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COUPLING REACTION BETWEEN METHYLPROPIONATE AND METHANOL TO FORM METHYLMETHACRYLATE OVER METAL ION-CONTAINED MAGNESIUM OXIDE CATALYSTS

Wataru UEDA,* Hideki KUROKAWA, Yoshihiko MORO-OKA,
and Tsuneo IKAWA

Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 227

Solid-base catalyst, MgO modified by metal ion promoted the cross-coupling reaction between methylpropionate and methanol to give methylmethacrylate. 65% selectivity to methylmethacrylate was attained by using 16.7 wt% Mn-MgO catalyst at 400 °C.

We recently developed the general synthetic method of α,β-unsaturated compound by using methanol, where methyl group at α-position of saturated ketones or nitrile was converted into vinyl group by the addition of methanol over metal oxide catalysts having solid-base property.[1,2] In the present communication, we wish to report a new synthetic process of methylmethacrylate by the coupling reaction between methylpropionate and methanol.

Various metal ion-contained magnesium oxide catalysts, M-MgO [M = Al(III), Cr (III), Mn(II), Co(II), Cu(II), Ni(II)], were prepared by impregnating magnesium oxide (Soekawa Rika, 99.92%) with the corresponding nitrate solution. All catalysts were heated in nitrogen stream for 2 h at 600 °C before the reaction. The reaction was carried out at atmospheric pressure in a conventional flow system. Reactant mixture was introduced into the flow line by a syringe pump and evaporated in a preheater tube. Nirtogen was used as the diluent and the flow rate was maintained at 70 ml/min. Products analysis was carried out by Gas-chromatography [Porapak T, 2m, 175 °C].

The activity of catalysts used reached the steady state after short deactivation periods. Table 1 shows methylpropionate conversion and selectivity for each product after the reaction for 4 hours. Methylmethacrylate (MMA) with two kinds of by-products was formed in each case. Methylisobutylate (MIB) may be fomred by the hydrogenation of MMA with molecular hydrogen formed in the reaction or by the hydrogen-transfer from methanol to MMA. Both diethylketone (DEK) and ethylisopropenylketone (MIPK) were formed through the homo-coupling reaction of methylpropionate. Unreacted methanol was recovered after the reaction with small amounts of the decomposition products, CO and CH_4.

Magnesium oxide showed the activity to some extent at elevated temperature to give MMA but mainly promoted the homo-coupling reaction to give DEK (run 1).

Table 1. Conversion and selectivity data for the catalytic formation of MMA over various metal ion-contained catalysts at 400 °C[a]

Run	Catalyst		Catalyst weight	Methylpropionate conversion	Selectivity/mol%		
	M-MgO M	wt%	g	%	MMA	MIB	Ketones
1	-	0	1	5.5	7.9	16.9	75.2
2	Al(III)	3.1	1	5.9	9.5	11.9	78.6
3	Co(II)	3.1	1	4.0	24.4	23.1	52.5
4	Ni(II)	3.1	1	2.5	23.4	39.0	37.6
5	Cu(II)	3.1	1	4.7	38.1	26.1	35.8
6	Cr(III)	0.48	1	6.8	23.7	23.1	53.2
7	Cr(III)	3.1	1	2.9	38.3	48.0	13.7
8	Cr(III)	11.0	1	1.9	36.8	49.5	13.7
9	Mn(II)	0.48	1	10.7	20.5	21.3	58.2
10	Mn(II)	3.1	1	10.5	47.8	17.3	43.9
11	Mn(II)	5.3	1	10.6	56.8	19.4	23.8
12	Mn(II)	16.7	0.1	2.5	64.8	17.2	18.0
13	Mn(II)	16.7	0.5	6.6	63.2	16.0	20.8
14	Mn(II)	16.7	1	10.2	60.8	15.5	23.7
15	Mn(II)	16.7	2	17.2	50.4	23.4	26.2

a) Reactant mixture: methanol 9%, methylpropionate 1%, remainder nitrogen.

For the purpose of improving the catalytic property, magnesium oxide was modified by the addition of various metal ion. As can be seen in Table 1, clear positive combination effect was observed except for Al-MgO catalyst. The addition of Cr(III) ion or Mn(II) ion showed the remarkable effect. Although the catalytic activity of Cr-MgO was low, high selectivity for the cross-coupling reaction of methylpropionate with methanol was attained (runs 6-8). Mn-MgO catalysts showed the most superior properties both in the conversion and the selectivity to MMA among the metal ion-contained catalysts tested in this investigation (runs 9-15). These combination effects were more appreciable on the catalysts with higher content of manganese (runs 9-11,13). By using high space velocity to avoid the hydrogenation of MMA and further C-C bond formation (runs 12,13), 65% selectivity to MMA was attained on 16.7 wt% Mn-MgO catalyst at 400 °C.

Since the coupling reaction of methanol with acetone or acetophenone having lower pKa of methyl-hydrogen proceeds easily over these solid base catalysts below 400 °C,[1,2] the key step of this reaction seems to be the abstraction of α-hydrogen of methylpropionate on surface base site. The combination effect of metal ion for improving the catalytic properties may be attributed to the cooperation of additive metal ion as Lewis acid site in the key step.

References

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2) W. Ueda, T. Yokoyama, Y. Moro-oka, and T. Ikawa, Ind. Eng. Chem. Prod. Res. Dev., in press.

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