JOURNAL OF CATALYSIS 12, 398–409 (1968)

Metal Chloride Promotion and Deactivation of Chromia-Alumina-Catalyzed Dehydrogenation of Cyclohexane

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Received July 15, 1968; revised September 19, 1968

As the concentration of the chloride of Li, Na, K, Mg, or Ca added to chromia-alumina increases, the catalyst activity for the dehydrogenation of cyclohexane passes through a maximum and eventually vanishes. The cation and the anion of these salts react with the chromia-alumina surface in equivalent, but small, amounts. Salt–surface reaction isotherms and plots of catalyst activity versus the amount of salt reacted with the surface are presented. For a given amount of reaction, the amount of activity depends upon the nature of the salt. The completion of the salt–surface reaction and the complete deactivation of the catalyst occur, within experimental error, simultaneously. The data suggest that both promotion and deactivation are due to the cation, and that both the unreacted salt in the catalyst pores (i.e., unreacted just before the solvent of the impregnating solution is removed) and some of the reacted salt do not contribute to deactivation.

I. INTRODUCTION

Chromia-alumina, usually prepared by depositing chromium oxide on an alumina surface, catalyzes both hydrocarbon dehydrogenation and acid-catalyzed reactions. In the dehydrogenation of cyclohexane and benzene, acid sites are probably responsible for the production of methylcyclopentane (MCP), which in turn produces a substance that irreversibly poisons dehydrogenation sites (*1*). A large number of metal oxides are known to promote chromia-alumina-catalyzed dehydrogenation of cyclohexane (*2*), and it has been suggested that this promotion is in reality a poisoning of the acid sites which produce a dehydrogenation poison (*1*). As the metal oxide concentration is increased, deactivation of the dehydrogenation sites is eventually observed (*1, 3*). Metal oxides may promote chromia-alumina catalysts prepared under oxidative conditions by stabilizing Cr^{6+} (*4*). In this article, only catalysts prepared using reduction conditions are considered.

We have been interested in salt-surface reactions and the relation of these reactions to the catalytic activity of the finished catalyst (*5–8*). Salts also react with the surface of chromia-alumina, and so the purpose of the present work was to study this reaction and to determine what the relation is between this reaction and the promotion and deactivation effects. Salts react with the surface of alumina (*9*), and NaOH and NaCl each remove acid sites responsible for alumina-catalyzed isomerization of cyclohexenes (*10*). In a chromia-alumina catalyst of about 7 wt % Cr, prepared by impregnation of alumina with chromic acid, it was shown by means of magnetic measurements that Cr_2O_3 covered only 20% of the alumina surface (*11*). It is therefore reasonable to suppose that at least part of the salt reaction with chromia-alumina is a removal of alumina acidity, accounting for at least some of the promotion effect of salts in cyclohexane dehydrogenation. There are also acid sites on the chromia of the chromia-alumina surface, and they may be responsible for promotion in a similar way.

The chromia acidity is sensitive to the extent the surface has been reduced (*12*), and therefore it is not surprising that the amount of alkali metal ion reaction with Cr in chromia-alumina depends upon the state of surface oxidation (*13*). Such a reaction may be responsible for the deactivation of dehydrogenation sites, sites which are known to be related to some chromium species present. Bridges, Rymer, and MacIver suggest that this deactivation is caused by either alkali metal ion reaction with dehydrogenation sites, decrease of chromia surface area, or physical blocking of sites (*1*). They suggest that the reaction of metal ion is an unlikely factor since the metal–chromia reaction product is stable only under oxidizing conditions, while usually reducing conditions prevail during dehydrogenation. They interpret their results to indicate that there is either a decrease in the area of chromia or a physical blocking of sites However, reaction between alkali metal ion and sites cannot be ruled out as a factor in deactivation merely because the presence of the reaction product is not detected by direct means. We note that in the cracking of cumene over silica-alumina the number of active sites is a few orders of magnitude lower than that which is normally observable by direct methods, and that low site densities have been reported in other catalytic reactions (*8*).

After a salt solution has reacted with the chromia-alumina surface, but before the solvent has been removed, some of the salt in the pores is dissolved in the pore-volume liquid and is therefore unreacted. In considering the properties of a finished catalyst, a distinction is usually not made between the salt which had reacted and that which had not reacted just before solvent removal. We did, however, find it profitable to make just such a distinction in a study of the salt poisoning of silica-alumina in the cracking of cumene. It was shown, contrary to what had earlier been accepted, that for a given amount of salt reaction with the surface, the extent of catalyst poisoning is independent of the nature of the salt (*8*). For this reason, an attempt was made to find what relation exists between the salt which reacts with the surface and the promotion and deactivation effects.

II. EXPERIMENTAL

Materials. Houdry chromia-alumina pellets, Grade 25Z, Series A, was used with and without a wash treatment. The washing consisted of successive equilibrations with 0.1 *M* NH_4NO_3 until sodium no longer could be detected by a flame test in the equilibrium solution. Washing removed a small amount of dichromate from the solid. The washed solid was heated in air at 170–200° for 24 hr, followed by hydrogen reduction for 5 hr and nitrogen for 0.5 hr, all at 500°. The unwashed material was treated similarly, except that the 170–200° step was omitted. Cr and Na analyses on the reduced materials were, respectively, 12.6% and 0.22% for the unwashed solid, and 12.6% and 0.08% for the washed solid. The pore volume (by water uptake) and surface area (BET) of the washed material were, respectively, 0.343 ml g^{-1} and 57 m^2 g^{-1}. Except where otherwise noted, washed chromia-alumina was used in all experiments.

Phillips Research Grade cyclohexane, 99.99 mole % minimum purity, was used. Other chemicals were reagent grade.

Solution–solid equilibration. Fifty milliliters of metal chloride solution was mixed with 50 g of chromia-alumina and let stand at 22° ± 3°, with occasional shaking, for at least 48 hr. The initial solutions and the equilibrium solutions were analyzed for chloride and, in some cases, for metal cation. During equilibration the pH of the solution changed no more than 0.5 pH unit in the pH range of 6.0 to 7.5. Tests for Cr^{3+} and Al^{3+} were negative for the several equilibration solutions examined. Some equilibration solutions contained dichromate, but the dichromate concentration was never higher than 0.002 *M*. The pellets were heated at 170–200° in air for 15 hr before they were ground to 100/200 mesh and given further heat treatment in the reactor prior to a dehydrogenation experiment. The catalyst not equilibrated with salt solution was given the same treatment, except that it was equilibrated with water instead of solution.

Analysis of solutions. Chloride was determined by $AgNO_3$ titration, using dichromate as indicator. Most results reported are averages of duplicate titrations of both the initial and equilibrium solutions. Calcium and magnesium were determined by EDTA titration, using Eriochrome Black T indicator. The aluminon test for aluminum in the equilibrium solutions was used. To test for aqueous Cr^{3+}, an attempt to precipitate $Cr(OH)_3$ was made after removal of dichromate. Dichromate was determined iodometrically.

Catalyst activities. Activities were determined in a flow-type differential reactor, with conversion never exceeding 1.5%. The reactor differed from the one described earlier (*8*) only in that the cyclohexane was fed to the reactor by means of a syringe driven by a constant-speed Series 249 Sage pump. All activity determinations were at 500°. Prior to a determination, the reactor containing the catalyst was flushed with N_2 for 0.5 hr at 500°. The only hydrogen in the system during a run was that produced by the reaction. The feed was pumped into the reactor at a rate of about 8 ml liquid/hr. The gas stream passed over 0.300 g of catalyst, after which it was cooled in a water condenser. The activity, on the basis of conversion per gram of catalyst per second, was independent of catalyst weight. A small mount of yellow deposit was always found at the beginning of the condenser. To determine an activity, the condensate of a 2-min interval was weighed and analyzed for cyclohexane, benzene, cyclohexene, and methylcyclopentane (MCP) in an Aerograph 90-P chromatograph, using a 12-ft column of 10% Ethofat on 40/60 Chrome T. No attempt was made to determine if the cyclohexene isomerized to methylcyclopentenes which could, if they formed, contribute to deactivation of the catalyst.

Most of the activities reported are averages of two determinations. The thermal rates of the production of benzene, cyclohexene, and MCP were, respectively, $< 0.2 \times 10^{-6}$, about 30×10^{-6}, and $< 10 \times 10^{-6}$ mmole sec^{-1}.

RESULTS

Solution–solid reaction. The amount of an ion in the pores of 1 g of chromia-alumina after equilibration, y_T, in millimoles per gram, is given by

$$y_T = \frac{c_i V - c_f(V - WP)}{W} \qquad (1)$$

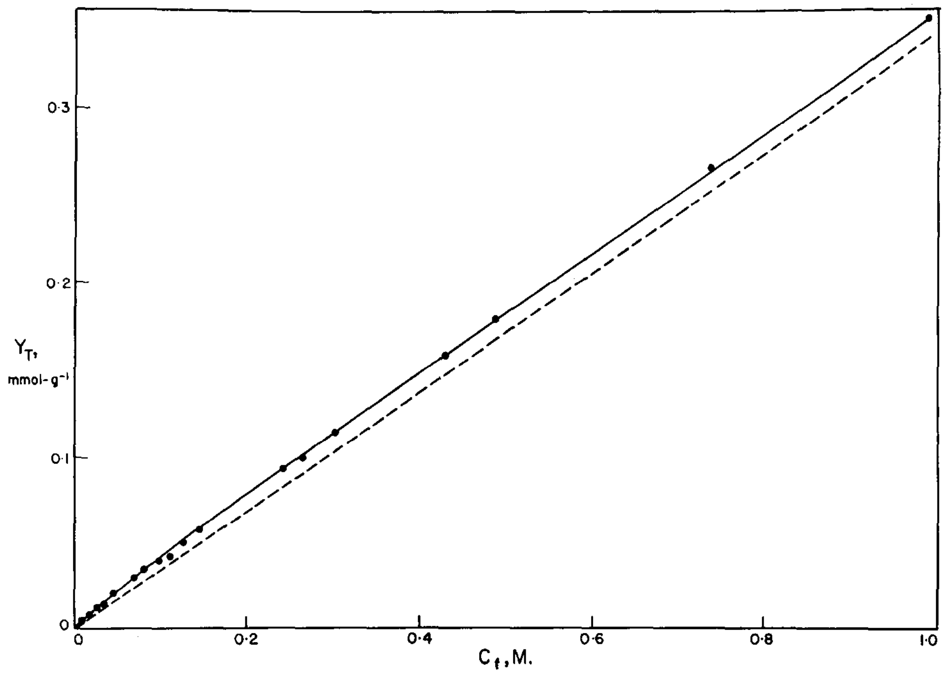

FIG. 1. y_T vs. c_f for NaCl-impregnated chromia-alumina. Dashed line gives y_T if there is neither reaction nor exclusion. Except where otherwise noted, all amounts of salt in the figures are in millimoles or moles and based on chloride analyses.

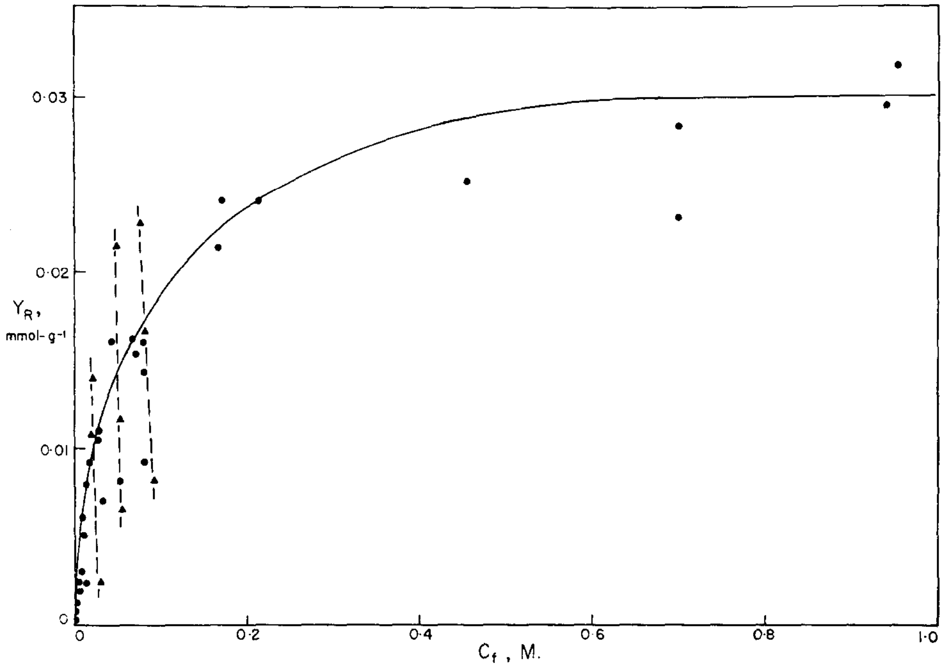

FIG. 2. Reaction isotherm for LiCl-impregnated chromia-alumina. Each vertical group of three triangular points is based on the same initial solution, with equilibration times of 2, 7, and 14 days for increasing y_T within each group. All other equilibration times are 6–7 days.

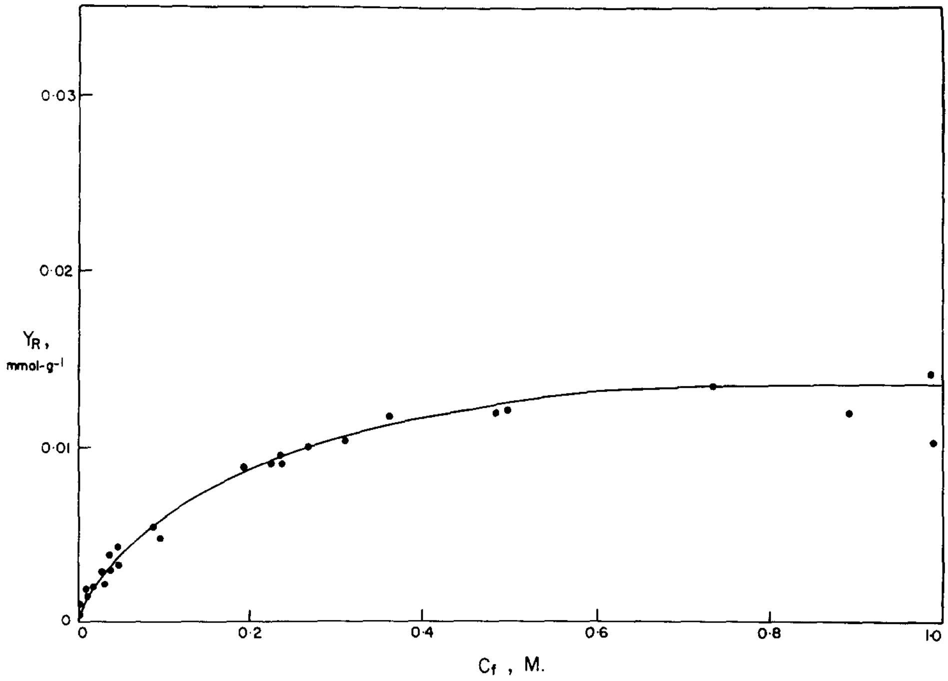

FIG. 3. Reaction isotherm for NaCl-impregnated chromia-alumina. Equilibration time, 2–7 days.

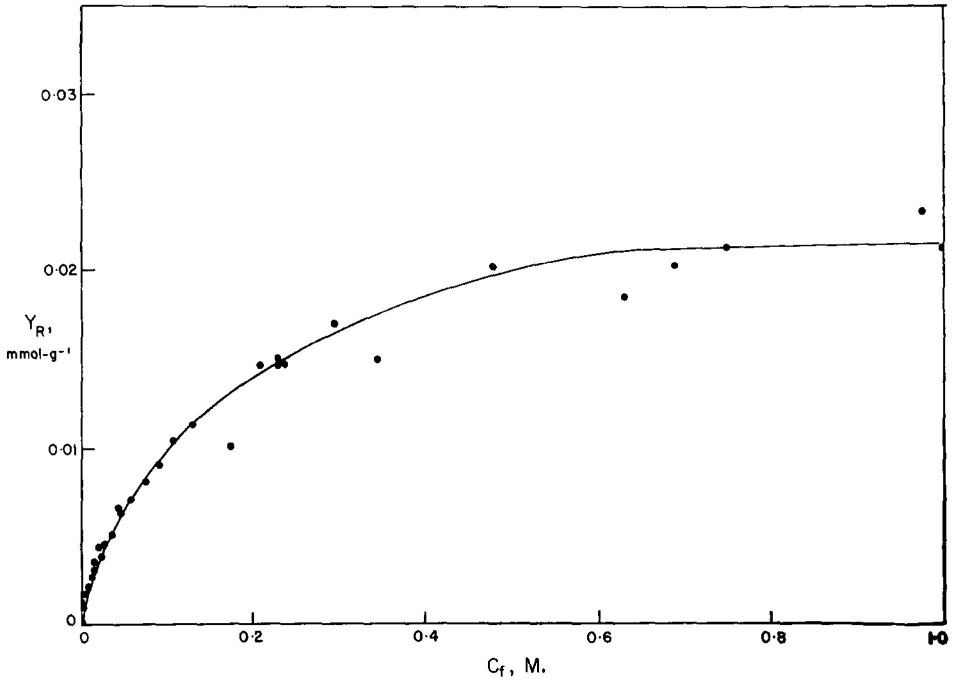

FIG. 4. Reaction isotherm for KCl-impregnated chromia-alumina. Equilibration time, 3–17 days.

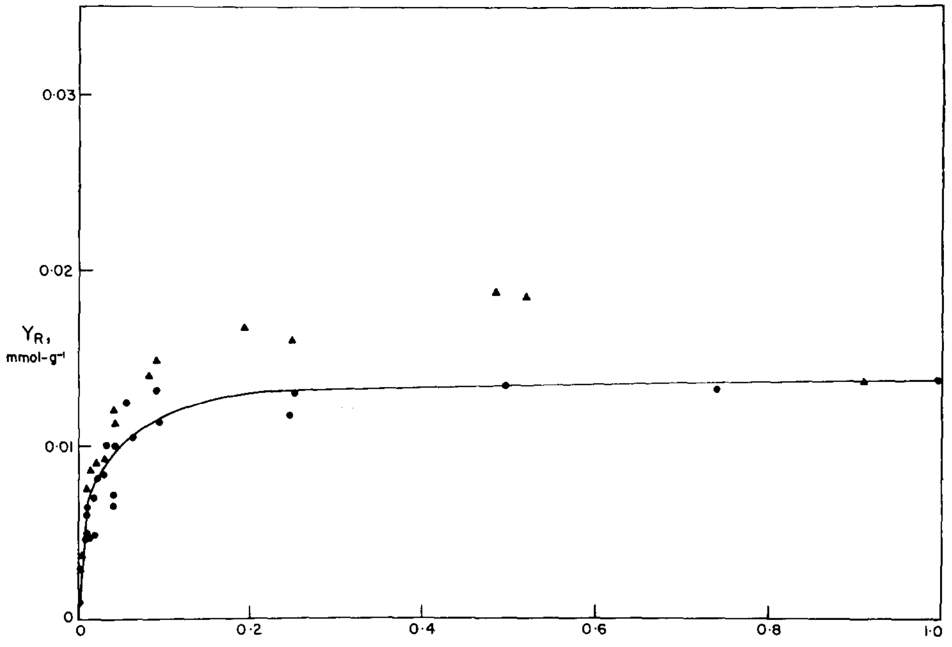

FIG. 5. Reaction isotherm for $MgCl_2$-impregnated chromia-alumina. Equilibration time, 3–18 days; ●, by Cl^- analysis; ▲, by Mg^{2+} analysis.

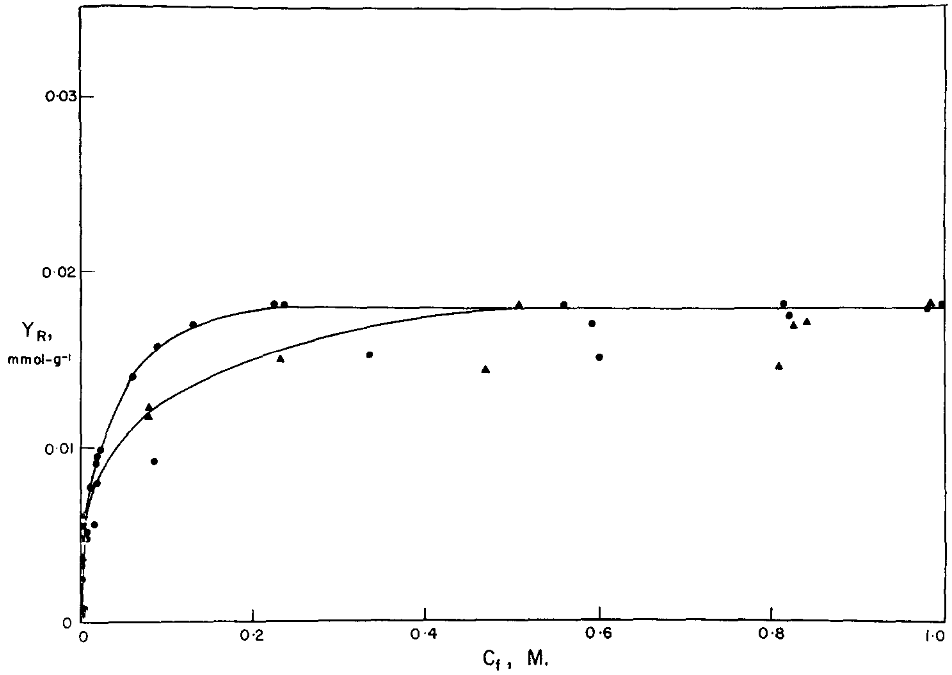

FIG. 6. Reaction isotherm for $CaCl_2$-impregnated chromia-alumina. Equilibration time, 3–4 days; ●, by Cl^- analysis; ▲, by Ca^{2+} analysis.

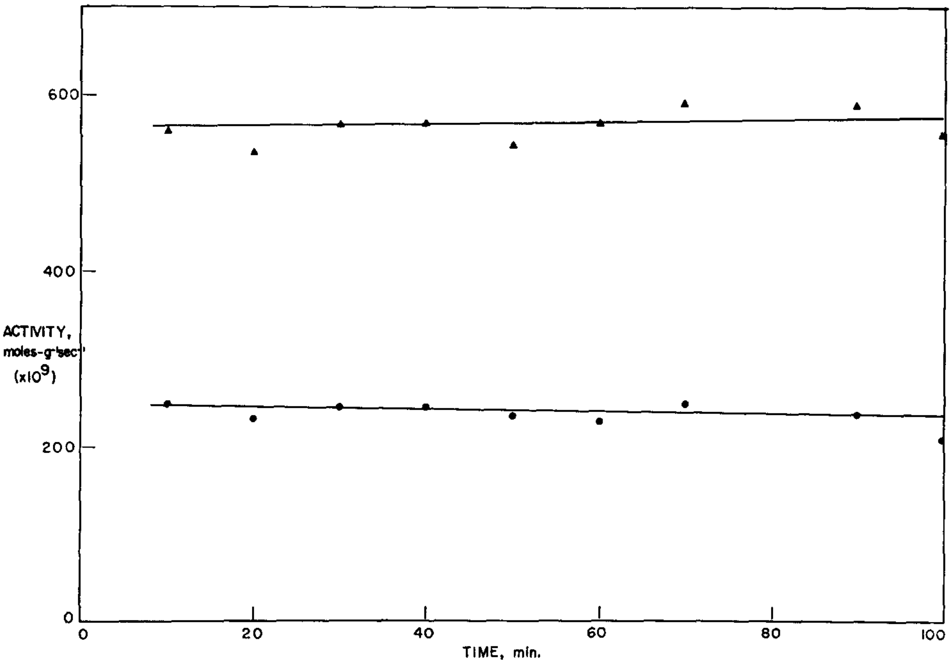

FIG. 7. Activity vs. time on stream for unpromoted chromia-alumina; ●, benzene production; ▲, cyclohexene production.

where V ml of solution of c_i ion molarity is mixed with W g of chromia-alumina of pore volume P ml/g, and c_f is the ion molarity after equilibration. The y_T vs. c_f isotherm for NaCl with chromia-alumina, in Fig. 1, is typical. A given value of y_T consists of ion dissolved in pore-volume liquid, y_D, and ion reacted with the chromia-alumina surface, y_R. With NaCl there is evidently no further reaction above $c_f = \sim 0.6\ M$, since at higher equilibrium concentration y_T vs. c_f is linear. In this range of concentration the increment in y_T is apparently due entirely to y_D. Thus, the dashed line in the figure, drawn parallel to the linear portion of the experimental curve and through the origin, is a plot of y_D vs. c_f. For any value of y_T, y_R is determined by diminishing y_T by y_D for the same value of c_f. But inspection of the dashed line reveals that $y_D = c_fP$, as is expected if the ion is not excluded from any part of the proe volume. [For a discussion of the exclusion question, see ref. (*14*) and references cited therein.] With all the ions studied, it was found that the relation

$$y_R = y_T - c_fP \qquad (2)$$

could be used.

In this way y_R vs. c_f isotherms were constructed, and they are shown for the five salts with chromia-alumina in Figs. 2–6. In Figs. 5 and 6 both cation and anion y_R vs. c_f isotherms are shown for $MgCl_2$ and $CaCl_2$. For convenience of comparison, chloride concentrations on both ordinates and abscissas are given in terms of moles, not equivalents, of salt.

Comparisons between salts and between metal ion and chloride ion are difficult because there is a large error in the determination of y_R in these systems. The reason for this difficulty is seen when Eqs. (1) and (2) are combined, with $V/W = 1$ ml g^{-1} in our systems

$$y_R = c_i - c_f \qquad (3)$$

This difficulty is particularly great at high c_f values: after y_R reaches its final value, c_i and c_f continue to increase. For example, in the Mg^{2+} isotherm of Fig. 5 at $c_f = 0.520\ M$, $c_i = 0.538\ M$ and $y_R = 0.018$ mmole g^{-1}. If c_i were measured correctly but c_f was

TABLE 1

ACTIVITIES OF SALT-IMPREGNATED CATALYSTS

Reacted salt, y_R (mmole g^{-1} × 10^3)[a]	Total salt, y_T (mmole g^{-1} × 10^2)[a]	Benzene activity (mole g^{-1} sec^{-1} × 10^9)[b]	Cyclohexene activity (mole g^{-1} sec^{-1} × 10^9)[b,c]
	LiCl		
3.5	0.50	290	615
4.4	0.48	300	600
5.4	0.58	255	575
6.1	1.1	300	670
7.0	1.0	305	590
9.0	0.92	315	660
9.5	1.5	310	645
11.0	2.0	270	633
12.2	2.8	258	570
13.0	2.6	235	550
16.2	4.2	220	585
16.5	4.3	200	575
23.2	10.3	110	392
23.3	15.2	70	365
25.8	17.4	45	250
25.8	18.1	45	275
28.0	26.3	12	255
28.0	27.1	11	200
30.0	35.9	0	75
30.0	63.9	0	170
	NaCl		
1.6	0.53	245	705
2.2	0.82	285	780
2.7	1.2	345	780
2.8	1.6	400	800
3.2	1.5	235	640
3.6	2.0	247	555
3.7	1.9	250	700
3.7	2.0	310	730
3.8	2.0	325	600
4.2	2.6	240	585
4.4	2.9	180	795
5.1	3.7	310	740
5.4	3.4	217	620
5.4	3.5	260	620
6.0	4.2	168	700
6.4	5.5	130	460
6.7	4.8	160	480
7.0	5.7	155	660
7.3	5.7	115	640
7.8	6.7	150	520
8.0	7.0	113	610
8.3	7.9	140	615
8.8	8.5	80	540
8.8	7.8	125	510
8.8	7.8	128	550
9.3	8.6	150	570
9.3	9.7	70	480
10.0	9.9	105	535

TABLE 1 (*Continued*)

Reacted salt, y_R (mmole g^{-1} × 10^3)[a]	Total salt, y_T (mmole g^{-1} × 10^2)[a]	Benzene activity (mole g^{-1} sec^{-1} × 10^9)[b]	Cyclohexene activity (mole g^{-1} sec^{-1} × 10^9)[b,c]
10.1	10.5	50	430
10.3	11.8	28	370
10.5	11.6	75	465
10.5	11.7	28	370
11.1	13.8	70	550
11.5	16.1	5	240
	KCl		
3.2	0.92	370	720
3.3	0.92	360	800
4.0	1.3	370	800
4.2	1.3	420	900
5.0	1.8	435	870
5.0	1.7	465	738
5.7	2.2	440	740
6.1	2.2	455	865
7.3	3.1	405	875
8.7	2.1	380	800
8.7	4.1	350	640
12.6	6.0	235	700
14.6	9.3	120	550
14.8	9.0	180	520
15.0	9.7	119	465
17.0	11.7	60	450
19.6	16.5	20	190
20.3	25.4	12	175
21.0	35.9	0	200
	$MgCl_2$		
0.28	0.045	245	700
0.78	0.089	340	875
1.3	0.16	320	800
1.7	0.23	455	864
2.4	0.30	430	840
2.9	0.70	280	660
6.2	1.1	222	600
6.2	1.2	190	520
7.2	1.5	225	670
7.2	1.0	170	545
8.0	1.2	165	510
8.2	1.6	210	535
9.0	1.9	155	560
9.1	2.0	187	555
9.7	2.4	130	460
9.8	2.2	115	480
11.5	4.1	75	400
11.6	4.1	70	380
13.0	9.8	40	370
13.0	9.6	40	250
13.6	18.3	28	280
14.0	26.6	12	130
14.0	36.1	0	120
14.0	36.3	0	160
14.0	26.7	5	195
16.8	4.3	77	400
	$CaCl_2$		
0.91	0.13	260	640
1.0	0.13	315	700
2.3	0.28	347	730
5.2	0.70	330	630
5.8	0.66	315	620
6.0	0.78	425	800
6.5	0.92	290	645
7.6	0.97	300	750
9.5	1.6	360	700
10.5	1.9	255	640
11.0	2.1	270	730
11.5	2.3	215	700
11.8	2.4	305	680
14.3	8.6	170	600
14.3	3.7	170	580
16.3	9.6	50	365
16.6	10.0	70	380
17.2	18.7	0	220
17.5	36.8	0	155
17.8	28.0	0	170

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[a] Expressed in millimoles of salt and based on chloride analyses.

[b] The anomalies which arise because the catalysts are arranged in order of increasing y_R, a quantity which can be significantly in error at high c_f values, vanish if the more reliable y_T values are considered.

[c] May include one or more of the isomeric methylcyclopentenes.

actually 0.77% higher than determined, y_R would actually be 0.014 mmole g^{-1}, 22% less than what was found. If there were such an error in the data of Fig. 5, the metal ion and chloride ion isotherms would coincide even at high concentrations. Even so, the agreement between ions is fairly good at low concentrations in Fig. 5, and at all $CaCl_2$ concentrations in Fig. 6.

Catalyst activities. A plot of activity vs. time, with respect to both cyclohexene and benzene production, is shown in Fig. 7 for the chromia-alumina catalyst containing no added salt. There is evidently no aging in at least the 1st hr, and therefore all activities reported are averages of two to four activities for times between 30 and 70 min after the run started. Activities with respect to

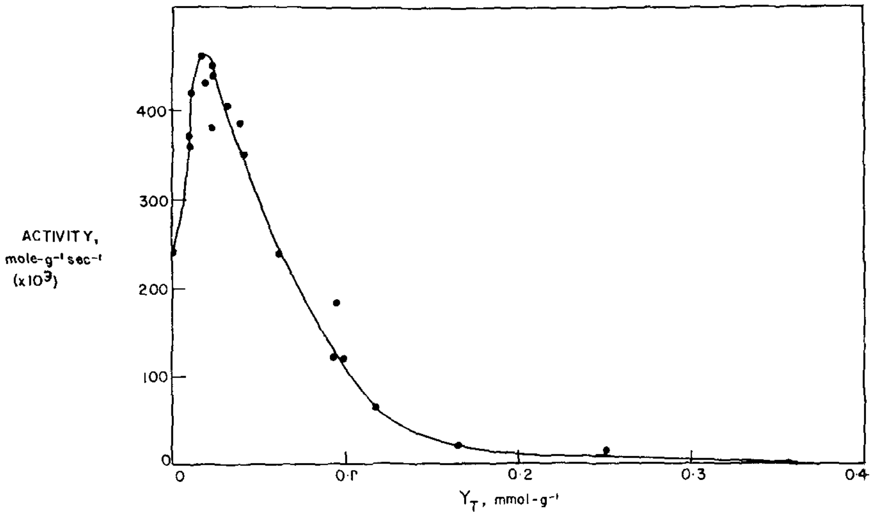

FIG. 8. Benzene activity of KCl-impregnated chromia-alumina catalysts as a function of y_T.

both cyclohexene and benzene production for all catalysts, along with y_T and y_R values, are given in Table 1. When the rates are corrected by subtracting out the thermal rates (see Experimental), the cyclohexene and benzene activities depend upon the experimental variables in about the same way, with greater scatter in the cyclohexene activities. Therefore, only benzene activities are discussed in the remainder of this article.

In Fig. 8, a plot of activity vs. y_T for the KCl-chromia-alumina catalysts is given. Similar plots, with the experimental points omitted (but found in Table 1) to avoid confusion, are given for all five sets of catalysts in Fig. 9. Activity vs. y_R for the KCl-chromia-alumina catalysts is plotted in Fig. 10 and similar plots without experimental points for all five sets of catalysts are shown in Fig. 11.

The activities of the unwashed catalyst, the washed catalyst which was not treated with water analogous to the salt solution treatment, and the washed catalyst which

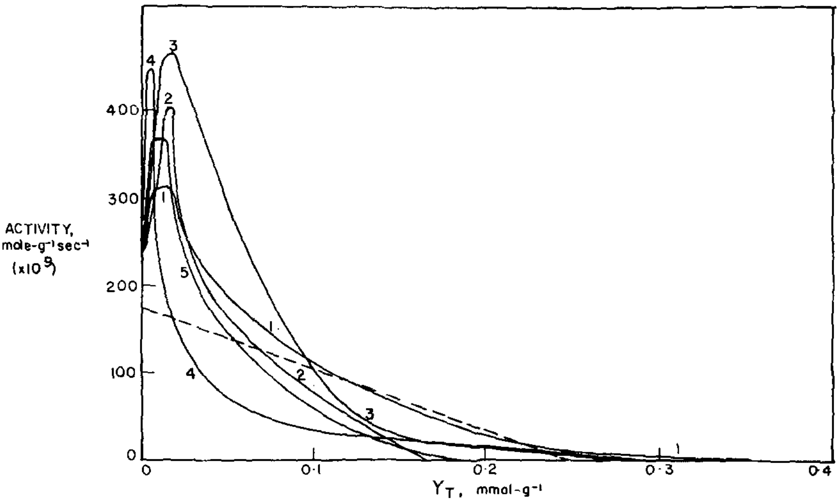

FIG. 9. Benzene activity for chromia-alumina catalyst impregnated with various salts, as a function of y_T; 1, LiCl; 2, NaCl; 3, KCl; 4, $MgCl_2$; 5, $CaCl_2$. Dashed line is approximate extrapolation of part of LiCl curve to $y_T = 0$.

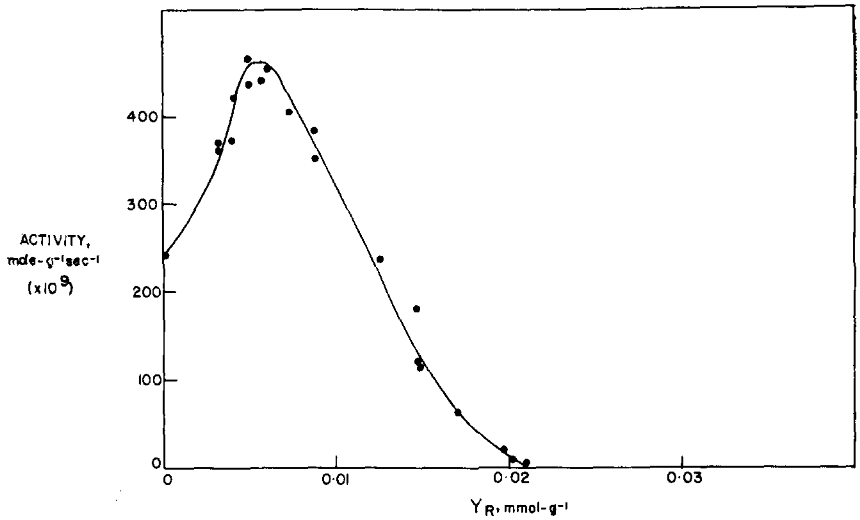

FIG. 10. Benzene activity of KCl-impregnated chromia-alumina catalysts as a function of y_R.

was so treated, were, respectively, 925, 450, and 245 × 10^{-6} mmole g^{-1} $sec.^{-1}$.

The rate of MCP production varied, in 91 catalysts studied, from the thermal rate up to only 80% more than the thermal rate. There was little, if any, correlation with the experimental variables.

DISCUSSION

Solution–Solid Isotherms

The existence of a time-invariant shoulder in the isotherms of Figs. 3–5 indicates the salt reaction with the surface is reversible. Because of our earlier inability to obtain a time-invariant shoulder in the LiCl-alumina isotherm, we concluded that the reaction may be irreversible (*9*); from the data of Fig. 2, it is evident that the same conclusion can be made for the reaction of LiCl with chromia-alumina. With both alumina and chromia-alumina, the amount of reaction with LiCl is greater than would be expected from a comparison with the other alkali

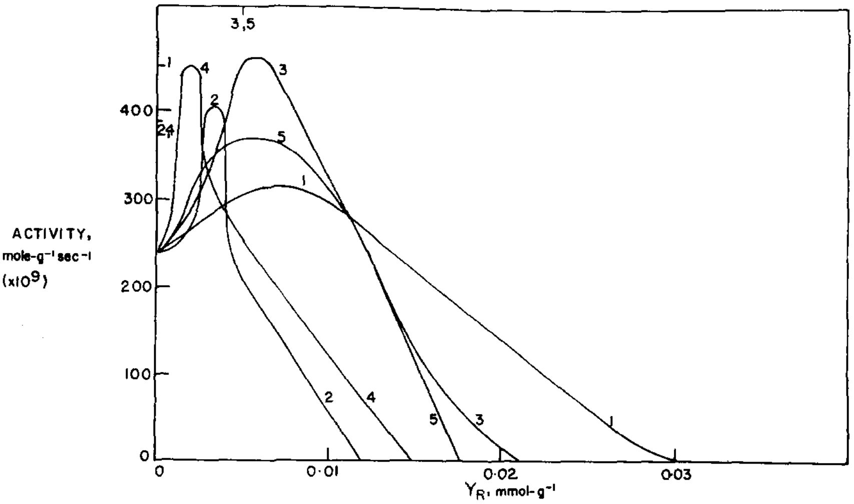

FIG. 11. Benzene activity for chromia-alumina catalyst impregnated with various salts, as a function of y_R; 1, LiCl, 2, NaCl, 3, KCl; 4, $MgCl_2$; 5, $CaCl_2$. Numbers at edge of plot indicate extrapolated values of indicated curves.

metal chlorides, suggesting that the slow reaction is a second, additional reaction, beyond the rapid, reversible reaction which occurs with the other alkali metal chlorides and presumably also with LiCl. Except for LiCl, the amount of reaction in each group increases with increasing cation atomic number, since the maximum y_R values (Figs. 2–6) are in the order NaCl < KCl < LiCl for the alkali metal chlorides, and $MgCl_2$ < $CaCl_2$ for the alkaline earth chlorides.

For no salt was there found in the equilibrium solution a significant concentration of ions other than the salt ions; the pH's of the initial and equilibrium solutions were about the same; the dichromate concentration was always less than 0.002 *M*; and Al^{+3} and Cr^{3+} were not detected. Therefore, it is concluded that there was equivalent anion–cation addition in all cases, and that any differences between the chloride and cation isotherms in Figs. 5 and 6 arise because of the difficulty of obtaining accurate y_R values (see Results). [Langmuir plots, not shown, were linear within experimental error; to the extent they are linear, they also indicate equivalent anion–cation exchange, with the production of solvent anion and cation (*14*).]

Promotion and Deactivation, a Cation Effect

If the promotion of chromia-alumina catalysis in the dehydrogenation of cyclohexane occurs because salt cations remove surface acidity (see Introduction), then metal chlorides, as well as oxides, should be promoters. Figures 8–11 show that promotion by metal chlorides does indeed occur.

The amount of MCP produced was always small, and this amount did not decrease enough as metal chloride was added to account for the promotion effect. However, we have shown (unpublished results) by adding MCP that the catalyst is poisoned irreversibly under our reaction conditions. Therefore, the MCP product we observed (not much more than the thermally produced MCP) may have played only a minor role in poisoning the acid sites, with the significant poisoning effect arising from MCP never released to the gas phase.

Since both metal oxides and metal chlorides deactivate the dehydrogenation sites, it is suggested that this effect is also caused by the cation. Dehydrogenation proceeds in two steps, with cyclohexene the detectable intermediate (*15*). Since the production of both cyclohexene and benzene is affected by cation addition in approximately the same way when the thermal rates are taken into account, the cation apparently reacts with the sites which produce cyclohexene if its effect is one of reaction with specific sites.

Promotion and Deactivation Considered Quantitatively

It is assumed that at high concentrations the salt has completely removed acid sites. An inspection of the activity vs. y_T curves above $y_T \approx 0.10$ mmole g^{-1} in Fig. 9 is instructive. If the number of dehydrogenation sites deactivated is proportional to the number of salt "molecules" ("komes") in the pore volume, then the last part of the curve would be linear, and an extrapolation back to $y_T = 0$ (the LiCl extrapolation is shown as a dashed line in the figure) would give the activity of the salt-free catalyst if there were no poisons found on acid sites. But in some of the cases such an extrapolation yields an activity *lower* than the highest observed activity, contrary to what would be expected. Furthermore, some of the observed curves are nonlinear at high y_T values, contrary to what would be found if y_T in this range were proportional to the extent of deactivation.

If, however, similar extrapolations are made in the activity vs. y_R curves (Fig. 11), the extrapolated activites at $y_R = 0$ are much higher than in the y_T extrapolations. At high y_R values the curves are more nearly linear than are the y_T plots. The extrapolated activities should agree, since at $y_R = 0$ all catalysts are identical. But they do not agree, and furthermore it appears that two extrapolated values (for NaCl and $MgCl_2$) are lower than the highest maxima. Thus, while it seems certain that the number of active sites is appreciably less than the lowest y_T values for which the activity is zero, there is no assurance that the salt addition reaction involves only catalytically active sites.

With the salt poisoning of silica-alumina in cumene cracking it was found that the amount of poisoning for a given amount of salt–surface reaction is independent of the salt chosen (*8*). The curves of Fig. 11 are similar, but by no means do they coincide, and so for a given amount of salt–surface reaction the amount of poisoning does depend upon the nature of the salt. Interestingly, the LiCl curve is not essentially different from the others, even though this salt reacts differently with the surface.

For a given salt the approximate y_R value at the point the surface is completely poisoned (Fig. 11) is about the same as the maximum value of y_R in Figs. 2 to 6. The salt and these two y_R values (in mmole g^{-1}) are, respectively, LiCl, 0.030, 0.030; NaCl, 0.012, 0.014; KCl, 0.021, 0.022; $MgCl_2$, 0.015, 0.014; $CaCl_2$, 0.018, 0.018. Because of the scatter of the points in these curves, the agreement is obviously partly fortuitous. Even so, it seems likely that the salt–surface reaction which deactivates the dehydrogenation sites is at least roughly parallel to the salt–surface reaction described by the isotherms of Figs. 2 to 6. While it is unlikely that an isotherm represents a single reaction, the deactivating reaction is complete at about the same equilibrium salt concentration necessary for the completion of any other salt–surface reactions.

The various aluminum and chromium species of the surface are probably chemically similar, reacting in a similar way with an aqueous salt. It has been suggested that one of the species on the reduced catalyst, Cr(II), is responsible for the catalysis of dehydrogenation reactions (*16*). Our data suggest that one (or more) of the similar salt–surface reactions deactivates some chromium species of the reduced catalyst. It is *possible* that the number of catalytically active sites is several orders of magnitude less than the number of sites which reacts with salt, as with silica-alumina-catalyzed cracking of cumene (*8*). From our data, we cannot conclude more than the idea that the number of active sites is not the same as the number of salt reaction sites.

ACKNOWLEDGMENTS

This work was partially supported by Atomic Energy Commission Contract AT (11-1)-1354. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; and one of us (H. V.) is indebted to the National Science Foundation for support in the Research Participation Program for High School Teachers.

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