

## Dehydrogenation of Methanol to Methyl Formate over Cu-SiO<sub>2</sub> Catalysts Prepared by Ion Exchange Method

It has been reported that the dehydrogenation of methanol to methyl formate occurs over Cu catalysts through the bimolecular reaction of formaldehyde as follows (1, 2):  $2\text{CH}_3\text{OH} \rightarrow 2\text{HCHO} \rightarrow \text{HCOOCH}_3$ . Furthermore, it has been recently indicated that the Cu catalysts are effective for the steam reforming of methanol (3, 4). However, deactivation of Cu is a serious problem in the dehydrogenation of methanol, as has been reported previously (2). In our preliminary experiments, it was found that a Cu-SiO<sub>2</sub> catalyst prepared by an ion exchange method shows a longer life for methanol dehydrogenation, as compared with those obtained by other methods such as impregnation or precipitation (5). Hereupon, Fig. 1 indicates aging curves for the two catalysts employed in Ref. (2) and this study. According to these results, it was suggested that highly dispersed Cu particles on the support cannot be easily aggregated during the reaction. In this paper, the dynamic parameters such as apparent activation energy, turnover frequency, and selectivity were studied from the viewpoints of the interactions between the Cu particles and SiO<sub>2</sub> support for this reaction.

The Cu-SiO<sub>2</sub> catalysts with various Cu-loading were prepared by ion exchange in the following way. First, an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> (Wako Pure Chemical Industries Ltd., extra pure grade) was added to an adequate amount of NH<sub>4</sub>OH. The pH of an aqueous Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> complex was adjusted to 12, using NH<sub>4</sub>OH and monitoring the solution pH with a pH meter (Toa Electronics Ltd., Model HM-7B). A proper quantity of SiO<sub>2</sub> (Snowtex, Nissan Kagaku Inc., surface area = 438 m<sup>2</sup>/g) was mixed with an aqueous solution of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>

complex obtained at pH 12 for 24 h at ambient temperature. The resultant precipitate was filtered and then thoroughly washed with distilled water. This washed precipitate was dried at 393 K, calcined in air at 773 K for 2 h, and then subjected to a reduction in a flow of H<sub>2</sub> gas at 573 K for 2 h in order to obtain a high dispersion of Cu prior to the reaction. In this case, the protons of surface hydroxyl groups on the SiO<sub>2</sub> support were exchanged by Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> complexes and the degree of Cu ion exchange was measured by ultraviolet spectra of the solution, using a UV spectrophotometer (Shimadzu Seisakusho Ltd., Model UV-200A) to monitor.

The dehydrogenation of methanol over various Cu-SiO<sub>2</sub> catalysts was carried out using a conventional flow system with a fixed catalyst bed. Methanol (Wako Pure Chemical Industries Ltd., extra pure grade) was fed at a rate of 0.123 mol/h over 0.3-3.0 g of catalyst by means of a microfeeder; helium at 30 ml/min was used as a carrier gas. The reaction products were periodically analyzed by a gas chromatograph connected to the reaction system.

Using a method similar to that of Scholten and Konvalinka (6), the reaction between N<sub>2</sub>O and Cu surface atoms was performed by a pulse technique at 363 K. The stoichiometry is  $\text{N}_2\text{O} (\text{gas}) + 2 \text{Cu} \rightarrow \text{Cu}_2\text{O} + \text{N}_2 (\text{gas})$ . The specific surface area of Cu ( $S_{\text{Cu}}^\circ$ ) was calculated from the assumption by Sunquist (7) for a stoichiometry of N<sub>2</sub>O/surface Cu.

The specific surface area and dispersion of Cu before the reaction, depends on the Cu-loading, as illustrated in Fig. 1. Both the surface area and the dispersion gradually decreased with increasing Cu content.

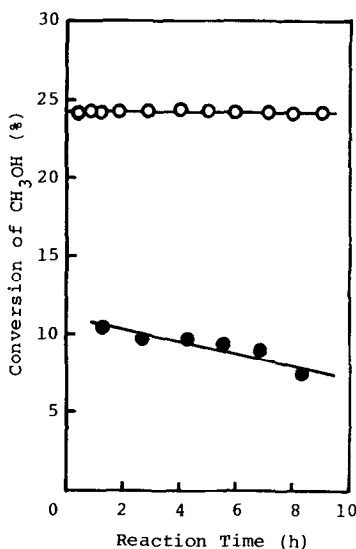


FIG. 1. Profiles of catalyst deactivation with reaction time. (●) Standard data in Ref. (2), (○) data observed in this study using 1.5 wt% Cu-SiO<sub>2</sub> catalyst. Reaction conditions: reaction temperature, 453 K; initial partial pressure of CH<sub>3</sub>OH, 1 atm, W/F = 6.0 g-cat · h/mol.

Figure 2 indicates the effects of Cu-loading upon the reaction rate and the selectivity to methyl formate over Cu-SiO<sub>2</sub> catalysts. The rate of methanol dehydrogenation (*r*) first increased with Cu-

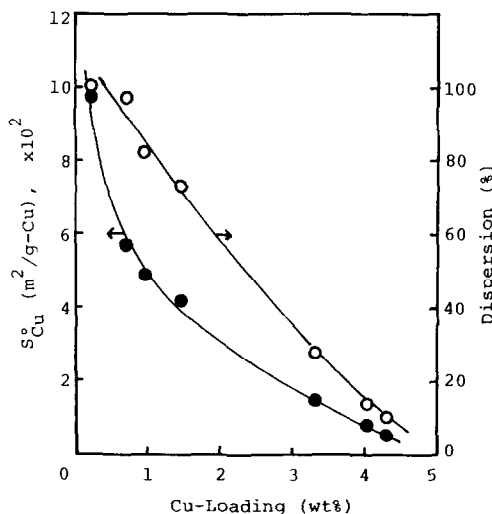


FIG. 2. Relationship between specific surface area of Cu ( $S_{Cu}^o$ ) or dispersion and Cu-loading of Cu-SiO<sub>2</sub> catalysts prepared by the ion exchange method. (●) Specific surface area of Cu ( $S_{Cu}^o$ ), (○) dispersion of Cu.

loading, attained a maximum near 1.5 wt% and then gradually decreased with increasing Cu content. The catalysts having lower Cu-loading showed lower rates. This should decrease since rate is per gram of catalyst of Cu and/or decreases as go to lower loading. On the contrary, the catalysts having higher Cu-loading exhibited lower rates, because the fraction of Cu metal not participating in the reaction increases as the Cu content increases.

Each catalyst showed a selectivity to methyl formate higher than 75% at constant conversion. It was confirmed that the selectivity gradually decreased with the amount of Cu supported on SiO<sub>2</sub>, attained a minimum around 1.5 wt% Cu-loading, and then increased gradually with the Cu-loading. The catalysts with Cu-loading below 1 wt% showed high selectivities. The higher the reaction temperature is, the lower the selectivity to methyl formate is, because the decomposition of methyl formate to CO is enhanced.

Catalyst deactivation is a serious problem in the dehydrogenation of methanol as has been reported previously (2). How-

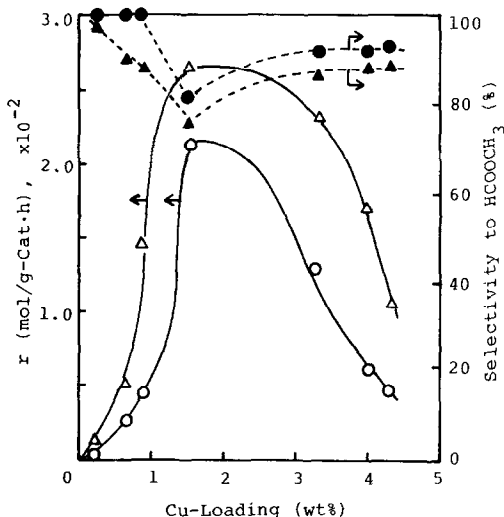


FIG. 3. Effects of Cu-loading upon reaction rate and selectivity to HCOOCH<sub>3</sub> over various Cu-SiO<sub>2</sub> catalysts. (○, ●) 463 K, (△, ▲) 483 K. Initial partial pressure of CH<sub>3</sub>OH: 0.605 atm. (○, △) Reaction rate, (●, ▲) selectivity to HCOOCH<sub>3</sub>.

ever, none of the Cu-SiO<sub>2</sub> catalysts prepared by ion exchange exhibited deactivation, because highly dispersed Cu particles on the support cannot be easily aggregated during the reaction (5).

An example of Arrhenius plots for the reaction over Cu-SiO<sub>2</sub> catalysts, for three Cu-loading, is illustrated in Fig. 3, where the reaction rate is regarded as zero-order because the reaction rate remains constant in the methanol partial pressure range of 0.43 to 1.0 atm. The apparent activation energies for the reaction over the catalysts with 0.23, 1.5, and 4.0 wt% Cu were estimated to be 88, 42, and 63 kJ/mol, respectively. This indicates that the activation energies depend on Cu-loading. The activation energy was the smallest at 1.5 wt% Cu.

In conclusion, the relationship of log-log plots between the Cu surface area and the turnover frequency calculated from the reaction rate is shown in Fig. 4. The turnover frequency was approximately constant to about 400 m<sup>2</sup>/g-Cu, then decreased rapidly with further increase in Cu surface area (Fig. 5). It is assumed that the catalysts

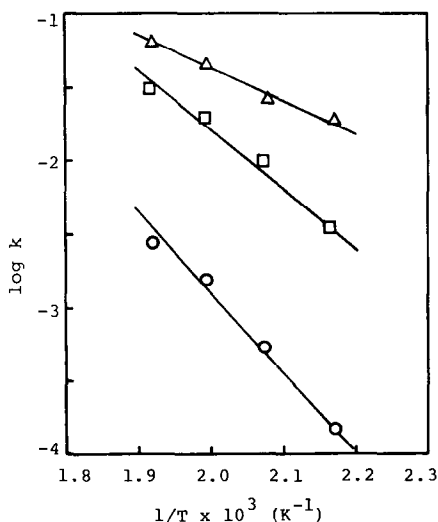


FIG. 4. Arrhenius plots for dehydrogenation of methanol over various Cu-SiO<sub>2</sub> catalysts prepared by the ion exchange method. Cu-SiO<sub>2</sub>: (○) 0.23 wt%, (△) 1.5 wt%, (□) 4.3 wt%.

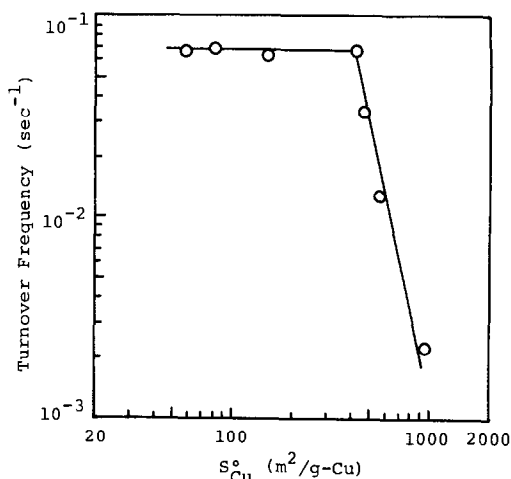


FIG. 5. Plots of turnover frequency against specific surface area of Cu for Cu-SiO<sub>2</sub> catalysts prepared by the ion exchange method. Reaction temperature: 483 K.

having Cu surface areas above 400 m<sup>2</sup>/g-Cu show smaller turnover frequencies because of smaller Cu particles and stronger interactions between the Cu metal and the SiO<sub>2</sub> support.

From the results mentioned above, it can be concluded that methyl formate formation in the dehydrogenation of methanol over Cu-SiO<sub>2</sub> catalysts prepared by an ion exchange method is a structure-sensitive type of catalytic reaction, because the dynamic parameters such as the apparent activation energy, turnover frequency, and selectivity depend on the specific surface area of Cu.

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*Received November 13, 1984*