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CATALYTIC ACTIVITIES OF COPPERS IN THE VARIOUS OXIDATION STATES FOR THE DEHYDROGENATION OF METHANOL

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The catalytic activities of coppers for the conversion of methanol are individually different by their oxidation states. Cu(II) ion and Cu(0) catalyze the dehydrogenation to form methyl formate and formaldehyde, respectively, while Cu(I) ion is inactive.

Fluoro tetrasilicic mica (TSM)1) is a particularly appropriate carrier for use in the study of intrinsic activities of metal ions.2) In the preceding paper,3) we have reported that Cu(II) ion exchanged form of TSM, Cu(II)-TSM, catalyzes the dehydrogenation of methanol to yield methyl formate selectively and shows no decay in the catalytic activity. The excellent performance of Cu(II)-TSM catalyst is caused by both no acidity of TSM and the reduction resistivity of Cu(II) ions in the interlayer spaces of TSM. It is, however, still ambiguous how the oxidation state of copper is related to the selectivity in the dehydrogenation of methanol, where three kinds of products, methyl formate, formaldehyde, and carbon monoxide, are possible, as illustrated in Fig. 1. Therefore, we examined catalytic activities of Cu(II)- and Cu(I)-TSM for the conversion of methanol, and Cu(0) supported on TSM as well.

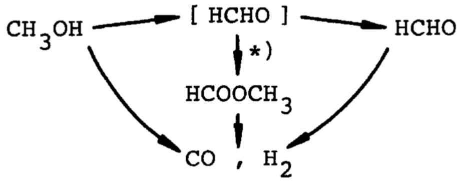

Fig. 1. Possible products in the dehydrogenation of methanol. *) Dimerization of [HCHO]'s or reaction between [HCHO] and surface methoxide.

Cu(II)- and Cu(I)-TSM were prepared by the cation exchange method described in the preceding paper.3) An intercalate of olygomeric cations of cupric hydroxide was prepared by precipitating the hydroxide into the interlayer spaces of TSM

Table 1. Activities of various catalysts for the dehydrogenation of methanol

Run No.	Catalyst	Temperature	Conversion	Selectivity / %		
		°C	%	$HCOOCH_3$	CO	H_2CO
1	Cu(II)-TSM	220	21.1	100	0	0
2		240	44.8	100	0	0
3		400	11.0	6.7	13.3	80.0
4	Cu(I)-TSM	220	1.1	100	0	0
5		240	4.3	100	0	0
6	Cu(0)-TSM	240	1.6	0	0	100
7		300	2.0	0	0	100
8		400	6.1	0	0	100
9	Cu(0)/SiO_2	400	36.9	0	54.3	45.6
10		240	1.8	50.0	tr	50.0
11		300	7.1	45.0	6.5	48.6

from aqueous solution of cupric perchlorate by the titration method reported by Yamanaka and Brindley.4) No Cl^- was detected in any catalyst samples after washing repeatedly by X-ray fluorescence analysis. The intercalate was decomposed in a stream of nitrogen at 400 °C, and reduced with methanol with raising temperature slowly up to 300 °C. The reduction was further conducted at 300 °C for 2.5 h and finally at 400 °C for 4.5 h to obtain Cu(0)-TSM. The copper contents of the catalysts were about 5, 10, and 7 wt% for Cu(II)-, Cu(I)-, and Cu(0)-TSM, respectively. The reaction was carried out with a fixed bed flow reactor. The catalyst sample (0.7 g) was exposed to a stream (58 ml/min) of mixture of methanol and nitrogen (1 : 2 in molar ratio).

The results are summarized in Table 1, where the values of selectivity were calculated on the methanol basis. Cu(II)-TSM catalyzed the dehydrogenation to methyl formate selectively at the temperatures below 240 °C (Runs 1,2). ESR studies showed that Cu(II) ions in Cu(II)-TSM are not reduced at all during the reaction. The results are in good agreement with the previous observations.3) At the higher temperatures, the catalytic activity and the selectivity to methyl formate formation decreased with time on stream, while formaldehyde and a small amount of carbon monoxide were formed. When the reaction was carried out at 400 °C, the deactivation almost stopped within 1.5 h giving the constant value of 11% for the conversion of methanol (Run 3). The value is lower than that obtained for the reaction at 220 °C. The decline of the catalytic activity is inferred to be caused by the reduction of Cu(II) ions in Cu(II)-TSM during the reaction. ESR spectra of fresh and used catalyst, however, showed only a small decrease in the intensity of the signal assigned to Cu(II) ions, suggesting that only a part of Cu(II) ions, which might be located near the outer surface of Cu(II)-TSM and effective for the catalysis, is reduced during the reaction.

The catalytic activity of Cu(I)-TSM was much lower than that of Cu(II)-TSM and produced methyl formate selectively (Runs 4,5). In the ESR spectrum for Cu(I)-TSM, a weak signal due to Cu(II) ions was observed. We, therefore, inferred that the low activity observed for Cu(I)-TSM is ascribed to the small amount of Cu(II) ions contained as an impurity and Cu(I) ion has no activity for the conversion of methanol.

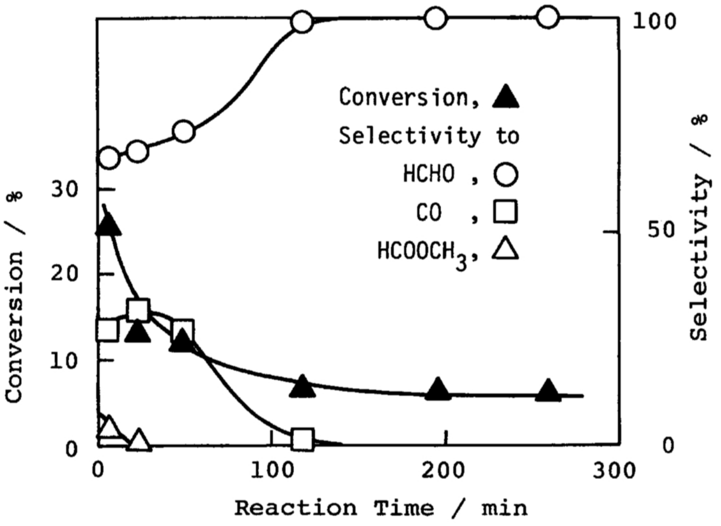

Fig. 2. Change in the activity and the selectivity during the final reduction at 400 °C to obtain Cu(0)-TSM.

In the preparation of Cu(0)-TSM, the reduction of the intercalate of cupric hydroxides was carried out with the same feed as that used in the activity measurements. The reaction of methanol was traced during the final treatment of the reduction at 400 °C. The result is shown in Fig. 2. Water was not detected throughout the reaction, indicating that the oxygen of cupric hydroxide had been removed completely in the preceding treatments. As seen in Fig. 2, the conversion of methanol decreased with the reaction time and kept a constant value at 6.1% after 120 min, while the selectivity to formaldehyde formation increased and attained the value of 100%. The formation of a small amount of methyl formate in the initial period of the reaction might be due to the presence of a trace amount of Cu(II) ions which were not reduced under the reduction conditions at 300 °C. A strong ESR signal assigned to Cu(II) ions was observed for the intercalate of cupric hydroxides. The signal disappeared after the reduction at 400 °C. In X-ray diffractogram with the reduced sample, broad and small peaks were observed and assigned to a metallic phase of copper. As seen in Table 1, Cu(0)-TSM thus obtained catalyzed the dehydrogenation to form formaldehyde selectively in the whole range of temperature studied (Runs 6-8).

The results clearly show that the selectivity in the dehydrogenation of methanol over copper catalyst is quite different depending on the oxidation state of copper, *i.e.* Cu(II) ion and Cu(0) catalyze the dehydrogenation to form, respectively, methyl formate and formaldehyde selectively, while Cu(I) ion is inactive for the conversion of methanol.

We have reported that the activity of a silica gel supported Cu(II) catalyst, Cu(II)/ SiO_2, prepared by the conventional cation exchange method is unstable in the dehydrogenation of methanol because the Cu(II) ions are easily reduced to Cu(0) or Cu(I) during the reaction even at the temperature as low as 200 °C.3) In an attempt to get Cu(0) supported on SiO_2, Cu(II)/ SiO_2 was reduced in the same procedure as that applied in the preparation of Cu(0)-TSM. The final reduction was conducted at 400 °C with monitoring the reaction of methanol. The conversion of methanol and the selectivity to the products did not change appreciably after 4 h, to give the values shown in Table 1 (Run 9). ESR studies showed that the intensity of a signal assigned to Cu(II) ions decreased considerably by the reduction and remained in some extent after the reduction. Shimokawabe *et al.*5) and Gentry and Walsh6) have found that some Cu(II) ions interact strongly with SiO_2 and are not reduced easily by hydrogen at 400 °C. Although it is obvious that there are at least two species, Cu(II) and Cu(0), on the reduced sample, we designated the sample as Cu(0)/SiO_2 for convenience. Cu(0)/SiO_2 exhibited the stable activities at 240 and 300 °C and catalyzed the reactions to form formaldehyde together with methyl formate and carbon monoxide (Runs 10,11). The results with Cu(0)/SiO_2 clearly show that the presence of coppers in various oxidation states causes the low selectivity in the dehydrogenation of methanol. It is likely that the high selectivity observed with Cu(II)- TSM and Cu(0)-TSM for the formation of methyl formate and formaldehyde, respectively, reflects uniformity in the state of copper supported in the interlayer spaces of TSM.

References

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