

The effect of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts with different phosphorus content for selective oxidation of propane to acrolein

Huachang Jiang^a, Weimin Lu^{a,*}, Huilin Wan^b

^a Institute of Catalysis, Zhejiang University (Xixi Campus), Hangzhou 310028, PR China

^b Department of Chemistry, Xiamen University, Xiamen 361005, PR China

Received 2 April 2003; received in revised form 18 July 2003; accepted 21 July 2003

Abstract

Several $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts with different P-content were prepared. These catalysts showed a definite activity for the selective oxidation propane to acrolein at 773 K, and the maximum yield of acrolein attained to 21.9% as the content of phosphorus equaled to 0.15. The catalysts were examined by X-ray diffraction (XRD) and H_2 -temperature programmed reduction (TPR) studies. The experimental results revealed that the addition of phosphorus not only change the crystalloid phases of the catalysts but also affect the redox capability of the catalysts, which greatly improved the performance of the catalyst.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Acrolein; Mixed metal oxides catalysts; Selective oxidation; Propane

1. Introduction

The use of mixed metal oxides for the partial oxidation of olefins was already well established, with the high selective processes for producing butadiene, isoprene and acrolein about 40 years ago. Because of the current abundance and low cost of alkanes, recently, however, more and more interests have been generated in the oxidative catalytic conversion of alkanes other than olefins to produce oxygenates and nitriles in both petroleum and petrochemical industries, although it was well known that those alkanes were low reactive because they had no lone pairs of electrons, no empty orbital and the polarity of the C–H bonds was very little.

Researches had shown that the mixed metal oxides, especially Mo–V–M–O (M = Al, Ga, Bi, Sb and Te) [1–4] and Mo–V–Te–Nb oxides [5–11] were highly catalytically active for the selective oxidation/ammoxidation of propane to acrylic acid/acrylonitrile. For economic and ecological reasons, the direct synthesis of acrolein from propane in a single-stage process attracted much attention [12–16]. Such a technical process could not be realized up to now. In the most case for selective oxidation of propane to acrolein,

both selectivity and yield of acrolein were very low because propane was very inactive and acrolein was easily further oxidized under the reaction condition. One of the major problems that prevent the technical application of the reaction is the availability of the catalyst that transforms the propane with high yield into the desired product acrolein. While high selectivity has often been obtained for the reaction at a low conversion level, the selectivity towards the desired acrolein decreased dramatically with increasing conversion.

It has been reported that phosphorus, as one of the content of the mixed metal oxides, could affect on selective oxidation of propane [17,18]. In our study on the series catalysts of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$, we not only obtained the maximum yield of acrolein as high as 21.9% which has not been reported before, but also found that addition of phosphorus could change the phases of the catalysts and greatly affect the redox of the catalysts, which may be one of the reasons improving the performance of the catalyst.

2. Experimental

2.1. Catalysts preparation

All the reagents were commercially obtained and used without further purification.

* Corresponding author. Tel.: +86-571-8827-3495; fax: +86-571-8827-3283.

E-mail address: weimwlu@mail.hz.zj.cn (W. Lu).

Into three flasks each with 30 ml of water, 0.8828 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 0.2641 g $\text{H}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$ and 0.1755 g NH_4VO_3 were added, respectively and heated at 353 K. After dissolved, the three solutions were mixed and became a rose solution. Into the mixed solution, different amount (0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00 mmol) of phosphoric acid was added. The solution was evaporated to dryness at 353 K, dried at 423 K, and calcined at 873 K in a stream of nitrogen for 2 h, respectively. Some black metal oxides were formed and the formula of which were $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$ and 0.4). As a comparison, MoO_n and VO_n catalysts were also prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and NH_4VO_3 with the same preparation condition, respectively.

2.2. Catalytic activity tests

Selective oxidation of propane to acrolein was carried out in a tubular fixed bed flow reactor made of quartz (i.d. = 6 mm) under atmospheric pressure. Analysis of reactants and products were carried out by gas chromatography, using two column types: (i) Porapak Q (2.0 m \times 1/8 in.); (ii) molecular sieve 13 Å (2 m \times 1/8 in.). Carbon balance was always more than 95%.

The catalytic reaction condition was as follows: amount of the catalysts 100 mg, feed gas molar ratio $\text{O}_2:\text{C}_3\text{H}_8 = 1:1$, GSHV 6000 h^{-1} , and the catalysts were not reduced or diluted further prior to reaction.

2.3. Catalyst characterization

X-ray diffraction (XRD) analysis was carried out using a Rigaku-D/max-B automated power X-ray diffractometer by the continuous scanning ($4^\circ/\text{min}$) with Cu K α radiation (45 kV, 40 mA).

H_2 -temperature programmed reduction (TPR) experiment was carried out on the AMI-200 catalyst characterizing system, 5.0 mg of catalyst was charged each time into a U-shaped quartz micro reactor (i.d. = 4 mm). After purged with Ar gas from 323 to 573 K with ramp of 20 K/min, held in 573 K for 30 min, cooled to 373 K, the sample was reduced in a 5% H_2/Ar stream (25 ml/min). The reduction temperature was uniformly ranged from 373 to 1023 K with

ramp of 20 K/min. The H_2 consumption was monitored by a TCD connected to PC data station.

3. Results and discussion

3.1. Catalytic performance

The reaction results of selective oxidation from propane under different temperature were showed in Table 1. As Table 1 showed, the reaction was greatly affected by the reaction temperature. Both conversion of propane and selectivity of acrolein were low when the temperature was less than 673 K. When the reaction temperature was higher than 773 K, CO and CO_2 were main product and yield of acrolein was also low. The suitable temperature for the reaction was 773 K.

The performance of the $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts for selective oxidation of propane to acrolein was studied in the range of x value from 0 to 0.4. Conversion of propane and selectivity of products were shown in Table 2, including the reaction results of MoO_n and VO_n catalysts.

As Table 2 showed, the conversion of propane was very low by using MoO_n catalyst (1.6%). This meant that the oxidizability of MoO_n catalyst was very little. As to VO_n catalyst, the major products were CO and CO_2 with high conversion of propane (53.1%), while acrolein could not be detected. The performance of VO_n and MoO_n showed that each of them was in prejudice of the reaction of selective oxidation propane to acrolein.

The catalytic performance of mixed metallic oxide $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ for selective oxidation of propane to acrolein was obviously better than that of single-content metallic oxide, as Table 2 showed, but both the conversion (12.5%) of propane and the selectivity (33%) of acrolein were also lower when there was no phosphorus in the Mo–V–Te–O catalysts.

The addition of phosphorus content greatly affected the formation of acrolein. The selectivity increased with the addition of phosphorus content and was up to 47.0% when phosphorus content was 0.15. The selectivity of acrolein decreased if phosphorus content continued increasing. Contrary with most of cases, the conversion of propane on the

Table 1

The reaction results of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_{0.15}\text{O}_n$ catalysts under different temperature (reaction temperature: 773 K; $\text{O}_2:\text{C}_3\text{H}_8 = 1:1$; GSHV = 6000 h^{-1})

Temperature (K)	Conversion of propane (%)	Selectivity (%)				
		CO	CO_2	C_2H_4	Acrolein	Acrylic acid
573	0	0	0	0	0	0
623	0.3	66.5	33.5	0	0	0
673	2.95	34.1	29.5	4.2	32.2	0
723	18.7	28.1	28.6	7.2	36.1	0
773	46.6	35.0	6.2	3.6	47.0	8.1
793	49.6	54.7	10.0	10.6	22.2	2.4
813	59.4	57.5	12.4	17.3	12.7	0

Table 2

The reaction results of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts with different phosphorus content (reaction temperature: 773 K; $\text{O}_2:\text{C}_3\text{H}_8 = 1:1$; $\text{GSHV} = 6000\text{h}^{-1}$)

	Reaction/production	MoO_n	VO_n	Value of x						
				0	0.05	0.1	0.15	0.2	0.3	0.4
Conversion (%)	Propane	1.6	53.1	12.5	43.6	44.2	46.6	37.3	31.4	32.2
Selectivity (%)	CO	0	71.1	42.7	38.3	40.7	35.0	41.6	44.9	48.8
	CO_2	32.6	21.7	8.1	11.2	9.5	6.2	6.4	7.0	7.8
	C_2H_4	21.7	0	7.2	11.5	5.2	3.6	5.6	8.0	9.6
	Acrolein	43.4	0	33.0	27.8	35.7	47.0	36.1	31.2	24.8
	Acrylic acid	0	0	9.0	11.2	9.0	8.1	10.3	9.2	9.0

catalysts of Mo–V–Te–P–O did not descend while phosphorus content added, but also aggrandized from 12.5 to 46.6% with the addition of phosphorus content. Trend of the conversion was like that of the selectivity and the maximum yield of acrolein was 21.9% when phosphorus content equaled to 0.15.

The major products in the selective oxidation of propane were CO and acrolein. Besides these, a small amount of acrylic acid, ethylene and CO_2 were also obtained as by-products. Propene was detected in this reaction.

3.2. H_2 -TPR

H_2 -TPR profiles and amount of H_2 consumption of MoO_n , VO_n and $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts were shown in Fig. 1 and Table 3, respectively. As Fig. 1 showed, two peaks in the H_2 -TPR pattern of pure MoO_n showed at temperature of 948 and 995 K (pattern b), corresponding to the step-wise reduction of $\text{Mo}^{6+} \Rightarrow \text{Mo}^{4+}$ and $\text{Mo}^{4+} \Rightarrow \text{Mo}^0$, respectively [19,20]. The TPR profile of pure VO_n could be observed at temperature of 913 and 943 K (pattern a). The amount of H_2 consumption of VO_n was larger than that of MoO_n .

The H_2 -TPR profile of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{O}$ was almost uniform as that of MoO_n (pattern c) with two peaks situated at 945 and 991 K and the peaks could mainly be ascribed to the reduction of V and Mo species. When phosphorus was added into the catalysts with x from 0.05 to 0.4, the two peaks incorporated to one and shifted to low temperature from the range of 901 to 925 K (patterns d–i). The board peak became sharper and consumption of hydrogen rapidly decreased from 59 to 4 along with the addition of phosphorus increased (Table 3).

Kinetic studies had confirmed that C–H bond activation step using lattice oxygen limits the rate of propane oxida-

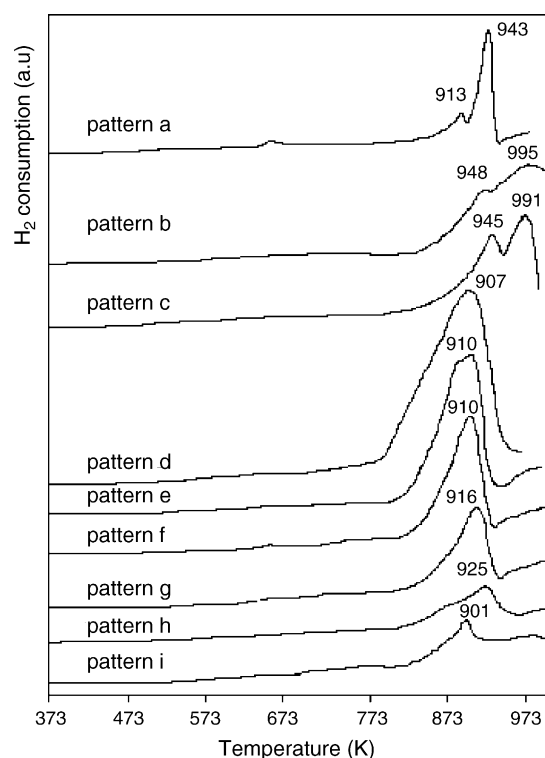


Fig. 1. The H_2 -TPR profiles of Mo–V–Te–P mixed metal oxides catalysts with different phosphorus content (pattern a: VO_n ; pattern b: MoO_n ; the phosphorus contents in $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts from patterns c to i were 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, respectively).

tion dehydrogenation on V- and Mo-based catalysts [21,22]. C–H bond dissociation process related with the incipient redox property of metal oxide catalysts. As we knew, the technical production of acrolein from propane was carried out in two separate steps with propylene as intermediate. Propylene could not be detected in our experiment, which implied

Table 3

The H_2 -TPR results of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts with different phosphorus content

	Catalyst		Value of x						
	VO_x	MoO_n	0	0.05	0.1	0.15	0.2	0.3	0.4
Temperature (K)	913/943	948/995	945/991	907	910	910	916	925	901
Weight (mg)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
H_2 consumption (μmol)	6.4/7.1	3.4/4.2	20.6/7.4	58.9	33.4	24.0	14.5	7.9	4.0

that propylene could easily be converted to other product as soon as it was formed from propane. Suitable reducibility and oxidizability of the catalyst were needed for selective oxidation from propane to acrolein. The oxidability of MoO_n was too low to oxidize propane and that of VO_n was so high that the ultimate products were CO and CO_2 .

Phosphorus content in the $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts played an important role for selective oxidation of propane to acrolein. Lower H_2 -TPR of the catalysts containing phosphorus content indicated that Mo^{6+} and V^{5+} species were partly reduced to low oxidation states. In selective oxidation of propane to acrolein on the catalysts, the oxygen deficient site around unsaturated Mo^{5+} reacted with molecular oxygen to form lattice oxygen species that were active species for propane activation; simultaneously, the unsaturated Mo^{5+} was oxidized to Mo^{6+} [23]. The enhancement of reducibility was propitious to this process. The more the lattice oxygen deficient sites, the easier the diffusion of oxygen and the reducibility of the catalysts improved with the increase of the phosphorus content. It was noted that the selectivity of acrolein greatly decreased, selectivity of CO_x obviously increased and H_2 consumption of the catalysts in H_2 -TPR experiment rapidly cut down when phosphorus content was excess ($x = 0.15$) in the catalyst. It suggested that addition of excessive phosphorus broke up the balance of redox cycle, resulting in both the conversion of propane and the selectivity of acrolein depressing. Appropriate phosphorus content may adjust reducibility and oxidizability of the catalyst. When phosphorus content was 0.15, the catalyst materialized the best redox capability.

3.3. X-ray diffraction

The XRD patterns of mixed metal oxide were shown in Fig. 2. In order to compare with the Mo–V–Te–P–O catalysts, a sample of MoO_n (pattern a) was measured. Its characteristic XRD peaks situated at the 2θ angles of 12.7, 23.3, 25.6, 27.3 and 38.9° which could be attributed to MoO_3 (JCPDS 5-508). Although a new phase of $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$ with the diffraction peaks at 2θ of 22.1, 28.2, 36.1, 45.2 and 50.0° (JCPDS 31-1437) was detected, the major phase of Mo–V–Te–O catalyst (pattern b) was MoO_3 .

With the diffraction intensity of the phase MoO_3 decreasing, diffraction intensity of the phase $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$ was going more and more strong with the phosphorus increasing and gradually became the major phase of the catalysts after phosphorus content was more than 0.15.

According to the XRD patterns of the catalysts of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$, the addition of phosphorus could also greatly affect phases in the catalysts. When there was no phosphorus in the catalyst, the main phase was MoO_3 . The addition of phosphoric acid could bring on phase of $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$ and it was going more and more strong with the phosphorus increasing. The degree of crystallization of the catalysts ebbed by degrees and amorphous phase

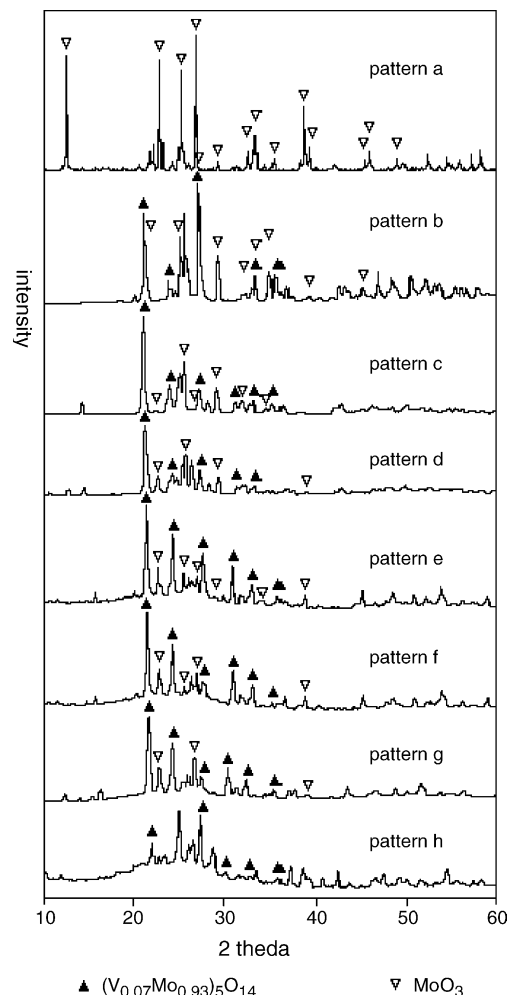
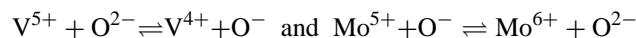


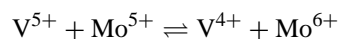
Fig. 2. The XRD patterns of Mo–V–Te–P mixed metal oxides catalysts with different phosphorus content (pattern a: MoO_n ; the phosphorus contents in $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_x\text{O}_n$ catalysts from patterns b to h were 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, respectively).

gradually emerged at the range of 2θ from 20 to 37° as the phosphorus contents above 0.2 (patterns f–h).

Existence of phase $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$ in the catalyst indicated that Mo and V species exhibited two kinds of oxidation states. Combination of the H_2 -TPR results might be $\text{Mo}^{5+}/\text{Mo}^{6+}$ and $\text{V}^{4+}/\text{V}^{5+}$. The two kinds of electron couples could be formed by a charge transfer:



And synergistic reaction could be occurred in the active phase by the equation:



4. Conclusion

The addition of phosphorus into the Mo–V–Te–O-based catalysts could greatly influence the formation of acrolein from partial oxidation of propane. The proper phosphorus

content in the catalyst improved the reducibility, increased the relative concentration of Mo^{5+} species and made intensity of phase $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$ suitable, which was in favor of the formation of the redox cycle ($\text{V}^{5+} + \text{Mo}^{5+} \rightleftharpoons \text{V}^{4+} + \text{Mo}^{6+}$) in the catalyst. Such effect in return greatly influenced the catalytic performance in selective oxidation of propane to acrolein. When the amount of phosphorus attained 0.15, the redox ability of the Mo–V–Te–P–O catalysts was best and the yield of acrolein attained 21.9%.

Acknowledgements

This work was supported by the National Natural Science Foundation of China and The State Key Laboratory for Physical chemistry of Solid Surface of Xiamen University.

References

- [1] W. Ueda, K. Oshihara, Appl. Catal. A: Gen. 200 (2000) 135.
- [2] K. Oshihara, T. Hisano, W. Ueda, Topics in Catalysis. 15 (2001) 153–160.
- [3] W. Ueda, K. Oshihara, D. Vitry, T. Hisano, Y. Kayashima, Catal. Surv. Jpn. 6 (2002) 33.
- [4] P. Botella, J.M. Lopez Nieto, B. Solsona, Catal. Lett. 78 (2002) 383.
- [5] H. Watanabe, Y. Koyasu, Appl. Catal. A: Gen. 194/195 (2000) 479–485.
- [6] M. Takahashi, S. To, S. Hirose, JP Patent 98,118,491 (1998).
- [7] J.N. Al-Saedi, V.V. Gulians, G. Pérez, M.A. Bñares, J. Catal. 215 (2003) 108.
- [8] E.K. Novakova, E.G. Derouane, J.C. Vedrine, Catal. Lett. 83 (2002) 177.
- [9] J.N. Al-Saedi, V.V. Gulians, Appl. Catal. A: Gen. 237 (2002) 111.
- [10] E. Balcells, F. Borgmeier, I. GriBtede, H.-G. Lintz, Catal. Lett. 87 (2003) 195.
- [11] E.K. Novakova, J.C. Vedrine, E.G. Derouane, J. Catal. 211 (2002) 235.
- [12] P. Kölsch, M. Noack, R. Schäfer, G. Georgi, R. Omorjan, J. Caro, J. Membr. Sci. 198 (2002) 119.
- [13] X. Zhang, H. Wan, W. Weng, X. Yi, J. Mol. Catal. A: Chem. 200 (2003) 291.
- [14] P. Kölsch, Q. Smejkal, M. Noack, R. Schafer, J. Caro, Catal. Commun. 3 (2002) 465.
- [15] X. Zhang, H. Wan, W. Weng, X. Yi, Catal. Lett. 87 (2003) 229.
- [16] J.M. Botella, L. Nieto, B. Solsona, J. Mol. Catal. A: Chem. 184 (2002) 335.
- [17] M. Takahashi, S. To, S. Hirose, JP Patent 98,120,617 (1998).
- [18] A. Kaddouria, C. Mazzocchia, E. Tempesti, Appl. Catal. A: Gen. 180 (1999) 271.
- [19] A. Parmaliana, F. Arena, F. Frusteri, Stud. Surf. Sci. Catal. 110 (1997) 347.
- [20] F. Arena, A. Parmaliana, J. Phys. Chem. 100 (1996) 19995.
- [21] K. Chen, et al., J. Phys. Chem. B 104 (2000) 1292.
- [22] K. Chen, et al., J. Catal. 195 (2000) 244–252.
- [23] M.M. Bettahar, G. Constantin, L. Savary, Appl. Catal. A 145 (1996) 1.