  Bull. Chem. Soc. Jpn., 56, 2203—2207 (1983)

Catalysis by "Copper Chromite". I. The Effect of Hydrogen Reduction on the Composition, Structure, and Catalytic Activity for Methanol Decomposition

Akira IIMURA,* Yasunobu INOUE,† and Iwao YASUMORI

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

†*Analytical Center, Nagaoka Technological University, Kamitomioka, Nagamine, Nagaoka, Niigata 949-54*

(Received November 27, 1982)

The effect of hydrogen reduction on the composition, structure, and catalytic activity of dichromium(III) copper(II) tetraoxide (copper chromite), $CuCr_2O_4$, was investigated. In this oxide, the surface and the bulk Cu^{II} was reduced into Cu^{I} and further to Cu^{0} by heating in hydrogen. The methanol decomposition on fresh copper chromite proceeded in a manner similar to that on metallic copper formed as the result of strong reduction and dispersed on chromium(III) oxide. The contribution of Cu^{II}, Cu^{I}, and Cu^{0} species to catalytic activity was examined and the similarity in the character of reaction on these two samples with different surface states was discussed. The role of Cr_2O_3 interacting with zerovalent copper was postulated.

Dichromium(III) copper(II) tetraoxide (copper chromite), $CuCr_2O_4$, having the spinel structure has been used as a catalyst for the hydrogenation[1-3] of carbonyl compounds or olefins and for the decomposition of alcohols.[4] The durability of $CuCr_2O_4$ to heat and inhibitor seems to be superior to that of metallic copper. The catalytic activities of this oxide, however, often vary with the method of preparation and the conditions of pretreatment.[5] Especially, under reductive conditions, surface or bulk reduction may occur, and the catalytic activity would be influenced by these processes. Accordingly, the study on the structural and activity changes, occurring in reduction treatment is considered to be important. Furthermore the study provides useful information on the structure of the active sites available for catalytic reactions.

Stroupe[6] found that Adkins' catalyst,[1,2] which is composed mainly of $CuO \cdot CuCr_2O_4$ and is active for the hydrogenolysis of esters, was reduced to Cu and $Cu_2Cr_2O_4$ during the course of reaction. Although there are several reports[6,7] on the reduction of the CuO/Cr_2O_3 system, few investigations about the changes of the surface structure of copper chromite by reducing treatments have been made.

Recently, Capece *et al.* reported that the structure of "copper chromite" was elucidated by means of X-ray photoelectron spectroscopy.[8] However, the changes in the surface structure of spinels by reduction have not been clearly discussed because the samples measured by them are commercial "copper chromite" catalysts which contain CuO as well as $CuCr_2O_4$. Thus, in the present study, the copper chromite catalyst was treated in various reducing conditions and the changes of the composition and the structure of the bulk and the surface of the catalyst were investigated. The difference of the catalytic activities between fresh and reduced catalysts was also examined by using the decomposition of methanol as a test reaction. The effect of reducing treatments on the composition and the structure of the simple oxides, CuO and Cr_2O_3 was also studied in comparison with that on $CuCr_2O_4$.

Experimental

Catalysts. $CuCr_2O_4$ was prepared by co-precipitation with aqueous ammonia from an aqueous solution of chromium(III) nitrate and an excess of copper(II) nitrate in relation to the stoichiometric amount of copper, followed by calcination in air at 600—650 °C for 6 h. The crude product was washed with 3 M HNO_3 (1 M = 1 mol dm^{-3}) until there was no detectable Cu^{II} species in the filtrate, and then heated in air at 400 °C for 4 h. This sample will be designated F catalyst in this paper.

The F catalyst was heated under an initial pressure of hydrogen of 50 Torr (1 Torr = 133.322 Pa) in a circulating system for 2 h at various temperatures. Then, the system was evacuated for a few minutes. After evacuation, the catalyst was heated to 500 °C in a closed system, and the water produced was collected in a trap cooled with liquid nitrogen. Finally, the sample catalyst was evacuated at 500 °C for 1 h. The temperatures chosen for the heating in hydrogen were 100, 200, 300, and 400 °C, and the catalysts obtained by these treatments were designated R100, R200, R300, and R400, respectively.

In order to obtain a strongly reduced copper chromite, the F catalyst was placed in a circulating reactor with a liquid nitrogen trap and heated in hydrogen at 500 °C until the rate of water formation became lower than 10 μmol/h g catalyst. Then the catalyst was evacuated for 1 h at the same temperature and was designated SR catalyst.

Commercial CuO(elemental analysis grade) was used for the experiment after pulverization. Chromium(III) oxide was prepared by decomposition of ammonium dichromate, followed by heating in air at 600—650 °C for 6 h.

Characterization of the Catalysts. The X-ray powder diffraction of the prepared catalysts was measured using the Cu $K\alpha_1$ line as an X-ray source.

XP spectra of these catalysts were recorded with a Hewlett-Packard 5950A ESCA Spectrometer. The monochromatized Al *Ka* line (1486.6 eV) was used as an X-ray source. The F catalyst sample was used for the measurement both without treatment and after evacuation at 500 °C in the XPS apparatus for 45 min. R200 and R400 catalyst sample were prepared by heating F catalyst at 200 and 400 °C, respectively in the preparation chamber of the spectrometer under 4 Torr of hydrogen followed by evacuation at 500 °C for 45 min. The SR catalyst was also used for the measurement after evacuation at 500 °C for 45 min in the XPS apparatus. The binding energy values of emitted electrons were corrected by using the carbon Cls value, 285 eV, as an internal standard.

BET surface areas of the catalysts were measured by the use of krypton at liquid nitrogen temperature.

Catalytic Activities. Catalytic activities were examined

for the decomposition of methanol and the initial reaction rates were measured in a circulating system of 470 ml in volume. The reaction was followed by analyzing the products with a gas chromatograph. A good reproducibility of catalytic activity was obtained by evacuation at the reaction temperature for one hour.

For purposes of comparison, the rates of propene hydrogenation on these catalysts were measured using the circulating system described above. To obtain reproducibility of rate measurement, the catalysts were evacuated at 500 °C for one hour before each experimental run of the hydrogenation.

Results

Reduction Behavior. In Fig. 1, the X-ray powder diffraction patterns of F, R100-R400, and SR catalysts are shown and the percentage fractions of reduction are summerized in the column 2 of Table 1. The latter values were estimated from the partial pressure of water formed, by assuming that the reduction was completed when all $CuCr_2O_4$ was turned into Cu and Cr_2O_3.

As shown in the figure, the diffraction lines assigned to $Cu_2Cr_2O_4$, which would be produced by the partial reduction of $CuCr_2O_4$, appeared in the pattern of R200, and the lines became more distinct on the patterns of R300 and R400. In the pattern of SR catalyst, however, the lines corresponding to $Cu_2Cr_2O_4$ completely disappeared and, on the contrary, only the lines assigned to copper metal and Cr_2O_3 appeared. As the (311) diffraction was most intense in all the diffractions of $CuCr_2O_4$, the values of full width at half maximum (FWHM) of this line and the crystallite sizes[9] calculated from these FWHM values are listed in column 3 and 4 of Table 1, respectively. The table shows that the decrease in the crystallite size takes place by reduction at temperatures between 200 and 300 °C. The degree of reduction of R300 is also largely different from that of R200.

It was found that simple oxides of copper, CuO and Cu_2O, were easily reduced into metallic copper by heating at 50 Torr of hydrogen at 300 °C, while the X-ray diffraction patterns of Cr_2O_3 were almost the same before and after heating in hydrogen at 500 °C.

In Fig. 2, $Cu2p_{3/2}$ X-ray photoelectron spectra for F, R200, R400, and SR catalysts are shown. In the spectrum of F catalyst, there are two peaks at about 936 and 940—945 eV which are characteristic of the Cu^{II} species and are assigned to a main peak and its shake-up satellite peak, respectively.[10] A peak which was assigned to photoelectrons from Cu^{I} or Cu^{0} species was also

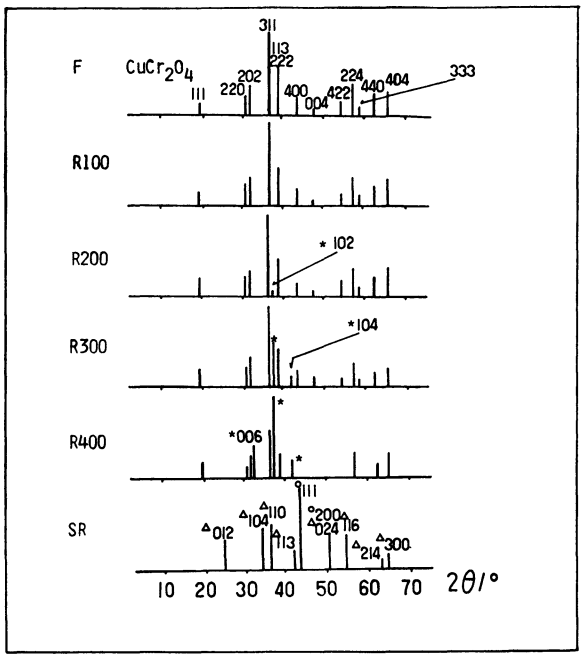

Fig. 1. Changes in X-ray diffraction patterns.
*: $Cu_2Cr_2O_4$, △: Cr_2O_3, ○: Cu.

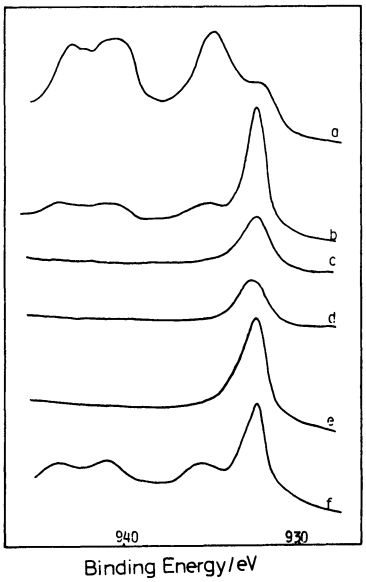

Fig. 2. $Cu2p_{3/2}$ XP spectra. (a) F catalyst, (b) F catalyst after heating at 500 °C, (c) R200, (d) R400, (e) SR catalyst, (f) reoxidized R400 (heated under 4 Torr of oxygen at 400 °C).

TABLE 1. REDUCTION PERCENTAGE, FWHM OF 311 LINE, CRYSTALLITE SIZE, AND SURFACE AREA OF F, R100—R400, SR, AND REOXIDIZED R400 CATALYSTS

Sample	Reduction/%	FWHM/°	D_{311}/Å	Specific surface area/$m^2\ g^{-1}$
F	0	0.24	347	5.7
R100	2	0.24	347	5.6
R200	4	0.24	347	5.9
R300	11	0.30	278	8.4
R400	20	0.42	199	9.9
SR	73	—	—	16.3
Reox.	—	0.42	199	6.4

observed at about 932 eV in all the spectra in the figure. For F, R400, and SR catalysts, peaks were observed at about 917.6, 916.8, and 919.1 eV of kinetic energies, respectively, and assigned to the $L_3M_{4,5}M_{4,5}$ Auger electrons from Cu^{II}, Cu^{I}, and Cu^{0}, respectively.[11] The intensity ratio was estimated at 2 : 1 : 5.

From the spectrum **a** in Fig. 2, the $Cu^{I}/(Cu^{I}+Cu^{II})$ intensity ratio was determined as about 0.15. By assuming that the cross sections of photoionization for Cu^{I} and Cu^{II} species were equal, it was estimated that 15% of the Cu species existed as Cu^{I} in the surface layer of the F catalyst.

Since photoelectrons from Cu^{II} species are scarcely observed in the spectrum of R200, the amount of Cu^{II} species existing in the surface layer of R200 is negligible.

In order to see the changes in the ratio of copper to chromium atoms existing in the surface layer, the intensity ratio of $Cu2p_{3/2}$ to $Cr2p_{3/2}$ in the XP spectra were determined. The results are shown in Table 2; the Cu/Cr ratios of R200 and R400 were significantly lower than that of F catalyst. This indicated that the Cr^{III} species was exposed preferentially to the surface of the catalyst when F was reduced into R200 or R400. The Cu/Cr ratio of SR was the highest all over the catalysts, so that it is concluded that the metallic copper produced by strong reduction is enriched in the surface layer. Therefore, it seems that the SR catalyst has the structure of dispersed metallic copper on Cr_2O_3.

In the bottom of the figure, the spectrum of an R400 sample heated at 400 °C in 4 Torr of oxygen for a further 45 min is shown. The observed main peak at about 936 eV and the satellites at 940—945 eV indicate clearly that the sample surface was partly reoxidized.

Table 2. XPS Intensity ratio of $Cu(2p_{3/2})$ to $Cr(2p_{3/2})$

Sample	$Cu(2p_{3/2})/Cr(2p_{3/2})$
F	1.6
R200	0.2
R400	0.2
SR	1.7
Reoxidized R400	0.6

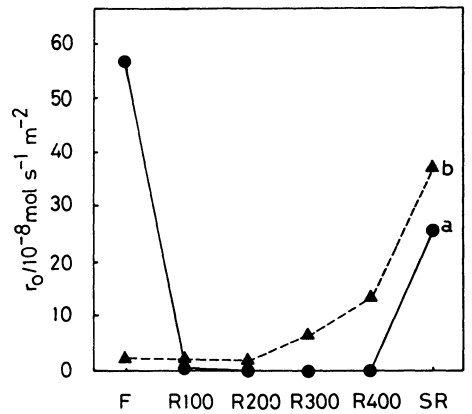

Fig. 3. Relationship between reduction conditions and initial rates of the reactions.
a: Decomposition of methanol at 200 °C, $p_0(CH_3OH) \simeq$ 20 Torr. b: Hydrogenation of propene at 0 °C, $p_0(C_3H_6) \simeq p_0(H_2) \simeq 17$ Torr.

In the spectrum of copper(II) oxide, CuO, no characteristic peaks of the Cu^{I} species were observed.

Catalytic Activities. In Fig. 3, the initial rates of methanol decomposition and propene hydrogenation on F, R100—R400, and SR catalysts are shown. In the case of methanol decomposition, the initial pressure of methanol and reaction temperature were fixed at 20 Torr and 200 °C, respectively. The rates were evaluated from the initial decreases in the partial pressure of methanol. As shown in the plot **a** of the figure, the catalytic activity decreased abruptly on increasing the degree of reduction to 2% (F→R100), and the decomposition did not occur on R200, R300, and R400 catalysts. However, on SR catalyst which was the highest in the extent of reduction, the catalytic activity was observed. The hydrogenation of propene was examined at 0 °C using a equimolar mixture of H_2 and C_3H_6, 35 Torr in total pressure. The product of the hydrogenation was found to be propane only. The reaction rate was evaluated by the initial decrease in the total pressure of the reactant. The plot **b** of the figure shows that the rates of propene hydrogenation were relatively low on F, R100, and R200, whereas the rate became higher on R300 and attained the highest point on the SR catalyst.

Typical runs of methanol decomposition on F and SR catalysts are shown in Fig. 4. The reaction products consisted of methyl formate, hydrogen, and carbon monoxide and there was no obvious difference between the courses of reaction on these catalysts. The changes in the composition of the gaseous product during the course of reaction on F and SR catalysts are appreciably different from that for the reaction on copper wire reported by Miyazaki and Yasumori;[12] the decay of methyl formate as the intermediate was faster than that in the reaction on copper wire.

The initial rates, r_0, of the decomposition on these catalysts were both expressed in the form as

$$r_0 = kKp/(1+Kp),$$

where p is the partial pressure of methanol, k and K are the rate constant and the adsorption constant, respectively: the linear relationships between $1/r_0$ and $1/p$ hold as shown in Fig. 5. From the dependence of ln k against $1/T$, the true activation energies of the reactions on F and SR were evaluated as 62 ± 5 and 60 ± 4 kJ mol^{-1},

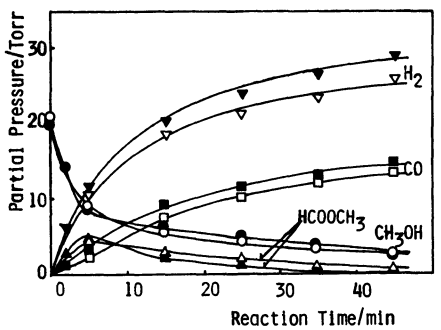

Fig. 4. Courses of methanol decomposition on F and SR catalyst.
Catalyst amount: 1.5×10^{-3} mol. ○△□▽: F catalyst at 200 °C. ●▲■▼: SR catalyst at 180 °C.

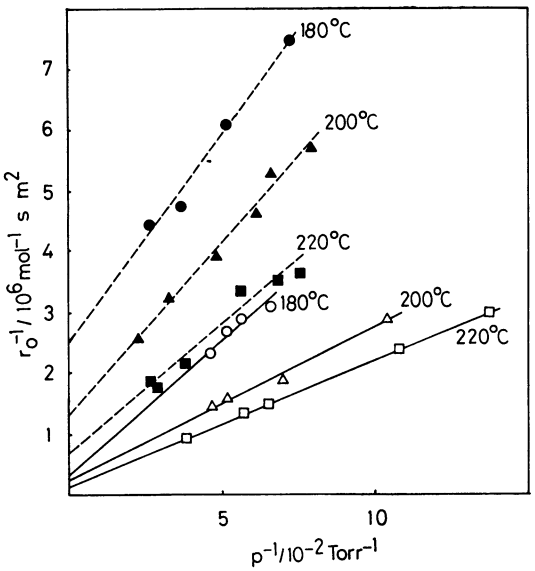

Fig. 5. Relationship between $1/p$ and $1/r_0$.
○△□: F catalyst, ●▲■: SR catalyst.

respectively.

The reactions of methanol on CuO and Cu_2O were examined at 200 °C. In these cases, the formation of CO_2, H_2O, and H_2 was observed in the initial stage of the reaction and methyl formate was produced later. This result shows that the reduction of the oxides proceeded simultaneously with the methanol decomposition, and, the reaction became similar to that on copper wire after the completion of reduction.

The decomposition of methanol on Cr_2O_3 was not observed up to 250 °C.

Discussion

Reduction-Reoxidation Behavior. The present work revealed the details of the effect of reduction conditions upon the composition and structure of copper chromite, $CuCr_2O_4$. Namely;

i) When the catalyst was heated in hydrogen below 200 °C, the bulk composition remained unchanged (Fig. 1 and Table 1), while Cu^{II} ions in surface layer were reduced to the state of Cu^{I} as revealed by the XPS data.

ii) The data shown in Table 1 indicated that the effects of hydrogen reduction began to penetrate deeper at about 300 °C. Under such conditions, the reaction,

$$2CuCr_2O_4 \xrightarrow{H_2} Cu_2Cr_2O_4 + Cr_2O_3 + H_2O, \quad (1)$$

was considered to occur even in the bulk, and the crystallites of starting material, $CuCr_2O_4$, would became smaller. Absence of the Cr_2O_3 lines on the X-ray diffraction chart indicated that the Cr_2O_3 produced by Reaction 1 did not crystallize.

iii) On heating at 500 °C, the catalyst was further reduced to Cu and Cr_2O_3. This suggested that $Cu_2Cr_2O_4$ produced in the Reaction 1 was converted to metallic copper and Cr_2O_3,

$$Cu_2Cr_2O_4 \xrightarrow{H_2} 2Cu + Cr_2O_3 + H_2O. \quad (2)$$

The X-ray data showed that Cr_2O_3 began to crystallize under this condition. On SR catalyst, therefore, the fine crystals of metallic copper were considered to be dispersed over Cr_2O_3.

The reoxidation of the reduced sample provides us with additional information about the structure of the catalyst. When R400 was heated in 25 Torr of oxygen at 400 °C for 1 h, the bluish green sample changed to black in color. The X-ray diffraction pattern of this reoxidized sample was similar to the pattern of R400; the positions, the widths, and the intensity ratios of the diffraction lines of the former sample were almost identical with the corresponding values of the latter sample. This result suggests that reoxidation scarcely occurred in the bulk of R400 under the conditions described above. However, as shown in Fig. 2, reoxidation occurred in the sample surface even under milder conditions. In addition, Table 1 shows that the surface area of the R400 sample decreased appreciably on heating at 400 °C in oxygen. On the basis of these findings, the reduction-reoxidation processes of the present copper chromite catalyst are indicated as follows;

i) The starting material F: The catalyst is the aggregates of polycrystalline particles of $CuCr_2O_4$. Since a small amount of Cu^{I} species is contained in the surface layer of the particles, $Cu_2Cr_2O_4$ and amorphous Cr_2O_3 coexists with $CuCr_2O_4$.

ii) Reduction to R100-R200: Oxygen atoms are removed from the catalyst surface by reduction with hydrogen and Cu^{II} ions are converted into Cu^{I} ions on the surface. The Cr_2O_3 produced covers most of the catalyst surface.

iii) Reduction to R300-R400: Oxygen atoms at the grain boundaries in the polycrystalline particles are also removed; the surface area of the catalyst increases since the original polycrystalline particles are divided into smaller ones.

iv) Reoxidation: When the reduced catalyst to the stage (iii) is heated in oxygen, Cu^{I} ions are oxidized to Cu^{II} ions in the surface layer, and the polycrystalline particles are sintered, so that the surface area of the catalyst decreases again. The crystallite size of $CuCr_2O_4$ in the catalyst particle which is covered with $Cu_2Cr_2O_4$ does not change because the reoxidation occurs only in a few layers of $Cu_2Cr_2O_4$ near the surface. These processes are illustrated by Fig. 6.

As described in the preceding section, the simple oxides of copper, CuO and Cu_2O, were more sensitive to hydrogen treatments than F catalyst, and metallic copper readily formed by heating in hydrogen at 200 °C. Thus it is possible to consider than Cu^{II} ions are somewhat stabilized in the bulk of the spinel structure of $CuCr_2O_4$. The Cu^{I} ions in $Cu_2Cr_2O_4$ are also stable up to 400 °C in 50 Torr of hydrogen, whereas Cu_2O

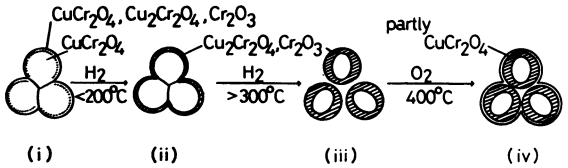

Fig. 6. Reduction-reoxidation process of $CuCr_2O_4$.

is reduced into metallic copper at 200 °C in the same pressure of hydrogen.

Cr_2O_3 formed on the catalyst surface was stable against reduction in the hydrogen treatment under conditions of the present study.

Catalytic Activities. For the decomposition of methanol, high activities were observed only on F and SR catalysts. Cu^{II} species exists only on the F catalyst. On R200—R400, the surface concentration of Cu^{I} species became quite small and methanol decomposition did not occur. These results indicate that Cu^{I} and/or Cu^{II} species are responsible for the methanol decomposition on F catalyst.

From the data of XPS intensity in Table 2, it is considered that the surfaces of R200—R400 catalysts are almost covered with amorphous Cr_2O_3. Therefore, their poor activities may be attributed to the low degree of exposure of Cu^{I} species or the absence of Cu^{II} species.

In SR catalyst, the main surface component is metallic copper; the Auger spectrum of SR catalyst indicates that the Cu^{I} species were rarely exposed on the surface. It is well known[12] that metallic copper has an activity for methanol decomposition, so it is possible to consider that metallic copper is the active component in the SR catalyst.

It has been reported by several authors that olefin hydrogenation proceeds on dehydrated chromium oxide gel,[13] and metallic copper:[14] The high activity of SR catalyst for propene hydrogenation reflects the formation of the dehydrated Cr_2O_3 and Cu^0 species on the surface.

The rate equation applied to the decomposition on these catalysts indicates that the rate determining step of the reaction is a unimolecular process on the catalyst surface. Wachs and Madix[15] reported that, in the reaction of methanol over oxygen preadsorbed Cu(110), a stable surface intermediate, CH_3O, existed on the catalyst below room temperature. By taking their results into consideration, it can be suggested that the O–H bond in methanol adsorbed on F and SR catalysts is weakened to some extent. Accordingly, the sequence of reaction on these catalysts can be represented as follows:

$$CH_3OH(g) \rightleftarrows CH_3O\cdots H(a),$$
$$CH_3O\cdots H(a) \nrightarrow H_2CO(a) + 2H(a),$$
$$2H_2CO(a) \rightleftarrows HCOOCH_3(g),$$
$$2H(a) \rightleftarrows H_2(g).$$

The results obtained for methanol decomposition show that the characteristics of the reaction on F and SR catalysts are very similar to each other, although the surface compositions and the valence states of copper are greatly different between these catalysts. The view that chromium ions act as the main active sites is excluded since the reaction was not observed on Cr_2O_3. Thus these similarities in the catalytic activities have to be attributed to the similarity in the nature of Cu^0 on Cr_2O_3 and that of Cu^{I} or Cu^{II} in F catalyst. Although the characteristics of methanol decomposition of F and SR catalysts (the rate equation and the value of real activation energy) are similar to those for the reactions on copper wire reported by Miyazaki and Yasumori,[12] the changes in the composition of the gas phase product during the course of the reaction are appreciably different. Wachs and Madix[15] reported that the ability of the copper surface to chemisorb methanol was greatly enhanced by surface oxygen. It is expected that Cu^0 on SR catalyst shows characteristics similar to that of Cu^{I} or Cu^{II} species if the oxygen atoms of Cr_2O_3 interact strongly with metallic copper under the present reaction conditions.

In order to reveal clearly the reason for the poor activities of R100-R400 as well as the mechanisms of catalyses by F and SR, it is necessary to analyze precisely the adsorbed state of reactant molecule and its behavior on the catalyst surfaces.

This study was supported by Grant-in-Aid for Special Project Research No. 56119004 from the Ministry of Education, Science and Culture.

References

1) H. Adkins, *J. Am. Chem. Soc.*, **72**, 2626 (1950).
2) H. Adkins and R. Connor, *J. Am. Chem. Soc.*, **53**, 1091 (1931).
3) Z. Kyrideo, *J. Am. Chem. Soc.*, **68**, 1385 (1946).
4) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y. (1939), Vol. XIX., pp. 31—35.
5) W. A. Lazier and J. V. Vangen, *J. Am. Chem. Soc.*, **54**, 3080 (1932).
6) J. D. Stroupe, *J. Am. Chem. Soc.*, **71**, 589 (1949).
7) É. É. Rachkovskii and G. K. Boreskov, *Kinet. Catal.*, **11**, 1036 (1970).
8) F. M. Capece, V. Dicastron, C. Furlani, G. Mattogno, C. Fragale, M. Gargano, and M. Rossi, *J. Electron Spectrosc. Relat. Phenom.*, **27**, 119 (1982).
9) B. E. Warren, *Z. Krist.*, **99**, 488 (1938) and references therein.
10) N. S. McIntire and M. G. Cook, *Anal. Chem.*, **47**, 2208 (1975).
11) P. E. Larson, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 213 (1974).
12) E. Miyazaki and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **40**, 2012 (1967).
13) R. L. Burwell, Jr., A. B. Littlewood, M. Cardew. G. Pass, and C. T. H. Stoddart, *J. Am. Chem. Soc.*, **82**, 6272 (1960).
14) E. Nishimura, Y. Inoue, and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **48**, 803 (1975).
15) I. E. Wachs and R. D. Madix, *J. Catal.*, **53**, 208 (1978).