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Condensation of formaldehyde and methyl formate to methyl glycolate and methyl methoxy acetate using heteropolyacids and their salts

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Abstract

Catalytic performances of heteropolyacids and their salts in the condensation of formaldehyde and methyl formate to methyl glycolate and methyl methoxy acetate have been studied. $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were found to have high activities for the formation of methyl glycolate and methyl methoxy acetate. The acidic salts of heteropolyacids also showed the activities in the condensation reactions, but the neutral salts of $H_3PW_{12}O_{40}$ and of $H_4SiW_{12}O_{40}$ were inactive. Thermal treatment of heteropolyacids was found to show a positive effect on the catalytic activities, and the most suitable pretreatment temperature was 300°C in the range 100–350°C. The investigating results of the influence of the reaction conditions showed that the molar ratios of formaldehyde to methyl formate and the reaction temperatures greatly affected the reaction. It was also found that the coexistence of water in the reaction system showed a negative effect on the catalytic activity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methyl glycolate; Methyl methoxy acetate; Formaldehyde; Methyl formate; Condensation; Heteropoly compounds

1. Introduction

Formaldehyde and methyl formate are produced in large quantity by the coal chemical industry and natural gas chemical industry. Both of them are important organic chemical materials. In China, the productive abilities of formaldehyde and methyl formate are constantly increasing. Therefore, it has become an urgent matter to develop novel products of the lower reaches of formaldehyde and methyl formate [1].

Several novel products of the lower reaches can be obtained from formaldehyde and methyl formate. One of them is methyl glycolate, which is used for the manufacturing of glycolic acid, DL-glycine, malonate ester, and in particular, for producing ethylene glycol (this new process for the manufacturing of ethylene glycol from C_1 chemistry route is a promising and encouraging subject) [2]. Methyl glycolate can be synthesized by the condensation of formaldehyde and methyl formate in the presence of a strong liquid acid catalyst such as H_2SO_4 or CH_3SO_3H [3] or by the carbonylation of formaldehyde with CO in a strong liquid acid (H_2SO_4 or HF)-catalyzed process [4]. On the other hand, methyl methoxy acetate, which is also an important chemical intermediate, was also formed

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at the same time as one of two desired products in the condensation of formaldehyde and methyl formate in the presence of an acid catalyst [3]. Methyl methoxy acetate is usually used as the raw material of medicines, and can also be converted to ethylene glycol by the catalytic hydrogenation and hydrolysis. However, with the use of liquid acids as catalysts in the production of methyl glycolate or methyl methoxy acetate, there are problems of the equipment corrosion and environmental pollution. Therefore, it is necessary to use solid acids instead of liquid acids as catalyst for the synthesis of methyl glycolate and methyl methoxy acetate. Heteropolyacids, as solid acid catalysts, have been paid growing attention in the acidic catalytic processes.

Recently, we have tried to apply heteropolyacids and their salts as catalysts for the synthesis of methyl glycolate and methyl methoxy acetate in the condensation of formaldehyde and methyl formate. In the present study, the catalytic performance of heteropolyacids and their salts was investigated. In addition, the effects of the reaction conditions, pretreatment temperatures and water on the activities of heteropolyacids were also examined.

2. Experimental

2.1. Materials

$H_4SiW_{12}O_{40}$ (abbreviated as SiW_{12}), $H_3PW_{12}O_{40}$ (PW_{12}) and $H_3PMo_{12}O_{40}$ (PMo_{12}) were purchased from Beijing Xinhua Chemical Reagent (analyzed grade, containing 24–26 molecules of crystallization water) and were directly used as catalysts, but in some case SiW_{12} and PW_{12} were pretreated in air at the chosen temperature for 3 h when necessary. $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$) was synthesized from Na_2MoO_4 and Na_2SiO_3 by a traditional way according to [5].

The salts of PW_{12} were prepared according to method in [6]. Namely, required amounts of the corresponding compounds containing the counter cation metal (aqueous solution) were added to the aqueous solution of PW_{12}. The resultant solution or suspension was kept under stirring for 30 min, and it was then evaporated at about 70°C to remove water. The obtained solid was calcined in air at 300°C for 3 h. The compounds (analyzed grade) were Na_2CO_3, K_2CO_3, Li_2CO_3, Ag_2CO_3, $CsNO_3$, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$, $2ZnCO_3{\cdot}3ZnO{\cdot}4H_2O$ and $NH_4HCO_3{\cdot}NH_2COONH_4$. The prepared salts of PW_{12} were denoted as $M^{n+}_{x/n}H_{3-x}PW_{12}O_{40}$ (abbreviated as $M^{n+}_{x/n}H_{3-x}PW_{12}$, here M refers to metal cation or NH_4^+, x=1–3). The salts of SiW_{12} were prepared in the same method as those of PW_{12}.

Two liquid acids, H_2SO_4 (analyzed grade, purchased from Beijing Xinhua Chemical Reagents) and CH_3SO_3H (analyzed grade, purchased from Beijing Kehua Special Reagents Center) were used for comparison. Trioxane (analyzed grade, purchased from Fluka Chemika-BioChemika Switzerland) was used as a source material of formaldehyde. Other reagents were purchased from Beijing Chemical Reagents.

2.2. Reaction procedure and analysis

For the condensation of formaldehyde (hereafter abbreviated as FA) and methyl formate (MF), a 20 ml autoclave was used. The reactions were carried out at 120–200°C for 1–8 h. The typical reaction procedure was as follows: the autoclave was placed with 3.75 g of trioxane, 3.00 g of MF and 1.00 g of heteropolyacid (SiW_{12}) as a catalyst. The mixture was stirred for 5 h at 160°C. The reaction mixture was qualitatively analyzed by GC–Mass (Hewlett-Packard 5890) and quantitatively analyzed by gas chromatography (Shimadzu GC-14B, Poropak N column). Ethylene glycol dimethyl ether was used as an internal standard for the GC quantitative analysis.

The IR spectra of the catalysts were measured by using a Perkin-Elmer 2000 FT-IR spectrometer.

3. Results and discussion

3.1. Conformation of the structure of heteropolyacids and their salts

The IR spectra of heteropolyacids and their salts were recorded between 4000 and 400 cm^{-1}. In the range 500–1100 cm^{-1}, the observed bands (for example, 1081, 987, 890, 810, 596 and 525 cm^{-1} in the case of $KH_2PW_{12}O_{40}$) of IR spectra were very similar to one another, and were assigned to belong to Keggin structure after comparing the data with [7].

3.2. Activities of heteropolyacids in the condensation reactions

When FA reacted with MF at 120–200°C for several hours in the presence of acid catalysts, desired products, methyl glycolate (hereafter abbreviated as MG) and methyl methoxy acetate (MMAc) were formed. The reaction byproducts were methanol and formic acid. The yields of MG and MMAc were calculated and used for evaluating the activities of the catalysts.

The catalytic activities of four kinds of heteropolyacids in the condensation of FA and MF are shown in Table 1. All of them showed activity for the formation of MG and MMAc under the given conditions. It was found that PW_{12} showed higher activity under the condition of 160°C, 5 h and 2.5 molar ratio of FA/MF (7.1 mmol of MG and 8.9 mmol of MMAc were formed on the basis of per gram of catalyst). The activities of SiW_{12} were close to that of PW_{12} (7.2 mmol of MG and 8.6 mmol of MMAc were formed on the basis of per gram of SiW_{12}). However, the activities of heteropolyacids containing Mo atom, $SiMo_{12}$ and PMo_{12}, were much lower than those of PW_{12} or SiW_{12}.

SiW_{12} and PW_{12} showed in Table 1 (Runs 1 and 2) were samples pretreated in air at 300°C for 3 h. On the other hand, as for the non-pretreatment SiW_{12} and PW_{12}, they also showed relatively high activities. For example, the yields of MG and MMAc were 6.2 and 5.7 mmol/g-cat., respectively, for non-pretreatment SiW_{12} under the reaction condition of 160°C, 5 h and 2.5 molar ratio of FA/MF. Furthermore, it is interesting that the yield of MMAc was higher than that of MG for all of four heteropolyacids. By comparing the total yields of MG and MMAc, the order of the activity of the four kinds of heteropolyacids was $PW_{12} \cong SiW_{12} \gg SiMo_{12} > PMo_{12}$.

Heteropolyacids possess purely Brønsted acidity. The strong acids were favorable for the formation of MG and MMAc [8,9]. We consider that protons attack H_2CO first in the condensation of FA and MF (Scheme 1). The high acid strength may be favorable for the attacking by protons.

It is generally considered that the acid strength of heteropolyacids are in the following order: $PW_{12} > SiW_{12} \geq PMo_{12} > SiMo_{12}$ [10], or $PW_{12} > PMo_{12} \geq SiW_{12} > SiMo_{12}$ [11]. On the other hand, polyanions are soft bases [12]. We think that the softness of heteropolyacids also plays an important role in the condensation of FA and MF. As shown in Scheme 1, we consider that heteropolyanion, $SiW_{12}O_{40}^{4-}$ reacts with $HCOOCH_3$ to form a complex ($SiW_{12}O_{40}^{4-} \cdots HCOOCH_3$), and then to give an intermediate ($^{-}COOCH_3$). That SiW_{12} showed comparably high activity in this reaction is perhaps due to its relatively high softness. The softness of heteropolyacids has been found to have the following order: $SiW_{12} > PW_{12} > PMo_{12} > SiMo_{12}$ [13]. Therefore, the catalytic activities of heteropolyacids in the conden-

Table 1
Catalytic activities of heteropolyacids and comparison with liquid acids

Run	Catalyst[a]	Temperature (°C)	Time (h)	FA/MF[c]	Yield (mmol/g-cat.)			TON[e]
					MG	MMAc	Total[d]	
1	SiW_{12}[b]	160	5	2.5	7.2	8.6	15.8	11.7
2	PW_{12}[b]	160	5	2.5	7.1	8.9	16.0	15.8
3	$SiMo_{12}$	160	3	2.5	3.6	3.8	7.4	4.2
4	PMo_{12}	160	3	2.5	1.8	2.3	4.1	3.1
5	H_2SO_4	120	4	1.0	6.8	7.1	13.9	0.7
6	CH_3SO_3H	160	4	1.0	8.0	4.5	12.5	1.2

[a] Catalyst 1.0 g.

[b] The sample was pretreated in air at 300°C.

[c] Molar ratio, MF 3.0 g.

[d] Total yield of MG and MMAc.

[e] Turn over number (total mole of MG and MMAc/mol-H^+ of catalyst used).

$$H_2C{=}O + H^+ \rightarrow H_2C{=}O\cdots H^+ \rightarrow H_2C^+\text{-}O\text{-}H$$

$$\begin{array}{l} H\text{-}COOCH_3 + SiW_{12}O_{40}^{4-} \rightarrow SiW_{12}O_{40}^{4-}\cdots H\text{-}COOCH_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad\qquad H\text{-}SiW_{12}O_{40}^{3-} + {}^{-}COOCH_3 \end{array}$$

$$H_2(HO)C^+ + {}^{-}COOCH_3 \rightarrow HO\text{-}CH_2\text{-}COOCH_3$$

Scheme 1.

sation of FA and MF may be related to the coordination of protonic acidity and soft basicity.

As shown in Table 1, among the four kinds of heteropolyacids, Mo-containing ones exhibited lower levels of activity. This may be related to the oxidative property of Mo-containing heteropolyanions. Kozhevnikov and Matveev [11] reported that the oxidative ability of Mo-containing heteropolyacids is higher than that of W-containing ones. On the other hand, the higher the valence of the central atom is, the higher the oxidative ability of heteropolyacids is. That is, the oxidative ability of PMo_{12} is higher than that of $SiMo_{12}$. Owing to the reductive property of FA, the oxidative property of heteropolyacids was negative for the condensation.

On the other hand, the activities of H_2SO_4 and of CH_3SO_3H, which were obtained under the best reaction conditions in the previous studies [14,15], are also listed in Table 1 in order to compare the heteropolyacids with these liquid acids. It is clear that the activities of PW_{12} and of SiW_{12} were much higher than those of the liquid strong acids on the basis of per weight catalyst. In addition, the reactions using SiW_{12} or PW_{12} as catalyst resulted in high turn over numbers (TON), while those using H_2SO_4 or CH_3SO_3H as catalyst were in low TON (Table 1, Runs 1, 2, 5 and 6). TON of the reaction with PW_{12} was nearly 23 times of that with H_2SO_4. Even for $SiMo_{12}$ and PMo_{12}, they showed higher TON than H_2SO_4 and CH_3SO_3H. From these results, it is suggested that the efficiency of the catalytic circulation of protons was higher for heteropolyacids than for H_2SO_4 and CH_3SO_3H.

3.3. *Effect of reaction conditions on the yield*

The effect of molar ratio of FA to MF was examined in the range 0.5–3.4 at 160°C, 3 h using SiW_{12} as the catalyst. The results are shown in Table 2 (Runs 1–7). It was found that when the reaction was carried out at a

Table 2
Effect of reaction conditions on yield of MG and of MMAc[a]

Run	Temperature (°C)	Time (h)	Molar ratio of FA/MF	Yield (mmol/g-cat.)		
				MG	MMAc	Total[b]
1	160	3	0.5	1.0	1.1	2.1
2	160	3	1.0	1.6	2.0	3.6
3	160	3	1.5	3.3	4.0	7.3
4	160	3	2.0	4.7	5.9	10.6
5	160	3	2.5	5.2	7.9	13.1
6	160	3	3.0	5.0	6.2	11.2
7	160	3	3.4	2.9	3.2	6.1
8	120	3	2.5	0.8	2.7	3.4
9	140	3	2.5	3.8	5.8	9.6
10	180	3	2.5	6.9	7.0	13.9
11	190	3	2.5	6.0	6.5	12.5
12	200	3	2.5	4.3	3.6	7.9
13	160	1	2.5	3.7	4.3	8.0
14	160	5	2.5	6.2	5.8	12.0
15	160	7	2.5	3.3	2.6	5.9

[a] Catalyst: SiW_{12}(non-treatment) 1.0 g, MF 3.0 g.

[b] Total yield of MG and MMAc.

low ratio of FA/MF, the yields were comparatively low (Runs 1 and 2). The yield increased with an increase in the FA/MF ratio up to 2.5. But further increase of the ratio led a decrease of the yields. Therefore, the suitable ratio of FA/MF was about 2.5.

The effect of temperature on the formation of MG and MMAc was also examined in the molar ratio of FA/MF=2.5 using SiW_{12} as the catalyst (Table 1, Runs 5 and 8–12). MG and MMAc were formed in the whole temperature range of 120–200°C. The yields of MG and of MMAc were low when the reaction temperature was low (Table 1, Run 8). The yields of MG and MMAc increased with an increase of temperature, and reached a maximum yield near 180°C for MG and 160°C for MMAc. When the reaction was carried out at high temperatures (over 190°C), the yield of both MG and MMAc decreased. Therefore, most suitable reaction temperature range for the formation of MG and MMAc was about 160–180°C.

The effect of reaction time in the batch process was also examined at 160°C and FA/MF=2.5 with SiW_{12} in the range 1–7 h (Table 2, Runs 5 and 13–15). It was found that the suitable reaction time for the formation of MG and MMAc was 3–5 h.

3.4. *Effect of pretreatment temperature of heteropolyacids*

It was found that the activities of non-pretreatment heteropolyacids were lower than that of pretreated heteropolyacids at 300°C. For example, in the case of non-pretreatment SiW_{12}, 6.2 mmol MG and 5.7 mmol MMAc were formed, respectively, on the basis of per gram of catalyst used, while 7.2 mmol MG and 8.6 mmol MMAc were formed, respectively, in the case of SiW_{12} pretreated at 300°C.

In order to investigate the effect of the pretreatment temperature of heteropolyacids on the catalytic activities, the purchased SiW_{12} and PW_{12} were heated in air at different temperatures ranging from 100°C to 350°C for 3 h, and then used for the reactions to examine the variation of activities. The results are shown in Fig. 1. It was clearly shown that the catalytic activities of both SiW_{12} and PW_{12} increased with an increase of pretreatment temperature up to 300°C. But further increase of the treatment temperature led to a decrease in the yields. This is probably due to a slight destruction of the structure of the polyanion when samples were pretreated at 350°C. It was also reported that the heteropolyacids decompose at around 350–600°C [12]. SiW_{12} and PW_{12} pretreated at 300°C were found to have the highest activity for the formation of MG and MMAc among those pretreated at the range 100°C to 350°C. When SiW_{12} was pretreated at a low temperature (100°C), the total yield was 11.6 mmol/g-cat., which did not change so much compared to non-pretreatment SiW_{12} (for example, the total yield was 11.9 mmol/g-cat. for non-pretreatment SiW_{12}).

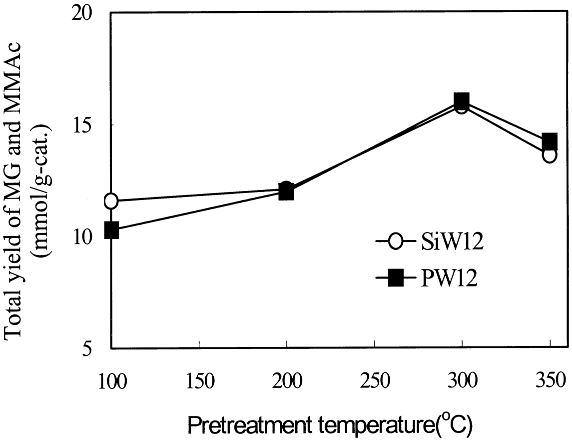

Fig. 1. Effect of pretreatment temperature of heteropolyacids on activity. Catalyst (pretreated in air for 3 h) 1.00 g; reaction conditions: 160°C, 5 h, MF=3.00 g, FA/MF=2.5.

It is known that heteropolyacids lose their crystallization water when heated at some temperatures. It was reported that $H_3PW_{12}O_{40}{\cdot}H_2O$ lost most of their crystallization water when heated to 300°C [16]. Therefore, the effect of pretreatment temperature of heteropolyacids on the reactions can be considered as that of the content of crystallization water. Brown et al. [17] reported that each $H_5O_2^+$ bridges four polyanions in the secondary structure in the case of $H_3PW_{12}O_{40}{\cdot}6H_2O$. Namely, protons are combined with water by hydrogen bonds. Therefore, in the dehydrated PW_{12}, the protons perhaps have comparably high mobility, and exhibit relatively high activity.

3.5. *Influence of water addition to the reaction system*

As it can be seen from the results mentioned above, the contents of crystallization water were found to

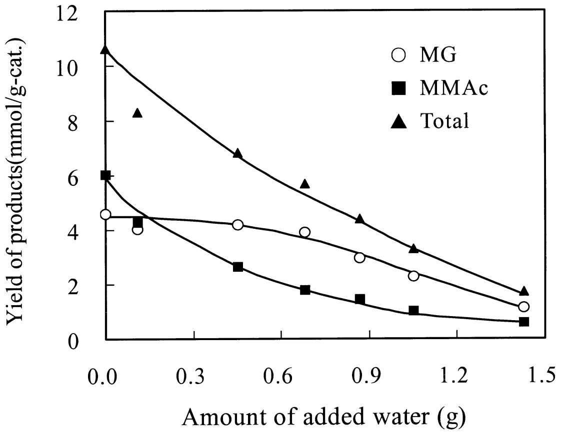

Fig. 2. Influence of water addition to the reaction system. Catalyst: PW_{12}(non-pretreatment) 1.00 g; reaction conditions: 160°C, 5 h, MF=3.00 g, FA/MF=2.5.

affect the catalytic activities for the condensation of FA and MF. Therefore, it was suggested that water contained in reaction system may also affect the activities of the catalysts.

In order to check the influence of water contained in reaction system on the catalytic activities, different amounts of water were added to the autoclave together with the substrates and catalyst. The results are shown in Fig. 2 in the case of PW_{12}. It was clearly demonstrated that water is unfavorable for the formation of MG and MMAc. The yields of MG and MMAc decreased with an increase in the amount of water in the range 0.11–1.43 g. Particularly, the decreasing degree of the yield of MMAc was more severe than that of MG. Similarly, a negative effect of water was also observed in the case of SiW_{12} (the total yields of MG and MMAc decreased from 11.9 to 6.1 mmolg-cat. when 0.40 g of water was added to the reaction system).

It was reported that the effects of water on the catalytic activities of heteropolyacids were found to be complex [12]. Ai [18] reported that the activity for acid-catalyzed reactions (such as the isomerization of 1-butene, the dehydration of 2-propanol and so on) decreased, while the activity for oxidations (such as that of butadiene to maleic anhydride and so on) increased with an increase in the content of water. Okuhara et al. [19] also indicated that when free acid of PW_{12} was used for the dehydration of 2-propanol, the conversion decreased with adding water, but an acceleration of the rate was also observed in the case of Cu salts.

3.6. *Catalytic activities of acidic salts of heteropolyacids*

The catalytic activities of the acidic alkali metal (Li, Na, K and Cs), alkali-earth metal (Mg), ammonium and transition metal (Zn, Ag) salts of PW_{12} were examined at 160°C and FA/MF=2.5. As it can be seen in Table 3, all of these acidic salts were found to be active for the formation of MG and MMAc. Com-

Table 3
Activities of acidic salts of PW_{12} for formation of MG and MMAc[a]

Run	Catalyst	Yield (mmol/g-cat.)		
		MG	MMAc	Total[b]
1	PW_{12}	7.1	8.9	16.0
2	LiH_2PW_{12}	4.7	5.2	9.9
3	NaH_2PW_{12}	5.7	6.2	11.9
4	KH_2PW_{12}	8.2	7.6	15.8
5	$Cs_{2.5}H_{0.5}PW_{12}$	7.1	5.1	12.2
6	$Mg_{0.5}H_2PW_{12}$	4.6	5.4	10.0
7	$Zn_{0.5}H_2PW_{12}$	4.8	5.9	10.7
8	$(NH_4)H_2PW_{12}$	7.1	7.2	14.3
9	Ag_2HPW_{12}[c]	3.2	5.4	8.6

[a] Catalyst (pretreated in air at 300°C for 3 h) 1.0 g, MF 3.0 g, molar ratio of FA/MF=2.5, temperature 160°C, 5 h.
[b] Total yield of MG and MMAc.
[c] FA/MF=2.0.

paring these acidic salts with their parent acid PW_{12}, it was found that the total yields of MG and MMAc of every salt was lower than that of PW_{12}. However, the yield of MG was higher when KH_2PW_{12}, rather than the parent acid, was used as catalyst. As for the alkali metal salts containing the same amount of metal cation, the activities were found to be in the following order: KH_2PW_{12}>NaH_2PW_{12}>LiH_2PW_{12}. It is known that the electronegativity of alkali metals exhibits the following order: Li>Na>K>Rh>Cs. Therefore, there is a relationship between the activity of the acidic alkali metal salts and the electronegativity of the corresponding metal. Namely, the lower the electronegativity of the alkali metal is, the higher the activity of the salts of PW_{12} is, except for $Cs_{2.5}H_{0.5}PW_{12}$ because the content of Cs in the salt was different from other alkali metal salts.

The activities of several salts of SiW_{12} were also examined at the same conditions as in the case of PW_{12}. Comparably high activities were also found in the condensation reactions. For example, KH_2SiW_{12}, NaH_2SiW_{12} and $Zn_{0.5}H_2SiW_{12}$ showed 12.2, 11.1 and 10.9 mmol/g-cat. of the total yield, respectively.

3.7. *Effect of content of counter cation in salts on the activities*

The variation of the catalytic activities of the $K_xH_{3-x}PW_{12}O_{40}$ with the K content is shown in Fig. 3. When the K content, x, was in the range 0.5–2.0, the acidic salts showed higher activity for the formation of MG than the parent acid (PW_{12}), and the highest level of activity was observed at x=0.5. When the K content x>2, the activity for the formation of MG decreased with an increase in the K content. On the other hand, the yield of MMAc decreased with an increase in the K content in whole range. When all of the protons were replaced by K, the formed neutral salt ($K_3PW_{12}O_{40}$) lost the activity for the formation of MG and MMAc in the condensation reaction.

4. Conclusion

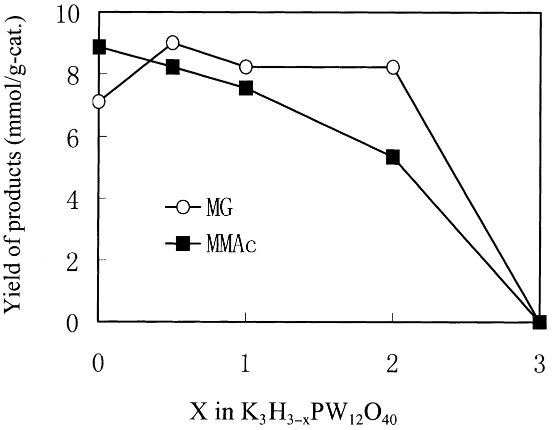

Fig. 3. Effect of K content in $K_3H_{3-x}PW_{12}O_{40}$ catalyst (pretreated in air at 300°C for 3 h) 1.00 g; reaction conditions: 160°C, 5 h, MF=3.00 g, FA/MF=2.5.

Heteropolyacids and their acidic salts were active in the condensation of formaldehyde and methyl formate to methyl glycolate and methyl methoxy acetate. In particular, PW_{12} and SiW_{12} showed high activities. The order of the activity of the four heteropolyacids was $PW_{12}\cong SiW_{12}\gg SiMo_{12}>PMo_{12}$. The neutral salts of heteropolyacids were inactive.

Suitable thermal treatments of heteropolyacids were favorable for catalytic activities, and the most suitable pretreatment temperature was 300°C among the range 100–350°C. The molar ratios of formaldehyde to methyl formate and the reaction temperatures greatly affected the reaction, and the suitable reaction conditions were 160°C, 3–5 h and FA/MF=2.5. The coexistence of water in the reaction system showed a negative effect on the catalytic activities.

References

[1] J. Liu, Q. Zhu, Huaxue Jinzhan (Chinese) 8 (1996) 251.
[2] J.S. Lee, J.C. Kim, Y.G. Kim, Appl. Catal. 57 (1990) 1.
[3] L.E. Ingo, A.H. Jurgen., Ger. Patent DE 2652072.
[4] Y. Souma, Japan Patent, Japan Kokai 82-46934 (1982).
[5] E.O. North, W. Haney, Inorg. Synth. 1 (1939) 127.
[6] G.A. Trigdinos, Ind. Eng. Chem., Prod. Res. Div. 13 (1974) 267.
[7] D.C. Rocchiccioli, Spectrochim. Acta A 32 (1976) 587.
[8] K. Wada, Japan Patent, Japan Kokai 82-46934 (1982).
[9] S.Y. Lee, J.C. Kim, J.S. Lee, Y.G. Kim, Ind. Eng. Chem. Res. 32 (1993) 253.
[10] I.V. Kozhevnikov, Catal. Rev.-Sci. Eng. 37 (1995) 311.
[11] I.V. Kozhevnikov, K.I. Matveev, Appl. Catal. 5 (1983) 135.
[12] M. Misono, Catal. Rev.-Sci. Eng. 29 (1987) 269.
[13] Y. Izumi, K. Matsuo, K. Urabe, J. Mol. Catal. 18 (1983) 299.

[14] D. He, W. Huang, M. Zhou, J. Liu, Q. Zhu, Proceedings of the Eighth Chinese National Conference on Catalysis, Xiamen, 16–20 October 1996, p. 955.

[15] W. Huang, D. He, J. Liu, Q. Zhu, Proceedings of the Fifth Chinese National symposium on Complexing Catalysis, Guangzhou, 11–15 November, 1997, p. 16.

[16] M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konisi, K. Sakata, T. Okuhara, Y. Yoneda, Bull. Chem. Soc. Jpn. 55 (1982) 400.

[17] G.M. Brown, M.R. Neo-Spiret, W.R. Busing, H.A. Levy, Acta Cryst. B 33 (1977) 1038.

[18] M. Ai, J. Catal. 71 (1981) 66.

[19] T. Okuhara, T. Hashimoto, T. Hibi, M. Misono, J. Catal. 93 (1985) 224.