

STUDIES ON SYNTHESIS OF METHYL GLYCOLATE AND METHYL METHOXY ACETATE FROM THE COUPLING OF FORMALDEHYDE AND METHYL FORMATE

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Abstract — Catalytic performance of various acids in the coupling reaction of formaldehyde and methyl formate to produce methyl glycolate and methyl methoxy acetate has been studied. The influence of reaction conditions, such as catalyst amount, reaction temperature, reaction time, and molar ratio of formaldehyde to methyl formate, has also been investigated. The results showed that the acid strength had great influence on the reaction, namely, stronger acids had higher activities. It was also found that the reaction temperature and time had significant effect on the reaction, and the preferable conditions were quite different as different acids were used.

Key words : Methyl Glycolate, Methyl Methoxy Acetate, Coupling, Formaldehyde, Methyl Formate

INTRODUCTION

Methyl glycolate (MG) and methyl methoxy acetate (MMA) are important chemical materials. MG is used for manufacturing glycolic acid, DL-glycine, and malonate ester. MMA is used for producing ethylene glycol monomethyl ether and medicine such as vitamins. In particular, both MG and MMA can be used for producing ethylene glycol (EG) [Lee et al., 1990]. At present, commercial EG is produced from the hydration of ethylene oxide that is formed by the catalytic oxidation of ethylene. However, because of the limited storage of petroleum resources, it becomes important to develop a new manufacturing process of EG [Lee et al., 1993]. Synthesis of MG via the coupling of formaldehyde (FA) and methyl formate (MF), which are produced from coal, is a new route for the production of EG [Liu et al., 1996]. In this paper, the catalytic activities of various acid catalysts for the coupling of FA and MF have been investigated, and the influence of reaction conditions has also been studied.

EXPERIMENTAL

The coupling of FA and MF was performed in a 20 ml autoclave. Trioxane was used as a source of FA. A typical procedure is as follows: the autoclave was placed with 1.5 g of trioxane(50 mmol of FA), 3.0 g of MF (50 mmol), and 1.0 g of methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) as a catalyst, the mixture was stirred for 4 hours at 160 °C, and the reaction mixture was analyzed by gas chromatography using Porapak N column on a Shimatsu GC-14B instrument. When FA reac-

ted with MF at 100-180 °C for several hours in the presence of acid catalysts, desired products, MG and MMA, were formed. The reaction products also included methanol (MeOH), formic acid, dimethoxy methane, and other unknown by-products.

RESULTS AND DISCUSSION

1. The Activities of Different Acids

The catalytic activities of various acid catalysts for the formation of MG and MMA from the coupling of FA and MF are compared in Table 1. Among those liquid acids, strong acids showed higher activity for the formation of MG and MMA. For example, when $\text{CH}_3\text{SO}_3\text{H}$, sulfuric acid (H_2SO_4), and chlorosulfonic acid (ClSO_3H) were used as catalysts, 7.73, 6.73, and 4.41 mmol of MG were formed, respectively, on the basis of per gram of catalyst, and at the same time, 4.43, 6.95, and 4.63 mmol of MMA were formed, respectively (Table 1, No. 1-3). On the other hand, weak acids such as sulfosalicylic acid (SSA) and p-toluene sulfonic acid (p-TsOH) showed lower activity for the formation of MG and MMA. By comparing the total amount of MG and MMA on the basis of per proton site, the activity order of mineral acids was $\text{H}_2\text{SO}_4 > \text{CH}_3\text{SO}_3\text{H} > \text{ClSO}_3\text{H} > \text{p-TsOH} \sim \text{SSA}$.

The activities of solid acid catalysts, such as cation exchange resins and heteropolyacids, were also tested. Though the activities of cation exchange resins were much lower than those of strong liquid acids on the basis of per gram of catalyst, they were rather high by comparing the amount of MG and MMA formation on the basis of per equiv. proton. For example, when polystyrenesulfonic acid resins, such as Amberlite IR-120, Dowex 50W×8, and D001×7 (offered by Nankai Univ., China) were used as catalysts, the total amounts of MG and MMA were 0.29, 0.33, and 0.11 mmol-equiv. H^+ , respec-

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Table 1. Catalytic activities of various acid catalysts for the formation of MG and MMA^a

No	Catalyst	Temp. (°C)	Time (h)	MG ^{b)} (mmol/gc)	MMA ^{b)} (mmol/gc)	MG ^{c)} (mol/H ⁺ eq)	MMA ^{c)} (mol/H ⁺ eq)	Total ^{d)} (mol/H ⁺ eq)
1	CH ₃ SO ₃ H	160	4	7.73	4.33	0.74	0.42	1.16
2	H ₂ SO ₄	120	4	6.73	6.95	0.66	0.68	1.34
3	ClSO ₃ H	160	4	4.41	4.63	0.51	0.54	1.05
4	SSA ^{c)}	160	4	0.74	0.29	0.19	0.07	0.26
5	p-TsOH	160	4	1.14	0.57	0.20	0.10	0.30
6	Amberlite IR 120	120	4	0.60	0.71	0.13	0.16	0.29
7	Dowex 50W×8	120	4	0.63	0.86	0.14	0.19	0.33
8	D001×7	120	4	0.30	0.24	0.06	0.05	0.11
9	Nafion NR-50	160	4	4.14	3.16	0.98	0.70	1.68
10	SiW ₁₂ ^{h)}	160	5	7.15	8.50	5.30	6.31	11.61
11	PW ₁₂ ^{h)}	160	5	6.98	8.24	6.91	8.16	15.07

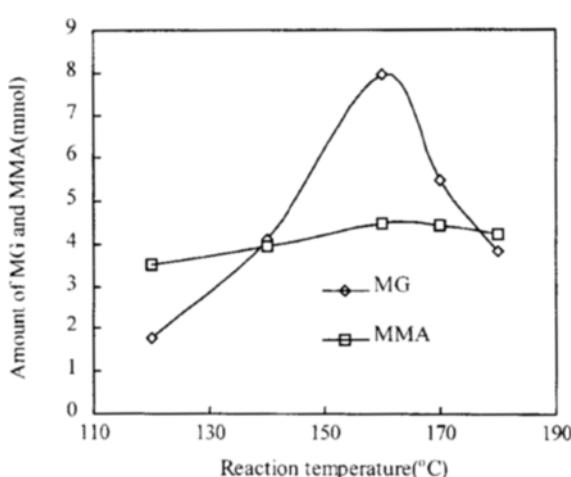
^{a)}Reaction conditions: MF, 50 mmol; FA/MF=1/1; Catalyst, 1.0-3.5 g, ^{b)}mmol/g catalyst, ^{c)}mol-equiv.H⁺, ^{d)}total amount of MG and MMA, mol-equiv.H⁺, ^{c)}SSA=sulfo-salicylic acid, ^{h)}MF=50 mmol, FA/MF=2.5

tively, which were comparable to that of p-toluenesulfonic acid or sulfo-salicylic acid. More interestingly, the activity of perfluorinated cation exchange resin such as Nafion NR-50 was much higher than that of sulfuric acid on the basis of per proton site.

Heteropolyacids, 12-silicotungstic acid (SiW₁₂) and 12-phosphotungstic acid (PW₁₂) also showed higher activities on the basis of per proton site, which were 11.61 and 15.07 mmol-equiv.H⁺, respectively, nearly ten times of that of H₂SO₄.

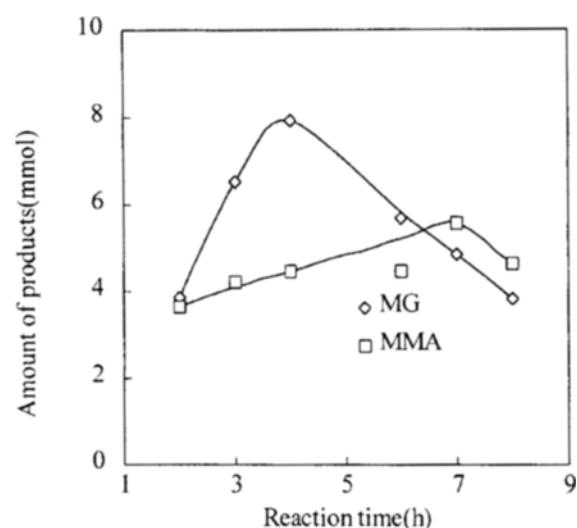
2. The Influence of Reaction Conditions

The influence of reaction conditions was tested using CH₃SO₃H as a catalyst. Fig. 1 showed the influence of temperature on the formation of MG and MMA. MG and MMA were formed on the whole temperature range of 120-180 °C when FA reacted with MF for 4 hours. The amount of MG increased with temperature first, reached a maximum near 160 °C, and then decreased with temperature. Meanwhile, the influence of temperature on the formation of MMA was very little. In the temperature range of 120-160 °C, the amount of MMA increased slightly; above 160 °C, the MMA formation tended to reach a constant level.

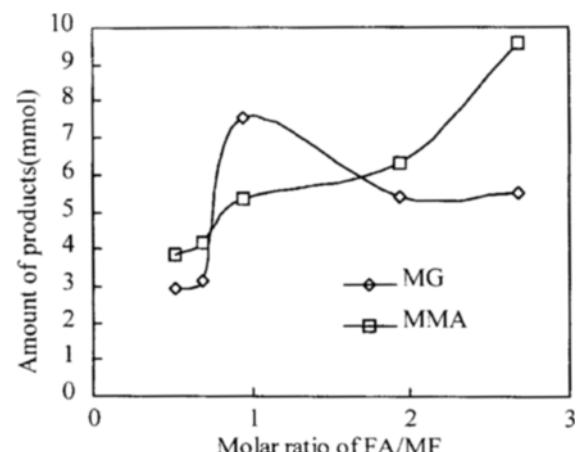
**Fig. 1. Influence of reaction temperature.**

(CH₃SO₃H, 1.0 g; FA=50 mmol; FA/MF=1/1; 4 h)

The effect of reaction time on the formation of MG and MMA is shown in Fig. 2. The amount of MG increased with reaction time, reaching maximum after 4 hours. In contrast,

**Fig. 2. Influence of reaction time.**

(CH₃SO₃H, 1.0 g; FA=50 mmol; FA/MF=1/1; 160 °C)

**Fig. 3. Influence of molar ratio of FA/MF.**

(CH₃SO₃H, 1.0 g; FA=50 mmol; 4 h; 160 °C)

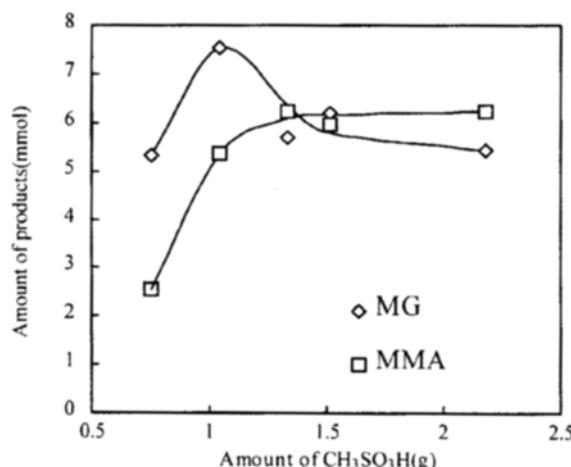


Fig. 4. Influence of catalyst amount.

(MF=50 mmol; FA=50 mmol; 4 h; 160 °C)

the maximum yield of MMA was obtained after 7 hours of the reaction at 160 °C.

The influence of molar ratio of FA to MF was examined at 160 °C. As shown in Fig. 3, the amount of MG increased with FA/MF ratio, reaching a maximum at FA/MF ratio of 1/1. On the other hand, the amount of MMA increased with FA/MF ratio, and a higher FA/MF ratio was more advantageous for the formation of MMA.

The effect of the amount of catalyst on the reaction was examined at 160 °C, with the reaction time being 4 hours and

FA/MF being 1/1. The result (Fig. 4) showed that the amount of MG increased first and then decreased with the amount of catalyst, while that of MMA increased first and then plateaued. The most desirable amount of the catalyst for MG formation was 1.0 g; for more $\text{CH}_3\text{SO}_3\text{H}$ used, the amounts of MG and MMA had nearly no change.

We also studied the influence of reaction conditions using sulfuric acid as a catalyst. The most preferable temperature was 120 °C and the appropriate reaction time was 4 hours. Compared with $\text{CH}_3\text{SO}_3\text{H}$, lower temperature and less time were needed to get similar results, probably because sulfuric acid is stronger than $\text{CH}_3\text{SO}_3\text{H}$. In the case of H_2SO_4 catalyst, the molar ratio of FA/MF had little effect on the formation of MG and MMA when it was maintained between 1 and 2.

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