Thermal Decomposition of Chromic Anhydride Supported on Alumina

By Yoshio MATSUNAGA

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In our previous papers[1,2] we have described the anomalous oxidation of supported chromia associated with its highly dispersed structure and have presented a new method of examining the structure of chromia-alumina and chromia-zinc oxide catalysts. In the infinite two-dimensional dilution of chromium, it has been 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 to chromia. The anomalous stability of the plus-six oxidation state of chromium in a highly dispersed state has been explained by the relative importance of surface oxidation of chromia. The present work has as its purpose the confirmation of this stabilization of the higher oxidation state by a study of the thermal decomposition of supported chromic anhydride.

Experimental

Gamma-alumina prepared by the method described in the previous paper[1] was chosen as a carrier because of its high surface area and of its lack of reactivity. Samples were prepared by impregnation with chromic acid solution. They were allowed to stand overnight, filtered, and dried at 110°C. Thermal decomposition was carried out in a stream of oxygen for five hours at 300, 350 and 450°C. A part of the sample, heated at 350°C, was reduced in a stream of hydrogen for five hours at 360°C for the purpose of applying the susceptibility-composition isotherm method[3] to the product. The magnetic susceptibility measurements and the determination of the mean oxidation number of chromium were described previously. The alumina used in this work was found to have a susceptibility of -0.36×10^{-6} per gram.

Results and Discussion

Fig. 1 shows the mean oxidation number of chromium, determined by an iodometric titration, plotted against the chromium content. Glemser et al.[4] showed that chromic anhydride begins to decompose in a stream of oxygen above 250°C, the products being $CrO_{2.6}$ in the temperature range from 283 to 314°C, $CrO_{2.4\sim5}$ from 334 to 388°C, and $CrO_{1.6}$ above 400°C. As the chromium content increases, it would be expected that the compositions of the products in the present system would become close to those reported by Glemser provided that samples are heated in the same temperature ranges. We chose 300, 350, and 450°C as the representative conditions of the above-mentioned three temperature ranges. The curves in Fig. 1 indicate clearly that the plus-six oxidation state is stabilized by the dispersed structure and even at 450°C chromic anhydride in the infinite two-dimensional dilution does not decompose at all. On the other hand, in the higher content range of chromium, the compounds $CrO_{2.6}$ and $CrO_{2.4\sim5}$ which appear in the thermal decomposition of massive chromic anhydride, are not found in our samples. These intermediate oxides seem to be insufficiently stable to exist in the dispersed state.

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[1] Y. Matsunaga, This Bulletin, **30**, 868 (1957).

[2] Y. Matsunaga, ibid., **31**, 58 (1958).

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

[4] O. Glemser, U. Hauschild and F. Trüpel, *Z. anorg. u. allgem. Chem.*, **277**, 113 (1954).

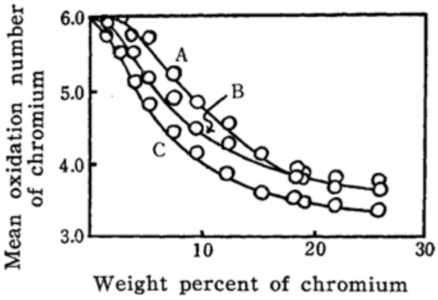

Fig. 1. Relation of oxidation number of chromium supported on gamma-alumina to its content.

A, chromic anhydride was decomposed at 300°C; B, at 350°C; C, at 450°C.

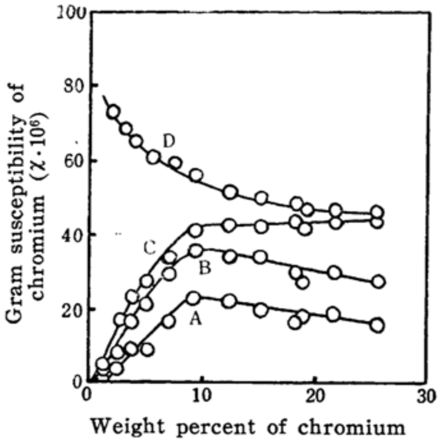

Fig. 2. Susceptibility-composition isotherm for chromium in its oxides supported on gamma-alumina.

A, chromic anhydride was decomposed at 300°C; B, at 350°C; C, at 450°C; D, reduced to chromia.

The gram susceptibility of the chromium ion, calculated on the assumption that the magnetic contributions of the chromium, aluminum, and oxygen ions are additive, is shown in Fig. 2. The chromium in the plus-six oxidation state has no unpaired electron and the estimated susceptibility based on the value for chromic anhydride[5] is 1×10^{-6}, so the decrease of the susceptibility value to almost zero, accompanying the dilution, means an increase of oxidation number to plus-six.

The relationships of the oxidation number and the magnetic susceptibility of chromium to its content in the samples treated at 450°C bear close resemblance to the similar ones shown in the previous paper. It is suggested that the same product is given by the heat-treatment at 450°C regardless of the starting materials; chromic anhydride or chromic oxide. The oxidation number in the series treated at 300 and 350°C are appreciably higher than four in the content range of chromium, less than that corresponding to point *l* in the susceptibility-composition isotherm of the reduced samples. Although we can not find any marked difference between the oxidation numbers of chromium in the samples decomposed at 300 and at 350°C, which contain more than 15% of chromium, the susceptibility values in the series treated at 350°C are significantly larger than thsoe in the series treated at 300°C. Such an increase of susceptibility value without the change of oxidation number suggests the occurrence of a structural change in chromium oxide. The samples containing less than 15% of chromium continue to lose a considerable amount of oxygen between 300 and 350°C.

As shown in Fig. 3, the thermal decomposition of chromic anhydride in the dispersed state occurs continuously, and it seems that the oxidation state of chromium changes from plus-six to plus-three without taking intermediate oxidation states. This view is consistent with the fact that there is only one kind of catalytically-active center for the decomposition of aqueous hydrogen peroxide on the surface of the oxidized chromia-alumina catalysts throughout the range of mean oxidation number of chromium from 3.12 to 5.65[6].

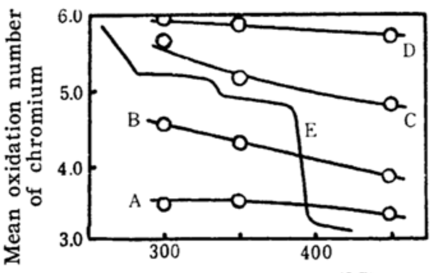

Fig. 3. Relation of oxidation number of chromium to treated temperature in the thermal decomposition of chromic anhydride.

Chromium content A, 27 percent; B, 12.5 percent; C, 5.5 percent; D, 1.8 percent; E, massive chromic anhydride (after Glemser et al.).

Consequently, it appears that the relatively large and thick aggregates of chromic anhydride on the surface of alumina

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[5] F. W. Gray and J. Dakers, *Phil. Mag.*, **11**, 297 (1931).

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

lose the greater part of their active oxygen below 300°C and only a small amount between 350 and 450°C. (cf. curve A in Fig. 3) This anomaly seems to be due to the instability of the intermediate compounds $CrO_{2.6}$ and $CrO_{2.4\sim5}$. There is no loss of oxygen between 300° and 350°C, but the product continues the structural change to chromia in this temperature range and completes it between 350° and 450°C. As described in the previous paper, the surface-accessible sites and some vacant sites due to lattice defects accommodate excess of oxide ions so the apparent oxidation number in the final product is always higher than plus-three. The smaller aggregates of chromium oxide are more defective and have higher surface area, so they have larger accommodation capacity for excess of oxygen. Therefore, the stabilization of the plus-six oxidation state becomes more effective as the chromium content decreases and the size of aggregates becomes smaller. The continuous loss of oxygen throughout the whole temperature range suggests that the product from small aggregates is highly defective and has no definite structure. (cf. curves C and D in Fig. 3)

In the previous paper we showed that the study of the oxidation of the chromia-alumina catalyst system by chemical analysis may be as useful as the susceptibility-composition isotherm method proposed by Selwood. However, the thermal decomposition of chromic anhydride on alumina is a step which takes place practically in the preparation of this catalyst and we can point out easily the position of point *l* in curves B and C in Fig. 1 and curves A, B and C in Fig. 2. Therefore, in the process of preparation, it is possible to get directly the same useful information about the degree of dispersion of chromium as from the oxidation of the final products either by the chemical method or by the magnetic method.

Summary

The thermal decomposition of chromic anhydride supported on gamma-alumina at 300°, 350° and 450°C was examined by chemical analysis and by magnetic susceptibility measurements. The stabilization of the plus-six oxidation state of chromium in a highly dispersed state was confirmed by the present experiments. In addition, by comparing the oxidation number and the magnetic susceptibility of chromium, it was found that the behavior of supported chromic anhydride in large aggregates is also anomalous. Contrary to the case of the thermal decomposition of massive chromic anhydride, the intermediate oxides $CrO_{2.6}$ and $CrO_{2.4\sim5}$ were not found. The large aggregates of chromic anhydride on alumina lose the greater part of their active oxygen at relatively low temperatures and crystallize continuously into chromia with further loss of oxygen.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo