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Vinylation of Methyl Acetate and Methyl Propionate with Methanol in the Presence of Oxygen on Metal Ion-Exchanged Forms of Fluoro Tetrasilicic Mica

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Among metal ion-exchanged forms of fluoro tetrasilicic mica (M-TSM's), Ti(IV)-TSM showed the highest catalytic activity at 350 °C for the vinylation of esters with methanol in the presence of oxygen. The values of selectivity for the vinylation of methyl acetate to methyl acrylate and that of methyl propionate to methyl methacrylate attained 87 and 64%, respectively.

We have reported that ketones, esters of carboxylic acids, and nitriles are vinylated with methanol over magnesium oxide modified with transition metal ions (M/MgO) to form corresponding α,β-unsaturated compounds.[1-3] Recently, we have found that Ti(IV) ion-exchanged form of fluoro tetrasilicic mica is effective as a catalyst for the vinylation of acetone in the presence of oxygen to give methyl vinyl ketone at 85% selectivity.[4] We report here the vinylation of methyl acetate or methyl propionate with methanol over the metal ion-exchanged forms of fluoro tetrasilicic mica (M-TSM's).

M-TSM's were prepared from Na-TSM by a simple ion exchange method described elsewhere.[5] The reaction was carried out in a conventional fixed bed flow reactor. An amount of 1.0 g of M-TSM was pretreated at 350 °C for 2 h in a stream of nitrogen and exposed to a stream of reactant mixture diluted with nitrogen at the same temperature. The feed rates were maintained to be (methyl acetate or methyl propionate + methanol) : O_2 : N_2 = 3 : 5 : 15 $ml \cdot min^{-1}$ and the mole ratio of methyl acetate or methyl propionate/methanol was adjusted to 1/4, 1/1, or 4/1.

The reaction of methanol and methyl acetate (mole ratio = 1/1) was conducted with various M-TSM's in the presence of oxygen. The typical results are summarized in Table 1, where the values of conversion and selectivity are calculated on the methyl acetate basis. Na-TSM showed no activity for the reaction. As seen in Table 1, the reaction over Ti(IV)-, Mn(II)-, Cr(III)-,

Table 1. Reaction of Methanol and Methyl Acetate over M-TSM's in the Presence of Oxygen

Metal ion	Conv. of acetate / %	Selectivity / %			
		MA	MP	AA	others
Ti(IV)	8.2	35.0	1.9	48.7	14.4
Cr(Ⅲ)	1.0	2.9	2.2	92.5	2.4
Mn(II)	2.2	17.9	tr	78.3	3.8
Sn(IV)	4.1	28.1	4.5	54.0	13.4

and Sn(IV)-TSM gave methyl acrylate (MA), methyl propionate (MP), acetic acid (AA), and "others" including acrylic acid (Acr.A), propionic acid, propionaldehyde, and methyl methacrylate. Ti(IV)-TSM was most active and selective for the vinylation of methyl acetate to give MA at 35% selectivity. The hydrolysis of esters took place considerably over M-TSM's to form AA at high selectivity. Acr.A formed by the hydrolysis of MA occupied a larger part of "others" and was formed at 9.4% selectivity over Ti(IV)-TSM.

Since the carboxylic acid are easily esterified back to the corresponding methyl esters with methanol over an acid catalyst, AA and Acr.A can be regarded as equivalents of methyl acetate and MA, respectively. The selectivity for vinylation is, therefore, calculated by the equation, 100 x (selectivity to MA + Acr.A)/(100 - selectivity to AA). The values are as high as 87% with Ti(IV)-TSM at any methanol/methyl acetate ratio. The rates calculated for the formation of MA over Ti(IV)-TSM were 102-105 μmol/h·g-cat and again independent on the substrate ratio. We also investigated the reaction over M/MgO catalyst and observed total oxidation of substrates in the presence of oxygen and homo-coupling of methyl acetate to form acetone in the absence of oxygen.

The results of the reaction between methanol and methyl propionate over Ti(IV)-TSM in the presence of oxygen are summarized in Table 2, where the selectivity for vinylation is calculated by the equation, 100 x [selectivity to methyl methacrylate (MMA)]/[100 - selectivity to propionic acid (PA)]. The major products were PA, MMA, and isobutyraldehyde (IBA) which are shown in Table 2. The minor products were AA, methyl acetate, methacrylic acid, and MA. The value of the selectivity for MMA formation attains 64% at the substrate ratio of 1/4, which is comparable to that attained with Mn(II)/MgO.$^{2)}$ The rate of MMA formation is a bit lower than that of MA formation in the reaction of methyl acetate. However, MMA is expected to be produced more efficiently when the reaction is conducted at the lower substrate ratio, since the rate and the selectivity for MMA formation increase with decreasing the substrate ratio.

Table 2. Formation Rates of Products at Various Methanol/Methyl Propionate Ratios

Methanol /Ester	Selectivity for vinylation / %	Rate / μmol·h^{-1}·g-cat^{-1}		
		MMA	PA	IBA
1/4	63.6	74	340	9.2
1/1	59.2	40	180	8.2
4/1	45.6	25	44	25

Acetonitrile is vinylated to acrylonitrile at high selectivity (95%) over Cr/MgO.$^{3)}$ Supplemental studies with Ti(IV)-TSM showed that acetonitrile was not vinylated with methanol but hydrolyzed predominantly to methyl acetate by the water produced in the oxidation of methanol. The preceding report$^{4)}$ and the present results suggest that Ti(IV)-TSM is effective for the vinylation of methyl or methylene group adjacent to carbonyl group, while M/MgO is suitable for the vinylation of nitriles.

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