



Highly effective synthesis of methyl glycolate with heteropolyacids as catalysts

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ABSTRACT

Methyl glycolate (MG) was synthesized successfully from the carbonylation of HCHO using heteropolyacids (HPAs) as catalysts, followed by esterification with methanol. The catalytic activities of different HPAs and effect of solvents and water amount in the reaction system were investigated with an autoclave under optimized reaction conditions. The stability and reusability of the catalysts were tested after separating the ingredients from the reaction system by distillation under vacuum. MG yield above 89% could be obtained when $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and sulfolane are employed as catalyst and solvent, respectively. The performance of catalysts did not show any significant deterioration after 10 times recycle.

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1. Introduction

Ethylene glycol is a high volume and widely used chemical product, one of its main uses being in the production of polyester plastics and fibers. It is widely manufactured by the hydration of ethylene oxide that is obtained by the oxidation of ethylene [1].

An alternative method of producing ethylene glycol that avoids the need for an ethylene derivative, and consequently the need for a steam cracker to produce ethylene, is to use C1 compounds as feedstock. Such processes include the reaction of HCHO with CO, which results in the formation of glycolic acid, which is then converted into ethylene glycol through processes such as hydrogenation, optionally after first being converted into methyl glycolate (MG) [2,3].

Du Pont Company firstly developed a commercial production route of ethylene glycol via MG by using H_2SO_4 as catalyst at 90 MPa. However, the process was discontinued in 1968 due to the rigorous reaction conditions and serious corrosion. It has been proven that carbonylation could proceed under extremely mild conditions when strong acid catalysts, such as HF or concentrated H_2SO_4 and copper carbonyls, were employed [4–6]. To overcome the disadvantages of rigorous reaction conditions and serious corrosion, a new method to synthesise MG has been developed by car-

bonylation of formaldehyde using methyl formate (MF) instead of gaseous CO [7–12]. This route shows a potential prospect because the reaction could be performed under the mild conditions. Nevertheless, the slow release of CO and the higher cost of MF might be the major drawbacks from the viewpoint of industrial application. Therefore, it is interesting and necessary to develop a novel process to MG by carbonylation of formaldehyde with gaseous CO under the mild condition since CO is cheap and widely used in various industrial processes. Recently, MG has been synthesized with a catalytic system consisting of p-toluenesulfonic acid, transition metal complex $\text{CF}_3\text{SO}_3\text{Ag}$, and ionic liquid $\text{BMIm}[\text{PF}_6]$ under 135 °C and 10 MPa of CO [13]. Solid acids, such as resins, have also proved being effective for the carbonylation of HCHO [14–16]. MG yield up to 78% could be obtained at a high initial CO pressure of 24 MPa [16].

In this study, the green and reusable heteropolyacids (HPAs) were used as catalysts for highly effective synthesis of MG.

2. Experimental

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (abbreviated as PW_{12}), $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12}) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo_{12}) (Sinopharm Chemical Reagent, AR) were directly used as catalysts. $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (SiMo_{12}) was synthesized from Na_2MoO_4 and Na_2SiO_3 by the traditional way according to the literature [17]. Paraformaldehyde (Tianjin Kermei Chemical Reagent) was used as the source of HCHO. All solvents (Sinopharm Chemical Reagent, CP) were used without further purification.

Weight change curves were recorded under flowing air on a Perkin–Elmer TGA high-resolution thermogravimetric analyzer.

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Acid properties of HPAs in acetone were determined by the electrical conductivity method [18].

The carbonylation of HCHO with CO was carried out using a 100 ml autoclave with a Teflon liner and a magnetic stirrer. In a typical reaction, paraformaldehyde (6.7 mmol), acidic catalysts (0.35 mmol), water (6.7 mmol) and solvent (20 ml) were charged into the reactor, and then CO was introduced with initial 4.0 MPa CO pressure at room temperature. The reactions were performed at 120 °C. After 4 h of reaction, the autoclave was cooled to room temperature and depressurized. The contents of autoclave after carbonylation were poured into methanol (67 mmol) and refluxed for 2 h at 70 °C, to esterify the glycolic acid into MG. The products were identified and quantitatively analyzed by a GC/MS (HP 6890-5973N) and an Agilent 6890N GC equipped with FID and TCD detectors, respectively. For quantitative analysis, a known amount of dimethyl sulfoxide or isopropanol was added as an internal standard to the product mixture before the GC analysis.

HCHO conversion and MG selectivity were calculated according to the following equations:

$$\text{Conversion of HCHO} = (M_{\text{in}} - M_{\text{out}}) / M_{\text{in}}$$

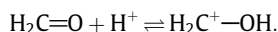
$$\text{Selectivity to MG} = M_{\text{MG}} / (M_{\text{in}} - M_{\text{out}})$$

where M_{in} and M_{out} are the amount (mol) of HCHO fed in and remaining in the solution after reaction, respectively, and M_{MG} is the amount (mol) of the product MG detected in solution after reaction.

3. Results and discussion

3.1. Effect of solvent

The acid-catalyzed reaction of HCHO with CO belongs to the known Koch reaction. The activation of HCHO is [4]



The easiness with which the Koch reaction takes place depends on how easily the substrate is protonated. Protonation of HCHO requires a strong acid, such as HPAs, to generate hydroxyl carbonium ion and a solvent to provide an ionic environment suitable for stable existence of carbonium ion. So, several polar aprotic-type reagents were selected as solvents for the synthesis of MG, and the results are shown in Table 1. From the data in Table 1, it was found that the MG yield increased with the solvent polarity (dipole moment). When sulfolane, the highest polar strength solvent, was used, about 99.6% HCHO conversion and 89.6% MG selectivity could be achieved, which are much higher than using other solvents. Correspondingly, the highest MG yield (89.3%) appears in the reaction with sulfolane as the solvent. For sulfolane, the non-

Table 1
Effect of solvent on the carbonylation of HCHO.

Solvent	HCHO conversion (%)	MG selectivity (%)	MG yield (%)	Dipole moment (μ^{D}) [19]
Sulfolane	99.6	89.6	89.3	16.0
1,4-Dioxane	42.3	81	34.2	1.5 ^b
Dimethyl sulfoxide	10	77	7.7	13.5
Formamide	8.4	75	6.3	11.2
Tetrahydrofuran	5.8	69	4.0	5.8

^a Dipole moment in Coulombmeter (Cm), measured in benzene, tetrachloromethane, 1,4-dioxane, or *n*-hexane at 20... 30 °C. 1 Debye = 3.336×10^{-30} Cm.

^b Due to the possible self-association and/or internal compensation, the dipole moment of 1,4-dioxane determined from bulk dielectric constant measurements will not give a true indication of the strength of any polar interaction that might take place with another molecule.

polar stability of four carbon ring and the high polarity of sulfur-oxygen double bond may favor the formation of stable carbonium ion, and enhance HCHO conversion.

3.2. Catalytic activities of different HPAs

The catalytic performances of different HPAs on the carbonylation of HCHO are shown in Table 2. All HPAs exhibited catalytic activities for the carbonylation reaction. As acid strength of HPAs increased, MG yield improved. The PW₁₂ showed the best performance among the HPAs because high acid strength accelerated the formation of hydroxyl carbonium ion. When acid strength was approximately equal, the molybdc acids gave low MG yield compared to the tungstic acids. This might be attributed to the greater reducibility of the molybdc acids [20]. Since reduced HPAs are more basic [20], their effectiveness as acid catalysts is diminished. Reduction of the HPAs during reaction was evidenced by the blue color of post-reaction solutions containing SiMo₁₂ and PMo₁₂, indicating the formation of reduced “heteropoly blues”. The reactant HCHO may be the reducing agent. So, PW₁₂ was selected as catalysts due to its excellent activity and stability for further investigation.

3.3. Effect of water

Water acts not only as crystal water of HPAs, but also as reactant for formation of glycolic acid. The moving ability of the protons within the HPA crystal is dominated by the level of hydration [21]. So, the amount of water in the reaction system could affect the catalytic activity of HPAs. Thermal gravity analysis of PW₁₂ provides important information about water in the catalysts, as the curves are shown in Fig. 1. It is verified that the PW₁₂ loses the absorbed water and the crystal water at 60 and 170 °C, respectively. The structures of PW₁₂ are destroyed when calcination temperature is over 500 °C.

PW₁₂ calcined at different temperatures was used as catalyst for the carbonylation reaction, and the results are shown in Table 3. To

Table 2
Catalytic activities of different HPAs on the carbonylation of HCHO.

HPA (Keggin)	pK ₁ (acetone)	MG yield (%)
H ₃ PW ₁₂ O ₄₀	1.6	89.3
H ₄ SiW ₁₂ O ₄₀	2.0	89.0
H ₃ PMo ₁₂ O ₄₀	2.0	65.0
H ₄ SiMo ₁₂ O ₄₀	2.1	39.8

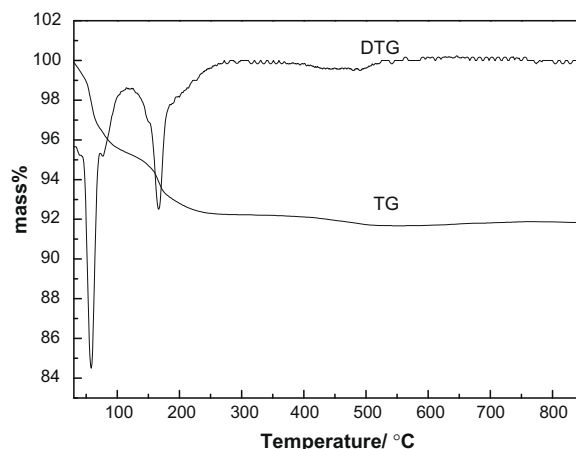


Fig. 1. TG and DTG curves of the PW₁₂.

Table 3
Effect of calcination temperature of PW₁₂ on MG yield^a.

Calcination temperature (°C)	MG yield (%)
Uncalcined	89.3
100	82.1
200	79.0
500	7.6

^a No water is added into the reaction system.

eliminate the water effect from reactants, the solvent sulfolane was dried with anhydrous MgSO₄, and CO was dried with 3 Å molecular sieves before fed into the reactor. When the catalyst was calcined at 100 °C, corresponding to the losing of absorbed water (see, Fig. 1), the MG yield decreased from 89.3% to 82.1%. MG yield decreased to 79% when the catalyst losing of both absorbed and crystal water at 200 °C. The destruction of the PW₁₂ structure at 500 °C would dismiss the acidity of the materials, resulting in the loss of activity for the carbonylation reaction.

Fig. 2 gives the reaction scheme of carbonylation of HCHO and CO. It is evident that water participates in the reaction as one reactant. Therefore, the different amounts of water in reaction system may have a great influence on the performance of carbonylation reaction. Table 4 gives the effect of water on the MG yield. The amount of HCHO and PW₁₂ was kept constant in these runs when the molar ratios of water to HCHO were changed. One can see that the MG yields hardly changed when the ratio of H₂O/HCHO was in the range from 0.8 to 2.0. The highest MG yield (90.0%) could be obtained when the ratio of H₂O/HCHO was 2.0. However, MG yield would decrease sharply with the increase of the ratio of H₂O/HCHO when it was above 2.0. The results indicate that the excess water would act partly as solvent, which is unfavorable for the formation of glycolic acid.

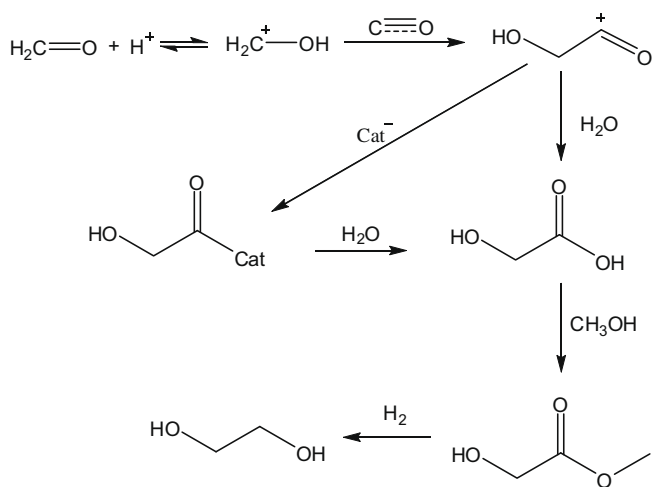


Fig. 2. Reaction scheme of carbonylation of HCHO and CO.

Table 4
Effect of additional water on the carbonylation of HCHO.

H ₂ O/HCHO ratio (mol)	MG yield (%)
0.8	89.1
1.0	89.4
1.5	89.3
2.0	90.0
2.2	64.8
2.6	46.2
2.9	30.8
6.9	8.3

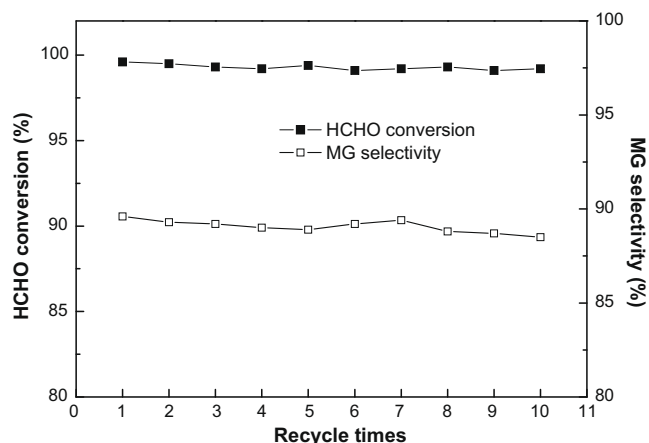


Fig. 3. HCHO conversion and MG selectivity after consecutive batches.

It has been reported that the effects of water on the catalytic activities of HPAs were found to be complex [22]. Sulfolane is a polar aprotic solvent, while water is a polar protic solvent, so the solvent effect of them is radically different. Sulfolane has advantages over water in providing a favorable ionic environment for stabilizing the hydroxy carbonium ion generated by activated HCHO. Excess amount of water would weaken the influence of sulfolane as the solvent, and leads to the difficulty in the formation and stabilization of carbonium ion. Thus, activation of HCHO may become controlling step.

4. Reusability of catalysts and solvents

In order to test the stability and reusability of the catalysts, the ingredients (including unreacted HCHO, excessive methanol and formed products) were separated from the reaction system by distillation under vacuum at 100 °C after carbonylation and esterification. PW₁₂ and sulfolane were recovered and reused for a new batch reaction under the same conditions. Fig. 3 shows the results of 10 consecutive tests. It is deserved to point out that the catalytic system did not show any deactivation in both activity and selectivity even after 10 times recycle. HCHO conversion and MG yield were kept at about 99% and 88% in consecutive runs, respectively. The results indicate that the catalytic system consisting of PW₁₂ and sulfolane in process of carbonylation of HCHO with CO is stable under the reaction operation, and distillation is an effective method to separate products from the reaction system.

5. Conclusion

An efficient catalytic system consisting of HPA catalysts and sulfolane solvent has been established in batch reactors to manufacture MG from HCHO and CO. Ninety percentage of MG yield could be obtained under optimized reaction conditions. Excess amount of water (H₂O/HCHO ratio above two) would decrease the MG yield sharply, due to the fact that water, acting partly as solvent, is unfavorable for the formation of glycolic acid. Moreover, the performance of catalysts did not show any significant deterioration after 10 times recycle. This process provides a useful and economically potential way for industry application of ethylene glycol manufacture.

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