Study on Zinc Oxide-Chromium Oxide Catalyst. IV. Dependency of Catalytic Activity on Catalyst Structure

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(Received November 13, 1958)

Our previous paper[1] reported that chromium oxide in a catalyst for methanol synthesis played two roles of promoting actions, intercrystalline on the one hand, and intracrystalline on the other hand. For the purpose of understanding the promoting actions from a structural viewpoint of the catalyst, this study has been made, and presents results on catalyst structures such as the crystal- and the macroscopic geometrical structure. On the basis of available data, the relationship between the catalytic activity and the catalyst structure is considered.

Taking the information thus obtained into consideration, we have attempted to prepare a catalyst of the higher activity for the methanol synthesis.

Experimental

Specimens of the same catalysts as described in our previous paper have been used in the present study. The catalysts were divided into three groups, catalysts A, B, and a catalyst S. A catalyst of the first group was a direct preparation from a paste of zinc oxide powder kneaded with a chromic acid solution, while one of the second group was produced from the solid matter remaining after washing of the paste with acetone. This last was prepared from a residue obtained by treating a reduced preparation of catalyst B with nitric acid. Table I shows Cr/Zn ratio determined for each catalyst, with its denotation. The previous paper[1] reported their catalytic activities for the methanol synthesis and decomposition, together with specific surface areas after reduction.

Part of the catalysts, both the raw and the reduced ones, were subjected to an X-ray study by means of a Geiger-counter spectrometer using filtered copper K_α ray.

Experimental data for the specific surface areas were supplemented with those determined on the raw catalysts by the BET method. From an extent of the surface area S, an average diameter d of particles in the catalyst granules was calculated by the aid of the relation of $d=6/(\rho S)$, where ρ was a catalyst density determined by the water-displacement method. Moreover, pore size distributions in three reduced preparations of the catalysts were determined by applying Barret's method[2] to nitrogen desorption isotherms at -195°C.

Experimental Results

Crystal Structure from X-ray Diagram. —Catalyst structures as revealed by X-ray diagrams are listed in Table II. Even the raw catalysts of a very low chromic

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

2) E. P. Barret, L. G. Joyer et al., *J. Am. Chem. Soc.*, 73 373 (1951).

TABLE I. CHEMICAL COMPOSITION OF THE CATALYST

Catalyst	A-0	A-1	A-2	A-3	A-4	A-5	A-6
Cr/Zn ratio	0	0.05	0.10	0.18	0.25	0.33	0.40
Catalyst	—	B-1	B-2	—	B-4	B-5	B-6
Cr/Zn ratio	—	0.05	0.09	—	0.23	0.31	0.36
Catalyst	A-7	A-8	A-9	A-10	A-11		
Cr/Zn ratio	0.50	0.67	1.00	1.10	1.50		
Catalyst	B-7	B-8	B-9	B-10	B-11		
Cr/Zn ratio	0.38	0.47	0.50	0.50	0.50		

TABLE II. CRYSTALLITES IN RAW CATALYSTS FROM X-RAY DIAGRAMS

Catalyst	Crystallites	Catalyst	Crystallites
A-2	ZnO(s), II_β, II_α, III_β	B-2	ZnO(s), II_β, II_α, III_β
A-6	I_β	B-4	ZnO(w), II_β, II_α, III_β
A-7	I_β	B-5	ZnO(very w), II_β(b)
A-9	complicated pattern	B-7	I_β
A-10	probably of Zn bichromate	B-8, -9,	I_β
		B-11	I_β

s, strong: w, weak: b, broad.

acid content (catalysts A-2, B-2) give diffraction patterns of zinc-hydroxychromates, such as III_β, II_α and II_β besides the strong pattern of zinc oxide[3]. As the chromic acid content increases, the pattern due to I_β begins to appear in place of the foregoing hydroxychromates, and that due to zinc oxide becomes weaker, disappearing finally (catalysts B-4, -5). The diagrams taken of catalysts B-7, -8, -9 and -11 of the highest chromic acid content (Cr/Zn ratio of 0.5) among the catalysts of to B series show only the sharp pattern due I_β, whereas the one taken of catalyst A-7 of the same Cr/Zn ratio gives, besides the above, a complicated pattern, which appears stronger in the diagram taken of catalyst A-8. The complicated one seems to refer to zinc bichromate, and presumably comes from the solid layer of a much higher chromic acid content which the liquid in the paste has left behind on the original solid particles (refer to 1).

The crystal structure of the catalyst is appreciably altered by reduction. Although the diagrams taken of the raw catalysts give patterns of various kinds of zinc-hydroxychromates and bichromate, those taken of the reduced catalysts give only two kinds of patterns referring to zinc oxide and zinc chromite spinel. Within a range of Cr/Zn ratio less than 0.5, the pattern of zinc oxide becomes the weaker and the broader for the increaing Cr/Zn ratios, whereas that of zinc chromite maintains a definite degree of broadening, notwithstanding the fact that the intensity is increasing. Catalyst A-10 of a high Cr/Zn ratio gives much sharper patterns of both kinds, and catalyst S, though it has a Cr/Zn ratio (1.6) a little less than the stoichiometric ratio (2) of zinc chromite spinel, gives the pattern due to zinc chromite spinel alone[5].

Rough calculations of linear dimensions D of zinc oxide and zinc chromite spinel crystallites have been made by the aid of Scherrer's formula, $D=k\lambda/\beta\cos\theta$, where k is a constant approximately 0.9, λ is wave length of an X-ray, β is diffraction breadth of a line, and θ is Bragg angle. In the calculation, respective (102) and (400) reflections of zinc oxide and zinc chromite spinel were employed.

In Fig. 1 linear dimensions of crystallites of zinc oxide and zinc chromite spinel are plotted as a function of Cr/Zn ratio, respectively. As Cr/Zn ratio increases, the crystallite size of zinc oxide which originally was as large as 500 Å in linear dimension diminishes rapidly. In this respect, the crystallites of zinc chromite spinel contrast sharply with the above, the linear dimension being kept within a narrow range of 60~100 Å. With an addition of the further increasing amounts

3) By Feitknecht et al.[4], the diffraction patterns as well as chemical formulae of zinc-hydroxychromates were given. The formulae are as follows:
III_β: $ZnCrOr_4\cdot 3Zn(OH)_2\cdot 4Zn(OH)_2$, II_α: $ZnCrO_4\cdot 2.5Zn(OH)_2\cdot 2H_2O$, II_β: $ZnCrO_4\cdot 2.5Zn(OH)_2$, I_β: $ZnCrO_4\cdot Zn(OH)_2$

4) W. Feitknecht and L. Hugi-Carmes, *Helv. Chim. Acta.*, **37**, 2107 (1954).

5) Our results have revealed more kinds of zinc-hydroxychromates than those found by Kawamura et al.[6] with their catalysts, which they prepared by a little different procedure from ours.

6) M. Kawamura, T. Irie, Y. Shiraishi et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 162 (1957).

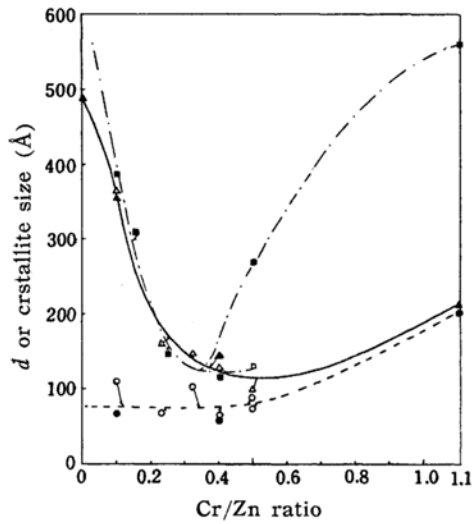


Fig. 1. Average particle diameter and crystallite size as function of Cr/Zn ratio.
—·—·—, average particle diameter: ——, size of ZnO crystallite: ·····, size of zinc chromite spinel crystallite. ●▲■, catalyst A: ○△□, catalyst B.

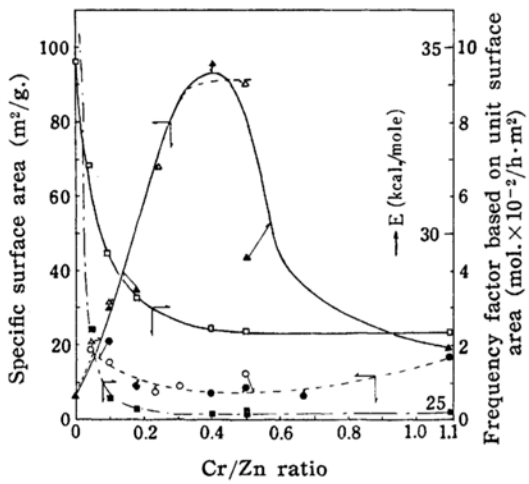


Fig. 2. Specific surface area, activation energy, and frequency factor as function of Cr/Zn ratio.
specific surface area: ●, raw catalyst (catalyst A), ○, (B), ▲, reduced catalyst (A), △, (B). □, activation energy for the synthesis, ■, frequency factor

of chromic acid beyond a Cr/Zn ratio of 0.5, the crystallites of both kinds grow to quite large ones.

Specific Surface Area and Average Size of Particles. — Specific surface areas of the raw catalysts as well as those of the reduced ones are shown as the function of Cr/Zn ratio in Fig. 2. Change in the areas of the former is small, the areas ranging from 7 to 20 m²/g., while the one in the area of the latter gives a remarkable peak at a Cr/Zn ratio of about 0.4～0.5, where the areas are five to ten times larger than those of the corresponding raw catalysts.

Granules of the raw catalysts are built up of particles as large as 1000～3000 Å in diameter. After reduction, the average size of the particles diminishes more or less remarkably according to chromic acid contents in the catalysts. Fig. 1 presents also the relationship between them. It shows that in a range of Cr/Zn ratio, less than 0.4, an average size of the particles is approximatly equal to the size of zinc oxide crystallites, and that in a range of higher Cr/Zn ratio, the particles are of much larger size than the crystallites of zinc oxide as well as zinc chromite spinel. The latter fact indicates that a particle is made up of a number of crystallites.

The growth of the particles as well as the crystallites, appearing in the catalysts of higher Cr/Zn ratios than 0.5, may be ascribed to thermal sintering[7] due to the glowing phenomenon that was once pointed out by Kawamura et al.[8] The glow has been found actually in the catalyst bed

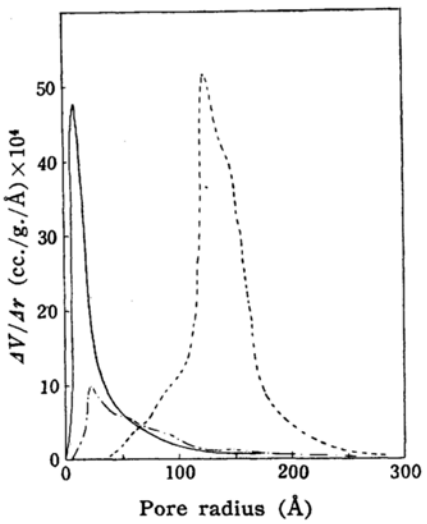


Fig. 3. Pore size distribution.
——, catalyst A-6: —·—·—, A-2: ····, A-10.

7) An assumption is also possible that crystallites of zinc chromite spinel are apt to aggregate with each other to become a large one, since there are not such a large number of zinc oxide crystallites as would be sufficient to prevent the aggregation. However, the assumption can not explain the simultaneous growth of zinc oxide crystallites.

8) M. Kawamura and T. Irie, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 166 (1957).

during reduction tending to appear more readily in the catalysts of the higher Cr/Zn ratios. It necessarily accompanies the growth to a greater extent.

Pore Size Distribution.—The results are shown in Fig. 3. Volumes of pores smaller than 300 Å in radius are 0.0588, 0.1178 and 0.2814 cc./g. for catalysts A-2, -6 and -10, respectively. A greater pore volume is not always associated with a larger extent of specific surface area, but the greater pore volume of extremely small pores with the larger extent of specific surface area.

Discussion

Intercrystalline Promoting Action of Chromium Oxide. — The intercrystalline promoter is a structural one responsible for production of a high-area structure. In this study, experimental evidences have been presented that a marked increase in the specific surface area takes place after reduction of the catalyst, and that well-grown particles of zinc-hydroxychromates in the raw catalysts disintegrate after reduction into extremely fine particles, which are often as small as the individual crystallites of zinc oxide and zinc chromite spinel[9], provided that scarcely any glow phenomenon has occurred during reduction. It has thus appeared that the formation of large particles of zinc-hydroxychromates in the raw catalysts is a requisite necessary for production of the extremely fine particles in the reduced catalysts, namely for the intercrystalline promotion of the activity by a chromic acid addition.

This picture[10] of structures of the raw and the reduced catalysts is consistent with the observations made by Matsui[12] on preparations of zinc-hydroxychromate II_β and its thermal decomposition products under an electron microscope. In his observations, the crystallites (100~500 Å, 500~600 Å in diameter for zinc chromite spinel and zinc oxide, respectively) were much larger in size than the ones defined in the present study. This may have been due mainly to a higher temperature (500°C), at which zinc-hydroxychromate II_β was decomposed, than to the reduction temperature in our study.

Compensation Effect in Catalytic Reactions[13].—We have found that catalyst S consists of zinc chromite spinel alone, and that a surface of the reduced zinc oxide-chromium oxide catalysts contains only two kinds of crystallites, crystallites of zinc oxide and zinc chromite spinel. As a consequence of the findings, we can expect according to the statement by Cremer[14] the compensation effect at the catalytic reactions on a series of the catalysts, under a reasonable assumption that crystallites of the different kinds simultaneously act as sites of a catalytic reaction[15]. On the other hand, the findings lead to the following expression of the intracrystalline promoting action of chromium oxide[1]; namely both the activation energy and the frequency factor based on unit surface area simultaneously fall with increasing proportions of zinc chromite spinel in the surface, the highest levels being thore of zinc oxide and the lowest levels being those of zinc chromite spinel (refer to Fig. 2). The expression coincides with the concept of the compensation effect by Cremer.

According to the aforegoing concept, an overall rate constant, k, is given by

$$k = F_1 A_1 \exp(-E_1/RT) + F_2 A_2 \exp(-E_2/RT) \quad (1)$$

where F is a fraction of the surface, subscripts 1 and 2 mean zinc oxide and zinc chromite spinel, respectively, and hence F_1 and F_2 stand for fractions of the surface occupied by zinc oxide and zinc chromite spinel, respectively. E is an activation energy, and A is a frequency factor based on unit surface area. Moreover, the finding in this study presents the following relationship,

$$F_1 + F_2 = 1 \quad (2)$$

As each value of A_1, A_2, E_1 and E_2 has already been known (refer to 1), F_1 and F_2 for any catalyst of the series can be evaluated from Eq. 1 and 2 by employing a value of k at a high temperature.

9) Comparatively large values of both the zinc oxide crystallite size and the average particle size determined for the catalysts of low Cr/Zn ratios are due to the presence of original large crystals of zinc oxide which have not been brought to a reaction with chromic acid.

10) The picture dose not exactly agree with the one for our previous catalysts[11], which were prepared by a somewhat different procedure from the present one.

11) H. Uchida and Y. Ogino, This Bulletin, **29**, 587 (1956).

12) T. Matsui, *J. Research Inst. Catalysis, Hokkaido University*, **4**, 109 (1956).

13) In this study the reactions include the methanol synthesis and decomposition.

14) E. Cremer, "Advances in Catalysis", Vol. VII, Rheinhold Publishing Corporation, New York (1956), p. 85.

15) According to the statement by Cremer, the compensation effect can be expected at the catalytic reactions on a series of the catalysts whose surface contains different activation energies, and in which the proportions of the sites are shifted with the chemical composition.

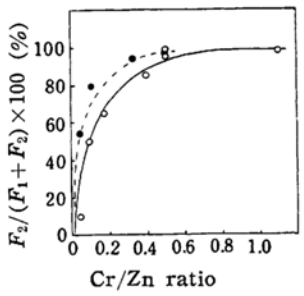


Fig. 4. Fraction of surface occupied by zinc chromite spinel as function of Cr/Zn ratio.
○, calculated from rate constant of synthesis, ●, calculated from rate constant of decomposition.

The results are shown in Fig. 4 as plots of $F_2/(F_1+F_2)$ vs. Cr/Zn ratio. This suggests migration of chromium ions from the particle interior into the surface taking place during reduction of the catalyst, but we can say nothing decisive in this respect as yet.

Attempt to Prepare Catalyst of Higher Catalytic Activity.—From the result that zinc chromite spinel yielded the lowest activation energy of the synthesis, it occurred to us first that a catalyst made of the spinel would be expected to give high activity, if it were provided with a large extent of surface area. However, an addition of chromic acid excessive to the amount corresponding to I_β always caused considerable decline in the surface area due to glowing in reduction. In this connection, we have made various efforts, e.g., reduction processes in hydrogen containing appropriate amounts of steam, to carry out the reduction without the glowing, but with no success. Another procedure, the simultaneous precipitation of hydroxides of zinc and chromium from a mixed solution of the nitrates with ammonia, yielded a catalyst of the desired chemical composition, but scarcely any evidence of zinc chromite spinel has been found unless the precipitate was heated at temperatures higher than 600°C[16]. The heating reduced the activity to a large extent, and we were unsuccessful in putting our first expectation into practice.

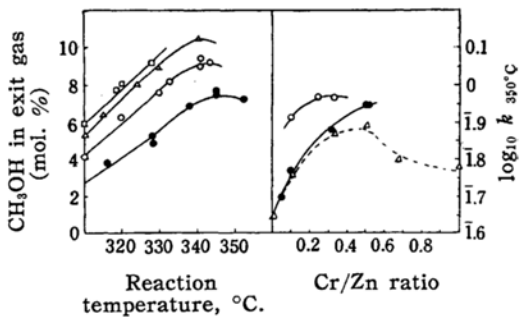
Our results[1] furthermore demonstrate that the specific catalytic activity, i. e., the activity based on unit surface area, for the methanol synthesis is increased appreciably by an addition of a small amount of chromic acid to such a level that is only a little lower than that of zinc chromite spinel. Natta[17], on the other hand, pointed out that zinc oxide produced by decomposition of zinc acetate was of a smaller crystallite size, and consequently showed higher activity than the usual ones. In view of the facts, it can next be expected that a catalyst of even a low chromic acid content may give higher activity, when it happens to have contained zinc acetate in the raw material. In producing a catalyst along with this expectation, the amount of chromic acid should be kept so low as not to provoke glowing during reduction, and hence a paste of the rather small Cr/Zn ratio of 0.25 has been chosen as a starting material, during the kneading of which appropriate amounts of acetic acid are added[18].

The results are given in Table IV, and Figs. 5A and 5B. A comparison of the

TABLE III. INCREASE IN SPECIFIC SURFACE AREA BY ACETIC ACID ADDITION

Catalyst	A-4	A-41	A-411	A-4111
CH_3COOH/ZnO (mol. ratio)	0	1/6	1/2	5/6
Specific surface area, m^2/g.	80	76	98	111
$k^{a)}\cdot10^2$	6.9	10.1	12.4	14.2
$k/WS^{b)}\cdot10^5$	7.75	10.5	10.0	8.3

a) a rate constant of the synthesis based on 10 cc. of the catalyst at 330°C.
b) the rate constant based on unit surface area.



Figs. 5A and 5B. Effect of acetic acid addition on catalytic activity.
A, synthesis. (left).
●, catalyst A-4, ○, A-41, △, A-II, □, A-4III.
B, decomposition. (right).
○, catalyst after acetic acid addition.
△, catalyst A, ●, catalyst B.

16) Even though the catalyst had not been heated at high temperatures, it could not give such a high activity for the methanol synthesis as the one obtainable with the catalyst in this study.

17) G. Natta, "Catalysis", Vol III, Rheinhold Publishing Corporation, New York (1955), p. 349.

18) By an acetic acid addition, the more violent glowing comes to take place.

table with the figures indicates a nearly parallel increase in the activities to the increasing extent of surface area. The figures disclose that the activity for decomposition rises more remarkably than the synthetic activity does. This leads to a premise that the addition of acetic acid does not result in surface enlargement of zinc chromite spinel, but results in that of zinc oxide whose synthetic activity is apt to decline rapidly with time (refer to 1). The premise can be confirmed from a constant value, 28.8 kcal./mol., of the activation energy of the synthesis independent of amounts of acetic acid added.

Summary

So far as catalysts made from pastes of zinc oxide powders kneaded with chromic acid solutions are considered, granules in the reduced ones are built up of extremely fine particles which usually are as small as individual crystallites of zinc chromite spinel as well as zinc oxide. The fine particles appear by way of the large particles of zinc-hydroxychromates in the raw catalysts. However, once the raw catalyst comes to contain a greater amount of chromic acid than that corresponding to zinc-hydroxychromate I_β, the granules in the reduced one are composed of the larger particles, an individual one of which is an assembly of a number of the crystallites.

On the basis of the results available on the catalyst structures, the intracrystalline promoting action of chromium oxide can be explained from Cremer's viewpoint of the compensation effect. The catalytic activity can be increased by adding an appropriate amount of acetic acid into the paste, the increase being nearly parallel to an increasing extent of the specific surface area. The increase by the addition, however, is expected only with the catalyst produced from the paste of a low chromic acid content.

The authors wish to express their sincere thanks to Messrs. S. Kato and M. Taniguchi of Tokyo Institute of Technology for their taking X-ray diagrams.

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