

Effects of Metal Acetate Salts on the Catalytic Cracking of Cumene over Silica-Alumina

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A study was made of the effects of metal acetate salts on the ability of a commercial silica-alumina catalyst to promote the conversion of cumene to benzene and propylene. The typical effect of the salts was to reduce the conversion. The extent of this reduction was determined by the amount, size, valence, and chemical type of the poisoning cation. Graphs of percent conversion versus the area (or volume) of catalyst surface actually covered by poisoning metal ions showed three distinct activity curves with the alkali metals exhibiting greatest, the alkali earth metals poorest, and zinc and cadmium an intermediate poisoning ability. Very small amounts of divalent metal cations showed a small promoting action. Acetic acid had no effect on conversion. The results suggest that cracking occurred on acid sites present in clusters on the catalyst surface and that site blocking and chemical neutralization both contributed to the poisoning of the catalyst.

INTRODUCTION

It is generally accepted that silica-alumina cracking catalysts act through a carbonium ion mechanism. This conclusion is based upon the acidic nature of these catalysts and the fact that they promote a number of reactions that are catalyzed by strong acids at low temperatures. There is disagreement, however, about the types of acid sites involved in the cracking reaction. Cracking activity has been attributed to Bronsted acid sites (1-8), Lewis acid sites (9, 10), Coulomb effects (11), and even to the negative charges on the catalyst surface (12, 13). Recent papers discuss acid properties (3-5, 8, 14, 15) and charge effects (11) as the major factors determining the activity of cracking catalysts. It has been shown that only partially dehydrated forms of catalysts are active in catalytic cracking. Both the completely hydrated and the completely dehydrated catalysts have been found to be inactive (16).

A useful method of studying cracking

catalysts consists of systematic poisoning of active centers by various alkali cations (3, 4, 16, 17, 18). The resulting loss in activity may then be evaluated in terms of the changes in total catalyst acidity, its acid strength distribution, the dimensions of the poisoning cations, and the mechanism of the cracking reaction. The purpose of this work was to make such a study of an amorphous silica-alumina bead catalyst and to establish, if possible, some general relationship between catalyst cracking activity and poisoning cation size, valence, and chemical type. The conversion of cumene was chosen as test reaction because it was known to give a clean reaction on silica-alumina, yielding almost exclusively benzene and propylene (1, 19-22).

EXPERIMENTAL

Cumene (Dow Chemical Company, Midland, Michigan) was purified by distillation. The fraction boiling at 152-153°C was used for the studies described below. Sorbead W, grade H, a commercial silica-

alumina (Socony-Mobil Oil Company, Paulsboro, New Jersey), was used as cracking catalyst. It was obtained in the form of $\frac{1}{8}$ -inch-diameter pellets. Some properties of these pellets, after heat-treating for 16 hr at 600°C to obtain a standard stock material, are shown in Table 1. All catalyst poisons were pure, reagent-grade metal acetate salts. The lithium acetate came from the G. Frederick Smith Chemical Company, Columbus, Ohio. All the other salts were obtained from Mallinckrodt Chemical Works, St. Louis, Missouri.

TABLE 1
PROPERTIES OF CATALYST PELLETS^a

X-ray	Amorphous Structure
Al ₂ O ₃ (%)	10.3
SiO ₂ (%)	86.9
Na ₂ O (%)	0.095
Apparent bulk density (g/cc)	0.87
Water absorption (%)	37
Surface area (m ² /g)	203
Skeletal density (g/cc)	2.29
Pore volume (cc/g):	
0 to 120 Å diameter	0.19
0 to 200 Å diameter	0.20
0 to 350 Å diameter	0.20
0 to 700 Å diameter	0.20
0 to 1000 Å diameter	0.20
0 to 10 000 Å diameter	0.24

^a Poisoning and calcination did not change any measured physical property of the catalyst samples.

The control catalyst sample was prepared by impregnating (23) the stock material with distilled water. The poisoned catalyst samples were prepared by impregnating the stock material with 0.1, 0.3, 0.6, and in some cases 1.2 meq of hydrogen, lithium, sodium, potassium, magnesium, calcium, barium, cadmium, and zinc ions per gram of catalyst. The poisons were added as acetate solutions in distilled water. All impregnations were followed by 24-hr air-drying and then by 12-hr calcination at 580°C to stabilize catalyst activity.

Cracking activity was determined by measuring the conversion of cumene to benzene in a stainless steel reactor containing 30 cc of catalyst at 425°C. Cumene

was pumped to the top of this reactor at an average rate of 2 cc/min. The temperatures of the catalyst samples were held within $425^\circ \pm 2^\circ\text{C}$ during all the valid runs. The temperature gradient across the catalyst bed was $3^\circ\text{--}5^\circ\text{C}$.

Percent conversion was calculated for benzene from gas chromatographic analysis of the liquid reaction products, and for propylene from the amount of gas evolved in the reaction assuming that this gas was 100% propylene and behaved ideally. Good checks were obtained. The data presented here were calculated from analyses of the liquid reaction products assuming that these products contained benzene and cumene exclusively. Conversion was plotted as a function of equivalent area or volume in order to compensate for the differing valences of the poisoning cations. Overall precision of the experiments was $\pm 1.5\%$.

RESULTS

Cracking was found to depend on the quantity, size, valence, and type of acetate salt cation with which the catalyst was impregnated. Most metal ions acted as poisons. However, very small amounts of divalent cations were found to promote catalyst activity. Acetic acid had no effect on cumene conversion. These results are tabulated in Table 2 and presented graphically in Fig. 1. No effect of reaction time was found. There was no evidence of thermal cracking in these test attempts.

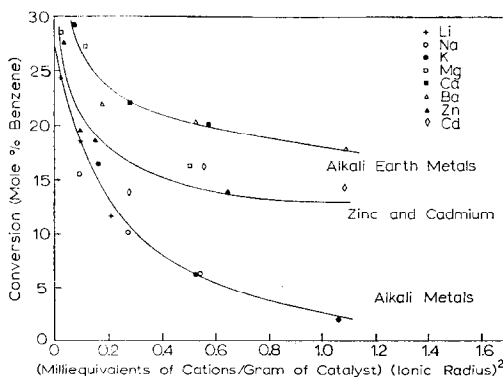


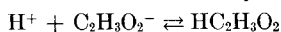
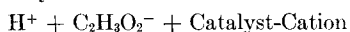
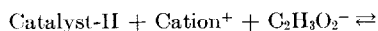
Fig. 1. Dependence of cracking activity on equivalent area of poisoning cations adsorbed on the catalyst surface.

TABLE 2
 SUMMARY OF THE ACTIVITY DATA

Type of sample (meq. poison/g. catalyst)	Ionic radius (Å)	Surface area coverage (m ² /g)	Conversion (mole %)	
			Propylene	Benzene
Control	—	—	25.0	27.2
0.1 H ⁺	—	—	24.4	26.8
0.3	—	—	25.9	26.0
0.6	—	—	24.1	27.1
0.1 Li ⁺	0.60	0.679	20.9	24.2
0.3	—	2.04	19.3	18.4
0.6	—	4.08	8.2	11.7
0.1 Na ⁺	0.95	1.71	13.7	15.7
0.3	—	5.13	7.7	10.4
0.6	—	10.3	5.5	6.5
0.1 K ⁺	1.33	3.34	14.7	16.6
0.3	—	10.0	4.6	6.1
0.6	—	20.0	3.0	1.8
0.1 Mg ²⁺	0.65	0.40	25.2	28.3
0.3	—	1.20	24.5	27.3
1.2	—	4.80	17.0	16.5
0.1 Ca ²⁺	0.99	0.924	26.0	29.1
0.3	—	2.77	20.7	22.0
0.6	—	5.54	21.4	20.1
0.1 Ba ²⁺	1.35	1.72	21.0	22.2
0.3	—	5.16	18.4	20.3
0.6	—	10.3	14.8	17.8
0.1 Zn ²⁺	0.74	0.52	30.0	27.6
0.2	—	1.04	19.7	19.6
0.3	—	1.56	19.5	18.5
0.6	—	3.12	21.3	15.8
1.2	—	6.24	15.1	14.1
0.3 Cd ²⁺	0.97	2.66	19.1	13.8
0.6	—	5.31	20.5	16.5
1.2	—	10.62	21.3	14.3

DISCUSSION

Metal acetate salts should react preferentially with Bronsted acid sites (5, 16, 24) and hydrated Lewis acid sites (8, 16). The simplified Bronsted acid interaction with the acetate cation is (24, 25)



It was assumed that exchange would take place on these acid sites in preference to the metal cations simply depositing in the pores of the catalyst. It was also assumed that there could have been hydration of some forms of Lewis acids during the exchange which hydrated forms could also exchange. According to this model, conver-

sion of cumene to benzene and propylene should have been an inverse linear function of the quantity of poison with which the catalyst was treated. Divalent cations should have been twice as effective poisons as monovalent cations, and acetic acid should have had no influence on conversion. Some of these effects were found. However, all cations of similar valence did not behave alike, and the divalent cations inhibited the conversion of cumene less than did the monovalent cations. Cracking activity loss was not a linear function of the amount of poison with which the catalyst was treated.

Considerable order was brought to the results when the sizes of the poisoning cations were taken into account. Thus, the data for catalysts poisoned by the alkali

metal, alkali earth metal, zinc and cadmium, and hydrogen ions fell on four distinct activity curves when conversion was plotted as a function of the equivalent area or volume of cation presumed adsorbed on the catalyst surface. This implies that the poisons functioned not only through chemical interaction with acid sites but also by physical blocking of adjacent, unreacted sites on the catalyst surface.

Two explanations may be offered for the poor poisoning ability of divalent metal cations. First, it has been shown (3, 11, 12, 26, 27) that by exchanging alkali metal ions with alkali earth metal ions, the cracking activity of molecular sieves can be significantly improved. The improvement is generally attributed to asymmetric placement of divalent cations with respect to the neutralized sites, resulting in the creation of both positively and negatively charged centers. These centers are claimed to be responsible for the different effects of monovalent and divalent cations on the cracking activity of these crystalline aluminosilicates and may also be responsible for the differences noted in this work. The second explanation is that of Hirschler (3), who found differences between the effects of alkali and alkali earth metal cations on the cracking activity of both crystalline and amorphous aluminosilicates and suggested that the polarizing action of the poisoning cation may tend to free a proton of a hydroxyl group that is attached to an adjacent aluminum or silicon atom and thus induce acidity on the catalyst surface. The same effect could be obtained by releasing a proton from a water molecule adsorbed on the cation itself. The greater the field strength of the cation, the stronger should be the resultant acidity. Thus, poisoning cations of different valence should have different effects on catalyst cracking activity, as was observed in this work. Hirschler's explanation, or at least the opposing effects on cracking of divalent metal cations, is supported by the results of this, and other (28, 29) studies, which show a promoting action for small amounts of divalent metal ion catalyst "poisons."

The reason why catalyst samples poi-

soned with zinc and cadmium behaved differently than catalyst samples poisoned with the alkali earth metals may possibly be explained in terms of asymmetry and field strength. Zinc and cadmium, like alkali earth metal ions, should react with two catalyst sites. However, the tendency of zinc and cadmium to form covalent bonds may lead to more symmetric location of these cations between the two sites which should result in weaker charge effects, weaker acidity, and weaker catalyst activity. This idea is reinforced by the fact that magnesium, which also had some slight covalent character, showed behavior as a poison midway between that of zinc and cadmium and that of the typical alkali earth metals, calcium and barium.

Catalyst activity decreased sharply in the early stages of the poisoning treatments. Activity loss became less pronounced when larger areas of the catalyst surface were covered by poisons. Previously suggested (16, 18) explanations are based upon the idea that the accessible strong acid sites assumed to contribute most to catalytic cracking are the same sites which, because of their accessibility and acidity, are poisoned first. These explanations are probably correct. However, this work suggests that another important factor is the blocking of one catalytically active site by a metal ion exchanged with another adjacent site. Thus, the data show that 0.6 meq of potassium ions was required to effectively neutralize the cracking activity of one gram of catalyst. This implies that there were approximately 3.6×10^{20} active centers on the surface of 1 g of catalyst. Since the surface area of the catalyst was 200 m²/g, a calculation shows that the average density of active centers was 0.018 center/Å². If these active centers had been randomly distributed, then the size of the poisoning ions should not have had any effect on catalyst activity. However, such a dependency was found, and Table 2 shows that activity was completely destroyed when only 10% of the catalyst surface was covered by potassium ions. The active sites must have been located in clusters on the catalyst surface and these

clusters must have occupied only 20 m² of the 200 m² area of 1 g of catalyst. Calculation shows the average density of active centers in such clusters to be 0.18 center/Å², a very reasonable density to explain the observed effects of poisoning cation size. The exact structure of catalytically active site clusters is as yet undefined, though it is clear that they are regions of some type of local order. Hirschler (30) has suggested that they may be a network of alternating silicon and aluminum atoms connected by oxygen bridges as in the X zeolite.

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