

One-step synthesis of methylmethacrylate from methacrolein over Keggin-type heteropoly compounds

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Abstract—One-step synthesis of methylmethacrylate (MMA) using heteropoly compounds (HPCs) as catalysts was demonstrated by feeding a mixture of methacrolein (MAL), air, water, nitrogen and MeOH (methanol). The HPCs with different counter-ions, such as $H_{1.7}Cs_{1.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$ ($CsPMo_{11}VO_{40}$), $H_{1.7}La_{0.7}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$ ($LaPMo_{11}VO_{40}$) and $H_{1.7}K_{1.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$ ($KPMo_{11}VO_{40}$), were studied in oxidation of MAL, esterification of methacrylic acid (MAA) and one-step synthesis of MMA from MAL, respectively. The selectivity of MAA was up to 45.7% and MMA was 44.6% with 93.3% MAL conversion over $CsPMo_{11}VO_{40}$.

Key words: Methylmethacrylate, Methacrolein, HPCs, Counter Ions

INTRODUCTION

Methylmethacrylate (MMA) is an important chemical intermediate used mainly in the production of plastics. Its conventional production routes are acetone-cyanohydrins processes (ACH) with a share of about 85% of production capacity in the world. However, since the transport of hydrogen cyanide is dangerous and the disposal of by-products like ammonium sulfate is expensive, processes for the replacement of ACH are being developed constantly, among which C_4 process is attractive for its environmental benignancy. C_4 processes, using isobutene or *tert*-butyl alcohol as raw material, consist of a two-stage oxidation process and one stage esterification: (1) isobutene to methacrolein (MAL), (2) MAL to methacrylic acid (MAA) and (3) MAA to MMA. Moreover, direct methylate processes that prepared MAL from isobutene, and then produced MMA from MAL in one-step were developed, where palladium as main active component of the catalysts was employed [1-3]. It is believed that a process using a coupling reaction is effective to alleviate the jam of equipment by avoiding high melting point by-products, including aromatics or/and oligomer from dimeric reaction or polymerization of MAA.

Heteropoly compounds (HPCs), known as environmentally benign catalysts with little causticity to equipment, have been applied in some selective oxidation reactions or acidic catalytic reactions [4,5]. Usually, changes of the secondary structure of HPCs would affect its catalytic performance. For example, HPCs used in the commercial process for the oxidation of MAL to MAA were presumably $Cs_xH_{3+y-x}PV_yMo_{12-x}O_{40}$ ($x=0-2$, $y=1-2$), in which formation of Cs acidic salts increased the surface area and the thermal stability of the catalyst remarkably [6-13]. In other studies [14], the presence of Cu^{2+} played an important role in supplementing lattice oxygen from gas oxygen, which was believed to be a rate-determining step. In addition, introducing an arsenic (As) component into the HPCs

results in an increase of selectivity of MAA and conversion of MAL [15].

HPCs are typical ionic crystals and have a small surface area, which effect catalytic activation when HPCs are used as catalysts. Pore expanding is an effective approach to enhance the surface area and the mechanical strength by adding ammonium nitrate or organic base, such as urea, pyridine, or quinoline [16].

A report about one-step synthesis of MMA from MAL using HPCs as catalysts has not been found up to now. In the present study, HPC catalysts with various counter-ions like $CsPMo_{11}VO_{40}$, $LaPMo_{11}VO_{40}$ and $KPMo_{11}VO_{40}$ were prepared and used in oxidation reaction of MAL, esterification reaction of MAA and coupling reactions from MAL to MMA. To improve catalytic activities, a certain content of Cu and As was added in the above-mentioned HPCs [13,17-19]. Moreover, the contents of Cu^{2+} and As^{5+} were fixed at 0.2 and 0.1 by the experiments of MAL oxidation. Thus, effects of the different main counter-ions on catalytic performance were investigated in the reactions.

EXPERIMENTAL

1. Raw Material and Catalyst Preparation

MAL (C_4H_6O , A. R.) was provided by J&K Chemical LTD. Detailed preparation procedure for $H_4PMo_{11}VO_{40} \cdot 14.5 H_2O$ was referred to the literature [20]. 20 g of $H_4PMo_{11}VO_{40} \cdot 14.5 H_2O$ was dissolved with 8 ml of deionized water (solution A); 4 g of quinoline was dissolved in 8 ml 5% diluted nitric acid solution (solution B). Next, solution A was added to solution B, where 2.60 g of $CsNO_3$ (or 2.70 g $La(NO_3)_3 \cdot 6 H_2O$, 1.28 g KNO_3), 0.59 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.21 g of H_3AsO_3 (60% aqueous solution) were added, and stirred strongly for 30 min. Then, the water was removed by heating the mixture in an oven at 120 °C. The dried mixture was pressed, smashed and sieved to particles with a diameter of 0.30-0.45 mm, and finally calcined in nitrogen flow at 400 °C for 3 h and air flow at 350 °C for 3 h. The HPCs theoretical compositions were $H_{1.7}Cs_{1.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$ ($CsPMo_{11}VO_{40}$), $H_{1.7}La_{0.7}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$ ($LaPMo_{11}$

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VO₄₀), H_{1.7}K_{1.5}Cu_{0.25}As_{0.1}PMo₁₁VO₄₀ (KPMo₁₁VO₄₀), respectively.

2. Characterization

The chemical composition of the samples was determined by using ICP (IRIS Intrepid II XSP, Thermo). IR spectra were recorded on a Bruker Tensor FT-IR with potassium bromide (KBr) at the ratio 1 : 150. Surface areas of the samples were measured by using a Thermo Sorptomatic surface area analyzer and standard multi-point BET analysis methods. The acid properties of the HPCs were measured by IR-pyridine adsorption using a Bruker Tensor FT-IR. Reduction properties of the HPCs were explored by H₂-TPR with a Thermo TPD/R/O 1100 Series.

3. Reaction Study

All the reactions were conducted in a 10 mm inner diameter stainless steel tubular reactor. Typically, 3 ml of catalyst that was diluted with 3 ml of inert quartz in the same size was loaded in the reactor to give a catalyst bed about 6 cm in height. An electrical furnace equipped with a temperature controller heated the reactor. The flow rate of air and N₂ was controlled by mass flow controllers. Water and methanol (MeOH) were fed by a mini-pump in certain proportion. MAL was saturated in a nitrogen gas flow and fed with gaseous reactants. A blank test showed that no reaction occurred in the absence of catalyst. Gaseous substances were analyzed by a TCD gas chromatograph equipped with a TDX-01B column. The liquid condensate of MMA, MAL, MAA, MeOH and acetic acid was analyzed by an FID gas chromatograph using a PEG-20M column. The oxidation of MAL and esterification of MAA were also performed by using the above-mentioned equipment with some modification. MeOH was removed from the above-mentioned reactants in oxidation of MAL, and only a mixture of certain ratio of MAA/MeOH was fed by mini-pump into the reactor in esterification of MAA.

RESULTS AND DISCUSSION

1. Catalyst Characterization

1-1. Chemical Compositions and Surface Area

The chemical compositions of the HPCs were determined by ICP (IRIS Intrepid II XSP, Thermo). Analysis results of ICP from Table 1 showed that the actual chemical compositions were close to theoretical compositions.

The surface area was measured by N₂-adsorption/desorption. As shown in Table 1, HPCs with alkaline metallic ions acting as counter-ions, especially, Cs-containing HPCs, had larger surface area than that of LaPMo₁₁VO₄₀ and KPMo₁₁VO₄₀. In general, HPC with bigger bulk of metallic ions as counter-ions, such as Cs⁺, Ag⁺, had more surface area, while HPCs with less bulk of metallic ions had less surface area, such as La³⁺ [21].

Table 1. Surface area and chemical compositions of the HPCs catalysts

Theoretical composition	Surface area (BET) (m ² ·g ⁻¹)	Practical atomic ratio			
		Mo	P	V	Cs/La/K
CsPMo ₁₁ VO ₄₀	54.5	11.0	1.2	1.3	1.6
LaPMo ₁₁ VO ₄₀	20.4	10.7	1.0	1.0	0.6
KPMo ₁₁ VO ₄₀	25.8	11.6	0.9	0.8	1.4

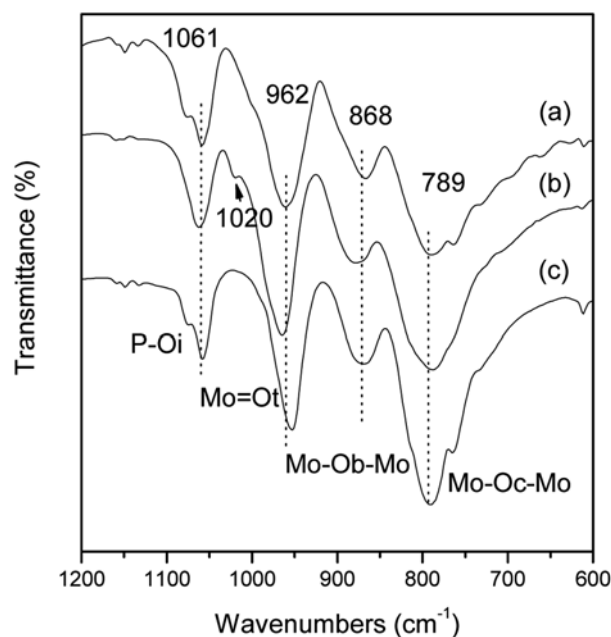


Fig. 1. IR spectra of the HPCs. (a) CsPMo₁₁VO₄₀; (b) LaPMo₁₁VO₄₀; (c) KPMo₁₁VO₄₀.

1-2. FT-IR

The CsPMo₁₁VO₄₀, LaPMo₁₁VO₄₀ and KPMo₁₁VO₄₀ exhibited four main characteristic FTIR bands at 1,061 cm⁻¹, 962 cm⁻¹, 868 cm⁻¹ and 789 cm⁻¹ from Fig. 1, attributable to ν_{as} (P-Oi), ν_s (Mo=Ot), ν_s (Mo-Ob-Mo), and ν_s (Mo-Oc-Mo), respectively, which proved the characteristic Keggin structure of the HPCs [12,22-26].

Note that two minor peaks at about 1,079 cm⁻¹ and 766 cm⁻¹ were observed over CsPMo₁₁VO₄₀ and KPMo₁₁VO₄₀, which are characteristic of V atoms substituting for Mo in the Keggin anions [10,22,26]. However, the two peaks disappeared over LaPMo₁₁VO₄₀, and a small peak at about 1,020 cm⁻¹ occurred over LaPMo₁₁VO₄₀, which was ascribed to the band $\nu(V=O)$ in free V₂O₅ [26]. It indicated that a part of V atoms had segregated from the Keggin anions and had formed the free V₂O₅ or else V species over LaPMo₁₁VO₄₀. Therefore, alkaline metallic ions as counter-ions, such as Cs and K, HPCs had a better structural stability.

1-3. Acidity Properties

MAL oxidation reaction was a surface-type reaction, where the greater surface area of the catalysts led to a higher catalytic oxidation activity. Moreover, it was also a concerted catalysis of acid and redox [27,28]; the acid properties of catalysts affected the catalytic activity of not only MAL oxidation, but also MAA esterification and the coupling reaction of one-step synthesis MMA from MAL.

Acidity properties of the HPCs were measured by IR-pyridine adsorption. The IR spectra of the HPCs that adsorbed pyridine at room temperature and desorbed at 200 °C are shown in Fig. 2. The bands at 1,450 cm⁻¹ were attributable to L-acid sites, and the bands at 1,540 cm⁻¹ were attributable to B-acid sites. The correction factors of B-acid sites and L-acid sites were 1.13 and 1.28, respectively [29]. Surface area of B-acid sites and L-acid sites was given in Table 2. LaPMo₁₁VO₄₀ and CsPMo₁₁VO₄₀ had many more B-acid sites than KPMo₁₁VO₄₀. HPCs with small bulk counter-ions, such as La³⁺, whose properties were similar to the original heteropolyacids

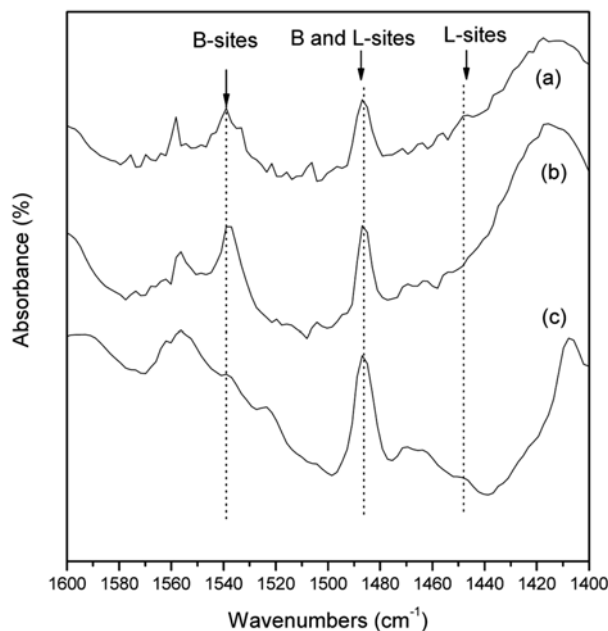


Fig. 2. IR-pyridine spectra of the HPCs. (a) CsPMo₁₁VO₄₀; (b) LaPMo₁₁VO₄₀; (c) KPMo₁₁VO₄₀.

Table 2. Relative area of the IR-pyridine adsorption on the HPCs

Catalysts	B-acid sites (1,540 cm ⁻¹)	L-acid sites (1,450 cm ⁻¹)
CsPMo ₁₁ VO ₄₀	18.6	1.2
LaPMo ₁₁ VO ₄₀	28.5	1.1
KPMo ₁₁ VO ₄₀	2.6	2.1

[28], had more B-acid sites. And the fewer B-acid sites of KPMo₁₁VO₄₀ may be ascribed to less K⁺ ionic radius.

1-4. H₂-TPR

The reduction activities of the HPCs were measured by H₂-TPR [12]. Song et al. studied the redox of cation-exchanged Keggin-type heteropolyacid catalysts [31]. The TPR profiles of CsPMo₁₁VO₄₀, LaPMo₁₁VO₄₀ and KPMo₁₁VO₄₀ after pretreatment are shown in Fig. 3. A single reduction peak was observed over CsPMo₁₁VO₄₀ and over KPMo₁₁VO₄₀ at 591 °C and 551 °C during 500-700 °C, respectively. However, LaPMo₁₁VO₄₀ had a complicated profile that can be decomposed into three main peaks at about 589 °C, 648 °C and 687 °C. Generally, reduction peaks in the 550-730 °C range are ascribed to the reduction of Mo⁶⁺ to Mo⁴⁺ [31,32]. Moreover, the reduction peak at about 589 °C was ascribed to (PMo₁₁VO₄₀)⁴⁻ (16%). And the peaks at 483 °C, 648 °C and 687 °C can be ascribed to the reduction peaks of V₂O₅ (7.8%), (PMo₁₂O₄₀)³⁻ (57.8) and MoO₃ (17.5%). According to the lower reduction temperature corresponding to a higher reduction activity, the prepared catalysts in this study had higher reduction activity than catalysts from literature with the same heteropolyanions and different counter-ions [33]. Thus, CsPMo₁₁VO₄₀ had a higher redox activity than LaPMo₁₁VO₄₀. Moreover, the active sites from single (PMo₁₁VO₄₀)⁴⁻ can lead to a higher selectivity over CsPMo₁₁VO₄₀.

2. Catalyst Testing

2-1. Oxidation of MAL

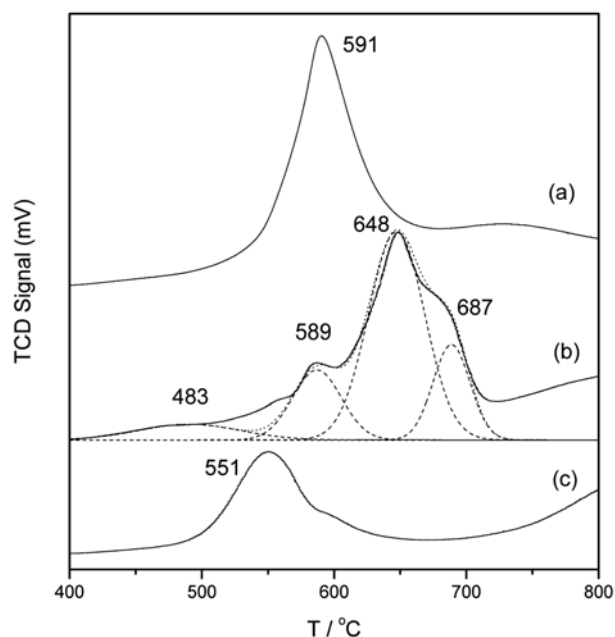


Fig. 3. H₂-TPR of the HPCs. (a) CsPMo₁₁VO₄₀; (b) LaPMo₁₁VO₄₀; (c) KPMo₁₁VO₄₀.

Table 3. Synthesis of MAA from MAL over different HPC catalysts at 300 °C

Catalysts	GSV (h ⁻¹)	MAL conversion (%)	Selectivity (%)		
			MAA	Ace.A	CO _x
CsPMo ₁₁ VO ₄₀	1,200	88.6	94.9	0.6	4.5
LaPMo ₁₁ VO ₄₀	1,200	82.2	94.7	0.2	5.1
KPMo ₁₁ VO ₄₀	1,200	82.6	90.3	1.2	8.5
CsPMo ₁₁ VO ₄₀	800	92.4	92.0	0.8	7.2
LaPMo ₁₁ VO ₄₀	800	85.1	88.6	2.5	8.9
KPMo ₁₁ VO ₄₀	800	87.0	85.2	4.2	10.6

Feed composition, MAL/air/N₂/H₂O=5/62.5/12.5/20 (molar ratio)

GSV-Gas Space Velocity; Ace.A-Acetic Acid; CO_x-CO and CO₂

The catalytic performance over CsPMo₁₁VO₄₀, LaPMo₁₁VO₄₀ and KPMo₁₁VO₄₀ is shown in Table 3. Each of the data points presented is an average of at least three separate product analyses.

The HPCs catalysts had better catalytic activity for MAL oxidation. The selectivity of MAA was up to 92% with 92.4% MAL conversion over CsPMo₁₁VO₄₀, which is better than the catalysts from literature where MAL conversion is from 70-90% and selectivity of MAA is from 80-85% [16,27,28,34]. The reason for the better catalytic performance may lie in the greater surface area and the stronger redox activity of CsPMo₁₁VO₄₀.

Effects of temperature on catalytic performance are shown in Fig. 4. With increasing temperature, the MAL conversion increased and the selectivity of MAA decreased when temperature was higher than 300 °C. Space velocity affected obviously the catalytic performance over CsPMo₁₁VO₄₀, as shown in Fig. 5. With the increasing of space velocity, the MAL conversion decreased while MAA selectivity slightly increased, and the formation of acetic acid, CO and CO₂ decreased gradually.

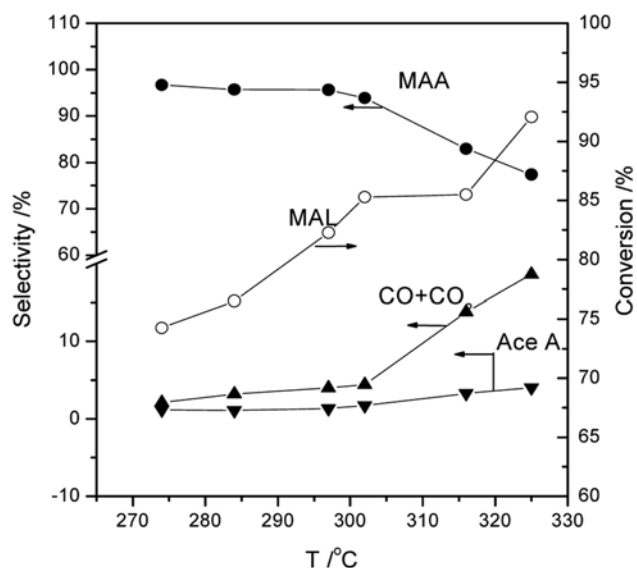
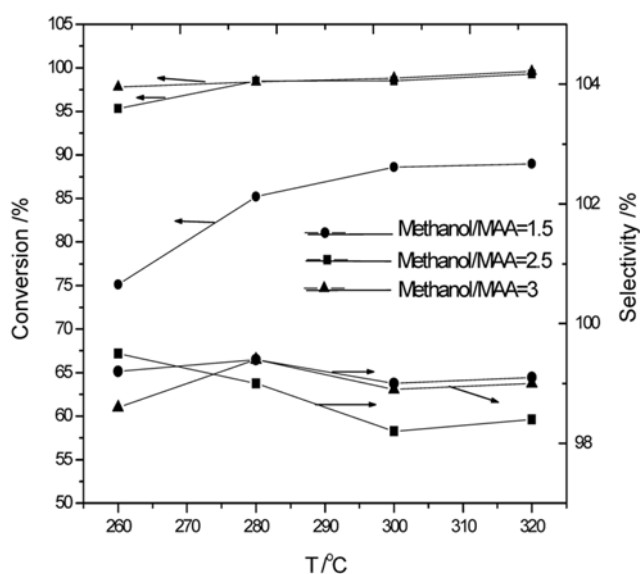
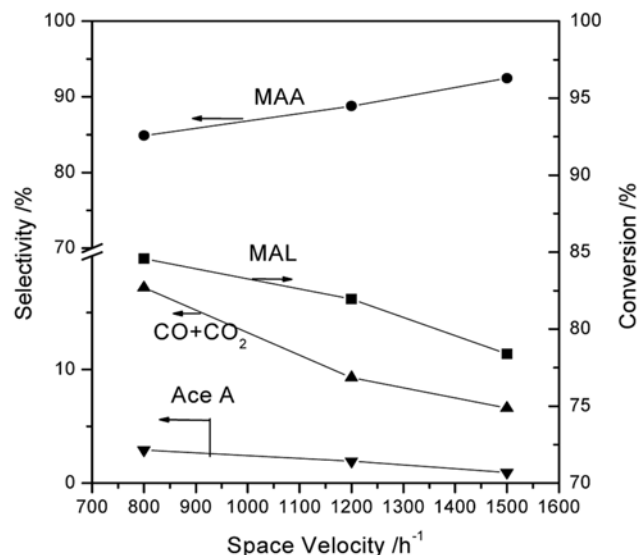
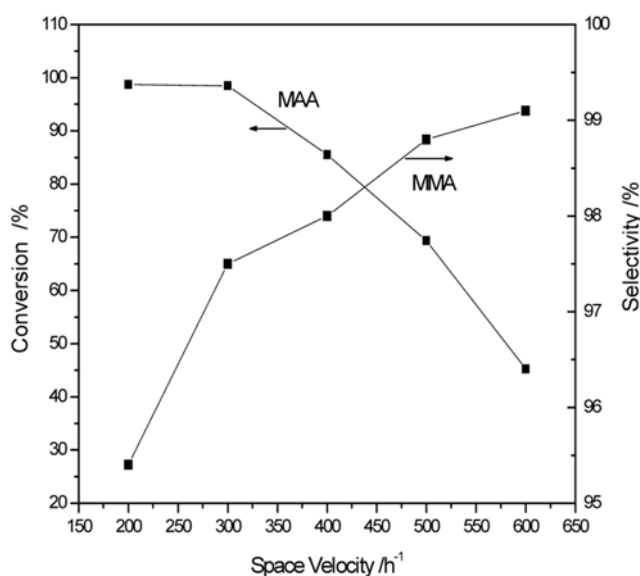
Fig. 4. Effect of temperature on MAL oxidation over CsPMo₁₁VO₄₀.Fig. 6. Effect of temperature and ratio of MeOH/MAA on esterification over CsPMo₁₁VO₄₀.Fig. 5. Effect of space velocity on MAL oxidation over CsPMo₁₁VO₄₀.Fig. 7. Effect of space velocity on esterification over CsPMo₁₁VO₄₀.

Table 4. Synthesis of MMA from MAA over different HPC catalysts at 300 °C

Catalysts	MAA conversion (%)	MMA selectivity (%)
CsPMo ₁₁ VO ₄₀	100	98.2
LaPMo ₁₁ VO ₄₀	100	97.5
KPMo ₁₁ VO ₄₀	82.2	98.8

2-2. Esterification of MAA

Production of MMA from esterification of MAA and MeOH adopted acid cation resins as catalysts in industrial processes [35], where the reaction temperature was mild but a longer reaction time was required. Compared with acid cation resins, the HPCs catalysts were advantageous to produce on a large scale.

When the reactant gas mixture was MeOH/MAA=2.5 (molar ratio), as shown in Table 4, the MMA selectivity and MAA conversion were close to 100% over the HPCs, except for KPMo₁₁VO₄₀.

Operation parameters, such as temperature, ratio of MeOH/MAA and space velocity were studied over CsPMo₁₁VO₄₀. The conversion of MAA increased gradually with the increasing temperature, and selectivity of MMA decreased in the whole temperature range from 260 °C to 300 °C. It was generally recognized that the ratio of MeOH and MAA was a key factor for preparing MMA. The optimal value of MeOH/MAA (molar ratio) was 2.5. As shown in Fig. 6, if the value was less than 2.5, selectivity to MMA declined. On the other hand, the excessive MeOH may decrease productivity of MMA. Effect of space velocity on catalytic performance is shown in Fig. 7 over CsPMo₁₁VO₄₀. When space velocity was less than

Table 5. One-step synthesis of MMA from MAL over different HPC catalysts at 300 °C*

Catalysts	MAL conversion (%)	Selectivity (%)			
		MMA	MAA	Ace.A	CO _x
CsPMo ₁₁ VO ₄₀	93.3	44.6	45.7	4.4	5.3
LaPMo ₁₁ VO ₄₀	88.4	47.6	28.3	5.8	18.3
KPMo ₁₁ VO ₄₀	85.5	24.4	55.8	9.5	9.3

*Feed composition, MAL/air/N₂/H₂O/MeOH=5/50/22.5/10/12.5 (molar ratio).

300 h⁻¹, almost 100% conversion to MAA could be achieved.

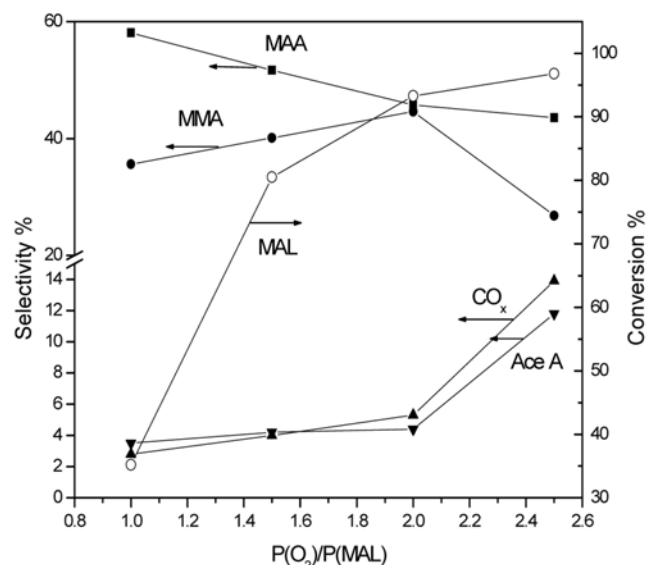
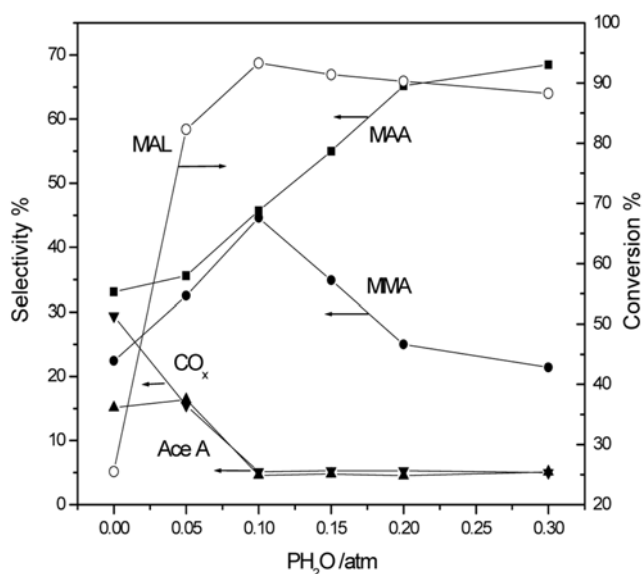
2-3. Coupling Reaction

The HPCs were effective catalysts for both oxidation and esterification reactions. Thus, the HPCs were used as catalysts in coupling reaction of one-step synthesis MMA from MAL.

Catalytic performance for the coupling reaction of MAL catalyzed by the HPCs is shown in Table 5. The total selectivity of MMA and MAA was up to 90.3% and selectivity of MMA was 44.6% with 93.3% MAL conversion over CsPMo₁₁VO₄₀. The coupling reaction improved the conversion of MAL by comparing the MAL conversion in Table 3 with Table 5. The reason may be that the fractional pressure of MAA was decreased due to esterification promoting the oxidation speed of MAL.

Moreover, selectivity of MMA over LaPMo₁₁VO₄₀ 47.6% of MMA selectivity and 88.4% of MAL conversion was obtained. As a result, it is obvious that MMA selectivity was influenced by their quantity of acid sites of catalysts. And a greater quantity of acid sites induced a higher MMA selectivity.

The coupling reactions over CsPMo₁₁VO₄₀ were performed in either oxygen-rich or hydrocarbon-rich atmosphere, as shown in Fig. 8. The HPCs catalysts were more active but had less selectivity to MMA and MAA in an oxygen-rich atmosphere. The oxygen-rich atmosphere enhanced deep oxidation to carbon oxides. In

**Fig. 8. Effect of O₂/MAL on the coupling reaction over CsPMo₁₁VO₄₀.****Fig. 9. Effect of steam on the coupling reaction over CsPMo₁₁VO₄₀.**

this study, a higher yield to MMA and MAA could be obtained when the volume ratio of partial pressure of O₂ and MAL was 2.

It was accepted that steam played an important role in partial oxidation over HPC catalysts; its presence can cause significant improvement in oxygenate selectivity [6,7,11,12,36-40]. From Fig. 9, the presence of steam caused an increase in MAA selectivity with a notable drop in CO_x formation; however, excess water caused a reduction of selectivity to MMA. 10% of steam was a suitable choice in the range of 0-30%.

When MeOH was added into the reaction system in one-step synthesis MMA from MAL, it might have caused a waste of MeOH or difficulty in separating MMA from products due to side-reactions of MeOH. All of reactants of the coupling reaction, except for MAL, were fed into the reactor by using CsPMo₁₁VO₄₀ as catalyst; the MeOH conversion was rather low. The main products were CO and CO₂. So, effects of MeOH on the coupling reaction were negligible.

CONCLUSIONS

The HPCs catalysts were not only applied to the both oxidation and esterification reactions, but could be used in the coupling reactions from MAL to MMA.

When the reaction temperature was at 300 °C, space velocity was 400 h⁻¹ and MAL/air/N₂/H₂O/MeOH was equal to 5/50/22.5/10/12.5, the 44.6% selectivity of MMA and 45.7% selectivity of MAA with 93.3% conversion of MAL could be achieved over CsPMo₁₁VO₄₀ in coupling reaction.

Cs-containing HPCs showed better structural stability and catalytic performances. CsPMo₁₁VO₄₀ had the best catalytic activities to MAL oxidation, MAA esterification and one-step synthesis MMA from MAL.

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