# Catalytic Activity of V-Substituted $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$ Heteropoly Compounds in Selective Oxidation of Isobutane<sup>1</sup>

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**Abstract**—A series of  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$  (x = 0-3) heteropoly compounds has been prepared and tested in the partial oxidation of isobutane. Catalytic tests show that at 350°C very high selectivity to meth-acrylic acid (60.1%) can be achieved at isobutane conversion of 12.2% over a  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$  catalyst with only one molybdenum atom per unit cell substituted by vanadium. The presence of Te<sup>4+</sup> in the heteropoly compounds appears to interfere with the dehydrggenation step and favor the formation of methacrolein and methacrylic acid.

DOI: 10.1134/S0023158412030068

Harold and Samuel first described the selective oxidation of isobutane with heteropoly catalysts in 1979 [1]. Later, several research groups carried out the oxidation of isobutane catalyzed by heteropoly compounds [2–11]. Many investigations have been done on the modification of molybdophosphoric salts with the Keggin structure. The salts can be modified by substituting protons with potassium or cesium, substituting transition metal ions such as Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup> for counter-cations, or by altervalent replacement (typically V-substitution for Mo). Improvement of catalytic behavior can be observed due to an effective modification process. In addition, other catalytic systems, such as V/MCM-41 and Te-Mo-based mixed oxides have also been used as catalysts for this reaction [12-20]. It has been found that high selectivity to methacrolein (MAL) can be achieved over Te-Mobased mixed oxide catalysts, while high selectivity to methacrylic acid (MAA) was observed with heteropoly compounds.

Earlier we were able to show that tellurium is a very important element that serves to achieve high selectivity to MAL, whereas a phase containing V–Te<sup>4+</sup> is active and selective component in the Mo–V–Tebased oxide catalysts for selective oxidation of isobutane to MAA [12–15], The mixed oxide catalysts appear to have a multifunctional surface structure; Mo<sup>6+</sup> or V<sup>5+</sup> ions are responsible for the activation of isobutane and abstraction of methylene hydrogen, while the abstraction of the methyl hydrogen and  $\alpha$ -hydrogen (from isobutene) is associated with Te<sup>4+</sup> cation and the chemisorption of olefin and insertion of oxygen occur on Mo<sup>6+</sup> ion [12, 21, 22]. However, available information is not sufficient to understand the effect of Te in the heteropoly compounds on the activity and selectivity of catalysts in the partial oxidation of isobutanc. Especially the role of Te in V-substituted heteropoly compound system is far from being understood.

The aim of the work reported here was to explore the ways leading to improvement of selectivity to a desired product in the oxidation of isobutane over heteropolyacid catalysts.

## **EXPERIMENTAL**

## Catalyst Preparation

A series of  $H_{3+x}PMo_{12-x}V_xO_{40}$  (x = 0-3) heteropoly compound catalysts was prepared using already described methods [23], In a typical synthesis, 7.1 g of  $Na_2HPO_4$  was dissolved in 100 mL water and mixed with NaVO<sub>3</sub> that had been dissolved in 100 mL of hot water. The mixture was cooled and acidified to a red color with 5 mL of concentrated sulfuric acid. To this mixture a solution of  $Na_2MoO_4$  was added. Finally, this solution was vigorously stirred while 85 mL of concentrated sulfuric acid was added slowly. Once the water solution was cooled the heteropolyacid was extracted with 400 mL of ethyl ether. After separation, a stream of air was passed through the heteropolyetherate layer to free ether. The solid was dissolved in 50 mL of water, and then allowed to crystallize. The formed crystals were collected by nitration, washed with water, and dried in air.

A series of  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$  heteropoly compounds were prepared as follows. An aqueous solution of telluric acid was added dropwise to an aqueous solution of  $H_{3+x}PMo_{12-x}V_xO_{40}$ , followed by the addition of aqueous solution of cesium carbonate at 80°C. The resulting suspension or solution was evapo-

<sup>&</sup>lt;sup>1</sup> The article is published in the original.



Fig. 1. XRD patterns of  $Cs_2Te_{0.2}H_{0.6 + x}PMo_{12 - x}V_xO_n$ heteropoly compounds.

rated to dryness at 80°C. The powder samples were collected, dried at 110°C for 12 h, and then calcined at 320°C for 2 h. The actual composition of the samples may be  $Cs_2Te_{0.2}H_vPMo_{12-x}V_xO_z$ , but in this paper the catalysts are designated as  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$ .

### Catalyst Characterization

Powder X-ray diffraction patterns (XRD) were collected using a Shimadzu XRD-6000 scanning (4°/min) with Cu $K_{\alpha}$  radiation (40 kV, 30 mA). The Fourier transform infrared spectra (FT-IR) were recorded at room temperature using a NICOLET Impact 410 spectrometer. Specific surface areas of the catalysts were computed using the BET adsorption isotherms of  $N_2$  measured at  $-196^{\circ}C$  (Micronieritics ASAP2010). Scanning electron micrographs (SEM) were taken through a FESEM XL-30 field emission scanning electron microscope. X-ray, photoelectron spectra (XPS) were recorded on aVG ESCA LAB MK-II. X-ray electron spectrometer using  $AlK_{\alpha}$  radiation (1486.6 eV, 10.1 kV). The binding energies for the samples in spectra were referenced to the C1s line at 284.7 eV. The measurement error of the spectra was ±0.2 eV.

## Catalytic Tests

The reaction was performed in a stainless steel tubular fixed bed reactor (16 mm i.d., 400 mm long) at atmospheric pressure. A mass flow controller regulated reaction feed, and a mini-pump fed water. The catalytic reaction conditions was as follows: molar ratio of the feed gas  $i-C_4H_{10}: O_2: N_2: H_2O = 1:1:2:1$ , gas hourly space velocity 1000 mL  $h^{-1}g_{cat}^{-1}$ . The experiments were carried out at 350°C. The products were



Fig. 2. The FT-IR spectra of  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$ heteropoly compounds:  $I-Cs_{2.0}Te_{0.2}H_{0.6}PMo_{12}O_n$ , 2- $Cs_{2.0}Te_{0.2}H_{1.6}Mo_{11}VO_n$ , 3- $Cs_{2.0}Te_{0.2}H_{2.6}PMo_{10}V_2O_n$ , 4- $Cs_{2.0}Te_{0.2}H_{3.6}PMo_9V_3O_n$ .

then fed via heated lines to an on-line gas chromatography for analysis. Methacrolein, methacrylic acid,  $CO_x$  (CO, CO<sub>2</sub>), and acetic acid (HAC) were the main products. Mass balance of carbon  $\geq 97\%$  was typically observed.

# **RESULTS AND DISCUSSION**

# XRD and FT-IR Studies

The X-ray diffraction patterns of the  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$  heteropoly compounds are shown in Fig. 1. Only the diffraction lines typical to molybdophosphoric salts with, a cubic structure [2-6] were present on the diffractograms. No peaks due to MoO<sub>3</sub> were observed on the XRD patterns.

The FT-IR spectra of catalysts are compared in Fig. 2. The bands at 1.060, 965, 866 and 797 cm<sup>-1</sup> can be readily seen which, are characteristic of a Keggin structure [2–6].

The SEM images of  $Cs_{2.0}Te_{0.2}H_{0.6}PMo_{12}O_n$  and  $Cs_{2,0}Te_{0,2}H_{3,6}PMo_9V_3O_n$  are shown in Fig. 3. Sphere morphology of the samples can be easily recognized. The average particle size of the  $Cs_{2,0}Te_{0,2}H_{0,6}PMo_{12}O_n$ spheres near to 1.1 µm can be estimated, while the average particle size of the  $Cs_{20}Te_{0.2}H_{3.6}PMo_9V_3O_n$ spheres appears to be about  $2.6 \,\mu m$ .

Table 1 shows the specific surface area ( $S_{\text{BET}}$ ) of the catalysts. It can be seen that for all samples the surface area of the  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$  catalysts gradually decreases with increasing level of substitution of Mo by V. Moreover, the  $S_{\text{BET}}$  values slightly decrease as the content of Cs in the Cs<sub>2.0</sub>Te<sub>0.2</sub>H<sub>0.6</sub>PMo<sub>12</sub>O<sub>n</sub> catalyst increases.

To gain further insight into the surface structure and properties of these heteropoly compounds. XPS spectra of Cs  $3d_{5/2}$ , Mo  $3d_{5/2}$ , V  $2p_{3/2}$ , Te  $3d_{5/2}$  and P 2p



Fig. 3. SEM images of  $Cs_{2.0}Te_{0.2}H_{0.6}PMo_{12}O_n$  (a) and  $Cs_{2.0}Te_{0.2}H_{3.6}PMo_9V_3O_n$  (b).

region with binding energies were investigated and the results are given in Table 1.

The Mo  $3d_{5/2}$  peak of the catalysts could be resolved into two components at 231.7 and 232.8 eV, which can be assigned to Mo<sup>5+</sup> and Mo<sup>6+</sup> species, respectively [11, 12]. The positions of the peaks indicate that Mo<sup>6+</sup> cations are the main surface species present on the surface of the Cs<sub>2</sub>Te<sub>0.2</sub>H<sub>0.6+x</sub>PMo<sub>12-x</sub>V<sub>x</sub>O<sub>n</sub> catalysts along with small amounts of Mo<sup>5+</sup> ions [Mo<sup>5+</sup>/(Mo<sup>5+</sup> + Mo<sup>6+</sup>)  $\leq$  0.1].

The V  $2p_{3/2}$  peak of the Cs<sub>2</sub>Te<sub>0.2</sub>H<sub>0.6+x</sub>PMo<sub>12-x</sub>V<sub>x</sub>O<sub>n</sub> catalysts could be resolved into two components at 516.2 and 517.3. eV, which can be related to V<sup>4+</sup> and V<sup>5+</sup> species, respectively [11, 12]. It can be thus inferred that vanadium exists on the surface of the Cs<sub>2</sub>Te<sub>0.2</sub>H<sub>0.6 + x</sub>PMo<sub>12 - x</sub>V<sub>x</sub>O<sub>n</sub> catalysts essentially as V<sup>5+</sup> ions.

The Te  $3d_{5/2}$  peak of catalysis could be fitted with two components at 576.2 and 577.3 eV, which can be ascribed to Te<sup>4+</sup> and Te<sup>6+</sup> species, respectively [11, 12]. It can be suggested that a Te<sup>4+</sup> cation occurs in the catalyst surface as the main tellurium ion. At the same time the presence of Te<sup>0</sup> (binding energy of 573 eV) was not observed on the catalysts.

The P 2*p* binding energies of surface phosphorus are very similar (ca. 133.7 eV) for all of the samples, which indicate that P atoms are mainly present as  $P^{5+}$  in the Cs<sub>2</sub>Te<sub>0.2</sub>H<sub>0.6+x</sub>PMo<sub>12-x</sub>V<sub>x</sub>O<sub>n</sub> catalysts [11].

The Cs  $3d_{5/2}$  binding energies of surface cesium are centered on 724.1 eV for the Cs<sub>2</sub>Te<sub>0.2</sub>H<sub>0.6+x</sub>PMo<sub>12-x</sub>V<sub>x</sub>O<sub>n</sub> catalysts, which indicate that Cs<sup>+</sup> cations are the most important surface Cs species [11].

### Catalytic Properties

Table 2 shows the catalytic data for isobutane oxidation over  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$  obtained at different reaction temperatures. The conversion of isobutane gradually increases, while selectivity to MAL and MAA progressively decreases with the increasing reaction temperature. At relatively low reaction temperatures, small amounts of isobutene can be observed, while at higher temperatures isobutene is readily oxidized, it suffers further transformations and cannot be found among the reaction products.

The catalytic results obtained for the oxidation of isobutane over the  $Cs_2Te_{0.2}H_{0.6+x}PMo_{12-x}V_xO_n$  catalysts at 350°C (Table 3) indicate that heteropoly compounds with incorporated the Te-ions are active and selective catalysts in the partial oxidation of isobutane. The conversion of isobutane and selectivity to MAA is considerably improved by substitution of vanadium for molybdenum in the molybdophosphoric system. However, the best catalytic performance can be achieved over  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_{40}$  catalyst with, one molybdenum in the extent of vanadium substitution for molybdenum in the extent of vanadium substitution for molybdenum in the extent of vanadium substitution for molybdenum in the heteropoly compound

Table 1. BET surface area and XPS data for the heteropoly compounds

Sample	$S_{\rm BET},$ m <sup>2</sup> /g	Binding energy, eV					Atomic ratios			
		Cs 3 <i>d</i> <sub>5/2</sub>	Mo 3 <i>d</i> <sub>5/2</sub>	$V 2p_{3/2}$	Te 3 <i>d</i> <sub>5/2</sub>	Р 2р	Cs/P	Mo/P	V/P	Te/P
Cs <sub>2.0</sub> Te <sub>0.2</sub> H <sub>0.6</sub> PMo <sub>12</sub> O <sub>n</sub>	8.8	724.1	233.0	_	577.2	134.3	1.8	11.6	_	0.18
$Cs_{2.5}Te_{0.2}H_{0.1}PMo_{12}O_n$	7.5	724.2	233.2	—	577.2	134.3	2.3	11.7	_	0.18
$Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$	7.3	724.1	233.1	516.7	577.2	134.2	1.9	10.5	0.8	0.19
Cs <sub>2.0</sub> Te <sub>0.2</sub> H <sub>2.6</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>n</sub>	6.2	724.2	233.2	516.8	577.3	134.2	1.9	9.7	1.8	0.17
$Cs_{2.0}Te_{0.2}H_{3.6}PMo_9V_3O_n$	4.5	724.1	233.2	516.9	577.1	134.2	2.0	8.8	2.5	0.18

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Reaction temperature,°C	Conver- sion, %	Selectivity, %								
		$i-C_4^=$	MAL	MAA	СО	CO <sub>2</sub>	$C_3^=$	HAC		
300	5.2	2.2	9.3	69.1	10.3	8.4	traces	0.6		
310	6.5	1.3	9.1	68.2	11.7	8.8	traces	0.8		
320	7.8	0.8	8.9	66.8	12.7	9.7	traces	1.0		
330	9.3	0.5	8.6	64.6	14.2	10.8	traces	1.2		
340	10.8	traces	8.3	62.5	15.5	12.1	traces	1.5		
350	12.2	traces	8.0	60.1	16.8	13.3	traces	1.7		
360	14.6	traces	6.5	55.2	19.3	15.6	0.8	2.5		

**Table 2.** Catalytic properties of  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$ 

Note: Experimental conditions: contact time 3.6 s, catalyst weight 2 g,  $i-C_4H_{10}: O_2: N_2: H_2O = 1:1:2:1$ .

**Table 3.** Isobutane oxidation at 350°C

Catalyst	Conversion %	Selectivity, %							
Catalyst		MAL	MAA	СО	CO <sub>2</sub>	HAC			
Cs <sub>2.0</sub> Te <sub>0.2</sub> H <sub>0.6</sub> PMo <sub>12</sub> O <sub>n</sub>	8.5	9.3	38.3	26.7	18.7	6.7			
$Cs_{2.5}Te_{0.2}H_{1.1}PMo_{11}VO_n$	6.6	7.7	15.4	21.2	23.1	26.1			
$Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$	12.2	8.0	60.1	16.8	13.3	1.7			
$Cs_{2.0}Te_{0.2}H_{2.6}PMo_{10}V_2O_n$	10.7	7.8	52.7	22.3	15.6	1.5			
$Cs_{2.0}Te_{0.2}H_{3.6}PMo_9V_3O_n$	9.6	7.6	48.9	23.5	16.2	3.7			

catalysts deteriorates the catalytic behavior. Furthermore, by comparing the catalytic performance of  $Cs_{2.0}Te_{0.2}H_{0.6}PMo_{12}O_n$  and  $Cs_{2.5}Te_{0.2}H_{1.1}PMo_{11}VO_n$  it can be readily recognized that  $Cs_{2.5}$ -containing heleropoly compound shows poor catalytic properties, indicating that activity and selectivity decrease when more than two cesium cations per unit cell are introduced in exchange for protons.

Figure 4 shows the results of the isobutane oxidation catalyzed by  $Cs_2H_{2.0}PMo_{11}VO_{40}$  and  $Cs_{2.0}Te_{0.2}-H_{1.6}PMo_{11}VO_{40}$  at 350°C. It can be seen that the substitution of protons by tellurium in the cesium salt has a strong positive effect on the selectivity to MAA and MAL. At the same time, a minor increase in activity was observed for the Te-substituted heteropoly compounds.

It has been generally accepted that the isobutane activation is associated with the presence of  $Mo^{6+}$  surface site [21], while  $V^{4+}$  ion can enhance catalytic activity and favor the formation of the redox cycle  $V^{4+} + Mo^{6+} \leftrightarrow V^{5+} + Mo^{5+}$  to improve the redox capability of Mo species. In addition, a  $(Mo^{6+})_2$  site is associated with the insertion of oxygen atom. Our previous experiments indicated that Te-Mo-based mixed oxides are very active and selective in the partial oxidation of.isobutane [13–16]. However, in contrast to the results obtained over heteropoly compounds, the main product in the isobutane oxidation over Te-Mo-based mixed oxides was MAL rather than MAA, Therefore,

the role of tellurium is less than completely understood. Over the cesium salts, the selectivity to MAL and MAA increases with the introduction of small amount of tellurium. This observation implies that the main role of  $Te^{4+}$  ions lies in the transformation of the reaction intermediate into MAA, which accounts for a considerable increase in selectivity to MAA. It appears that  $Te^{4+}$  cations are active in the dehydrogenation



**Fig. 4.** Selective oxidation of isobutane over CS  $Cs_2H_{2.0}PMo_{11}VO_{40}$  (A) and  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$  (B) catalysts at 350°C.

step, because the efficiency of these ions in the abstraction of hydrogen has already been repeatedly reported for many oxidation reactions of alkenes and alkanes [22].

The data outlined above suggest that by substituting one vanadium atom per unit cell for molybdenum it is possible to improve catalytic activity of the molybdophosphoric system in the selective oxidation of isobutane. However, an increased level of replacement of protons by cesium deteriorates the catalytic performance. It was found that the substitution of protons by small amounts of tellurium in the cesium salt is favorable for the formation of MAL and MAA. Under the reaction conditions used, the  $Cs_{2.0}Te_{0.2}H_{1.6}PMo_{11}VO_n$ catalyst showed the best selectivity to MAL + MAA (68.1%) with yield of 8.3% at 350°C.

This work was supported by Jilin province (20090591 and 201105006), Jilin University (450060445017) and Specialized Research Fund for the Doctoral Program of Higher Education (20100061120083).

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