Catalytic Activity for Methanol Synthesis of Zinc Oxide-Chromium Oxide-Copper Oxide Catalysts and its Structural Dependency

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Because of their higher catalytic activity for methanol synthesis than that of zinc oxide-chromium oxide catalysts, three component catalysts, consisting of oxides of zinc, chromium, and copper, are in industrial use in this country. A few papers[1-3] have already appeared dealing with the catalysts. However, only the papers by Natta and Ivanov described the catalysts from a structural view point, and dependency of catalytic activity upon catalyst structures has remained unclarified as yet. The present study attempts to assemble a number of experimental data in this respect, and to approach complete understanding of the promoting action of copper oxide in the three component catalysts.

In this paper a preparative procedure somewhat different from the usual ones is proposed. The major part of the determinations on catalyst structures as well as on catalytic activity are made on the catalysts prepared by the procedure.

Experimental

Preparations of a series of zinc oxide-chromium oxide-copper oxide catalysts of varying chemical compositions were made by a procedure somewhat different from the usual ones: namely, a commercial zinc oxide powder was kneaded with a chromic acid solution, in which an appropriate amount of cupric oxide had been dissolved, into a paste, which was allowed to dry at room temperature. The resulting cake was crushed, and screened to 2 to 2.5 mm. granules. Another catalyst, denoted by catalyst R, manufactured by a usual procedure was also prepared. According to the procedure, a mixture of powders of zinc oxide and copper oxide was kneaded with a chromic acid solution into a paste, which was then treated similarly to finished catalyst granules.

Chemical compositions of the catalysts used in this study are listed in Table I. Because of rather poor solubility of copper oxide in a chromic acid solution, a catalyst of Cu/Zn ratio in excess of 0.25 could not be obtained.

Catalytic activity for the methanol synthesis was determined according to the same procedure as described in the previous paper[4]. Among the by-products of the synthesis, formaldehyde was determined by a chemical analysis, while water and higher alcohols were determined by means of a gas chromatography.

Catalyst bed density was determined on the catalyst after the synthesis as follows: an amount of the catalyst granules was placed in a graduated cylinder, which was vibrated by hand till no more reduction in volume of the catalyst bed was observed. The density is given by the value of catalyst weight (g.) divided by volume (cc.) at the end of the vibration.

Specific surface area of the catalyst was determined from nitrogen adsorption data plotted according to the BET theory. In addition, volumes were measured by the water- and the mercury-displacement method[5], from values of which true and bulk densities, and pore volume could be evaluated.

Some of the catalysts, the raw as well as the reduced ones, were subjected to an X-ray study by means of a Geiger-counter spectrometer using filtered K_α ray.

TABLE I. CATALYST COMPOSITION

Catalyst	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Cr/Zn, mol.	0.39	0.39	0.44	0.49	0.49	0.49	0.49
Cu/Zn, mol.	0.09	0.16	0.17	0.08	0.13	0.16	0.21

Catalyst	No. 8	No. 9	No. 10	No. 11	No. 12	No. 13	R
Cr/Zn, mol.	0.49	0.55	0.55	0.65	0.65	0.65	0.49
Cu/Zn, mol.	0.25	0.13	0.16	0.21	0.16	0.25	0.16

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1) M. R. Fenske and P. K. Frolich, *Ind. Eng. Chem.*, **21**, 1052 (1929).

2) G. Natta and his coworkers, "Catalysis", III, Rheinhold Publishing Corp., New York (1955), p. 375.

3) K. N. Ivanov. ibid., p. 375.

4) H. Uchida and Y. Ogino, This Bulletin, **31**, 49 (1958).

5) A. J. Juhola and E. O. Wiig, *J. Am. Chem. Soc.*, **71**, 2078 (1949).

Results

Catalytic Activity for Methanol Synthesis.— Some of the results are exemplified in Fig. 1 which, for the sake of comparison, includes the authors' previous results⁶⁾ on a zinc oxide-chromium oxide catalyst. Besides the well-known fact that an addition of copper oxide is very effective in improving the catalytic activity of a zinc oxide-chromium oxide catalyst, the figure reveals that a zinc oxide-chromium oxide-copper oxide catalyst exists in either one of two states, A or B, of different activities. State-A appears immediately after reduction of the raw catalyst at temperatures lower than 280°C, and it is not until the reduced catalyst is heated above this temperature that catalytic activity is decreased to a lower level. Being heated beyond 280°C, the catalyst suffers a rapid activity decline until a steady state, state-B, is established. There is little tendency to further decrease in activity, even though the catalyst in state-B heated as high as 360°C.

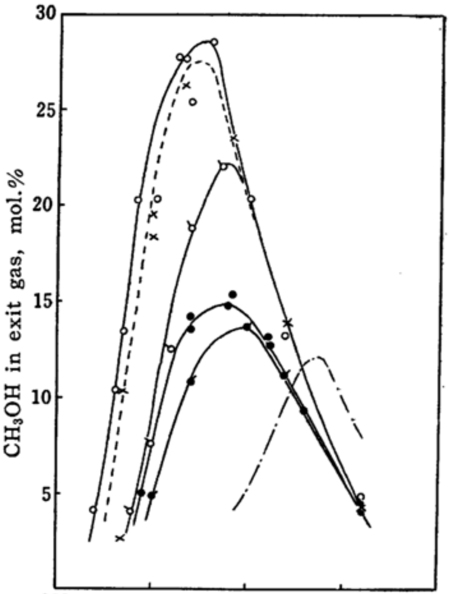

Fig. 1. Methanol concentration as a function of reaction temperature at 150 kg./cm² and S. V. of 1.10⁴.
○, cat. No. 6 (state A), ♁, cat. No. 6 (B), ×, cat. No. 6 (A′), ●, cat. R (A), ♁, cat R (B), —·—, a zinc oxide-chromium oxide catalyst.

Fig. 1 also indicates that after slow oxidation at low temperatures the catalyst in state-B recovers the activity to such a level that it is approximate to the initial activity in state-A (catalyst in state-A′). Being compared with catalyst No. 6, catalyst R of the same chemical composition as, but of a different manufacturing procedure from, catalyst No. 6 gives a considerably lower activity.

It is more desirable to express catalytic activity in terms of the rate constant of the synthesis than the methanol concentration in the exist gas. The reason for this is the difficulties of arranging experiments at a constant space velocity (based on catalyst bed volume after the synthesis), since the catalyst bed volume is apt to shrink, during the synthesis, in an extent that can not exactly be predicted before the synthesis. Usually the extents of shrinkage are in the range of 15 to 25% of the original bed volume of the raw catalyst. The rate constant can be calculated from a methanol concentration by the aid of the rate equation proposed by the present authors⁴⁾.

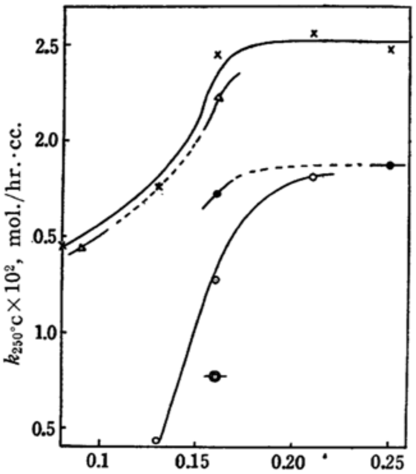

Fig. 2. Catalytic activity as a function of Cu/Zn ratio.
×, Cr/Zn=0.49, △, Cr/Zn=0.89,
●, Cr/Zn=0.65, ○, Cr/Zn=0.55,
◎, cat. R.

The activity thus defined is plotted as a function of chemical composition of the catalysts in Fig. 2. Regarding a series of catalysts of Cr/Zn ratio of 0.49 with varying Cu/Zn ratios, curves in the figure show a rapid initial increase in activity with increasing Cu/Zn ratio, followed by a portion with a smaller slope, and finally

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6) Y. Ogino, M. Oba and H. Uchida, This Bulletin, 32, 284 (1959).

no further increase in the range of Cu/Zn ratios higher than 0.17, while with a series of catalysts with the fixed Cu/Zn ratio of 0.16 and with varying Cr/Zn ratios they show a maximum activity appearing at the Cr/Zn ratio of 0.49.

By-products, such as water and isobutanol, are extremely small in amount (less than 0.7%) in the products at temperatures lower than 270°C, and it makes little difference, whether the catalyst is in state-A or state-B. At higher temperatures the amounts become greater, e. g. attaining to contents of 10% water and 1.4% isobutanol in the product at 360°C. There have been found no alcohols other than isobutanol. Very small quantities of formaldehyde (less than 0.1%) have always been found in the products of the present study.

Catalyst Bed Density. — The catalyst bed density after the synthesis is plotted against the chemical composition of the catalyst in Fig. 3, in which it may be seen that the bed density rises with Cr/Zn ratio up to the high value of 1.47 for a catalyst of an appropriate composition. In contrast to this, catalysts of the usual manufacturing procedures, such as catalyst R and a pelleted catalyst in an industrial use, give lower bed densities of 0.808 and 1.15, respectively.

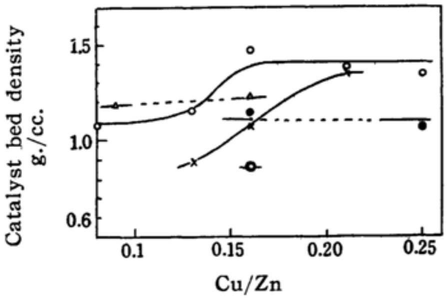

Fig. 3. Catalyst bed density as a function of Cu/Zn.
○, Cr/Zn=0.49, △, Cr/Zn=0.39,
×, Cr/Zn=0.55, ●, Cr/Zn=0.65,
◎, cat. R.

Naturally the catalyst bed density parallels the bulk density of catalyst granules. It is not because the true density of catalyst granules is high, but because the pore volume in the granules is extremely small, that the present catalyst gives a high value of the bulk density (refer to Table III). As shown in the table, the bulk density of a raw catalyst can not be correlated directly to that of a reduced one, since the raw one contains an appreciable indefinite quantity of crystallization water.

Specific Surface Area. — Specific surface areas of the raw and the reduced catalysts are summarized in Table II. The table discloses that the specific surface area is enlarged remarkably by reduction of the raw catalyst to state-A, and further, but in less degree, by subsequent reduction to

TABLE II. CATALYST BED DENSITY AND SPECIFIC SURFACE AREA

Catalyst		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Catalyst bed density, g.*/cc.		1.297	1.231	1.423	1.082	1.328	1.470
Specific surface area (raw), m²/g.		—	10.85	0.54	8.90	5.65	1.69
Specific surface area	A	112	132	133	115	113	113
(reduced), m.²/g.	B	—	—	—	124	151	147

Catalyst		No. 7	No. 8	No. 10	No. 11	No. 12	R
Catalyst bed density, g.*/cc.		1.381	1.328	1.067	1.361	1.162	0.808
Specific surface area (raw), m²/g.		1.08	0.24	9.20	—	5.67	26.5
Specific surface area	A	104	113	104	101	116	94
(reduced), m.²/g.	B	120	151	120	—	140	137

* With reduced catalysts.

TABLE III. DENSITIES AND PORE VOLUME OF CATALYSTS No. 6 AND R

Catalyst		Bed density g./cc.	Density g./cc.	Bulk density g./cc.	Pore volume cc./g.	Average pore dia. Å
No. 6 (raw)		1.78	3.4122	3.0883	0.0307	728
R (raw)		1.03	2.9813	1.1849	0.5085	768
No. 6 (reduced)	A	1.47	4.7325	3.042	0.1190	21
	B	1.43	5.4079	2.806	0.1725	23
R (reduced)	A	0.808	4.9221	2.9716	0.1333	28
	B	0.799	5.4477	1.8609	0.3538	52

state-B. The present catalysts give much higher surface areas than the zinc oxide-chromium oxide catalysts in the authors' previous paper.

A high extent of specific surface area once obtained on a catalyst in state-B is diminished, by slow oxidation of state-B to state-A, to a smaller area which is approximate to the former area of the catalyst in state-A, with simultaneous recovery of the activity.

Loss and Gain of Oxygen with Reduction and Oxidation of Catalyst.—The different states of a catalyst, state-A, −B, and −A′, appeared to be related to different oxygen contents of the catalyst. In this respect, changes in weight of catalyst No. 6 with repeated reduction and oxidation have been pursued in some detail. The results are given in Fig. 4, in which changes in weight are expressed in per cent increase based on the catalyst weight in state-B. By reduction of the raw catalyst at 250°C, decrease in weight takes place to a remarkable extent, the major part of which is presumably due to release of crystallisation water from the raw catalyst. Subsequent reduction from state-A to state-B accompanies the further decrease in weight, whose major part may probably be due to loss of oxygen7). After slow oxidation of the resulting catalyst in dry air at room temperature, gradual take-up of oxygen takes place till it, after a week, attains to as great an amount as 11.3% weight increase. The major part of the oxygen can readily be liberated by reduction at 250°C, and state-A′ is established. On the other hand, it should be emphasized that the gradual oxygen take-up is also observed for zinc oxide-chromium oxide catalysts, though it is of a much smaller amount, e. g. 2.4% increase for a catalyst of Cr/Zn ratio of 0.5.

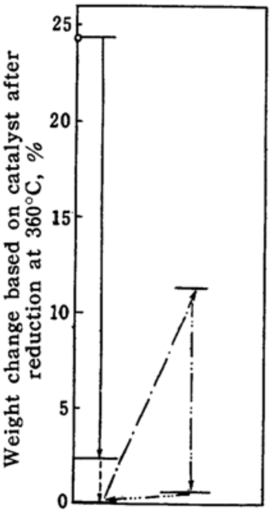

Fig. 4. Changes in weight of catalyst with reduction and oxidation.

○, raw catalyst, ——, reduction at 250°C, ------, reduction at 360°C, —·—·, oxidation at room temperature, —··—··, reduction at 250°C, —···—, reduction at 360°C.

Catalyst Structure Revealed by X-ray Diffraction Patterns. — Among the catalysts, catalysts No. 6 and R were subjected to an X-ray examination. Both of the raw catalysts gave diffraction lines due to zinchydroxychromates Iβ and IIβ, with no signs of oxides of copper. With catalyst No. 6 the latter hydroxychromate develops to greater crystallites than the former one, whereas with catalyst R the situation is the opposite. In this respect the authors' previous paper reported that a catalyst of Cr/Zn ratio of 0.49, with no copper, consisted of zinchydroxychromate Iβ alone, and that zinchydroxychromate IIβ, together with zinchydroxychromate Iβ, appeared only in a catalyst of the smaller ratio. In the present catalysts of high Cr/Zn ratios, zinchydroxychromate IIβ may gradually appear, because the part of chromic acid is consumed by the preferential combination with copper oxide to produce copper chromate. However, no evidence of either copper chromate or cupric chromite has been found in the diffraction diagram, even after the sintering of the catalyst at 600°C8). The results also show that in the manufacturing of the present catalysts chromic acid tends to combine with copper oxide more readily than it does in that of catalyst R.

After the synthesis, catalysts No. 6 and R gave no diffraction lines other than the diffused ones due to cuprous oxide9). This does not necessarily indicate that the crystallite, such as those of oxides of zinc and chromium or those of zinc chromite, are completely absent in the catalyst

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7) The decreases are in the range of 1~3.5% for individual catalyst of the present series. No definite relationship between the extent of decrease and chemical composition has been found.

8) Refer to Stroupe's paper: J. D. Stroupe, *J. Am. Chem. Soc.*, **71**, 589 (1949).

9) The crystallites of cuprous oxide may perhaps be produced, during the taking of the diagram, by reoxidation of copper crystallites produced by reduction, though necessary care, such as the leaching of the specimen in methanol, has been taken.

granules, but that the crystallites are too finely dispersed to be detected by an X-ray examination. The diffration lines of cuprous oxide remain essentially unchaned, whether the catalysts are in state-A or state-B. From the diffusivity of the diffraction lines, a rough calculation of the width of cuprous oxide crystallites was made by the aid of Scherrer's formula. The width has proved to be about 50 Å.

Discussion

Catalytic Activity and Catalyst Bed Density.—Fig. 5. presents the relationship between the catalytic activity and the catalyst bed density, and an approximate proportionality has been found existing between them. The present catalyst owes the fact that it has such a high catalytic activity mainly to the high catalyst bed density. The high catalyst bed density is characteristic of the catalysts made by the present procedure.

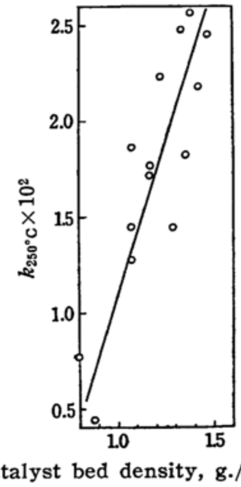

Fig. 5. Relationship between catalytic activity and catalyst bed density.

Specific Surface Area and Specific Catalytic Activity.—With the present catalysts, hardly any relationship between catalytic activity and the extent of the specific surface area has been found. On the other hand, specific activity, namely, activity expressed per unit surface area, tends to increase slowly with copper content throughout the range of the present study (refer to Fig. 6). The tendency, however, is only a minor factor influencing the catalytic activity which is considered on the basis of unit volume of the catalyst bed or unit mass of the catalyst granules. Catalyst R gives a very low specific activity.

Activation Energy and Frequency Factor of Synthesis.—Arrhenius' plots are linear with slopes corresponding to an activation energy of 16.6 kcal./mol. for individual catalysts in state-A, and another one of 21.9 kcal./mol. for individual ones in state-B, respectively. Present values of the activation energy are much lower than those of zinc oxide (34.6 kcal./mol.) and zinc oxide-chromium oxide catalysts (e. g. 27.4 kcal./mol. for a catalyst of the Cr/Zn ratio of 0.5).

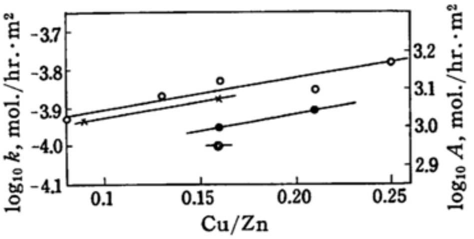

Fig. 6. Specific catalytic activity or frequency factor per unit surface area as a function of Cu/Zn.

○, Cr/Zn=0.49, ×, Cr/Zn=0.39,
●, Cr/Zn=0.55, ◎, cat. R.

By the choice of an adequate scale for the ordinate, the same straight line as cited in Fig. 6 can reveal the relationship between the frequency factor based on unit surface area and the Cu/Zn ratio, since the catalysts give a constant activation energy independently of the varying Cu/Zn ratios[10]. In contrast to the present catalysts, the zinc oxide-chromium oxide catalysts usually showed much higher values of the frequency factor per unit surface area (e. g. 0.5^{-2} mol./hr.·m^2 for the catalyst of Cr/Zn ratio of 0.5). This enables the authors to expect a steep rise of the frequency factor with decreasing Cu/Zn ratios in a range of the extremely low ratios, when the above mentioned straight line relationship is also taken into account. No experimental data, however, are available to demonstrate the expectation as yet.

The catalyst always changes its state from A to B with simultaneous increase of both the activation energy and the frequency factor per unit surface area.

State-A and State-B of Catalyst.—It is not because of the sintering of the catalyst granules that a decrease in catalytic

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[10] From the results, a premise is possible that all active centers are alike, appearing more frequently on the catalyst surface with increasing copper content.

activity appears with the change of the catalyst state from state-A to B, but it is because of a decrease in specific catalytic activity per unit catalyst surface. This is apparent from the rather larger specific surface area for the catalyst in state-B. At first sight, the sintering of copper crystallites, as revealed by the appearance of the diffraction lines due to cuprous oxide in the diagram, seemed to have a great influence upon the specific catalytic activity. This, however, can not be true, because the same diffraction lines appear in the diagram of the catalyst in state-A′ of an activity approximate to state-A.

Among structural factors of the catalyst here investigated, only the oxygen content of catalysts seems to have an influence upon the specific catalytic activity. Oxygen of this kind is remarkably increased in amount by an addition of copper oxide. It is increased to such an extent that it is much greater than that estimated to be produced by the reduction of cupric oxide to copper. The oxygen may thus come partly from copper oxide, but also from some other kinds of oxides of high oxidation stage at which the oxygen is rather loosely bound, namely, oxide of chromium. In this respect, the X-ray diffraction diagram has revealed that, by an addition of copper oxide, crystallites of chromium oxide or zinc chromite become more finely dispersed in the catalyst. Chromium oxide in extremely fine dispersion is reasonably expected to be capable of being oxidized more readily to high valency states (refer to the papers of Selwood(11) and others(12,13)).

Summary

A preparative procedure in which copper oxide is introduced into the catalyst by a different way from the usual ones has presented the catalyst of high catalytic activity for the methanol synthesis. The catalyst owes its high catalytic activity to three structural factors, namely, a high catalyst bed density, a larger extent of specific surface area, and a great amount of oxygen loosely bond in catalyst oxides, among which the first factor plays the most important role. The last is effective in improving the specific catalytic activity based on unit surface area, and is in a close relation to the two states, A and B, of different catalytic activities.

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11) P. W. Selwood, " Advances in Catalysis ", Vol. III, Academic Press, Inc., New York (1951), p. 42.

12) Y. Matsunaga, This Bulletin, **31**, 58, 145 (1958).

13) S. Sida et al., Abstracts of the 7th Annual Meeting of the Chemical Society of Japan, (1954), p. 157.