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Reaction of Methanol and Acetone over Metal Ion-Exchanged Forms of Fluoro Tetrasilicic Mica to Form Methyl Vinyl Ketone

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Methyl vinyl ketone was obtained at 30-40% selectivity by the reaction of methanol and acetone at 350 °C over Ti(IV)-, Cr(III)-, Mn(II)-, and Sn(IV)-exchanged forms of fluoro tetrasilicic mica (TSM). The addition of oxygen into the feed increased the conversion of acetone and the reaction over Ti(IV)-TSM converted 11% of acetone fed into methyl vinyl ketone at 85% selectivity.

Fluoro tetrasilicic mica (TSM) is a synthetic layer lattice silicate. We have reported that TSM has no acidity[1] and it's metal ion-exchanged forms (M-TSM's) show different activities for methanol conversion reactions depending on the metal ions.[2] Cu(II)-TSM catalyzes the dehydrogenation of methanol to form methyl formate selectively,[3] and Ti(IV)-TSM catalyzes the dehydration of methanol to form dimethyl ether suggesting that Ti-TSM acts as an acid catalyst.[4] In an extension of the studies, we have found that Ti(IV)-TSM is an effective catalyst for the reaction of methanol and acetone to form methyl vinyl ketone, especially in the presence of oxygen.

Metal ion-exchanged forms of TSM were prepared by the simple ion exchange method described elsewhere.[2] The reaction was carried out in a conventional fixed bed flow reactor. An amount of 1.0 g of catalyst was loaded in the reactor and pretreated at 350 °C for 2 h in a stream of nitrogen. A mixture of methanol and acetone vapor (mole ratio; 1:1) was fed at a constant rate of 3.0 ml/min together with nitrogen 20 ml/min or a mixture of nitrogen 15 ml/min and oxygen 5 ml/min.

The results of the reaction of methanol and acetone at 350 °C are summarized in Table 1, where the values of conversion and selectivity are calculated on the acetone basis. No reaction took place over the original form of TSM (Na-TSM). As seen in Table 1, the reaction over Ti(IV)-, Cr(III)-, Mn(II)-, and Sn(IV)-forms of TSM gave methyl vinyl ketone(MVK), methyl ethyl ketone (MEK), methyl acetate(AcOMe), and some compounds abbreviated to "others" including mesityl oxide, mesitylene, and a trace amount of heavier products. The activities of the M-TSM's were stable and the

Table 1. Reaction of Methanol and Acetone over Metal Ion-Exchanged Forms of TSM

Metal ion	Conv. of acetone	Selectivity / %			
		MVK	MEK	AcOMe	others
Ti(IV)	2.3	40.7	4.7	34.5	20.3
Cr(Ⅲ)	3.2	33.4	4.4	32.0	30.2
Mn(II)	1.4	27.2	4.2	19.1	49.5
Sn(IV)	2.1	41.1	6.5	52.4	tr

selectivity for MVK formation was about 40% over Ti(IV)- and Sn(IV)-TSM.

By the reaction over Ti(IV)-TSM in the absence of methanol, mesityl oxide and mesytilene were formed in the ratio of about 7:2 at 21% conversion and methyl acetate was not formed at all. The results show that mesityl oxide and mesitylene are formed by the condensation of acetone. Although the mechanism of methyl acetate formation is not clear yet, MVK is supposed to be formed through an aldol condensation between acetone and formaldehyde like species formed on the catalyst surface, as speculated for the vinylation of acetone with methanol over metal ion-containing MgO catalyst.5) We also studied the reaction of acetone and formaldehyde at 350 °C over Ti(IV)-TSM and found that MVK and divinyl ketone were formed at 95 and 4% selectivity, respectively. Cu(II)-TSM is an active catalyst for the dehydrogenation of methanol3) and showed higher activity (conversion = 8.6% at the initial period) and selectivity (82%) than the catalysts listed in Table 1. However, the interlayer Cu(II) ions were reduced during the reaction and the catalytic activity declined seriously with reaction time.

The results of the reaction of methanol and acetone in the presence of oxygen are summarized in Table 2. Na-TSM was again inactive and produced only a trace amount of products. As seen in Table 2, the values of conversion and selectivity for MVK formation increased remarkably by the addition of oxygen into the feed, while the acetone condensation was scarecely affected. The facts suggest that the presence of oxygen is favorable for the dehydrogenation of methanol to form formaldehyde-like species which reacts with acetone subsequently to form MVK. The catalytic activities of Ti(IV)- and Sn(IV)-TSM are twice as high as those of Cr(III)- and Mn(II)-TSM. The value of selectivity for MVK formation over Ti(IV)-TSM attains 85%, which is much higher than the value 55% attained with metal ion-containing MgO catalyst.5)

Table 2. Reaction of Methanol and Acetone in the Presence of Oxygen over Metal Ion-Exchanged Forms of TSM

Metal ion	Conv. of acetone	Selectivity / %			
		MVK	MEK	AcOMe	others
Ti(IV)	11.6	84.5	0.2	11.2	4.1
Cr(Ⅲ)	5.6	79.5	2.3	12.4	5.8
Mn(II)	5.6	58.4	tr	29.2	12.4
Sn(IV)	12.3	68.8	5.4	18.3	7.5

We also examined the reaction using Ti(IV)-exchanged form of hectorite (Hect) which is similar to TSM in the crystallographic structure and has acid sites on the silicate sheets. Ti(IV)-Hect showed higher activity (conversion=13%) than Ti(IV)-TSM. The reaction product contained larger amounts of methyl acetate and olygomerization products of MVK and the selectivity for MVK formation was as low as 70%. It is likely that TSM is preferable to the other silicate minerals to get a selective catalyst because the silicate sheets of TSM is chemically inactive and catalyzes no side-reactions such as olygomerization of MVK.

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