## Heteropolyacids as Efficient Catalysts for the Synthesis of Precursors to Ethylene Glycol by the Liquid-phase Carbonylation of Dimethoxymethane

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Methyl methoxyacetate (MMAc), a precursor to ethylene glycol (EG), was synthesized successfully via the liquid-phase carbonylation of dimethoxymethane (DMM) catalyzed by heteropolyacids (HPAs). The experiment results showed that  $H_3PW_{12}O_{40}$  (PW<sub>12</sub>) exhibited the best catalytic performance for the carbonylation of DMM, and its high catalytic activity was attributed to the synergistic effect between its superior acidic strength and the high polarity of the solvent.

Ethylene glycol (EG), one of the essential commodity chemicals, is widely used as a raw material in the production of polyester resins, fibers, medicines, antifreezes, and other products.<sup>1</sup> The main method of producing EG is the hydration of ethylene oxide, which can be obtained by the partial oxidation of ethylene.<sup>2</sup> However, as a result of the increasing shortage of petroleum, considerable attention has been paid to finding alternative starting materials, in place of ethylene, for producing EG. Synthesis gas, a less expensive mixture of CO and H<sub>2</sub> generated from fossil fuels and biomass, as a starting feedstock for producing EG is a hopeful alternative. EG can be produced from formaldehyde and syngas through the carbonylation of formaldehyde to glycolic acid, followed by esterification to methyl glycolate (MG) and hydrogenation to the target product.<sup>3–9</sup> However, since the reaction rate of formaldehyde carbonvlation is limited by the low solubility of CO in the used solvent, the reaction pressure has to be relatively high.<sup>10</sup>

Both formaldehyde and dimethoxymethane (DMM) are derivatives of the C1 compound of methanol. The carbonylation of DMM with carbon monoxide produces methyl methoxyacetate (MMAc) in contrast to the production of glycolic acid for formaldehyde carbonylation. MMAc and glycolic acid are both precursors to EG. MMAc can be readily converted into EG in two consequent steps,<sup>11,12</sup> the gist of which comprises the hydrogenation of MMAc to 2-methoxyethanol and the hydrolysis of 2-methoxyethanol to EG. Recently, Bell and co-workers reported for the first time the vapor-phase carbonylation of DMM over H-Faujasite (an acid zeolite) to synthesize MMAc with a selectivity of 79% and a yield of 20%.13 Liu and his partners tested a Nafion-H catalyst for the vapor-phase carbonvlation of DMM that exhibited a high MMAc selectivity of about 90% but a low DMM conversion of 15% at 80 °C and about 3 MPa.<sup>14</sup> Several attempts at the synthesis of MMAc through the carbonylation of DMM with CO have been carried out in the liquid phase.<sup>15-20</sup> In these cases, however, the use of severely corrosive strong mineral acid or very high reaction pressure could not be avoided. To our certain knowledge, few reports have been published on the carbonylation of DMM by heteropolyacids (HPAs).

In this work, a green and reusable heteropolyacid  $(PW_{12})$  was selected as an efficient catalyst for the synthesis of MMAc via the liquid-phase carbonylation of DMM under relatively mild conditions; the high catalytic activity of  $PW_{12}$  may be attributed to the synergistic effect between its superior acidic strength and the high polarity of the solvent.

In order to screen the best catalyst, four different HPAs (PW<sub>12</sub>, SiW<sub>12</sub>, PMo<sub>12</sub>, and SiMo<sub>12</sub>) and some other catalysts were examined preliminarily for the carbonylation of DMM with CO (Scheme 1). The final products were quantitatively analyzed by GC using a known amount of ethyl acetate as the internal standard (Table 1). The product, MG, probably originated from the hydrolysis of DMM to HCHO and methanol, followed by further carbonylation of HCHO with CO (Scheme 2). Because MMAc and MG are both precursors to EG, the total selectivity of MMAc and MG was calculated. The highest DMM conversion (99.1%) and total selectivity (80.9%) of MMAc and MG were obtained when using PW12 as the catalyst. As shown in Table 1, the total selectivity improved with increasing HPA acidic strength; therefore, the acid strength of the HPAs seemed to be a key parameter in the carbonylation of DMM. SiW<sub>12</sub>, PMo<sub>12</sub>, and SiMo<sub>12</sub> possessed approximately equal acidic strength, but the molybdic HPAs exhibited lower MMAc selectivity than the tungstic HPAs. This may be attributed to the greater reducibility of molybdic acids.<sup>9</sup> The deep blue color of the reaction solutions catalyzed by PMo12 and SiMo<sub>12</sub> provided evidence for the formation of heteropoly blues, which were a result of the reduction of molybdic acids. The reduction of HPAs leads to an increase in the basicity of the polyanion<sup>21,22</sup> and causes a further negative influence on acid catalytic activity. The catalytic performance of PW12 was clearly

$$\begin{array}{c} (\text{DMM}) \\ \text{HPAs:} \quad + \text{CO} \quad \overbrace{\text{solvent}}^{\text{HPAs}} \quad CH_3\text{OCH}_2\text{COOCH}_3 \\ (\text{MMAc}) \\ \text{HPAs:} \quad H_3\text{PW}_{12}\text{O}_{40} \text{ (abbreviate as PW}_{12}) \\ H_4\text{SiW}_{12}\text{O}_{40} \text{ (abbreviate as SiW}_{12}) \\ H_3\text{PMo}_{12}\text{O}_{40} \text{ (abbreviate as PMo}_{12}) \\ H_4\text{SiMo}_{12}\text{O}_{40} \text{ (abbreviate as SiMo}_{12}) \end{array}$$

**Scheme 1.** The carbonylation of DMM with CO catalyzed by heteropolyacids.



**Scheme 2.** Probable reaction route for the formation of MG from DMM.

Table 1. Catalytic activities of different catalysts on the carbonylation of DMM<sup>a</sup>

Catalyst	$pK_1$ (acetone) <sup>9</sup>	Conversion <sup>b</sup> /% -		MMAc and MG				
			MMAc	MG	MF	DME	Methanol	selectivity/%
PW <sub>12</sub>	1.6	99.1	63.9	17.0	5.6	12.3	1.2	80.9
SiW <sub>12</sub>	2.0	98.2	54.3	18.6	6.5	15.0	5.6	72.9
PMo <sub>12</sub>	2.0	99.8	47.4	11.0	7.0	17.1	17.5	58.4
SiMo <sub>12</sub>	2.1	23.6	40.0	15.8	20.0	14.2	9.8	55.8
CF <sub>3</sub> SO <sub>3</sub> H	$-14.1 (H_0^d)^{14}$	95.7	58.2	14.9	6.6	15.8	4.5	73.1
$H_2SO_4$	$-11.9 (H_0^d)^{14}$	56.1	43.8	13.2	9.2	12.7	21.1	57.0
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	$0.55 (H_0^d)^{14}$	12.2	21.9	5.3	3.7	5.7	63.4	27.2
H-ZSM-5		15.3	38.7	11.6	5.5	9.8	34.4	50.3

<sup>a</sup>Reaction conditions:  $PW_{12}/DMM = 0.065$  (H<sup>+</sup> equiv/mol), 10 mL sulfolane, 130 °C, 3.0 MPa CO, 3 h. <sup>b</sup>Conversion =  $[1 - 3M_{DMM}/(3M_{DMM} + 2M_{DME} + 2M_{MF} + M_{methanol} + 3M_{MMAc} + 2M_{MG})] \times 100\%$ . <sup>c</sup>Selectivity of MMAc =  $[3M_{MMAc}/(2M_{DME} + 2M_{MF} + M_{methanol} + 3M_{MMAc} + 2M_{MG})] \times 100\%$ , where  $M_i$  is the moles of component *i* in the reaction solutions. <sup>d</sup>H<sub>0</sub> is the value of Hammett acidity function.

Table 2.	Effect of	f solvents	on the	carbonylation	of DMM <sup>a</sup>
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Solvent	Dipole moment $(\mu)^{23}$ /10 <sup>-30</sup> C m	Conversion <sup>b</sup> /%	Selectivity <sup>c</sup> /%					MMAc and MG
			MMAc	MG	MF	DME	Methanol	selectivity/%
Sulfolane	16.0	99.8	72.8	11.6	4.7	10.7	0.2	84.4
DMF	12.7	9.3	16.5	0.2	2.5	6.7	74.1	16.7
THF	5.8	36.9	3.1	0.1	9.2	16.7	70.9	3.2
DMSO	13.5	13.1	2.6	0.5	2.9	0.9	93.1	3.1
Acetonitrile	13	8.4	2.7	0.5	2.2	6.9	87.7	3.2
Acetone	9.0	11.7	1.9	0.6	5.2	3.8	88.5	2.5
1,4-Dioxane	1.5	7.9	1.5	0	1.8	1.3	96.4	1.5
Toluene	1.0	4.8	1.7	0	1.6	0.9	95.8	1.7

<sup>a</sup>Reaction conditions:  $PW_{12}/DMM = 0.065$  (H<sup>+</sup> equiv/mol), 10 mL solvent, 120 °C, 3.0 MPa CO, 2 h. <sup>b</sup>Conversion =  $[1 - 3M_{DMM}/(3M_{DMM} + 2M_{DME} + 2M_{MF} + M_{methanol} + 3M_{MMAc} + 2M_{MG})] \times 100\%$ . <sup>c</sup>Selectivity of MMAc =  $[3M_{MMAc}/(2M_{DME} + 2M_{MF} + M_{methanol} + 3M_{MMAc} + 2M_{MG})] \times 100\%$ , where  $M_i$  is the moles of component *i* in the reaction solutions.

superior to the other catalysts for the carbonylation of DMM.

In addition to the target products, dimethyl ether (DME) and methyl formate (MF) were also simultaneously formed as byproducts. Based on the previous work and experimental results, the formation of DME and MF was deduced from the disproportionation of DMM; a proof for this conclusion was that the molar ratio of DME to MF was close to two.

The carbonylation of DMM may be a Koch-type mechanism,<sup>14</sup> starting with the protonation of DMM with protons from the HPAs to form methanol and the methoxymethyl cation.<sup>11</sup> The methoxymethyl species, which is rich in positive charges, can be stabilized by HPAs anions. In this step, the superior acidic strength of HPAs makes it easy to generate methoxymethyl species. Then, the nucleophile CO attacks the active species to produce the acylium cation, from which the resultant MMAc is generated by subsequent reaction with a DMM molecule, and consequently the methoxymethyl species is regenerated. According to the proposed Koch-type mechanism, the carbonylation of DMM is a typical acid-catalyzed process, and the efficiency of this carbonylation reaction therefore depends severely on the acidity of the catalyst.

With an active catalyst in hand, the influence of different solvents was studied and the results are summarized in Table 2. It can be seen that the effect of these different solvents on the carbonylation reaction exhibits a huge distinction. The dipolar aprotic solvent sulfolane showed distinct advantages as a medium for this reaction system. A far more excellent carbonylation performance, evident from the high DMM conversion (99.8%) and total selectivity (84.4%), was achieved in sulfolane than in the other organic solvents studied under the same conditions. The cause of the huge difference brought about by these solvents was unclear; however, we tried firstly to explain it based on solvent polarity. When solvent polarity was considered for its influence on DMM carbonylation, it was concluded that the conversion and selectivity increased roughly with solvent dipole moment. During the reaction process, the methoxymethyl and methoxyacetyl cations require a suitable ionic environment for stabilization. Therefore, the aprotic-type solvent sulfolane may favor DMM carbonylation by stabilizing the intermediates through its high polarity. The high polarity of the solvent and strong acidity of the catalyst seemed to exhibit a synergistic effect on the carbonylation of DMM with CO.

The effect of initial CO pressure and reaction time on DMM carbonylation catalyzed by  $PW_{12}$  was also studied (Supporting Information, Table S1). The experiment results showed that the total selectivity of MMAc and MG was obviously dependent on the CO pressure. By raising the CO pressure from 0.5 to 4 MPa, the conversion of DMM increased rapidly to nearly 100% at 1 MPa and the selectivity was maximum at 3 MPa. When the reactants were stirred for 0.5 h, the conversion of DMM and the



Figure 1. Reusability results of  $PW_{12}$  as catalyst for the carbonylation of DMM in solvent of sulfolane. Reaction conditions of carbonylation:  $PW_{12}/DMM = 0.065$  (H<sup>+</sup> equiv/mol), 10 mL sulfolane, 120 °C, 3.0 MPa CO, 2 h.

total selectivity could reach 60.6% and 69.8%, respectively, suggesting good catalytic activity of  $PW_{12}$ . After 2 h, the DMM conversion reached nearly 100% and the total selectivity showed a maximum of 83.1%.

We then investigated the temperature dependence of DMM carbonylation in the presence of PW12 at 3 MPa initial CO pressure (Supporting Information, Table S2). At 80 °C, the conversion of DMM and total selectivity of MMAc and MG were as low as 22.2% and 15.3%, respectively. The results showed that the contents of MF and DME rose with an increase in temperature from 80 to 90 °C. However, they dropped when the temperature went beyond 100 °C. This phenomenon may be explained by the fact that the carbonylation rate of DMM was seriously limited while the disproportionation of DMM was more favorable at low reaction temperature; therefore, the contents of MF and DME increased from 80 to 90 °C. With increasing reaction temperature, the carbonylation of DMM was significantly enhanced and the disproportionation of DMM was thus diminished. When the reaction temperature was 120 °C, the conversion and selectivity reached the maximum. However, further increase in temperature to 150 °C led to decreased total selectivity, but increased the contents of MF and DME. This was probably because the disproportionation of DMM was more susceptible to be promoted at high temperatures.

The ratio of DME/MF was about two below  $130 \,^{\circ}$ C; however, it reached greater values at higher temperatures (3.4 and 4.3 at 140 and 150  $^{\circ}$ C, respectively). This deviation in the ratio of DME to MF was probably caused by the decomposition of MF to methanol and subsequent dehydration of methanol to DME, according to Bell and co-workers.<sup>11</sup>

The possibility of the reuse of  $PW_{12}$  under mild conditions was also studied. After DMM and the formed products were separated from the reaction system under vacuum,  $PW_{12}$ dissolved in sulfolane was recovered and reused directly for a new batch reaction. As shown in Figure 1,  $PW_{12}$  exhibited good stability in both activity and selectivity for the carbonylation process of DMM after six cycles. In conclusion, some Keggin-type heteropolyacids were tested for the liquid-phase carbonylation of DMM to synthesize precursors to EG. Among the tested HPAs,  $PW_{12}$  was the most efficient for the carbonylation of DMM at 120 °C and 3 MPa CO pressure for 2 h in sulfolane. Almost 100% conversion of DMM was achieved with 84.4% total selectivity of MMAc and MG. The catalyst could be reused six times with no significant decline in catalytic performance. The present research shows that HPA catalysts possess potential for application in the production of ethylene glycol.

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Supporting Information is available electronically on J-STAGE.

## References

- 1 H. Yue, Y. Zhao, X. Ma, J. Gong, *Chem. Soc. Rev.* **2012**, *41*, 4218.
- 2 B. Li, S. Bai, X. Wang, M. Zhong, Q. Yang, C. Li, *Angew. Chem., Int. Ed.* **2012**, *51*, 11517.
- 3 S. A. I. Barri, D. Chadwick, *Catal. Lett.* 2011, 141, 749.
- 4 F. E. Celik, H. Lawrence, A. T. Bell, J. Mol. Catal. A: Chem. 2008, 288, 87.
- 5 Y. G. Kim, J. S. Lee, K. H. Lee, *Res. Chem. Intermed.* **1998**, 24, 197.
- 6 S. Y. Lee, J. C. Kim, J. S. Lee, Y. G. Kim, *Ind. Eng. Chem. Res.* 1993, 32, 253.
- 7 T. Li, Y. Souma, Q. Xu, Catal. Today 2006, 111, 288.
- 8 H. Song, F. Jing, R. Jin, Z. Li, J. Chen, *Catal. Lett.* 2014, 144, 711.
- 9 Y. Sun, H. Wang, J. Shen, H. Liu, Z. Liu, *Catal. Commun.* 2009, 10, 678.
- 10 F. E. Celik, T. Kim, A. N. Mlinar, A. T. Bell, J. Catal. 2010, 274, 150.
- 11 F. E. Celik, T.-J. Kim, A. T. Bell, J. Catal. 2010, 270, 185.
- 12 V. Shapovalov, A. T. Bell, *J. Phys. Chem. C* **2010**, *114*, 17753.
- 13 F. E. Celik, T.-J. Kim, A. T. Bell, Angew. Chem., Int. Ed. 2009, 48, 4813.
- 14 S. Liu, W. Zhu, L. Shi, H. Liu, Y. Liu, Y. Ni, L. Li, H. Zhou, S. Xu, Z. Liu, *RSC Adv.* **2014**, *4*, 40999.
- 15 H. J. Schmidt, H. J. Arpe, U.S. Patent 4501917, 1985.
- 16 H. J. Schmidt, H. J. Arpe, EP Patent 0071920 B1, 1984.
- 17 J. Robert, U.S. Patent 2273269, 1942.
- 18 T. Koyano, M. Tachikawa, K. Kumagai, EP Patent 0078162 A1, 1983.
- 19 F. E. Celik, T.-J. Kim, A. T. Bell, U.S. Patent 20100105947 A1, 2010.
- 20 K. Murata, A. Matsuda, T. Masuda, Bull. Chem. Soc. Jpn. 1985, 58, 2141.
- 21 I. V. Kozhevnikov, K. I. Matveev, Appl. Catal. 1983, 5, 135.
- 22 E. Papaconstantinou, M. T. Pope, *Inorg. Chem.* 1967, 6, 1152.
- 23 C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 3rd ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003. doi:10.1002/3527601791.