A Study of Zinc Oxide - Chromium Oxide Catalysts. VI. The Changes Brought about by Heat Treatment in the Activity for Methanol Synthesis and in the Structure of the Raw Catalysts

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A number of papers have appeared dealing with those methanol-synthesis catalysts which consist of the oxides of zinc and chromium.[1] However, most of these papers have described mainly the relation of the activity and of the catalyst structure to the chemical composition. The only exception is a series of papers by Kawamura and his associates,[3-6] who investigated the reduction process of the catalysts in detail and also the changes in the activity and in the structure of the reduced catalysts brought

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[1] See Ref. 2.

[2] G. Natta, "Catalysis," III, Reinhold Publ., N. Y. (1955), p. 349.

[3] M. Kawamura, T. Irie, T. Shiraishi and K. Tokunaga, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **60**, 162 (1957).

[4] M. Kawamura and T. Irie, ibid., **60**, 162 (1957).

[5] M. Kawamura and T. Irie, ibid., **60**, 170 (1957).

[6] T. Irie and T. Shiraishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 107 (1957).

about by heat treatment. In the course of our previous study⁷⁾ of the catalysts, it became evident that the activity declined considerably if a dry preparation from a slurry of zinc oxide powder in aqueous chromic acid was preheated in the air in the hope that the shrinkage of the catalyst bed during the synthesis might be avoided. This observation makes us suspect that a change in the catalyst structure might accompany this decline in activity. However, in order that a better understanding of the dependence of the catalyst performance upon the history of a catalyst may be obtained, a more detailed study on this subject is required.

Experimental

Catalyst Preparation and Activity Measurement.—Catalysts with different chromium/zinc atomic ratios were prepared from commercial zinc oxide powder and chromic acid in the following way. A slurry of the zinc oxide powder in aqueous chromic acid was spread over a glass plate and evaporated to dryness in the air at room temperature. The resulting cake was then ground to a 100-mesh powder, and the powder was pelleted (4 mm. in diameter by 4 mm. high). The chromium/zinc atomic ratios in the catalysts thus prepared were 0.1, 0.5, and 1.0. Also, a catalyst not containing chromic acid was prepared by pelleting the zinc oxide powder to the same size.

Every kind of catalyst was treated as follows. A lot of the catalyst was divided into two parts. One part was reduced in a vessel different from the methanol synthesis reactor⁷⁾ and then immediately tested in the reactor for catalytic activity. The other part was first heated in the air at 400°C for 5 hr., and then reduced in the methanol synthesis reactor and tested for catalytic activity in situ. In this paper, the former class of catalysts will be denoted by the symbol "A," and the latter class, by the symbol "B." Also, if necessary, the numerals, 1, 2, 3, and 4, will be attached to the above symbols to indicate the chromium/zinc ratios of 0, 0.1, 0.5, and 1.0 respectively. Thus we will have A-1, A-2, etc.

In all cases, the reduction was carried out in a current of $2H_2$-1CO synthesis gas under atmospheric pressure; in the earlier stages of reduction, the temperature was gradually raised to 350°C over a 1.5 hr., period so that the glow phenomenon due to the rapid reduction of sexivalent chromium might be prevented in the catalyst bed. This final temperature was maintained for 4 hr.

The activity for methanol synthesis was measured by the use of the same apparatus as has been described previously.⁸⁾ Five milliliters of a catalyst sample (1—2 mm.) was placed to the reactor in order to fill the annular space between the walls of the reactor and the centrally-placed stainless-steel thermocouple protection tube (4 mm. in OD and 2 mm. in ID). The catalyst bed formed was 18 mm. in OD, 4 mm. in ID, and 22 mm. high. The longitudinal temperature difference throughout the whole catalyst bed remained within 2°C when the activity measurements were made with a $2H_2$-1CO synthesis gas containing 4% nitrogen under the following conditions; pressure = 150 kg./cm², space velocity based on the feed rate (vol./hr. at S. T. P.) of synthesis gas $= 1\times10^4 \pm 50\ \text{hr}^{-1}$, and temperature range = 300—390°C.

In the experiments with the catalyst samples A-3 and B-3, the samples, once they had been used in the methanol synthesis, were heated in a hydrogen stream at 500°C for 8 hr.; then activity measurements were again made on these hydrogen-treated samples (designated as A′-3 and B′-3).

The Investigation of Catalyst Structures.—The specific surface area, S, was determined by applying the BET equation to the argon adsorption isotherm at −196°C. The density, ρ_t, was measured by the helium displacement method. From the values of S and ρ_t, the average particle diameter, $\bar{d}$, was calculated according to the formula $\bar{d}=6/\rho_t S$, on the basis of the assumption that the particles have the form of a sphere or cube. Moreover, the particle size and shape in catalyst granules were examined under an electron microscope of the JEM-6 type. The samples for the electron microscopic observation were prepared by grinding the catalyst with castor oil in a mortar.

The X-ray diffraction patterns for powdered samples of the catalysts were obtained with an

TABLE I. SAMPLES USED FOR THE INVESTIGATION OF CATALYST STRUCTURES

Sample	Cr/Zn atomic ratio	Remarks
A_0-1	0	Catalysts as prepared from slurries. (These are the original samples for the preparation of the othe series of samples listed in this table.)
A_0-2	0.1	
A_0-3	0.5	
A_0-4	1.0	
A_1-1	0	Reduced in $2H_2$-1CO gas stream under atmospheric pressure at temperatures below 350°C after the preparation from slurries.
A_1-2	0.1	
A_1-3	0.5	
A_1-4	1.0	
A_2-1	0	Reduced under the afore-mentioned conditions after the preparation from slurries and subsequently used for methanol synthesis.
A_2-2	0.1	
A_2-3	0.5	
A_2-4	1.1	
B_0-1	0	Heated in air at 400°C for 5 hr. after the preparation from slurries.
B_0-2	0.1	
B_0-3	0.5	
B_0-4	1.0	
B_1-1	0	Treated in the same manner as samples B_0 after the preparation from slurries and then used for methanol synthesis.
B_1-2	0.1	
B_1-3	0.5	
B_1-4	1.0	
A'_2-3	0.5	Obtained by heating samples A_2-3 and B_1-3 in hydrogen stream at 500°C for 8 hr.
B'_1-3	0.5	

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7) If reduced in the reactor, the catalyst bed shrinks with the progress of reduction and, consequently cannot be tested for catalytic activity in situ.

8) M. Oba, Y. Ogino and H. Uchida, *Rpt. Gov't, Chem. Ind. Research Inst., Tokyo*, **60**, 121 (1965).

X-ray diffractometer of the Geigerflex D-3F type. The nickel-filtered Cu*Kα* radiation from a sealed-off X-ray tube equipped with beryllium windows and operated at 40 kV. and 18 mamp. was used.

The above measurements and observations were conducted on catalyst samples taken at various stages of catalyst treatment. These samples are listed in Table I. In the nomenclature used here, subscript numbers are attached to the catalyst class symbols A and B in order to indicate the different treatments to which the catalysts, A and B, were subjected. Thus the symbols A_1 and B_1,, for example, stand for those samples of a catalyst of Class A or B which were subjected to a specified treatment.

Results

Activity for Methanol Synthesis.—The methanol concentration in the exit gas is plotted against the reaction temperature in Fig. 1 for the synthesis runs conducted with the catalysts of two series, A and B.[9] Also, for the purpose of a quantitative comparison of activities, the values of the rate constant of methanol synthesis at 330°C, k_{330}, taken as a measure of the activity are listed in Table II. The k_{330} values for synthesis with the catalysts A′-3 and B′-3 are also included in this table. The k_{330} values were calculated according to Eq. 1, which was in turn derived from Rate Eq. 2.[10]

$$k=\frac{SV}{273\boldsymbol{R}}\times \int_0^z \frac{\left[\nu_{\mathrm{CO}}\nu_{\mathrm{H_2}}{}^2 4P^3\{1+(1-n)z\}\left(\frac{n}{2}-z\right)\right]^{0.3}}{(1+2z)^2\left[\nu_{\mathrm{CO}}\nu_{\mathrm{H_2}}{}^2\frac{4P^3\{1+(1-n)z\}}{(1+n)^3}-\frac{\nu_{\mathrm{CH_3OH}}Pz}{K}\right]} \tag{1}$$

$$r=k\{(f_{\mathrm{CO}}f_{\mathrm{H_2}}{}^2)^{0.7}-f_{\mathrm{CH_3OH}}(f_{\mathrm{CO}}f_{\mathrm{H_2}}{}^2)^{-0.3}/K\} \tag{2}$$

In these equations, SV (hr^{-1}) is the space velocity based on the feed rate of the synthesis gas; $\boldsymbol{R}$, the gas constant; ν_i, the fugacity coefficient of the ith component; P (atm.), the total pressure of the H_2-CO gas; n the H_2/CO mol. ratio; z, the mole fraction of methanol in the exit gas; r (mol./hr.), the rate of methanol formation; f_i (atm.), the fugacity of the ith component, and K, the equilibrium constant of reaction. Both Fig. 1 and Table II show that the optimum chromium/zinc atomic ratio is 0.5 for each series of catalysts, and that all the catalysts of series A have higher activities than the corresponding catalysts of series B.

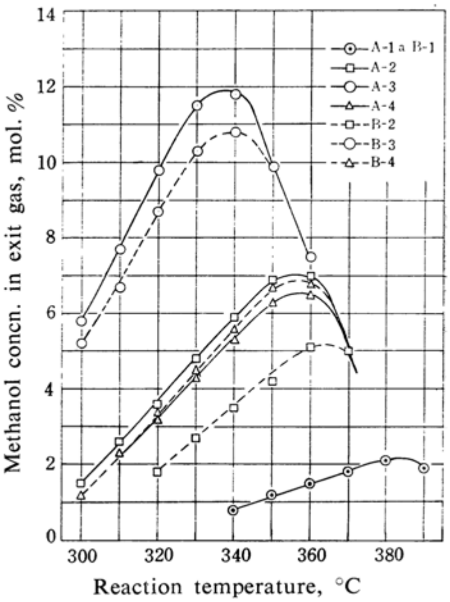

Fig. 1. Catalyst activity for methanol synthesis..

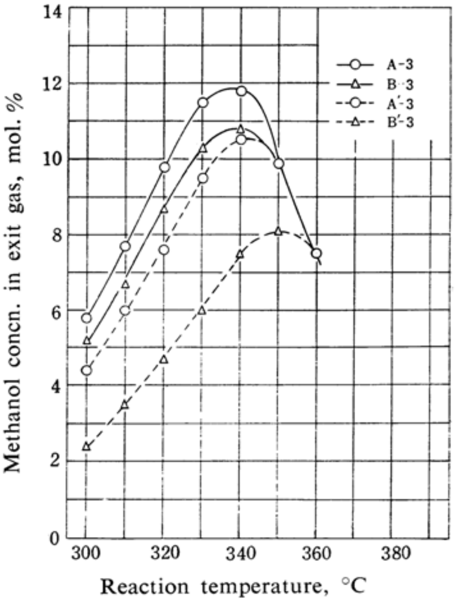

Fig. 2. Catalyst activity for methanol synthesis.

A comparison of the activity difference between catalysts A-3 and A′-3 with the difference between the catalysts B-3 and B′-3 (Fig. 2 and Table II) may give an approximate concept of the relative thermal stability of the two series, A and B. The stronger thermal stability of the catalysts of series A may be seen from the data.[11]

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[9] According to the nomenclature in Table I, these catalysts should be denoted by the symbols A_1 and B_0. However, for the sake of simplicitys, the symbols with the subscript numbers will not be used unless necessary.

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

[11] When catalysts A-3 and B-3 were heated in hydrogen for only 2 hr., their activities decreased to the same extent as when the catalysts were heated in the same medium for 8 hr.

TABLE II. RATE CONSTANT OF METHANOL SYNTHESIS AT 330°C (k_{330}), SPECIFIC RATE CONSTANT (k'_{330}), ACTIVATION ENERGY (E), AND FREQUENCY FACTOR PER UNIT SURFACE AREA (A')

Catalyst	k_{330} $atm^{-2.1}hr^{-1}$	k'_{330} $atm^{-2.1}ml.hr^{-1}m^{-2}$	E kcal./mol.	A' $atm^{-2.1}ml.hr^{-1}m^{-2}$
A-1	0.50×10^{-2}	1.65×10^{-4}	33	1.44×10^{8}
A-2	5.90×10^{-2}	11.5×10^{-4}	24	3.17×10^{5}
A-3	17.9×10^{-2}	18.2×10^{-4}	21	4.79×10^{4}
A-4	5.25×10^{-2}	4.29×10^{-4}	26	8.51×10^{5}
B-1	0.50×10^{-2}	1.69×10^{-4}	33	1.47×10^{8}
B-2	3.20×10^{-2}	1.43×10^{-4}	39	4.33×10^{10}
B-3	15.2×10^{-2}	6.32×10^{-4}	21	3.56×10^{4}
B-4	5.60×10^{-2}	2.64×10^{-4}	29	2.77×10^{6}
A'-3	13.5×10^{-2}	16.0×10^{-4}	22	1.36×10^{5}
B'-3	7.70×10^{-2}	18.7×10^{-4}	24	8.51×10^{5}

TABLE III. BED DENSITY (ρ_b), SURFACE AREA (S), HELIUM DENSITY (ρ_t), AVERAGE PARTICLE DIAMETER ($\bar{d}$), AND LATTICE CONSTANT (a)

Catalyst	ρ_b g./ml.	S $m^2/g.$	ρ_t g./ml.	$\bar{d}$, Å	a, Å		Identification[b]
					ZnO	$ZnCr_2O_4$	
A_0-1	2.10	3.8	5.47	2900	3.252	—	Z
A_0-2	1.44	3.0	3.78	5300	3.251	—	Z+IIIβ+Iβ(v.w.)
A_0-3	1.56	4.0	3.49	4300	—	—	Iβ
A_0-4	1.38	2.0	3.20	9400	—	—	Zn bichromate presumably
A_1-1	2.08	5.2	5.23	3300		—	Z
A_1-2	1.38	120	4.37	110	3.251	—	Z
A_1-3	1.17	128	3.69	130	3.250	8.482	Z+S(w.)
A_1-4	1.26	93	3.90	170	3.246	8.482	Z+S
A_2-1	2.08	13.5	5.47	810		—	Z
A_2-2	1.38	37	4.90	330	3.251	8.523	Z+S(v.w.)
A_2-3	1.17	83.5	4.46	160	3.249	8.397	Z+S
A_2-4	1.26	97	4.28	145	—		Z(v.w.)+S
B_0-2	1.33	14.3	5.04	830	3.251	—	Z
B_0-3	1.46	15	4.51	880	3.250	8.434	Z+S(v.w.)+?
B_0-4	1.24	6.2	3.62	2700	—	8.429	Z(w.)+S+?
B_1-1	2.18	13.5	5.50	810	3.249	—	Z
B_1-2	1.37	163	5.53	67	3.253	—	Z+S(w.)
B_1-3	1.41	170	5.18	68	3.252	8.460	Z+S
B_1-4	1.18	178	5.09	66	—	8.408	Z(v.w.)+S
A_2'-3	1.56	54	4.52	240	3.256	8.470	Z+S
B_1'-3	1.49	28	4.83	450	3.254	8.453	Z+S

b) The symbols Z and S stand for zinc oxide and zinc chromite while Iβ and IIIβ for zinc hydroxychromates Iβ and IIIβ respectively.

The liquid product of methanol synthesis, in general, contains small amounts of such by-products as dimethyl ether, methylformate, water, formaldehyde, and isobutanol. Therefore, the liquid products obtained in the synthesis runs conducted at 380°C with different catalysts were analyzed for such by-products.[12] The results show that the proportion of water in the liquid product obtained with a catalyst of a lower activity is greater than in the product obtained with a catalyst of a higher activity (e. g., 5% water in the case of the catalyst A-3 and 1.1% in the case of the catalyst A-1), whereas the proportions of the other by-products are nearly in dependent of catalyst species or of chromium content (0.7—1.5% dimethyl ether, 0.5—0.6% methylformate, and 0.1% formaldehyde).[13]

Surface Area and Average Particle Diameter.—The results of the surface-area determination are summarized in Table III. The surface areas of three original catalysts containing chromium, A_0-2, A_0-3, and A_0-4, are very small, even

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[12] The by-products were determined gas chromatographically except for formaldehyde, which was determined iodometrically.

[13] The percentages are based on the weight of the liquid product. In no cases was isobutanol detectable.

smaller than the surface area of the original zinc oxide catalyst, A_0-1. If these chromium-containing catalysts are reduced in the synthesis gas, the reduced catalysts (A_1-2, A_1-3, and A_1-4) show quite large surface areas, 30—50 times as large as the surface areas before reduction. However, when these reduced catalysts are used for methanol synthesis, the surface area decreases more or less according to the chromium content; the smaller the chromium content, the smaller the surface area. (Compare the surface areas of the samples A_1 with those of the samples A_2.) On the other hand, if the original catalysts are heated in the air at 400°C, the surface area of the chromium-containing catalysts is slightly increased (see the data for the samples B_0), while when these heat-treated catalysts are used for methanol synthesis, the surface areas of such samples (B_1) are greater than those of the samples A_2. It is worth noting here that the surface area is nearly the same for all the samples B_1, being independent of the chromium content. On the other hand, when two catalyst samples once used for methanol synthesis, A_2-3 B_1-3, are heated in hydrogen at 500°C for 8 hr., the surface areas are markedly decreased, the extent of decrease being greater in the case of the sample B_1-3 (see the data for A_2'-3 and B_1'-3).[14]

The density, ρ_t, is the highest for the catalyst samples with no chromium; it tends to decrease with an increase in the chromium content.

The values of the average particle diameter are also listed in Table III. Particles in the chromium-containing original catalysts (A_0) are quite large, much larger than the particles in the original zinc oxide catalyst. However, when these catalysts are reduced in the synthesis gas, the particles are split into very fine particles.

X-Ray Diffraction.—The results obtained are summarized in Table III. In the case of the chromium-containing catalysts A_0, if the chromium/zinc ratio is smaller than the ratio for zinc hydroxychromate Iβ ($ZnCrO \cdot Zn(OH)_2$, Cr/Zn=0.5), all the chromic acid added will react with zinc oxide to form zinc hydroxychromates. In fact, the X-ray diffraction pattern of the sample A_0-2 shows the presence of hydroxychromate IIIβ ($ZnCrO_4 \cdot 3\text{-}4Zn(OH)_2$), together with zinc oxide, whereas the diffraction pattern of the sample A_0-3 shows the presence of hydroxychromate Iβ alone. If the proportion of chromic acid is further increased, there appears another diffraction pattern which has not yet been identified. Kawamura et al.,[3] however, attributed this diffraction pattern to a bichromate.

When the chromium-containing original catalysts (A_0) are reduced in the synthesis gas or are used for methanol synthesis, the resultant catalysts give diffraction diagrams quite different from those for the original catalysts. In such diagrams, no crystalline phase other than those of zinc oxide and zinc chromite is observed. This indicates that hydroxychromates has undergone decomposition in the synthesis gas. The decomposition of hydroxychromates is also caused by the heat treatment of the same original catalysts in the air at 400°C, as is evidenced by the diffraction data obtained with the B_0 catalysts. However, the results of the differential thermal analysis and the thermogravimetric analysis of the sample A_0-3 (Fig. 3)[15] show that the decomposition occurring in the air is different in type from the decomposition in the synthesis gas. The former type of decomposition is endothermic and takes place at ca. 310°C, whereas the latter type is exothermic and, according to Kawamura and Irie,[5] begins to take place at a much lower temperature, i. e., 200°C. The endothermic peak observed is due to the conversion of sexivalent chromium oxide by oxygen removal into the

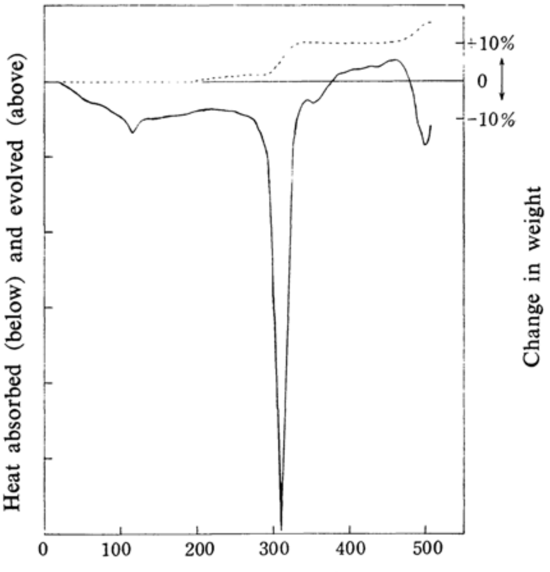

Fig. 3. Differential thermal analysis curve and thermogravimetric analysis curve.
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[14] When the catalysts A-3 and B-3 were heated in hydrogen for only 2 hr., the surface areas decreased to the same extent as when the catalysts were heated in the same medium for 8 hr.

[15] Similar results, though not the same as those reported here, were presented by Kawamura et al.[3] for a variety of zinc oxide-chromium oxide catalysts, but their results for a catalyst similar to the present one are not identical with ours.

trivalent oxide, which combines with zinc oxide to form zinc chromite.

Besides the diffraction patterns due to zinc oxide and zinc chromite, the diffraction diagram of the sample B_0-4 shows complicated patterns, which, though not identified, give evidence for the formation of intermediates in the decomposition process.

On the basis of diffraction lines due to the (110) plane of zinc oxide and the (400) plane of zinc chromite, the lattice constants for the two components have been calculated; they are listed in Table III. The lattice constants calculated for the zinc oxide in the catalyst samples vary little among the samples and agree with the literature value (a=3.249 Å).[16) whereas the lattice constants found for the zinc chromite[17) in the catalyst samples are, in general, greater than the literature values[18) (a=8.32, 8.20 Å).[16) According to Irie and Shiraishi,[6) the zinc chromite produced by the reduction of the hydroxychromates at low temperatures occludes zinc oxide, and its lattice is enlarged to form a stressed structure. By taking their view into consideration, the present observation may be interpreted as follows: Where there is a non-stoichiometric structure of zinc chromite, Zn^{2+} will enter the structure to occupy the empty interstices; as a result, the lattice will be enlarged, with stresses set up on it. The zinc chromite retains the enlarged lattice even when heated for a prolonged time in hydrogen at 500°C.

Electron Microscopic Picture.—Upon the addition of aqueous chromic acid to zinc oxide powder (Micrograph 1), the reaction between the two reagents takes place around the periphery of the powders. This fact can be seen, though not directly, from Micrograph 5 with reference to a low-chromium sample once used for the synthesis (the sample A_2-2). As the amount of chromic acid is increased, the reaction extends into the interior of the powders, producing large crystals of zinc hydroxychromate Iβ (see Micrograph 2 for the sample A_0-3). According to Feitknecht and Hugi-Carmes,[19) the crystal of this hydroxychromate grows to a thin hexagonal plate of large dimensions. The present observation is in agreement with their statement in that the crystal grows in the form of a layer-structure; the only difference is that the crystal is a thin plate of an irregular shape. The crystals here observed may be the fragments into which the original hexagonal plate has been broken as a result of grinding the catalyst in the preparation of samples for electron microscopic observation. On the other hand, the electron microscopic picture of a reduced catalyst (the sample A_1-3) is entirely different from that of the original (the sample A_0-3). Micrograph 3 for the sample A_1-3 shows a number of caterpillar-like particles within the original fringe of the hydroxychromate crystal, particles which are as fine as about 50 Å wide. Seemingly, the particle is an aggregate of a few crystallites of a spheroid structure (ca. 50 Å in diameter). When the reduced catalyst is used for methanol synthesis, the particles become greater and more gaps are formed between them, with no substantial change in the pattern visible in the original fringe of the crystal. (Compare Micograph 4 for the sample A_2-3 with Micrograph 3.) This phenomenon may be simply due to the progress of sintering during the synthesis run. It should here be noted that these electron microscopic pictures are quite different from that of the catalyst prepared from a mixed solution of the nitrates and ammonia (see Refs. 8 and 20).

In spite of the fact that zinc hydroxychromate undergoes thermal decomposition in the heat treatment of catalysts in the air at 310°C,

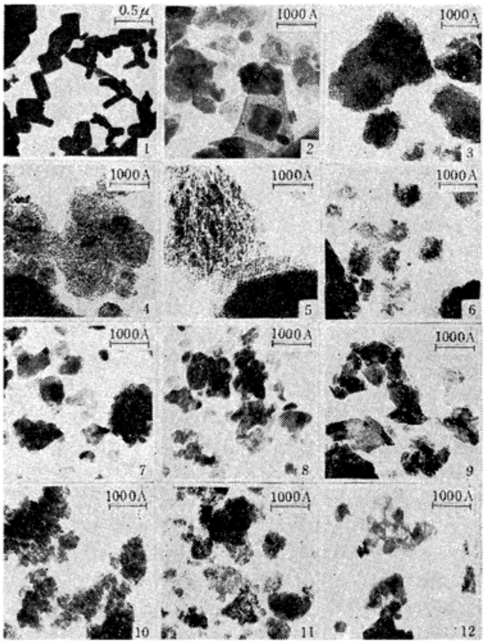

Fig. 4. Electron micrographs.

1, Sample A_0-1. 2, A_0-3. 3, A_1-3. 4, A_2-3. 5, A_2-2. 6, A_2-4. 7, B_0-3. 8, B_1-3. 9, B_1-4. 10, A'_2-3. 11, Residue from A_2-3. 12, Residue from B_1-3

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16) A. S. T. M. Special Technical Publication 48-L, The X-ray Powder Data File, 1962.

17) Irie and Shiraishi[6) designated this structure as R and distinguished it from zinc chromite.

18) A sample with a chromium/zinc ratio of 1.98 was found to give the value of 8.331 Å after it was reduced and then heat-treated in the air at 800°C for 40 hr.

19) W. Feitknecht and L. Hugi-Carmes, *Helv. Chim. Acta*, 37, 2093 (1953).

the electron microscopic picture of a heat-treated catalyst (the sample B_0-3) is not essentially different from the original catalyst (the sample A_0-3). The only differences are that the crystal fragments are smaller and that massive fragments of an irregular shape are more abundant in the case of the sample B_0-3 than in the case of the sample A_0-3.

In contrast to the structural difference observed between the samples A_0-3 and A_1-3, no remarkable difference is found between the electron microscopic pictures of the samples B_0-3 and B_1-3 (i. e., the sample once used for methanol synthesis after heat treatment in the air). In the sample B_1-3, such a pattern as is observed in the micrograph for the sample A_2-3 appears only within a very small portion of the original fringe of the thin plate-like crystal; the major part remains so homogeneous that the individual particles, if present, are indistinguishable. This is also the case with the two samples of a high chromium content, B_0-4 and B_1-4 (see Micrograph 9).

When two samples once used for methanol synthesis, A_2-3 and B_1-3, are heated in hydrogen at 500°C, a marked crystal growth occurs, leading to the production of large crystals (compare Micrograph 10 with Micrograph 4), the growth being more pronounced in the sample B_1-3.(20)

The Composition of Individual Particles.—It yet remained unclarified whether the catalyst particles in a sample once used for methanol synthesis consist of the single component, zinc oxide or zinc chromite, or whether each particle is a composite substance made up of the two. For the study of this problem, two samples containing a large excess of zinc oxide, A_2-3 and B_1-3, in which the $ZnO/ZnCr_2O_4$ mol. ratio was 3, were treated with an aqueous ammonium acetate solution for half an hour at room temperature and the free zinc oxide removed;(22) the residues were then examined under an electron microscope.

The residue from the sample A_2-3 was found to have a chromium/zinc ratio of 1.79, which is approximately the ratio for zinc chromite. Its electron microscopic picture does not differ essentially from that of the initial sample (compare Micrograph 11 with Micrograph 4), although the caterpillar-like particles in the residue are thinner than in the initial sample and more white areas are observed. Therefore, it follows that most of the particles are aggregates of zinc oxide and zinc chromite crystallites, whereas the others consist of zinc oxide alone or mainly of zinc oxide. This inference is also supported by a comparison of the X-ray diffraction diagram of the residue with that of the initial sample (Fig. 5). The X-ray diffraction diagram shows the presence of zinc chromite alone, and the diffraction lines due to zinc chromite are greatly broadened. The line-broadening effect is probably due to the stress imposed on the chromite lattice as a result of the removal of the zinc oxide initially present in the zinc chromite in excess of its stoichiometric proportion.

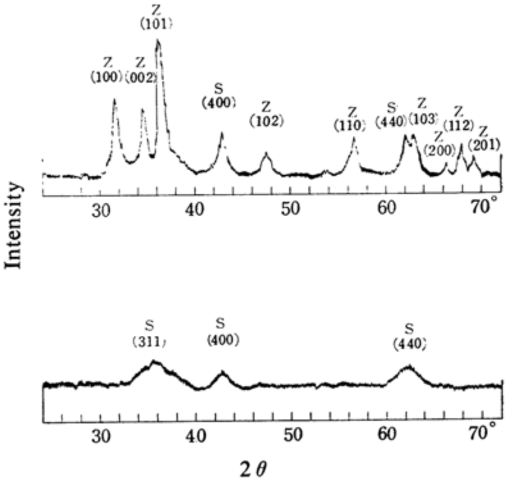

Fig. 5. X-Ray diffraction diagrams.
Above, sample A_3-3. Below, residue from sample A_3-3 after removal of zinc oxide.

The electron microscopic picture of the residue from the sample B_1-3 (Micrograph 12) is somewhat different from that of the initial sample (Micrograph 8). Within the original fringe of the crystal there appear wide openings, in which presumably zinc oxide particles have predominated. Accordingly, either zinc oxide crystallites or zinc chromite crystallites are more or less concentrated locally within the fringe, and the mutual penetration of the two components seems to have been achieved not as thoroughly as in the case of the sample A_2-3.

Discussion

The Size and Shape of Particles.—In general, the average particle diameter, $\bar{d}$, as calculated by use of the formula $\bar{d}=6/\rho_t S$, greatly differs from the size as estimated by electron microscopic observations. The shape one can imagine from the $\bar{d}$ for the particles in the sample A_0-3 is a sphere or cube about 4000 Å in diameter or in linear dimension. Similarly, the particle in the A_2-3 is considered to be a sphere or cube of the 160 Å size. However, electron

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20) J. E. Germain and L. Ponsole, *Bull. soc. chim. France*, **1961**, 1572.

21) Other electron micrographs will be presented elsewhere.

22) G. H. Osborn, *Analyst*, **76**, 114 (1951).

micrographs show a thin plate-like particle of several thousands Å size for the former sample, and a caterpillar-like particle about 50 Å in width for the latter. Such a discrepancy is also found in the case of the sample A_2-4. Particularly in the case of the sample B_1-3, the particle shape imaginable from the $\bar{d}$ differs markedly from the shape observed under the electron microscope. The $\bar{d}$ for the particles in this sample is calculated to be 70 Å. This size would be sufficiently large for the individual particles to be distinguished from one another in the electron micrograph if they could be assumed to be, for instance, spherical. However, most of the particles seen in the electron micrograph are relatively large and thin plates of a homogeneous structure.

These seemingly contradictory results may be interpreted as follows. In the sample A_0-3, thin plates of large dimensions are piled up, with no gaps between them, to form particles as thick as several thousand Å. These particles are more or less similar in shape to the one assumed in the calculation of $\bar{d}$; however, under the influence of the grinding action in the preparation of samples for electron microscopic observations, they collapse to yield thin plate-like particles. On the other hand, in the sample A_2-3, the particles are in the form of caterpillars and apparently different in shape from the one assumed in the calculation of $\bar{d}$; in the sample A_2-4, particles are of two different types, caterpillar-like particles and particles of irregular shape, whereas the particle shape assumed in the calculation is of a single type, a sphere or a cube. These considerations will account for the discrepancies noted above. However, it is not possible to give a satisfactory interpretation of the results for the sample B_1-3. At any rate, the $\bar{d}$ value is of minor significance for us in drawing the picture of individual particles.

The sum of the surface areas of all the particles in one gram of a catalyst, when calculated from their linear dimensions as estimated from the electron micrograph, can be considerably greater than the specific surface area of the same catalyst as measured by the BET method. In this respect, Nielsen[23] points out that the interfacial layers are apt to coalesce with the particles to a coherent surface, and that only where the distance between two particles, or the orientation, is too divergent does the interfacial layer split up in two surface areas. This coherent surface should be taken into consideration in attempting to understand the k in terms of the specific activity and the specific surface area, because this is the surface where the reactants in the methanol synthesis reach.

Specific Activity.—The specific activity based on unit accessible surface area at a given reaction temperature, k', is calculated by the following formula:

$$k' = k/\rho_b S \tag{3}$$

where ρ_b is the catalyst bed density (the values are listed in Table III). The k' depends on the chromium/zinc ratio in nearly the same manner as the k does.[24] From the Arrhenius plot of k', the activation energy, E, and the frequency factor per unit surface area, A', are calculated for each catalyst. The calculated values of k' at 330°C (k'_{330}), E, and A' are given in Table II.

In the case of the catalysts A, both the high k' value and the moderately large S value are responsible for the high k value. On the other hand, in the case of the catalysts B, k' is the sole factor affecting the k value, because the surface area, S, in this particular case is almost the same for all the catalysts.

A comparison of the data for k' values of the two series of catalysts show that the heat treatment of chromium-containing catalysts (the original catalysts, designated as A_0 in Tables I and III) in the air at 400°C results in a considerable decrease in k'. However, the heat-treated catalysts, after having been used for methanol synthesis, have a much greater surface area than the corresponding catalysts used for the synthesis without previous heat treatment in the air (see the data for S of the samples B_1 and A_2 in Table III). Therefore, the decrease in k' due to heat treatment is the main reason why the catalysts B have lower activities (k) than the catalysts A.

Structural Factors Affecting the Specific Activity.—The catalysts A have higher specific activtiies (k') than the corresponding catalysts B. Moreover, the two series of catalysts are quite different in their electron microscopic pictures. The structural difference between the two series of catalysts may stem from the difference in the way of the decomposition of zinc hydroxychromate into zinc oxide and zinc chromite. The decomposition of, or the removal of excess oxygen from, the hydroxychromate proceeds more slowly but to a greater extent in the heat treatment of catalysts in the synthesis gas than in the treatment in the air.

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[23] A. Nielsen, "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," Jul. Gjellerups Forlag. Copenhagen (1956), p. 167.

[24] The correlation between k' and the chromium/zinc ratio in the range of high chromium/zinc ratios is different from that described in the previous paper.[25] This is mainly due to the different values of S for the catalyst samples with a chromium/zinc ratio of 1.

[25] Y. Ogino, M. Oba and H. Uchida, This Bulletin, 32, 284 (1954).

According to Irie and Shiraishi,[6] the decomposition of the hydroxychromate in the synthesis gas begins to take place at a temperature as low as 200°C, and the rate of decomposition gradually increases as the temperature is raised. The excess oxygen, in this case, is removed exothermically as carbon dioxide. Therefore, it is here considered that, in the earlier stages of the heat treatment of catalysts in the synthesis gas (i. e., treatment at low temperatures), a number of fine crystallites of zinc oxide and zinc chromite appear in the layer-structure of hydroxychromate and that, in the latter stages (i. e., treatment at higher temperatures), these crystallites will serve as nuclei for the formation of large particles by the aggregation of newly-born crystallites. In these particles, the mutual penetration of zinc oxide and zinc chromite is likely to be achieved as thoroughly as possible.

On the other hand, in the treatment of catalysts in the air, the decomposition of the hydroxychromate, as is exemplified in Fig. 3 for the catalyst A-3, occurs suddenly at a higher temperature, i. e., at 310°C. In this case, the whole layer-structure of hydroxychromate will be decomposed instantaneously into a great number of very fine crystallites of zinc oxide and zinc chromite, the crystallites being scattered within the initial fringe of the layer-structure; the removal of excess oxygen will remain rather incomplete. Accordingly, once this structure appears in the heat treatment of a catalyst in the air, the complete transformation of this structure into one capable of forming large particles in the heat treatment in the synthesis gas may be difficult, even though the catalyst is subsequently heated in the synthesis gas at temperatures not much higher.

The lattice constant of zinc chromite in catalysts is, in general, considerably greater than the normal value,[26] it varies a little among the catalysts studied. However, the specific activities of the chromium-containing catalysts of Series A greatly differ, from the specific activities of the corresponding catalysts of Series B. Hence, the specific activity can, by no means, be correlated with the lattice constant. The difference in specific activity is considered attributable to the difference in the degree of the mutual penetration of zinc oxide and zinc chromite rather than to the difference in the lattice constants.

This consideration is not contradictory to the observation that the specific activity of the catalyst B′-3 can be increased to the level of specific activity for the catalyst A-3 by heat treatment in hydrogen at 500°C, because the heat treatment favors the progress of the mutual penetration of zinc oxide and zinc chromite.

Summary

The activity for methanol synthesis has been determined for two series of catalysts prepared from zinc oxide and chromic acid with and without subsequent heat treatment in the air. Also, the correlations between catalytic activity and other catalyst properties have been studied. Each catalyst series has consisted of four catalysts, three of them prepared from slurries of zinc oxide powder in aqueous chromic acid, and the other prepared directly from zinc oxide powder. The chromium/zinc ratios in the catalysts made from the slurries are 0.1, 0.5, and 1.0. The catalysts of one series have been heated in the air at 400°C after their preparation (the "heated series").

In both series, the activity and the specific activity have been found to be influenced by the chromium/zinc ratio. The catalysts not heated in the air after their preparation (the "unheated series") show higher activities than the corresponding catalysts of the heated series, though the former catalysts have much smaller surface areas.

The results of electron microscopic examination show that the two series of catalysts, after having been used for methanol synthesis, are structually different. The structural difference has been ascribed to the difference in the way of the decomposition of the layer-structure of zinc hydroxychromate. In the case of the unheated series, the layer-structure is decomposed into crystallites of zinc oxide and zinc chromite by reduction in the synthesis gas, whereas in the case of the heated series the layer-structure is decomposed by heat treatment in the air.

X-Ray diffraction data show that, in all cases, the lattice constant for the zinc oxide in catalysts is normal, whereas the lattice constant for the zinc chromite is larger than the normal value.

The average particle diameter as calculated from the surface area and density of catalysts does not agree with the size as estimated by electron microscopic observations.

The difference in specific activity between the two series may be due to the difference in the degree of the mutual penetration of zinc oxide and zinc chromite crystallites rather than to the variation in the zinc chromite lattice constant.

In addition, the effects upon the activity and

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[26] Irie and Shiraishi[6] state that the zinc chromite of the normal lattice constant shows scarcely any activity for methanol synthesis.

upon the catalyst structure of catalyst treatment in hydrogen at 500°C after methanol synthesis have been discussed.

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