

# Partially reduced heteropoly compound catalysts for the selective oxidation of propane<sup>☆</sup>

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## Abstract

Partially reduced multi-component heteropoly compound catalysts with the Keggin structure were prepared and used for the selective oxidation of propane. The influence of the pore diameter of the support on the reaction was also tested. Results show that the partially reduced heteropoly acid catalyst exhibits the highest activity for the selective oxidation of propane under the optimum reaction conditions:  $T = 390\text{ }^{\circ}\text{C}$ ,  $\text{C}_3\text{H}_8:\text{O}_2:\text{H}_2\text{O}:\text{N}_2 = 1:2:2:5$  (mol/mol) and space velocity =  $1500\text{ h}^{-1}$ . The maximum conversion of propane and the maximum yield of acrylic acid reached 38 and 14.8%, respectively. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Heteropoly compound; Partially reduced; Propane; Selective oxidation

## 1. Introduction

As a kind of important and versatile material in organic chemical industry, acrylic acid can be produced by many ways. Among them, the selective oxidation of propane has attracted much attention in recent years because it is cheap and plenty material [1]. Polyanions with the 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 [2–4]. Recently, the importance of the oxidation degree of addenda atoms in

heteropoly compounds was realized to be an important factor affecting on the catalytic performance. A partially reduced heteropoly acid treated by pyridine was reported to show best performance for the selective oxidation of alkanes [5]. We reported another kind of partially reduced heteropoly acid catalyst with the basic composition of  $\text{Cu}_{1.2}\text{-P-Mo}_{10}\text{-V}_2\text{-As}_{0.6}\text{-O}_{40}$  prepared by a newly designed method [6], of which the degree of the reduction was less than two electrons per Keggin structure. When used for the selective oxidation of propene, the reduced catalysts exhibited better catalytic activity and selectivity than the non-reduced ones. In this paper, partially reduced heteropoly acid catalysts were used for the oxidation of propane to acrolein and acrylic acid in a single step. The influence of the pore diameter of the support on the reaction and the optimum reaction conditions were also tested.

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## 2. Experimental

### 2.1. Catalyst preparation

Three catalysts of heteropoly compound with Keggin structure were prepared according to the method reported in our previous paper [7]. The heteropoly anions have the common composition of  $\text{P-Mo}_{10}\text{-V}_2\text{-As}_{0.6}\text{-O}_{40}$  with a different content of the metal ions. The partially reduced heteropoly acids were prepared using Cu as the reductant. The three catalysts are designated as A, B and C, corresponding to  $\text{H}_x\text{Cu}_{0.6}\text{Cr}_{0.6}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}$ ,  $\text{H}_x\text{Cu}_{1.2}\text{PMo}_{10}\text{V}_2\text{-As}_{0.6}\text{O}_{40}^*$  (partially reduced) and  $\text{H}_x\text{Cu}_{0.6}\text{Cr}_{0.6}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}^*$  (partially reduced). The typical procedure is shown as follows. A certain amount of  $\text{H}_3\text{PO}_4$  (85%),  $\text{H}_3\text{AsO}_4$  (85%),  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ , Cu and  $\text{Cr}_2\text{O}_3$  were mixed with water and the resultant mixture was refluxed at 70–80 °C for 48–72 h to form a homogeneous solution. 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 in a nitrogen atmosphere for 2 h to remove the water thoroughly.

The  $\text{SiO}_2$  supports were hydrothermally treated in an autoclave under different temperature to enlarge the pore diameter. The catalysts were loaded on the supports by impregnating with a load of 20 wt.%.

### 2.2. Catalytic reaction

Catalytic reactions were carried out in a tubular fix-bed microreactor. The volume of the catalysts was 2 ml (40–60 mesh). The products were analyzed on-line by a 102G gas chromatograph with a porapak-Q column ( $6 \times 2000 \text{ mm}^2$ ), TC and FI detector.

### 2.3. Catalyst characterization

IR spectra of the catalysts were taken on a Perkin-Elmer 683 IR Spectrometer by KBr tablet method. ESR spectra were collected on an ER200D-SRC Electron Spin Resonance Spectrometer. The operation conditions were: modulation frequency of 12.5 kHz, central field of 3450 G, scanning width of 3000 G, output power of 20.4 mW and modulation width of 6.3 Gpp. The characterization by TG and DTA was carried out on a PCT-1 (Beijing Optical

Instrument) differential thermal analyzer. The specific surface area and the pore diameter of the  $\text{SiO}_2$  supports were measured on a Soptomatic 1900 BET Adsorption Instrument by the adsorption of liquid  $\text{N}_2$ .

## 3. Results and discussion

### 3.1. Characterization of the reduced state

The IR spectra of the non-reduced and two partially reduced catalysts with different amount of Cu are shown in Fig. 1. Four strong absorption peaks near 1061, 958, 871 and 790  $\text{cm}^{-1}$ , which are attributed to the vibration of P–O bond, Mo=O bond and Mo–O–Mo bonds of different locations, respectively, show that three catalysts contain heteropoly anions of the 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 spectra is the different relative intensity of the Mo–O bonds versus the P–O bond. It appears that the relative intensity of the Mo–O bonds versus the P–O bond of the heteropoly compounds is decreased by the reduction, which indicates that the amount of the Mo–O bonds in the heteropoly anions is decreased by the reduction. There is no obvious change in the IR

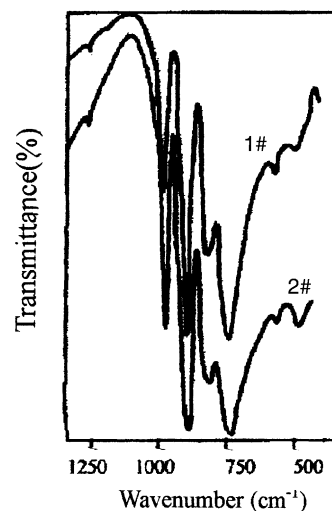


Fig. 1. IR spectra of the non-reduced (1#) and the partially reduced (2#) catalyst of the same composition  $\text{H}_x\text{Cu}_{0.6}\text{Cr}_{0.6}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}$ .

characterization of the catalysts because the reduction degree of the heteropoly compounds is lower than two electrons per the Keggin structure. There is no obvious change in color of the catalysts either. The newly made reduced catalyst was dark orange while the newly made non-reduced catalyst was bright orange. The former had a little deeper color than the latter. After the catalytic reaction, all catalysts became dark green or even dark blue probably due to the formation of molybdenum blue, and correspondingly the four characteristic IR absorption peaks became very small. It is known that molybdenum blue has the reduction degree of at least two electrons per the Keggin structure, being deeply reduced than the catalysts we made. The deeply reduced catalysts (dark green or dark blue) showed lower catalytic ability for the selective oxidation than the non-reduced catalyst [6].

The ESR spectra of the non-reduced and two partially reduced catalysts are listed in Fig. 2. The asymmetric peak appearing in the normal magnetic field is the signal of  $\text{Cu}^{2+}$ . The  $g_{\parallel}$  value 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  $\text{V}^{4+}$  ( $g_{\parallel}$  1.93,  $g_{\perp}$  1.98) due to the order of the redox potential,  $\text{Cu}^{2+} > \text{V}^{4+} > \text{Mo}^{5+}$ . The signals of  $\text{V}^{4+}$  are very weak because of the very strong signal of  $\text{Cu}^{2+}$  and

the coupling due to the coexistence of the multiple components. When the element Cr was added into the heteropoly compound, the signal of  $\text{V}^{4+}$  is even more difficult to be observed due to the two strong signals of Cu and Cr, and the fewer amounts of the reduced addenda atoms.

From the IR and ESR spectra we conclude that: (1) the catalysts we prepared are all heteropoly compounds with the Keggin structure, and (2) The reduced catalysts are partially reduced, which means the reduction degree is less than two electrons per the Keggin structure. During the reduction, 2.4 mol electrons transferred from  $\text{Cu}^0$  powder to the Keggin anions ( $1.2\text{Cu}^0 - 2.4\text{e}^- \rightarrow 1.2\text{Cu}^{2+}$ ;  $2[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}\text{As}_{0.6} + 2.4\text{e}^- \rightarrow 2[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{6.2}\text{As}_{0.6}$ ). The element As, which was added to partly take place the position of P, connecting the two Keggin structures. So in fact the amount of the electrons obtained per Keggin structure is 1.2.

### 3.2. Effect of the support

The heteropoly acid catalysts usually have small surface area and show low catalytic activity for the oxidation of alkanes without supports. Supports with large surface area ( $>200\text{ m}^2$ ) can help to increase the conversion of the alkanes. Meanwhile, the selectivity of the products can also be decreased by overoxidation or surface coke because of the small pore size of the supports. We use the hydrothermal treatment to enlarge the pore diameter of the support  $\text{SiO}_2$ . Results show that the pore size of the  $\text{SiO}_2$  increases by five times with increasing treating temperature, while the surface area decreases by four times (see Table 1).

Table 2 shows the catalytic activity of four types of  $\text{SiO}_2$  supports for the selective oxidation of propane. It appears that the optimum selectivity of acrylic acid and the conversion of propane were obtained when the  $\text{SiO}_2$  treated under  $220^\circ\text{C}$  was used as the support. It may be due to the proper pore size (around 16 nm), pore distribution and the surface area (around  $120\text{ m}^2/\text{g}$ ).

### 3.3. Choosing the optimum reaction conditions

The choosing of the optimum reaction conditions for the selective oxidation of propane is presented in

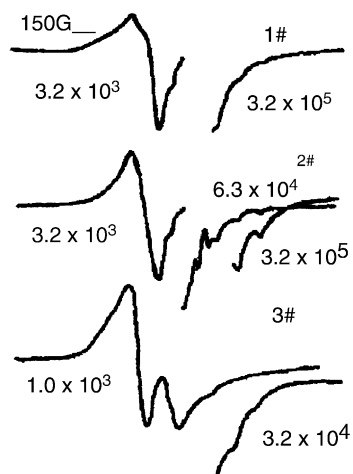


Fig. 2. ESR spectra of the non-reduced catalyst  $\text{H}_x\text{Cu}_{1.2}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}$  (1#), the partially reduced catalyst  $\text{H}_x\text{Cu}_{1.2}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}^*$  (2#) and  $\text{H}_x\text{Cu}_{0.6}\text{Cr}_{0.6}\text{PMo}_{10}\text{V}_2\text{As}_{0.6}\text{O}_{40}^*$  (3#).

Table 1

BET surface area and pore diameter of SiO<sub>2</sub> by hydrothermal treatment under different temperature<sup>a</sup>

SiO <sub>2</sub>	Saturated vapor pressure of water (atm)	Specific surface area (m <sup>2</sup> /g)	Specific pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
Without treatment	–	388.69	1.0985	4
Treated under 200 °C	15.3	130.11	0.9938	13
Treated under 220 °C	22.9	121.39	0.9858	16
Treated under 240 °C	33.0	95.17	0.8110	20

<sup>a</sup> The SiO<sub>2</sub> supports were hydrothermally treated in an autoclave under different temperature.

Figs. 4–7, which include the effects of temperature, C<sub>3</sub>O<sub>8</sub>/O<sub>2</sub> ratio, space velocity and the influence of water. All the tests were carried out on the partially reduced catalyst H<sub>x</sub>Cu<sub>0.6</sub>Cr<sub>0.6</sub>PMo<sub>10</sub>V<sub>2</sub>As<sub>0.6</sub>O<sub>40</sub>\* supported on the SiO<sub>2</sub> (BET specific surface area 121 m<sup>2</sup>/g) with a loading of 20 wt.%. Results show that the optimum reaction conditions for the selective oxidation of propane were  $T = 390\text{ }^{\circ}\text{C}$ , C<sub>3</sub>H<sub>8</sub>:O<sub>2</sub>:H<sub>2</sub>O:N<sub>2</sub> = 1:2:2:5 (mol/mol) and space velocity = 1500 h<sup>-1</sup>.

### 3.3.1. Temperature

The TG and DTA curves of the non-reduced and two partially reduced catalysts are listed in Fig. 3. All the curves of DTA have two endothermic peaks below 220 °C, corresponding to the dehydration of the molecular water and the crystallized water, respectively, and one or more exothermic peaks at the temperature range from 360 to 500 °C, corresponding to the decomposition of the catalysts. The dehydration temperature of the three catalysts (the maximum value all appear near 103.3 and 200.7 °C, respectively) are almost the same while the decomposition temperature of 1# (starting from 412.3 °C) is much higher than either that of 2# (starting from 365.8 °C) or 3# (starting from 384.4 °C). It indicates that the thermal stability of PMo heteropoly acid increases by adding the element

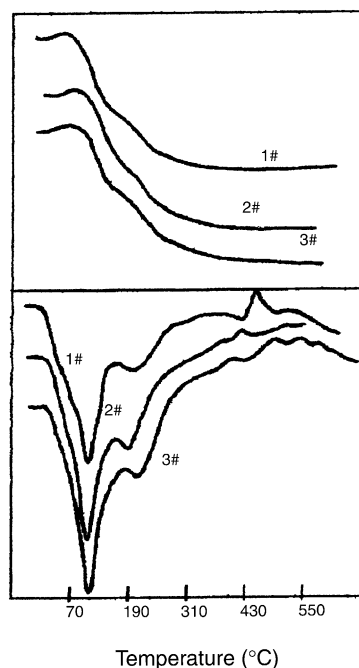


Fig. 3. TG–DTA diagrams of the three catalysts H<sub>x</sub>Cu<sub>0.6</sub>Cr<sub>0.6</sub>PMo<sub>10</sub>V<sub>2</sub>As<sub>0.6</sub>O<sub>40</sub> (1#), H<sub>x</sub>Cu<sub>1.2</sub>PMo<sub>10</sub>V<sub>2</sub>As<sub>0.6</sub>O<sub>40</sub>\* (2#), and H<sub>x</sub>Cu<sub>0.6</sub>Cr<sub>0.6</sub>PMo<sub>10</sub>V<sub>2</sub>As<sub>0.6</sub>O<sub>40</sub>\* (3#).

Table 2

Comparison of the catalytic activity of four types of SiO<sub>2</sub> supports for the selective oxidation of propane<sup>a</sup>

SiO <sub>2</sub>	Y <sub>AL</sub> (%)	Y <sub>acetone</sub> (%)	Y <sub>HAc</sub> (%)	Y <sub>AA</sub> (%)	Conversion (%)	S <sub>AA</sub> (%)
Without treatment	0.3	0.4	3.6	4.6	20	23
Treated under 200 °C	0.4	0.6	4.3	6.5	27	24
Treated under 220 °C	0.8	1.0	7.1	14.8	38	39
Treated under 240 °C	0.5	0.6	5.1	9.2	29	31

<sup>a</sup> AL: acrolein, HAc: acetic acid, AA: acrylic acid; the fixed composition of the catalysts were Cu<sub>0.6</sub>Cr<sub>0.6</sub>PAso<sub>6</sub>Mo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>; heteropoly acid/SiO<sub>2</sub> = 1/3 (wt/wt);  $T = 663\text{ K}$ ; propane:O<sub>2</sub>:N<sub>2</sub>:H<sub>2</sub>O = 1:2:5:2 (mol/mol); space velocity = 1500 h<sup>-1</sup>.

Table 3

Comparison of the catalytic activity of three catalysts for the selective oxidation of propane<sup>a</sup>

Catalyst	$Y_{AL}$ (%)	$Y_{acetone}$ (%)	$Y_{HAc}$ (%)	$Y_{AA}$ (%)	Conversion (%)	$S_{AA}$ (%)
A	0.3	0.1	1.1	0.2	9.0	2.0
B	0.9	0.4	2.5	9.3	30.0	31.0
C	0.8	1.0	7.1	14.8	38.0	39.0

<sup>a</sup> AL: acrolein, HAc: acetic acid, AA: acrylic acid; A:  $H_xCu_{0.6}Cr_{0.6}PMo_{10}V_2As_{0.6}O_{40}$ ; B:  $H_xCu_{1.2}PMo_{10}V_2As_{0.6}O_{40}^*$ ; C:  $H_xCu_{0.6}Cr_{0.6}PMo_{10}V_2As_{0.6}O_{40}^*$ ; heteropoly acid/SiO<sub>2</sub> = 1/3 (wt/wt);  $T = 663$  K; propane:O<sub>2</sub>:N<sub>2</sub>:H<sub>2</sub>O = 1:2:5:2 (mol/mol); space velocity = 1500 h<sup>-1</sup>.

Cr, which is consistent with Ref. [8], but decreases by the reduction.

Table 3 shows the catalytic activity of three catalysts for the selective oxidation of propane. It appears that the partially reduced catalysts B and C exhibit higher catalytic activity than the non-reduced catalyst A. The addition of Cr increases the stability of the catalyst, leading to low conversion and selectivity for the reaction, however. The oxidation of propane includes several unit reactions such as dehydrogenation and oxygen insertion steps. The heteropoly compounds suffer from the low thermal stability during the reactions, compared with the composite oxides. The suitable temperature range is usually 280–400 °C, above which the main structure of the heteropoly compound will be destroyed. One of the ways to enhance the thermal stability is to change the metal ions of the heteropoly compounds. From the TG–DTA diagrams, we can see that  $H_xCu_{0.6}Cr_{0.6}PMo_{10}V_2As_{0.6}O_{40}$  shows the best thermal stability than the other catalysts because of the addition of Cr. During the reaction, however, it shows the lowest catalytic performance among the three catalysts. Meanwhile, both the partially reduced catalysts  $H_xCu_{0.6}Cr_{0.6}PMo_{10}V_2As_{0.6}O_{40}^*$  and  $H_xCu_{1.2}PMo_{10}V_2As_{0.6}O_{40}^*$  show their best catalytic performances under 390 °C, which is in the range of the decomposition temperature of the heteropoly compounds (see Table 1 and Fig. 4). Here a question is raised. Why a partly destroyed heteropoly compound exhibits better catalytic activity than a non-destroyed catalyst? The decomposition of the heteropoly compound takes place gradually, starting from the reconstruction of the polyanions and ending up till the structural water is cleaned up. As the reconstruction happens, the number of the coordinated oxygen atoms in the polyanions may decrease, with a change in the coordinating environment of

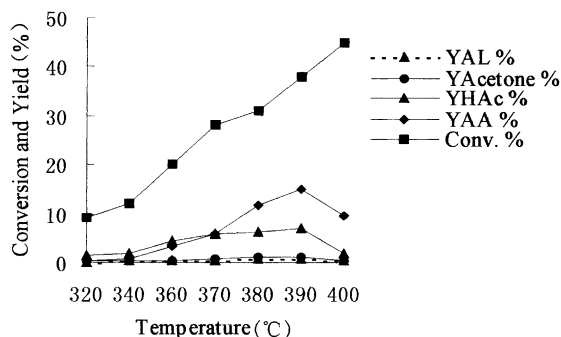


Fig. 4. Effect of the reaction temperature for the selective oxidation of propane. Reaction conditions: C<sub>3</sub>H<sub>8</sub>:O<sub>2</sub>:N<sub>2</sub>:H<sub>2</sub>O = 1:2:5:2 (mol/mol), space velocity = 1500 h<sup>-1</sup>.

the addenda atoms and a scarcity of the coordinated oxygen atoms. We assume that some specific active species with low coordinated oxygen number and aberrant polyhedron structure forms and benefits the oxygen insertion process during the reaction. The partly destroyed heteropoly catalysts, together with the partially reduced catalysts, both of which increase the amount of oxygen scarcity, which may maintain a good redox circle for the selective oxidation of alkanes.

### 3.3.2. Space velocity

Fig. 5 shows the effect of the space velocity for the selective oxidation of propane. The conversion of propane decreases gradually with the increase of the space velocity, while the selectivity of liquid products, especially that of the acrylic acid has a maximum value. It illustrates that the higher space velocity benefits sufficient contact between the catalyst and the reactant gases, but it also results in overoxidation since the delayed desorption of the products.

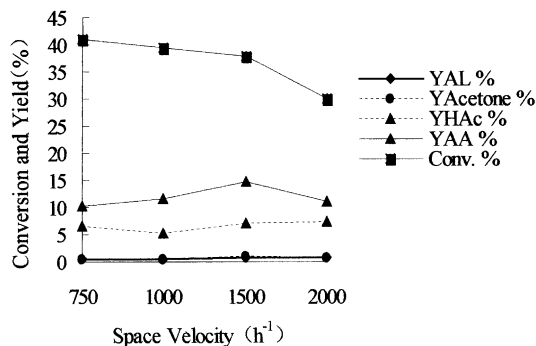


Fig. 5. Effect of the space velocity for the selective oxidation of propane. Reaction conditions:  $C_3H_8:O_2:N_2:H_2O = 1:2:5:2$  (mol/mol),  $T = 390^\circ C$ .

### 3.3.3. Propane/ $O_2$ ratio

Effect of the propane/ $O_2$  ratio for the selective oxidation of propane is shown in Figs. 6 and 7. It was reported that the concentration of propane in the feed gases influences the surface active sites of the catalyst [2]. Before the catalytic reaction, oxygen and propane were used to activate the newly made catalyst, respectively. The results show that propane maintains the reduced state that is beneficial to the reaction. However, the fuel-rich condition results in a low conversion of propane though the selectivity of AA may be higher. It is suggested that the reduced state is responsible for the activity and for the formation of acrylic acid in the propane oxidation. The partially reduced state is suitable for the oxidation because the reduced state provides not only coordinatively unsaturated Mo or V for the adsorption or stabilization of intermediate

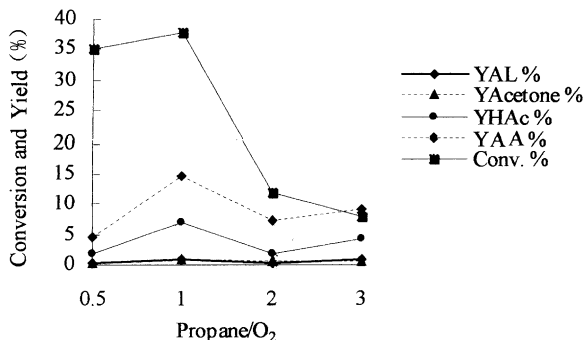


Fig. 6. Effect of the propane/ $O_2$  ratio for the selective oxidation of propane. Reaction conditions:  $N_2:H_2O = 5:2$  (mol/mol), space velocity =  $1500 h^{-1}$ ,  $T = 390^\circ C$ .

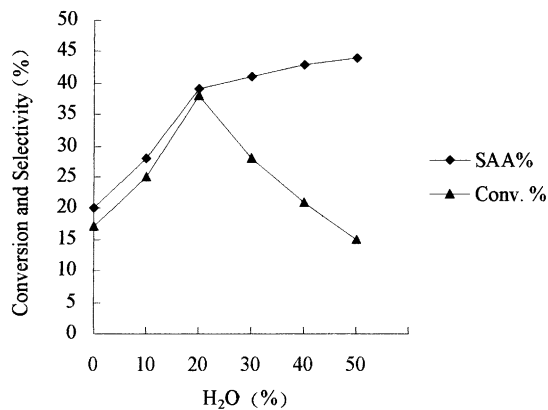


Fig. 7. Effect of the  $H_2O$  for the selective oxidation of propane. Reaction conditions:  $C_3H_8:O_2:N_2 = 1:2:5$  (mol/mol), space velocity =  $1500 h^{-1}$ ,  $T = 390^\circ C$ .

species but also basic lattice oxygen that may only be formed near the reduced Mo or V sites [5].

### 3.3.4. Water

Water plays an important role in the oxidation of propane. Water may enhance the desorption of acrylic or acetic acids from the surface of the catalysts to prevent them from being further oxidized to  $CO_x$ . Water may increase the concentration of hydroxyl groups on the catalyst surface and facilitate the reaction between the adsorbed acryloyl species and hydroxyl groups to form acrylic acid [3]. Water may also take away the heat produced during the reaction to avoid the hot area on the catalyst surface. When water was absent or present in very small quantities, propylene and  $CO_x$  were observed as the major products while only a trace amount of acrylic acid was obtained.

## 4. Conclusion

Multi-component, partially reduced heteropoly acid catalysts with the Keggin structure were prepared and used for the selective oxidation of propane. Results show that the optimum reaction conditions for the selective oxidation of propane were  $T = 390^\circ C$ ,  $C_3H_8:O_2:H_2O:N_2 = 1:2:2:5$  (mol/mol) and space velocity =  $1500 h^{-1}$ . Under such conditions, the conversion of propane and the yield of acrylic acid reached 38 and 14.8%, respectively.

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