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Poisoning and Nature of Alumina Surface in the Dehydration of Methanol

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The poisoning action of acids and bases on the catalytic activity of different acidic aluminas is studied for the methanol dehydration reaction. The inhibiting action of the basic poisons depends on their basicity and it is greater on the catalyst of stronger acidity. By means of isothermic adsorption-desorption and desorption with programmed temperature, it is found that methanol and *n*-butylamine or acetic acid are capable of displacing each other from most of the active sites on the alumina surface. Although alumina presents superficial heterogeneity, for the most part the active surface behaves as a homogeneous one with respect to these chemicals, and an interaction exists among the adsorbed molecules.

INTRODUCTION

The catalytic activity of alumina for methanol dehydration is associated with the Lewis acid–Lewis base pair formed during surface dehydration. As this acid–base pair is necessary for catalytic activity, it can be expected that both acid and basic substances will produce poisoning, as has been found by Jain and Pillai (*1*). The surface of alumina is heterogeneous regarding acidity and the acid strength distribution is a function of calcination temperature (*2*). The heat of adsorption of ammonia also indicates that the surface is heterogeneous (*3*): for low surface coverage the amount of heat evolved is large but it falls suddenly as large areas become covered.

This paper refers to the mechanism of poisoning by organic acid and bases of the reaction of methanol dehydration over commercial aluminas. The types of alumina used showed great differences in their acid strength. Runs with simultaneous injection of poison were carried out and to analyze the phenomenon which occurs at the catalyst surface, the isothermal adsorption and desorption of methanol and poisons were studied. The technique of desorption at programmed temperatures was also used. The last two techniques have been recently described (*4, 5*) and are very useful tools for studying the phenomena which occur on a catalyst surface.

The importance of the acid strength of active sites on alumina has been noted by several authors who found that poisoning by nitrogen bases affect differently alcohol dehydration and the isomerization of the olefin produced (*6–9*). This difference was attributed to the different acid strength of active sites. The relatively strong sites are required for the dehydration of alcohols to olefins and for the secondary isomerization of the olefin and are irreversibly poisoned. This type of acid site is only found in aluminas of great purity. The relatively weak sites are active only for the alcohol dehydration and are poisoned reversibly. It is also known that very pure alumina is active in hydrogen–deuterium exchange, ethylene hydrogenation, isomerization, and cracking of hydrocarbons, the catalyst being poisoned by water vapor (*10–14*). Therefore another type of active site may be present, which is poisoned by water and therefore does not participate in reactions in which water is formed, as in the dehydration of alcohols.

EXPERIMENTAL

Runs with Simultaneous Poisoning

Materials. The catalysts used were γ-alumina T-126 and γ-alumina F-110. Their properties are given in Table 1. The specific surface was measured by the continuous method and the acid strength distribution by means of the technique described in a previous paper (*15*). The poisons used were a strong base (diethylamine, $pK_a = 11.0$), a weak base (pyridine, $pK_a = 5.3$) and two acids (phenol, $pK_a = -6.7$ and acetic acid, $pK_a = -6.1$). These poisons as well as the methanol employed were pure grade reagents and were used as received.

TABLE 1

SPECIFIC SURFACE AREA AND ACIDITY DISTRIBUTION OF THE ALUMINAS

Alumina	Provided by	Specific surface area	meq/g H_0 acidity (pK_a)				
			−8.2	−5.7	−3.0	1.5	3.3
T-126	Girdler Catalyst	210 m^2/g	0.12	0.18	0.21	0.21	0.24
F-110	Alcoa	155 m^2/g	0	0.13	0.21	0.21	0.21
992 C	W. R. Grace & Co.	222 m^2/g	0.12	0.12	0.17	0.17	0.19

Procedure. Standard runs were carried out as previously described (*15*). Two hr after the run had begun, the pure methanol feed was substituted by a mixture of the poison in methanol. This mixture was allowed to pass for two hours and then pure methanol was passed again. The feed flow rate was kept constant throughout the experiment.

Isothermic Adsorption-Desorption and Desorption at Programmed Temperature

Materials. Two aluminas were used: γ T-126 and η 992C. Their properties are given in Table 1. Distilled *n*-butylamine and glacial acetic acid were used as poisons.

Apparatus. A scheme of the apparatus is given in Fig. 1. It consists of a stainless steel catalytic microreactor 0.9 cm in diameter and 12 cm long, packed with 0.5 g of 30–80 mesh catalyst. The outlet pipe from the microreactor is connected to a thermal conductivity cell and, whenever desired, the gases are routed to the chromatograph by means of the sampling valve. The reagents are fed to the reactor in a nitrogen stream, the mixture being obtained by bubbling the nitrogen through the liquid at constant temperature. The oven of the microreactor is connected to a linear temperature programmer for controlling the heating rate. The microreactor temperature is measured by a chromel–alumel thermocouple, the output from which is continuously recorded.

Analysis. The analysis of effluents was carried out in an 810 Perkin Elmer chromatograph with thermal conductivity and flame ionization detectors. A ¼″ × 3m column of Triton 101 + 10% NaOH on 60–80 mesh Chromosorb P was used for experiments with *n*-butylamine and a ¼″ × 1.8m column of Porapak Q in the case of acetic acid.

Procedure. Two types of experiments were carried out: (a) The catalyst was introduced into the reactor and activated in situ at 500°C for four hr in a stream of dry air. Then it was taken to a temperature of 230°C in the presence of nitrogen. At this temperature a stream of methanol in nitrogen (obtained by bubbling nitrogen through methanol at 0°C) was passed until the catalyst was in equilibrium with the gas phase. This was verified by observing the response of the chromatograph and of the conductivity cell. Then keeping the temperature constant at 230°C, nitrogen was passed, resulting the isothermal de-

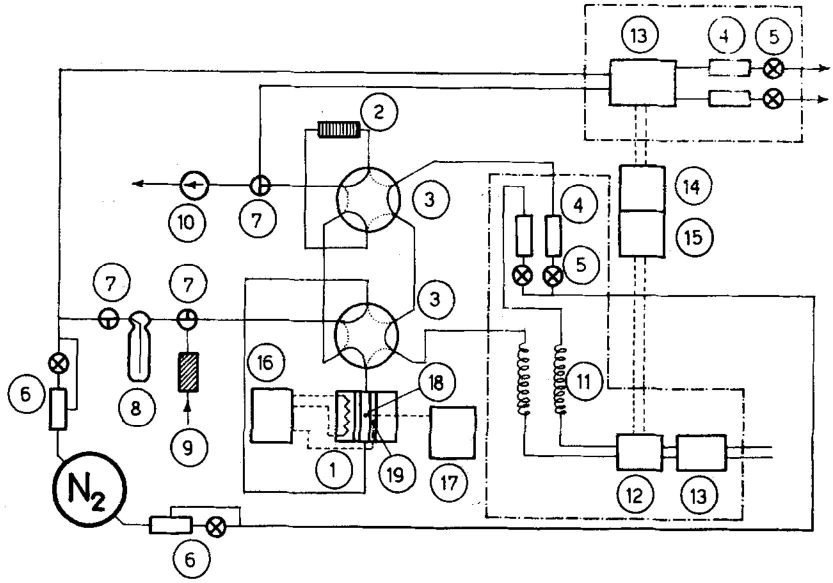

FIG. 1. Scheme of the apparatus: 1, microreactor and oven; 2, sampling volume; 3, sampling valve; 3′, microreactor valve; 4, flow-meters; 5, needle valves; 6, flow-regulator; 7, three way stopcock; 8, bubbling flask; 9, anhydrone drier; 10, circulation pump; 11, chromatographic columns; 12, flame ionization detectors; 13, conductivity detectors; 14, continuous conductivity recorder; 15, chromatographic recorder; 16, controller; 17, temperature recorder; 18, measure thermocouple; 19, control thermocouple.

sorption of methanol and reaction products. In a similar way, a stream of poison in nitrogen (obtained by bubbling nitrogen through *n*-butylamine at 0°C or acetic acid at 20°C) was passed for ten min. Then nitrogen was passed to sweep away the poison that desorbed from the surface. After this, methanol in nitrogen was again fed to the reactor until constant response was attained and then nitrogen was used alone. This procedure was repeated several times. After the last isothermal desorption of methanol, when at the normal working temperature no reactant was detected in the exit stream, the programmed temperature desorption was carried out using a rate of 13.6°C min^{-1} up to 500°C.

(b) Over the catalyst, activated as in procedure (a), a stream of poison in nitrogen was passed and maintained until there was a constant response from the chromatograph and the thermal conductivity cell. Then nitrogen was fed overnight, and followed by methanol and nitrogen, the temperature was maintained at 230°C. Finally programmed temperature desorption was carried out.

RESULTS

Runs with Poisoning

Figures 2–6 show how the activity of the alumina for methanol dehydration is affected by the passage of poison. The amount of dimethyl ether formed per unit time is taken as a measure of activity be-

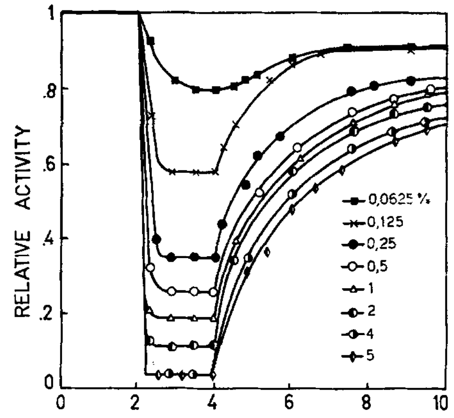

FIG. 2. Relative activity of the γ-alumina T-126 during the poisoning with solutions of diethylamine in methanol.

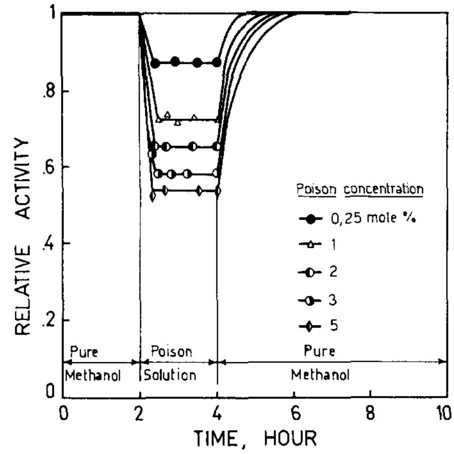

FIG. 3. Relative activity of the γ-alumina T-126 during the poisoning with solutions of pyridine in methanol (experimental points during activity recovering not shown to avoid blurring).

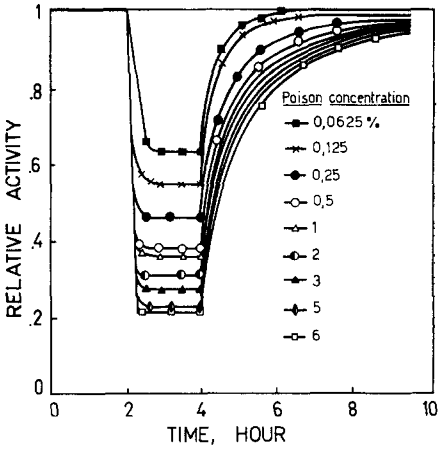

FIG. 5. Relative activity of the γ-alumina F-110 during the poisoning with solutions of diethylamine in methanol.

cause at working conditions it is a zero order reaction (*16*). The activity of the catalyst with pure methanol is taken as unity and relative activity is plotted when feeding with different concentrations of poison in methanol.

Figure 2 shows that since T-126 is a strongly acid catalyst the poisoning produced by the stronger base is very pronounced. Activity is only recovered very slowly and there remains a residual poisoning which is very difficult to eliminate due to the strong bonds between diethylamine and the strong acid sites. Pyridine (Fig. 3), being a weaker base, produces less poisoning and the activity is recovered rapidly. Poisoning by phenol (see Fig. 4) seems to be in part irreversible or that it recovers very slowly. This could be due to the bonds formed with very strong basic sites or to the formation of heavy substances on the catalyst surface.

Because alumina F-110 has less strong acid sites the adsorption of bases is not so strong and the activity is recovered quickly, as can be seen in Figs. 5 and 6.

The results show that the poisoning of alumina by organic bases and acids is reversible; activity is recovered when there

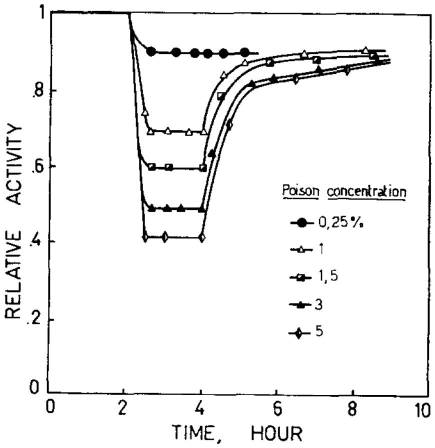

FIG. 4. Relative activity of the γ-alumina T-126 during the poisoning with solutions of phenol in methanol.

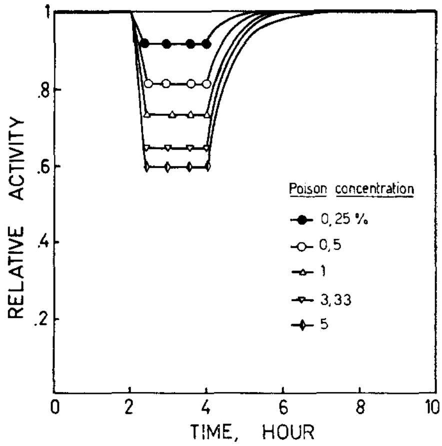

FIG. 6. Relative activity of the γ-alumina F-110 during the poisoning with solutions of pyridine in methanol.

is no poison in the feed. It is possible to accept for the poisoning the approach made by Knözinger (*17*) for the adsorption of pyridine on alumina at 230°C: the catalyst and the poison form an "external complex," which has a weak bond that is weakened by the simultaneous adsorption of water. Then methanol is able to expel the base from the surface.

The poisoning action of the bases depends on their basicity and the acid strength of the catalyst. For a particular base, the weaker acid sites are only covered at relatively high vapor pressures and their activity is recovered rapidly when there is no more base in the feed.

Isothermic Adsorption-Desorption and Desorption at Programmed Temperature

Results of runs carried out with *n*-butylamine as poison are shown in Figs. 7 and 8, where the amount of methanol, ether, and *n*-butylamine are represented as functions of the corresponding peak heights obtained in the chromatographic analysis. The peak heights read were corrected by its attenuations and different molar response of the reactants. In the case of dimethyl ether, the heights represented the methanol conversion in accordance to $200n_e/(2n_e + n_m)$, where n_e = number of ether moles, and n_m = number of methanol moles. During the desorption the heights are related to the higher conversion. Studying *n*-butylamine adsorption, 100 is the higher value obtained, and during its desorption relative values are taken. Semilogarithmic coordinates are used to show up the low values, and the time scale has been truncated. The flame ionization detector was used for greater sensitivity, then water was not monitored, only dimethyl ether, methanol, and *n*-butylamine.

Figure 7 shows the results of procedure (a) for the γ-alumina T-126. On passing methanol, dimethyl ether and the unreacted methanol are both observed in the reactor outlet. Ether and methanol desorb to the nitrogen stream when the passage of methanol is stopped. On passing *n*-butylamine for 10 min, some of the methanol is displaced from the surface. During the first minutes of passage the amine reacts with the adsorbed methanol since the chromatogram shows the presence of several products. Butylamine is then eliminated by the passage of nitrogen until it cannot be detected with the chromatograph.

For a certain time no more *n*-butylamine is detectable, but when methanol is again passed, it expels some *n*-butylamine which was not desorbed during the passage of the carrier gas. Once the *n*-butylamine is de-

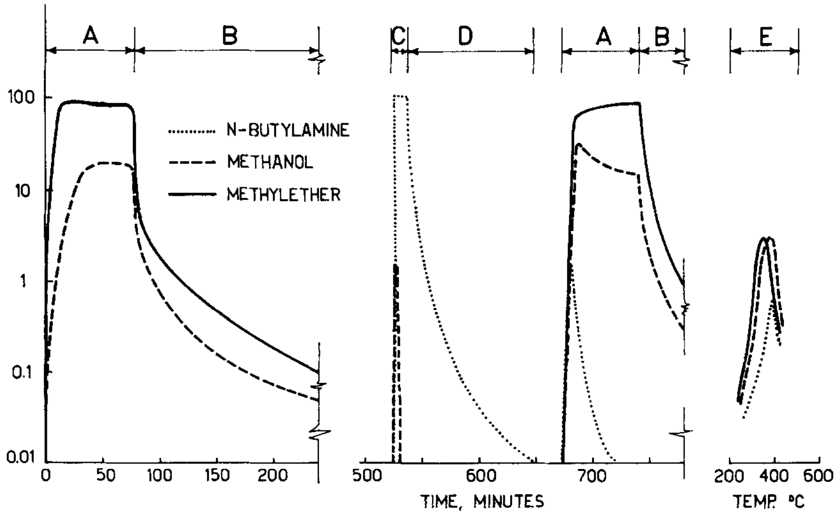

FIG. 7. Representation of procedure (a) for γ-alumina T-126. A, methanol adsorption; B, methanol desorption; C, *n*-butylamine adsorption; D, *n*-butylamine desorption; E, temperature programmed desorption.

sorbed, the conversion to ether reaches the original level. After passing the carrier until no more methanol and ether can be detected at the outlet, and then raising the temperature, methanol, ether, and *n*-butylamine, which are irreversibly adsorbed at 230°C, start coming off again. Similar results were obtained with η-alumina 992 C.

The possibility of displacement between similar molecules and the reaction between surface groups has been recently shown out by means of IR studies (*18*): if methanol is passed over a surface where ethanol has been preadsorbed, diethyl ether is produced first, then methyl ethyl ether and finally dimethyl ether.

Figure 8 refers to procedure (b) used with γ-alumina T-126. In this case *n*-butylamine is passed first and then carrier is passed overnight to desorb it. After this, passage of methanol displaces part of the *n*-butylamine from the surface and dehydration of the alcohol occurs but with a somewhat lower activity than in the case of procedure (a) where methanol was passed before the *n*-butylamine. This shows that there are sites where it is difficult for *n*-butylamine to adsorb under the conditions of procedure (a). A certain amount of amine, greater than for the case of procedure (a), is not displaced by methanol, as is shown by the programmed temperature desorption. Similar results were found with η-alumina 992 C.

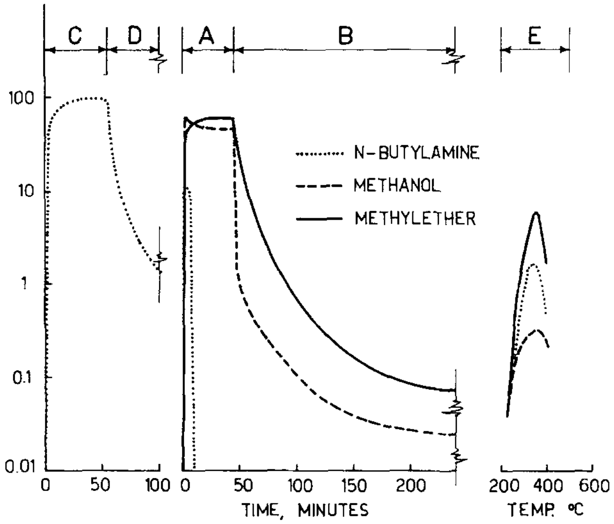

FIG. 8. Representation of procedure (b) for γ-alumina T-126. A, methanol adsorption; B, methanol desorption; C, *n*-butylamine adsorption; D, *n*-butylamine desorption; E, temperature programmed desorption.

Curves with the same characteristics as those of Figs. 7 and 8 were obtained when acetic acid was used as poison. Using procedure (a) it was seen that acetic acid can displace some methanol from the catalytic surface, even though this methanol was not removed by the nitrogen stream over a period of several hours. When methanol is again passed after desorbing acetic acid isothermally, it is observed that methanol is able to displace more acetic acid from the surface, either as such or in combination with methanol. The initial activity is thus recovered. But methanol does not eliminate all the acetic acid, because on effecting the desorption at programmed temperature the presence of ether, methanol, acetic acid and other compounds is detected in the exit stream.

DISCUSSION

The phenomenon observed shows that after the passage of poison the initial activity is recovered, this may mean (1) that the poison is not adsorbed, (2) that it is adsorbed on nonactive sites, or (3) that it has been adsorbed on active sites and has afterwards been displaced by methanol.

The first possibility can be ruled out since it has been shown by our programmed desorption results (Figs. 7 and 8), by IR studies and other methods (*19*), that both acids and bases are adsorbed irreversibly over alumina. The second postulate is also not valid because, as can be seen in Figs. 2–6, the activity falls during the passage of poison, which means that the poison affects active sites. Therefore, it may be inferred that the acids and the bases can be adsorbed on the active sites of the surface, but the alcohol is capable of displacing them, or transferring them to sites catalytically inactive, from where they can be desorbed when temperature is increased.

The alcohol and both the base and the acid adsorb on the acid–base pair of alumina and between them there is established an adsorption equilibrium which depends on the individual adsorption constants. The poisoning action of bases and acids is due to the competing action for the sites of the acid–base pair.

When after adsorbing methanol, pure carrier gas is used, part of the methanol desorbs but some remains attached to the alumina surface. Nevertheless, when a stream of *n*-butylamine or acetic acid is passed, more methanol is desorbed. This fact can be explained by supposing that there is some form of molecular interaction at the surface of alumina. During passage of methanol vapors, a greater part of the alumina surface is covered with it and a gas-surface equilibrium is maintained. The activation energy of adsorption is small and because of the small heat of adsorption at high surface coverage, the desorption activation energy is also small. When no more methanol vapor is passed, it desorbs and the surface covering diminishes. The methanol passes to a lower energy level requiring a higher activation energy for desorption and consequently the desorption process practically stops. When new molecules of the same or another alcohol, or of an acid or a base, reach the surface they adsorb and increasing the surface coverage they raise the energy level of the preadsorbed molecules. Adsorption–desorption equilibrium is again attained and so methanol can now desorb. The same effect is observed when methanol is passed after adsorbing and desorbing *n*-butylamine or acetic acid. This behavior is typical of a homogeneous surface with interaction between the adsorbed substances, and is similar to that found by Weber and Laidler (*20*) for metals.

This concept of a homogeneous surface with interaction would also explain the results of Kishi, Ogawa, and Hirota (*21*) for the case of formic acid over nickel and the observations made by Knözinger: water irreversibly adsorbed on alumina is partially displaced by ethanol, ethanol irreversibly adsorbed is displaced by water (*22*), and also, water and pyridine can displace each other (*17*).

Neither superficial heterogeneity nor homogeneity with interaction can totally explain the behavior of alumina. Measurement of acidity by titration (Table 1) and the variations of heats of adsorption (*3*) indicate that sites with very different acid strengths exist. The fact that *n*-butylamine or acetic acid both remain after methanol is passed for a long time, indicates heterogeneity, i.e., there are sites on which no interchange with methanol takes place. This would indicate that some of the surface adsorbs the poison irreversibly: such sites would not be active in the dehydration of methanol and would be on these, that the poison adsorbs with a significant decrease of energy. When methanol was first passed followed by *n*-butylamine for a period of ten minutes, the amine was not able to cover all the very strong acid sites: however it does cover them when it is passed over a bare alumina surface.

Kummer and Emmett (*23*) observed similar behavior when adsorbing carbon monoxide on iron catalysts. They found that 50% of the surface behaved homogeneously with interaction between the adsorbed molecules, and that the other 50% retained the monoxide which was first adsorbed, without later exchange with new carbon monoxide molecules.

In conclusion, it may be said that the surface of alumina is heterogeneous but that the active sites for the dehydration of methanol in great part behave homogeneously; and that an interaction exists between the adsorbed molecules.

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