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CONVERSION OF METHANOL TO LOW MOLECULAR WEIGHT HYDROCARBONS OVER Ti ION EXCHANGED FORM OF LAYERED SILICATE MINERALS

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The acid amount on layered silicate minerals increases remarkably by exchanging the interlayer cations with Ti ions. The catalytic activity of the minerals for the conversion of methanol is also improved markedly by the treatment. Over Ti ion exchanged form of activated clay, methanol is selectively converted to lower olefins and the chain growth is limited at C_6.

Previously, we investigated the catalytic activities of various metal ion exchanged forms of fluor tetrasilisic mica (Me-TSM's) for the conversion of methanol and found that Me-TSM's show characteristic activities for decomposition, dehydration or dehydrogenation of methanol.[1)] It is of particular interest that none but Ti-TSM catalyzed the dehydration to produce dimethyl ether. This fact suggests that the silicate sheets of fluor tetrasilisic mica have no acid sites and Ti-TSM acts as an acid catalyst distinctively. Although it is not clear yet whether the interlayer Ti ions act as acid sites or induce the acidity on the silicate sheets, the catalytic activity of acidic layered silicate minerals is expected to be largely improved by exchanging the interlayer cations with Ti ions. Accordingly, we investigated the acidity of Ti ion exchanged form of layered silicate minerals by TPD of adsorbed ammonia and the catalytic activity of the minerals for the conversion of methanol.

The minerals employed in this study are listed in Table 1. TSM and Hect were kindly supplied by Topy Industries. The synthesis and the properties of these minerals have been studied extensively by Kitajima and Daimon.[2)] Mont is a natural clay mineral. Each mineral was dispersed into distilled water to obtain 0.06% aquosol. Proton exchanged form of the minerals was prepared by passing the aquosol

Table 1. Layered Silicate Minerals Employed

Minerals		Chemical Formula
TSM	(Tetrasilisic Mica)	$Na[Mg_{2.5}Si_4O_{10}F_2]$
Hect	(Hectorite)	$Li_{1/3}[Mg_{8/3}Li_{1/3}Si_4O_{10}F_2]$
Mont	(Montmorillonite)	$Na_{1/3}[Al_{5/3}Mg_{1/3}Si_4O_{10}(OH)_2]$
Mont*	(Activated Clay)	Acid treated montmorillonite

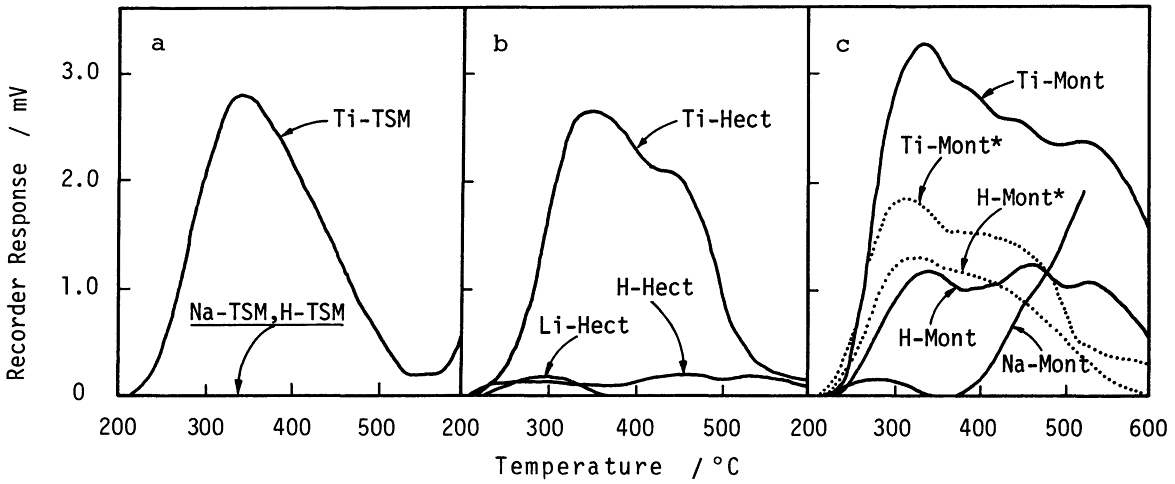

Fig. 1. TPD spectra of ammonia adsorbed on various layered silicate minerals.

through a column packed with an acid form of ion exchange resin (Amberlite IR-120). Ti ion exchanged form of the minerals was prepared by mixing the aquosol and aqueous solution of titanium trichloride. The resulting suspension of each of H and Ti form of the minerals was filtered, washed well with distilled water, and finally dried in an oven at 100°C. H-Mont* was kindly supplied by Mizusawa Chemicals. Ti-Mont* was prepared similarly from the suspension of H-Mont*. All the samples were pretreated in a stream of helium or nitrogen at 350°C for 2 h before the TPD measurement and the reaction were conducted, respectively.

In the TPD experiment, ammonia was fully adsorbed on the sample (0.01 g) at 200°C to exclude weakly adsorbed ammonia from the TPD. TPD spectra were recorded up to 600°C at a heating rate of 10°C/min. The flow rate of carrier gas (He) was maintained at 20 ml/min. A considerable amount of water was desorbed in the temperature region above 350°C. In order to eliminate the contribution of the water to the TPD spectra, a cold trap immersed in a dryice-methanol bath was settled between the sample tube and a thermal conductivity cell.

The reaction was carried out with a fixed bed flow reactor equipped with gas-sampling valves for gas chromatographic analysis. An amount of 2.0 g of the catalyst sample was loaded in a reactor and exposed to methanol vapor diluted to 15% with nitrogen at a contact time of 7.2 s.

TPD spectra obtained with various samples are illustrated in Fig. 1. The TPD from most samples gives complex spectra. The desorbed gases at the temperature below and above 350°C were separately collected in traps cooled by liquid nitrogen and proved by mass spectroscopic analysis to be only ammonia and a mixture of ammonia and a small amount of carbon dioxide, respectively. As shown by an arrow in Fig. 1a, ammonia desorption was not observed at all with Na-TSM and even with H-TSM. The facts strongly support that TSM has no acid sites. On the other hand, a large desorption peak appeared at around 320°C in the TPD for Ti-TSM, suggesting that a considerable amount of acid sites is generated by exchanging the interlayer Na ions with Ti ions. The amount of ammonia desorbed was estimated from the peak area to be less than 0.255 mmol/g-Ti-TSM. The value corresponds to one-tenth of the cation exchange capacity of TSM (2.54 meq/g). All the Ti ions in TSM would not be

Table 2. Catalytic Activity of Various Layered Silicate Minerals for the Conversion of Methanol

Catalyst	300°C Conv. of Methanol (%)	300°C Conv. to Hydrocarbons (%)	350°C Conv. of Methanol (%)	350°C Conv. to Hydrocarbons (%)
Na-TSM	0	0	0	0
H-TSM	0	0	0	0
Ti-TSM	35.2	2.2	50.8	14.2
Li-Hect	0	0	0	0
H-Hect	11.2	0	15.1	0.6
Ti-Hect	87.3	7.2	90.4	38.0
Na-Mont	10.5	0	59.8	0
H-Mont	82.0	0	84.1	8.7
Ti-Mont	89.6	8.9	93.2	58.6
H-Mont*	90.3	3.6	92.5	5.6
Ti-Mont*	87.8	6.3	95.2	89.5

effective for the adsorption of ammonia, although the location of acid sites is not clear yet. The feature was also observed in the TPD spectra with the other minerals. As seen in Fig. 1b, the amount of ammonia desorbed at the temperature below 350°C was increased scarcely by changing Li-Hect into H form but dramatically by changing it into Ti form. Fig. 1c shows that the acid amount on Mont increases by exchanging the interlayer Na ions with H or Ti ions and the amount of acid sites on Ti-Mont is much larger than that on H-Mont. The acidity of acid treated Mont (H-Mont*) which is sometimes called activated clay is further improved by the additional treatment with Ti ions (see dotted lines in Fig. 1c).

The reaction of methanol conversion was conducted with the minerals for 6 h at 300 and 350°C. The catalytic activities did not change appreciably throughout the reaction. The results are summarized in Table 2. As seen in Table 2, no reaction took place over Na- and H-TSM and the considerable activity was observed with Ti-TSM to produce dimethyl ether with a small amount of hydrocarbons. The results are in conformity with the TPD measurement and the previous observations with using a pulse system1). In the series of cation exchanged form of Hect and Mont, Na or Li form of the minerals is not active for the conversion of methanol. The activity of H forms of the minerals is fairly high but produced dimethyl ether predominantly. The activity of the activated clay, H-Mont*, did not largely differ from that of H-Mont.

As expected from the results of TPD measurement, the activities of these minerals were remarkably improved by exchanging the interlayer cations with Ti ions. The values of conversion attained about 90% with Ti-Hect the original form of which, Li-Hect, showed no activity. The values of the conversion to hydrocarbons are as high as 38.0 and 58.6% at 350°C with Ti-Hect and Ti-Mont, respectively. Ti-Mont* showed the highest activity which converted 90% of the fed methanol to hydrocarbons at 350°C. A product distribution in the hydrocarbons is shown in Fig. 2. The hydrocarbons produced over Ti-TSM was methane for the most part, suggesting that the substantial amount of carbonaceous species was accumulated on the surface. With

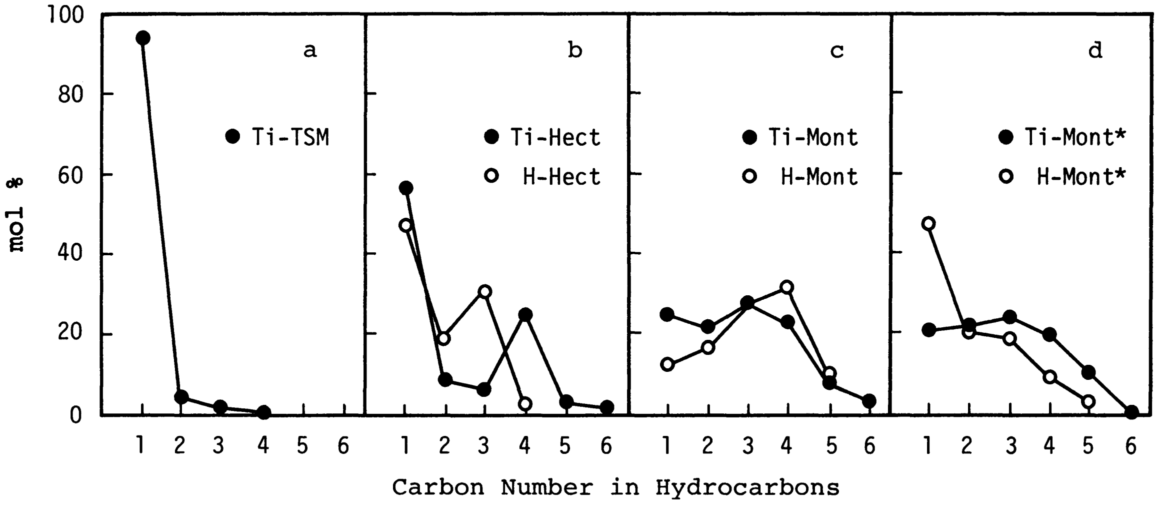

Fig. 2. Product distribution in hydrocarbons produced over H or Ti exchanged form of layered silicate minerals at 350°C.

Ti-Hect, the hydrocarbons with a chain length longer than C_2, C_2+, were formed in some extent but methane accounts for nearly 60% of hydrocarbons produced. The facts suggest that the acid sites generated on the minerals by intercalation of Ti ions are active enough to dehydrate methanol to dimethyl ether and/or methane but do not facilitate the formation of C–C bonds by themselves. With Ti-Mont and Ti-Mont*, C_2+ were produced considerably, in which only a trace amount of C_7 was detected. In addition, fractions of olefin in C_2 and C_3 were 88 and 96% with Ti-Mont and 90 and 96% with Ti-Mont*, respectively. Kaeding and Butter investigated the conversion of methanol to hydrocarbons over ZSM-5 class zeolite and reported that the modification of the zeolite with phosphorus compounds increased the yield of lower olefins and the selectivity to C_2-C_4 olefins was 65-75% at 80-100% conversion.[3] The rest was mostly C_5-C_{10} aliphatics and aromatics. It is interesting that over Ti-Mont*, methanol was selectively converted to olefins and the chain growth was virtually limited at C_6. Ti-Mont* seems to be a better catalyst than zeolitic one to yield lower olefins selectively.

Many problems remain ambiguous at this stage of investigation. Further investigation should be made especially on the role of Ti ions in the acid properties of Ti exchanged form of minerals and the mechanism of the dehydration of methanol over the catalysts. It is, however, noteworthy that the intercalation of Ti ions greatly improved the acidity of sheet silicate minerals. The method might be applicable to modify the acidity of the other minerals and useful to design a solid acid catalyst.

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