

# Effect of cesium content on the structure and catalytic performances of heteropoly compounds in one-step synthesis of methylmethacrylate from methacrolein

Xiaojun Guo<sup>†</sup>, Chongpin Huang, and Yingxia Li

State Key Laboratory Chemical Resource Engineering, Beijing University of Chemical Technology,  
Box 35#, Beijing, 100029, China

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**Abstract**—Keggin-type heteropoly compounds (HPCs)  $H_{3.2-x}Cs_xCu_{0.25}As_{0.1}PMo_{11}VO_{40}$  ( $x$ , 0-2.5) were used as catalysts for coupling reaction of methylmethacrylate (MMA) from methacrolein (MAL) in this study. And the catalytic performance of the HPCs was investigated in the oxidation-esterification coupling reaction. Moreover, the HPCs were characterized by  $NH_3$ -TPD, TG-pyridine-adsorption/desorption,  $N_2$ -adsorption/desorption, ICP, TG-DSC, FT-IR, XRD and TPR. These reactive results have been correlated to the acidity, surface area and reducibility. With the increasing of Cs content, surface area of the HPCs increased, while the acidity and reducibility decreased. Difference of the quantity of acid sites originated from the hydration protons being substituted by  $Cs^+$ . Effects of  $Cs^+$  content on the reducibility of the HPCs indicated that  $Cs^+$  changed the structural stability of V as coordinating atoms and the proportion of the different reducible states of  $Mo^{6+}$ .

Key words: Heteropoly Compounds (HPCs), Cesium, Methylmethacrylate, Methacrolein, Coupling Reaction

## INTRODUCTION

In recent years, many known and new Keggin-type HPCs with adjustable structures and properties have been applied in some selective oxidation reactions or acidic catalytic reactions. These HPCs were regarded as environmentally benign catalysts for little causticity to the equipment [1-3]. There have been already several industrial processes utilizing heteropoly catalysts [4-7]. Especially, the  $C_4$  green clean processes of MMA production, in which HPCs were used as catalysts for synthesis of methacrylic acid (MAA) from MAL oxidation, were industrialized in the 1980s. The conventional production routes of MMA are acetone-cyanohydrins processes (ACH) that have potential menace to the security of the environment. And the successful replacing of the  $C_4$  processes against ACH has greatly improved the environmental security in MMA production.

Generally, the  $C_4$  process consists of a two-stage oxidation process and one stage esterification, i.e., (a) isobutene to MAL, (b) MAL to MAA and (c) MAA to MMA. However, since the high melting point by-products from dimeric reaction or polymerization of MAA, could lead to the jamming of equipment, a modified  $C_4$  process in which the steps of the (b) and (c) had been accomplished through a coupling reaction has been developed in Asahi Kasei Corporation [6]. The modified  $C_4$  process employs palladium as the main active component of the catalysts. Similarly, the coupling reactions of synthesis MMA from MAL have been carried out over the HPCs catalysts [8].

Cs-containing HPCs exhibited outstanding catalytic performance in one-step synthesis MMA from MAL; however, how and how much Cs functioned on HPCs were not discussed in the former work [8]. A series of different Cs content of Keggin-type HPCs  $H_{3.2-x}Cs_xCu_{0.25}As_{0.1}PMo_{11}VO_{40}$  ( $x$ , 0-2.5) were prepared and used as catalysts

in the coupling reactions, and effects of the different cesium (Cs) content on catalytic performance were investigated in this paper. Moreover, the HPCs were characterized by  $NH_3$ -TPD, TG-pyridine-adsorption/desorption,  $N_2$ -adsorption/desorption, ICP, TG-DSC, FT-IR, XRD and TPR.

## EXPERIMENT

### 1. Preparation of Catalysts

MAL ( $C_4H_6O$ , A. R.) was provided by J&K Chemical LTD. Detailed preparation procedure for  $H_4PMo_{11}VO_{40} \cdot 14.5 H_2O$  is referred to the literature [9]. 25 g of  $H_4PMo_{11}VO_{40} \cdot 14.5 H_2O$  was dissolved with 10 ml of deionized water (solution A), a (0 g, 1.08 g, 3.25 g, 5.40 g) of  $CsNO_3$ , 0.74 g of  $Cu(NO_3)_2 \cdot 3H_2O$ , 0.26 g of  $H_3AsO_3$  (60% aqueous solution) and 5.0 g quinoline was dissolved in 15 ml 5% diluted nitric acid solution, respectively (solution B). Next, solution A was added to solution B and stirred strongly for 30 min. Then, the water was removed by heating the mixture in an oven at 393 K. 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 673 K for 3 h and in airflow at 623 K for 3 h. The HPCs compositions were  $H_{3.2}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$  (Cs0),  $H_{2.7}Cs_{0.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$  (Cs0.5),  $H_{1.7}Cs_{1.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$  (Cs 1.5) and  $H_{0.7}Cs_{2.5}Cu_{0.25}As_{0.1}PMo_{11}VO_{40}$  (Cs 2.5), respectively.

### 2. Reaction Study

All of reactions were conducted in a 10 mm inner diameter stainless steel tubular reactor. Typically, 3 ml of catalyst was loaded in the reactor to give a catalyst bed about 3 cm in height. An electrical furnace equipped with a temperature controller heated the reactor. Mass flow controllers controlled the flow rate of air and  $N_2$ . Water and Methanol (MeOH) were fed by a mini-pump in a certain proportion. MAL (containing 100 ppm hydroquinol) 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 sub-

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: xiajunguo@sohu.com

strates were analyzed by an on-line TCD gas chromatograph equipped with a TDX-01B column for  $N_2$ ,  $O_2$ , CO and  $CO_2$  at 313 K. The liquid condensates of MMA, MAL, MAA, acetic acid and MeOH were analyzed by an FID gas chromatograph using a PEG-20M column. The carbon balance usually exceeded 94%. The main by-products of the coupling reaction were analyzed and their nature determined by a VARIAN HPLC and a SHIMADZU-QP5000 GC-MS.

### 3. Characterization

The chemical composition of the samples was determined by using ICP (IRIS Intrepid II XSP, Thermo). Surface areas of the samples were measured with a Thermo Sorptomatic surface area analyzer and standard multipoint BET analysis methods. IR spectra were recorded on a Bruker Tensor FT-IR with potassium bromide (KBr) at the ratio 1 : 150. XRD was characterized by Bruker D-8 Focus. TG-DTA was measured by Beijing Hengjiu Instruments. The acid properties of the HPCs were studied by TG-pyridine-adsorption/desorption using Beijing Hengjiu Instruments. TPD and TPR were carried out by using Thermo TPD/R/O 1100 Series.

## RESULTS AND DISCUSSION

### 1. Catalyst Characterization

#### 1-1. Acid Property, Chemical Compositions and Surface Area

Acid properties of the HPCs with different Cs content were ex-

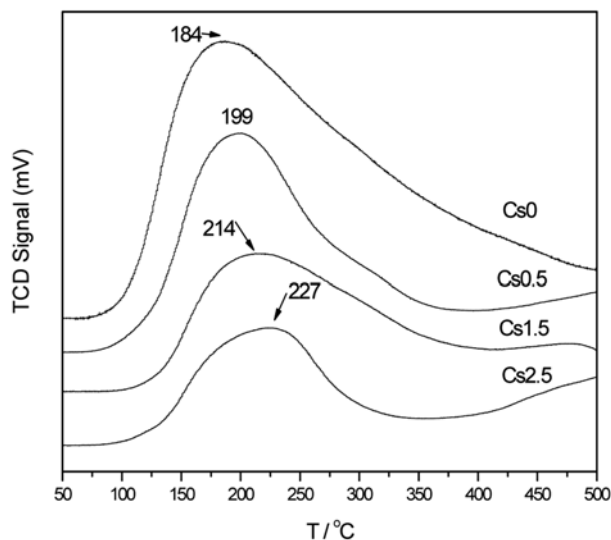


Fig. 1. TPD of the HPCs.

plored by  $NH_3$ -TPD and TG-pyridine-adsorption/desorption to determine the quantity of acid sites and the distribution of acid strengths of the HPCs [10]. Fig. 1 shows the profiles of  $NH_3$  desorbed of the HPCs. All samples presented a broad profile, revealing that the acid property including both bulk acid sites and surface acid sites was widely distributed. With the increasing of Cs content, the acid strength of catalysts increased gradually, the culminations of the desorbed ammonia peaks of Cs0, Cs0.5, Cs1.5 and Cs2.5 were located at 184 °C, 199 °C, 214 °C and 227 °C, respectively. The quantity of acid sites of the HPCs is exhibited in Table 1. The results of TPD and TG-pyridine-adsorption/desorption showed a similar trend that the quantity of acid sites decreased from Cs0 to Cs 2.5. On the other hand, the surface area of the HPCs increased with the increasing of Cs content, which was similar to the reports of the literature [11].

#### 1-2. TG-DTA

Cs0, Cs0.5, Cs1.5 and Cs2.5 that had been dehydrated at 100 °C for 0.5 h were studied by TG-DSC. As shown in Fig. 2, an obvious difference occurred between Cs0 and the other three kinds of Cs-containing HPCs. The reason may be that  $Cs^+$  modified the crystal structure of the  $H_4PMo_{11}VO_{40}$  due to their bigger ionic radius.

The weight loss peaks of Cs0, Cs0.5, Cs1.5 and Cs2.5 are shown in Table 2; the peaks at near 200 °C (L.T.) were 75.2%, 65.8%, 49.5% and 43.6% of the total weight loss, respectively. Generally, the water lost weight at near 200 °C was connected with protons by hydrogen bonds and formed hydrogen protons [5]; the quantity of hydrogen protons determined the main acid amount of catalysts. Cs0 and Cs0.5 had more weight loss peaks of water than Cs1.5 and Cs2.5 at near 200 °C, which well corresponded with the acid amount of TPD in Table 1. And the weight loss peak of M.T. was attributed to weight loss of all of water. Comparing TG-DTA of pure  $H_4PMo_{11}VO_{40}$  with that of Cs0, the weight loss peak of H.T. might be ascribed to gasification of quinoline, which was added into the HPCs to improve the surface area and structural stability but decreased the quantity of acid sites of the HPCs [8].

#### 1-3. FT-IR

Heteropoly anions (primary structure of oxoanions) can be determined by FT-IR. V atoms, as coordinating atoms or else V species, can also be determined by FTIR [11]. Effects of V atoms on catalytic performance of HPCs are related to surrounds of V atoms' location. Jing et al. reported that V atoms located in primary structure of oxoanions as coordinating atoms had the best catalytic performance [12]. Fig. 3 shows infrared spectra of the HPCs with different Cs content after pretreatment. The catalysts exhibited four main characteristic FT-IR bands at 1,054-1,064  $cm^{-1}$ , 954-961  $cm^{-1}$ , 860-880  $cm^{-1}$  and 740-790  $cm^{-1}$ , attributable to  $\nu_{as}$  (P-Oi),  $\nu_s$  (Mo=

Table 1. Surface area, acidity and chemical compositions of the HPCs

Theoretical composition	S (BET) (m <sup>2</sup> )	Site·g <sup>-1a</sup> 10 <sup>-19</sup>	Acidity <sup>b</sup> Mol(NH <sub>3</sub> )g <sup>-1</sup> ·10 <sup>-4</sup>	Practical atomic ratio			
				Mo	P	V	Cs
Cs0	4.2	7.30	50.4	11.6	0.8	1.0	0
Cs0.5	15.6	3.17	38.9	11.2	0.8	0.8	0.48
Cs1.5	38.2	1.62	29.5	11.0	1.2	1.3	1.60
Cs2.5	64.5	0.61	25.0	11.3	0.9	0.9	2.38

<sup>a</sup>The quantity of acid sites was obtained from TG-pyridine-adsorption/desorption.

<sup>b</sup>The quantity of acid sites was obtained from  $NH_3$ -TPD.

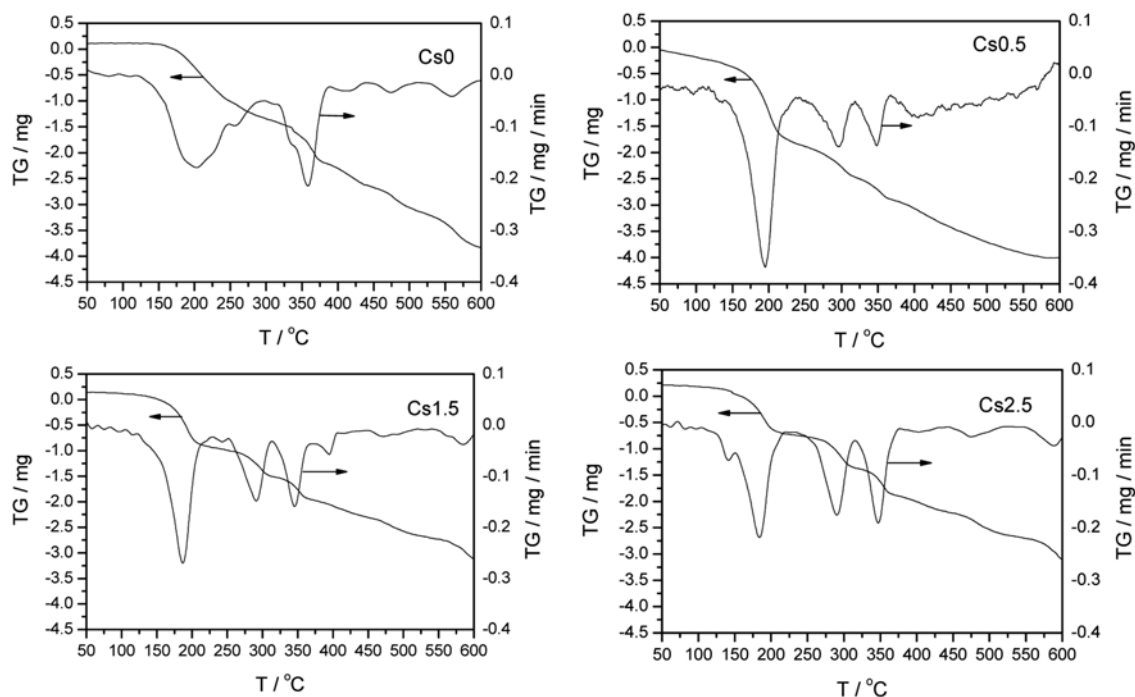


Fig. 2. TG-DSC of the HPCs.

Table 2. Weight loss proportion of the HPCs

HPCs	L.T. (200 °C)	M.T. (300 °C)	H.T. (350 °C)
Cs0	75.2%	--	25%
Cs0.5	65.8%	19.1%	15%
Cs1.5	49.5%	26.6%	23.9%
Cs2.5	43.6%	30.9%	25.5%

L.T.-Low Temperature; M.T.-Middle Temperature; H.T.-High Temperature

Ot),  $\nu_s$  (Mo-Ob-Mo), and  $\nu_s$  (Mo-Oc-Mo), respectively [13-17]. Oi refers to O atom common to  $\text{PO}_4$  tetrahedron and a trimetallic edge shared  $\text{MoO}_6$  octahedra, the  $\text{Mo}_3\text{O}_{13}$  triplet; Ob refers to the O atom connecting two  $\text{Mo}_3\text{O}_{13}$  units by corner sharing; Oc refers to the O atom connecting two  $\text{MoO}_6$  octahedra inside a  $\text{Mo}_3\text{O}_{13}$  unit by edge sharing; and Ot refers to the terminal O atom. Note that a minor peak at about  $1,034\text{ cm}^{-1}$  was observed over Cs0, which was characteristic of the band  $\nu(\text{V}=\text{O})$  in free  $\text{V}_2\text{O}_5$ . And another peak at  $1,076\text{ cm}^{-1}$  occurred over Cs0.5, Cs1.5 and Cs2.5, which was ascribed to the band of V atom substituting for Mo as coordinating atoms in the primary structure of oxoanions. With the increasing of Cs, an increasing trend of the band at  $1,076\text{ cm}^{-1}$  in intensity can be observed [11,17-18]. Meanwhile, the vibration frequency of  $\nu_s$  (Mo=O) shifted down when Cs substituted for hydration proton.  $\text{Cs}^+$  improved the structural stability of Cs-containing HPCs. However, Cs0 was unstable; the partial V species segregated from the Keggin anion and formed free  $\text{V}_2\text{O}_5$  in secondary structure of Cs0. 1-4. XRD

Primary structure of HPCs is stable, while the secondary structure (crystal structure) is unstable and easy to change according to surroundings. We can get the data of the HPCs' secondary structure by XRD. As shown in Fig. 4(A), the XRD data were collected

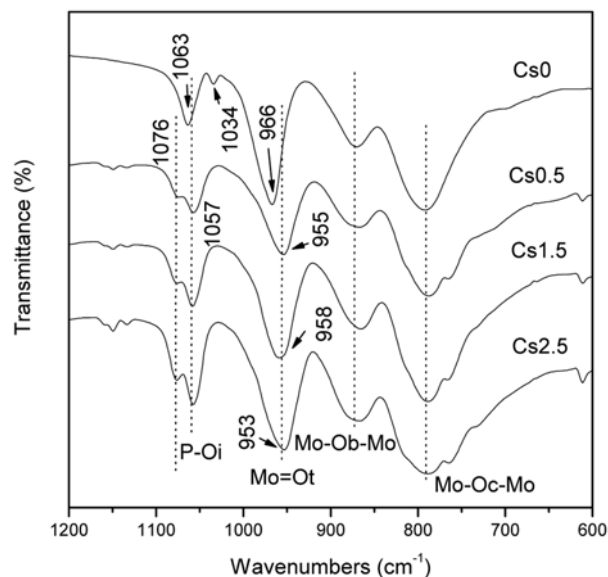


Fig. 3. FT-IR of the HPCs.

over the HPCs before pretreatment to investigate the phase composition as well as the structural stability. The main XRD lines were at  $2\theta=7.2^\circ, 7.5^\circ, 8.4^\circ, 8.9^\circ, 9.3^\circ, 28.0^\circ, 28.5^\circ, 29.0^\circ$ , which might be assigned to hydrogen protons of the secondary structure. With the increasing of  $\text{Cs}^+$  substitution, the amount of hydrogen protons decreased, and the intensity of the lines decreased obviously, too. Another phase that was detected in the HPCs with  $2\theta$  diffraction bands at  $10.7^\circ, 18.5^\circ, 23.9^\circ, 26.2^\circ, 30.4^\circ, 35.8^\circ$  and  $39^\circ$ , were assigned to  $\text{Cs}^+$ -substituted HPCs [11,16,19]. After pretreatment, the XRD data of HPCs are shown in Fig. 4(B); the lines at  $2\theta=7.2^\circ, 7.5^\circ, 8.4^\circ, 8.9^\circ, 9.3^\circ, 28.0^\circ, 28.5^\circ, 29.0^\circ$  disappeared. However, the intensity of lines

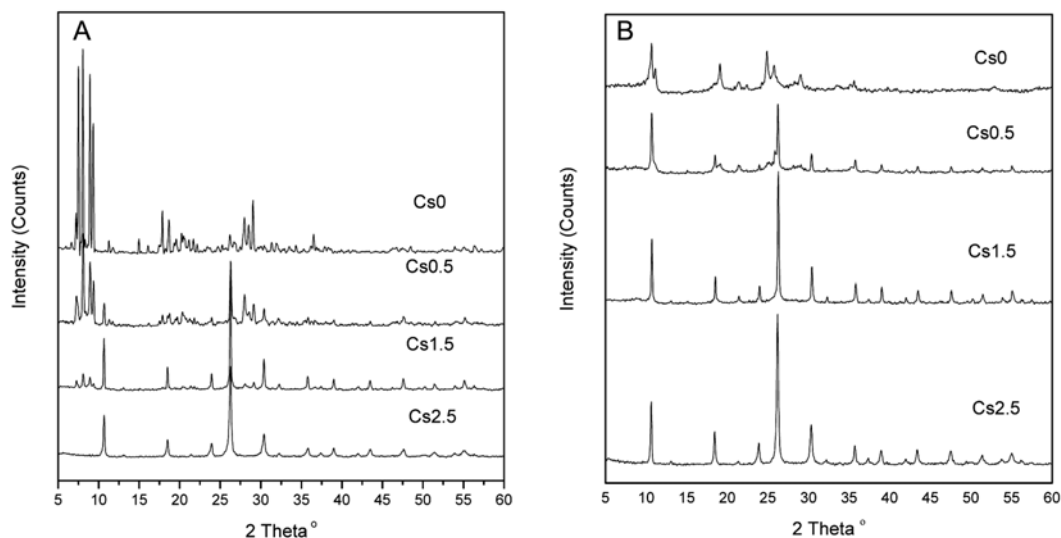


Fig. 4. XRD of the HPCs. A Before pretreatment; B After pretreatment.

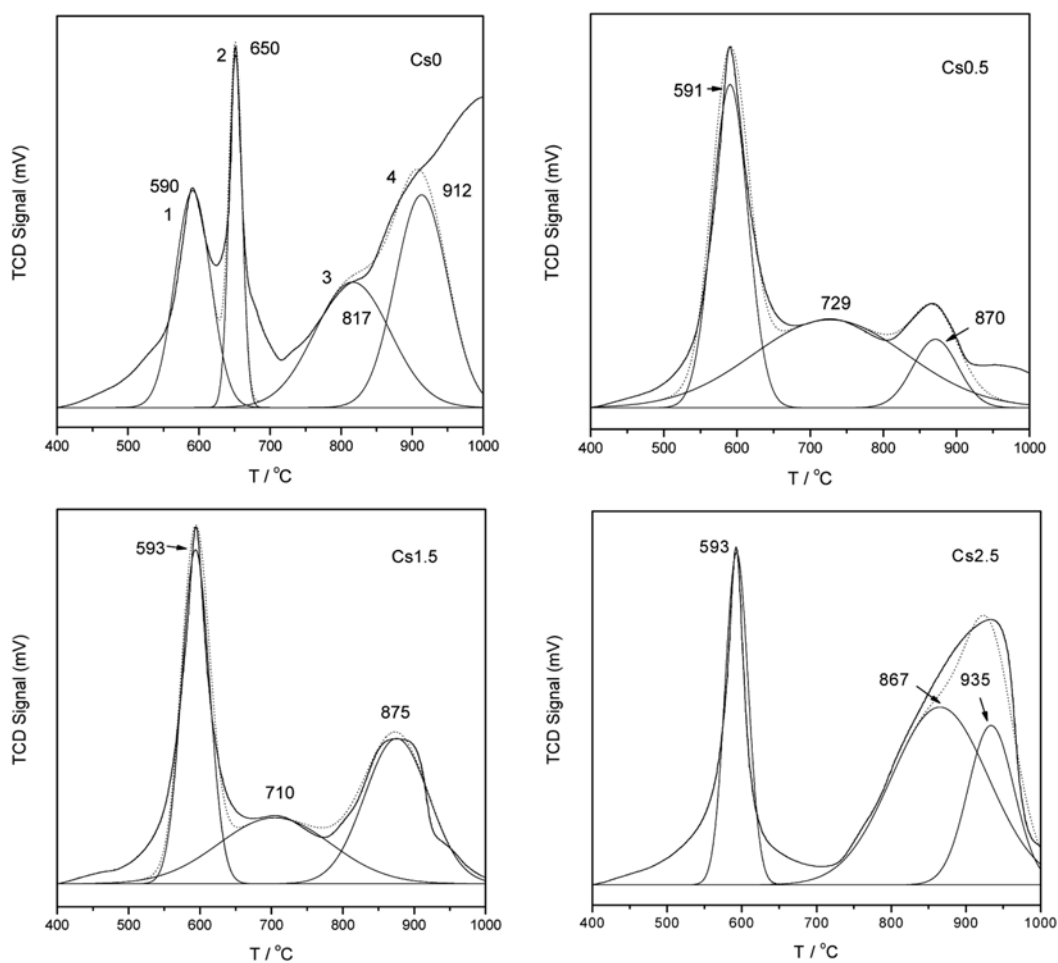


Fig. 5. TPR of the HPCs.

at 10.7°, 18.5°, 23.9°, 26.2°, 30.4°, 35.8° and 39° increased with the increasing of Cs content. As a result, Cs-containing HPCs had better crystal stability than Cs0; moreover, the greater content of Cs corresponded to a more stable crystal structure.

#### 1-5. TPR

Redox property of the HPCs can be measured by scanning tunneling microscopy (STM), UV-visible spectroscopy or H<sub>2</sub>-TPR [20, 21]. The redox property of the HPCs was measured by H<sub>2</sub>-TPR in

**Table 3. TPR peaks proportion of the HPCs**

HPCs	L.T. (591 °C)	M.T. (729 °C)	H.T. (870 °C)
Cs0.5	41.2%	47.9%	10.9%
Cs1.5	35.7%	28.5%	35.8%
Cs2.5	24.1%	53.2% (867 °C); 22.7% (935 °C)	

L.T.-Low Temperature; M.T.-Middle Temperature; H.T.-High Temperature

this paper. TPR profiles of the HPCs are presented in Fig. 5. With the increasing of Cs content, the reductive peaks of Cs0.5, Cs1.5 and Cs2.5 showed a regular change, as shown in Table 3. The HPC with higher Cs content corresponded to a small reductive L.T. peak and a large reductive H.T. peak. On the contrary, the HPC with lower Cs content corresponded to a large L.T. reductive peak and a small H.T. reductive peak. However, the reductive peaks over Cs0 exhibited an irregular TPR profile; the reason may be ascribed to its lower structural stability.

Mo as main coordinating atom in the primary structure of oxoanions occurred in three kinds of states of  $\text{Mo}^{6+}$ ,  $\text{Mo}^{4+}$  and Mo [22]. The location and the percentage of the reductive peaks over Cs0.5, Cs1.5 and Cs2.5 are shown in Table 3. The L.T. reductive peaks at near 591 °C were 41.2%, 35.7% and 24.1% of the total reductive peaks, respectively. The larger peak of L.T. corresponded to a higher reductive activity. As a result, Cs0.5 had the best reductive activity. However, Cs2.5 had the higher structural stability, its L.T. reductive peak was the least, and its reductive peaks of M.T. and H.T. shifted up to high temperature. Therefore, Cs improved the structural stability and decreased reducibility of the HPCs; and the difference of structural stability may lie in that  $\text{Cs}^+$  improved the structural stability of V as coordinating atoms and changed the proportion of the different reduction states of Mo ions.

## 2. Catalytic Testing

Catalytic performance of the HPCs with different Cs content is shown in Table 4. Analyses of products were collected when the reaction was at a steady state. Each of the data points over a certain catalyst was an average of at least of three separate product analyses.

The Cs-containing HPCs had better catalytic performance than Cs0. In particular, the total selectivity of MMA and MAA was up to 90.3%, and the selectivity of MMA was 44.6% with 93.3% MAL conversion over Cs1.5. Generally, MAL oxidation was a surface-type reaction [5,6]. And a greater acid amount improved the selec-

tivity of MMA in the coupling reaction. As known from Table 1 and Table 4, a greater surface area corresponded to a higher MAL conversion.

FT-IR indicated that V atoms segregated from the primary structure of oxoanions over Cs0 and formed free  $\text{V}_2\text{O}_5$  in secondary structure of Cs0. The by-products, such as  $\text{CO}_2$  or CO, formed easily over  $\text{V}_2\text{O}_5$ , which was a more intense oxidant, because of the lower total selectivity over Cs0. However, V atoms were located in positions of coordinating atoms in the primary structure of oxoanions over Cs0.5, Cs1.5 and Cs2.5, indicating higher structural stability and total selectivity of MMA and MAA than those over Cs0.

Due to the stronger structural stability and the weaker reducibility of Cs2.5, MAL conversion over which was less than that of Cs1.5 though Cs2.5 had the most surface area. On the contrary, Cs0.5 had more intense reducibility and less surface area than Cs1.5 and Cs2.5; MAL conversion over Cs0.5 was less than that of Cs1.5, Cs2.5. As a result, effects of surface area on catalytic activity may be more than that of reducibility.

The commercial catalysts were utilized in synthesis of MAA from MAL, where MAL conversion was from 70 to 90% and selectivity to MAA was from 80 to 85% in MAL oxidation reaction of  $\text{C}_4$  processes [5,6,23,24]. And the Cs-containing HPCs used in the coupling reaction had usually the higher MAL conversion and the total selectivity than those of the commercial catalysts for synthesis of MAA from MAL. The reason was that MAA transformed rapidly into MMA and decreased the partial pressure of MAA, which improved MAL conversion and the total selectivity of MMA and MAA.

## CONCLUSIONS

With the increasing of Cs content, MAL conversion increased in the beginning and then decreased, and the total selectivity of MMA and MAA showed a similar trend. The maximum of MAL conversion and the total selectivity occurred simultaneously over Cs1.5. And a greater quantity of acid sites corresponded to a higher selectivity of MMA. With the increasing of Cs content, the surface area of the HPCs increased, while reducibility and the quantity of acid sites decreased gradually. XRD data of hydrogen protons in the secondary structure were determined in this paper. Cs-containing HPCs had better crystal structural stability. Moreover, the content of Cs was greater, and the crystal structure was more stable.

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**Table 4. Catalytic performances of the HPCs in the coupling reaction\***

HPCs	Conversion of MAL (%)	Selectivity (%)			
		MMA	MAA	Ace.A	$\text{CO}_x$
Cs0	60.5	38.7	27.7	17.0	16.6
Cs0.5	84.6	45.3	37.8	8.5	9.4
Cs1.5	93.3	44.6	45.7	4.4	5.3
Cs2.5	88.6	30.8	55.6	8.6	5.0

\*Above HPCs catalysts with the same mass; Temperature, 300 °C; space velocity was  $400 \text{ h}^{-1}$  and MAL/air/ $\text{N}_2$ / $\text{H}_2\text{O}$ /MeOH was equal to 5/50/22.5/10/12.5 (molar ratio)

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