SCHEME 1

The curves in Fig. 2, where the differential adsorption heats are reported as a function of the amount adsorbed, are composed of three regions. At the very beginning a sharp decrease in q_{diff} is observed, as in similar cases (*18*), which may be assigned to the adsorption on few very strong sites possibly arising from surface defects. In the intermediate region, a plateau or a slight decrease in q_{diff} values is observed, corresponding to the heats released during adsorption on the predominant surface sites. At the end, a further sharp decrease is observed, corresponding to the saturation of the chemisorption sites and to the formation of small amounts of physisorbed or liquid-like species.

The comparison of the q_{diff} values measured in the intermediate region may be taken as a criterion to compare the basic strength of the main exposed sites. From the data reported in Fig. 2 the following basicity scale may be proposed: $ThO_2 \geq MgO > Fe_2O_3 > TiO_2 > Al_2O_3$ (973 K) $> Al_2O_3$ (773 K) $\gg SiO_2$.

As regards the first adsorption region, we should remark that our data are less accurate here, mainly in the cases of the low-surface-area oxides (MgO and Fe_2O_3). This is due to our particular apparatus, which permits only a limited amount of powder in the cell, imposing a compromise between the amount of vapor that must be introduced to be accurately measured and the amount of exposed sites, which is directly related to the oxide surface area. This may be a serious limitation of the present work, because it is possible that the few sites of very high strength are those predominantly active in catalysis, although they would also be the first to be poisoned and to become inactive; however, it seems reasonable that the scale of the basicity of the defect sites would roughly reflect that of the normal sites. In any case this method allows a characterization of these sites in higher-surface-area powders.

It seems remarkable to us that the basicity scale we have reported, based on the calorimetric measurements, is the inverse of the scales of the values of $P_{\max}$, the alcohol vapor pressure at saturation, reported in Table 1. This is not really unexpected: in fact, in a simplified treatment of the adsorption of the same adsorbate on different surfaces, the adsorbate partial pressure at constant coverage θ is expected to be inversely proportional to the adsorption equilibrium constant, which is determined mainly by the enthalpy factor. This is the case of the Langmuir theory of reversible adsorption, with the Langmuir equation written as $K P_{\mathrm{ad}} = \theta/(1 - \theta)$.

The basicity scale of the main sites on the different oxides we have proposed may be compared with literature data concerning measurements made at the gas/solid interface. For instance, the stability of the surface carbonates can also be related to the surface basicity of the oxides. Accordingly, we observe that evacuations at 873 and 773 K are necessary to cause almost complete desorption of CO_2 from thoria and magnesia, respectively, while much milder treatments are sufficient to desorb it from Fe_2O_3 (*19*), TiO_2 (*20*), and Al_2O_3 (*21*). The very strong basicity of thoria and magnesia is also related to the particular ability of these oxides to cause radical coupling of CO if pretreatments at very high temperatures are carried out (*22, 23*).

As for the other ionic oxides, we note that on iron oxide dissociation of very weak acidic molecules such as toluene (*24*) and ammonia (*25*) has been observed, as on MgO (*26*), while these reactions are not observed on titania (*17, 27*). This justifies that iron oxide has a basicity intermediate between those of magnesium and titanium oxides.

Concerning alumina, we may note the effect of raising the activation temperature, which increases the strength of the basic sites more than their number. This result goes together with the increase in surface acidity well known to take place upon increase of the evacuation temperature (*28*). On such an oxide it seems that a very small amount of very strong basic sites is also present.

Finally, the different behavior of silica, not unexpected indeed, points to the almost complete absence of basicity on this covalent oxide.

As regards measurement of the *number* of basic sites, our method is certainly limited by the relative ratio between the area of the adsorbed molecule and the density of the adsorption sites, even assuming a homogeneous distribution of sites. The maximum amount of adsorbed alcohol as measured in our volumetric/calorimetric apparatus ranges from about 2 to 3.2 μmol/m^2 on ionic oxides, which corresponds to about 80–50 Å^2 per molecule. This value is comparable to that evaluated for the cross-sectional area of this molecule (*29*).

Concluding, the microcalorimetric study of the adsorption of fluoroalcohols, such as hexafluoroisopropanol seems to represent a useful method to investigate the basic character of oxide catalyst surfaces, especially those having high surface areas where detailed information also at low coverages may be obtained.

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