JOURNAL OF CATALYSIS 21, 70–77 (1971)

Acid Strength of the Active Sites on Silica-Alumina Catalyst for Cracking of Cumene, Dehydration of Methanol and Methylation of Methylaniline Studied by the Poisoning Technique

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Received May 19, 1970

The active sites on a silica-alumina (13% Al_2O_3) catalyst were studied to obtain information on which to base predictions of catalytic activity. The poisoning technique was used with three different reactions: cracking of cumene at 350°C, dehydration of methanol, and methylation of methylaniline at 230°C. In catalysts poisoned with NaOH the activity for methylation is proportional to the total Hammett acidity. Cracking activity is proportional to the acidity stronger in equivalence than 72% H_2SO_4; dehydration requires the presence of even stronger acid sites. More basic reactants need weaker acid sites. The elimination of acidity with *n*-butylamine at reaction temperatures is highly selective. The decrease of activity during poisoning follows the decrease of acidity.

INTRODUCTION

Knowledge of the active sites of a catalyst for a given reaction and of substances which destroy the activity of these sites is very important for industrial application of heterogeneous catalysis. From such studies it may be possible, first, to predict catalytic activity for catalysts of the same type and secondly, to obtain information about the poisons which either diminish the activity and/or modify the selectivity of the catalyst. The last International Congress on Catalysis (Moscow, 1968) had as the main subject the prediction of catalytic activity, and it was shown that the problem is far from being solved.

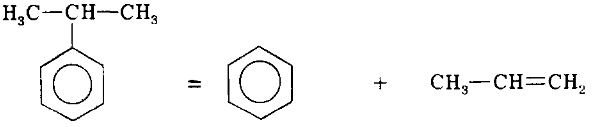
The technique of destroying or modifying the activity of catalysts by poisoning and then observing how other properties are changed is very useful in studying the active sites and in shedding light on the phenomenon of poisoning. This technique is applied in the present work to the study of silica-alumina catalyst in three different reactions: dehydration of methanol, cracking of cumene and methylation of methylaniline.

It is a known fact that the active sites of silica-alumina have acid nature, and the alkalies and organic nitrogen bases react with them and cause poisoning of the catalytic activity. The three named reactions are typical ones catalyzed by acid materials and, as they are quite different, they may require active sites of different acid strength.

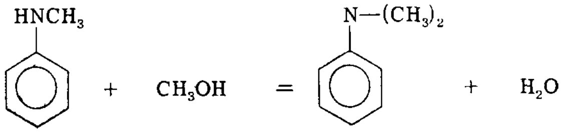
Reactions Studied and Measure of Activity

The three reactions studied were the following: see top of page 71.

The conversion in reactions 1 and 2 was determined by measuring gas-flow rate in the reactor effluent. Since there are no gas products formed other than those shown in the reactions this gives a direct measure of conversion, which was checked by chromatographic analysis of the liquid product. As the conversions for reactions 1 and 2 were small, they were taken as a measure



$$2\,CH_3OH = (CH_3)_2O + H_2O$$



of catalytic activity. For reaction 3 the conversion was not low; nevertheless, it was used to evaluate the catalyst activity because it varies in a manner similar to that of the kinetic constant in the rate equation (*1*).

Catalysts

Houdry S-90 silica-alumina was used. The cylindrical pellets were ground and the 40–80 mesh fraction used. The specific surface area of the activated catalyst, determined by adsorbing N_2 by the flow method, was 370 m^2/g and the pore volume by the water–mercury method, was 0.64 cm^3/g.

To obtain catalysts poisoned with NaOH, the fresh catalyst was impregnated with alkali solutions of several concentrations (0–5 *N*). The volume of solution employed was enough to fill all the pores, plus 5% in excess. After 24 hr the catalyst was dried at 120°C, and before use it was calcined in the usual way.

Reactants

The methanol was ERBA (>99.9%). The methylaniline was BDH (>99%), previously distilled in vacuum and kept in an inert atmosphere at 0°C in the absence of light. The cumene was BDH and infrared and chemical analysis showed that it did not contain hydroperoxide. The methanol–methylaniline molar ratio in the mixture for reaction 3 was 2:1.

Catalyst Acidity

Catalyst acidity was determined in the catalyst, previously heated to 500°C, by titrating at room temperature with a 0.1 *N* solution of *n*-butylamine in benzene, as described previously (*2*). A series of Hammett indicators (H_0 acidity) were used. The milliequivalents of *n*-butylamine used per g-catalyst up to the indicators color change was taken as the acidity stronger than that corresponding to the color-change point. The acid strength at each point on the scale is expressed as equivalent to the concentration of an aqueous solution of H_2SO_4 with the same pK_a (*2*).

The acidity titration method has some difficulties because of uncertainties in the end points and in the interpretation of the kind of acidity. Nevertheless, it is an easy way to follow the acidity variation and the acid strength distribution. Some authors state that the H_0 is a measure of the total acidity (*3*). The H_R acidity according to Hirschler (*4*) is protonic and according to Covini, Fattore and Giordano (*5*) is aprotonic. A recent paper (*6*) that refers to H_R stated that "evidently, adsorption-indicators titrations do not unambiguously distinguish between Brönsted and Lewis sites." Finally, it must be remembered that the acidity is measured on the bare surface and at room temperature, but at reaction conditions one kind of acidity may be transformed into the other form.

Both kinds of indicators give values of acidity that can be compared with the catalytic activity; the one which proportionally fits better can be used as an index without meaning a particular kind of acidity. In this work the H_0 indicators were used because the experimental determinations are more accurate than when using the H_R, and the H_0 are more easily avail-

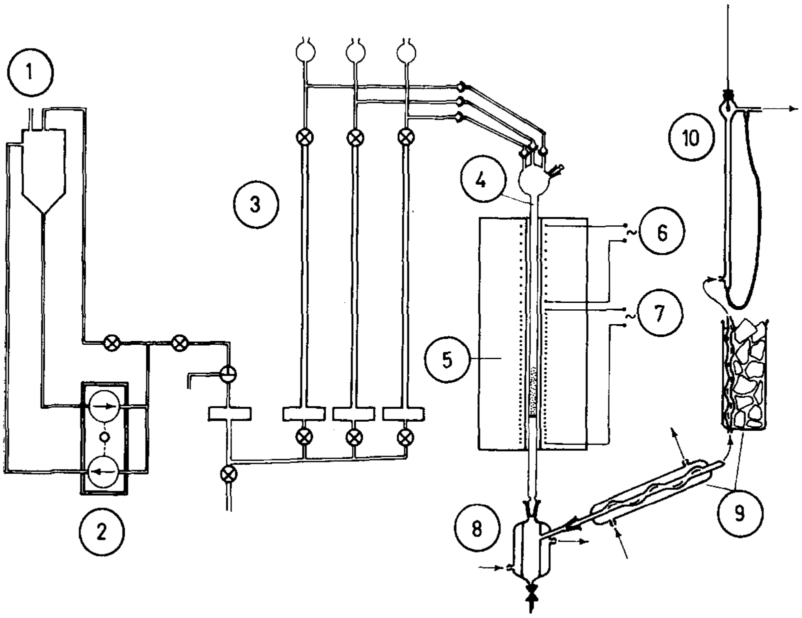


FIG. 1. Diagram of the equipment: 1, oil reservoir; 2, two gear Zenith pump; 3, feeding burettes; 4, reactor; 5, oven; 6, preheating-vaporization zone; 7, reaction zone; 8, liquid collector; 9, condenser; 10, soap-film gas-meter.

able. The H_0 acidity is taken as an index number for comparison of the acid strength distribution of the different catalysts with the catalytic activity.

Equipment for Determination of Catalytic Activity

The equipment used is shown in Fig. 1 and provided continuous operation. A constant flow rate was attained by means of two gear pumps (Zenith, Model QF) connected in differential form. Oil was pumped to displace mercury, which in turn displaced the reactants, feeding them to the reactor from one of three available burettes. The reactor employed was the same for the three reactions and had a preheating and a reaction zone. The temperature of the preheating zone was manually controlled and that of the reaction zone was monitored by a proportional controller. The products were condensed in a thermostatically controlled condenser to minimize solution of the gaseous products of reactions 1 and 2. In reactions 1 and 3, the condenser was used to collect product samples which were then analyzed by gas chromatography. Following this condenser was a second one kept at 0°C, from which the gases passed to a soap-film flowmeter.

Working Conditions

The catalyst was activated in the reactor for 4 hr at 500 ± 2°C using a stream of dry air, and then cooled to the reaction temperature in a stream of dry nitrogen. All the reactions were studied with a W/F value equal to 0.30, expressed as (g-catalyst)/(ml feed/hr). The reaction temperatures were 230 ± 1°C for reactions 2 and 3, and 350 ± 1°C for reaction 1. (The catalyst are selective for the reactions at these temperatures.) To minimize effluent gas solubility, the condenser was maintained at 70°C for reaction 1 and at 55°C for reaction 2.

The determinations of activity for the catalysts poisoned with NaOH were carried out 40 min after the run had begun. In the case of poisoning of reactions 1 and 2 with *n*-butylamine, they were carried out after each pulse of poison, when activity remained constant.

Analysis of Products

The gas-flow rate at STP in reactions 1 and 2 was taken as a measure of the activity. For reaction 3 the liquid collected was analyzed chromatographically for dimethylaniline. To check selectivity and conversion of reaction 1, samples of the liquid product were also analyzed. For both liquid analysis a 810 Perkin-Elmer gas chromatograph was used, with the flame ionization detector and a 0.6 cm × 3 m column of Triton 101 + 10% NaOH on 60–80 mesh Chromosorb P.

CATALYSTS POISONED WITH NAOH

Acidity Distribution

For the different catalysts obtained by impregnation with NaOH solutions the values of H_0 acidity stronger than those equivalent to 90% and 72% H_2SO_4 are close to each other, as is the case for the values of acidity stronger than 48% and than 3×10^{-4}% H_2SO_4. The last indicator is the weakest; therefore the acidity measured with it can be considered as the total. We can divide acidity into two zones: strong H_0 acidity, i.e., greater than 72% H_2SO_4, and weak H_0 acidity, of strength between 72% and 3×10^{-4}% H_2SO_4.

The acid strength distributions are shown in Fig. 3, and in Fig. 2 the total, weak, and strong acidity are shown. It can be seen that when a small amount of NaOH is added (up to 0.30 meq/g), there is a sharp fall in the strong H_0 acidity. At the same time the weak acidity increases, keeping the total acidity constant. This weakening of the acid sites by the alkali has already been cited by Hirschler (*4*).

When the amount of NaOH added is between 0.30 and 1.30 meq/g the decrease of strong acidity continues and the increase of weak acidity is correspondingly smaller, resulting in a fall of the total acidity. With more than 1.30 meq/g the strong acidity is zero, and the addition of more alkali produces a large fall in the weak acidity until it is finally destroyed.

The amount of NaOH necessary to eliminate the acidity stronger than 90% H_2SO_4 is greater than the value of this acidity measured with *n*-butylamine at room temperature. This might indicate that the NaOH does not adsorb in a very selective manner; part of it goes to sites which are not acidic. Also this could be explained as some part of the alkali producing a weakening of the acid sites, but keeping their strength between the ones of the same indicators. Then, according to our method of measuring the acidity, this part of the alkali does not produce any noticeable change on acidity or acid strength.

There is no replacement of a surface proton by a sodium ion (7); this ion attaches itself to the surface in such a way that it reduces the acid strength. Upon adding more sodium, the weakening process continues until all the acidity is destroyed.

Catalytic Activity

By impregnation with NaOH, catalysts of quite different acidity distributions were

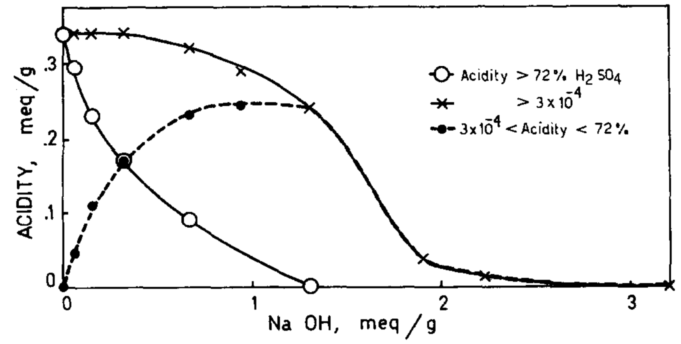


FIG. 2. Modification of the H_0 acid strength distribution as a function of the NaOH concentration on the silica-alumina.

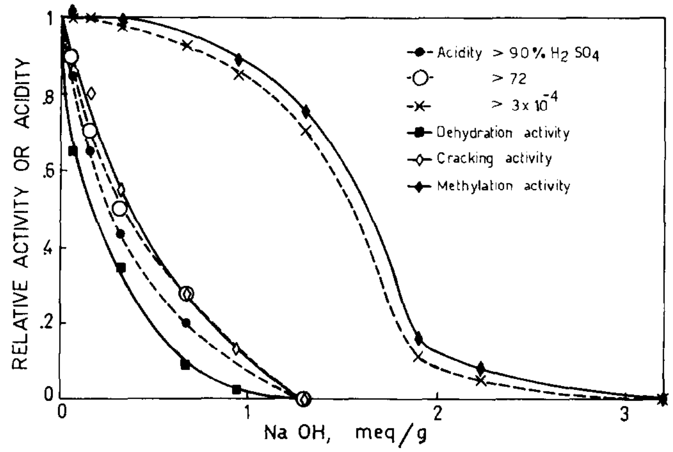


FIG. 3. Relative acidities and relative activities of the catalysts poisoned with NaOH as a function of the poison concentration.

obtained. It is possible that they have different catalytic activities in the reactions under study, depending on which is the active zone for the reaction. Independent runs were therefore carried out with each catalyst to determine the activity for each reaction.

Figure 3 shows the activity, plotted together with the H_0 acidity, as a function of the amount of NaOH on each catalyst. The relative activity and relative acidity of each catalyst are taken with reference to the values corresponding to the unpoisoned catalyst. NaOH by itself is inactive; by impregnating silica gel with NaOH solutions, inactive materials were obtained.

It can be seen that the activity for cracking of cumene follows the same variation as the acidity stronger than 72% H_2SO_4. The activity for the dehydration of methanol falls more rapidly than the acidity stronger than 90%, so it must require still stronger acid sites. The activity for methylation is nearly the same for the catalyst with 0–0.30 meq/g, even though in this region the stronger acidity decreases to a low value and the weak acidity rapidly increases. For catalysts dosed with higher levels of NaOH, the activity falls in a manner similar to that of the total acidity (stronger than $3 \times 10^{-4}\%$ H_2SO_4), from which it is inferred that the methylation reaction is related to all the acid sites.

The results can be explained taking into account the basidity of the reactants: methylaniline is a strong base and will be adsorbed in an activated form on all the acid sites, weak or strong; cumene is less basic and requires sites stronger than 72% H_2SO_4 to be adsorbed in an activated form; and methanol, which is a very weak base, will be adsorbed in an activated state only on very strong acid sites. This is in accordance with the ideas of Taylor as long ago as 1925 (*8*): "The amount of surface which is catalytically active is determined by the reaction catalyzed."

According to the acidity titrations, the surface of the original catalyst is heterogeneous in terms of acid strength; but only with the observation of the decay of activity as a function of the amount of poison added, it is not possible to obtain information on the heterogeneity of the original catalyst regarding its catalytic activity. This is so because the poison changes the distribution of the acid strength. In other words, it produces an induced heterogeneity, and the drop of acidity is not linear with the amount of poison added.

The nearly proportional relation between activity for a given reaction and acidity greater than a determined value would indicate that for that reaction all the sites are equally active and that only an acid strength greater than a certain value is required. Truly this correlation does not necessarily imply that the surface sites are at the same time acid and active. Both properties may correspond to different surface sites that are proportionally related in the different catalysts because they are destroyed by the poison in the same way. As for methylation of methylaniline, the activity is related to the total acidity, weak or strong; perhaps methylaniline weakens the strong sites, and during the reaction all the sites are weak and have the same activity.

Some authors (*4*, *5*, *9*) reported that H_0 acidity does not correlate with cracking activity and found that H_R acidity does better. Topchieva and Rosolovskaya (*10*) used H_0 indicators and quoted that acid sites of medium acid strength (72%–90% H_2SO_4) are the active ones.

POISONING WITH *n*-BUTYLAMINE

Acidity

After catalyst activation, dry nitrogen was passed over the catalyst at the temperature of the reaction (230 or 350°C), and pulses of *n*-butylamine were injected with a syringe at the reactor inlet. After each pulse, nitrogen was passed for 30 min, and then the catalyst bed was well mixed and samples were taken to determine acidity.

Figure 4 shows the acidity distribution as a function of the amount of *n*-butylamine added to the catalyst at 230°C. After the first injection the catalyst did not give an acid color with the indicator which changes at 90% H_2SO_4. As with NaOH, the strong acidity falls rapidly, but the increase of weak acidity is of a smaller magnitude. After adding 0.3 meq/g of *n*-butylamine new additions affect the acidity little. Possibly the base is not adsorbed because of the very small contact time of the pulses and the high activation energy of adsorption at certain sites. This should make the adsorption on them very slow at this temperature, and most of the amine could be taken out by the carrier gas.

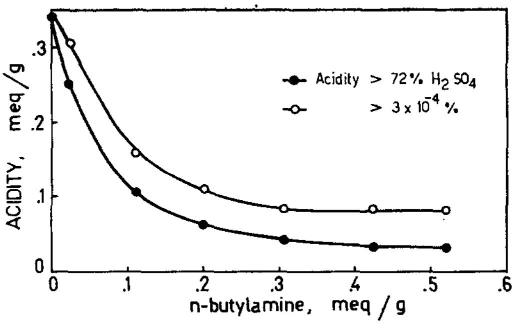


FIG. 4. Acid strength distribution as a function of the amount of *n*-butylamine added to the catalyst at 230°C.

The first addition of *n*-butylamine at 230°C caused a fall of acidity, measured at room temperature, greater than the amount of base added. At high temperature the adsorption will be more selective than during titration; alternatively the type of bond formed at high temperature may lead one base molecule to act over several acid sites, thus decreasing the acidity more than at room temperature. At both temperatures the weak acidity is little affected even after addition of great amounts of *n*-butylamine. This could be caused by the displacement of the adsorption equilibrium by temperature on the weak sites.

At 350°C (see Fig. 5) only 0.14 meq/g are required for the catalyst not to give an acid color with the indicator of strength equivalent to 72% H_2SO_4 (while at room temperature 0.34 meq/g are necessary to attain the same effect). At 350°C this strong acidity can be totally cancelled by adsorption of *n*-butylamine; probably at this temperature there is no kinetic limitation, and the adsorption is fast enough to adsorb the base on all the strong acid sites in the small contact time. In some of the experiments at 350°C the acidity stronger than 72% H_2SO_4 was not totally destroyed, or it was zero when titrated immediately after the addition of the poison and later recovered part of the value.

The difference between poisoning with NaOH and *n*-butylamine may be due to the different methods of addition. All the NaOH added remains on the catalyst but part of each pulse of *n*-butylamine vapor may not be adsorbed, being taken out by the carrier gas.

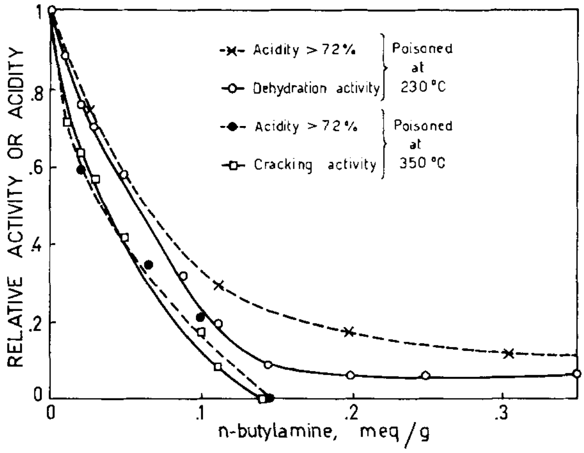


FIG. 5. Relative acidities stronger than 72% and relative activities for cumene cracking at 350°C and methanol dehydration at 230°C, as a function of the amount of *n*-butylamine added at corresponding temperature.

Catalytic Activity

The effect of *n*-butylamine on catalytic activity was investigated by carrying out standard runs and injecting pulses of the base. Figure 5 compares the fall of activities with that of strong acidities. The activity for the cracking of cumene has an analogous behavior to that found when poisoning with NaOH; it follows the same curve as that for acidity stronger than 72% H_2SO_4. The activity for dehydration of methanol falls more markedly than this acidity, but it is not zero although, the catalysts in the acidity measurement experiments do not give values stronger than 90% H_2SO_4.

To see if the reason for this disagreement with the NaOH poisoning is because the surface was covered with methanol prior to poisoning, 0.06 meq/g of *n*-butylamine were added to the catalyst before the run. Passing methanol, it was found that dehydration activity was completely destroyed. In another experiment the run was started and later the 0.06 meq/g were added with the activity falling to half of the original, in agreement with Fig. 5. The *n*-butylamine in the pulses is not able to displace methanol from all the active sites; this depends on contact time.

For the same reason the fall of activity for methylation cannot be verified by the pulse method with *n*-butylamine because methylaniline and dimethylaniline are stronger bases than methanol and have a high boiling point. Therefore it is more difficult for the *n*-butylamine to displace them from the surface, and the poisoning which it produces is much less than the decay of total acidity obtained when injecting the pulses on the catalyst without preadsorbed substances.

In agreement with NaOH poisoning, the activity for cracking of cumene is related to the acidity stronger than 72% H_2SO_4. This is because at 350°C little cumene is adsorbed on the catalyst; so, the *n*-butylamine is able to reduce the acidity and activity of the catalyst during the cracking in the same way as it is able to reduce the acidity of the bare surface. Although in some cases the acidity stronger than 72% H_2SO_4 did not reach zero, it remained with a small value, while the cracking activity always went to zero.

CONCLUSIONS

The poisoning of silica-alumina by impregnation with solutions of NaOH is different to that produced by adsorption of vapors of *n*-butylamine. NaOH first transforms strong acidity into a weak form and then continues its action on the weak acidity until neutralization is complete. Butylamine destroys the strong acidity and the weak one which appears remains unaltered. But for both types of poisoning, the catalytic activity follows the modification of the acidity, and the strength of the acid sites required for each reaction is a function of the reactants basidity. A small addition of poison modifies in a very different way the catalytic activities for the three reactions, and it seems that all the active sites for one particular reaction have the same activity.

A silica-alumina with high total acidity, be it strong or weak, will be good for methylaniline methylation, but it will require a high proportion of strong acidity to show high activity for methanol dehydration or cumene cracking.

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