BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1981—1986 (1967)

# The Zinc Oxide-Copper Catalyst for Carbon Monoxide-Shift Conversion. I. The Dependency of the Catalytic Activity on the Chemical Composition of the Catalyst

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(Received February 3, 1967)

The zinc oxide-copper catalysts under investigation included a series of catalysts of different copper contents prepared by kneading zinc oxide powder with copper hydroxide cake (the "kneaded series"), and two other catalysts prepared by the impregnation and the coprecipitation methods. Only the catalysts of the kneaded series show a high activity in the carbon monoxide-shift conversion, provided the catalysts contain appropriate amounts of copper. The observed dependency of the catalytic activity on the copper content can be interpreted in view of the catalyst scheme in which the copper forms its own fine particles among the original zinc oxide particles. On the basis of this picture, the study was then extended to other copper-containing catalysts; an active alumina-copper catalyst could be produced by kneading the cake with alumina powder with a high specific surface area.

Although the zinc oxide-copper catalyst is of considerable importance in industry because of its high activity in the carbon monoxide-shift conversion, no paper has appeared dealing with this catalyst[3] and little knowledge has been obtained on this matter. The present study has been undertaken in an attempt to understand the role played by copper in increasing the catalytic activity, in the light of the comprehensive knowledge available on this catalyst. The study was conducted mainly on a particular series of catalysts. These catalysts were prepared by kneading copper hydroxide with zinc oxide powder; the catalysts differed in copper content. In this connection, Kuraishi[4] had already stated that some of the catalysts prepared by the kneading process show high activity in the carbon monoxide-shift conversion. The present paper will describe how the activity depends on the chemical composition of the catalyst and also on the method of preparation. The catalyst structures will be described in the next paper.

## Experimental

**Catalyst Preparation.** A series of catalysts differing in copper content were prepared by kneading zinc oxide powder (c.p.) with a copper hydroxide cake (the "kneaded series"). The cake was prepared by precipitation in the following way; into a vessel containing 8 *l* of a dilute aqueous ammonia solution, while the solution was being stirred rapidly, an aqueous solution of copper nitrate (3 mol concn.) was added at a constant feed rate (9 m*l*/min), while simultaneously there was added, at the same feed rate, that of an aqueous ammonia solution whose concentration was equivalent to that of the nitrate solution. In this way, the precipitation was always conducted at a fixed pH value of 6.5 (for detailed procedures, Ref. 5). After washing with a dilute aqueous ammonia solution, a portion of the precipitate,[6] which formed a cake consisting 70—75% of water, was kneaded with some zinc oxide powder to produce a mixed slurry. This slurry was air-dried, crushed, and pelleted to cylinders of 4 mm in diameter by 4 mm high.

In addition, a couple of zinc oxide-copper catalysts with an approximate copper content were prepared by processes other than the kneading process; one (the impregnated catalyst) was a pelleted catalyst from zinc oxide powder, which had been impregnated with a copper nitrate solution, while the other (the coprecipitated catalyst) was a pelleted catalyst from a precipitate obtained by adding an aqueous ammonia solution to a mixed solution of nitrates of zinc and copper.

The catalyst pellets were usually heat-treated in the air at 250°C for 4 hr in the hope of avoiding shrinking with use in the reaction. The choice of 250°C as the heat-treatment temperature was made on the basis of the thermogravimetric analytical result that no more loss in the weight of a sample took place at temperatures above 250°C.

Besides the above treatment (treatment A) to avoid shrinking, two other treatments were used; the catalyst pellet was reduced, prior to introduction into a reactor,

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[3] A few papers have, indeed, appeared dealing with use of the zinc oxide-copper catalyst in methanol synthesis, but not in carbon monoxide-shift conversion.

[4] M. Kuraishi (Japan Gas Chemical Co.), private communication.

[5] M. Oba, Y. Ogino and H. Uchida, *Rpt. Gn't. Chem. Ind. Research Inst., Tokyo,* **60**, 121 (1965).

[6] According to the X-ray diffraction diagram, the precipitate proved to contain some $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ in addition to $Cu(OH)_2$.

TABLE 1. CHEMICAL COMPOSITIONS OF THE CATALYSTS

| Catalyst No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 21[a] | 22[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu/Zn (atomic ratio) | ZnO | 0.09 | 0.25 | 0.45 | 0.68 | 0.90 | 1.98 | 2.95 | 9.70 | Cu | 0.34 | 0.40 |

a) An impregnated catalyst. b) A coprecipitated catalyst.

with $2H_2+1CO$ gas at 250°C (treatment B), the powder was reduced with the gas at 250°C before being pelleted (treatment C). The respective samples, A, B, and C, which had been subjected to the specified treatments, A, B, and C, were then examined for their catalytic activity of carbon monoxide shift conversion; sample A was found to have the highest activity.[7] All the catalyst samples were, therefore, subjected to treatment A.

The catalyst pellet was crushed, and granules from 1 to 2 mm size were used for the activity test. All the samples were examined for zinc as well as for copper, their chemical compositions, as expressed by the Cu/Zn atomic ratio, are listed in Table 1.

**Measurement of Catalytic Activity.** The measurements were made by the use of a flow reactor containing a fixed catalyst bed. The reactor consisted of a stainless steel tube (20 mm ID, 1 mm in wall thickness, and 1000 mm high); it was immersed in a bath of fluidized iron oxide powder. The bath was then heated electrically. Ten milliliters of the catalyst sample were introduced into the reactor to form a ring-shaped catalyst bed between the walls of the reactor and the centrally-placed stainless steel thermocouple well (4 mm OD and 2 mm ID). The bed formed was 33 mm high. The whole space below the bed was filled with glass beads (3 mm in diameter) in order to reduce the dead volume of the reactor.

A gas mixture of $2H_2+1CO$ (hereafter designated as the initial dry gas) was supplied at a constant feed rate from a bomb, through a needle valve and a flowmeter, to a stainless steel mixer, where liquid water was introduced from a syringe (connected to a constant speed-driving device) and evaporated. The mixer contained a stainless steel gauze and was maintained at 150°C. The mixture of water vapor and gas passed through the reactor containing a preheating zone, and then the catalyst bed. Before starting the measurements the catalyst was reduced in a current of dry gas at 250°C for 4 hr. The longitudinal temperature difference throughout the whole catalyst bed remained within 2°C when the activity measurements were made under the following conditions; pressure=1 atm, space velocity of initial dry gas at S. T. P.$=500\ \mathrm{hr}^{-1}$, $H_2O/CO$ molar ratio=3, and temperature range=140—500°C.

The exit gas from the reactor was cooled in order to remove water by condensation, and was then passed through a gas meter. A small portion of the gas was withdrawn for analysis for carbon dioxide by the usual volumetric method. The percentage conversion of carbon monoxide, $x$, in the reaction of $CO+H_2O=CO_2+H_2$ was calculated according to the formula;

$$x=\left[\frac{V'_{CO_2}}{(100-V'_{CO_2})}\times\frac{1}{V_{CO}}\right]\times 100$$

where $V'_{CO_2}$ is the volume percent of carbon dioxide in the exit gas free from water and where $V_{CO}$ is the volume percent of carbon monoxide in the initial dry gas.

**Measurement of the Bed Density and the Specific Surface Area.** These measurements were always conducted on the samples after they had been used in the activity test. The bed density was calculated from the volume and weight of the catalyst sample used to form a 10 m$l$ bed. The specific surface area was determined by applying the BET equation to the nitrogen isotherm at −96°C.

## Experimental Results

**The Catalytic Activity in Carbon Monoxide-shift Conversion.** Figures 1 and 2 present the results of the activity tests as plots of the percentage of carbon monoxide conversion against the reaction temperature. All the plots for the kneaded series refer to the catalyst sample after stabilization at 400°C for 2 hr. In fact, immediately after reduction at 250°C, the catalyst shows a higher activity than the plot in the figure, but this initial activity tends to decrease to a constant level at a higher temperature. As regards catalyst 4, this level was finally attained after a 10 hr period at 400°C, as is shown in Fig. 3. The activities might thus have been compared more strictly on the basis of the activity at this level, but the further loss of the activity after the stabilization was so slow that the

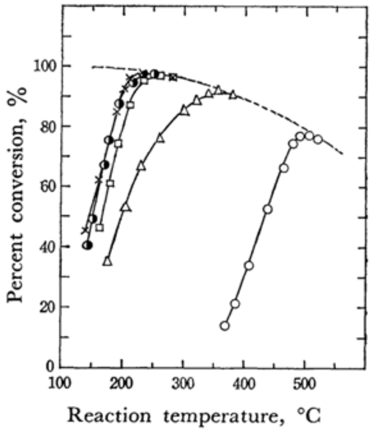

Fig. 1.

○ Cat. 1. △ Cat. 2. □ Cat. 3.
× Cat. 4. ◑ Cat. 5.

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[7] The percentage conversion of carbon monoxide, determined at 180°C under the reaction conditions described in the next section, were 78.5, 68, and 73% for the samples A, B, and C respectively, all with the same copper content (Cu/Zn atomic ratio of 0.45).

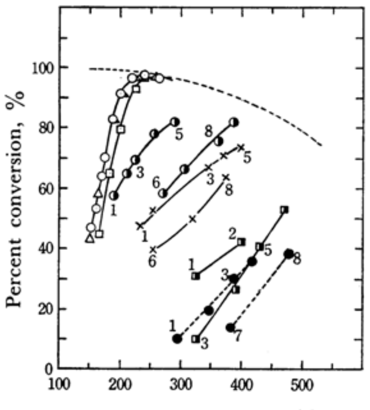

Fig. 2.

○ Cat. 6. □ Cat. 8. ◨ Cat. 9.
● Cat. 10. × Cat. 21. ◑ Cat. 22.

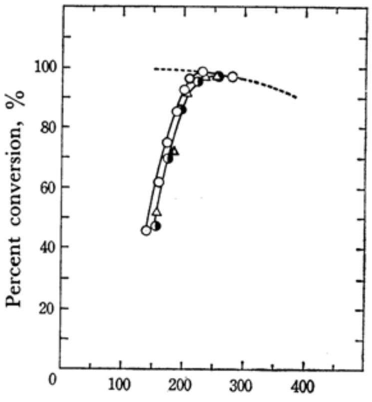

Fig. 3. Catalyst 4 after various periods of running at 400°C.

—○— 400°C, 2 hr. —△— 400°C, 4 hr.
—◑— 400°C, 10 hr.

Figs. 1—3. Percent conversion of carbon monoxide as function of reaction temperature. $H_2O/CO=3$, $S.V.(H_2+CO)=500\ hr^{-1}$

present plots may serve for reasonable purposes of comparison. In contrast, the plots for catalyst 21 (the impregnated catalyst) and 22 (the coprecipitated catalyst) in Fig. 2 refer to the samples immediately after reduction at 250°C, the numerals along the plots indicating the sequence of the measurements. These two catalysts, even at earlier stages of the reaction, show much lower activities than the kneaded series and, moreover, are liable to readily lose their activity at relatively low temperatures. Accordingly, no practicable zinc oxide-copper catalyst for the carbon monoxide-shift conversion can be prepared by either the impregnation method or the coprecipitation method.[8)]

The catalytic activities for the kneaded series will be compared quantitatively later in this paper in terms of the rate constant of a rate equation.

**The Bed Density and Specific Surface Area.** Figure 4 shows the bed density, $\rho_b$, as a function of the Cu/Zn atomic ratio, while Fig. 5 shows the specific surface area, $S$ ($m^2$/g catalyst), as such. As the copper content is increased, the $\rho_b$ first decreases rapidly and then more slowly to reach an almost constant value, which is much higher than that of catalyst 10, consisting of copper alone. Both catalysts, 21 and 22, give lower $\rho_b$ values than the corresponding catalysts of the kneaded series. The $S$ remains almost invariable within the range of the Cu/Zn atomic ratio of 2, but then it decreases rapidly. The impregnated

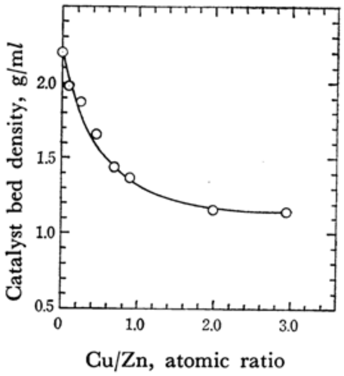

Fig. 4. Catalyst bed densities dependent on chemical compositions.

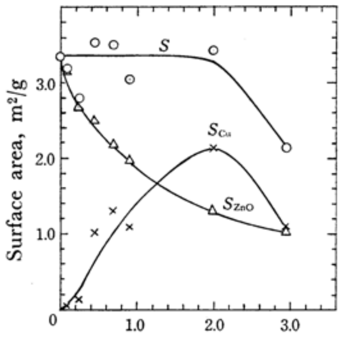

Fig. 5. Total surface area and surface areas of zinc oxide and copper as function of chemical composition.

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8) The activity of a coprecipitated catalyst could be increased to a higher and more stable level if the catalyst contained a greater amount of copper; *e. g.*, a coprecipitated catalyst 22′ (Cu/Zn=1.03, $\rho_b=1.02$ g/m*l*, $S=6.8\ m^2/g$) gave the $k_{180}$ value, as defined in the next chapter, of $27.5\times10^{-3}$. However, this level still remains considerably lower than that of the corresponding catalyst (catalyst 6, $k_{180}=64.5\times10^{-3}$) of the kneaded series. The activities of impregnated catalysts were low and unstable over the range of Cu/Zn atomic ratios below 0.97.

catalyst gives a considerably lower $S$, while the coprecipitated catalyst gives a little higher $S$, than the corresponding catalysts of the kneaded series.

## Discussion

**The Specific Activity.** For the purpose of making a quantitative comparison of activities, the rate constant, $k$, in the Kul'kova-Temkin rate equation for carbon monoxide-shift conversion, Eq. (1),[9] was taken as a measure of the activity.

$$r = k\left[p_{\mathrm{CO}}\left(\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}}\right)^{1/2} - \frac{p_{\mathrm{CO_2}}}{K}\left(\frac{p_{\mathrm{H_2}}}{p_{\mathrm{H_2O}}}\right)^{1/2}\right] \tag{1}$$

In Eq. (1), $r$ (mol m$l$ cat$^{-1}$ hr$^{-1}$) is the reaction rate; $p_i$ (atm), the partial pressure of the $i$th component, and $K$, the equilibrium constant of the reaction. The unit of the $k$ is (mol atm$^{-1}$ m$l$ cat$^{-1}$ hr$^{-1}$). On the basis of 1.0 mol of the initial dry gas, $a$ mol of carbon monoxide in the initial dry gas, $x$ mol of carbon monoxide converted, and $na$ mol of water added to the initial dry gas, the $p_i$'s may be written as:

$$\left.\begin{aligned} p_{\mathrm{CO}} &= P(a-x)/(1+na) \\ p_{\mathrm{H_2O}} &= P(na-x)/(1+na) \\ p_{\mathrm{H_2}} &= P(1-a+x)/(1+na) \\ p_{\mathrm{CO}} &= Px/(1+na) \end{aligned}\right\} \tag{2}$$

where $P$ (atm) is the total pressure. The substitution of Eq. (2) into Eq. (1) and subsequent rearrangement gives:

$$r = \frac{kP}{(1+na)}\left(\frac{na-x}{1-a+x}\right)^{1/2} \times \left[a - x - \frac{x(1-a+x)}{K(na-x)}\right] \tag{3}$$

Eq. (3) is simplified to Eq. (4) when $x/a$ is replaced by $y$, which is the degree of carbon monoxide conversion, and $(1-a)/a$ by 2, which is the $H_2O$/CO molar ratio of the initial dry gas:

$$r = \frac{kaP}{(1+na)}\left(\frac{n-y}{2+y}\right)^{1/2}\left[1 - y - \frac{y(2+y)}{K(3-y)}\right] \tag{4}$$

On the other hand, the rate, $r$, for a steady-state flow reactor is usually given by:

$$r = F\frac{\mathrm{d}y}{\mathrm{d}v} \tag{5}$$

where $F$ (mol hr$^{-1}$) is the feed rate of the reactant (CO in this case), and $v$ (m$l$), the catalyst bed volume. By replacing the $F$ with $V_0$, the feed rate in m$l$ at S. T. P. of initial dry gas per hr, Eq. (5) takes the form:

$$r = \frac{V_0 a}{273\boldsymbol{R}}\frac{\mathrm{d}y}{\mathrm{d}v} = \frac{a}{273\boldsymbol{R}}\frac{\mathrm{d}y}{\mathrm{d}(1/SV_0)} \tag{6}$$

where $\boldsymbol{R}$ is the gas constant, and $SV_0$ (hr$^{-1}$), the space velocity as defined by $V_0/v$. The combination of Eq. (4) with Eq. (6) and subsequent integration yields the rate constant as a function of $y$, when $P=1$ atm:

$$k = \frac{(1+na)SV_0}{273\boldsymbol{R}} \times \int_0^y \frac{\mathrm{d}y}{\left(\frac{n-y}{2+y}\right)^{1/2}\left[1 - y - \frac{y}{K}\left(\frac{2+y}{n-y}\right)\right]} \tag{7}$$

where $n=3$ and $SV_0=500$ hr$^{-1}$, as has been described previously. For a convenient comparison of activities, the $k$ at 180°C, $k_{180}$, calculated according to Eq. (7) using the $y$ measured at this temperature, was taken, but in a few cases where the catalytic activity was too low to permit the measurement, the $k_{180}$ value was obtained by extrapolating the Arrhenius plot of $k$'s at higher temperatures. The $k_{180}$ values are shown in Fig. 6 as a function of the Cu/Zn atomic ratio. The additions of small amounts of copper up to a Cu/Zn atomic ratio of 0.4 cause a rapid increase in the activity, whereas additions of amounts greater than a ratio of 2 cause a rapid decrease. In the intermediate range, the activity decreases slowly with the copper content after passing through a maximum at a ratio of about 0.4.

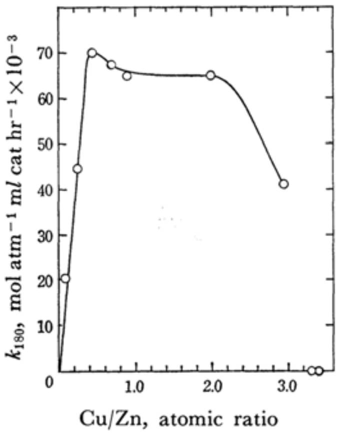

Fig. 6. Plot of rate constant at 180°C *vs.* chemical composition.

As regards the kneaded series, the specific activity, *i. e.*, the activity per unit of surface area, $k'$, may be defined in two different ways, Eq. (8) and Eq. (9):

$$k' = k/\rho_b S \tag{8}$$

$$k'_{\mathrm{Cu}} = k/\rho_b S_{\mathrm{Cu}} \tag{9}$$

In the above equations, $S_{\mathrm{Cu}}$ (m$^2$/g cat) is the surface area of copper for 1 g of a catalyst, and $k'_{\mathrm{Cu}}$ stands for the specific activity based on the unit of area

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[9] N. V. Kul'kova and M. I. Temkin, *Zhur. Fiz. Khim.*, **23**, 695 (1949).

of this copper surface. In Eq. (8), a uniform specific activity over the whole catalyst surface was assumed. In contrast, in Eq. (9) the catalyst surface area was assumed to be the sum of the surface area of zinc oxide particles and that of copper particles, of which only the copper surface was considered effective in the reaction because of the extremely low activity of catalyst 1 as compared with the copper-containing catalysts. According to Eq. (8), we can picture copper as dispersed homogeneously over the surface of every original zinc oxide particle (model I), whereas according to Eq. (9) we can picture particles consisting of copper alone being distributed among the orginal zinc oxide particles (model II).10) The $S_{Cu}$ in Eq. (9) is then calculated by the following formula:

$$S_{Cu} = S - S_1 \times [\mathrm{ZnO}/(\mathrm{ZnO} + \mathrm{Cu})\ \text{in weight}] \tag{10}$$

where $S_1$ is the specific surface area of catalyst 1, *i. e.*, the catalyst consisting of zinc oxide alone. Moreover, this calculation is subject to the further assumptions that the zinc oxide powder does not disintegrate in the course of being kneaded with the copper hydroxide cake and that, hence, the zinc oxide powder in the copper containing catalysts occupies the same extent of specific surface area ($m^2$/g ZnO) as that of catalyst 1.

Figure 5 presents a plot of the $S_{Cu}$ against the Cu/Zn atomic ratio, together with a similar plot of the $S_{ZnO}$, which is the zinc oxide surface area for 1 g of a catalyst. The $S_{ZnO}$ was calculated from the formula of $S_{ZnO} = S - S_{Cu}$. The $k'$ and $k'_{Cu}$ values calculated on the basis of the $k_{180}$ values, *i. e.*, $k'_{180}$ and $k'_{Cu180}$ respectively, are plotted against the Cu/Zn atomic ratio in Fig. 7, resulting in curves A and B respectively. Depending on whether model I or II is taken into account, quite different trends appear in the change in the specific activity with the copper content; curve A increases, but curve B decreases, with the copper content.

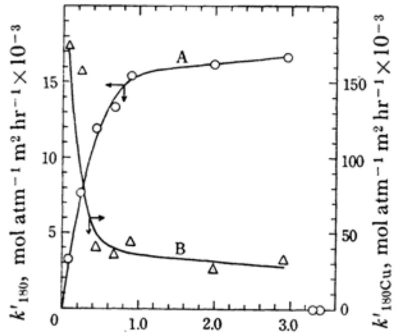

Fig. 7. Specific activities per unit surface area and per unit copper surface area plotted against chemical composition.

Possible explanations for both curves may be offered from the view point of the models proposed. As regards curve A, based on model I, the specific activity increases in proportion to the surface concentration of copper crystallites until the surface is saturated with the crystallites (the first explanation). As regards curve B, based on model II, the specific activity is higher when the growth of copper particles is arrested more considerably by the presence of a greater number of zinc oxide particles and, hence, a greater stress is imposed on the surface of the copper particles; it tends to decrease with the particle growth (the second explanation). The first explanation, however, can not apply to the finding that the impreganted and the coprecipitated catalyst both give very poor activities (Ref. Fig. 3; at an early period, $k'_{180} = 1.07$ and 0.81 mol atm$^{-1}$ hr$^{-1}$ m$^{-2}$ × $10^{-3}$ for catalysts 21 and 22 respectively) as compared with the corresponding catalysts of the kneaded series. Model II will be visualized more definitely in the next paper.

**Activation Energy of the Reaction.** The activation energies of the carbon monoxide-shift conversion were calculated according to the Arrhenius plot of $k$'s; the energies for the kneaded series are plotted in Fig. 8 as a function of the Cu/Zn atomic ratio. By the addition of a very small amount of copper, the activation energy is decreased considerably; then it increases slowly with the further addition of copper until it reache a constant level of 14 kcal/mol for Cu/Zn atomi ratios above 1.0. This decrease and subsequent increase in the activation energy is another evidence in favor of model II; the surface of the copper particles, whose growth is arrested to a greater extent, may perhaps have a higher surface energy and may, as a consequence, give a lower activation energy of the reaction.

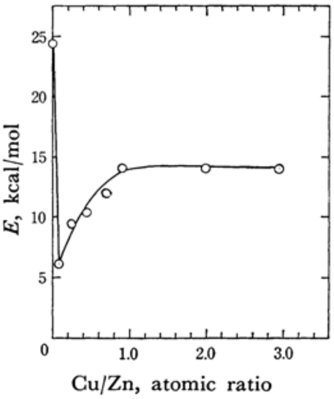

Fig. 8. Activation energy as function of chemical composition.

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10) There is probably an additional model in which the original zinc oxide particle is incompletely covered with patches of copper. This model could not be taken into account, however, because it was difficult to distinguish the extent of the effective copper surface from that of the ineffective surface of zinc oxide.

**Activity of the Alumina-Copper Catalyst.** Model II led us to expect that an active catalyst, whether the oxide-component was zinc oxide or another oxide, might be produced if it included a great number of very fine copper particles. With this expectation in mind, the copper hydroxide cake was kneaded with alumina powder with a high specific surface area, in the hope that the copper cake might be divided into particles as fine as possible, while a pelleted alumina - copper catalyst (catalyst 31, Cu/Al atomic ratio=0.25) was prepared in the usual way. The alumina was a precipitate from a sodium aluminate solution with carbon dioxide. It gave a high specific surface area, 245 m$^2$/g, even after heat-treatment in the air at 400°C for 4 hr. As expected, catalyst 31 showed a high activity (Ref. Fig. 9). Moreover, a three - component alumina - zinc oxide - copper catalyst (catalyst 32, Al : Zn : Cu atomic ratio= 1.0 : 0.5 : 0.48) also showed a high activity (Ref. Fig. 9 also), though the activity was a little lower than that of catalyst 31. This catalyst is characterized by its stronger thermal stability. The $\rho_b$, $s$, $k_{180}$, and $E$ values for catalysts 31 and 32 were as follows; $\rho_b=0.96$ and 1.13 g/m$l$, $S=123$ and 84.5 m$^2$/g, $k_{18}=82$ and 60 mol atm$^{-1}$ m$l$ cat$^{-1}$ hr$^{-1}\times 10^{-3}$, and $E=8.9$ and 11.7 kcal/mol respectively.

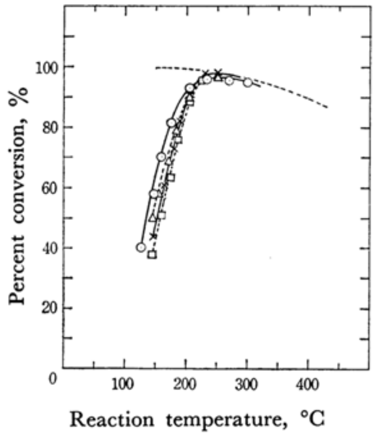

Fig. 9. Percent conversion of carbon monoxide as function of reaction temperature.

○, △ Cat. 31 (Cu : Al=0.25 : 1)
×, □ Cat. 32 (Cu : Al : Zn=0.48 : 1 : 0.5)
Full line. After running at 400°C for 2 hr
Dotted line. After running at 400°C for 4 hr

Moreover, an iron oxide - copper catalyst (Cu/Fe atomic ratio=0.23) and a chromium oxide-copper catalyst (Cu/Cr atomic ratio=0.55), both prepared by the kneading process, were tested for the activity of the carbon monoxide-shift conversion. In its earlier stages, the former catalyst[11] compares in activity with catalyst 3 of the zinc oxide-copper series, but the activity decreases more readily with the reaction duration (conversion value at 200°C; 81% after 2 hr, 71.7% after 10 hr). The latter catalyst shows a very poor activity (conversion value at 400°C; 65% even immediately after reduction).

The authors wish to express their thanks to Mr. Tadashi Hattori of Nagoya University for his participation in a part of this study.

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[11] The catalyst was pretreated in a stream of $2H_2+1CO$ gas added with water in a $H_2O/CO$ molar ratio of 3 at 400°C.