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DIFFERENCE IN THE CATALYTIC ACTIVITIES FOR THE CONVERSION OF METHANOL BETWEEN TRIVALENT AND TETRAVALENT Ti ION EXCHANGED FORMS OF LAYERED SILICATE

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The catalytic activities of Ti ion exchanged forms of layered silicate minerals are completely different by the ionic valencies. Methanol was dehydrated to dimethyl ether and hydrocarbons over Ti(IV) forms of the minerals, whereas dehydrogenated to methyl formate and methylal over Ti(III) forms of the minerals. It is of particular interest that acetone is formed from methanol over Ti(III) form of fluoro tetrasilicic mica (Ti(III)-TSM).

In the preceding paper,[1)] we reported that the acidity of layered silicate minerals is markedly enhanced by exchanging the interlayer cations with Ti ions and the catalytic activity of the minerals for the conversion of methanol into lower olefins is improved remarkably by the treatment. It is, however, still ambiguous how the enhancing effect of Ti ions is related to the oxidation state of the ions. Accordingly, we investigated the catalytic activities of trivalent, Ti(III), and tetravalent, Ti(IV), Ti ions exchanged forms of the minerals for the conversion of methanol, and found that Ti ion catalyzes different kinds of reactions by the ionic valencies. The results are reported in this communication.

Three kinds of layered silicate minerals were employed, i.e., fluoro tetrasilicic mica (TSM), hectorite (Hect), and montmorillonite (Mont). The structures and the properties of these minerals have been mentioned elsewhere.[2)] It is to be noted that TSM has no acid site and the acid amount on Hect is less than that on Mont. Ti(III) ion exchanged forms of the minerals were carefully prepared in an atmosphere of nitrogen, because Ti(III) is easily oxidized by gaseous oxygen into Ti(IV). The aquosol (0.1 wt%) of each mineral was deoxygenized by boiling and mixed with the calculated amount of aqueous solution of $TiCl_3$. The mixture was stirred for 2 h and the resulting Ti(III) form of the mineral was filtered, washed well with deoxygenized distilled water, and finally dried in vacuo

Table 1. Catalytic Activities of Ti(IV) Exchanged Forms of Layered Silicate Minerals

Catalyst (0.1 g)	Ti(IV)-TSM		Ti(IV)-Hect		Ti(IV)-Mont		TiO_2
Temperature (°C)	250	300	250	300	250	300	300
Conversion (%)	1.2	19.3	1.0	43.0	19.3	69.3	51.1
Product distribution (%)							
Dimethyl ether	100	99.1	100	95.2	85.7	70.7	100
Hydrocarbons	0	0.9	0	4.8	14.3	29.3	0
Methane		0.9		0.3	1.1	2.8	
C_2				1.6	8.1	8.0	
C_3				2.6	2.0	5.7	
C_{4+}				0.3	3.1	12.8	

at room temperature. Ti(IV) forms of the minerals were prepared by the same way but with the aqueous solution of $Ti(SO_4)_2$.

The reaction was carried out with a conventional flow reactor. An amount of 1.0 g of the catalyst sample was pretreated at 350 °C for 2 h in a stream of nitrogen and exposed to methanol vapor diluted to 15% with nitrogen at a reaction temperature. The space velocity was adjusted at 35 ml/min·g.

The results obtained with Ti(IV) ion exchanged forms of the minerals are summarized in Table 1. All of the catalyst samples catalyzed the dehydration of methanol to dimethyl ether. The catalytic activity of Ti(IV)-Mont was highest of all and produced considerable amount of hydrocarbons at 300 °C. The activity of Ti(IV)-TSM was poor and produced a small amount of hydrocarbons, mainly methane. The results are in conformity with the previous observations.1) We also examined the catalytic activity of TiO_2 (reference catalyst; JRC-TID-1) and found that the activity was higher than that of Ti(IV)-TSM and Ti(IV)-Hect, and the reaction product was only dimethyl ether. The facts suggest that the acidity of TiO_2 is weaker than that of acid sites generated on the silicate sheets by the intercalation of Ti(IV) ions.

The catalytic activities of Ti(III) ion exchanged forms of the minerals are summarized in Table 2. Surprisingly, no dimethyl ether but the other oxygenated compounds, methyl formate, methylal (dimethoxy methane), and acetone, were formed over Ti(III)-TSM at 250 °C. At 300 °C. methane was formed and accounted for about 70% of the products but only a trace amount of dimethyl ether was detected. The activity of Ti(III)-Hect was higher than that of Ti(III)-TSM and showed the similar features in the product distribution, which exhibits substantial formation of methyl formate and methylal. The dehydration of methanol to dimethyl ether took

Table 2. Catalytic Activities of Ti(Ⅲ) Ion Exchanged Forms of Layered Silicate Minerals

Catalyst (0.1 g)	Ti(Ⅲ)-TSM		Ti(Ⅲ)-Hect		Ti(Ⅲ)-Mont	
Temperature (°C)	250	300	250	300	250	300
Conversion (%)	1.9	7.2	4.0	43.0	24.3	9.8
Product distribution (%)						
Dimethyl ether	0	t	8.0	15.1	98.4	82.8
Hydrocarbons	0	72.3	t	46.7	1.6	17.2
Methane		72.3	t	46.0	0.4	3.2
C_2		t		0.7	1.2	4.9
C_3				t	t	4.2
C_{4+}						5.9
Methyl formate	26.8	1.1	59.0	32.0	0	0
Methylal	50.2	25.2	33.0	6.2	0	0
Acetone	23.0	1.4	0	0	0	0

place to some extent over Ti(Ⅲ)-Hect but the distribution in the hydrocarbons was far from that observed with Ti(IV)-Hect (see Table 1). The results indicate that Ti(Ⅲ) ions catalyze the dehydrogenation of methanol preferentially. It is inferred that formaldehyde is firstly formed as an intermediate and is dimerized or reacts with methanol to form methyl formate. The former was proposed by Yasumori and Miyazaki3) for the reaction over copper wire. The formation of methylal also suggests the intermediacy of formaldehyde, since aldehydes readily react with alcohols to form acetals.

As seen in Table 2, the catalytic activity of Ti(Ⅲ)-Mont was much higher and quite different in the selectivity from those of the other two Ti(Ⅲ) forms of minerals. Methanol was dehydrated preferentially over Ti(Ⅲ)-Mont to form dimethyl ether with producing hydrocarbons by subsequent reactions. Both of methyl formate and methylal were not found in the products. The activity is rather similar to that of Ti(IV)-Mont. Since methanol is dehydrated to dimethyl ether but not to hydrocarbons over the original form of Mont (Na-Mont), Ti(Ⅲ) ions in the interlayer spaces are considered to enhance the acidity of Mont probably by their high charge density or electronegativity. The resulting strong acidity might obscure the intrinsic activity of Ti(Ⅲ) ions. The formation of no dimethyl ether over Ti(Ⅲ)-TSM suggests that the activity of Ti(IV)-TSM for the dehydration of methanol is due to Ti(IV) ions themselves, in other words, Ti(IV) ions act as acid sites.

ESR spectra of the Ti(Ⅲ) forms of minerals ($g = 1.95$) well agreed with that of Ti(Ⅲ) exchanged form of zeolite observed by Ono et al.4) When the sample was exposed to air at room temperature, the ESR signal was readily disappeared and the characteristic color of Ti(III) ions, somber purple, changed into white. The sample once exposed to the air did not catalyze the dehydrogenation any more but the dehydration to form dimethyl ether and hydrocarbons. Considering that TiO_2 exhibited no activity to produce hydrocarbons, the interlayer Ti(III) ions seem to be oxidized mostly to Ti(IV) ions. It is speculated that the oxidation is accompanied with the formation of a portion of TiO_2 (e.g., Eq. 1), because total

$$4\ Ti^{3+} + O_2 = 3\ Ti^{4+} + TiO_2 \qquad (1)$$

charges of interlayer cations remain necessarily unchanged to balance with the negative charges of the silicate sheets.

The unexpected differences have been observed in the catalysis by Ti(III) and Ti(IV) ions exchanged forms of the minerals and are inferred to be caused by the characteristic activity of each ion. The formation of acetone in the conversion of methanol is rather unusual. Although the yield of acetone is not high enough in this experiment and the optimum reaction conditions are still in investigations, the reaction is believed to have a potential in C_1 chemistry.

References

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