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Methanol Conversion to Oxygenated Compounds over the Catalyst Containing Ti Ion as a Main Ingredient

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Methanol was converted into a variety of oxygenated compounds including esters, ketones, and aldehydes at 350 °C over Ti ion-based catalysts, for which Zn and Cl ions were effective additives.

We have reported that the solid acidity of layer lattice silicates is enhanced remarkably by exchanging the interlayer cations with Ti ions, and Ti ion-exchanged montmorillonite catalyzes the dehydration of methanol to produce lower olefins selectively.1) In an extension of the studies, we found a novel type of methanol conversion to produce a variety of oxygenated compounds.

A heteroion-exchanged fluoro tetrasilicic mica (TSM), Ti-M-TSM, was prepared by exchanging the interlayer Na ions of TSM with Ti and other metal ion, M, by adding a mixed solution of Ti and M chrolide (equivalent ratio = 9:1) to an aquosol of TSM, followed by washing the precipitate with distilled water and drying it. Ti-Zn-TSM/Cl was obtained by drying the precipitate without the washing. Ti-M-SiO_2 was prepared similarly but with an aqueous suspension of silica gel.

The reaction was conducted at 350 °C in a fixed-bed flow reactor. An amount of 1.0 g of catalyst was pretreated at 450 °C for 2 h in a stream of nitrogen and exposed to a stream (35 mL/min) of methanol vapor diluted to 15 vol% with nitrogen.

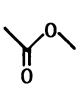
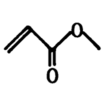
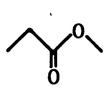
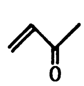
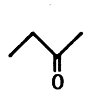
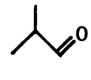
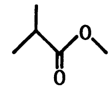
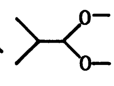
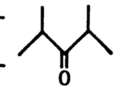
Table 1 summarizes the results of the methanol conversion, where the values of selectivity were calculated on the methanol basis. The formation of dimethyl ether, methane, and/or CO was easily predicted from the results of the methanol

Table 1. Methanol Conversion over Catalysts Containing Ti and Other Metal Ion

Catalyst	Conversion	Selectivity / % a)						
	%	DME	CH_4	CO	CO_2	MF	DMM	C_{3+}-O
Ti-VO-TSM	35.0	32.5	54.0	8.9	3.4	1.1	0.1	0
Ti-Ni-TSM	33.2	0	6.5	93.5	0	0	0	0
Ti-Zn-TSM	8.3	71.3	25.8	0	0	0.7	1.3	0.9
Ti-Zn-TSM+Cl	14.0	12.6	3.9	33.0	6.3	39.4	0.1	4.7
Ti-Zn-TSM/Cl	60.1	43.8	13.9	0	3.3	17.2	0.5	21.3
Ti-VO-SiO_2	67.5	14.9	65.1	14.2	0	2.9	0.4	2.5
Ti-Ni-SiO_2	64.7	28.8	19.6	50.6	0	0.2	0.2	0.6
Ti-Zn-SiO_2	36.0	23.1	20.2	21.9	1.5	10.2	5.2	17.9
Ti-Zn-SiO_2/Cl	74.1	33.4	7.7	0	1.4	2.1	0.4	55.0

a) DME = Dimethyl ether, MF = Methyl formate, DMM = Dimethoxymethane.

Table 2. Product Distribution (mol%) in C_{3-7} Oxygenates

Catalyst											others
Ti-Zn-TSM/Cl	2.8	2.7	2.9	4.4	0.8	0.5	43.1	21.3	4.0	7.3	10.3
Ti-Zn-SiO_2/Cl	9.1	10.4	5.2	0.9	6.3		17.2	7.2	6.0	4.5	33.2

conversion over homoion-exchanged TSM (M-TSM).$^{2)}$ However, the formation of a small amount of methyl formate and dimethoxymethane was not expected because Ti-, VO-, and Ni-TSM do not catalyze the dehydrogenation and Zn-TSM shows no activity for methanol at 350 °C.$^{2)}$ It is of particular interest that a variety of C_{3+} oxygenates (C_{3+}-O) including esters, ketones, and aldehydes were found in the products. We did not succeed in identifying the products heavier than C_8 individually but their mass spectra were completely different from those of hydrocarbons. The values of selectivity for C_{3+}-O were therefore calculated from mass balance. We also employed Mg, Cr, Mn, Fe, Co, or Cu ion as M for Ti-M-SiO_2 and observed no appreciable formation of C_{3+}-O over the catalyst. As seen in Table 1, the combination of Ti and Zn is most effective in TSM or SiO_2 system to yield C_{3+}-O.

In the initial period of the reaction over Ti-Zn-TSM/Cl or Ti-Zn-SiO_2/Cl, considerable amount of CH_3Cl was detected in the products, suggesting that the Cl ions retained on the catalyst were removed by the reaction with methanol. The formation of CH_3Cl decreased and stopped in 4 h. After that, we continued the reaction for 10 h and observed no appreciable decline in the catalytic activity. As seen in Table 1, Ti-Zn-TSM/Cl and Ti-Zn-SiO_2/Cl are more active and effective to give C_{3+}-O than the corresponding Cl free catalysts. We treated Ti-Zn-TSM with CCl_4 vapor at 350 °C and found the treatment enhanced the activity to form C_{3+}-O (Ti-Zn-TSM+Cl in Table 1). These facts suggest that the presence of Cl ion is essential to obtain C_{3+}-O at high yield by this novel methanol conversion.

The typical product distributions in C_{3-7} oxygenates are shown in Table 2, where unidentified products (others) are evaluated quantitatively by FID gas chromatography assuming the relative sensitivity for the molecular formula determined by GC-mass spectrometry. As seen in Table 2, methyl acetate is an only product having one C-C bond and is formed as a minor product. We can find pairs of unsaturated and it's hydrogenated compound in the products having two or three C-C bonds. Branched compounds are formed abundantly, which have two methyl groups at α-carbon. Although the reaction mechanism is not clear yet, these features lead us to speculate on the routes for the formation of some products by analogy with the vinylation with methanol over Ti-TSM$^{3)}$ or M-MgO catalysts.$^{4)}$ The formation of methyl formate and dimethoxymethane suggests that formaldehyde or formaldehyde-like species is formed on the catalyst as a reaction intermediate and a succesive aldol condensation with the intermediate is supposed to take place over acid sites.

References

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