

## Partial reduced heteropoly compound catalysts for the selective oxidation of propene

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### Abstract

A newly designed procedure was used for the preparation of partial reduced heteropoly compound catalysts. The catalytic activities of the partial reduced catalysts for the selective oxidation of propene were tested. IR, Raman, ESR, TPO and TPR were used for the characterization. The  $\text{Cu}_{1.2}\text{V}_2$  catalyst seems to be the most active catalyst due to the most containing of  $\text{V}^{4+}$ . © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The catalytic function of heteropoly compounds (HPCs) has attracted much attention in the last two decades [1]. There are already several industrial processes in which heteropoly catalysts are utilized. Many known and new heteropoly compounds are being applied to a wide variety of reactions. It is evident that the research activity on heteropoly catalysis is very high and still growing [2].

HPCs in the solid state are ionic crystals consisting of large polyanions, counter-cations, water of crystallization, and other molecules. The structure of polyanions, the 3-D arrangement, and the structure of solid HPCs as assembled, such as the size of the parti-

cles, the pores structure, and the distribution of HPCs in supports, etc. are described as the primary structure, the secondary structure and the tertiary structure of HPCs, respectively. Different polyanions and counter-cations greatly influence the structure of solid HPCs, which leads to various catalytic functions [3].

Polyanions with Keggin structure are well known as oxidation and acid catalysts, in which the redox and acid–base properties can be modified by choosing different heteroatoms, addenda atoms or substituting the addenda atoms with altermultivalent atoms [4]. In recent years, considerable attention has been paid to the modification of oxidative properties by the substitution of the addenda Mo atoms by the altermultivalent atoms. The mixed molybdovanadophosphate  $\text{H}_{3+x}[\text{PMo}_{12-x}\text{V}_x\text{O}_{40}]$  is found to be most selective in the oxidation of low hydrocarbons [5].

Recently, the importance of the oxidation degree of addenda atoms in HPCs used as heterogeneous oxidation catalysts was realized, in addition to other key

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factors affecting on catalytic performance of HPCs catalysts mentioned above. It has been found that a partial reduced HPC shows best performance for the selection oxidation of alkanes [6].

In this paper, partial reduced HPCs were prepared by a newly designed procedure, which exhibited enhanced catalytic activity and selectivity in the oxidation of propene to acrolein and acrylic acid in a single stage.

## 2. Experimental

### 2.1. Catalyst preparation

Four catalysts of heteropoly compound with Keggin structure were prepared according to our previous work. They have the common composition of  $H_x-Cu_{1.2}-P-Mo_{10}-V_2-As_{0.6}-O_{40}$ . The P, Mo, and V were active elements for the oxidation of low hydrocarbons. Earlier studies have shown that the addition of As increased the selectivity, and the redox properties of  $Cu^{2+}$  made HPCs more active.

Among four catalysts, three are partial reduced HPCs, and one is non-reduced HPC. In order to control the degree of reduction, the partial reduced HPCs were prepared using Cu, pentaerythritol, Cu and pentaerythritol as reductant, respectively. The typical procedure is shown as following. A certain amount of  $H_3PO_4$ ,  $H_3AsO_4$ ,  $MoO_3$ ,  $V_2O_5$ , Cu or CuO were mixed by molar ratio (P:As:Mo:V:Cu = 1:0.6:10:2:1.2) with water and refluxed at 70–80°C for 48–72 h to form a homogeneous solution. Then 0.8 mol pentaerythritol was added into the solution by stirring. The heteropoly compound was crystallized from the solution by the evaporation in a water bath at 100°C. The crystal was dried at 100°C and calcined at 300°C under a nitrogen atmosphere for 2 h to remove the water and the pentaerythritol thoroughly. The supported catalysts were prepared by conventional impregnating procedures on porous  $SiO_2$  with a loading of 25 wt.% HPCs.

### 2.2. Catalytic reaction

Catalytic reactions were carried out in a tubular fix-bed microreactor-gas chromatography. The volume of the catalysts was 2 ml (40–60 mesh). The products

were analyzed online by a 102G gas chromatography with a porapak-Q column, a 5 Å molecular sieve column ( $\Phi$ : 6 × 2000 mm), and a FID detector. The reaction conditions were:  $N_2/O_2/propene = 43/9/4$ ,  $T = 633$  K.

### 2.3. Catalyst characterization

IR spectra of the catalysts were taken on a Perkin-Elmer 683 IR Spectrometer by KBr tablet method. Raman spectra were obtained on a LabRamI Laser Microscope-Raman Spectrometer using an Ar ion laser (wavelength 514.5 nm). The operation conditions were 50 times of magnification of lens, 20 W of output power, 20 s of scanning time, and twice accumulations. ESR spectra were carried out on an ER200D-SRC Electron Spin Resonance Spectrometer. The operation conditions were modulation frequency 12.5 kHz, central field 3450G, scanning width 3000G, output power 20.4 mW, modulation width 6.3 Gpp. The characterization of TPO and TPR was carried out on a BET instrument. The samples were pretreated at 250°C under Ar atmosphere for 30 min. The TPO experiments were carried out under an atmosphere of mixed  $O_2$ -Ar containing 5% (v/v)  $O_2$ . The final temperature was 400°C; And the samples with the same pretreatment as above were used for TPR experiments as well. The TPR experiments were carried out under an atmosphere of mixed  $H_2$ -Ar containing 10% (v/v)  $H_2$  with a temperature rate of 10, 20, 30°C  $min^{-1}$ , respectively. The final temperature was 600°C.

## 3. Results and discussion

### 3.1. IR

The IR spectra of the four catalysts are shown in Fig. 1. Four strong absorption peaks near 1061, 958, 871 and 790  $cm^{-1}$ , which are attributed to the vibration of P–O bond, Mo=O bond, and Mo–O–Mo bond of different locations, respectively show that four catalysts all contain heteropoly anions of Keggin structure. The vibration of V–O bond could not be seen because of the very strong absorption of Mo–O bond. The only difference between the four spectra is the different relative intensity of the Mo–O bonds versus the P–O

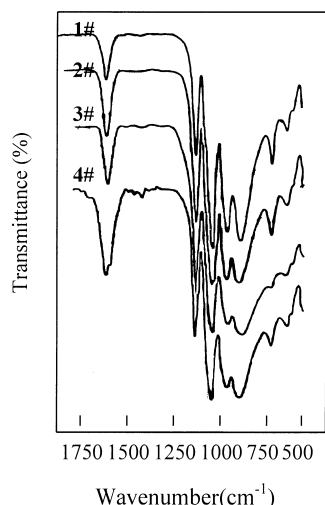


Fig. 1. IR spectra of four catalysts. (1#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$ ; (2#)  $\text{Cu}_{1.2}^0\text{V}_2$ ; (3#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$  and pentaerythritol; (4#)  $\text{Cu}_{1.2}^0\text{V}_2$  and pentaerythritol.

bond. It appears that the relative intensity of the Mo–O bonds versus the P–O bond of the heteropoly compounds gradually decreases with the deeper reduction, which indicates that the amount of the Mo–O bonds in the heteropoly anions is decreased by reduction.

### 3.2. Raman

The Raman spectra of the four catalysts are shown in Fig. 2, and the main absorption peaks are shown in Table 1. Generally the bands in the frequency range of  $310\text{--}370\text{ cm}^{-1}$  are for Mo=O bending,  $500\text{--}650\text{ cm}^{-1}$  for symmetric Mo–O–Mo or Mo–O–V deformations,  $700\text{--}850\text{ cm}^{-1}$  for antisymmetric Mo–O–Mo or Mo–O–V stretching,  $900\text{--}1000\text{ cm}^{-1}$  for symmetric and antisymmetric Mo=O or V=O stretches. There are two strong absorbing peaks near  $999$  and  $973\text{ cm}^{-1}$  in the spectra of  $\text{Cu}_{1.2}^{2+}\text{V}_2$  and  $\text{Cu}_{1.0}^0\text{V}_2$ ,

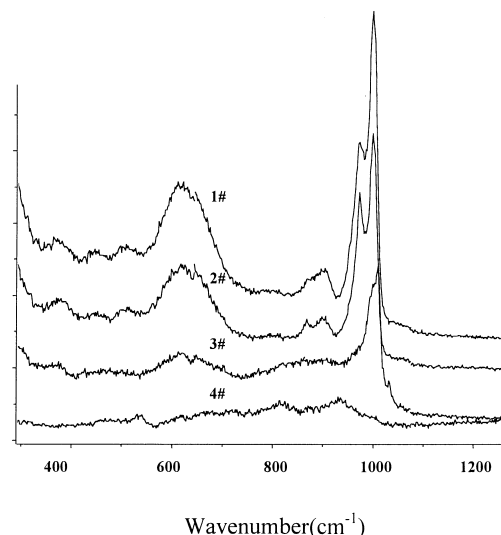


Fig. 2. Raman spectra of four catalysts.

and the two peaks become weak or disappeared when the pentaerythritol was used. In addition, the sample  $\text{Cu}_{1.2}^{2+}\text{V}_2$  and pentaerythritol produces a peak near  $1001\text{--}1015\text{ cm}^{-1}$ , which is attributed to  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  phases. And in the spectrum of the sample  $\text{Cu}_{1.2}^0\text{V}_2$  and pentaerythritol, the characteristic peaks of the heteropoly compound can hardly be observed. It indicates that single and homogeneous phase of heteropoly compound does not exist when the pentaerythritol is used as reductant. Molybdenum oxide or vanadium oxide may due to the destruction of the polyanion structure of the heteropoly compound.

### 3.3. ESR

The ESR spectra of the four catalysts are listed in Fig. 3. The asymmetric peak appeared in the normal

Table 1  
Main Raman absorbing peaks of four catalysts

Entry	Catalysts	Wave number ( $\text{cm}^{-1}$ )
1#	$\text{Cu}_{1.2}^{2+}\text{V}_2$	999, 973, 896, 617, 508, 447, 364
2#	$\text{Cu}_{1.2}^0\text{V}_2$	999, 973, 898, 867, 617, 510, 452, 379
3#	$\text{Cu}_{1.2}^{2+}\text{V}_2$ and pentaerythritol	1013, 1010, 614, 375
4#	$\text{Cu}_{1.2}^0\text{V}_2$ and pentaerythritol	931, 822, 721, 676, 662, 537, 532

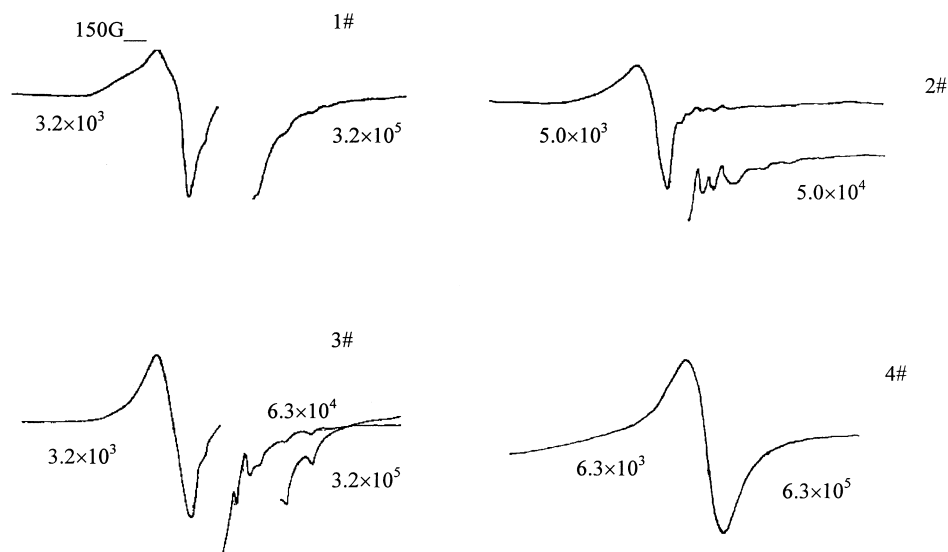


Fig. 3. ESR spectra of four catalysts. (1#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$ ; (2#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$  and pentaerythritol; (3#)  $\text{Cu}_{1.2}^0\text{V}_2$ ; (4#)  $\text{Cu}_{1.2}^0\text{V}_2$  and pentaerythritol.

magnetic field is the signal of  $\text{Cu}^{2+}$ . The  $g_{\parallel}$  value of  $\text{Cu}^{2+}$  ion is 2.23–2.27 and the  $g_{\perp}$  value is around 2.07–2.08. The asymmetric peak shows an aberration in the octahedron coordination of  $\text{Cu}^{2+}$ . The resolved lines observed on the right-hand side of the  $\text{Cu}^{2+}$  signal can be attributed to  $\text{Mo}^{5+}$  and  $\text{V}^{4+}$ . The signals of  $\text{Mo}^{5+}$  and  $\text{V}^{4+}$  are very weak because of the very strong signal of  $\text{Cu}^{2+}$ . The most strong signal of  $\text{V}^{4+}$  appears in the spectrum of the sample 3#, which results from the high amount of  $\text{V}^{4+}$  in  $\text{Cu}_{1.0}^0\text{V}_2$ . Strangely, in the sample 4#, the signal of  $\text{Mo}^{5+}$  and  $\text{V}^{4+}$  can hardly be observed, and the signal of  $\text{Cu}^{2+}$  shows a symmetric octahedron coordination of  $\text{Cu}^{2+}$  ions. During the reduction by Cu Powder, 2.4 mol electrons transferred from the  $\text{Cu}^0$  to the Keggin anions ( $1.2\text{Cu}^0 - 2.4e \rightarrow 1.2\text{Cu}^{2+}$ ,  $2[\text{PMo}_{10}^{6+}\text{V}_2^{5+}\text{O}_{40}]^{5-}\text{As}_{0.6} + 2.4e \rightarrow 2[\text{PMo}_{10}^{5+}\text{V}_2^{4+}\text{O}_{40}]^{6.2-}\text{As}_{0.6}$ ). The element As, which was added to partly substitute the position of P, connected two Keggin structures into one. So in fact the amount of the electrons obtained per Keggin structure is 1.2.

### 3.4. TPO and TPR

The TPO curves of the four catalysts are shown in Fig. 4 and Table 2. It shows that the heteropoly

compounds prepared by Cu and  $\text{Cu}^+$  pentaerythritol have consumption peaks of  $\text{O}_2$  in the range of the lower temperature (below  $220^\circ\text{C}$ ), while all the four catalysts have a consumption peak of  $\text{O}_2$  in the range of the higher temperature (above  $220^\circ\text{C}$ ). Among them, the heteropoly compounds prepared by Cu has two peaks near 75 and  $150^\circ\text{C}$ ; the catalyst reduced by Cu powder and pentaerythritol has no peaks appeared near  $75^\circ\text{C}$ , but only a small peak near  $150^\circ\text{C}$ , and the consumption of  $\text{O}_2$  is much lower than that

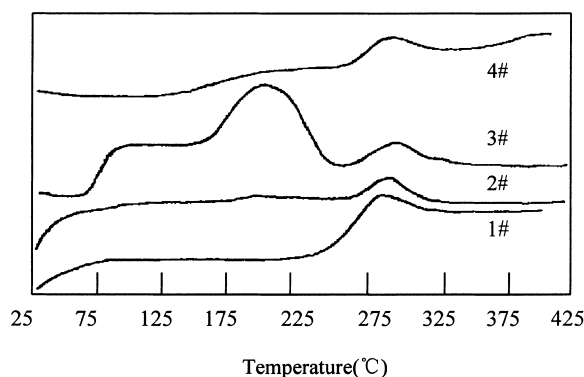


Fig. 4. The TPO curves of the four catalysts. (1#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$ ; (2#)  $\text{Cu}_{1.2}^{2+}\text{V}_2$  and pentaerythritol; (3#)  $\text{Cu}_{1.2}^0\text{V}_2$ ; (4#)  $\text{Cu}_{1.2}^0\text{V}_2$  and pentaerythritol.

Table 2  
TPO value of four catalysts

Catalysts	$T_m$ ( $^{\circ}\text{C}$ )	$\text{O}_2$ consumption of catalyst per unit weight ( $\mu\text{mol g}^{-1}$ )
$\text{Cu}_{1.2}^{2+}\text{V}_2$	287.5	271.2
	90	287.0
$\text{Cu}_{1.2}^0\text{V}_2$	205	891.7
	300	205.8
$\text{Cu}_{1.2}^{2+}\text{V}_2$ and pentaerythritol	290	170.4
	200	29.5
$\text{Cu}_{1.2}^0\text{V}_2$ and pentaerythritol	295	173.5

on the catalyst reduced by Cu powder; The catalyst reduced by pentaerythritol only has oxidation peaks in the range of the higher temperature. Compared to that of the non-reduced catalyst, the temperatures of oxidation peaks of the three partial reduced heteropoly compounds in the range of the higher temperature all shift to higher temperature, starting around  $263^{\circ}\text{C}$ , and the apex is around  $296\text{--}300^{\circ}\text{C}$ . From the results we can conclude that: 1. The heteropoly compounds exist in a reduced state when prepared by reductants, either Cu powder or pentaerythritol. 2. There are three types of reduction centers on the surface of the heteropoly acid catalysts. New reduction center was produced when Cu powder was used. When pen-

taerythritol was used, however, the reduction center disappeared.

The TPR characterization with and without pretreatment and the activation energy of  $\text{H}_2$  of the four catalysts are shown in Figs. 5 and 6 and Table 3. It is shown that two peaks appeared over  $400^{\circ}\text{C}$  for both catalysts with and without pretreatment. However, no reduction peak appeared in the range of  $150\text{--}350^{\circ}\text{C}$  if the catalysts were pretreated by  $\text{O}_2$  to  $400^{\circ}\text{C}$ , while two peaks appeared in the range of  $150\text{--}350^{\circ}\text{C}$  if the catalysts were not pretreated by oxidation. It is suggested that the reduction peaks in the range of  $150\text{--}350^{\circ}\text{C}$  may be attributed to the redox procession between the HPC with higher assembly structure and the hydrogen,

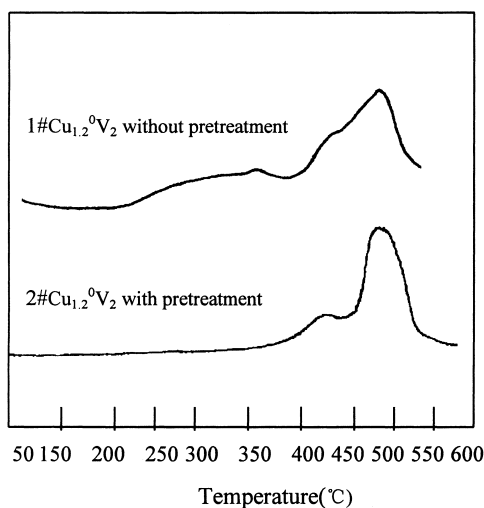


Fig. 5. The TPR of  $\text{Cu}_{1.2}^0\text{V}_2$  with and without pretreatment. Temperature rate:  $30^{\circ}\text{C min}^{-1}$ .

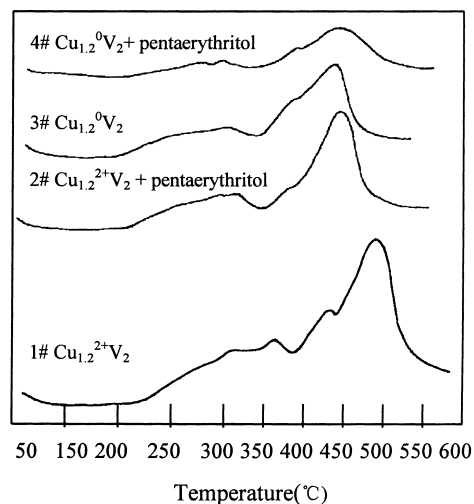


Fig. 6. The TPR of four catalysts without pretreatment. Temperature rate:  $10^{\circ}\text{C min}^{-1}$ .

Table 3  
Reduction temperature and activation energy of H<sub>2</sub> of four catalysts

Catalysts	$T_m$ (°C)	$E_a$ (kJ mol <sup>-1</sup> )	$T_m$ (°C)	$E_a$ (kJ mol <sup>-1</sup> )
Cu <sub>1.2</sub> <sup>2+</sup> V <sub>2</sub>	374.0	138	506.1	194
Cu <sub>1.2</sub> <sup>0</sup> V <sub>2</sub>	322.7	43	461.1	80
Cu <sub>1.2</sub> <sup>2+</sup> V <sub>2</sub> and pentaerythritol	346.2	124	477.8	58
Cu <sub>1.2</sub> <sup>0</sup> V <sub>2</sub> and pentaerythritol	309.6	49	463.0	122

Table 4  
Catalytic activity of four catalysts for the selective oxidation of propene<sup>a</sup>

Catalyst	Color (before reaction)	Color (after reaction)	Conversion (%)	Selectivity (%)			
				Acrolein	Acetone	Acetic acid	Acrylic acid
Cu <sub>1.2</sub> <sup>0</sup> V <sub>2</sub>	Dark yellow	Dark green	72	3.5	0.1	21.0	52.1
Cu <sub>1.2</sub> <sup>2+</sup> V <sub>2</sub>	Orange	Dark yellow	61	4.1	0.1	11.5	28.7
Cu <sub>1.2</sub> <sup>2+</sup> V <sub>2</sub> and pentaerythritol	Dark yellow	Dark green	76	3.3	0.1	19.7	39.5
Cu <sub>1.2</sub> <sup>0</sup> V <sub>2</sub> and pentaerythritol	Dark green	Dark blue	88	1.8	–	2.2	2.2

<sup>a</sup> The results were obtained after the reactions had carried out for 7 h.

while the reduction peaks appearing over 400°C may be attributed to the decomposition procession of the HPC from higher assembly structure to the lower assembly structure until the oxides eventually. The starting temperature of the catalyst reduced by Cu powder is 165.4°C, which is lower than that of other catalysts (all around 190°C). It appears that Cu<sub>1.2</sub><sup>0</sup>V<sub>2</sub> is more reducible than the others. And the lowest activation energy of H<sub>2</sub> in the range of the lower temperature on this catalyst (see Table 3) also proves that.

### 3.5. Catalytic reaction

Table 4 shows the color before and after the reaction, and the catalytic activity of four catalysts for the selective oxidation of propene. The color and the IR spectra of the catalysts show that the catalysts prepared by reductants are only partial reduced, since the Keggin structure of the heteropoly compounds remains intact in all catalysts, and the degree of the reduction is relatively smaller than the molybdenum blue, which is reduced by at least two electrons per Keggin unit. During the reaction, even under the oxidative atmosphere, the catalysts become more deeply reduced compared to their original states, which can be explained according to the redox mechanism of

the heteropoly compounds. When the selective oxidation takes place at high temperature, the reactants are oxidized by the lattice oxygen (O<sup>2-</sup>) in the surface of the heteropoly compound catalyst, which will be supplied by molecule oxygen through the bulk. The slow reoxidation will result the scarcity of the lattice oxygen in the bulk, which is shown by the deeper color in appearance.

The reaction results also show that when Cu<sub>1.2</sub><sup>0</sup>V<sub>2</sub> was used, the optimum selectivity of acrylic acid was obtained. The acetone and the acetic acid, produced by the reaction of the reductive species and the adsorbing oxygen, is lower than the acrolein and the acrylic acid, which are the products of the reductive species and the lattice oxygen. When the more deeply reduced heteropoly compound catalyst — Cu<sub>1.2</sub><sup>0</sup>V<sub>2</sub> and pentaerythritol was used, the conversion of the propene also increased while the selectivity of liquid products decreased. It suggests that a proper reduced catalyst is favorable for the selective oxidation, probably because a good redox circle is maintained to supply the lattice oxygen properly during the reaction. It also indicates that the element Cu, which is ready to be re-oxidized and accelerates the reoxidation of the catalyst, plays an important role in the catalytic oxidation. The study on the relationship between the structure and the activity is under way.

#### 4. Conclusion

Partial reduced catalysts were prepared and used for the selective oxidation of propene. Compared to the non-reduced catalyst, the partial reduced catalysts were more active and selective. The more deeply reduced catalyst leads to an increase in the conversion of propene, but lower selectivity of acrylic acid. The  $\text{Cu}_{1.2}^0\text{V}_2$  catalyst seems to be the most active catalyst due to the most containing of  $\text{V}^{4+}$ . The oxidation and reduction behaviors of partial reduced heteropoly compounds catalysts was studied using the temperature programmed reduction (TPR) and oxidation (TPO). Results show that the catalyst reduced by Cu powder has the lowest activation energy, which is consistent to the results of the selective oxidation.

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