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A Promoting Effect of Phosphorus-Addition to Cu/SiO$_2$ on Selective Synthesis of Formaldehyde by Dehydrogenation of Methanol

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Copper supported on SiO$_2$, which was prepared from Cu(OCOCH$_3$)$_2$ and to which P was added, was a selective catalyst (80-85% at about 50% conversion) for the formation of HCHO by the dehydrogenation of CH$_3$OH at 500 °C. Among various additives such as P, B, K, Li, Mo, and Zn, the addition of P to the Cu/SiO$_2$ significantly enhanced the rate for the formation of HCHO with an increase in the selectivity.

Formaldehyde is an important raw material in polymer industry. At present, formaldehyde is commercially produced by oxidative dehydrogenation of methanol using a Ag catalyst or a MoO$_3$-Fe$_2$O$_3$ catalyst.1) However, since the product of this process is an aqueous solution of formaldehyde, an energy-consuming separation process is necessary to obtain pure formaldehyde. Direct dehydrogenation of methanol to formaldehyde has been attempted by use of Cu-Zn-S2) or Cu-Zn-Se3) catalysts at 650 °C, but they are not sufficiently active or selective. Cu exchanged fluoro tetrasilicic mica produced HCHO selectively by this reaction, but the conversion was very low.4)

We report here that a Cu/SiO$_2$ catalyst promoted by phosphorus exhibited a high activity and selectivity at rather high conversions for the dehydrogenation of methanol to formaldehyde at 500 °C. Cu/SiO$_2$ has been known as a good catalyst for the reforming of methanol and water to hydrogen5) and dehydrogenation of methanol to methyl formate.6)

The Cu/SiO$_2$ catalysts were prepared by two different methods by using SiO$_2$ gel (Kokusan Kagaku, No. 322899, 150 m^2•g^{-1}, pore volume; 0.35 cm^3•g^{-1})7). The first method is an incipient wetness impregnation of an aqueous solution of copper acetate (Cu(OCOCH$_3$)$_2$) (abbreviated as Cu(Ac)/SiO$_2$),8) or an aqueous solution of Cu(NO$_3$)$_2$ (abbreviated as Cu(N)/SiO$_2$). The second is an ion-exchange method using an aqueous solution of Cu(NH$_3$)$_4$(NO$_3$)$_2$ (Cu(Am)/SiO$_2$). For comparison, another catalyst was prepared by the ion-exchange method from ID gel (SiO$_2$ gel, Fuji Davison, 142 m^2•g^{-1}), which was denoted as Cu(Am)/ID. In all cases, the amount of Cu loaded was 1.9 wt%.

After Cu(Ac)/SiO$_2$ was dried at 100 °C, various additives such as P, B, K, Li, Mo, and Zn were loaded by impregnating it with an aqueous solution of H$_3$PO$_4$,

H_3BO_4, an ethanol solution of K or Li acetate, an aqueous solution of ammonium molybdate, and a methanol solution of $Zn(NO_3)_2$. The atomic ratio of the additives to Cu was usually fixed to 0.2. Only in the cases of P and K, the amounts were varied. The P or K-added $Cu(Ac)/SiO_2$ catalysts were denoted as P-$Cu(Ac)/SiO_2$ or K-$Cu(Ac)/SiO_2$. The catalysts were dried at 100 °C, pretreated in He at 300 °C for 1 h, and reduced in a flowing H_2 at 300 °C for 1 h.

Catalytic dehydrogenation of methanol was carried out in a conventional flow reactor at 500 °C and 1 atm. Methanol (about 380 Torr; 1 Torr = 133 Pa) was supplied into a carrier gas (He) by use of a micropump, and a total flow rate was 30 $cm^3 \cdot min^{-1}$. The conversion was controlled by changing the catalyst weight. The products were analyzed by gas chromatography using an APS-201 column (100 °C) for HCHO, CH_3OH, dimethyl ether (DME), methyl formate (MeF), and CO_2. An activated carbon column (100 °C) was used for CO, CH_4, and CO_2. For a part of these catalysts, particle size of Cu was measured by transmission electron microscopy (TEM), and the surface area of the Cu particles was determined by the decomposition of N_2O at 90 °C using a pulse technique.[9)] The reliability of the last method was assured for a fine Cu particle (13 $m^2 \cdot g^{-1}$).

The conversion of methanol decreased gradually with time and reached stationary values after about 4 h for all catalysts. The stationary conversions were between one-third and one-half the initial values. At the initial stage of the reaction, CO as well as HCHO was appreciably formed, mainly due to the high conversion. Then CO decreased gradually with time, and HCHO increased. A stationary selectivity was reached after 4 h. Therefore, the activity and selectivity were estimated from the data at 6 h. The activity was about three times as high as those of $Cu(Ac)/SiO_2$ and $Cu(N)/SiO_2$.

Figure 1 shows the dependence of the selectivity to HCHO on the conversion over Cu/SiO_2 catalysts. An appreciable amount of DME (the selectivity was 7-40% at 24-90% conversion) was formed over $Cu(Am)/SiO_2$ and Cu(Am)/ID, while the formation of DME was less than 5% for $Cu(Ac)/SiO_2$ and $Cu(N)/SiO_2$ up to 80% conversion. The selectivity given in Fig. 1 is calculated for the products other than DME. At low conversions, the selectivity was high for all catalysts. However, the selectivities for $Cu(Am)/SiO_2$ and Cu(Am)/ID decreased rapidly as the conversion increased, due to its conversion to CO. On the other hand, in the other cases, the selectivity decreased much less with the conversion. The difference between the two groups may be due to the difference in the dispersion and/or oxidation state of Cu. Here, we attempted to improve the catalytic performance of $Cu(Ac)/SiO_2$ by several additives.

The results are summarized in Table 1. The additions of B, Zn, Mo, K, and Li did not influence the activity much and slightly lowered the selectivity. Contrary to these additives, P enhanced remarkably the formation of HCHO; the activity increased by a factor of about 7 (from the correlation of conversion-W/F at low conversions), and the selectivity to HCHO retained its high values (≥80%) at higher conversions. When the selectivity was compared at the same conversion level, the selectivity was also a little improved (Fig. 1).

The influence of the atomic ratio of P to Cu on the activity and the selectivity is shown in Fig. 2. The activity showed a maximum value at P/Cu = 0.2 and decreased markedly at P/Cu $\geq$ 0.66. As for the selectivity to HCHO, it was about 80% in the range of 0 $\leq$ P/Cu $\leq$ 0.4, but was very low for P/Cu $\geq$ 0.66, at which DME was mainly formed. For comparison, the influence of K/Cu ratio in K-Cu(Ac)/SiO_2 was examined. When K/Cu increased from 0 to 1, both activity and selectivity decreased greatly.

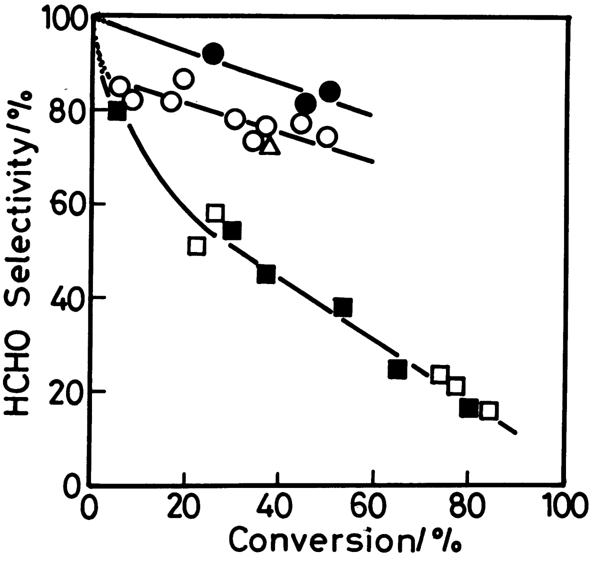

Fig. 1. Dependence of HCHO selectivity on the %-conversion of dehydrogenation of methanol over Cu/SiO_2 catalysts (500 °C). ○:Cu(Ac)/SiO_2, △:Cu(N)/SiO_2, □:Cu(Am)/SiO_2, ■:Cu(Am)/ID ●:P-Cu(Ac)/SiO_2 (P/Cu = 0.2) (see text). The selectivity was calculated in the products other than dimethyl ether.

Table 1. Effect of Additives to Cu(Ac)/SiO_2 on the Activity and Selectivity in Dehydrogenation of Methanol at 500 °C

Additives[a]	W/F[b]	Conv./%	Selectivity/%[c]					
			HCHO	CO	CO_2	CH_4	DME[d]	MeF[e]
None	4.3	15.0	82.2	11.9	1.1	5.2	0	0
	8.3	30.0	81.8	10.6	1.0	5.6	0	0.6
P	0.8	24.8	91.6	1.2	0.4	4.0	0	2.8
	4.2	51.5	83.8	6.7	0.7	5.6	0.3	2.9
B	8.3	36.8	79.6	12.2	1.7	6.2	0.3	0
K	8.3	31.0	71.7	21.1	0.9	6.3	0	0
Li	8.3	38.2	78.2	13.9	1.8	6.1	0	0
Zn	8.3	28.4	73.2	14.6	2.8	5.2	1.1	3.1
Mo	8.3	20.9	70.4	18.1	1.5	9.2	0.8	0

a) Additives/Cu = 0.2 in atomic ratio. b) $g\text{-cat}\cdot h\cdot mol^{-1}$.
c) On the basis of C_1. d) Dimethyl ether. e) Methyl formate.

The average particle sizes measured by TEM were 35 Å and 48 Å for Cu on Cu(Ac)/SiO_2 and P-Cu(Ac)/SiO_2 having P/Cu = 0.2, respectively, showing that the difference in the particle size was small. The surface area of Cu on Cu(Ac)/SiO_2 was 157 $m^2\cdot g^{-1}$ as determined by the N_2O decomposition method.[9)] This value corresponds to the particle size of about 43 Å, which is nearly equal

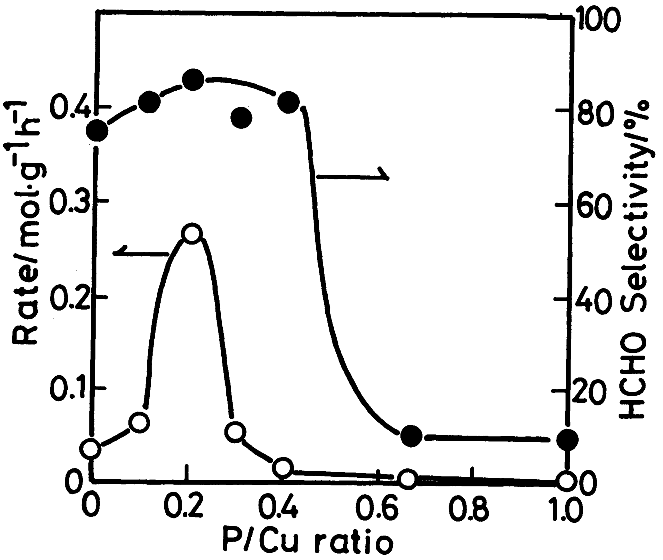

Fig. 2. Effect of the P/Cu ratio on rate and selectivity in dehydrogenation of methanol over P-Cu/SiO_2 catalyst (500 °C). The conversions were 50, 40, 52, 35, 15, 3, and 8% for P/Cu ratio of 0, 0.1, 0.2, 0.3, 0.4, 0.66, and 1.0, respectively.

to that obtained from TEM. On the other hand, the surface area of Cu on the P-Cu(Ac)/SiO_2 determined by the N_2O method was only 7 $m^2 \cdot g^{-1}$, while the particle size from TEM little changed. This great decrease of the surface area indicates that a certain phosphorus compound such as $Cu_3(PO_4)_2$ which was formed during the preparation process covered the surface of the Cu particle and kept Cu in an oxidized state in the case of P-Cu(Ac)/SiO_2, and inhibited the decomposition of N_2O.

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References

1) M. Chono and T. Yamamoto, Shokubai, 23, 3 (1981).
2) Jpn. Patent 51-1407; 51-76209.
3) Jpn. Patent 52-215.
4) K. Takagi, Y. Morikawa, and T. Ikawa, Chem. Lett., 1985, 527.
5) H. Kobayashi, N. Takezawa, and C. Minochi, J. Catal., 69, 487 (1981).
6) T. Sodesawa, M. Nagacho, A. Onodera, and F. Nozaki, J. Catal. 102, 460 (1986).
7) This SiO_2 contained the following impurities; Na_2O (0.17% in weight), CaO (0.07%), Fe (0.02%), and Al_2O_3 (0.04%).
8) N. Kakuta and A. Kazusaka, J. Chem. Soc., Faraday Trans. 1, 80, 3245 (1984).
9) J. J. F. Scholten and J. A. Konvalinka, Trans. Faraday Soc., 65, 2465 (1969).

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