

Effect of Different Dopant in the Mo-V-Te-O Catalyst on the Performance of Selective Oxidation Propane to Acrolein

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Abstract: Several Mo-V-Te-O mixed metal oxides catalysts with different dopant were prepared and used for catalytic oxidation propane to acrolein. It was revealed that the addition of P could greatly improve the performance of the Mo-V-Te-O catalyst. The catalysts were examined by XRD and H₂-TPR. The XRD characteristic of the Mo-V-Te-P-O showed that the addition of P could aggrandize the (V_{0.07}Mo_{0.93})₅O₁₄ phase. H₂-TPR illuminated that the MoV_{0.3}Te_{0.23}P_{0.15}O_n catalyst took on the best redox ability.

Keywords: Acrolein, mixed metal oxides catalysts, selective oxidation, propane, XRD.

Mo-V based catalysts used for selective oxidation of propane to acrylic acid or acrylonitrile have generated much recent interest¹⁻³. It was found that structural differences of the catalysts could greatly influence the performance of catalysts. W. Ueda *et al.* prepared a series of Mo-V-M-O (M = Al, Ga, Bi, Sb and Te) oxides by hydrothermal synthesis method⁴. They claimed that all the synthesized solids were rod-shaped crystallites and gave a common XRD peak corresponding to 4.0 Å d-spacing and they reckoned that the XRD characteristics of the oxides were almost independent of added metal cations.

Our works found that the addition of P into the Mo-V-Te-O based catalysts could greatly improve the existence and intensity of the phase (V_{0.07}Mo_{0.93})₅O₁₄ and influence the performance of partial oxidation propane to acrolein accordingly.

Experimental

Into three flasks each with 30 mL of water heated at 353 K, a define amount of (NH₄)₆Mo₇O₂₄•4H₂O, H₂TeO₆•2H₂O and NH₄VO₃ were added, respectively. After dissolving, the three solutions were mixed. The mixed solution was divided into three parts and phosphoric acid or potassium nitrate was added into the two solutions, respectively. Nothing was added into the third solution. After evaporated to dryness at 353 K, each solution was dried at 423K and calcined at 873 K in a stream of nitrogen for 2

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h, respectively. Three black metal oxides were got and the formula of which were $\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_{0.15}\text{O}_n$, $\text{MoV}_{0.3}\text{Te}_{0.23}\text{K}_{0.15}\text{O}_n$ and $\text{MoV}_{0.3}\text{Te}_{0.23}\text{O}_n$.

Selective oxidation of propane to acrolein was carried out in a tubular fixed bed flow reactor made of quartz (ID = 6 mm) under atmospheric pressure. Analysis of reactants and products were carried out by gas chromatography, using two type columns: (i) Porapak Q (2m × 1/8 in.); (ii) molecular sieve 13A (2m × 1/8 in.).

X-ray diffraction (XRD) analysis was carried out using a Rigaku-D/max-B automated power X-ray diffractometer by the continuous scanning (4°/min) with Cu(α) radiation (45 KV, 40 mA). TPR experiments were carried out on the AMI-200 catalysts characteristic system instrument, 5.0 mg of catalyst was charged into a U-shaped quartz micro reactor (ID = 4 mm). After purged with Ar gas from 323K to 573K with ramp of 20K/min and then held in 573K for 30 minutes, the sample was cooled to 373K and reduced in a 5% H_2/Ar stream (25 mL/min). The reduction temperature was uniformly ranged from 373K to 1023K with ramp of 20K/min.

Results and Discussion

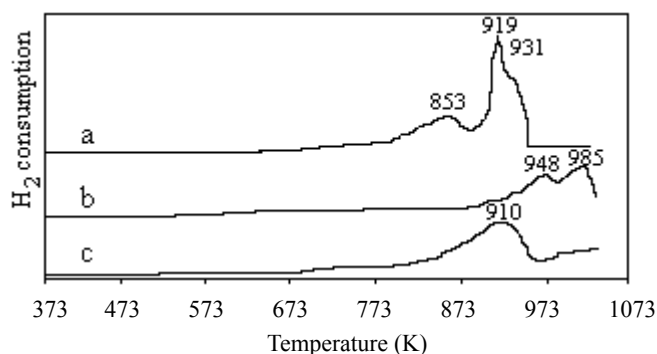
Table 1 The results of partial oxidation propane on Mo-V-Te-O based catalysts

Catalysts	Conversion (%)			Selectivity (%)		
	C_3H_8	CO	CO_2	C_2H_4	Acrolein	Acrylic acid
$\text{MoV}_{0.3}\text{Te}_{0.23}\text{P}_{0.15}\text{O}_n$	46.6	35.0	6.2	3.6	47.0	8.1
$\text{MoV}_{0.3}\text{Te}_{0.23}\text{O}_n$	12.5	42.7	8.1	7.2	33.0	9.0
$\text{MoV}_{0.3}\text{Te}_{0.23}\text{K}_{0.15}\text{O}_n$	27.5	67.4	25.5	1.2	5.9	--

Reaction temperature: 773K; $\text{C}_3/\text{O}_2=1:1$; GSHV=6000; weight of catalyst: 0.1000g

The results of selective oxidation propane were showed in **Table 1**. When there was no dopant in the Mo-V-Te-O based catalyst, conversion of propane was only 12.5% with the selectivity of acrolein being 33.0%. Although the addition of potassium into the Mo-V-Te-O based catalyst could greatly improve the conversion of propane (27.5%), but the selectivity of acrolein (5.9%) greatly decreased. The addition of P, however, improved not only the conversion of C_3H_8 (46.6%), but also the selectivity of acrolein (47.0%).

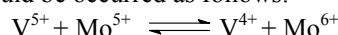
The H_2 -TPR profiles of Mo-V-Te based catalysts were shown in the **Figure 1**. In the H_2 -TPR profile of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{O}_x$ catalyst, two peaks could be detected situated at 948K and 985K which assigned to the step-wise reduction of $\text{Mo}^{6+} \rightarrow \text{Mo}^{4+}$ and $\text{Mo}^{4+} \rightarrow \text{Mo}^0$, respectively^{5,6}. The peaks shifted to low temperature with the addition of potassium and three peaks situated at 853、918 and 931K could be detected in the H_2 -TPR profile of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{K}_{0.15}\text{O}_x$ catalyst. Low reduction peaks and high H_2 consumption might cause the improvement of oxidizability of Mo-V-Te-K catalyst. Along with the addition of phosphorus, the two peaks in the H_2 -TPR profile of $\text{MoV}_{0.3}\text{Te}_{0.23}\text{O}_x$ catalyst incorporated into one peak and shifted to low temperature. The one peak in the H_2 -TPR profile might mainly arouse by one phase of the catalyst.

Figure 1 The H₂-TPR profiles of Mo-V-Te based catalysts(a: MoV_{0.3}Te_{0.23}K_{0.15}O_x; b: MoV_{0.3}Te_{0.23}O_x; c: MoV_{0.3}Te_{0.23}P_{0.15}O_x)

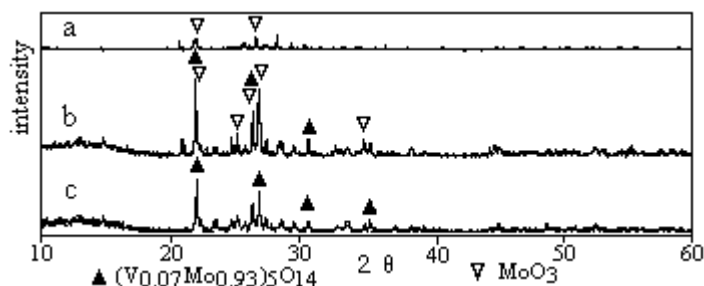
The **Figure 2** showed the XRD patterns of Mo-V-Te based catalysts. When there was no dopant in the Mo-V-Te catalyst, the main phase was MoO₃ (JCPDS 5-508), (V_{0.07}Mo_{0.93})₅O₁₄ phase was little with the diffraction peaks at 2θ of 22.1, 28.2, 36.1, 45.2 and 50.0° (JCPDS 31-1437) (pattern b). The addition of K extraordinarily promoted the formation of amorphous phase (pattern a). The addition of phosphorus apparently promoted the formation of (V_{0.07}Mo_{0.93})₅O₁₄ phase and lowered the MoO₃ (pattern c) phases. M. Lin *et al.* suggested that the effective catalysts for the oxidation reaction should have XRD peaks at angles of 22.1, 28.2, 36.2, 45.2 and 50.0°⁷. We thought that the redox ability of the catalyst played an important role for selective oxidation of propane. Existence of phase (V_{0.07}Mo_{0.93})₅O₁₄ in the catalyst indicated that Mo and V species exhibited two kinds of oxidation states. Combination of the H₂-TPR results, they might be Mo⁵⁺/Mo⁶⁺ and V⁴⁺/V⁵⁺. The two kinds of electron couples could be formed by a charge transfer:



And the synergistic reaction could be occurred as follows:



The cooperation between the two electron couples improved the redox ability of Mo-V-Te-P catalyst induced the selective oxidation of propane.

Figure 2 The XRD profiles of Mo-V-Te based catalysts(a: MoV_{0.3}Te_{0.23}K_{0.15}O_x; b: MoV_{0.3}Te_{0.23}O_x; c: MoV_{0.3}Te_{0.23}P_{0.15}O_x)

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