Study on Zinc Oxide-Chromium Oxide Catalyst. III. Promoting Effect of Chromium Oxide on Catalytic Activities for Methanol Synthesis and Decomposition

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Several papers have appeared dealing with the promoting effect of chromium oxide in zinc oxide-chromium oxide catalysts on the catalytic activities for the methanol synthesis and decomposition. However only Natta's paper has been able to discuss the subject from the kinetic view point, since there had not been any rate equation of the methanol synthesis before the one given by Natta[1,2]. Recently the authors of this paper have proposed a rate equation that gives the rate constant of the synthesis from a relatively small number of measurements[3]. By the aid of this rate equation a quantitative expression of the activity becomes available more easily. This leads us to a further understanding of the promoting effect of chromium oxide.

Our previous paper[4] described the activity for the methanol decomposition in connection with the catalyst composition along with its structural dependence, but the catalyst used in the study proved to have such a poor activity that an accurate determination on the synthesis was somewhat difficult. In the present study the catalyst has been prepared by a procedure different from the previous one, and necessary attention has been paid to obtain homogeneous structure of the catalyst.

Experimental Procedure

Catalyst Preparation.—The catalysts were made by treating a commercial zinc oxide powder (grade, pure) with an appropriate chromic acid solution. The mixture was kneaded into a paste, which was divided into two portions. One of them was allowed to dry immediately at room temperature, while the other was washed with acetone before drying. According to the

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[1] G. Natta, P. Pino et al., *La Chimica e L' Industria*, **35**, 705 (1953).

[2] G. Natta, "Catalysis III," 345 (1955) (Edited by P. H. Emmett, Rheinhold Publishing Corp., New York).

[3] H. Uchida and Y. Ogino, This Bulletin, **31**, 45 (1958).

[4] H. Uchida and Y. Ogino, ibid., **29**, 587 (1956).

paper by Feitknecht et al.,[5] the washing furnished a means for separating a solid product from a liquid product in the paste without decomposition. The dried cakes were powdered and pressed into tablets, which were crushed and screened to 2 to 3 mm. particles. The catalyst produced directly from the paste is denoted catalyst A, while the one from the separated solid is denoted catalyst B.

Further, another catalyst, denoted catalyst S, was prepared. A preparation of the catalyst B-9 whose chromic acid content was equivalent to Cr/Zn ratio of 0.5 was reduced in hydrogen at 350°C, and was leached with nitric acid at room temperature till any dissolution of uncombined oxide of zinc or chromium was hardly detectable. The remainder, according to the statement by T. Sato[6], was to give the crystal structure of zinc chromite spinel with no sign of either zinc oxide or chromium oxide. It was then treated in the same way as described above. The Cr/Zn ratio in the catalyst S was determined 1.6 by chemical analysis.

Catalytic Activities for Synthesis and Decomposition of Methanol. — A reactor as described in our previous paper[3] was used for the determination of catalytic activity for the methanol synthesis. The syntheses were conducted at several different temperatures from 300 to 360°C at a constant pressure (150 kg./cm^2 of $2H_2+1CO$ gas) and space velocity (about $1 \cdot 10^4$). Methanol concentration in the exit gas from the reactor gave a measure of the activity. On the other hand, activity for the methanol decomposition was given by a rate of carbon monoxide evolution, or percent of methanol decomposition, during a constant feed through a catalyst bed. The measurements were made at several different temperatures from 300 to 400°C. By-products in the synthesis as well as in the decomposition were determined by analytical methods as usually employed[*1].

Specific Surface Area.—The specific surface area was determined from nitrogen adsorption data plotted according to the BET theory.

Results

Chemical Composition of Catalysts B.—In order to determine the time of kneading necessary for completion of the reaction between zinc oxide and chromic acid solution, change in chemical composition of the solid in the paste with kneading times was pursued. It appeared that after only one hour of the kneading both Cr/Zn ratio and the crystallisation-water in the solid attained respective values which were held approximately constant during the prolonged kneading extending twenty hours. The results clearly show that to the utmost two hours of the kneading are sufficient for completion of the reaction considered, and for producing a solid of homogeneous structure.

In Fig. 1, the Cr/Zn ratio in the catalysts B is plotted against the ratio in the original pastes after kneading for two hours. The full line in Fig. 1 illustrates the fact that the quantity of chromic acid which is removable from the paste by washing with acetone becomes larger according to the increasing ratio of Cr/Zn in the paste. The catalyst B, or the solid in the paste, can thus contain no more chromic acid than that equivalent to the Cr/Zn ratio of 0.5. The results also show that the solid is in equilibrium with the liquid of a higher chromic acid concentration, the amount of which becomes larger according to the increase in chromic acid content in the paste[*2].

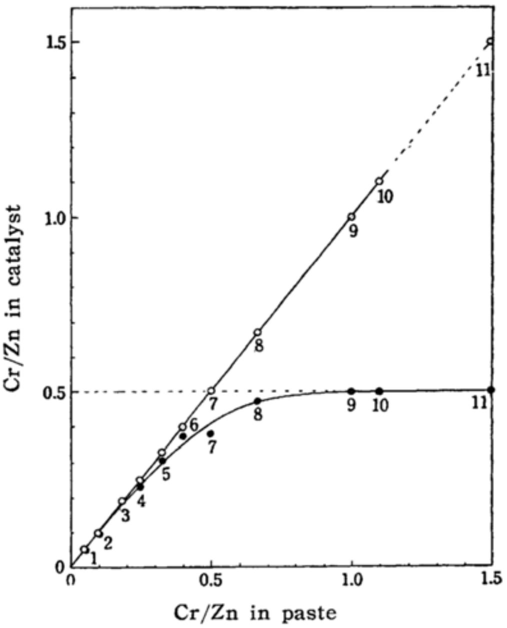

Fig. 1. Catalyst composition.

○ catalysts A; ● catalysts B

A plot corresponding to the series of

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

[6] T. Sato, Lecture at the Fourth Symposium on Catalysis, 1956.

[*1] Refer to our previous paper[3,4], and also the paper by Brown et al. (*Ind. Eng. Chem.*, **21**, 310 (1929)) for analysis of dimethylether.

[*2] Chromic acid concentration of the liquids actually existing in equilibrium with the solids was determined, which follows:

Cr/Zn in paste	1/3	1/2	1/1.5	1	1.5	2.0
Cr/Zn in solid	0.31	0.38	0.47	0.50	0.50	0.50
Cr/Zn in liquid	0.82	1.17	1.78	1.85	1.89	1.95

The results are essentially in agreement with those by Groeger[7].

[7] M. Groeger, *Z. anorg. Chem.*, **70**, 135 (1911).

catalysts A gives the straight line in the figure.

Catalytic Activity for Methanol Synthesis and Decomposition.—Part of the results is shown in Fig. 2 presenting the methanol concentration as a function of the reaction temperature. From the data available, rate constants, k, have been calculated by the aid of the following rate equation proposed by us[3],

$$r = k(p_{CO}p^2_{H_2})^{0.7} - p_{CH_3OH}\cdot(p_{CO}p^2_{H_2})^{-0.3}/K$$

where K is the equilibrium constant of the synthesis, and are given in Fig. 3 as a function of Cr/Zn ratio in the catalysts. The figure reveals that the series of catalysts A exhibits maximum activity at the Cr/Zn ratio which is a little less than 0.5, whereas catalyst B-10 of Cr/Zn ratio of 0.5 gives activity higher than the catalyst A-7 of the same Cr/Zn ratio.

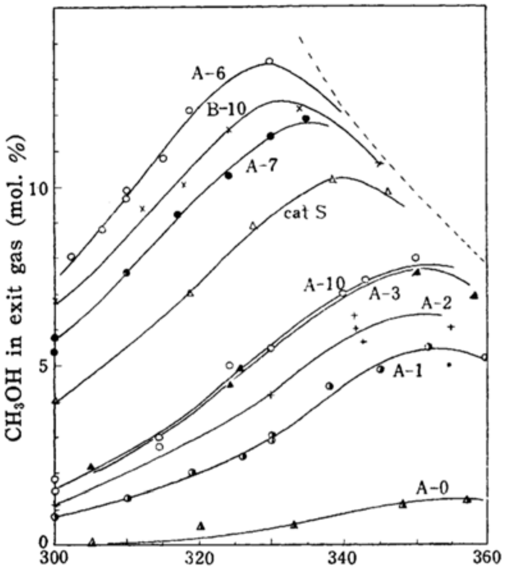

Fig. 2. Methanol concentration as a function of reaction temperature at 150 kg./cm² and S. V. of 0.95—1.05·10⁴.

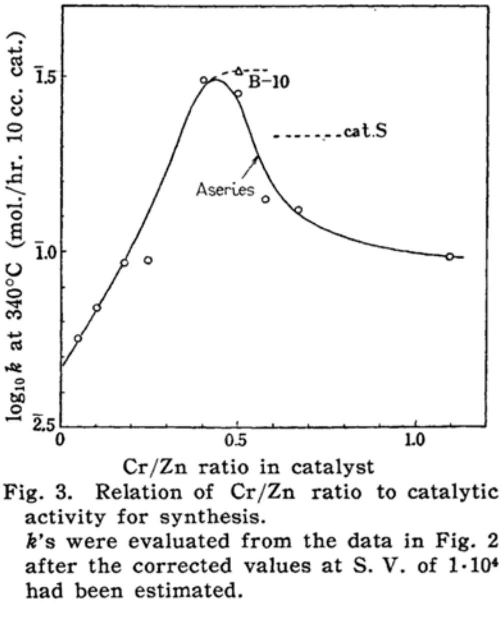

Fig. 3. Relation of Cr/Zn ratio to catalytic activity for synthesis.
k's were evaluated from the data in Fig. 2 after the corrected values at S. V. of 1·10⁴ had been estimated.

Molstad et al.,[8] and Frolich et al.[9] have done comprehensive work on the activity correlated to the Cr/Zn ratio in a wider range. The present results give a maximum activity at the same Cr/Zn ratio as pointed out by the former, but differ from the work of the latter in giving the maximum activity at a somewhat higher Cr/Zn ratio. The difference may mainly be due to our mode of catalyst preparation which is different from theirs.

Catalyst S is of intermediate activity between catalyst B-10 and catalyst A-10. Catalytic activity for the methanol decomposition is shown in Fig. 4 as a function of Cr/Zn ratio in the catalyst. Tendencies similar to those found in the synthesis are found in the decomposition. Furthermore an asymptotic rise of the activities of catalysts B with the increasing Cr/Zn ratios up to 0.5 can be seen more clearly. The similarity between the changes in activity for the synthesis and for the

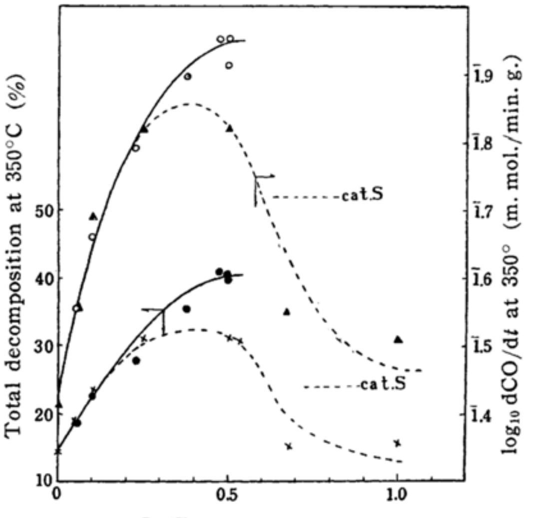

Fig. 4. Relation of Cr/Zn ratio to catalytic activity for decomposition.
dotted lines, A series; full lines, B series.

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[8] M. C. Molstad and B. F. Dodge, *Ind. Eng. Chem.*, **27**, 134 (1935).

[9] P. K. Frolich and D. S. Cryder, ibid., **21**, 867 (1929).

TABLE I

SPECIFIC SURFACE AREAS OF CATALYSTS

Catalyst	A-0	A-0	A-1	A-2	A-3	A-6	A-7
Specific surface area[a)], m^2/g.	5.8[b)]	6.3	40	29	35	96	44
Catalyst	A-10	B-1	B-2	B-4	B-9	S	
Specific surface area[c)], m^2/g.	20	40	31	68	90	43	

a), numerals listed, except b), show the specific surface areas determined on the catalysts after having been used in the synthesis: b) is the area determined on the catalyst A-O before the synthesis. c), the specific surface areas of catalysts B were determined on the specimens reduced in hydrogen at 320~350°C.

decomposition with the Cr/Zn ratios was once reported by Frolich et al..[*3]

Selectivity in Synthesis and Decomposition.—In the synthesis, gaseous products such as carbon dioxide and methane were produced in extremely small amounts: increase in carbon dioxide concentration in the gas after the synthesis did not exceed one percent, and hardly any methane was detectable. Among the liquid products both formaldehyde and methylformate were usually found to be very small in amount (0.1% and 0.5% respectively), and because of the too small quantity of dimethylether produced, no accurate determination was probable by the method employed in this work. On the other hand, the zinc oxide catalyst gave the highest yield of water, which diminished rapidly with the increasing Cr/Zn ratios in the catalysts (refer to Fig. 5). Anyhow, hardly any kind of effect of chromic acid addition undesirable to the selectivity of the synthesis has been found.

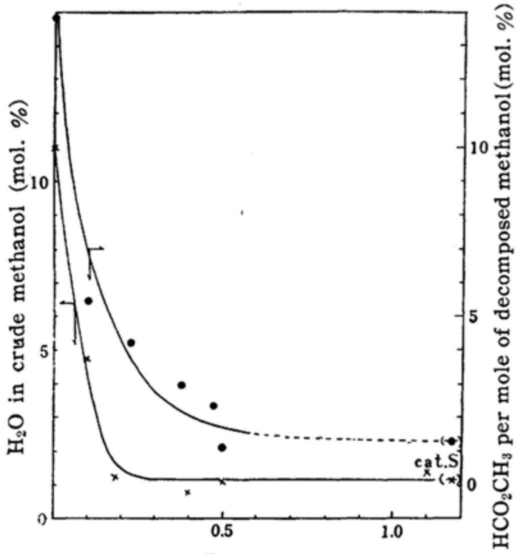

Fig. 5. Cr/Zn ratio in catalyst and selectivity in reactions.

In the methanol decomposition, small quantities of carbon dioxide and formaldehyde were produced, independent of the Cr/Zn ratios in the catalysts, whereas the production of methylformate seemed closely correlated to the ratio (refer to Fig. 5). The correlation appeared remarkable on the series B of the catalysts: the yield was the greatest on the zinc oxide catalyst, and tended to decline regularly with the increasing Cr/Zn ratios. As for the series of the catalysts, a slight minimum of the yield appeared at a relatively small Cr/Zn ratio.

Specific Surface Area. — The specific surface areas which were determined on the catalysts after the synthesis are listed in Table I. With respect to the series A the area passes through a maximum at the Cr/Zn ratio of 0.4. The individual catalysts of the B series show a larger specific surface area than the corresponding ones of the series A.

Discussion

Catalyst Composition and Catalytic Activity.—In the course of our manufacturing the catalysts A, the liquid which contained chromic acid more abundantly than the solid in the paste left after drying the surface layer of higher chromic acid content at the back of the original solid particle, and the particle surface became more enriched with chromic acid than the particle interior. Therefore the chemical composition of the catalysts A can not indicate the real surface concentration of chromic acid. On the other hand, the chemical composition of the catalysts B can directly predict the concentration considered, since the catalyst was produced from the solid, free of the liquid. Only the B series of the catalysts thus gives a correct relation of the catalytic activity to the chemical composition.

[*3] In this respect any similarity was hardly found by Storch (*J. Phys. Chem.*, **32**, 1743 (1928)).

For the reason mentioned above, a maximum of the activity appearing at the Cr/Zn ratio shortly before 0.5, which was usual in the previous work, is not the necessary relation between the activity and the chemical composition. An excessive addition of chromic acid may certainly cause decrease in the activity, since chromic acid alone is no more an active catalyst than zinc oxide alone, but an exact representation of the activity change in the intermediate range of the Cr/Zn ratio has not been established as yet[*4].

Catalyst Composition and Specific Catalytic Activity per Unit Surface Area.—By dividing the activity per gram of the catalyst by the specific surface area, the specific catalytic activity per unit surface area is obtained, and is plotted against the Cr/Zn ratio of the catalyst in Fig. 6. Over a wide range of the relatively high ratios, the specific activities for both the synthesis and the decomposition vary a little, gradually approaching either one of catalyst S. However, in the range of the low Cr/Zn ratio the specific activity for the synthesis rises with the increasing Cr/Zn ratios, whereas the one for the decomposition indicates the opposite.

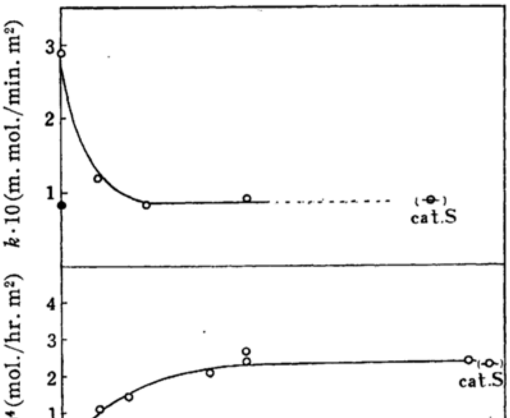

Fig. 6. Relation between Cr/Zn ratio in catalyst and specific activity per unit surface area.
above, decomposition; below, synthesis.
● shows the specific activity determined on catalyst A-0 after having been used in the synthesis.

It was at first sight apparently difficult to explain the results thus seemingly inconsistent with each other, but soon the following fact could shed some light upon the subject: the catalysts without and with a little chromic acid content turned gray after having been used in the synthesis for a few days, and came to give far lower activity for the decomposition than the original one having the clean surface, while regarding the catalyst of the higher chromic acid content neither darkening of the catalyst nor decrease in the activity for the decomposition occurred. This shows easier contamination of the surface of the former catalyst with carbon from carbon monoxide decomposition during the synthesis. If the catalyst surface remained clean, the series of catalysts with none and with a little chromic acid content should show the downward tendency of the activity for the synthesis with the increasing chromic acid contents.

At any rate change in the activity based on unit surface area is far smaller than that in the activity based on unit mass (volume) of the catalyst. This suggests an apparent proportionality of the catalytic activity to the extent of the specific surface area, and furthermore, when combined with the relation of the specific surface area to the Cr/Zn ratio, an intercrystalline promoting effect of chromic acid.

Relation of Catalyst Composition to Activation Energy and Frequency Factor in Methanol Synthesis and Decomposition.—From Arrhenius' plots of the rate constants of the synthesis and the decomposition, the constants being based on unit specific surface area, the activation energy and frequency factor have been evaluated[*5]. Fig. 7 shows the plots of the energy and factor vs. the Cr/Zn ratio in the catalyst. Both of the plots similarly fall with the increasing Cr/Zn ratio rapidly at first, and then asymptotically approach respective minimum values of catalyst S[*6].

The addition of chromic acid thus causes decreases in both the frequency factor and the activation energy. The decrease in the former necessarily results in the fall

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[*4] In this respect a catalyst prepared by coprecipitation of hydroxides of zinc and chromium from a mixed solution of the nitrates was at first expected to give information, however it has proved difficult to obtain a catalyst of homogeneous structure as well as one of moderate activity by this procedure of preparation.

[*5] In our previous paper the plots on the rate of decomposition were given on the catalysts of a different procedure of preparation, and were found intersecting with each other at a definite $1/T$. In the present results the plots certainly show different slopes, but no intersection appears in the temperature range which is far lower than that in the previous paper.

[*6] Although the syntheses were not always conducted on the clean catalyst surface, the present tendency may be considered still inherent to the clean one.

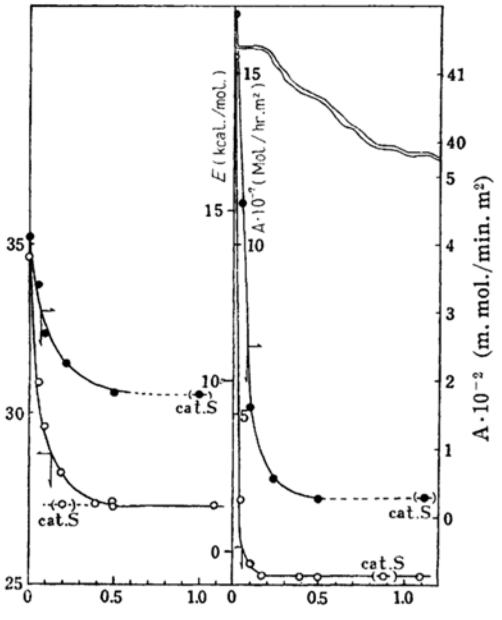

Fig. 7. Relation of Cr/Zn ratio in catalyst to activation energies and frequency factors of reactions.
○, synthesis: ●, decomposition.

of the specific activity per unit surface area, which is simultaneously compensated with decrease in the latter. Consequently the specific activity per unit specific surface area can be maintained at the level of catalyst S, presumably a zinc chromite spinel, of moderate activity.

At first sight one may be apt to consider chromic acid simply an intercrystalline promoter, namely a structural promoter responsible for production of high-area structure, but closer investigation as mentioned above leads us to the conclusion that chromic acid behaves not only as an intercrystalline but also as an intracrystalline promoter, namely a promoter modifying the structure of the catalyst advantageously for preservation of the specific activity*7. Moreover, we should like to emphasize the effect of chromic acid addition upon the improvement of the selectivity and prevention of carbon monoxide decomposition on the catalyst surface, which are suggestive rather of a intracrystalline than an intercystalline promoting effect.

Summary

The catalysts have been prepared from pastes of zinc oxide powder kneaded with chromic acid solutions of different concentrations. From the pastes two series of the catalysts have been produced, namely the one directly from the paste and the other from the solid, free of the liquid, in the paste. Only the results on the latter series can give the correct relation of the catalyst composition to the catalytic activity, which indicates the activity rising with the higher chromic acid contents to an asymptotic maximum at the Cr/Zn ratio of 0.5.

The catalytic activity on the catalysts of different Cr/Zn ratios almost parallels the specific surface area of the catalysts, while the specific activity based on unit specific surface area of the catalysts changes in a far less degree than the change in activity per unit gram of the catalyst. These suggest an intercrystalline promoting effect of chromic acid. Moreover the closer investigation on the activity reveals that both the activation energy and the frequency factor of the reactions which are based on unit surface area show a downward tendency with the increasing Cr/Zn ratios asymptotically to their respective minimums of presumable zinc chromite spinel. This shows besides an intracrystalline promoting effect of chromic acid.

Within the range of the present study, hardly any effect of chromic acid addition undesirable to the selectivity in the synthesis has been found.

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*7 Natta stated that chromium oxide was an intercrystalline promoter because of there being little change in the activation energy of the synthesis by the addition.