Studies on Fused Iron Catalyst for Alcohol Synthesis by Hydrogenation of Carbon Monoxide. III. Function of Copper in the Catalyst

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Introduction

Though the fused iron catalyst had been used in the I. G. Farbenindustrie A. G.,[1] and thereafter by R. B. Anderson,[2-4] et al. for the Fischer-Tropsch- as well as Synol-synthesis, it had never been a special catalyst for the synthesis in high yield of alcohols, but the ordinary catalyst for ammonia synthesis.

In this respect, we have been conducting a series of experiments in order to shed some light upon the fused iron catalyst for alcohol synthesis. Our preceeding experiment[5,6] revealed that the fused iron catalysts could be divided into two groups. The catalysts in one group contained Al_2O_3 and K_2O as principal promoters, and those in another group had SiO_2, MgO and K_2O as such. The catalysts of the first group could sometimes be found highly active, and gave alcohol-rich products when the synthesis was conducted at low temperatures. In the facility of producing alcohol-rich products, the catalysts in the second group, however, stood behind those of the first group, even though the synthesis could be undertaken at a considerably low temperature.

A consideration of this result has led us to expect that a catalyst suitable for alcohol synthesis may be obtained if it contains other promoters together with those found in the highly active catalyst of the first group.

The present paper deals with the experiments of the expectation, and shows the effect of the addition of copper ont he behaviour of the catalyst. The effect is to make the catalyst favorable for the production in high yield of oxygenated compounds, but to cause a decrease in the activity in water-gas synthesis.

Experimental Procedure

The contribution of promoters in the fused iron catalyst was examined both by the activity measurement and by the analysis of synthesis products obtained with the catalyst.

Surface properties of the catalyst were simultaneously studied, in order that a better knowledge of the effect and role of the promoter might be obtained.

Preparation of Catalyst and the Synthesis.—The catalyst was prepared according to the method previously reported,[7] and was subsequently crushed to granules of 1–2 mm. diameter. Figs. 1, 2, 3, and Table I illustrate the composition of the promoters. The numerals listed in the row for promoter-composition indicate the weight percentages of the promoters which might be present in the catalyst when iron could be exactly oxidized to Fe_3O_4.

The synthesis was carried out in an electrically heated 15 mm. I. D. catalyst testing reactor into which was inserted a 7 mm. O. D. thermocouple well. Before the synthesis, the catalyst (60 cc.) was reduced in a hydrogen stream under a pressure of between 20 to 40 kg. per cm^2 at a space velocity of between 3,000 to 5,000 per hour. The temperature was in the range of 470–500°C. The reaction was made under a pressure kept at 25 kg. per cm^2 and at a space velocity for the synthesis gas ($H_2:CO=1:1$) of 500 per hour. It was started from a temperature where the gas contraction* could be kept below 20% for the initial 2 or 3 days, and was continued with a gradually rising temperature, until a gas contraction of 50% was attained. The temperature required for maintaining this contraction in the continued operation was taken as a measure of the relative activity.

The oily products were distilled into fractions** of a temperature difference of 20°C and subsequently analysed for alcohols, esters and carbonyl compounds by the method previously reported[5]. At the same time, the contents of carbon monoxide, hydrogen, methane, and of gaseous olefins in the exit gas were determined.

Microscopic Observation.—A preparation of a catalyst was observed under a microscope, after having been thoroughly polished and subsequently

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[1] P.B.R. 98, 165.

[2] R.B. Anderson, and J.F. Shultz et al., *J. Am. Chem. Soc.*, 72, 3503 (1950).

[3] R.B. Anderson, and B. Seligman et al., *Ind. Eng. Chem.*, 44, 391 (1952).

[4] R.B. Anderson, and J. Feldman et al., ibid., 44, 2418 (1952).

[5] H. Uchida, and N. Todo et al., *J. Chem. Soc. Japan*, (*Ind. Sect.*), 56, 487 (1953) (in Japanese).

[6] H. Uchida, and K. Ogawa et al., ibid., 57, 100 (1954).

[7] G. Shima and H. Uchida, *Rep. Chem. Ind. Res. Inst. Tokyo*, 45, 369 (1950) (in Japanese).

* Defined as $(1-E/F)\times100\%$, where E is the volume of exit gas containing CO_2 at S.T.P. and F is the volume of feed gas at S.T.P. (30l./hr.).

* The fractional distillation was continued first under the atmospheric pressure, and then under a reduced pressure of 5 mm Hg, until the final distillation temperature attained to 200°C and 190°C respectively.

etched by hydrochloric acid. Observations were made at a definite time interval on the same region of the specimen throughout the reduction. In addition, a replica stripped from the etched surface was subjected to the electron microscopic observation.

Determination of Surface Properties of the Catalyst.—The speciments having been used for the activity measurement in the ammonia synthesis at 100 kg./cm^2, were employed for the surface area determination by means of B E T method from the physical adsorption isotherms of CO_2 at −78°C. The surface concentration of K_2O (+CaO)* was also estimated according to the procedure by P. H. Emmett.8) After the measurements with CO_2, the chemisorption of CO was undertaken at −78°C according to S. Brunauer9) in order to estimate the surface concentration of iron. The pore volumes were measured by water- and mercury-displacement method10) to calculate the average pore radius.

Experimental Results

Activity and Oxygenated Compounds.—Cat. 101 was highly active, as shown in Fig. 1. The addition of CuO to the Cat. 101, producing Cat. 301, reduced the activity markedly, but, in turn, increased the quantity of the oxygenates in the products. The detailed measurement of the activity in relation to varying amounts of CuO and K_2O, showed that the activity tended to decrease with the increasing amount of CuO (0.25–0.5–1.0%) but remained unaffected by the varying amount of K_2O (0.5–1.0%). A small amount of 0.25% of CuO was sufficient to increase the content of oxygenates. Among the catalysts of the first group, Cat. 302 (CuO, 0.5%) seemed to produce a maximum of oxygenates which attained to one half of the products (Fig. 5). Therefore it follows by no means that the products obtained with the catalysts of high activity are necessarily rich in the oxygenates. More oxygenates, however, were

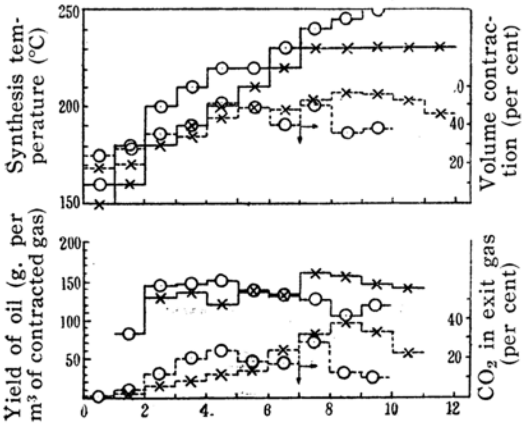

Fig. 1–3 Above; Temperatures of operations required to maintain constant contraction.
Below; Yields of oil products, g./m^3 of contracted gas and CO_2 in exit gas.
×; Cat. 101 ($2Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $1K_2O$)
○; Cat. 301 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$)

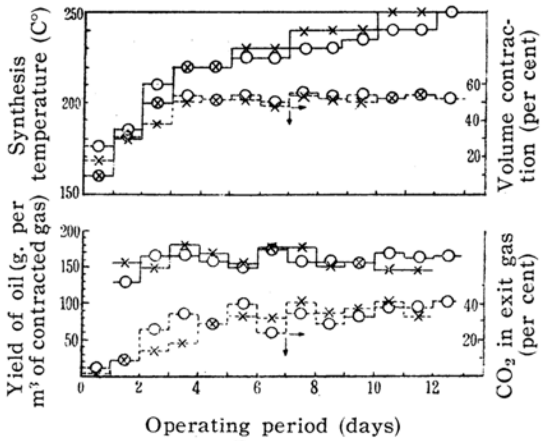

Fig. 2.
×; Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$)
○; Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$)

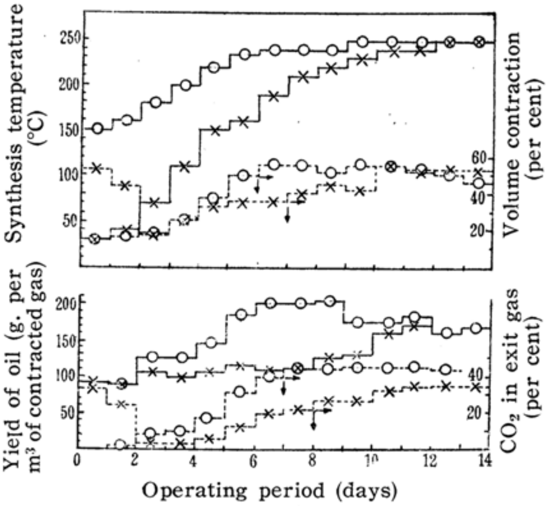

Fig. 3.
×; Cat. 330 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, $2.5K_2O$)
○; Cat. 331 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, 1CuO, $2K_2O$)
The ordinates below in Figs. 1–3 indicate a×1000/(*F*−*E*); a, oil per *F* litres of feed gas, *E*, volume of exit gas containing CO_2.

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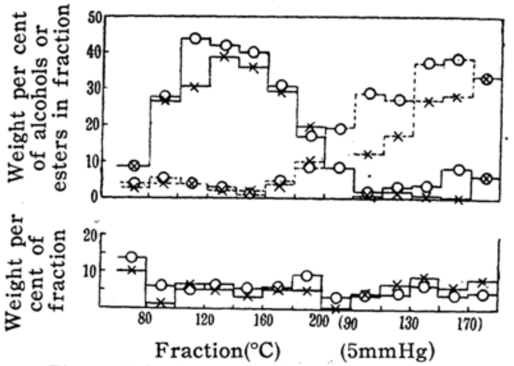
* CaO behaves similarly with K_2O in the physical and chemical adsorption of CO_2. (H. Uchida and T. Sato, ibid., **46**, 103 (1951)).

8) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 310 (1937).

9) S. Brunauer and P.H. Emmett, ibid., **62**, 1732 (1940).

10) A. Juhola and E.O. Wiig, ibid., **71**, 2078 (1949).

produced with Cat. 304 (Fig. 5). at lower reaction temperatures than at higher temperatures. The results may be interpreted to mean that in the case of a given catalyst, the lower the operation temperature is, the higher the yield in oxygenates is. The carbonyl compounds increased with the increasing amount of alcohols plus esters and amounted to an extent of from 4 to 7% in the fractions of between 100–200°C. Throughout the syntheses, with the catalysts of the first group, CO_2 in the exit gases remained small in amount at low operation temperatures and increased up to 40% with rising temperature. The higher temperature was favourable for the formation of gaseous olefins and methane, each attaining in amount to 2–3% and 7–9% respectively in the exit gas at 240–250°C. Aqueous products were usually about one half of the oily products in weight and contained 7–12% of alcohols*, and acids equivalent in amount to 2–2.7% acetic acid.



Figs. 4–6 Above; Contents of alcohols and esters in oil products. Full line, alcohols; dotted line, esters.
Below; Weight per cent of fractions.
×; Cat. 101 ($2Al_2O_3$. 1CaO, 1MgO, $1WO_3$, $1K_2O$)
(React. temperat., 180–230°C)
○; Cat. 301 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$)
(,, ,, ,180–230°C)

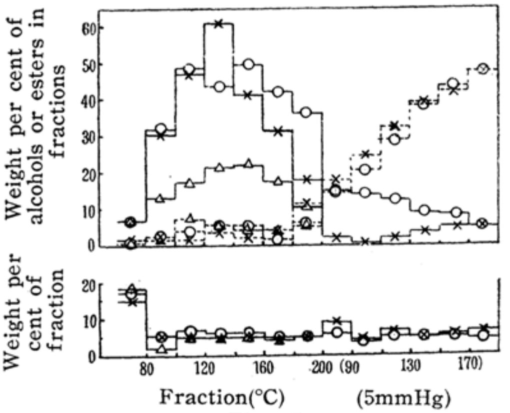


Fig. 5.
×; Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$) (180–230°C)
△; ,, (,,) (240–250°C)
○; Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$) (170–250°C)

Among the catalysts of the second group, a particular catalyst (2.5 SiO_2, 2MgO, 1CaO, $1WO_3$, $1K_2O$) was active at low temperatures of 70–100°C.⁶⁾ A catalyst containing Al_2O_3 together with SiO_2, MgO, CaO, and K_2O (Cat. 330) was again highly active producing the oil at 30–50°C with 50% of the gas contraction (Fig. 3). The activity lasted only for 2 days, and the temperature of 170–180°C was required to maintain the contraction at 40% in the continued operation. With this catalyst, the product below 120°C contained very small amounts of alcohol (Fractions; 120–140°C, 4.4%, 140–160°C, 4.1%, 160–180°C, 6.0%), while that at higher temperatures (130–250°C) the somewhat greater amount (14.0%, 10.6%, 3.9%, of the respective fractions). The catalyst seemed rather less suitable for the alcohol synthesis than those of the first group. In this connection, H. Tramm¹¹⁾ had already avoided a large quantity of diatomite earth in the precipitated iron catalyst for the alcohol synthesis. By the addition of CuO to Cat. 330 (Cat. 331), the activity was lowered (Fig. 3), while the somewhat higher yield of alcohols was obtained (Fig. 6), yet not very significantly. Similar behaviour was also found with the catalysts containing SiO_2, MgO, CaO, and K_2O with (Cat. 320) and without CuO (Cat. 209).

Among the precipitated iron catalysts, a catalyst promoted by MgO, CaO, CuO, and K_2O, but by neither Al_2O_3 nor SiO_2 was frequently used in the Fischer-Tropsch synthesis by H. Koelbel¹²⁾. A fused catalyst of the similar promoter-composition (Cat. 311) was employed in the present experiment. It was found to be of a low activity, and produced a very small amount of oxygenates (Fig. 6) with a large quantity of high boiling fraction (Table I).

Microscopic Structure.—Large grains develop on the etched surface of Cat. 101 containing Al_2O_3, CaO, K_2O etc. and no CuO. The grains are divided into finer sub-grains by regular orientations of narrow grain boundaries (Photo. 1). These grains appeared as fine crystallites with sharp facets in the electron microscope (Photo. 2), their dimen-

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* The water-soluble alcohols obtained with Cat. 301, comprised 0.4%-C_1, 7.0%-C_2, 1.2%-C_3, 0.4%-C_4.

11) H. Tramm, *Brennstoff Chem.*, **33**, 21 (1952).

12) H. Koelbel, and P. Ackermann et al., *Chem. Ing. Tech.*, **23**, 183 (1951).

TABLE I

PROMOTER-COMPOSITION AND FRACTION OF THE PRODUCT DISTILLED BELOW 200°C

Catalyst	101	301	302	303
Promoter-composition	$2Al_2O_3$, 1CaO $1WO_3$, 1MgO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $0.5K_2O$
Fraction below 200°C wt. % (Reaction temperature °C)	37.3 (180–230)	51.3 (180–250)	52.0 (170–250)	53.2 (180–230) 56.5 (240–250)
Catalyst	304	311	209	210
Promoter-composition	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$	3MgO, 1Cao, $1WO_3$, 1CuO, $1K_2O$	$2.5SiO_2$, 2MgO, 2CaO, $1K_2O$	$2.5SiO_2$, 2MgO, 2CaO, $1K_2O$, 0.5CuO
Fraction below 200°C wt. % (Reaction temperature °C)	43.2 (180–230) 48.1 (235–250)	27.0 (180–270)	45.7 (180–250)	40.5 (180–250)
Catalyst	330			
Promoter-composition	$3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, $2.5K_2O$			
Fraction below 200°C wt. % (Reaction temperature °C)	67.8 (30–110) 47.0 (130–250)			

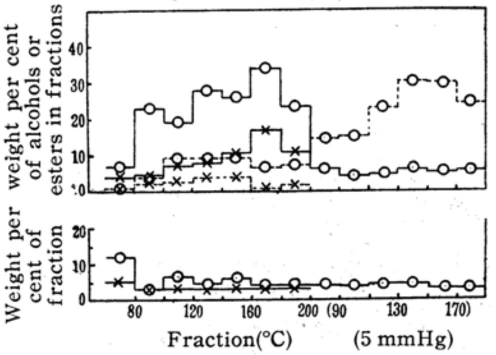

Fig. 6.

×; Cat. 311 (3MgO, 1CaO, $1WO_5$, 1CuO, $1K_2O$) (180–270°C)

○; Cat. 331 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, 1CuO, $2K_2O$) (150–250°C)

sions being a few microns in the smallest. By the addition of a small amount of CuO (0.25%), the narrow grain boundaries disappeared (Photo. 3, 4). Increasing amounts of CuO caused the gradual appearance of intergranular inclusions (Photo. 5), which revealed the metallic lustre of copper before the etching (Cat. 303). Copper added in excess of the quantity which permitted the copper to dissolve into the grains, thus segregated along the grain boundaries. Quite different from those of the first group were the catalysts of the second group, containing glassy inclusions between the grains as previously reported[13,14] (Photo. 7), and not possessing well-developed cleavage surfaces (Photo. 8). This is a significant feature of the catalyst of the second group. The addition of copper gave no remarkable change in the microscopic structures of these catalysts. After the reduction in hydrogen, cracks wider than those of the catalysts of the first group appeared, probably because of stronger shrinkage of the grains. Cat. 330 which contained SiO_2 and Al_2O_3 with a large amount of K_2O, showed the regular orientations of narrower boundaries as well as the crystalline inclusions (Photo. 9 and 10).

Determination of Surface Properties of the Catalyst.—The results are summarised in Table II. The addition of copper seemed to bring about increase in the surface area. With respect to the surface concentration of K_2O, the data were not sufficient to give any definite effect of copper. The adsorption of CO by copper might prevent the S. Brunauer's[9] procedure for the estimation of the surface concentration of iron from the direct use of the method for the catalysts containing copper. Preliminary measurements of adsorption of CO at −78°C were, therefore, carried out with copper supported on Al_2O_3. Nearly the same amount of CO

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[13] Z.W. Wilchinsky, *Anal. Chem.*, **21**, 1188 (1949).

[14] H. Uchida, N. Todo et al., *Rep. Chem. Ind. Res. Inst. Tokyo*, **46**, 11 (1951) (in Japanese).

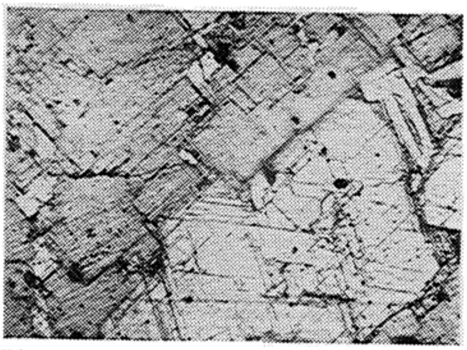

Photo. 1. Cat. 101 ($2Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $1K_2O$) ×100

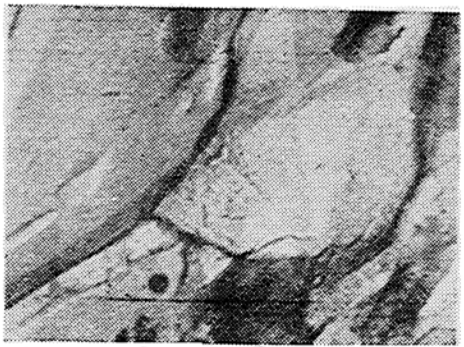

Photo. 2. Cat. 101 Replica ×5.000

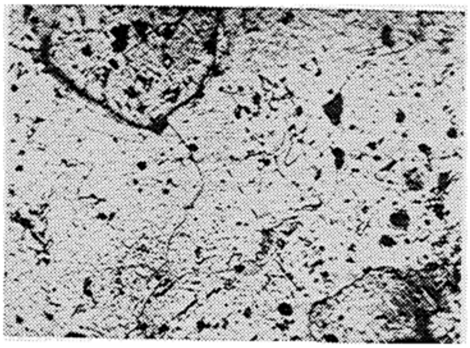

Photo. 3. Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$)

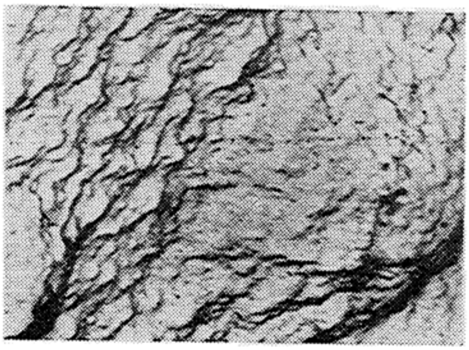

Photo. 4. Cat. 304 Replica

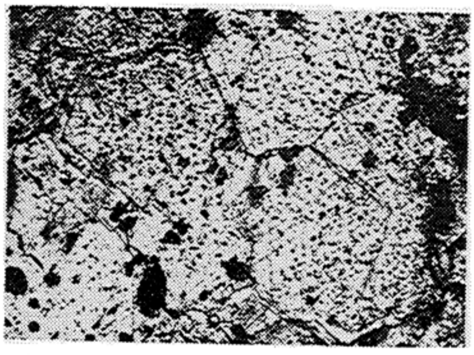

Photo. 5. Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO $1K_2O$)

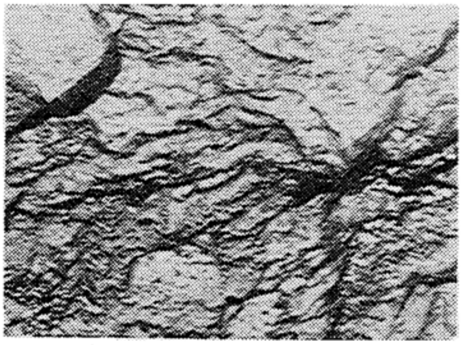

Photo. 6. Cat. 302 Replica

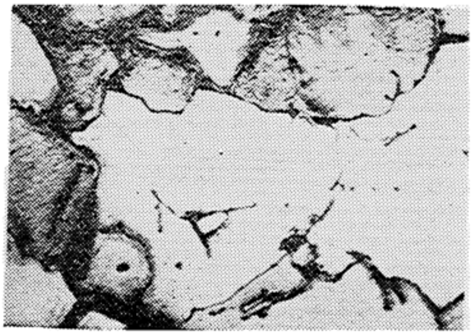

Photo. 7. Cat. 209 ($2.5SiO_2$, 2MgO, 2CaO, $1K_2O$)

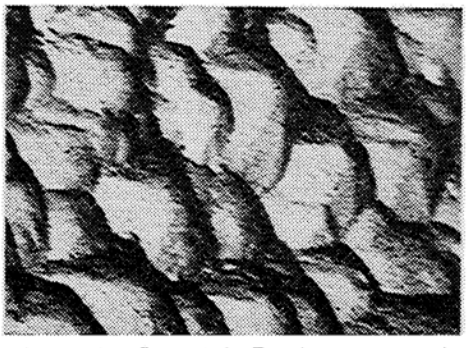

Photo. 8. Cat. 209 Replica

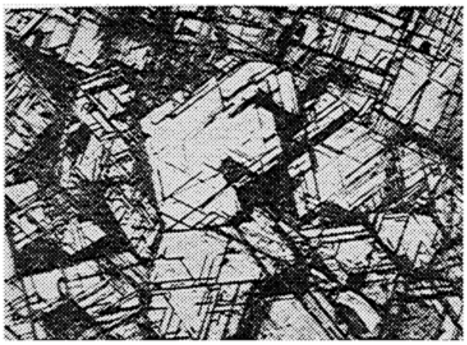

Photo. 9. Cat. 330 ($3Al_2O_3$, $2SiO_2$, ICaO, lMgO, $2.5K_2O$) ×100

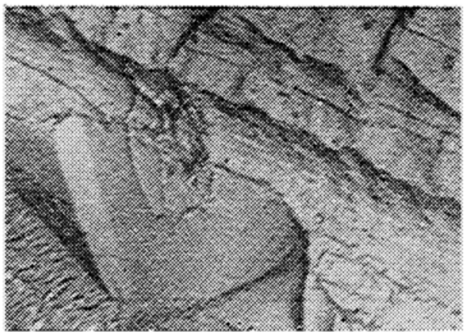

Photo. 10. Cat. 330 Replica ×5.000

was adsorbed at the following successive adsorptions; the one immediately after a degassing at 500°C and the one succeeding after an evacuation at 0°C for one hour (8.2 cc./g.Cu at the first and 7.9 cc./g.Cu at the second at 50 mm Hg). In contrast to the above, the major part of CO adsorbed at −78°C remained adsorbed through the evacuation at 0°C with Cat. 101. The difference between the first and the second measurements ($V_{CO}-V'_{CO}$) might be assumed, for convenience, to represent the surface concentration of iron with respect to the catalysts containing copper. The values of ($V_{CO}-V'_{CO}$) for the catalysts of the second group (Cat. 209, 320) were smaller than those for the first group, while the values of V_{CO} per unit area for the former were larger than those of the latter. The values of 1-A in Table II might express the surface concentration of the promoters, as of Al_2O_3, Cu, exclusive of both iron and K_2O (+CaO). In the case of the catalysts of the first group (with an exception of Cat. 302), the values increased with the addition of copper. This fact suggested that copper might concentrate on the surface.

TABLE II

SURFACE PRORERTIES

Catalyst	101	301	302	303	304	311	209	210	330
Surface area $m^2/g.$	3.3	8.9	7.5	12.5	13.5	1.6	4.3	3.7	6.0
V_{cCO_2}/V_{mCO_2}	0.59	0.32	0.61	0.36	0.37	0.57	0.45	0.28	0.74
Pore volume cc./g.	0.120	0.112	0.122	0.112	0.124	0.123	0.136	0.102	0.138
Average pore radius Å	1385	465	600	355	325	2710	1100	1215	720
V_{CO} (at −78°C)	0.29	0.69	0.61	1.09	0.88		0.63	0.55	0.53
V'_{CO} (at −78°C)	0.096	0.24	0.24	0.39	0.36		0.43	0.28	0.12
1-A*	0.13	0.45	0.16	0.39	0.45		0.24	0.38	--0.04

* $A=(V_{CO}-V'_{CO}+V_{cCO_2})/V_{mCO_2}$, V_{mCO_2}; volume of CO_2 forming the monolayer on the surface, V_{cCO_2}; volume of CO_2 chemisorbed at −78°C.

Discussion

According to the study by H. Koelbel,[12] the addition of 0.05% of copper to iron caused a complete activation during the induction (or the formation) of the precipitated catalysts as well as a marked change in character of the products. On the other hand, according to S. Kodama,[15] 25% of copper to iron was needed for a sufficiently high yield of the oil. The present experiments have shown that a small amount of CuO was enough to bring about a considerable increase of the oxygenates. The microscopic structure, the surface area, and the chemisorption of CO changed also appreciably at the addition of this amount. These results were more like those of H. Koelbel. Since an excess addition of copper causes the segregation along the grain boundaries, it may be right that the further tendency for alcohols to increase considerably, should not be predicted.

In the case of the precipitated iron catalysts for the hydrocarbon synthesis, the promoting action of copper was ascribed by H. Koelbel[12] to an easier formation of iron-carbon com-

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[15] S. Kodama, and H. Tawara et al., *J. Chem. Soc. Japan*, (*Ind. Sec.*) **45**, 1268 (1942) (in Japanese).

pounds. In this connection, S. Kodama[16] attributed it to an increase in number of the active centers at which iron carbides were formed. D. Gall,[17] and E. J. Gibson[18] assumed the synthesis mechanism to involve step-wise addition of methylene radicals to one end of a growing chain terminated by a hydroxymethylene radical or methylene radical to produce alcohols or alcohols and olefins as the initial, desorbed products. Therefore, primarily, the surface structures which may increase or favour the survival of hydroxymethylene radicals, and secondarily, those on which alcohols are not easily adsorbed to be converted to hydrocarbons, may be expected to increase the yield in alcohols. Since the alcohols have been shown to be increased by copper on the surface, copper may contribute to an easier formation of these structures. The structures might be ascribed to the carbides of iron, so far as the considerations by H. Koelbel and by S. Kodama were adopted. The assumption may be also consistent with the fact that the products obtained with Cat. 330 at low temperatures contain an extremely small amount of alcohols, while rather more abundant alcohol has been produced with increasing temperatures in the additional continued operation, during which the formation of the carbides may be achieved.

The low activity of Cat. 311 containing neither Al_2O_3 nor SiO_2 is expected, to a certain extent, due to its extremely small surface area. Since the catalyst has produced a large amount of high molecular fraction, Al_2O_3 together with SiO_2 are also effective in the shortening of carbon chains. On the other hand, Al_2O_3 and SiO_2 showed the promoting actions different from each other in the synthesis. Their microscopic structure as well as their behaviour for the chemisorption of CO differed also greatly between Al_2O_3 and SiO_2. Consequently, some structural difference of the surface may be supposed between the catalysts promoted by either Al_2O_3 or SiO_2.

Summary

Among the fused iron catalysts for the syntheses from water-gas, those containing Al_2O_3 and K_2O as principal promoters behaved differently from those containing SiO_2, MgO, and K_2O as such. With the former, it was well known that the products rich in oxygenates were obtained when the synthesis could be carried out at low temperatures. In the present study, an addition of copper has proved to bring about an increase in oxygenates with a simultaneous decrease of the activity. A marked effect of copper on the yield of alcohols has already been realized at the addition of 0.25% of CuO into the catalyst, while no further remarkable effect has been easily observed with its increasing amounts. The observations of microscopic structures, such as the area, the chemisorption of CO_2, and CO showed also considerable changes at this amount of addition. An excess amount of copper is liable to segregate along the grain boundaries and hence seems to contribute little for the promotion.

By the addition of Al_2O_3 together with SiO_2 besides the usual promoters such as CaO, K_2O etc., a catalyst of the high activity, though of short durability, was obtained. In the product obtained with this catalyst at low temperatures, oxygenates have been extremely small, while those obtained by the additional operation at higher temperature are greater in amount.

A particular promoting action, quite different from that of Al_2O_3, has been ascribed to SiO_2.

Acknowledgment

The authors' thanks are due to Mr. Tadasuke Hosoya for his cooperation. He has been carrying out a part of this experiment.

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Meguro

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[16] S. Kodama, and S. Matsumura et al., ibid., **47**, 3 (1944).

[17] D. Gall, and E. J. Gibson et al., *J. Appl. Chem.*, 2, 371 (1952).

[18] E. J. Gibson and C. C. Gall, ibid., **4**, 49 (1954).