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Formation of methyl methacrylate from methyl propionate and methanol

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Abstract

The formation of methyl methacrylate (MMA) was studied in a vapor-phase reaction between methyl propionate (MP) and methanol without using any sources of formaldehyde. Silica-supported CsOH doped with a small amount of silver Ag was found to be the best catalyst. The optimum Ag/Cs/Si atomic ratio was 4–10/20–25/1000. When the reaction was performed in the absence of oxygen in the feed, the main product was methyl isobutyrate (MIB) at the beginning of the reaction; MMA was not obtained. As the time-on-stream increased, the formation of MIB fell, while that of MMA increased, showed a maximum, and then decreased gradually. In the case of the reaction performed in the presence of oxygen, the catalytic activity was stable. As the amount of oxygen increased, the yield of MMA increased, while the selectivity fell. The performances were further improved by the combination of a small amount of Ag–Cs/SiO_2 catalyst and a large amount of Cs/SiO_2 catalyst.

Keywords: Methyl methacrylate formation; Vapor-phase aldol-condensation; Methanol dehydrogenation; Methyl propionate

1. Introduction

Methyl methacrylate (MMA) is a monomer of polymethyl methacrylate, which is a raw material of the so-called organic glasses. Therefore, patented works have been making devoted to investigation on the aldol-condensation-type reaction of propionic acid (PA) and methyl propionate (MP) with formaldehyde (HCHO) to obtain methacrylic acid (MAA) and MMA, respectively [1–3].

$$CH_3CH_2COOH + HCHO \rightarrow CH_2{=}C(CH_3)COOH + H_2O \tag{1}$$

$$CH_3CH_2COOCH_3 + HCHO \rightarrow CH_2{=}C(CH_3)COOCH_3 + H_2O \tag{2}$$

As the source of HCHO, formalin (aqueous solution of HCHO), trioxane [$(HCHO)_3$], and methylal [$CH_2(OCH_3)_2$] are used. It is known that the use of formalin is not preferred as the source of HCHO, because both the reaction rate and the selectivity are decreased by the presence of water in the reaction feed. The reaction of MP with HCHO, i.e. the reaction (2), is generally performed in the presence of a large amount of methanol in the reaction feed to avoid the hydrolysis of MMA and MP.

About the reaction (1), several papers have been published [4–10], besides patents. On the other hand, there are only two papers reporting on the reaction (2); the one reports the performances obtained using solid acids (V–Si–P oxides) as the catalysts and methylal as the source of HCHO [11], and the other reports the results obtained using silica-supported CsOH catalysts and formalin as the source of HCHO [12].

In this study, we tried to discover effective catalyst-systems for production of MMA directly from MP and methanol without using any source of HCHO, according to the following reactions:

$$CH_3CH_2COOCH_3 + CH_3OH \rightarrow CH_2{=}C(CH_3)COOCH_3 + H_2O + H_2 \tag{3}$$

$$CH_3CH_2COOCH_3 + CH_3OH + 0.5O_2 \rightarrow CH_2{=}C(CH_3)COOCH_3 + 2H_2O \tag{4}$$

The catalyst-systems have to promote two different reactions: (1) aldol-condensation and (2) conversion of methanol to HCHO. As for the first reaction, silica-supported CsOH catalysts doped with a small amount of Zr cations as a promoter was

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Table 1
Performances obtained in the absence of oxygen

Time-on-stream (h)	MP base (%)			CH_3OH base (%)		
	Conversion of MP	Yield of MMA	Selectivity to MMA	Conversion of CH_3OH	Yield of MMA + HCHO (%)	Selectivity to MMA + HCHO (%)
1.0	32.86	1.27	4	55.97	–	–
2.5	30.73	3.93	13	36.34	–	–
4.0	20.73	11.59	38	28.91	16.46	57
7.0	15.10	11.59	76	15.92	11.24	71
8.5	12.90	10.18	79	13.53	9.68	72
10.0	9.06	8.02	89	8.75	7.42	85
11.5	7.77	7.16	92	8.70	7.03	81

used, because it has been known that CsOH gives the highest performance among hydroxides of alkali metal [9,12], and that the addition of a small amount of foreign metal cations into the silica enhances a little the yield of MMA [3]. The stress was laid on finding out effective catalysts for the conversion of methanol to HCHO, which do not spoil the activity for the aldol-condensation and also which do not convert MP to side-products. After screening tests of catalysts, it was concluded that the silica-supported CsOH catalysts doped with a small amount of Ag show the best performance.

2. Experimental

2.1. Catalysts

Silica-supported CsOH catalysts doped with Ag and Zr cations (Ag–Zr–Cs/SiO_2) were prepared by the following procedures. First, dry gel of silica doped with Zr cations was prepared by evaporating water from an aqueous colloidal silica containing a required amount of zirconium oxy nitrate [$ZrO(NO_3)_2$]. The colloidal silica used was ''Cataloide S 20LE'', which was offered kindly by Mitsubishi Rayon Co. The dry gel was ground and sieved to get the 8–20 mesh-size portion. It was calcined at 400 °C for 4 h in a stream of air, and then it was impregnated with an aqueous solution containing a desired amount of $AgNO_3$. The wet gel was dried in an oven and calcined again at 400 °C for 6 h. The resulting solid was impregnated again with an aqueous solution containing a desired amount of CsOH, and the wet gel was dried in an oven and calcined again at 400 °C for 6 h.

2.2. Reaction procedures

The reaction was carried out with a continuous-flow-system. The reactor was made of a stainless steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. The catalyst sample was placed near the bottom of the reactor, and porcelain cylinders, 3 mm long and 1.0 mm i.d./3.0 mm o.d, were placed both under and above the catalyst sample. Unless otherwise indicated, the amount of catalyst used was 20 g and the reaction temperature was 360 °C. Nitrogen was fed in from the top of the reactor with a fixed rate of 100 ml/min (250 mmol/h). A mixed solution of MP and methanol was introduced into the reactor using a syringe pump and a fine stainless steel tube. The feed rates of MP and methanol were 50 and 75 mmol/h, respectively. The contact time was in the range of 12–15 s.

The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water-soluble compounds. After 1 h on run, the contents of the water scrubbers were collected (100 ml). HCHO was analyzed by iodometry, and the other products were analyzed by GC.

The conversion of MP was defined as: 100 × [1 − (moles of unreacted MP + produced PA)/(moles of MP fed)]; the conversion of MP to PA was not counted as the conversion. The conversion of methanol was defined as: 100 × [1 − (moles of unreacted methanol − produced PA − produced MAA)/(moles of methanol fed)]; a correction was made for methanol formed by the formation of PA and MAA.

The yield of MMA + MAA based on the MP feed was defined as: 100 × (moles of MMA + MAA)/(moles of MP fed), and the yield of MMA + MAA based on the methanol feed was defined as: 100 × (moles of MMA + MAA)/(moles of methanol fed). The selectivity was defined as: 100 × (yield)/(conversion). The contact time (s) was defined as: (volume of catalyst used)/(volume of overall reaction gas mixture per second).

3. Results and discussion

3.1. Reaction in the absence of oxygen

A mixture of MP and methanol was introduced using nitrogen as the carrier gas over a 20 g portion of catalyst with a Ag/Zr/Cs/Si atomic ratio of 4/10/22/1000 at a temperature of 360 °C. The feed rates of MP/methanol/N_2 were 50/75/250 mmol/h. Typical results are shown in Fig. 1 and the detailed performances are also listed in Table 1.

At the beginning of the reaction, methyl isobutyrate (MIB) was almost the sole product besides small amounts of CO and hydrogen, which was formed by the decomposition of methanol; MMA was not obtained. As the time-on-stream increased, the formation of MIB sharply decreased, while the formation of MMA increased, showed a maximum, and then decreased gradually. The selectivity from MP to MMA increased steadily with the time-on-stream.

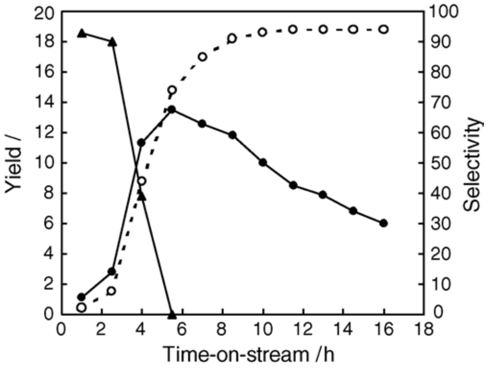

Fig. 1. Reaction of MP and methanol. Feed rates: MP/methanol/nitrogen = 50/75/250 mmol/h. (▲) Yield of MIB (MP base), (●) yield of MAA (MP base), (○) selectivity to MMA (MP base).

The following consideration was led from the results:

1. Methanol is dehydrogenated to HCHO

$$CH_3OH \rightarrow HCHO + H_2 \qquad (5)$$

2. MMA is formed by the condensation of MP and HCHO; the reaction (2).
3. The produced MMA is hydrogenated very quickly with methanol to form MIB and HCHO

$$CH_2{=}C(CH_3)COOCH_3 + CH_3OH \rightarrow (CH_3)_2CHCOOCH_3 + HCHO \qquad (6)$$

4. HCHO is formed from both the reactions (5) and (6).
5. The catalytic activities for both the reactions (5) and (6) are deactivated slowly with the time-on-stream.
6. The activity for the reaction (6) is very high at the beginning of the reaction, but it is deactivated much more quickly than that for the reaction (5).
7. It is known that the activity for the reaction (2) is very stable [12].

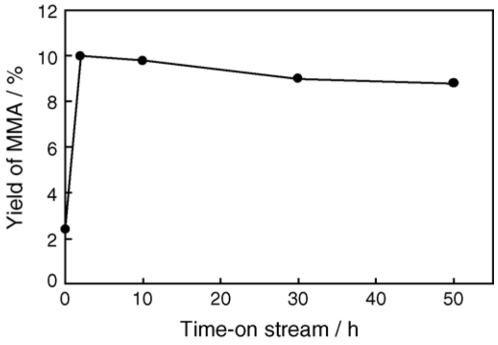

Fig. 2. Effects of oxygen on the yield of MMA (MP base). Oxygen was added after 20 h on stream in the absence of oxygen. Feed rates: MP/methanol/oxygen/nitrogen = 50/75/10/250 mmol/h.

3.2. Reaction in the presence of oxygen

In order to overcome the fall of catalytic activity for methanol dehydrogenation, i.e. the reaction (5), a small amount of oxygen was added into the reaction feed after 20 h on stream in the absence of oxygen. The Ag–Zr–Cs/SiO_2 catalyst, which had already been completely deactivated for the dehydrogenation of methanol, showed a very high activity for the oxidative dehydrogenation of methanol to HCHO

$$CH_3OH + 0.5O_2 \rightarrow HCHO + H_2O \qquad (7)$$

As the results, the formation of MMA markedly increased. Further, the catalytic activity became stable. The results are shown in Fig. 2.

The typical performances are also collected in Table 2.

3.3. Oxygen addition into the fresh catalyst

It has been found in our preliminary studies that, unlike Ag/SiO_2 catalysts, the fresh Ag–Zr–Cs/SiO_2 catalyst is very active for the decomposition of methanol to CO and H_2 regardless of the presence of oxygen [13]. However, the results shown in the section above suggest that, when MP is present in the reaction feed, the fresh Ag–Zr–Cs/SiO_2 catalyst is inert for the decomposition of methanol and it promotes selectively the oxidative dehydrogenation of methanol to HCHO. Therefore, oxygen was introduced into the fresh catalyst together with MP and methanol. The results are summarized in Table 3. As the amount of oxygen increased, the yield of MMA increased, but the selectivity decreased.

3.4. Effect of the contact time

The effects of the amount of catalyst used, i.e. contact time, on the product distributions were studied. The results are shown

Table 2
Effects of oxygen added after 20 h on stream in the absence of oxygen

Catalyst batch	O_2		MP base (%)		CH_3OH base (%)		
	Feed (mmol/h)	Conversion of MP	Yield of MMA	Selectivity to MMA	Conversion of CH_3OH	Yield of MMA + HCHO	Selectivity to MMA + HCHO
1	5	15.7	12.1	77	15.3	11.2	74
2	5	14.1	11.1	79	14.8	11.2	76
3	5	14.5	12.4	86	15.7	12.4	79
1	10	18.4	14.3	78	18.5	13.4	73
2	10	18.0	14.5	80	21.1	14.8	70
3	10	18.8	14.7	78	20.2	14.2	71

Table 3
Effects of the amount of oxygen feed on the performances

O_2 feed (mmol/h)	MP base (%)			CH_3OH base (%)			
	Conversion of MP	Yield of MMA	Selectivity to MMA	Conversion of CH_3OH	Yield of MMA	Yield of HCHO	Selectivity to MMA + HCHO
2.5	7.16	6.41	89.5	4.80	4.28	0,60	–
5.0	10.60	8.79	82.9	8.10	5.86	1.79	94.3
7.5	15.32	10.93	71.3	12.51	7.29	2.82	88.7
10	17.82	12.84	72.1	16.67	8.56	3.93	74.9
15	21.03	15.04	71.5	21.51	10.03	5.11	70.4
20	25.30	16.27	64.3	26.42	10.85	7.18	68.2
25	28.21	16.83	59.7	31.03	11.23	8.73	64.3

Table 4
Effects of the amount of catalyst used

Catalyst amount (g)	MP base (%)			CH_3OH base (%)			
	Conversion of MP	Yield of MMA	Selectivity to MMA	Conversion of CH_3OH	Yield of MMA	Yield of HCHO	Selectivity to MMA + HCHO
0.62	3.79	0.65	17.2	14.03	0.43	10.43	77.2
1.25	4.42	1.98	44.8	16.71	1.32	12.20	80.9
2.5	8.37	4.98	59.5	17.09	3.32	10.20	79.1
5.0	12.62	8.15	64.6	17.57	4.53	8.81	81.0
10	14.62	10.45	71.5	15.69	7.49	4.29	75.1
20	18.30	13.12	72.0	16.67	8.56	3.93	74.9

The feed rates of MP/methanol/O_2/N_2 were 50/75/10/250 mmol/h.

Table 5
Effects of the combination of Ag–Cs/SiO_2 catalyst (1 g) and Cs/SiO_2 catalyst (20 g)

O_2 feed (mmol/h)	MP base (%)			CH_3OH base (%)			
	Conversion of MP	Yield of MMA	Selectivity to MMA	Conversion of CH_3OH	Yield of MMA	Yield of HCHO	Selectivity to MMA + HCHO
5	12.56	10.58	84.2	9.54	6.88	1.24	85.4
10	20.10	14.50	72.1	14.51	9.67	2.61	84.6

The feed rates of MP/methanol/O_2/N_2 were 50/75/5 or 10/250 mmol/h.

in Table 4. It was found that the rate of oxidative dehydrogenation of methanol to HCHO is much more rapid than that of aldol-condensation, that is, almost all of oxygen is consumed with a very small amount of catalyst, while a large amount of catalyst is require to consume a large part of the produced HCHO.

3.5. Combination of Ag–Zr–Cs/SiO_2 catalyst and Cs–Zr/SiO_2 catalyst

It was found from the results shown in the section above that the amount of the Ag–Zr–Cs/SiO_2 catalyst required for the oxidative dehydrogenation of methanol to HCHO is very small, while a large amount of catalyst is required for the aldol-condensation. Therefore, a very small amount (1.0 g) of the Ag–Zr–Cs/SiO_2 catalyst was placed on a large amount (20 g) of Cs–Zr/SiO_2 catalyst. The results are summarized in Table 5. The values of selectivity in the both reactions are improved to a certain extent.

4. Conclusion

With Ag–Zr–Cs/SiO_2 catalysts, MMA is obtained from MP and methanol in the presence of a small amount of oxygen, without using any sources of HCHO. The catalytic activity is stable enough. As the amount of oxygen increases, the yield of MMA increases, while the selectivity to MMA decreases. The performances are further improved by the combination of a small amount of Ag–Zr–Cs/SiO_2 catalyst and a large amount of Cs–Zr/SiO_2 catalyst. The performances are almost the same as those obtained in the reaction of MP with HCHO (formalin) over Cs–Zr/SiO_2 catalysts.

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