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CONVERSION OF METHANOL OVER METAL ION EXCHANGED FORMS OF FLUOR TETRA SILISIC MICA

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The catalytic activities of metal ion exchanged form of fluor tetra silisic mica (Me-TSM) were tested for the conversion of methanol. Although Na- and H-TSM have no activities, some Me-TSM's show characteristic activities. Ti-TSM exclusively catalyzes the dehydration reaction like an acid catalyst. Cu-TSM dehydrogenates methanol to produce methyl formate selectively.

Layered silicate minerals consist of negatively charged silicate sheets which are electrostatically connected by interlayer cations. The interlayer cations in the swelling silicate minerals, mostly Na^+ or Ca^{++}, are exchangeable with any desired cations and the interlayer spaces act as "host" for water and a variety of polar organic molecules to form intercalated complexes. Intercalation of bulky compound enlarges the interlayer distance and sometimes, produces new materials with the expanded interlayer spacing. In spite of the interesting natures, a little attention has been paid to their catalytic behavior.

Fluor tetra silisic mica (Na-TSM) is a swelling mica with the chemical formula of $NaMg_{2.5}Si_4O_{10}F_2$. It was synthesized by Kitajima and Daimon[1] and the layer structure shown in fig. 1 was cristalographically established by Toraya et al.[2] In this communication, we report the catalytic activities of the cation exchanged TSM with various metal ions (Me-TSM) for the conversion of methanol.

Na-TSM was kindly supplied by TOPY Ind. Co. It was further refined before use to be free from crystobalite and other nonswelling portions. A portion of Na-TSM, 0.6 g, was dispersed into 200 ml of distilled water with vigorous stirring and to the dispersion was added

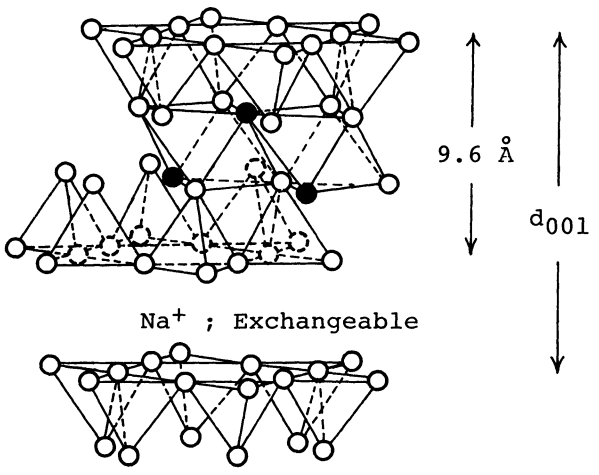

Fig. 1. Oxygen network of fluor tetra silisic mica : o Oxygen , ● Fluorine

dropwise the calculated amount (1.6 meq) of the metal chloride or nitrate solution. Me-TSM was readily precipitated after the addition of the solution and the mixture was continuosly stirred for 10 hr to complete the exchange reaction. The resulting precipitate of Me-TSM was washed well with distilled water and dried in an oven at 100°C.

The catalytic activities of various Me-TSM's were tested for the conversion of methanol by means of the pulse technique. An amount of 30 mg of catalyst sample was loaded in a microreactor and pretreated in a helium stream (20 ml/min) at 400°C for 1 hr. After the treatment, the reactor was cooled down to a reaction temperature (300 – 400°C) and 0.2 or 1.0 µl of extra pure grade CH_3OH was injected.

Possible conversions of CH_3OH are illustrated in Fig. 2. Na- and H-TSM did not show any activities, suggesting that the silicate sheet of TSM has no activities in itself. Since the metal ions in Me-TSM are firmly held by the electrostatic force among the catalytically inactive sheets, Me-TSM is favorable to characterization of the inherent activities of metal ions. The activities of Me-TSM determined are summarized in Table 1, where the values for selectivity to H_2O formation were calculated by the equation, 100 x H_2O formed/CH_3OH reacted. As seen in Table 1, the selectivity was higher than 50% with some Me-TSM's and even attained to the value of 100% with Sn-

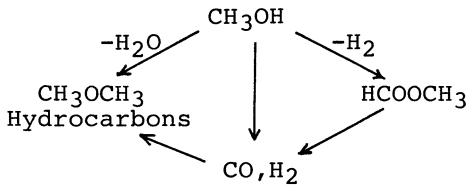

Fig. 2. Possible reactions in the conversion of methanol.

Table 1. Catalytic Activities of Metal Ion Exchanged Form of Fluor Tetra Silisic Mica (Me-TSM) for the Conversion of Methanol[a)]
(Reaction Temperature , 300°C ; Pulse Size , 0.2 µl)

Me	Conversion of CH_3OH (%)	Selectivity to H_2O formation (%)	Products[b)]
Ti	44.8	69.7	$\underline{CH_3OCH_3}$, CH_4
Sn	10.7	100	$\underline{CH_4}$, C_2H_4, C_2H_6
Ag	6.5	100	
Cr	9.8	68.6	
Fe	7.7	56.6	
Rh	50.3	40.1	$\underline{CO + H_2}$, $\underline{CH_4}$, C_2H_6
Pd	72.4	7.7	$\underline{CO + H_2}$, CH_4
Ru	64.1	6.3	
Ni[c)]	75.9	7.1	
Ce[c)]	21.6	2.5	$\underline{CO + H_2}$, CH_4, C_2H_4, C_2H_6, C_3H_6
Ir[c)]	25.7	0	$\underline{CO + H_2}$, CH_4, C_2H_4

a) Mg-, Ca-, Mn-, Co-, Zn-, La-, and Th-TSM exhibithed no activities.
b) The major products are indicated by underlines.
c) Reaction temperature , 400°C.

and Ag-TSM. The reaction products besides H_2O were mostly CH_4 with Sn-, Ag-, Cr-, and Fe-TSM, suggesting considerable accumulation of carbonaceous deposit over the catalysts. It is of particular interest that Ti-TSM showed a high activity to produce CH_3OCH_3 preferentially. Considering that the dehydration of CH_3OH over zeolites and heteropoly acids is always accompanied by the formation of CH_3OCH_3, Ti-TSM is likely to act as an acid catalyst. These facts lead us to expect that the catalytic ability of acidic layered silicate minerals should be improved by exchanging the interlayer cations with Ti ions. Indeed, Ti exchanged form of each of montmorillonite and hectorite shows a high activity for the conversion of CH_3OH to produce hydrocarbons. The details of the results will be reported elsewhere.

The activities of Ru-, Rh-, Pd-, and Ni-TSM were much higher than those of Me-TSM's described above, but the formation of CO and H_2 was rather predominant over these catalyst samples (see Table 1). Supplemental studies with a flow reaction system revealed more clearly that CH_3OH was selectively decomposed to CO + $2H_2$ over all the samples (selectivity 98%) and the subsequent methanation reaction fairly took place over Ru-TSM. The high activity of Rh-, Pd-, and Ni-TSM for the selective decomposition of CH_3OH is attractive, because CO and H_2 may be transported in the form of CH_3OH.

Cu-TSM was one of the most active catalysts employed in this study and exclusively catalyzed the dehydrogenation to $HCOOCH_3$ (see Fig. 2).[3] The results are shown in Table 2, where the values for selectivity were calculated on the CH_3OH basis. In the studies with a flow reaction system, the value of the selectivity to $HCOOCH_3$ formation was kept at 100% up to 50% conversion. The selectivity gradually decreased with raising temperature, while the formation of CO and H_2 increased simultaneously, suggesting that the subsequent decomposition of $HCOOCH_3$ took place. The results with Al_n- and Cu·Al_n-TSM were also summarized in Table 2. Al_n-TSM was prepared in the same way as the other Me-TSM but with a solution of olygomeric cations of aluminium hydroxide (Al_n). Cu·Al_n-TSM was obtained by two step exchanges, that is, firstly with Al_n and secondly with Cu ions. An extent of the cation exchange was approximately adjusted

Table 2. Catalytic Activities of Cu Exchanged Form of Fluor Tetra Silisic Mica (Cu-TSM) and Effect of Intercalated Aluminium Hydroxide (Al_n)

Catalyst	Reaction Temperature (°C)	Conversion of CH_3OH (%)	Selectivity to $HCOOCH_3$ (%)	Selectivity to CH_3OCH_3 (%)
Cu-TSM	300	53.0	67.5	0
	350	72.1	58.0	0
	400	82.1	31.8	0
Cu·Al_n-TSM	250	71.1	76.1	0
	300	84.1	64.8	2.2
Al_n-TSM	300	29.2	0	100
	350	39.5	0	100

Pulse Size, 1.0 µl

in the ratio of 2 : 3. In the pulse experiment, an amount of 50 mg of Cu·Al_n-TSM was loaded in the microreactor, so that the amount of Cu loaded was equal to that of Cu-TSM. As seen in Table 2, the activity of Cu·Al_n-TSM was much higher than that of Cu-TSM : the conversion was the same as that of Cu-TSM at a higher teperature by 100°C. Furthermore, the selectivity of Cu·Al_n-TSM was as high as that of Cu-TSM. This high activity of Cu·Al_n-TSM seemed not to originate in the intercalated Al_n species, because Al_n-TSM was also active for the conversion of CH_3OH but gave only dehydration products (see Table 2). Recently, Shabtai et al.[4] and Yamanaka and Bridley[5] reported that the bulky compound intercalated into a layer mineral acted as a pillar to expand the interlayer distance and to increase the BET surface area dramatically. We think that the high activity of Cu·Al_n-TSM is due to an increase in effective surface sites by the pillar effect of intercalated Al_n.

References

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