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ACIDITY OF OXIDE CATALYSTS IN THE PRESENCE OF REACTANTS

By

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Abstract

The acidity of synthetic alumina and silica-alumina, both before and after the passage of different reagents at 230°C, has been determined.

Unactivated aluminas gave a basic color with bromothymol blue and phenolphtalein. Upon activation, the basic color disappeared and their reaction was acidic even with very strong indicators. Silica-aluminas never showed a basic color with the basic indicators. Also their acidity was less affected by the ambient humidity.

At 230°C, alumina adsorbed vapors of *n*-butylamine (a base) and phenol (an acid) while silica-alumina only adsorbed *n*-butylamine. After such adsorption, the catalysts lost their original acidity and the extent of the inhibition was found to be a function of the basicity of the reactant. The amounts adsorbed on the catalysts did not give a measure of catalytic activity or the type of acidity.

Introduction

The insulating oxides are important in industry on account of their use as supporting agents or as catalysts; their use has increased in recent years. Alumina and silica-alumina are particularly important for cracking, alkylation and isomerization of hydrocarbons, gasoline reforming, dehydration of alcohols, *etc.*

The catalytic activity is associated with the acidic properties of the surface. Alumina presents Lewis-type acid sites which are formed during the dehydration process by combination of two surface hydroxyl groups.[1] The accepted mechanism[2] for dehydration of alcohols on alumina involves an acid and a basic site. For example, in the case of methanol and ethanol, the alcohols are adsorbed by dissociation on both types of site and the combination of two neighbouring alkoxide groups leads to the formation of the ether.[3,4]

Silica-alumina has acid-sites of the Lewis and Brönsted types. The Brönsted type is able to give away a proton, in such a way that the mechanism of the dehydration reaction may be of the ionic type.[3] Certain authors

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remark that silica-alumina, like alumina, also has basic sites.[5,6,7]

It has been found that in alumina the catalytic activity follows a similar law to that for basicity.[8] According to several authors, the catalytic activity of aluminas and silica-aluminas for different reactions is usually proportionally related to acidity[9-16]; for this reason we have used the acidity as measured by volumetric titration as an indication of the state of the catalyst surface.

This titration-method with a liquid base may be criticized on various accounts: firstly, the reaction may not be quantitative and equilibrium may not be reached; secondly, there may be physical and chemical adsorption simultaneously; thirdly, the results may depend on the base used for titration; and fourthly, it is not really konwn which type of acidity is measured. Also, since the method depends on the visual observation of the change in color of an absorbed molecule, the method is restricted to the use of indicators which produce an intense coloration: this limits the number that can be used and hence the range of acidity values that can be explored. Some authors[17] have demonstrated that several problems arise in titration with certain H_0 indicators.

In fact, the titration technique measures the capacity of the solid to react with a base at low ambient temperatures, *i.e.*, a property which is not necessarily indicative of the acidity under reaction conditions. Nevertheless, experience shows that it is possible to correlate acidity and activity. In many cases they are proportional, the proportionality factor being different for different catalysts. Thus, the acidity titration gives an empirical number when working under standard experimental conditions, and the rumber so obtained can be used as a guide to the actual acidity under reaction conditions.

In the present paper a study of the acidity of the surface of alumina and silica-alumina catalysts, after exposure to ambient conditions or after the passage of various chemicals, is reported. The conditions used for the latter experiments are the same as those used in a previous paper for the dehydration of methanol to dimethyl ether.[3] The action of poisons for this reaction, such as *n*-butylamine and other chemicals of different basicity, on the acid strength distribution is also studied.

Experimental

Acidity determination: The acidity was determined by titration of the catalysts activated at 500°C, with a 0.1 N *n*-butylamine solution in benzene using a series of H_0 indicators, according to a technique previously described.[3] In order to obtain reproducible values and to reach the adsorption equilibrium at the surface of the catalyst, the *n*-butylamine solution was added very slowly with very strong agitation to a finely divided sample of the solid.

Adsorption capacity measurements: In order to determine the amount of substance that the catalyst was able to adsorb, a column aproximately 50 cm long and 1/4″ in diameter was filled with a 60–80 mesh catalyst, After activation it was then used as a chromatographic column in an 810 Perkin Elmer gas-chromatograph. Next, known volumes of a given substance were injected until there was no further retention; at this point a signal was obtained from the ionization detector. The amount added in milliequivalents/gram of adsorbed substance up to this point was then calculated.

Catalysts: The catalysts used were the following synthetic aluminas and silica-aluminas: gamma alumina T–126, $Sg=210\,m^2/g$, supplied by Girdler Catalyst; gamma alumina F–110, $Sg=155\,m^2/g$, supplied by Aluminum Company of America; eta alumina 992C, $Sg=222\,m^2/g$, supplied by W. R. Grace & Co.; silica-alumina S–90, $Sg=370\,m^2/g$, supplied by Houdry process and Chem. Co.; and silica-alumina Aerocat, $Sg=513\,m^2/g$, supplied by American Cyanamid. The specific surface area, Sg, was determined by the flow method with the catalyst activated at 500°C.

The poisoned catalysts were obtained from material previously activated in air at 500°C and then cooled to 230°C in a nitrogen current to which the poisons were added and later nitrogen was passed for three hours. The liquid reagents were either directly vaporised into the nitrogen current or vaporized by bubbling nitrogen through bottles containing the liquid. In the latter case the temperature of the bottle was the one required to have 100 mmHg as partial pressure of the poison. Both methods gave similar results on titration for acidity.

Reagents: All the reagents were pure grade and were used without purification, except for the *n*-butylamine which was distilled before use.

Results and Discussion

Commercially prepared aluminas, which have been exposed to the atmosphere, do not exhibit an acid color, even to butter-yellow ($pKa=+3.3$; but they do show a basic greenish color to bromothymol-blue ($pKa=+7.1$) and pink to the phenolphtalein ($pKa=+9.2$). On adding water, the pink color is lost. Upon activation by heating acidity appears and the basic character disappears, as shown in Table 1.

It has previously been pointed out that alumina basicity measured by the bromothymol-blue increases up to a certain value upon the addition of water.[18] The fact that moist alumina at ambient temperature turns a basic color in the presence of an indicator does not prove the existence of cataly-

TABLE 1. Influence of pretreatment on acidity and basicity of aluminas and silica-aluminas

Catalyst		Meq/g of H_0 acidity (*pKa*)					Basicity (*pKa*)	
		−8.2	−5.7	−3.0	+1.5	+3.3	+7.1	+9.2
Alumina 992 C	A	0	0	0	0	0	+	+
	B	0.12	0.12	0.17	0.17	0.19	−	−
Alumina T-126	A	0	0	0	0	0	+	+
	B	0.12	0.18	0.21	0.21	0.24	−	−
Alumina F-110	A	0	0	0	0	0	+	+
	B	0	0.13	0.13	0.13	0.21	−	−
Silica-alumina S-90	A	0	0	0	0.06	0.21	−	−
	B	0.30	0.34	0.34	0.34	0.34	−	−
Silica-alumina Aerocat	A	0	0	0	0	0.03	−	−
	B	0.30	0.32	0.34	0.34	0.34	−	−

A : commercial catalyst in the state in which it was received.
B : catalysts activated at 500°C

tically active basic sites under the reaction conditions. However, it gives some indication of the existence of basic sites. Now, it is known already that both acids and bases poison aluminas.[19] The ability of alumina to adsorb acids and bases is also shown by the data in Table 2, which summarizes the results obtained when n-butylamine (a base) or phenol (an acid) are passed over a column filled with activated catalyst in the chromatograph at 230°C. The figures show a great decrease of acidity compared with that for the activated material, the values for which are shown in Table 1.

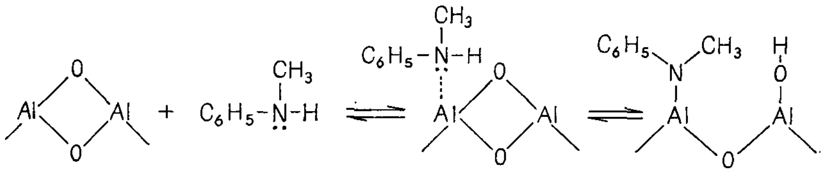
It will be noted that the amount of phenol adsorbed by F-110 alumina (0.80 meq/g) is higher than the amount of butylamine (0.13 meq/g). This does not necessarily means that the concentration of basic sites is higher than that for the acid ones, as established by SCHWAB and KRAL,[5] since it is necessary to take into account a) the relative acidic or basic strength of each material, b) their boiling points and c) the possibilities of decomposition or polymerization. Some explanation of the fact that the basic sites on alumina, are not show up with the indicators must also be given. It could be possible that an adequate indicator has not yet been found or that the basic sites acquire "strength" after the attack on the acid center. This attack could increase the electronic density and basicity of the sites, as is shown in the following mechanism. A nucleophilic reactant attack the alumina

TABLE 2. *n*-butylamine and phenol adsorption capacity of different catalysts and the effect on H_0 acidity

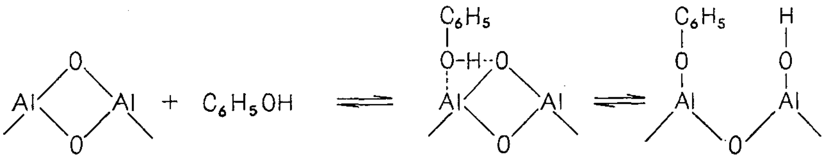
Catalysts		meq/g adsorbed at 230°C	Meq/g of H_0 acidity (*pKa*)				
			−8.2	−5.7	−3.0	1.5	3.3
Alumina 992 C	A	0.24	0	0	0	0	0
Alumina T-126	A	0.26	0	0	0	0	0
Alumina F-110	A	0.13	0	0	0	0	0
	B	0.80	0	0	0	0	0
Silica-alumina S-90	A	0.12	0	0	0.06	0.08	0.11
Silica-alumina Aerocat	A	0.15	0	0	0	0.09	0.10
	B	0	×	×	0.34	0.34	0.34

A : activated catalyst on which *n*-butylamine was adsorbed.
B : activated catalyst on which phenol was adsorbed.
× : impossible to determine because of the catalyst color after phenol treatment.
(The values for the activated catalysts are shown in Table 1).

and is adsorbed; then it dissociates to form new superficial groups. With methylaniline, for example:



The basic site represented by the superficial oxygen does not color the bromothymol blue but in spite of this, it can adsorb phenol. It may be that phenol, being more acidic than methylaniline starts simultaneously the attack to the oxygen and to the aluminum, covering the acid-basic pair:



Thus acid sites are covered and although phenol is an acid, alumina will not exhibit acidity after the passage of phenol as found in alumina F-110 (see Table 2).

Synthetic silica-aluminas never exhibit a basic character to the indicators, they give acid color only to the weaker acid indicators when they have not been activated. Activation increases their acid character (see Table 1). The dehydration of methanol on silica-alumina is irreversibly poisoned by bases but not by acids; this is because bases do not allow methanol adsorption on strong acid sites, by a mechanism in which a proton takes part.[3] This type of catalyst irreversibly adsorbs a base but not phenol, as shown in Table 2.

The amount of poison adsorbed from the gas phase by the alumina and silica-alumina catalysts is not necessarily a measure of its catalytic capacity, since the adsorption may take place on catalytically non-active sites, or on sites which would not adsorb it in the presence of the reactants. Apparent inconsistences in adsorption of bases on alumina and in their effect on activity have been found by different authors.[20-22] When *n*-butylamine is passed over activated alumina or silica-alumina in a nitrogen stream at 230°C until equilibrium is reached, and then the carrier alone is passed at constant temperature for several hours, some *n*-butylamine still remains adsorbed. This can be seen on carrying out desorption at higher temperatures, the amine together with other products can be detected. On carrying out the same experiments with methanol, it is observed that methanol also remains adsorbed, either unreacted, or as dimethyl ether and water; these materials desorb at increased temperatures. This means that during the reaction and afterwards, the catalyst surface is never free but occupied by molecules of reactant and/or products which prevent the strong acid sites from coloring the indicators. Nevertheless, the catalyst maintains its total activity.

In order to find out the state of the surface under reaction conditions, the effect on acid strength distribution by treating the catalysts at 230°C with *n*-butylamine, methanol and other chemicals was determined. The results of the different experiments are shown in Table 3. When the catalysts were colored after the treatment it was not possible to use indicators of strong acidity, which only show a weak change in color. On methanol treated silica-alumina, the response to highly acidic indicators was low and a quantitative result could not be obtained.

Since alumina and silica-alumina have acidic active-sites, it is logical to suppose that the greater the basicity of the reagent, the greater its inhibiting power. However, it must not be forgotten that the basicity-order may not be preserved under reaction conditions, since the temperature is high and the reagents are adsorbed on the catalyst surface.

On T–126 alumina it is observed that all the reagents eliminate all response to the indicator with $pKa = -8.2$. The action at other pKa values increases in intensity and extent as the basic nature of the reagent increases;

TABLE 3. Surface acidity after the passage of different reactants at 230°C

Catalyst	Treatment	Meq/g of H_0 acidity (*pKa*)				
		−8.2	−5.7	−3.0	1.5	3.3
Alumina T-126	Without treatment	0.12	0.18	0.21	0.21	0.24
	Propanol	0	0.14	0.18	0.18	0.18
	Methanol	0	0.09	0.19	0.19	0.22
	Water	0	0.08	0.13	0.13	0.21
	Tert-butanol	×	×	0.11	0.11	0.13
	Methylaniline	0	0	0	0.05	0.11
	Pyridine	0	0	0	0	0.04
	n-Butylamine	0	0	0	0	0
Silica-alumina S-90	Without treatment	0.30	0.34	0.34	0.34	0.34
	Propanol	×	×	0.27	0.27	0.30
	Methanol	>0	>0	0.27	0.27	0.27
	Water	×	×	0.25	0.25	0.29
	Tert-butanol	0	0	0.21	0.21	0.24
	Methylaniline	0	0	0.10	0.10	0.10
	Pyridine	×	0.23	0.23	0.23	0.30
	n-Butylamine	0	0	0.19	0.19	0.24

× : colored catalyst.

with butylamine, acidity is completely neutralized.

On silica-alumina, methanol is able to neutralize a great part of the acidity determined by the $pKa = -8.2$ indicator, but some the other chemicals are able to destroy it. Even the strongest base cannot totally eliminate the acidity, it is weakened.

If both catalysts are compared, it is seen that the action varies in extent, but in all cases the catalyst does not recover its initial acidity.

Similar experiments in which the activated catalyst was put in contact with acetic acid, methanol, water, piridine and butylamine during five days into a desiccator at 20°C and then nitrogen was passed during three hours, were carried out. The adsorption was found to be less selective, and in all cases the acidity was neutralized, except when acetic acid or methanol was adsorbed on silica-alumina. Similar results were obtained recently by MATSUZAKI, NITTA and TANABE[23] working with silica-alumina.

It may be concluded that under reaction conditions and after use, the surface of the catalyst is never bare but always covered to different extents by molecules of reactants and/or products, depending on their basicity and the type of catalyst. Consequently, during the reaction the acidity of the catalyst is different in value from that of the activated material which has not been in contact with reactants. But as different authors have correlated catalytic activity with the acidity measured in the activated material, it can be inferred that the state of the substances adsorbed on the surface during the reaction will still depend on the acidity of the bare material.

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