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Reactions of Several Aqueous Chlorides with Silica-Alumina Catalysts

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The cations of aqueous LiCl, NaCl, KCl, $BaCl_2$, and NH_4Cl exchange with some of the aluminum of cogelled, catalytic silica-alumina. Even at 2–5 *M* salt concentration no other reaction involving the surface could be observed. The extent of cation exchange over a wide concentration range is reported. The maximum amount of exchange was 4.4% of the aluminum present, corresponding to 1.5×10^{13} aluminum ions released per square centimeter of surface, or a distance of 26 Å between surface aluminum atoms (assuming uniform distribution) which could be released. A comparison with catalytic cracking results reported earlier indicates there are far fewer active sites for cracking than there are aluminum atoms which can be released under the conditions of the exchange experiments.

Hydrochloric acid destroys part of the silica-alumina structure; consequently the HCl-surface reaction must be very different from that of the salts.

Some foreign cations poison the surface of silica-alumina for catalytic cracking activity (*1*). We are extending our study of the cracking reaction (*2–4*), by using the method of Horton and Maatman, to determine by a kinetic method the relationship between activity site density and concentration of reacted cation. We report here results concerning the nature and amount of reacted cation for several aqueous chlorides with two silica-aluminas, one of which was studied by Horton and Maatman (*4*) for the purpose of determining the surface density of catalytically active sites. The reactions of various aqueous ions with different forms of silica-alumina have been studied (*1, 5–13*). The systems considered were generally unlike ours. In particular, in our systems at equilibrium a large fraction of the ions in the pores is unreacted. Thus, mere uptake of salt is not a proper measure of reaction. Nor does it seem possible to devise a washing procedure which would remove only and all the unreacted ions. This is especially a problem since there is some interest in differentiating between adsorbed and exchanged ions. We have therefore made this study using a method designed for problems of this type (*14*).

EXPERIMENTAL

Materials. Cogelled Houdry S-90 silica-alumina 4 × 4-mm pellets and Socony-Mobil white silica-alumina beads were used. The catalyst, per cent Al_2O_3, BET surface area, and pore volume are, respectively: Houdry S-90, 12.4%, 440 m^2/g, and 0.74 ml/g; Socony-Mobil bead, 10%, 393 m^2/g, and 0.47 ml/g. The Socony-Mobil catalyst was used by Horton and Maatman (*4*). We determined the pore volume by water absorption; the other data are the manufacturer's. Before use and before pore-volume measurement the catalysts were heated 450° for 2 hr in air.

Procedure. Solutions were equilibrated with solids by frequent shaking over a

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period of at least 48 hr. Aliquots of both initial and final solutions were analyzed. The temperature of all experiments was 20–22°. With the Houdry catalyst the ratio of solution volume to catalyst weight was 1.67 ml/g; usually 30 g of catalyst was used. With the Socony-Mobil catalyst the ratio was 1.75 ml/g with usually 20 g of catalyst being used. No time effect could be found in the salt experiments, even though in some cases the contact time varied from 3 days up to several weeks. In the hydrochloric acid experiments analyses of the solution external to the porous solid indicated a steady state condition was obtained only after 10 days' contact time.

Analytical. Solutions containing barium ion were analyzed for aluminum with a direct EDTA titration using hematoxylin as indicator. Other aluminum analyses were carried out with a zinc chloride back titration of excess EDTA. Chloride analyses were made by silver nitrate titration, using dichlorofluorescein as indicator. Beckman Zeromatic and GS pH meters were used to measure pH values.

RESULTS AND DISCUSSION

Calculation of the Extent of Reaction

A description of the treatment of the data of the lithium chloride-Houdry catalyst system is given to illustrate the method used. The amount of chloride ion within the pores of 1 g of catalyst at equilibrium, y_{Cl}, is given by

$$y_{\text{Cl}} = [c_iV - c_f(\text{Cl})(V - WP)]/W \quad (1)$$

where V ml of solution of c_i (molar) salt concentration is mixed with W g of catalyst of P ml/g pore volume, and where $c_f(\text{Cl})$ is the molar concentration of chloride at equilibrium. Curve 1 of Fig. 1 is y_{Cl} vs. c_f (Cl). To calculate the amount of lithium ion in the pores of 1 g of catalyst, y_{Li}, the molar concentration of lithium ion at equilibrium in the external solution, $c_f(\text{Li})$, is needed.

The calculation made depends upon the assumption that there are essentially no hydrogen ions produced upon equilibration. With reaction the LiCl solution pH dropped from 5–6 to no less than 3 (a change typical of all systems studied), a drop probably caused by hydrolysis of aluminum (0.01–0.02 *M* in equilibrium solutions). The formation constant of HCl at 25° is only $10^{-6.1}$ (*15*); thus even with a very high chloride concentration pH measurement is an approximate measure of $(\text{H}^+) + (\text{HCl})$. Therefore, there are essentially no cations in solution besides the lithium and aluminum ions and the electroneutrality condition in the external solution is

$$c_f(\text{Cl}) = c_f(\text{Li}) + 3c_f(\text{Al}) \quad (2)$$

where $c_f(\text{Al})$ is the molar concentration of the aluminum ion at equilibrium. The value of $c_f(\text{Li})$ determined from Eq. (2) is used in an equation similar to Eq. (1), where y_{Li} and $c_f(\text{Li})$ replace the corresponding chloride values. Curve 2 of Fig. 1 is y_{Li} vs. $c_f(\text{Li})$. The fraction of a y_{Li} value representing unreacted lithium ion in the pores is determined according to the procedure given earlier (*14*). To use this procedure it is assumed that in the linear high concentration region of the curve the increase in y_{Li} is due entirely to the increase in unreacted lithium ion in the pores. Then Curve 3, the amount of reacted lithium ion in the pores vs. $c_f(\text{Li})$, can be produced. Curve 4 shows the amount (in milliequivalents) of aluminum ion released per gram of catalyst during the lithium chloride equilibrations.

Curve 4 could be constructed from equilibrium aluminum ion concentrations only if it was assumed that aluminum chloride did not itself adsorb on the catalyst. To determine whether or not aluminum chloride adsorbs, there were carried out 19 equilibrations of Houdry catalyst with aluminum chloride alone, where the final salt concentration varied from 0.08 to 2.4 *M*. In this series y_{Al} vs. c_f (Al) (not shown) is linear, with the curve passing through the origin. This is different from the characteristic curvature of Curve 2 of Fig. 1, and the aluminum chloride results indicate this salt does not react with the surface even at high concentrations.

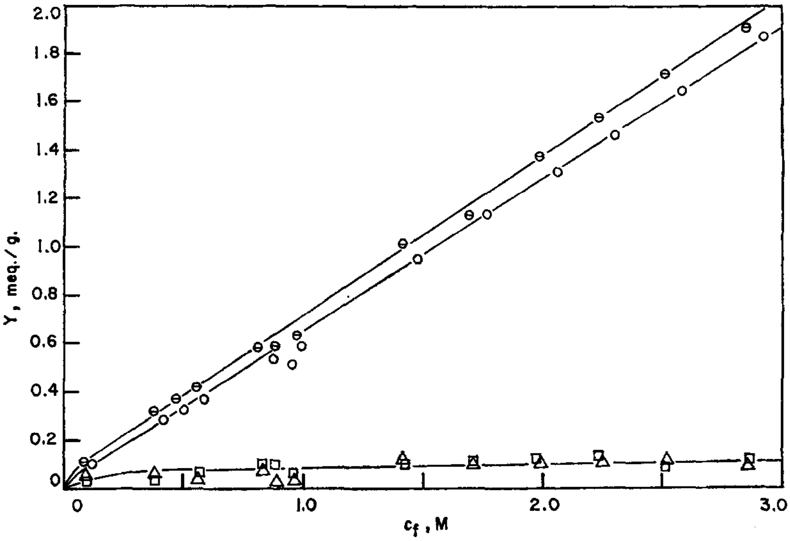

Fig. 1. Plot of y vs. c_f for LiCl-Houdry catalyst system. See text; ○, Curve 1; ⊖, Curve 2; △, Curve 3; □, Curve 4.

The curves of Fig. 1 are typical of the salt systems studied. The maximum amounts of aluminum ion release are summarized in Table 1.

TABLE 1
Maximum Amounts of Exchange

Catalyst	Salt	Conc.[a] (M)	No. of expts.	Max. exchange (meq/g)[b]
Houdry	LiCl	0.09–2.9	13	0.10
Houdry	NaCl	0.07–4.8	23	0.15
Houdry	KCl	0.04–2.1	13	0.30
Houdry	NH_4Cl	0.05–1.9	22	0.32
Houdry	$BaCl_2$	0.08–1.6	12	0.16
Socony	LiCl	0.25–2.1	8	0.13
Socony	NaCl	0.25–1.9	8	0.16
Socony	KCl	0.2–2.0	8	0.26

[a] Range of final concentration of salt in experiments indicated in next column.

[b] Average of values of Al^{3+} release on plateau of exchange isotherm; error, ±10%.

Nature and Extent of the Reaction

To the extent that Curves 3 and 4 agree, the amount of metal ion reacted is equivalent to the amount of aluminum ion released. The extent of agreement and the point scatter are typical of all the systems studied. Curve agreement is difficult to establish because Curve 3 is calculated from large differences in small numbers; better evidence for equivalence is the absence of observable exchange of solution cation for surface hydrogen. On the other hand, there are references in the literature to metal-ion poisoning of Bronsted acid sites of the silica-alumina surface. The existence of such poisoning has been offered as proof of the existence of Bronsted acid sites. Had we observed such a reaction, the metal ion of the solution would have replaced a surface proton, not a surface aluminum ion. Concerning the Bronsted acid question, Basila, Kantner, and Rhee (*16*) concluded from the infrared spectrum of potassium-silica-alumina that potassium blocks Bronsted acid sites. There are at least two important differences between their potassium-impregnated solid (similar to the solids others have studied) and ours, and consequently our data should be used with care in any attempt to settle the controversial Bronsted acid question. First, they studied the dried solid; we do not know what would happen to our reacted (or the relatively large amount of unreacted) metal ion were the solid to be dried. Second, they (and others) used a strongly basic anion (the acetate ion in the case cited), causing considerably more exchange of the metal ion with surface hydrogen than there was in our experiments, where the chlorides were used. Actually, the cations used in our work exchange slightly with the hydrogen of the surface silanol groups of silica gel (*17*) and there is probably similar exchange with the silanol groups of silica-alumina. The amount of this reaction is apparently small enough to be masked by aluminum exchange and subsequent hydrolysis.

The maximum amount of aluminum ion released is small compared to the total amount of aluminum present. The most aluminum ion released in any system of Table 1 (NH_4Cl with the Houdry catalyst) was only 4.4% of the aluminum present. This is 1.5×10^{13} aluminum ions released per square centimeter of surface. If there is a uniform, square distribution of these ions over the surface before release, they are 26 Å apart. While the density of aluminum ions released is small, it is still orders of magnitude larger than the density of the catalytically active sites found by Horton and Maatman (*4*). The density of aluminum ions which can be released by the electrolyte solutions used in this study is, however, of the order of magnitude of the site densities found by several methods, including chemisorption methods, summarized by Hirschler and Hudson (*18*). Shishniashvili and Bastanadze showed that the amount of aluminum which can exchange is small and a function of composition, with none exchanging in a purified silica-alumina gel containing 50.7% Al_2O_3(*19*).

The reaction of the cations of the salts of Table 1 is quite different from the reaction of the hydrogen ion with the aluminum of silica-alumina. Sixteen hydrochloric acid–Houdry catalyst experiments were carried out, with the acid initially 0.2–3.5 *M*. The amount of aluminum ion released increased continuously over the whole acid concentration range, with 48% of the total aluminum of the catalyst released at the highest concentration and 3.9% at the lowest. The acid attack apparently changed the skeleton itself: The pore volume of the catalyst changed from 0.74 ml/g to 0.78 ml/g when it was in contact for 7 days with hydrochloric acid initially 2.0 *M*.

The ion order and approximate amount of reactivity given in Table 1 is the same for the two catalysts. The ion order, except for barium, agrees with the conclusions of Raychaudhuri and Ghani (*6*) and also with the conclusion of Birrell (*12*) that the larger the effective ion size, the less exchange there is with the silica-alumina surface.

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