Oxidation of Chromia Supported on Alumina

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Since 1946 Selwood and his coworkers[1] have carried out a detailed study of the magnetic properties of certain catalysts. By determining susceptibility-composition isotherms for a variety of supported oxides of transition elements, they deduced the oxidation state, the interaction covalence, and the dispersion of the paramagnetic ions. In the case of chromia on alumina[2], they concluded that, while the moment is nearly constant over the whole composition range, the change in susceptibility of chromium is almost entirely brought about by a change in the Weiss constant, namely the degree of dispersion. Selwood stated that the plus-three oxidation state of chromium is probably stabilized by the inductive action of the alumina support.

On the other hand, chromia has been known as a p-type semiconductor in an ordinary atmosphere and contains an excess of oxygen. The surface oxidation of chromia and chromia-alumina catalysts has been studied by many workers. Weller and Voltz[3] showed that the amount of excess of oxygen after treatment with oxygen at 500°C corresponds to the coverage of about one third of the total surface of the chromia. However, their study was concerned with only one commercial chromia-alumina catalyst, so it seems of interest to examine the correlation between the degree of dispersion and the stability of chromia towards oxidation at various temperatures.

Experimental

Preparation of Catalysts—The alumina and the chromia-alumina catalyst used in this study were prepared by a method similar to that described by Eischens and Selwood. Aluminum was dissolved in a ten per cent. solution of potassium hydroxide, then precipitated by acidification with a stream of carbon dioxide. The washed precipitate was dried and calcined at 600 °C for twelve hours. The product was identified as gamma-alumina by X-ray diffraction. Alpha-alumina was prepared by further heat-treatment at about 1100°C for two weeks. The magnetic susceptibilities were found to be -0.37×10^{-6} for gamma-alumina and -0.33×10^{-6} for alpha-alumina. These values were independent of the field strength.

Catalyst samples were prepared by the impregnation method with chromic acid solution. By modifying the concentration of the chromic acid solution, catalysts with chromium concentration from about 1 to 33 per cent. were obtained. Samples were dried for eight hours at 350°C and reduced in a stream of hydrogen for five hours at 360°C. Analysis of each catalyst sample was carried out as follows. The samples were dissolved in hot concentrated sulfuric acid and diluted. The chromic ion was oxidized with potassium persulfate using silver nitrate as catalyst and the excess of the oxidant was decomposed by boiling the solution. After cooling, an excess of ferrous ammonium sulfate was added and the solution was titrated with standard dichromate solution, using diphenylamine in concentrated sulfuric acid as indicator.

Oxygen Treatment—The reduced catalysts were cooled in a stream of hydrogen and oxidized with air at room temperature. Further oxidations were carried out in a stream of oxygen for five hours at 250, 350 and 450°C.

Determination of Oxidation Number of Chromium—An iodometric method was employed for this purpose as described by Weller and Voltz[3]. A weighed amount from 100 to 300 milligrams of the sample was placed in about 30 cc. of distilled water and to it were added about two grams of potassium iodide and 10 cc. of distilled hydrochloric acid. The mixture was allowed to stand for about thirty minutes and the suspension was titrated with standard sodium thiosulfate solution (0.02N) with the use of starch solution as indicator. The mean oxidation number of chromium was calculated on the assumption that chromic ions equivalent to the active oxygen are present in a valent state higher than three.

Magnetic Measurement—The susceptibilities were measured at room temperature using a Gouy balance as previously described[4]. The field was calibrated at two constant current strengths with distilled water. When samples exhibited field strength dependence of susceptibility,

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[1] P. W. Selwood, "Catalysis" vol. 1 ed. by P. H. Emmett, Reinhold Pub. Corp., New York, 1954, p. 353.

[2] R. P. Eischens and P. W. Selwood, *J. Am. Chem. Soc.*, **69**, 1590, 2698 (1947).

[3] S. W. Weller and S. E. Voltz, ibid., **76**, 4695, 4701 (1954) and references cited there.

[4] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

the ferromagnetic effect was calibrated by the formula⁵⁾,

$$\chi_H = \chi + 2\sigma c/H$$

where χ_H is the apparent susceptibility observed at the field strength H, σ the saturation magnetization of the ferromagnetic impurity, c its concentration, and χ the susceptibility free from ferromagnetism.

The gram susceptibility of chromium was evaluated on the assumption that the susceptibility contributions of chromium, aluminium, and oxygen ions are additive, and those of the last two are independent of concentration.

Results

The first series to be considered is that in which gamma-alumina is used as a carrier. Fig. 1 shows the apparent oxidation number of chromium, determined by the chemical analysis, plotted against the concentration of chromium. The specific susceptibilities of chromium derived by direct application of the Wiedemann additivity law from the values per gram of catalyst samples are conveniently shown graphically in Fig. 2. Eischens and Selwood chose to call such curves "susceptibility-composition isotherms". Similar data for the second series, in which chromic acid is impregnated on alpha-alumina, are shown in Figs. 5 and 6.

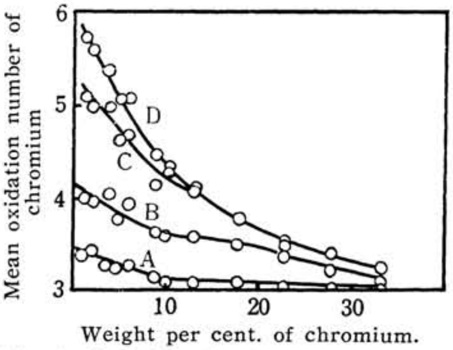

Fig. 1. Relation of oxidation number of chromium supported on gamma-alumina to its concentration: A, oxidized at room temperature; B, at 250°C; C, at 350°C; D at 450°C.

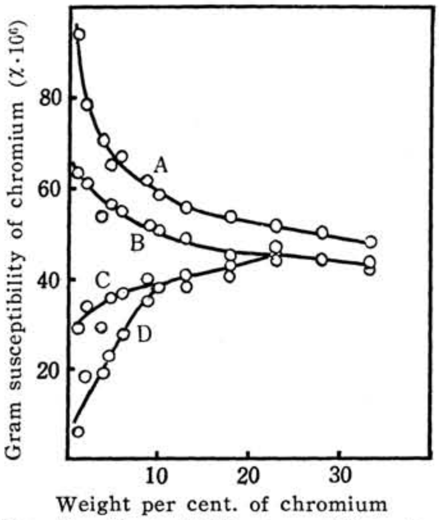

Fig. 2. Susceptibility-composition isotherms for chromia impregnated on gamma-alumina: A, oxidized at room temperature; B, at 250°C; C, at 350°C; D, at 450°C.

Discussion

The reduced catalyst samples are green or bluish white in a stream of hydrogen, but those of low concentration of chromium change their color to grayish white or grayish green in a short time after contact with air. These color changes suggest that the oxidation proceeds perceptibly at room temperature and, as the concentration of chromium decreases, air reacts with the chromic ion more rapidly. By direct chemical analysis, chromium in an oxidation state higher than three was detected over the whole concentration range. As shown in Fig. 1 curve A, the mean oxidation number is appreciably higher than three in the catalyst samples which contain less than ten per cent. of chromium and the limiting value at infinite dilution seems to be about 3.5.

When the temperature of oxygen treatment is raised above 250°C, the catalyst samples in the concentration range of less than eight per cent. change their color to yellowish white and those in the range from eight to twenty per cent. show grayish brown color. These remarkable color changes indicate that a drastic increase in oxidation number of chromium is likely to occur during oxygen treatment at such high temperatures and the results of chemical analysis confirm this view. In the limiting case, infinite dilution of chromium, the oxidation number increases until it finally reaches six, namely chromia is oxidized completely to chromic anhydride. The oxidation of chromia found here is in sharp contrast to our knowledge of the thermal decomposition of chromic anhydride. Glemser and his coworkers⁶⁾ showed that chromic

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5) L. F. Bates, "Modern Magnetism" Cambridge Univ. Press, 1951, p. 135.

6) O. Glemser, U. Hauschild and F. Trüpel, *Z. anorg. allgem. Chem.*, **277**, 113 (1954).

anhydride begins to decompose in a stream of oxygen at about 250°C, the products being $CrO_{2.6}$ at temperature range from 283 to 314°C, $CrO_{2.4-5}$ from 334 to 388°C, and $CrO_{1.6}$ above 400°C. Therefore, the remarkable oxidation of supported chromia can not be attributed to a gross change in crystal nuclei, but the large surface area due to their dispersed structure may be responsible. It appears that the stabilization of the plus-three state of chromium by the inductive action of the alumina support is not effective enough for surface oxidation of chromia to be appreciably prevented.

To elucidate the shapes of the curves in Fig. 1, we must refer to the susceptibility isotherm method developed by Eischens and Selwood; this method revealed the dispersed structure of supported chromia from the magnetic data. Eischens and Selwood established that the susceptibility of chromium in supported chromia follows the Curie-Weiss law, $\chi=C/(T+\Delta)$, and noticed that the Curie constant C which relates to the oxidation state of chromium is almost constant but that the Weiss constant Δ is markedly dependent on the chromium concentration. According to Heisenberg's theory, the Weiss constant may be related to the exchange effect between neighboring paramagnetic chromium ions by the formula,

$$\Delta=-2JzS(S+1)/3k,$$

where J is the exchange integral, z the number of equidistant paramagnetic neighboring ions, S the vector sum of spin moments, and k the Boltzmann constant. Eischens and Selwood calculated the relationship between z and the number of layers of chromia on the assumptions that the variation in the exchange integral can be ignored and also that supported chromia has the corundum structure consisting of a hexagonal close-packed oxide-ion lattice with chromic ions in two thirds of the octahedral holes. Their calculations are reproduced graphically in Fig. 3. They pointed out that the graph of z against the number of layers changes its direction fairly sharply at about three layers and concluded that at the point where the susceptibility-composition isotherm changes its direction, the crystal nuclei of chromia spread on gamma-alumina are, on the average, three layers thick. In our results shown in Fig. 2 curve A, such a characteristic point which was called "point 1" is found at about ten per cent. of chromium. In the higher concentration range of chromium, these crystal nuclei tend to grow and to thicken. On the other hand, as the concentration of chromium decreases, the crystal nuclei shrink and, at the limit, chromium ions may be in two-dimensional atomic dispersion.

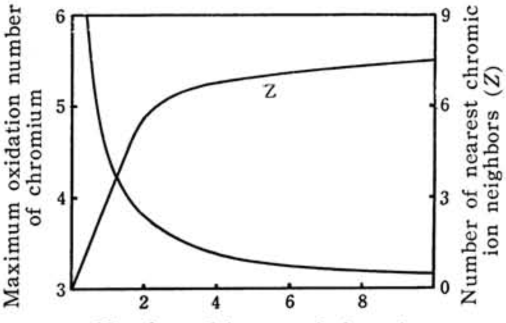

Fig. 3. Relation of maximum oxidation number of chromium and number of nearest chromic ion neighbors to number of layers of chromia.

It must be noted that the oxidation of chromia is especially marked in the concentration range of chromium less than that corresponding to point 1. The decrease in gram susceptibility of chromium means an increase of chromium in a valence state higher than three. Chromium ions in the plus-four and five states are less paramagnetic than those in the plus-three state and susceptibility of chromic acid may be nearly zero; therefore, the shapes of the susceptibility isotherms for the catalyst samples oxidized at higher temperatures (curves B, C and D in Fig. 2) are not only consistent with the above-mentioned view, but also show such a tendency more clearly. A chromium ion in the interior of crystalline chromia is completely surrounded by oxide ions and can not be oxidized directly with oxygen unless it migrates to the surface. But a chromic ion situated on the surface has not a sufficient number of oxide ions to enclose it and there is a possibility of suffering oxidation. The relationship between z and the number of chromia

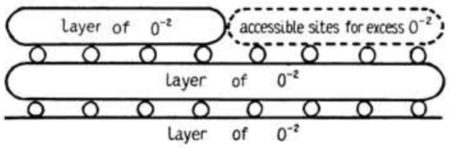

Fig. 4. Schematic representation of two layers of chromia, ○ Cr^{+3}.

layers is determined by the relative importance of the surface layer, hence, we can conclude easily that the degree of possible oxidation stands in close relation with z.

We shall examine the expected relation more quantitatively. Fig. 4 is a very schematic representation of supported chromia which is just two layers thick. Electroneutrality can be achieved in a chromia nucleus when the number of chromic ions situated in the outermost layer is the same as that in the layer just below, and half of them are not covered with oxide ions as shown in the model. The vacant sites on the surface can accommodate excess oxygen atoms until half of the chromic ions in the outermost layer are oxidized completely to the sexavalent state. Therefore, if sufficient oxide ions are supplied into such a space in the outermost oxide layer, the increase in the mean oxidation number of chromium must be $(6-3)/2\times2$ as shown in Fig. 4. Similar examination of a crystal model shows that the maximum value of the mean oxidation number of chromium has the following values; for one layer, +4.50; for three layers, +3.50; for five layers, +3.30; and for ten layers, +3.15. The possible oxidation numbers thus calculated are shown graphically in Fig. 3 for the purpose of comparing with the relation between z and the number of layers of chromia. The magnitude of the calculated values seems to be rather small. The disaccordance may be due to the existence of defects in the interior of the crystal which we ignored in the above examination. Some of them may contribute to oxidation directly and others may promote the migration of ions to the surface and create a further possibility of oxidation. Therefore, it is not too much to say that the possibility of surface oxidation explains satisfactorily the remarkable observed oxidation of supported chromia.

In the second series, the position of point 1 in the susceptibility isotherm for the catalyst samples oxidized at room temperature (Fig. 6 curve A) is not clear. However, by analogy to the first series, we can easily locate it in the isotherms for the catalysts oxidized at higher temperatures (Fig. 6 curves C and D) and also in the relations between the mean oxidation number and the concentration of chromium shown in Fig. 5. Point 1 is found at about two or three per cent. of chromium and its shift to a lower concentration of chromium may be due to a decrease in surface area of the carrier.

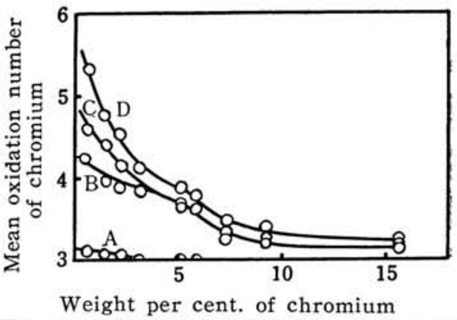

Fig. 5. Relation of oxidation number of chromium supported on alpha-alumina to its concentration: A, oxidized at room temperature; B, at 250°C; C, at 350°C; D, at 450°C.

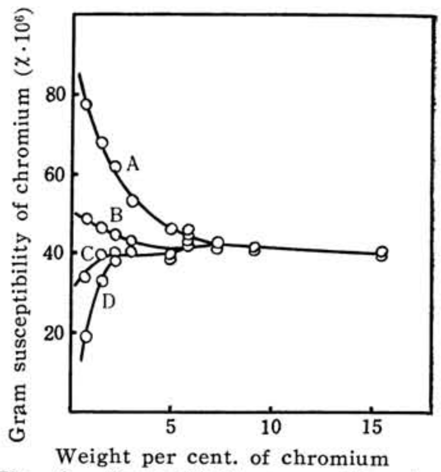

Fig. 6. Susceptibility-composition isotherms for chromia impregnated on alpha-alumina: A, oxidized at room temperature; B, at 250°C; C, at 350°C; D, at 450°C.

The susceptibility isotherms C and D in both the first and the second series show the existence of a characteristic point where the concentration of chromium is about twice that at point 1. The magnetic susceptibility of chromium in the catalyst samples oxidized at 350 and 450°C is nearly constant between these two points. At present the author can not give any explanation to this new point.

Although point 1 was shown at first in the susceptibility isotherm by Eischens and Selwood and its meaning was given on the basis of the magnitude of Weiss constant as clarified in the preceeding paragraphs, its position in the chromia-alumina catalyst system can be easily pointed out in the relation between the mean oxidation number and the concentration of chromium in the samples oxidized at the temperature higher than 350°C. The latter method may be more convenient than the magnetic method as it needs only the apparatus for the usual chemical analysis. Besides, at least in this catalyst system our chemical method has the possibility of giving a measure of the surface area of promoter. It is not yet clear whether or not the application of the method described here is limited to this case.

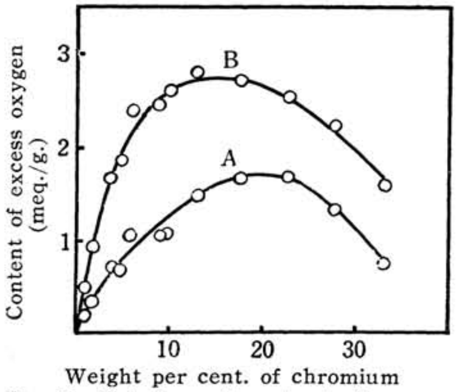

Fig. 7. Relation of content of excess oxygen in chromia-gamma-alumina catalysts to chromium concentration: A, oxidized at 250°C; B, at 450°C.

As the oxidation of supported chromia can be closely related to its high surface area, if we plot the content of excessive oxygen in one gram of the oxidized catalyst sample against the concentration of chromium, the composition at which the surface area of chromia per gram of catalyst reaches its maximum value will be indicated. As shown in Fig. 7, the catalysts which contain from 15 to 20 per cent. of chromium have the greatest values of excessive oxygen. Therefore, when we need to prepare the chromia-alumina catalyst in which the surface area of chromia is as high as possible, we must impregnate chromic acid solution on gamma-alumina, as the final concentration of chromium will be from 1.5 to 2 times that corresponding to point 1.

A similar study on the chromia-zinc oxide catalyst system was also made. The results will be presented in a later paper.

Summary

Oxidation of chromia supported on gamma- and alpha-alumina at room temperature, 250, 350 and 450°C was examined by chemical and magnetic method. The mean oxidation number of chromium in the oxidized catalyst samples was determined as a function of the concentration of chromium. In the extreme case, infinite two-dimensional dilution of chromium, it was shown that chromia is oxidized completely to chromic anhydride. This chemical change is in sharp contrast to our knowledge of the thermal decomposition of chromic anhydride. The remarkable property of supported chromia to suffer oxidation was attributed to the relative importance of surface oxidation and explained nearly quantitatively by comparing it with the conclusion deduced from the susceptibility-composition isotherm method developed by Selwood and his coworkers. Therefore, the study of oxidation of the chromia-alumina catalyst system by chemical analysis seems to be useful to the same degree as the magnetic method proposed by Selwood and more convenient for deducing the dispersed structure of supported chromia. Finally the condition of preparing the catalyst sample which has the greatest surface area of chromia per gram of catalyst was examined in reference to the above-mentioned conclusion.

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