[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Structure and Activity of the Chromium-Aluminum Oxide Catalyst System

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This paper describes the continuation of structure studies on the chromium-aluminum oxide catalyst system.[2] The change of surface area, as a function of chromium concentration, has been determined. Activity tests have been run, using the cyclization of *n*-heptane as the test reaction, and the results have been correlated with magnetic data previously reported.[3]

Experimental

Surface areas were obtained on the undiluted catalysts by low temperature nitrogen adsorption and the BET equation.

The activity tests were run on a series of catalysts which had been prepared by impregnating γ-alumina with chromic acid solution, followed by reducing with hydrogen.[3] The catalysts varied in concentration from 1.9% to 34.5% chromium after reduction. All catalysts with a chromium concentration of more than 2% were diluted down to 2% with γ-alumina before pelleting. The pellets were 4 mm. long and 5 mm. in diameter. The pelleted catalysts were heated at 500° for twenty hours as a pretreatment, and to burn off the stearic acid used as an aid in pelleting.

The catalytic apparatus was built according to specifications furnished by Dr. H. Pines of this Laboratory. The reactor block was made of aluminum-bronze and was heated electrically. Temperature control was obtained by means of the differential expansion of the block and a porcelain rod. A small bellows type pump was used.

The reactor was made of 20-mm. Pyrex tubing. It was 80 cm. long and had ground glass connections at both ends. The reactor top has two inlets, one for feed and one for the regeneration gas. A thermowell extended from the reactor top down into the catalyst bed. The lower 20 cm. of the reactor was filled with porcelain rings. The space above the catalyst bed was packed with Berl saddles.

The *n*-heptane, obtained from the Westvaco Chlorine Products Company, had a boiling point of 98.44°, a freezing point of −90.66°, a density of 0.68382 g. per ml. and a refractive index of 1.38779, 20°/D.

All tests were run at 490°. The temperature control was accurate to within two degrees. The space velocity was 50 cc. of liquid *n*-heptane per gram of chromium per hour. Since 25 g. of catalyst was used and the chromium concentration was 2%, this space velocity corresponds to a feed rate of 25 cc. per hour. The test duration was one hour.

The catalyst was regenerated and carbon determined by burning with air for ten hours at 490°. After the regeneration, hydrogen was passed through the reactor for one hour before each test was started.

The products were condensed in a water condenser and collected in a bulb cooled with ice-water. The non-condensable gases were collected over water in a calibrated bottle. The density of the gas was determined by comparing its weight with that of an equal volume of air under the same conditions.

The liquid product was analyzed for toluene by means of the refractive indices. It was assumed that everything in the product, except the toluene, had the same refractive index as *n*-heptane. A calibration curve for the analysis was obtained from a series of mixtures of toluene and pure *n*-heptane.

The results reported are the average of several runs. In each test the runs were repeated until three values were obtained in which the maximum difference was 2% toluene. This required at least four and usually five different runs because the activity of the first run in each series tended to be very low.

Results

The susceptibility isotherm for an impregnation type series is given in Fig. 1. This isotherm has been presented in a previous paper.

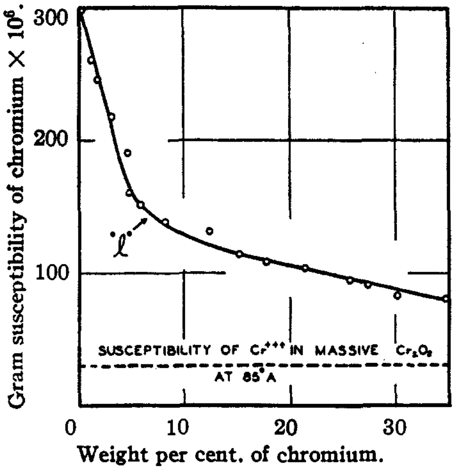

Fig. 1.—Susceptibility isotherm at 85° A. for chromia impregnated on alumina. The susceptibility of chromium in pure chromia at 85° A. is also shown.

The surface areas of catalysts of two impregnation series were measured. In one the carrier was γ-alumina; in the other it was *boehmite*. Figure 2 shows the results of these measurements.

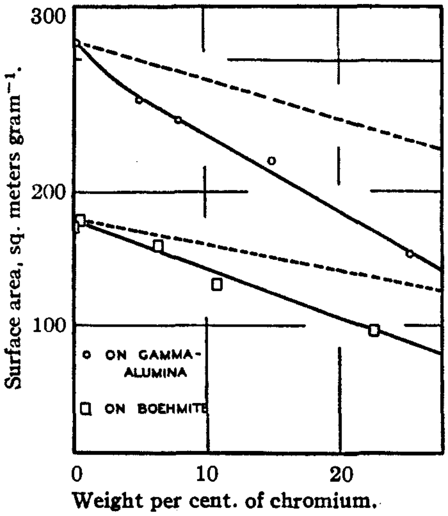

Fig. 2.—Effect of chromium concentration on surface area.

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[2] Eischens and Selwood, THIS JOURNAL, **69**, 2698 (1947).

[3] Eischens and Selwood, *ibid.*, **69**, 1590 (1947).

It is seen that the surface area falls off in practically a straight line for both series.

It has been shown that a point "l" of the isotherm only about one-ninth of the alumina surface could be covered by chromia and that the average chromium atom is in a crystallite about three atom layers thick.[3]

There are two possible pictures of the surface of the catalyst which could explain the fact that only a small part of the total surface is covered at the "l" point. In the first, the alumina surface is only covered in spots. Each of the spots is a crystal nucleus of chromium oxide. There are large areas of exposed alumina between the spots. A second possible representation of the surface would have a large part of the "nitrogen" area in regions inaccessible to the chromium. In this case the crystal nuclei might be touching.

The basic difference of these two extreme views lies in the manner in which they explain why only a small fraction of the alumina is covered. The first view assumes that there is enough attraction or lattice stability in the chromia nuclei so that the chromia will go together into piles rather than spread out evenly over the alumina surface. In the second case, the fraction of area covered represents all of the surface which the chromia is able to reach. The rest of the area is concealed in "caves" and "pores" and there is no exposed alumina.

If the chromia is gathered in piles on the alumina and the latter has large areas exposed, one would expect only a gradual decrease in the total area of the catalyst, as the chromium concentration is increased. At the "l" point only a small fraction of the alumina area would be covered and this decrease would be partially compensated by the area contributed by the chromia. If the entire available area were covered, it is probable that the chromia layer would cover and plug up some of the pores, making them inaccessible to the gas. In this case the area, as measured by the nitrogen, would decrease more rapidly before the "l" point than it would at higher concentrations. One would then expect a curve of area *versus* chromium concentration to have the same general shape as the susceptibility isotherm.

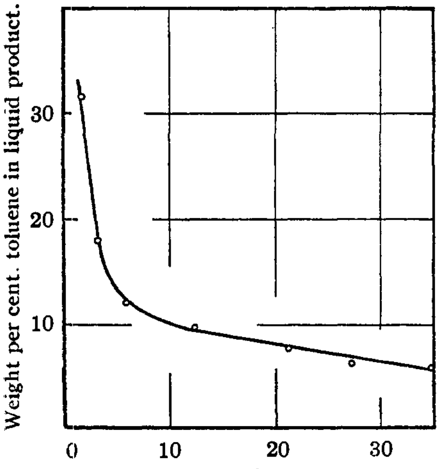

Fig. 3.—Catalytic activity as a function of chromium concentration.

The data presented in Fig. 2 shows that there is no sharp decrease in area in the low concentration region. It is, therefore, indicated that the view of the surface, as being covered with small piles of chromia, is the more nearly correct.

Since the surface area data are reported as square meters per gram of catalyst, one would expect a gradual dropping off of the area as the concentration of chromium is increased because the chromia contributes to the weight of the sample and probably has a much lower area than an equal weight of alumina.

If the assumption is made that the total area of the catalyst is due only to the alumina, one can calculate the apparent area per gram of alumina by dividing the observed area by the weight fraction of alumina. The results of these calculations are plotted by the dotted lines in Fig. 2. It is seen that, even with the above assumption, the apparent area per gram of alumina decreases as the chromium concentration is increased. This would indicate that more and more of the alumina area is covered as the concentration increases. Thus, there must be a spreading of the chromia clusters. The fact that these calculations are based on the probably invalid assumption that all of the area is due to the alumina does not invalidate the conclusion. The assumption is, in reality, the most severe test of the conclusion. If the chromia also contributes to the area, the alumina area drops off at a faster rate than indicated by the dotted line.

The results of the activity tests, reported as per cent. toluene in the liquid product, are given in Fig. 3. Pure alumina has no activity in this reaction. Since the magnetic data have been reported as susceptibility per gram of chromium, it was desirable to present the activity results so that a direct comparison could be made. To facilitate this, the same amount of chromium was used in each test. This also made it possible to have a constant space velocity without changing the pumping rate for the various samples.

On the average about 90% of the feed is recovered as liquid product. The carbon laydown accounts for a little less than 2%. Although the volume of gas formed appears to be roughly proportional to the amount of toluene in the liquid product, the weight per cent. of gas is not consistent. This is probably accounted for by the fact that small variations in the amount of cracking would not affect the volume of the gas nearly as much as they would affect the density. The cracking product gases have a much greater density than the hydrogen given off in the dehydrocyclization.

The supplementary data are given in Table I.

TABLE I

CATALYTIC ACTIVITY OF Cr_2O_3/Al_2O_3

Wt. % chromium[a]	Liters of gas[b]	Wt. % gas	Wt. % carbon[d]	Wt. % liq. prod.[d]	Wt. % toluene[c,d]
1.9/1.9	6.0	5.3	1.9	91	31.3
2.0/3.2	4.2	4.7	1.8	91	18.1
2.0/5.7	3.0	3.7	1.6	88	11.7
2.0/12.2	2.3	4.2	1.8	91	9.6
2.0/21.1	2.1	3.5	1.6	91	7.6
2.0/27.2	2.1	3.9	1.7	90	6.3
2.0/34.5	2.2	3.2	1.5	89	5.8

[a] The designation 2.0/5.7 means that the catalyst contained 2.0% Cr but that this was made by mechanically diluting a 5.7% Cr impregnate with an appropriate amount of γ-alumina. [b] 25°, 750 mm. pressure. [c] In liquid product. [d] The difference between 100 and the sum of columns 3, 4 and 5 is experimental error.

A comparison of Figs. 1 and 3 shows that there is apparently a close relationship between the activity of the chromia–alumina catalyst and the magnetic susceptibility of the chromium in the catalyst. It is important to remember that thus far this relationship has been shown to hold for a series of catalysts, the method of preparation of which is identical and which differ only in the concentrations of chromium. The only other catalysts tested were those for which the impregnation was carried out at different temperatures, as previously reported. In this case there also appeared to be a relationship between susceptibility and activity. However, these results were not extensive enough to warrant definite conclusions.

In order to discuss the relationship between the susceptibility and activity it is desirable to briefly review the work that has been done in this study of the chromium–aluminum oxide catalyst system.

First, it has been shown that the susceptibility per gram of the chromium in the catalyst varies with the concentration according to the susceptibility-composition isotherm. There is a sharp break in this isotherm at the "l" point. At concentrations below this point the slope of the curve is much greater than at higher concentrations. At this point there are important changes in the factors which determine the Weiss constant, Δ, in the Curie–Weiss law, $\chi = C/(T + \Delta)$. The Weiss constant is a measure of the interaction between electrons in adjacent atoms. The factors which determine the Curie constant (C) are also important in that the apparent valence of the chromium depends on the values of C. The shape of the isotherm has been interpreted on the basis of changes in the coördination number of chromium atoms with respect to other chromium atoms in the corundum structure. This interpretation leads to the belief that the chromia layer is three atom layers deep at the "l" point and that only a small fraction of the total alumina area is covered with chromia.

The weight of the evidence which has been gathered from many sources, such as the isotherm, Weiss constant measurements, and the effects of temperature of impregnation, heat treatment, and co-precipitation, points to the one basic fact, that the susceptibility in this system is a direct measure of the dispersion of the chromium. X-Ray studies verify these conclusions. It is commonly accepted that dispersion is an important factor, but of course not the only one, in the activity of catalysts, because it determines how much of the active element is exposed and available to the reactants. Thus, the conclusion may be drawn that the close relationship found between activity and susceptibility is due to the fact that they are both closely related to the underlying phenomenon of dispersion.

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Summary

Surface area measurements have been made which, when taken together with magnetic data, support the view that at the "l" point of the susceptibility isotherm, the chromia is scattered over the surface of the alumina in small piles approximately three atom layers deep. Activity tests of a series of chromium–aluminum oxide catalysts, used in the cyclization reaction, show that there is a close relationship between the magnetic susceptibility and the activity of the chromium in the catalyst.

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