Letter

The activity of $H_4SiW_{12}O_{40}$ for the coupling of formaldehyde and methyl formate to methyl glycolate and methyl methoxy acetate

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Abstract

The catalytic coupling of formaldehyde (FA) and methyl formate (MF) over 12-tungstosilicic acid and its salts has been investigated. $H_4SiW_{12}O_{40}$ and its acidic salts were active in the coupling of FA and MF to methyl glycolate (MG) and methyl methoxy acetate (MMAc). Among the acidic salts, LiH_3SiW_{12} and $Mg_{0.5}H_3SiW_{12}$ showed much higher activities. Water affected the activities of $H_4SiW_{12}O_{40}$ and was unfavorable for the formation of MG and MMAc. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In conventional acid-catalyzed processes, liquid acids (e.g., H_2SO_4, HF, etc.) have been mostly used as catalysts [1–10]. However, the common shortcomings of using liquid acids as catalysts are significant corrosion for equipment, difficulty in the separation between products and catalyst and pollution of the environment. Therefore, as the demands of environmental protection become increasingly strict, using solid acids instead of liquid acids as catalysts has become an important field to develop friendly catalytic-processes for the environment

[11]. Methyl glycolate (MG) and methyl methoxy acetate (MMAc) can be formed when formaldehyde (FA) reacts with methyl formate (MF) in the presence of a strong liquid acid catalyst such as H_2SO_4 or CH_3SO_3H [12]. However, it is now expected to use solid acids instead of liquid acids as catalysts for the synthesis of MG and MMAc. MG is popularly used for manufacturing of glycolic acid, DL-glycine, malonate ester, and in particular, for producing ethylene glycol [13]. MMAc is usually used as a raw material in medicines, and can also be converted to ethylene glycol by the catalytic hydrogenation and hydration. 12-Tungstosilicic acid ($H_4SiW_{12}O_{40}$), as a solid acid catalyst, more attention has been paid to it in the acid catalytic processes [14–16]. We now report that in the coupling of FA and MF, $H_4SiW_{12}O_{40}$ and

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its salts showed high activities for the formation of MG and MMAc. In addition, the effect of water on the activities was also examined.

2. Experimental

Purchased $H_4SiW_{12}O_{40}$ was preheated in air at 300°C for 3 h before using. The salts of $H_4SiW_{12}O_{40}$ were prepared according to the method in the literature [17] and were also calcined in air at 300°C for 3 h. On the other hand, other solid acids such as H-β zeolite, ion exchange resin (Amberlite IR-120) as well as a liquid acid (H_2SO_4) were also tested for the synthesis of MG and MMAc. A typical reaction procedure is as follows: the autoclave (20 ml) was placed with 3.75 g of trioxane (used as a source material of FA), 3.00 g of MF and 1.00 g of $H_4SiW_{12}O_{40}$ as a catalyst. The mixture was stirred for 5 h at 160°C. The liquid-phase prod-

ucts were qualitatively analyzed by GC–mass spectrometry (Hewlett Packard 5890) and quantitatively analyzed by gas chromatography (Shimatsu GC-14B, Porapak N column), but the gas-phase products (mainly CO) were not quantified. Ethylene glycol dimethyl ether was used as an internal standard material for the GC quantitative analysis.

3. Results and discussion

In the coupling of FA and MF in the presence of acid catalysts, besides the desired products MG and MMAc, the by-products methanol, formic acid and CO were also formed. The yields of MG and MMAc were used for evaluating the activities of catalysts in this study. The catalytic activities of $H_4SiW_{12}O_{40}$ and its salts as well as other acids in the coupling of FA and MF are shown in Table 1. Although a large

Table 1
Catalytic activities of $H_4SiW_{12}O_{40}$ and its salts as well as other acids[a]

Entry	Catalyst	Yield (mmol/g-cat.)				Yield[b] (total carbons/g-cat.)	
		MG	MMAc	CH_3OH	HCOOH	(MG + MMAc)	(CH_3OH + HCOOH)
1	$H_4SiW_{12}O_{40}$	7.2	8.6	8.0	10.9	56.0	18.9
2	H-β zeolite	2.1	2.3	3.7	6.2	15.5	9.9
3	Amberlite IR-120[c]	3.1	2.0	1.5	3.1	17.3	4.6
4	H_2SO_4[d]	6.8	7.1	4.0	0	48.8	4.0
5	H_2SO_4[e]	3.8	5.3	8.8	0	32.6	8.8
6	$LiH_3SiW_{12}O_{40}$	9.0	6.4	9.2	7.4	52.6	16.6
7	$NaH_3SiW_{12}O_{40}$	5.6	5.5	8.5	6.3	38.8	14.8
8	$KH_3SiW_{12}O_{40}$	6.0	6.2	8.2	6.0	42.8	14.2
9	$CsH_3SiW_{12}O_{40}$	7.2	6.8	17.2	9.3	48.8	26.5
10	$NH_4H_3SiW_{12}O_{40}$	5.6	7.2	20.2	7.8	45.6	28.0
11	$Mg_{0.5}H_3SiW_{12}O_{40}$	8.4	7.2	17.0	7.2	54.0	24.2
12	$Ni_{0.5}H_3SiW_{12}O_{40}$	6.0	6.6	19.1	9.5	44.4	28.6
13	$Zn_{0.5}H_3SiW_{12}O_{40}$	5.5	5.4	15.7	6.5	38.1	22.2
14	$Al_{1/3}H_3SiW_{12}O_{40}$	6.2	5.9	17.3	10.3	42.2	27.6
15	$La_{1/3}H_3SiW_{12}O_{40}$	4.0	4.8	8.9	7.6	31.2	16.5
16	$K_2H_2SiW_{12}O_{40}$	6.4	7.5	8.3	7.6	49.2	15.9
17	$K_3HSiW_{12}O_{40}$	4.7	3.0	11.0	17.3	26.1	28.3
18	$K_4SiW_{12}O_{40}$	0	0	9.7	10.5	0	21.3

[a]Reaction conditions: Catalyst = 1.0 g, molar ratio FA/MF = 2.5, MF = 3.0 g, 160°C, 5 h.
[b]Total carbons/g-cat. of (MG + MMAc) = (mmol/g-cat. of MG) × 3 + (mmol/g-cat. of MMAc) × 4; total carbons/g-cat. of (CH_3OH + HCOOH) = (mmol/g-cat. of CH_3OH) + (mmol/g-cat. of HCOOH).
[c]Catalyst = 2.0 g, 120°C.
[d]Catalyst = 2.0 g, 120°C, 4 h, FA/MF = 1.0.
[e]Catalyst = 2.0 g, 160°C, 4 h, FA/MF = 1.0.

amount of methanol and formic acid were formed in the coupling of FA and MF, $H_4SiW_{12}O_{40}$ and its acidic salts were active for the formation of MG and MMAc under the given conditions. The yield (total carbons/g-cat.) of MG and MMAc was much higher than that of by-products methanol and formic acid under the catalysis of $H_4SiW_{12}O_{40}$ or the most of its acidic salts. It was found that $H_4SiW_{12}O_{40}$ showed much higher activity under the condition of 160°C, 5 h and 2.5 molar ratio of FA/MF (7.2 mmol of MG and 8.6 mmol of MMAc were formed on the basis of per gram of catalyst, Table 1, Entry 1). H-β zeolite and Amberlite IR-120 ion exchange resin also showed activities for the formation of MG and MMAc (Table 1, Entries 2, 3), but their activities were lower than those of $H_4SiW_{12}O_{40}$. H_2SO_4 showed higher activities at 120°C than at 160°C in the coupling of MG and MMAc (Table 1, Entries 4, 5). However, after reaction, H_2SO_4 became a waste acid, and the corrosion of autoclave was serious.

The acidic salts of $H_4SiW_{12}O_{40}$, such as alkali metal salts (Li, Na, K and Cs), alkali-earth metal salt (Mg), ammonium salt and transition metal salts (Zn, Ag) as well as aluminum, lanthanum salt, also showed activities in the formation of MG and MMAc (Table 1, Entries 6–15). Comparing these acidic salts with their parent acid $H_4SiW_{12}O_{40}$, it was found that the yield (total carbons/g-cat.) of MG and MMAc for every salt was lower than that of $H_4SiW_{12}O_{40}$, but the yield (mmol/g-cat.) of MG was higher

for LiH_3SiW_{12} and for $Mg_{0.5}H_3SiW_{12}$ than for the parent acid (Entries 1, 6, 11).

The catalytic activities of the potassium salts ($K_xH_{4-x}SiW_{12}O_{40}$, $x = 1$, 2, 3 and 4) varied with the K content (Table 1, Entries 8, 16–18). $KH_3SiW_{12}O_{40}$ showed just lower activities than $K_2H_2SiW_{12}O_{40}$. However, when the K content increased, the acidic salts such as $K_3HSiW_{12}O_{40}$ showed lower activities in the formation of MG and MMAc. When all of the protons of $H_4SiW_{12}O_{40}$ were replaced by K, the resultant salt $K_4SiW_{12}O_{40}$ lost its activities in the coupling reaction.

In our experiments, it was also found that water might affect the activities of catalyst [18]. In order to check the influence of water contained in the reaction system on the catalytic activities of $H_4SiW_{12}O_{40}$, different amount of water was added to the autoclave together with the substrate and the catalyst. The results are shown in Table 2. It was clearly demonstrated that water was unfavorable for the formation of MG and MMAc. The yield of MG and of MMAc decreased with an increase in the amount of water. The amount of methanol and formic acid formed in the reactions increased with an increase in the amount of water (Table 2, Entries 2–4). The reason may be that adding water to the acid catalyzed reaction system may lead to the hydrolysis of MF and result in the decrease of yields of MG and MMAc. It was reported that the activity for acid-catalyzed reactions (such as the isomerization of 1-butane, the dehydration of 2-propanol and so on) decreased

Table 2
Influence of water on the activities of $H_4SiW_{12}O_{40}^a$

Entry	Catalyst	H_2O (g)	Yield (mmol/g-cat.)				Yield[b] (total carbons/g-cat.)	
			MG	MMAc	CH_3OH	HCOOH	(MG + MMAc)	(CH_3OH + HCOOH)
1	$H_4SiW_{12}O_{40}$	0	7.2	8.6	8.0	10.9	56.0	18.9
2	$H_4SiW_{12}O_{40}$	0.20	3.9	4.6	8.4	6.5	30.1	14.9
3	$H_4SiW_{12}O_{40}$	0.40	3.2	2.9	11.3	9.1	21.2	20.4
4	$H_4SiW_{12}O_{40}$	0.64	2.8	1.4	10.8	13.6	14.0	24.4

[a]Catalyst 1.0 g, FA/MF = 2.5, MF = 3.0 g, 160°C, 5 h.
[b]Total carbons/g-cat. of (MG + MMAc) = (mmol/g-cat. of MG) $\times$ 3 + (mmol/g-cat. of MMAc) $\times$ 4; total carbons/g-cat. of (CH_3OH + HCOOH) = (mmol/g-cat. of CH_3OH) + (mmol/g-cat. of HCOOH).

with an increase in the content of water [19]. Okuhara et al. [20] also indicated that when free acid of PW_{12} was used for the dehydration of 2-propanol, the conversion decreased with the addition of water.

In conclusion, $H_4SiW_{12}O_{40}$ and its acidic salts were active in the coupling of FA and MF to MG and MMAc. $H_4SiW_{12}O_{40}$, LiH_3SiW_{12} and $Mg_{0.5}H_3SiW_{12}$ showed much higher activities for the formation of MG and MMAc. Water affected the activities of $H_4SiW_{12}O_{40}$ and was unfavorable for the formation of MG and MMAc.

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