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The Decomposition of *n*-Butanol over Salt-Impregnated Alumina

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n-Butanol decomposes at 260°C to water, *n*-butyl ether, and butenes with alumina as catalyst. Impregnation of aqueous LiCl, NaCl, KCl, or $CaCl_2$ deactivates the alumina, although in some cases a promotional effect at low salt concentration was observed. In certain experiments there was a trace of dehydrogenation, with the formation of butyraldehyde. Activity as a function of the amount of salt added was studied. For both LiCl, which apparently reacts irreversibly with Al_2O_3, and the other salts, which react reversibly, the group of catalytic sites is within, and smaller than, the group of sites which react with salt. Probably alcohols as well as salts react with noncatalytic sites. Our results and certain conclusions others have made indicate that the alcohol–alumina reaction is complex. It is shown that the number of active sites may be very small. If so, the complexity of the alcohol–alumina reaction and the catalytic results are more easily reconciled.

In earlier work we made certain observations concerning the impregnation of catalysts active in cracking and in dehydrogenation. The present study was carried out to determine if similar conclusions hold for alcohol dehydration. We chose the low-temperature dehydration of *n*-butanol over Al_2O_3 for our study.

Several of our earlier observations are of interest in the present study. We noted, as have others, that there can be a maximum in the activity of a catalyst as salt is added to the surface of a solid which is active catalytically without added salt (*1*). In other cases, salt deactivates at all concentrations (*2*). We showed in these systems that the catalytically-active sites are within the group of sites which react with aqueous salt ions, i.e., the unreacted salt in the catalyst pores prior to removal of the solvent, does not contribute to deactivation even though such salt is deposited when the solvent is removed. It was also shown in these studies that some of the sites with which the salt reacts are not catalytically active.

In the present work we make similar conclusions for the dehydration of *n*-butanol over Al_2O_3 which has been impregnated with aqueous LiCl, NaCl, KCl, or $CaCl_2$. Furthermore, we show by means of analysis of certain literature data, that dehydration of alcohol on Al_2O_3 may take place on only a very small number of active sites.

EXPERIMENTAL METHODS

Houdry 200S Al_2O_3 (α-basic aluminum oxide, AlO(OH)) of surface area 159 $m^2\ g^{-1}$ (manufacturer's data) and pore volume 0.320 ml g^{-1} (water absorption) was used throughout. Before use, the Al_2O_3 was heated 2 hr in oxygen at 500°C. Usually 25-ml solution (of LiCl, NaCl, KCl, or $CaCl_2$) were mixed with 12.5 g Al_2O_3; the solution:solid ratio was always 2:1. The solution–solid contact time was always at least two days and the mixture was kept at room temperature. To determine the amount of salt reaction with the surface, the stock solutions and aliquots of the excess solution which had contacted alumina were analyzed for chloride by $AgNO_3$ titration, using a dichromate indicator. Analyses of aliquots taken at different times indicated that equilibrium was achieved in 2 days for all but the LiCl systems, where equilibrium was not necessarily achieved in even three weeks.

To activate the catalyst, the solid was drained of solution, dried at 120°C in air for 16 hr, ground to $-100 + 200$ mesh, and calcined at 490°C in N_2 for one hour in the catalytic reactor. Catalytic activities were measured in a differential reactor, similar to the reactor used earlier (*1*). A clock-driven syringe fed 4.31 ml of *n*-butanol (reagent grade, dried and stored over Linde 3A Molecular Sieves) per hour into the reactor, and alcohol vapor at 260°C passed over 0.300 g catalyst. All conversions were less than 3%, and there was no conversion when the catalyst was omitted. Unlike the reactor used earlier, the product stream was not condensed. Instead, the gas which left the catalyst passed directly into a heated 4-ml loop connected to a gas sampling valve. To measure activity, the gas in the loop was swept by helium carrier gas into the column (containing 10% ethofat on 30–60 Chrome T) of a gas chromatograph. The exit of the chromatograph and the exit of the chromatograph bypass, and consequently the reactor itself, were at atmospheric pressure. For liquid calibration, liquids were injected into the chromatograph injector port in the usual manner, and for butene calibration the reactor and the loop were flushed with butene before the gas in the loop was swept into the column.

In the dehydration reaction the products were water, *n*-butyl ether, and butene. (The butenes were left unresolved.) Traces of butyraldehyde were found in the product in some of the runs in which the catalyst contained a metal salt. The activity with respect to water, ether, and butene was measured at 20, 40, and 60 min after the run started, and the activity for the run was taken as the average of these measurements. Activity was not a function of time. At least two runs were made on each catalyst. The average deviation in activity was less than 10%.

RESULTS

The reaction of these aqueous salt solutions with the same kind of Al_2O_3 (but with a different pretreatment) was discussed earlier (*3*). It was shown that anion and cation react with the surface in equivalent amounts, and that it is therefore sufficient to follow the reaction by means of anion analysis of the solutions.

We distinguish between salt which reacts with the surface of Al_2O_3, y_R, in millimoles per gram, and the unreacted salt in the pore volume liquid when the liquid is removed. The total of the two kinds of salt is designated by y_T. We calculate y_T directly and obtain y_R from y_T, using a procedure given earlier (*4*). Thus, at high salt concentrations, where reaction with the surface is complete, increments in y_T with increasing c_f, the concentration of the salt in the contacting solution, are due only to increments in the amount of unreacted salt in the pores. Since some ions are larger than the average cluster of water molecules, the effective pore volume for an ion species may be less than the pore volume determined for water absorption (*4*). The effective pore volume for a salt is given by the slope of the y_T vs c_f plot in its high concentration, linear range. The effective pore volumes for LiCl (both sets), NaCl, KCl, and $CaCl_2$ solutions are, respectively, 0.299, 0.317, 0.320, and 0.303 ml g^{-1}. The deviations of these effective pore volumes for three of the four salts from the "effective" pore volume for water, 0.320 ml g^{-1}, were significant in the calculation of y_R,

TABLE 1
DEACTIVATION OF ALUMINA BY SALTS

Salt	y_T[a] mmol g^{-1}	y_R[a] mmol g^{-1}	Max y_R[b] mmol g^{-1}
LiCl (1 wk)	0.43–0.45	0.35–0.37	0.35
LiCl (3 wks)	0.45–0.47	0.41–0.43	0.46
NaCl	0.09–0.15	0.025–0.030	0.033
KCl	0.08–0.17	0.024–0.026	0.030
$CaCl_2$	0.25–0.26	0.075–0.080	0.080

[a] Range of values within which activity vanishes.

[b] Maximum amount of salt which reacts with surface.

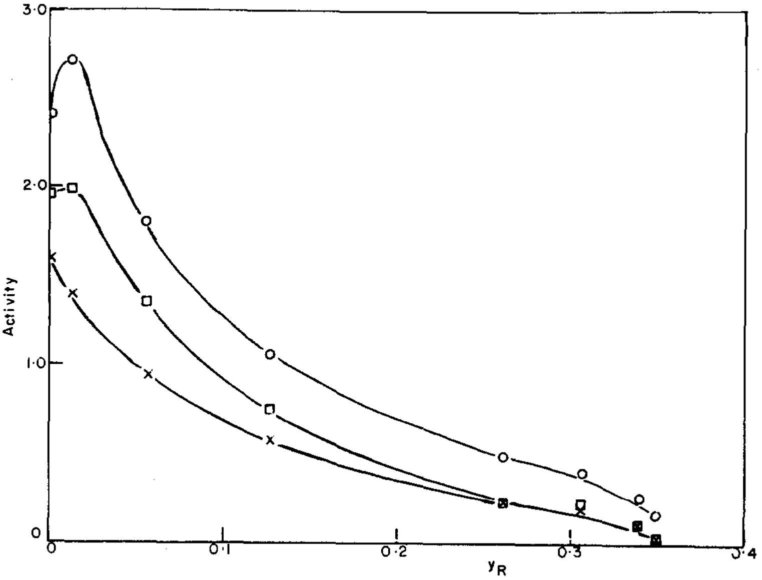

FIG. 1. Activity (mol g^{-1} sec^{-1} × 10^6) vs y_R (mmol g^{-1}) for the LiCl-impregnated Al_2O_3 in which the solution–solid contact time was 1 week. The products are water (○), *n*-butyl ether (×), and butenes (□).

which is given by the difference between y_T and the amount of unreacted salt.

Typical plots are given in Ref. (*3*). The maximum values of y_R for the various salts obtained in the present work are given in Column 4 of Table 1. (The Al_2O_3 batch and pretreatment are not the same as in the earlier work (*3*), and the maximum values are not precisely the same.) To minimize the effect of any scatter in the y_R–c_f plots (plots not shown), the y_R values usually used with the activity results reported below were those taken from the linear Langmuir plot.

In Figs. 1–6 the activity for the production of water, ether, and butene, as a func-

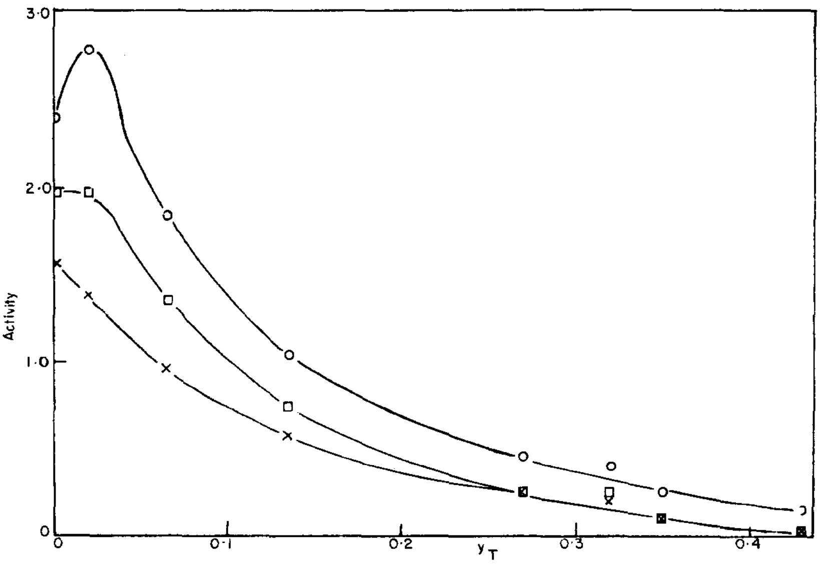

FIG. 2. Same as Fig. 1, but for y_T (mmol g^{-1}).

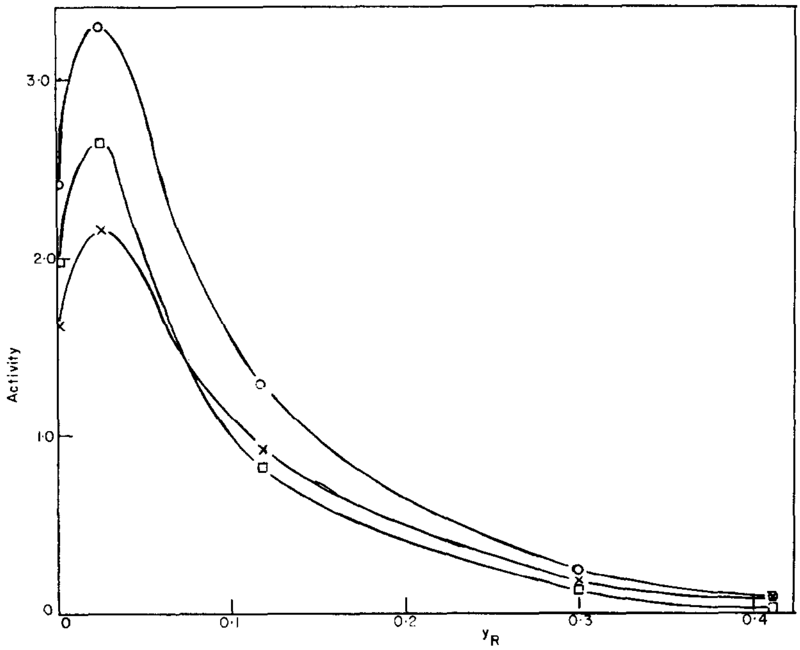

FIG. 3. Same as Fig. 1, but for a solution–solid contact time of 3 weeks.

tion of y_T and y_R, is given for the catalysts impregnated with LiCl and NaCl. (The plots for KCl and $CaCl_2$, not shown, are similar.) The activity recorded for a catalyst is an average of all the determinations made on that catalyst. The stoichiometric amount of water produced should equal the sum of the ether and butene amounts. The data in the figures indicate that generally a smaller amount of water was ob-

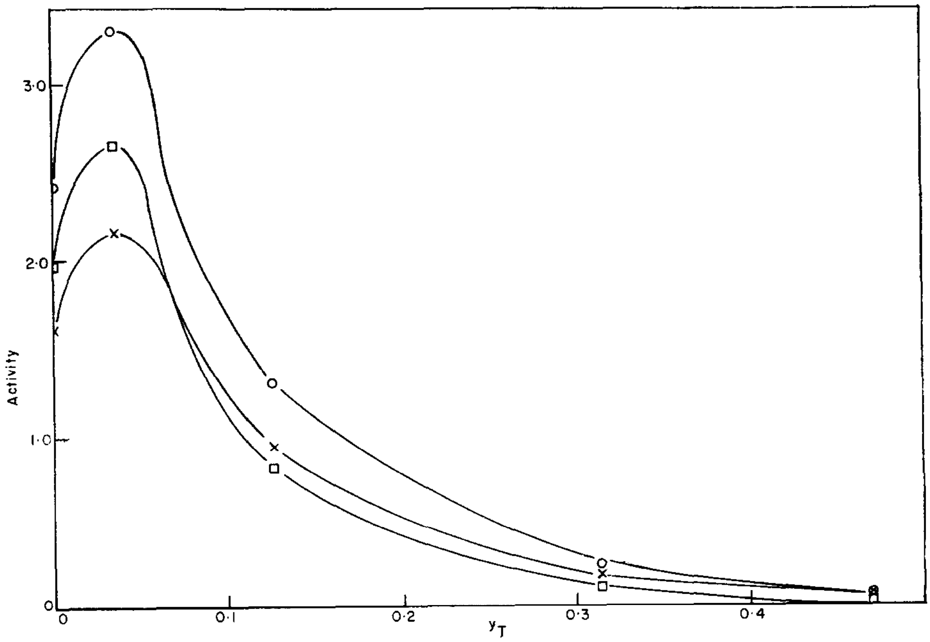

FIG. 4. Same as Fig. 2, but for a solution–solid contact time of 3 weeks.

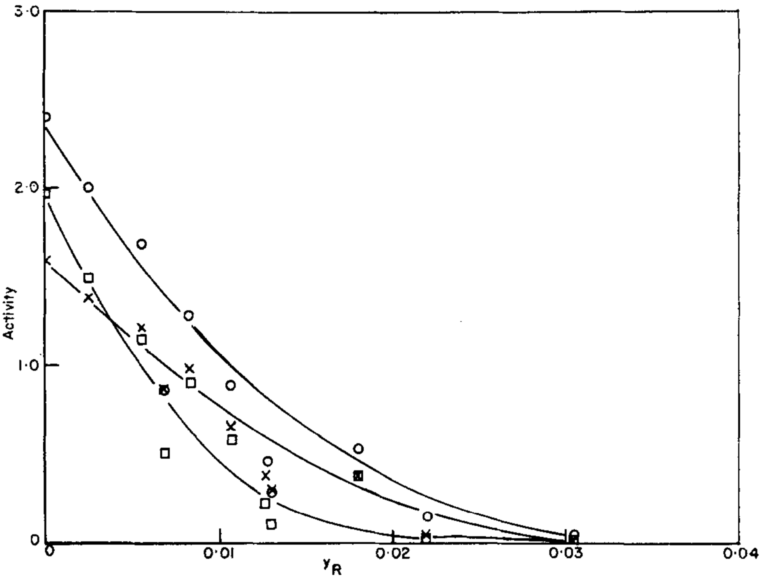

FIG. 5. Same as Fig. 1, but for the NaCl-impregnated Al_2O_3.

served, suggesting that the catalyst (calcined at 490 but used at 260°C) absorbed some of the water product. The water curves are therefore not as reliable as the others, and we base all of our conclusions on the ether and butene curves. In any case, the three kinds of curves in Figs. 1–6 are similar. The approximate y_T and y_R values at which activity vanishes are given in Columns 2 and 3 of Table 1.

DISCUSSION

As the effects of adding salts are discussed below, it will become evident that the alcohol-Al_2O_3 reaction is complex. We shall then show that the idea of complexity is also suggested by the results of those who have studied the mechanism of alcohol decomposition over Al_2O_3. Finally, we shall suggest how it might be possible to remove

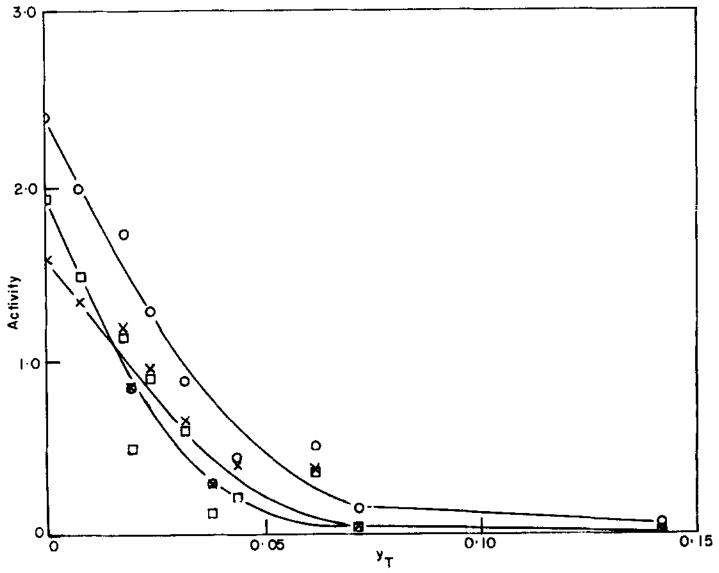

FIG. 6. Same as Fig. 2, but for the NaCl-impregnated Al_2O_3.

in catalytic studies some of the confusion which is a consequence of the complex nature of the alcohol–Al_2O_3 reaction.

Salt Effects

Four of the conclusions based on our results suggest that the alcohol–Al_2O_3 reaction is complex.

First, we found at low concentration of added LiCl or $CaCl_2$ that activity increases with increasing salt concentration, with deactivation occurring only at higher concentration of salt. Similarly, Pis'man and coworkers found a maximum in activity at low concentrations of KOH in Al_2O_3 for n-butanol dehydration (*5*, *6*). Pscheidl and Witzmann made a similar observation when Li^+-doped Al_2O_3 (as well as transition metal-doped Al_2O_3) was used in the dehydration of isopropanol (*7*). Second, we found traces of butyraldehyde, indicating dehydrogenation, when Al_2O_3 was impregnated with aqueous salt. Pis'man and coworkers found evidence of n-butanol dehydrogenation over KOH-treated Al_2O_3 (*5*, *6*), and Kay and Cares detected a small amount of acetaldehyde when ethanol was dehydrated over Al_2O_3 (*8*).

Third, the shape of the activity-added salt curves at the higher values of added salt indicates complexity. If each ion or "molecule" of the added salt were to destroy a catalytic site, a linear decrease in activity with increasing y_T might be expected. Or, if each ion or "molecule" of *reacted* salt were to destroy a catalytic site, a linear decrease in activity with increasing y_R might be expected. Some of the curves appear to be linear, but it is certain that neither the y_T nor the y_R group is linear at high concentration of salt for all four salts. Nonlinearity suggests that the salt reacts with some sites which are not catalytically active. Finally, the wide variation in the values of y_R at which activity vanishes (Table 1) also indicates that the salts react with noncatalytic sites. Thus, ~0.025 mmol of NaCl or KCl reacted (per gram Al_2O_3) removes all activity, while ~0.08 mmol of $CaCl_2$ or ~0.4 mmol of LiCl is necessary to achieve the same result. Alcohols would be expected to react with at least some of the noncatalytic sites with which salts react.

By means of our data, we can estimate whether y_R or y_T is the more meaningful measure of the destruction of active sites. For each salt the value of y_R at which activity vanishes (Column 3 of Table 1) is reasonably close to the value of y_R at which salt–alumina reaction is complete (Column 4). We conclude that the group of active sites is within the group of sites responsible for the salt–alumina reaction. Correlating activity with the *total* amount of salt in the pores, y_T, a procedure that is usually used, seems questionable.

Is it correct to assume, as we do, that the reaction of a "molecule" of salt in aqueous solution with an active site means that that site, and only that site, is poisoned after the catalyst is calcined? It seems that such an assumption is justified, since otherwise the closeness of the values in Column 3 to those in Column 4 of Table 1, just referred to, would be fortuitous. Furthermore, the same assumption concerning the reactions of salts with surfaces was consistent with, and necessary in order to interpret, the results obtained in earlier studies of ours, viz., in studies of the dehydrogenation of cyclohexane over salt-poisoned Cr_2O_3–Al_2O_3 (*1*), and (in spite of a difference in the mechanism of poisoning) the cracking of cumene over salt-poisoned SiO_2–Al_2O_3 (*2*).

Thus, our results suggest that there are sites on the surface of Al_2O_3 which catalyze dehydration, sites which catalyze dehydration when certain salts are used as promoters, sites which catalyze dehydrogenation, and sites which react with salt (and probably alcohol) which are catalytically inactive.

Dehydration Mechanism

Catalytic studies of others have also indicated that the alcohol-Al_2O_3 interaction is not simple. Some typical examples are given: Jain and Pillai (*9*) and others have suggested that olefins and ethers form on different sites. Bremer, Steinberg, and Wendlandt (using η-Al_2O_3) concluded that Brönsted and Lewis sites each act synergistically with certain surface hydroxyl groups (*10*). Knozinger and coworkers found the reaction to be bimolecular, with one molecule adsorbed as a surface alkoxide (*11, 12*). De Mourges *et al.* (*13*) and others showed that different acid-catalyzed reactions over Al_2O_3 (including alcohol dehydration) apparently do not occur over the same groups of sites, although the possibility that the groups overlap was not ruled out. It was deduced, from the composition of isotopically-exchanged desorption products, that there are several forms of alcohol–Al_2O_3 interaction (*14*). De Boer showed that both the Langmuir–Hinshelwood and the Rideal–Eley mechanisms are important in ethanol dehydration (*15*).

Number of Active Sites

The results of the present work and the earlier work cited may suggest the need for a reexamination of some of the ideas which have been held concerning the decomposition of alcohols over Al_2O_3. If there are many surface sites which are not catalytically active, and if (as has been indicated above) the complication of simultaneous catalyzed reactions exists, it might well be asked if correct assumptions are usually made concerning the number of *active* sites on the surface. Typical assumptions about the number of active sites have been made by Dzis'ke *et al.* (*16*) and Parera and Figoli (*17*). Dzis'ke *et al.* assumed for *n*-butanol dehydration over Al_2O_3 that a measure of the amount of NaOH reaction with the surface (or, alternately, indicator reaction with the surface) is a measure of the approximate number of active sites; values of the order of $10^{14}cm^{-2}$ were obtained. Parera and Figoli used nitrogen bases, which act as poisons, to study the active part of the surface, with the implication that all, or a large fraction of, the base adsorption sites are catalytically active.

If, however, the number of catalytically active sites is much smaller than is usually supposed, then much of the observed reaction between alcohol and Al_2O_3 is not related to catalytic activity. In this case, much of the confusion concerning the catalytic reaction is the result of a failure to distinguish between the reaction of alcohol with active sites and the reaction of alcohol with inactive sites. Furthermore, if only a small number of sites is responsible for one kind of catalytic reaction, it is then easily possible for several catalytic reactions to occur simultaneously, as they in fact do occur.

We calculated the number of active sites using absolute rate theory (*18*) for the dehydration of *n*-propanol, benzyl alcohol, isobutanol, and cyclohexanol over Al_2O_3, using the data reported by Knozinger, Buhl, and Ress (*12*). We have defended and explained earlier the procedure used (*19*). The reactions are zero order in alcohol pressure, regardless of the product or the kind of site, above an alcohol pressure of 30–80 mm (the value of the minimum zero-order pressure depending upon the alcohol). We therefore used Eq. 2 of Ref. (*19*) in the zero order region to determine the number of sites, and values varying from 9×10^9 to $5 \times 10^{11}cm^{-2}$ were found for the four alcohols. Naturally, care must be exercised in comparing systems involving different alcohols and different alumina catalysts. But since the total number of alcohol–Al_2O_3 reaction sites is $\sim 10^{14}cm^{-2}$, a serious question can be raised concerning whether or not studies in which active sites are not observed directly, are meaningful for catalytic work. (This does not invalidate the conclusion that the active sites are within a certain group of sites such as the group of sites which reacts with salt.) In our earlier work we showed that high densities of active sites may be too easily assumed for many catalytic systems. Many surface sites thought to be active may actually be inactive, with the active fraction of the surface being as low as 10^{-2}–10^{-6}% in some cases (*19*).

Reaction of LiCl with Al_2O_3

The LiCl–Al_2O_3 reaction is slow and extensive, and there is no evidence that it was complete even in our 3-week samples. Very likely the reaction is irreversible. Even though only a small fraction of the surface sites with which LiCl reacts is catalytically active, the data of Table 1 suggest that for the group in which there was more reaction (the 3-week catalysts), that there was more deactivation. As a first approximation, the data suggest that the fraction of LiCl-reacted sites which is catalytically active is the same in the first week of reaction with LiCl as in the following 2-week period.

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