

## Active Sites and Mechanisms of Dehydration of Methanol and Methylation of Methylaniline on Alumina and on Silica-Alumina

J. M. PARERA AND N. S. FIGOLI

*From the Facultad de Ingeniería Química, Santa Fe, Argentina*

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The active sites of alumina and silica-alumina catalysts for the dehydration of methanol, as well as the mechanisms of this reaction, were studied in a flow system at 228°C by poisoning the catalyst during the run with nitrogen bases. On alumina, methanol dissociates upon adsorption on the Lewis acid sites, and the random combination of surface groups gives the dimethyl ether. Poisons also adsorb and dissociate reversibly, and their poisoning action is caused by their strong adsorption on the acid sites, in competition with methanol. On silica-alumina protonic sites are involved and the nitrogen bases are irreversible poisons, because they form stable quaternary ions with the proton.

In the methylation of methylaniline, under the same working conditions as those of the methanol dehydration, the same active sites are involved and the mechanisms are also similar. For methylation, relatively weaker acid sites are necessary, and they are not poisoned by nitrogen bases.

The dehydration of alcohols and the alkylation of amines can be carried out by heterogeneous catalysis, using solid acids as catalysts and reactants in gaseous phase.

The dehydration of alcohols has been studied for many years. The two complete surveys published on the mechanism (1, 2) refer to alumina. Most authors have worked on the dehydration of ethanol on this catalyst, which gives diethyl ether and ethylene. Some of them propose the formation of a carbonium ion (3), others establish that dehydration takes place through a concerted mechanism in which an acid and a basic site take part (4), and Arai *et al.* show that surface ethoxide groups are formed as intermediates (5).

Particularly in the dehydration of methanol to give dimethyl ether, alumina (6, 7, 8), silica-alumina (8), and ion-exchange resins (9) have been used. For this reaction on alumina Jain and Pillai (7) proposed the concerted mechanism,

suitably adapted to the case. For the methylation of methylaniline, alumina and silica-alumina (10) have been used, the latter being the most active and selective catalyst.

This paper deals with the active sites on alumina and on silica-alumina for the dehydration of methanol and the methylation of methylaniline. They are studied by poisoning the catalyst with bases. Reaction mechanisms on the assumed sites are proposed.

### EXPERIMENTAL

#### *Apparatus and Procedure*

The catalytic activity was determined by performing standard runs at 228°C and 1 atm in the apparatus shown in Fig. 1.

Methanol leaves the calibrated constant head flask at a constant rate, which is regulated by a capillary resistance immersed in an ice bath. It is vaporized in a methyl salicylate boiling bath and

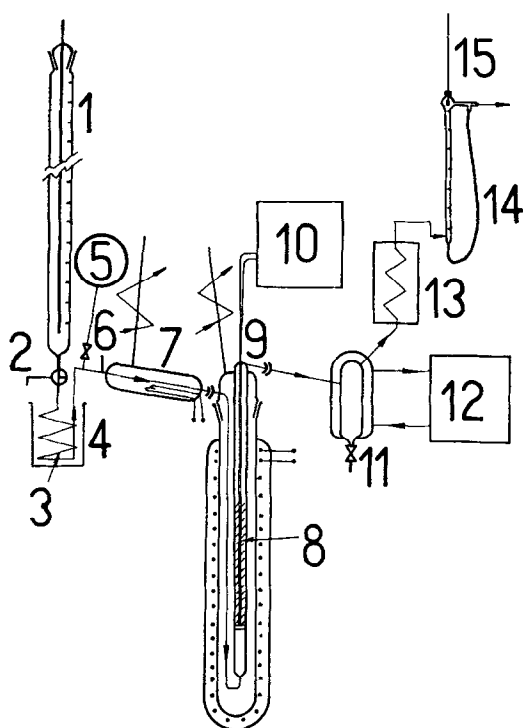


FIG. 1. Experimental apparatus: 1, constant head flask; 2, three-way stopcock; 3, capillary resistance; 4, ice bath; 5, nitrogen cylinder; 6, septum for syringe injections; 7, vaporizer; 8, reactor; 9, iron-constantan thermocouple; 10, potentiometer; 11, liquid condenser; 12, thermostatic bath; 13, ice bath; 14, soap-film flow meter; 15, mercury thermometer.

passes through the catalyst placed in the reactor tube (13-mm internal diameter), which is surrounded by boiling methyl salicylate. The temperature in the catalyst mass is measured with an iron-constantan thermocouple connected to a potentiometer. The effluent from the reactor goes to a

condenser heated to 56°C to decrease the solubility of dimethyl ether in the collected liquid mixture. The gaseous product passes through an ice bath refrigerator and then is measured in a soap-film flow meter.

Before the run, the catalyst was pretreated in the reactor by heating at 480°C during 6 hr in a dry air stream. It was cooled and kept in a nitrogen atmosphere. For this pretreatment the methyl salicylate bath was replaced by an oven.

#### Analysis

To study the methylation of methylaniline the liquid products were analyzed by gas chromatography for the mixture methylaniline-dimethylaniline. A flame-ionization detector was used and a 3-m by 1/4 inch column of Chromosorb P 30-60 mesh impregnated with a 20% mixture of 5% KOH in Dowfax 9N9.

For the dehydration of methanol, the activity was found by measuring the amount of gas (dimethyl ether) produced per unit time.

#### Catalysts

Four commercial catalysts were used; their acid strength distributions are listed in Table 1. The A T-126 catalyst is a pelleted  $\gamma$ -alumina (Girdler Catalyst, surface area 210 m<sup>2</sup>/g). The A 992 is a pelleted  $\eta$ -alumina (W. R. Grace & Co., surface area 222 m<sup>2</sup>/g). The S-A 980 is a pelleted silica-alumina with 13% alumina (W. R. Grace & Co., surface area 364 m<sup>2</sup>/g). The S-A Sy is a microspheroidal

TABLE 1  
ACID STRENGTH DISTRIBUTION

Catalyst	H <sub>0</sub> , pK <sub>a</sub>					H <sub>R</sub> , pK <sub>a</sub>		
	-8.3	-5.6	-3.0	+1.4	+3.3	-16.27	-13.3	-6.63
A T-126	0.12	0.18	0.21	0.21	0.24	0	0	0
A 992	0.12	0.12	0.17	0.17	0.19	0	0	0
S-A 980	0.32	0.32	0.34	0.34	0.45	0.07	0.30	0.33
S-A Sy	0.27	0.27	0.43	0.43	0.43	0.18	0.18	0.33
S-A 980 + NaOH	0.20	0.20	0.27	0.27	0.27	0	0.04	0.20
S-A Sy + NH <sub>3</sub>	0	0	0.25	0.25	0.25	0	0	0
A 992 + NaOH	0	0	0	0.02	0.02	0	0	0

silica-alumina with 13% alumina (Synclyst, J. Crosfield & Sons Ltd, surface area 460 m<sup>2</sup>/g). The pelleted catalysts were ground and the 50- to 60-mesh fraction was used. The microspheroidal catalyst was tableted and then ground and sieved.

**Surface area.** The BET surface area was measured at liquid nitrogen temperature by the flow method. The catalyst was degassed by the same procedure as that used in the pretreatment.

**Acid strength distribution.** The measurement of the acid strength distribution was carried out by dosing with a 0.1 *N* benzene solution of *n*-butylamine. About 0.1 g of 100–200 mesh catalyst was heated in the same way as in the pretreatment, then cooled and kept in a nitrogen atmosphere until the titration was performed. The indicators are shown in Table 2. They were commercial products, except the 4,4',4'' trinitrotriphenylmethanol, which was prepared by the procedure of Covini, Fattore, and Giordano (11).

TABLE 2  
p*K*<sub>a</sub> AND ACID STRENGTH OF AN AQUEOUS  
SO<sub>4</sub>H<sub>2</sub> SOLUTION EQUIVALENT TO THE  
INDICATORS USED

Indicator	p <i>K</i> <sub>a</sub>	H <sub>2</sub> SO <sub>4</sub> (wt %)
<b>H<sub>0</sub></b>		
Anthraquinone	-8.3	90
Chalcone	-5.6	72
Dicinnamalacetone	-3.0	48
Benzeneazodiphenylamine	+1.4	0.02
Butter yellow	+3.3	3 × 10 <sup>-4</sup>
<b>H<sub>R</sub></b>		
4,4',4''-Trinitrotriphenyl- methanol	-16.27	88
Diphenylmethanol	-13.3	77
Triphenylmethanol	-6.63	50

In the same pretreatment flask, a 0.2% benzene solution of the H<sub>0</sub> indicator (Hammet indicator) of lower p*K*<sub>a</sub> is added. Then, dropwise, the 0.1 *N* benzene solution of butylamine is added with constant agitation by a magnetic stirrer until the neutralization of the indicator. The indicators of larger p*K*<sub>a</sub> shown in Table 2 are then successively added and titrated. To check

the results, anthraquinone and chalcone are titrated separately, and in another sample, the other three H<sub>0</sub> indicators.

The H<sub>R</sub> indicators (carbonium ion indicators) are used independently one from another. Each determination is finished in approximately 24 hr. No interference between indicators in the successive titrations was found. The acidity is expressed in milliequivalents per gram of catalyst stronger than p*K*<sub>a</sub> given in Table 1.

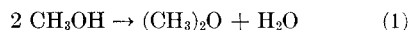
**Pretreatment with ammonia and NaOH.** The treatment of silica-alumina with ammonia was carried out by heating the pretreated catalyst to the temperature at which the run was to be made, then passing an ammonia stream for 5 min and finally nitrogen for 4 hr at the same temperature. The treatment with sodium hydroxide was carried out by impregnating the catalyst with a 1 *N* water solution, using the necessary amount to fill the pores with liquid. After standing overnight, the material was dried at 120°C and heated in the same way as in the pretreatment.

### Reagents

All the reactants, poisons, indicators, and gases were pure grade and were used without further purification.

### DEHYDRATION OF METHANOL

On alumina and silica-alumina, this is a clean reaction, and under the working conditions used (228–229°C) only the dehydration of methanol takes place:



Runs were carried out with each of the four catalysts. Each run began by feeding methanol during 2 hr, then displacing the alcohol with a stream of nitrogen, injecting 10 ml of a liquid base (pyrrole, methyl-aniline, dimethylaniline, quinoline, pyridine, piperidine, or diethylamine), purging with nitrogen, and finally passing methanol again to check the activity. All the bases irreversibly poisoned the silica-alumina, but they did not affect the alumina, which, after the base treatment, regained all, or nearly all, its original activity. The same

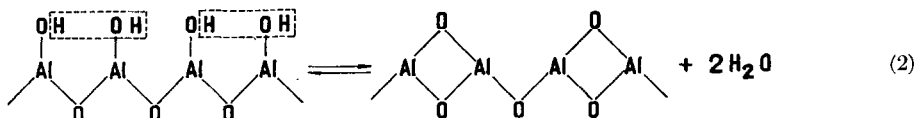
behavior was found on passing a stream of gaseous methylamine or ammonia instead of injecting a liquid base.

To study the progressive poisoning, several runs were made injecting a 0.1 *N* benzene solution of a base in the vaporizer inlet. This was done several times during the run using a syringe. Figure 2 shows a run with alumina and one with silica-alumina and dimethylaniline as basic poison. For simplicity, the catalytic activity is taken equal to the amount of gas (dimethyl ether) formed. As can be seen, the poisoning on alumina is reversible, while on silica-alumina it is irreversible. With the other catalysts and bases the behavior was similar.

#### Active Sites and Mechanism on Alumina Catalyst

Figure 2 shows that the alumina is poisoned reversibly by the nitrogen bases. To clarify this point further, the run of Fig. 3 was carried out, passing over the catalyst dilute solutions of diethylamine in methanol. The dehydrating activity drops, according to the partial pressure of the base, but a great part of the initial activity is restored when the input of base into the feed ceases. This behavior can be explained according to the structure and properties of the activated alumina proposed by Peri (12), which we adopt for the active sites and mechanism.

The activated alumina only has a Lewis type acidity. According to Peri (12) this acidity is formed during the dehydration of the surface of the hydrated alumina. The activated alumina formed can be rehydrated by dissociation of the water molecule in H and OH. Thus, the chemistry of the activated alumina may be considered as the rupture of the water molecule with reversible formation of surface OH [Eq. (2)].



It is here assumed that there is a similar behavior with the methanol molecule; this

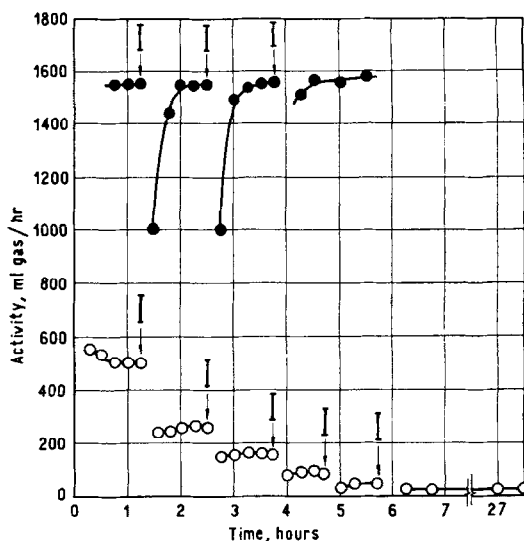
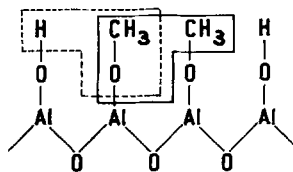


Fig. 2. Progressive poisoning of the catalysts for dehydration of methanol; dimethyl ether vs. time. I, injection of 0.5 ml of 0.1 *N* benzene solution of dimethylaniline; temperature, 228°C; ●, catalyst 7.5 g A T-126, feed 7 ml/hr; ○, catalyst 3 g S-A 980, feed 7 ml methanol/hr.

would originate OH and OCH<sub>3</sub> groups on the surface. The random combination of the surface groups may lead to desorption of methanol (shown by dotted line), dimethyl ether (shown by full line), or water:



The formation of the surface aluminum methoxide is in agreement with the fact that, upon adsorption on alumina, alcohols dissociate to form surface alkoxides (13), and with the data of Heiba and Landis (14), who found that aluminum alkoxides

dissociate to give the same products, as does the decomposition of alcohol and

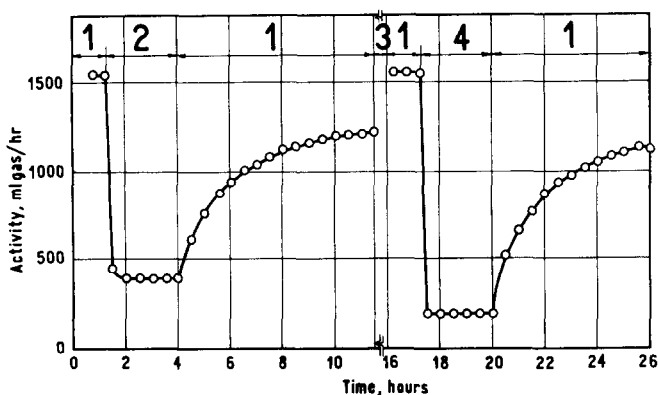


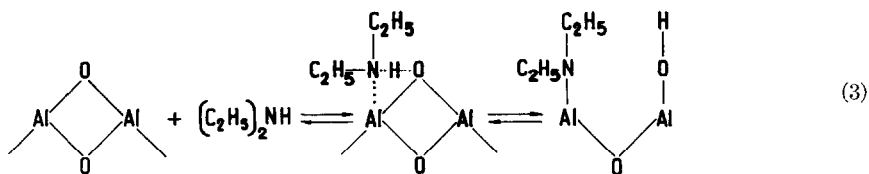
FIG. 3. Poisoning of alumina T-126 for dehydration of methanol. Dimethyl ether vs. time. Catalyst, 7.5 g; feed, 7 ml/hr; temperature, 228°C; 1, pure methanol as feed; 2, 0.5% molar solution of diethylamine in methanol as feed; 3, 100 ml/min air at 480°C; 4, 2% molar diethylamine in methanol as feed.

ether on alumina. Arai, Saito, and Yoneda (15) have also shown, by IR techniques, that, upon adsorption, diethyl ether is dissociated to form two surface ethoxide groups. On the other hand, the mechanism proposed comprises different steps from those described by Jain and Pillai (7), although it also implies "acid-basic" sites.

Regarding the reversible poisoning action of nitrogen bases, it is considered that they dissociate on adsorption on alumina, as Peri found in ammonia (16). For example, with diethylamine it is as shown in Eq. (3).

#### Active Sites and Mechanism on Silica-Alumina Catalyst

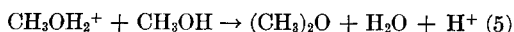
Figure 2 shows that the activity for methanol dehydration on silica-alumina is irreversibly poisoned and is not restored although heated to the working temperature (228°C) during many hours. As the conversion is small the activity is taken as the gas produced. The activity as a function of the amount of poison added drops following approximately an exponential law, similar to the one found in cracking of cumene on silica-alumina (13% Al<sub>2</sub>O<sub>3</sub>)



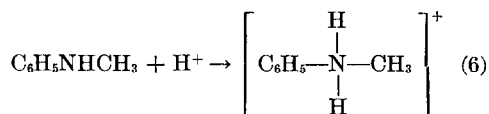
As the nitrogen from the base is more nucleophilic than the oxygen from methanol, its bond with aluminum is much stronger and the base covers a greater percentage of the surface than its molar percentage in the reagents stream. This adsorption on the greater part of the surface is reversible and varies according to the partial pressure of the base. When it is eliminated from the feed, it desorbs, leaving nearly the whole surface again free for the dehydration of methanol.

by Mills, Boedeker, and Oblad (17) and on zeolites by Topchieva *et al.* (18).

The acidity of the silica-alumina is caused by Brönsted and Lewis type centers. The type of poisoning of the dehydrating capacity of silica-alumina is different to the one of alumina, which only has Lewis acidity. It coincides with the poisoning of cumene cracking, a typical reaction catalyzed by Brönsted sites. For this reason it is possible to expect a mechanism involving a proton.



When a nitrogen base is present, it takes the proton irreversibly, forming a quaternary amine ion, in the case of methylaniline as follows:



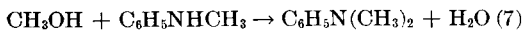
The bond between the base and the surface proton is so strong that the latter is unable to react with methanol according to Eq. (4). At 228°C the bases irreversibly hold the protons that were active in dehydration.

On the Lewis type centers of silica-alumina, located on the aluminum atoms, methanol can adsorb in a similar way as it does on alumina. According to Hirschler (19) the active part of the surface of silica-alumina could consist of a network of alternating silicon and aluminum atoms connected by oxygen bridges. Therefore, there is no formation of neighboring methoxy groups, which are necessary for the ether formation, and this rendered the Lewis sites inactive for this reaction.

Because of the poisoning, the distribution of the acidity of the silica-alumina is modified. Treating with ammonia it was found that the acidity did not disappear, but was weakened, as shown in Table 1. Most of the acidity in the catalyst without poison is stronger than 90%  $\text{H}_2\text{SO}_4$ ; on the other hand, when it is poisoned, strong acidity disappears and weak acidity appears instead. In other words, the poisoning action would be the weakening of strong acid centers. This action of the bases on acidity has already been cited by Hirschler (19).

#### METHYLATION OF METHYLANILINE

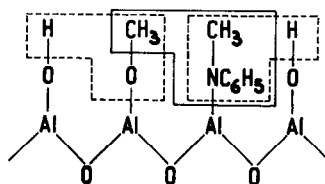
The methylation of methylaniline is a dehydration similar to reaction (3); but it involves one methanol molecule with one of a strong base [poison of reaction (3)], instead of two methanol molecules.



In a former paper (10) it was shown that reaction (7) takes place on alumina and on silica-alumina. On the first, methanol dehydrates, at the same time giving off ether according to Eq. (1). The production of ether is less than that which would correspond to the actual methanol pressure. On silica-alumina, only reaction (7) occurs; the dimethyl ether formed is negligible. Injecting ammonia and the other nitrogen bases during a run, it was found that they do not poison methylation either on alumina or on silica-alumina.

#### Mechanism on Alumina Catalyst

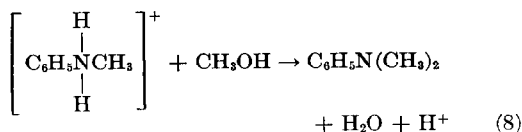
According to what has been said before, alumina presents Lewis sites and its chemistry is based on the dissociation of the molecules upon adsorption and on the random recombination of its parts. When methanol and methylaniline are adsorbed on the surface there are groups which upon desorption can give methanol (dotted line), methylaniline (dotted line), dimethylaniline (full line), or water.



In addition, two methoxy groups can produce ether; this occurs in a small proportion because a great part of the surface is covered by the methylaniline. The poisoning by nitrogen bases is reversible and it is due to a competition for the acid sites.

#### Mechanism on Silica-Alumina Catalyst

During the methylation of methylaniline this base poisons the dehydration of methanol, because it retains protons forming the complex of Eq. (6). This complex may react with methanol, in a way similar to reaction (5), to give dimethylaniline.



The free proton is captured by another methylaniline molecule according to Eq. (6).

Ammonia and the other nitrogen bases do not poison the methylation. This is due to the fact that the action of the poisons is to weaken the strength of the acid sites, and as methylamine is strongly basic, it is able to join a weakened protonic site and react, a thing that methanol cannot do because it is less basic.

#### STRENGTH OF THE ACID SITES

The poisoning action of bases in the dehydration of methanol on alumina would be due to a greater coverage of the acid sites by the bases. These are first adsorbed on the stronger sites and as their vapor pressure increases they are adsorbed on the weaker ones. Most of the active sites are reversibly covered by the diethylamine, but the coverage of the small portion of stronger sites is irreversible at the temperature at which the run is carried out. Heating to a higher temperature is needed to regain all the activity.

Something similar was found by Beranek *et al.* (20) and Pines and Col (4, 21, 22) in the dehydration of alcohols to olefins on alumina. They found two types of acid sites: the relatively strong ones, where isomerization of the olefin and dehydration take place, and which are poisoned irreversibly by the bases; and the relatively weak ones, where dehydration takes place and which are reversibly poisoned.

Upon impregnating alumina with sodium hydroxide, a catalyst with the acidity indicated in Table 1 was obtained. The amount of alkali was enough to cancel all of the dehydrating capacity of the alumina. Because very little methanol can be adsorbed, the possibilities to form ether are a minimum. On the other hand, the adsorption of methylaniline is still great and it reacts with the small amount of methanol present, the catalyst having a methylating activity equal to one-fourth that of the unpoisoned one.

It was stated that in the dehydration of methanol on silica-alumina, the poisoning action of the nitrogen bases consists in

weakening the acid sites. Methanol being a weak base, requires strong acid sites for its chemisorption and dehydration takes place on them. Methylaniline, instead, is a strong base and is strongly adsorbed on these sites, weakening them. In the weak sites existing in the catalyst, or in those formed by the weakening of the strong ones, methanol is not adsorbed. Methylaniline, instead, is adsorbed in a reversible way and they are the active sites for its methylation. This was verified by impregnating silica-alumina with sodium hydroxide. The acidity lowered, as shown in Table 1, and this produced a drop in the dehydrating activity of the catalyst to one-third of its value, while the capacity to methylate methylaniline was not altered.

#### CONCLUSIONS

The dehydration of methanol and the methylation of methylaniline on alumina take place through a mechanism which involves the adsorption and dissociation of the reactants; the recombination of the surface groups gives the products, which are desorbed. The poisoning action of nitrogen bases on dehydration reaction is caused by their greater adsorption equilibrium.

On silica-alumina both reactions take place in the protonic sites, the dehydration requiring strong acid sites. On the other hand, on account of the greater basicity of methylaniline, methylation requires relatively weak acid sites. The poisoning effect of bases in the dehydration of methanol is the result of the effect of their weakening action on the strength of the acid sites.

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