Dispersed Structure of Chromia-Zinc Oxide Catalyst System

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In the previous paper[1] the author has reported the correlation between the degree of dispersion of chromia which is supported on alumina and its stability towards oxidation at various temperatures. In the extreme case where chromium ions are in two-dimensional infinite dilution, it has been revealed that chromium can be oxidized completely to the hexavalent state, contrary to our knowledge of the thermal decomposition of chromic anhydride. This anomalous stability of the higher oxide on the surface of alumina has been explained nearly quantitatively by the relative importance of surface oxidation of chromia. Therefore, the determination of mean oxidation number of chromium in the oxidized chromia-alumina catalysts might be useful in the same way as the susceptibility isotherm method[2] to deduce the dispersed structure of supported chromia.

The magnetic method developed by Selwood was applied by Shida and his collaborators[3] to the chromia-zinc oxide catalysts prepared by the impregnation method. They found that chromic ions

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[1] Y. Matsunaga, This Bulletin, **30**, 984 (1957).

[2] R. P. Eischens and P. W. Selwood, *J. Am. Chem. Soc.*, **69**, 1590, 2693 (1947).

[3] S. Shida et al, Abstracts of the paper presented at the Annual Meeting of the Chemical Society of Japan, April 1954.

are dispersed more highly than in the chromia-alumina system and attributed this distinction to the three-dimensional dispersion of a part of the chromic ions associated with the formation of zinc chromate in the process of impregnation. The form of the susceptibility isotherm is concerned not only with the dispersed structure of chromia on the catalyst surface but also with the three-dimensional dispersion, so it seems to be difficult to deduce the structure of chromia in this catalyst system by the magnetic method alone. On the other hand, however, our chemical method described in the previous paper gives a measure of surface area of chromia; namely, it is concerned with the two-dimensional dispersed structure. Hence for the purpose of elucidating the structure of the chromia-zinc oxide catalyst more fully, the application of these two methods was extended to this catalyst system.

Experimental

Preparation of Catalysts.—Zinc oxide used in this work was prepared by a method similar to that described in our previous work on its diamagnetism[4]. After zinc sulfate solution had been carefully purified, the oxalate was precipitated, filtered and dried at 110°C. Non-sintered zinc oxide was prepared by the calcination of oxalate at 450°C for six hours and a sintered sample was obtained by heating at 850°C for three hours. The magnetic susceptibilitiy of both materials was found to be -0.33×10^{-6} and was independent of magnetic field strength.

Catalyst samples were prepared by the impregnation method in the similar way as in the case where alumina was used as a carrier. Instead of chromic acid solution ammonium bichromate solution was employed for this purpose because Shida et al. claimed that the latter is more suitable for achieving two-dimensional dispersion of chromia on the surface of zinc oxide. The samples with chromium content from about 1 to 17 per cent. were obtained by varying the concentration of the ammonium bichromate solution. The conditions of drying and reduction of the catalysts and the method of determination of the chromium content were the same as those used in the case of the chromia-alumina catalyst system.

Oxygen Treatment.—The reduced catalysts were cooled in a stream of hydrogen, then oxidized with air at room temperature. Further oxidations were carried out in a stream of oxygen for five hours at 250° and 450°C. The oxidation number of chromium in these oxidized catalysts was determined iodometrically.

Magnetic Measurements.—Measurements of the susceptibilities of catalyst samples were made at room temperature using a Gouy balance as previously described[5]. The field was calibrated at two constant current strengths with distilled water, and the field strength dependence of susceptibility was examined. No ferromagnetic effect, however, was found in any sample.

The gram susceptibility of the chromium ion was calculated on the assumption that the magnetic contribution of chromium, zinc, and oxygen ions are additive, and that of the last two is independent of the concentration of any constituent. This assumption seems to be justified by the fact that the change in concentration of lattice defect has no measurable effect on the diamagnetism of zinc oxide[4].

Results

The series in which non-sintered zinc oxide is used as a carrier will be considered at first. In Fig. 1 the mean oxidation number of chromium is plotted against its content. The value in the samples oxidized at room temperature is less than 3.1 in the whole range of chromium content. The degree of oxidation state reached by the treatment at higher temperature is appreciably smaller than that in the chromia-alumina catalyst similarly treated; besides, the forms of curves in these two catalyst systems are quite different.

The susceptibility per gram of chromium derived by direct application of an additivity rule is graphically shown in Fig. 2. In this figure the dissimilarity between the kinds of behavior of chromium in two systems, in which alumina and zinc oxide respectively are used as carrier, is more remarkable. For example, in the samples oxidized at room temperature, the susceptibility of chromium supported on alumina is markedly dependent on its content and the relation between these two variables gives information with regard to the dispersed structure of chromia. But in the case presented in this paper, its magnitude is constant regardless of the content of chromium, and we can not deduce a definite conclusion from these results. The susceptibility of chromium in the series oxidized at higher temperatures decreases as the content of chromium is decreased.

Similar data for the second series, in which sintered zinc oxide is used as the carrier, are shown in Figs. 3 and 4. The susceptibility of chromium in the series oxidized at room temperature shows a

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[4] Y. Matsunaga, This Bulletin, **30**, 680 (1957).

[5] H. Akamatu and Y. Matsunaga, ibid., **26**, 364 (1953).

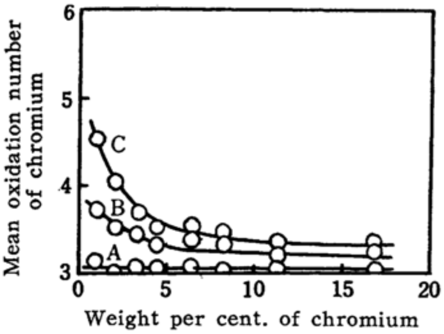

Fig. 1. Relation of oxidation number of chromium supported on non-sintered zinc oxide to its content.
A; oxidized at room temperature,
B; at 250°C, C; at 450°C.

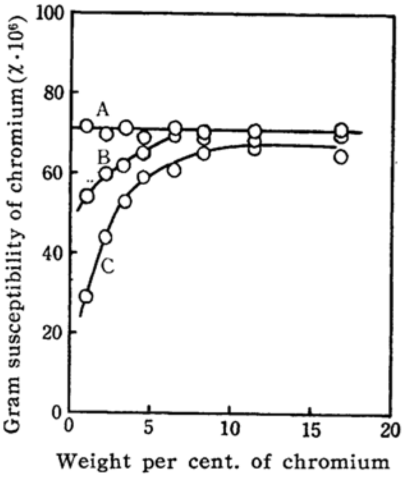

Fig. 2. Susceptibility-composition isotherms of chromia impregnated on non-sintered zinc oxide.
A; oxidized at room temperature,
B; at 250°C, C; at 450°C.

slight increase as its content decreases, and the value extrapolated to infinite dilution of chromia seems to be somewhat greater than that found in the first series. The dependencies of susceptibility and oxidation number in the series treated at higher temperature on the variation of the chromium content are less appreciable than those in the first series.

Discussion

According to the results given by Shida et al., the susceptibility of chromium (χ) in the present oxide-catalyst system follows the Curie-Weiss law expressed by

$$\chi = C/(T+\Delta)$$

where C, Δ are the Curie and the Weiss constants, and T is the absolute temperature. The Curie constant relates to the number of unpaired electrons in a paramagnetic ion, namely the oxidation number of chromium in this case, and the magnitude of the Weiss constant increases in proportional to the number of equidistant neighboring chromium ions as expressed by the formula,

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

where J is the exchange integral, z the number of equidistant neighboring chromium ions, S the vector sum of spin moments, and k the Boltzmann constant.

The susceptibility and the mean oxidation number of chromium for the samples of the first series oxidized at room temperature are independent of the composition of the catalyst. The moment of chromium ion is 3.8 Bohr magnetons at infinite magnetic dilution and the susceptibility value is about 115×10^{-6} at the temperature of measurement⁶⁾. Therefore, we can conclude that z is appreciably great and constant throughout the measured range of chromium content. It must be nine at the maximum value in massive chromia, and may decrease as the crystallite size of chromia decreases or as the neighboring chromic ion is displaced by a diamagnetic ion. The former case was found in the chromia-alumina catalyst system and discussed in detail by Eischens and Selwood. Furthermore, we have presumed that the anomalous oxidation of supported chromia is in close relation with the value of z and confirmed Selwood and Eischens' conclusion from this standpoint. The magnitude of z in the present catalyst system may be about five to six judging from the susceptibility value of chromium. If we wish to interpret this decrease of z by the shrinkage of the crystal nuclei of chromia, they must be, on the average, about three layers thick, regardless of the content of chromium. The mean oxidation number of chromium in such a case must be +3.6 or more as expressed in our previous paper¹⁾ when the samples are oxidized at higher temperatures. Besides, it must be constant throughout the whole range of chromium content. As shown in Fig. 1, however, such an increase in oxidation number is achieved only in the samples which contain less than four per cent. of chromium.

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6) P. W. Selwood, L. Lyon and M. Ellis, *J. Am. Chem. Soc.*, **73**, 2310 (1951).

In the present catalyst system, the displacement of a neighboring chromic ion by a diamagnetic zinc ion must also be considered. It seems highly likely that in the process of impregnation, basic zinc chromate is formed and, after heating and reduction, most of it is converted into zinc chromite and a small proportion of chromic ions are dissolved in the carrier. The estimated value of z seems to be consistent with this model, if the crystal nuclei of zinc chromite are so large that the effect on the magnitude of z of chromic ions situated on the surface can be left out of consideration even in the catalyst which contains only two per cent. chromium. However, such a large crystallite of zinc chromite can not be oxidized appreciably and this model is inconsistent with the apprecible oxidation appearing in the low content range of chromium. Thus it is suggested that the dependence of the oxidation number of chromium on the composition of the catalyst is not explainable without the combination of these two models mentioned above, namely the thin crystal nuclei of supported chromia and the relatively large crystallites of zinc chromite. In the catalyst samples containing a small amount of chromium, the promoter may be mainly in the form of a thin layer of chromia which must be responsible for the high surface oxidation. As the content of chromium is increased, the crystallites of zinc chromite appear and the surface oxidation of the chromia layer becomes less important.

We have shown in the previous paper that the chemical method developed by us gives no more information on the dispersed structure of chromia than that given by the susceptibility isotherm method if the promoter is situated only on the surface of the carrier. However, as described in the above paragraphs these two methods are complementary to each other in the present system so we can clarify more fully the structure of the catalyst by using both methods.

In the second series, the carrier is more or less compact as the result of being heated at higher temperature and may be less reactive than the non-sintered one. Consequently, the reaction between adsorbed chromate ion and zinc oxide becomes rather difficult and the crystal nuclei of chromia grow more easily on the surface of the carrier. The slight decrease in susceptibility of a chromic ion accompanying its increasing concentration in the catalyst must be attributed to this crystal growth. It seems to be consistent with this expectation that the chromic ion in this series is less active towards oxidation.

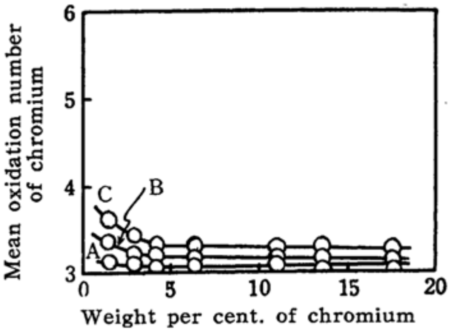

Fig. 3. Relation of oxidation number of chromium supported on sintered zinc oxide to its content.
A; oxidized at room temperature,
B; at 250°C, C; at 450°C.

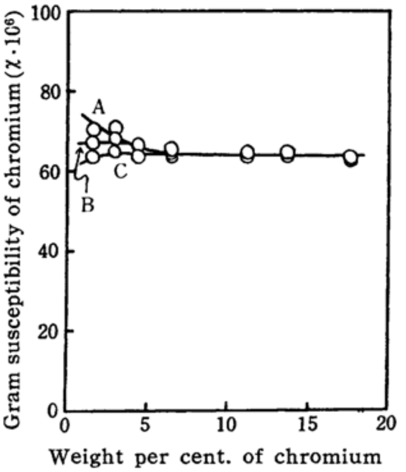

Fig. 4. Susceptibility-composition isotherms of chromia impregnated on sintered zinc oxide.
A; oxidized at room temperature,
B; at 250°C, C; at 450°C.

The cause of discrepancy between the forms of the susceptibility-composition isotherms reported by Shida et al. and by us is not yet accounted for. However, it appears that chromia-zinc oxide catalysts prepared by the impregnation method consist of zinc oxide, relatively large crystallites of zinc chromite, and a thin layer of supported chromia. If the carrier is less reactive than our sintered zinc oxide, the content dependence of susceptibility of chromium will resemble much more that found in the chromia-alumina catalyst system. This is probably due to the fact that chromia arises from the chromate ion adsorbed on the carrier but not combined with it throughout the processes of preparation, i.e. impregnation, drying, and heat treatment. The reactivity of zinc oxide depends on its state of subdivision and the degree of crystallinity as seen by comparison between our two cases. Moreover, it is expected to depend on the type and the concentration of lattice defects contained in the material because these factors govern the diffusion process by which reaction proceeds. For this reason the effect of impurity in zinc oxide must be one of the important causes which determine the structure of this catalyst system.

Summary

Chromia-zinc oxide catalysts have been prepared by the impregnation method using non-sintered and sintered zinc oxide as carriers. Measurements of magnetic susceptibility have been made for these two series of catalysts of varying composition. The values of gram susceptibility and the mean oxidation number of chromium in the samples oxidized with air at room temperature are nearly independent of the content of chromium. After oxygen-treatment at 250° or 450°C has been carried out, however, the surface oxidation becomes appreciable in the samples of low content of chromium, and the variations in the susceptibility and the mean oxidation number suggest that the dispersed structure of chromia depends on the composition of the catalyst. It appears that chromic ions are distributed in the two compounds, namely the thin layers of chromia on the catalyst surface and the relatively large crystallites of zinc chromite and, as the chromium content is decreased, the former becomes more important. By comparison between the two series examined in the present work, it is suggested that the form of the magnetic susceptibility-composition isotherm is governed by the reactivity of the carrier and the cause of the discrepancy between the results obtained by Shida et al and by us may be due to the difference between the kinds of chemical behavior of the zinc oxides employed as carrier.

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