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Cu-FLUOR TETRA SILISIC MICA. A NOVEL EFFECTIVE CATALYST FOR THE DEHYDROGENATION OF METHANOL TO FORM METHYL FORMATE

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Cu ion exchanged form of fluor tetra silisic mica (Cu-TSM) is remarkably active and selective for the dehydrogenation of methanol to methyl formate. The exclusive activity of Cu-TSM is caused by both no acidity of TSM itself and the high resistivity of exchanged Cu ions against the reduction to Cu metals. Cu-TSM eclipsed the patent catalysts especially by the selective activity.

The alkali metal ions in the interlayer spaces of layered silicate minerals are easily exchangeable with any desired metal ions. In the preceeding communication, we reported the catalytic activities of metal ion exchanged forms of fluor tetra silisic mica (Me-TSM's) for the conversion of methanol by means of the pulse technique.[1)] One of the interesting results obtained is the exclusive activity of Cu-TSM to dehydrogenate methanol to methyl formate selectively.

$$2\ CH_3OH \longrightarrow HCOOCH_3 + 2\ H_2 \qquad (1)$$

Since methyl formate is considered to be an important intermediate in C_1 chemistry, we examined the activity of Cu-TSM, Cu exchanged forms of the other silicate minerals, and the catalysts appeared in patents comparatively. In this communication, we report the results which promise the practical use of Cu-TSM for the synthesis of methyl formate.

TSM[2a)], taeniolite (Taen)[2b)], and hectorite (Hect)[2c)], supplied by Topy Ind. Co., are the synthesized silicate minerals with a layered structure. Bentonite (Bent)[2d)] is similar in the structure but a natural product. The alkali metal ions in the interlayer spaces of these minerals were exchanged with Cu ions by mixing the dilute aquosol of the minerals (0.3 wt%) and the solution of copper ammine complex or copper chloride (0.05 N). The mixture was continuously stirred for 10 hr and the resulting

Table 1. Activities of Cu exchanged forms of various silicate minerls

Catalyst prepared	Conversion (%)	Selectivity (%) $HCOOCH_3$	CH_3OCH_3	Conversion (%)	Selectivity (%) $HCOOCH_3$	CH_3OCH_3
with ammine complex		at 220°C			at 240°C	
Cu-TSM	38	100	0	52	92	0
Cu-Taen	7	100	0	14	100	0
Cu-Hect	12	19	81	34	16	84
Cu-Zeol	18	0	100	44	0	100
Cu-Bent				6	27	68
with aquocomplex						
Cu-TSM	4	100	0	5	100	0
Cu-Taen	0.2	0	100	0.3	0	100
Cu-Hect	40	0	100	45	0	100

precipitate was washed well with distilled water, filtered, and finally dried in an oven at 100°C. The Cu exchanged form of molecular sieve 13X (Cu-Zeol) was also prepared in the same way but with the suspension of the zeolite. Silica gel supported Cu catalyst (Cu-SiO_2) was prepared by the conventional cation exchange method.3)

The reaction was carried out with a flow reaction system. An amount of 0.7 g of the catalyst sample was treated in the reactor by passing nitrogen at 300°C for 2 hr and subsequently exposed to the stream of a mixture of methanol vapor and nitrogen (2 : 5) at the reaction temperature. The flow rate was maintained at 65 ml/min.

The activities of various catalyst samples prepared are summarized in Table 1, where the values of selectivity were calculated on the methanol basis. Although the layered structures of Taen, Hect, and Bent are similar to that of TSM, the activities of Cu exchanged forms of these minerals are quite different individually. Cu-TSM was most active for the dehydrogenation to methyl formate. The value of the selectivity was as high as 100% up to 50% conversion. At the temperature above 240°C, the selectivity decreased and carbon monoxide was simultaneously produced, suggesting that the methyl formate decomposed subsequently to carbon monoxide and hydrogen (2).

$$HCOOCH_3 \longrightarrow 2\ CO + 2\ H_2 \qquad (2)$$

The selectivity was also high with Cu-Taen prepared with ammine complex but the activity was much lower than that of Cu-TSM. With Cu-Hect, Cu-Zeol, and Cu-Bent, the dehydration of methanol (3) took place rather predominantly. Cu-Taen and Cu-Hect pre-

$$2\ CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad (3)$$

pared with Cu aquocomplex are also active only for the dehydration. These facts show that methanol is dehydrated preferentially on the acid sites of these minerals. Cu-Taen and Cu-Hect prepared with ammine complex solution are lower in the activity but give the dehydrogenation products. The ammonia in the solution and/or liberated from the ammine complex seems to block the acid sites of the minerals and facilitate the adsorption of methanol on the adjacent Cu ions.

Fig. 1 shows the changes in the activity of Cu-TSM and Cu-SiO_2 with the reaction time, where the time courses of the selectivity to methyl formate formation are also plotted. The activity of Cu-TSM was very stable and the selectivity (100%) did not change at all throughout the reaction conducted. The color of the used Cu-TSM was deep blue, suggesting that the interlayer Cu ions retain the initial oxidation state even under such a reducing atmosphere of the reaction. The activity of Cu-SiO_2 was higher than that of Cu-TSM and increased gradually with the reaction time. However, the value of the selectivity to methyl formate formation was as low as 75% at the initial period of the reaction and decreased to 25% in 300 min while the amount of carbon monoxide increased remarkably in the products. Carbon dioxide and dimethyl ether were always observed in the products but the amount of those produced were rather unchanged. The color of the Cu-SiO_2, which was light blue before being loaded in the reactor, changed into brown, suggesting that Cu ions on SiO_2 were reduced to Cu metals during the reaction. It is likely that the selective dehydrogenation to methyl formate is catalyzed not by Cu metals but by Cu ions. The high stability of Cu ions in Cu-TSM is consistently understandable with the crystal structure of TSM. The interlayer Cu ions are the constituent of the layer lattice structure of Cu-TSM, where the Cu ions should be balanced with the negative charges of the silicate sheets.

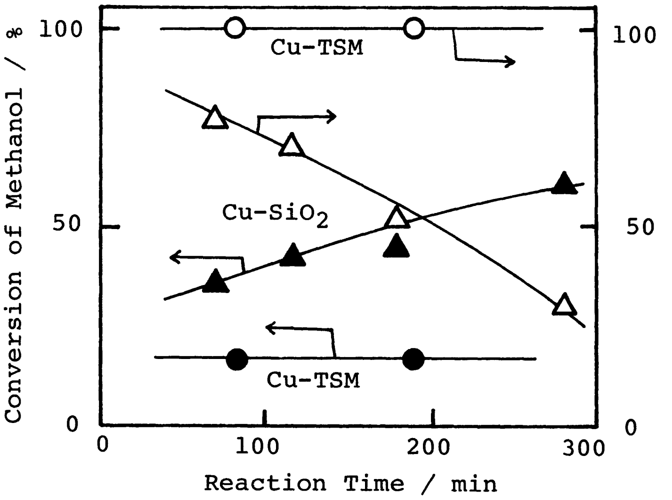

Fig. 1. Changes in the catalytic activities of Cu-TSM and Cu-SiO_2 with the reaction time.

The comparative studies revealed that Cu-TSM is an excellent catalyst for the dehydrogenation of methanol to methyl formate and this particular activity results from both no acidity of TSM and the reduction resistivity of Cu ions in Cu-TSM. The catalytic ability of Cu-TSM, especially the high selectivity, seemed to be favorable for the practical synthesis of methyl formate. Therefore, we examined the activity of the catalysts claimed in patents for comparison. The catalyst samples were prerared

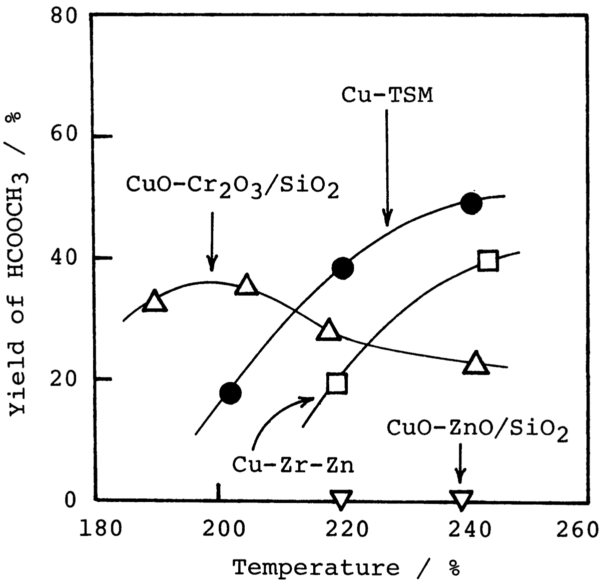

Fig. 2. Temperature dependence of the yield of methyl formate with Cu-TSM and the patent catalysts.

by the methods described in the patents. The results are shown in Fig. 2, where the yields of methyl formate are plotted against the reaction temperature.

As can be seen in Fig. 2, Cu-TSM is the most efficient catalyst to yield methyl formate. With Cu-TSM, the value of 100% of the selectivity was easily obtainable up to 50% conversion. $CuO-Cr_2O_3/SiO_2$ 4) was most active under a mild condition, but the value of the yield did not exceed 35% at any temperatures. Carbon monoxide and a small amount of formaldehyde were always produced besides methyl formate, so that the highest value of the selectivity to methyl formate was only 93% even at the low temperature of 190°C. Cu-Zr-Zn 5) catalyze the reaction selectively as well as Cu-TSM but the activity was lower than that of Cu-TSM. The activity of $CuO-ZnO/SiO_2$ 6) was so poor that the reaction could not be observed at the temperature below 300°C. The catalyst samples tested here have relatively high activities among the patent catalysts. Accordingly, we can conclude that Cu-TSM is superior to the patent catalysts and promissing for the practical use in the synthesis of methyl formate from methanol.

References

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2) a, $Na[Mg_{2.5}Si_4O_{10}F_2]$; b, $Li[Mg_2LiSi_4O_{10}F_2]$; c, $Li_{1/3}[Mg_{8/3}Li_{1/3}Si_4O_{10}F_2]$; d, $Na_{1/3}[Al_{5/3}Mg_{1/3}Si_4O_{10}(OH)_2]$.

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