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Article

An outstanding Cr-doped catalyst for selective oxidation of propane to acrylic acid

Aixin Xu^a, Yang Wang^a, Hanqing Ge^b, Shu Chen^a, Yanhua Li^a, Weimin Lu^{a,*}^a Institute of Catalysis, Zhejiang Provincial Key Laboratory of Applied Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China^b Lanzhou Chemical Research Center of Petrochemical Research Institute, China Petroleum, Lanzhou 730000, Gansu, China

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ABSTRACT

The catalytic performance of active MoVTenbO_x catalysts containing an M1 phase in the partial oxidation of propane to acrylic acid (AA) was greatly improved when an optimal amount of Cr was added. The catalyst containing Cr/Nb (molar ratio = 0.002) showed good selectivity (78.3%) and high AA yield (50.7%). The catalysts were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, O₂ and NH₃ temperature-programmed desorption, and oxidation of 2-propanol. The relationship between the catalyst structure and catalytic properties was investigated. The results indicated that the amounts of Mo⁶⁺, V⁵⁺ and Te⁴⁺ species on the catalyst surface were adjusted, and oxidation activity of the catalyst increased, as a result of doping with an appropriate amount Cr, which promoted propane activation. The acid strength became weaker, and the number of acid sites on the catalyst surface decreased, which suppressed AA oxidation and improved the selectivity for AA.

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1. Introduction

In recent years, with the rapidly growing demand for plastics, polymers, fibers, and organic rubbers in emerging markets, the demand for acrylic acid (AA) has risen sharply [1]. Currently, AA is produced commercially by the partial oxidation of propylene. The price of propylene has gradually risen with increasing demand. Propane is widely present in natural gas and crude oil but has not been much used although it is inexpensive [2]. Therefore, the direct transformation of propane to AA in one step has attracted much attention [3,4]. Mo-V-Te(Sb)-Nb-O mixed-metal oxide catalysts with M1 and M2 phases are the best catalysts for the selective oxidation of propane to AA that have been proposed to date [5,6]. The yield of AA reported by the Japanese Mitsubishi Company was 48%, which can be commercialized initially [7]. It is therefore important to explore

highly efficient catalysts with independent intellectual property rights in our country.

The selective oxidation of propane to AA is a two-step process according to the reaction path. In the first step, propane is activated and dehydrogenated to propylene; this is the rate-determining step (RDS). The second step starts with propylene, and acrolein is formed as an intermediate in the AA syntheses [5,8,9]. In the reaction, it is critical to maintain the oxidation-reduction ability of the catalysts and promote the RDS.

According to previous reports, MoVTenbO_x doped with a certain amount of W or Pd showed an improvement in the RDS of selective propane oxidation, and the catalytic performance of the catalyst was significantly modified; however, the yield of AA was not greatly increased [10,11]. In catalysts for oxidative dehydrogenation of propane to propylene, the deposition of

* Corresponding author. Tel: +86-13777462563; E-mail: luweimin@zju.edu.cn

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CrO_x on VO_x/Al₂O₃ led to a better catalytic performance than that of VO_x/Al₂O₃ at similar VO_x surface densities because the replacement of the V–O–Al or V–O–V structures with V–O–Cr increased the reducibility and catalytic reactivity of VO_x [12]. Research on CrO_x/TiO₂ catalysts for propane dehydrogenation to propylene has also been reported [13]. As Cr is beneficial for propane dehydrogenation and may play an important role when it combines with V species, we studied MoVTeNbO_x catalysts doped with Cr in the selective oxidation of propane to AA and explored the relationship between the catalytic properties and catalyst structure.

2. Experimental

2.1. Catalyst preparation

A model MoVTeNbO_x catalyst with the composition Mo/V/Te/Nb = 7.82/1.18/0.94/1 was prepared using a co-precipitation method. Certain amounts of ammonium molybdate, ammonium metavanadate, and tellurium acid were added to 20 mL of distilled water at 80 °C with stirring until the components dissolved, and then 20 mL of niobium oxalate solution was added to the mixture solution. The resulting solution was allowed to stand at 80 °C until the solvent evaporated, and then the residue was dried in an air-circulating oven at 80 °C for 12 h. Finally, the powder sample was calcined in N₂ atmosphere at 150 and 600 °C for 2 h in each case. The preparation of the catalysts doped with Cr, MoVTeNbCr_yO_x was similar except for the addition of chromium nitrate solution to the mixed solution (Cr/Nb molar ratio (y) = 0.002, 0.006, 0.008, 0.01) before the solution was dried. All the materials used in the experiments were commercially available and of analytical grade.

2.2. Catalyst test

Catalytic performance experiments were carried out in a tubular fixed-bed quartz reactor (i.d. 7.4 mm) under atmospheric pressure with about 0.6 g of sample. A gas line connecting the reactor with a gas chromatograph (GC) was maintained at 140 °C to prevent the products from possible condensation in the line during flow. The feedstock and reaction products were analyzed on-line using a GC equipped with a flame ionization detector for analyzing hydrocarbons and a thermal conductivity detector (TCD) for analyzing O₂ and carbon oxides. Two column types, Porapak QS (4.0 m × 3.2 mm) and TDX-01 (2.0 m × 3.2 mm), were used for product separation. The chromatographic data were calculated using the carbon normalization method.

2.3. Catalyst characterization

The phase composition of the catalysts was identified by powder X-ray diffraction (XRD) with a Rigaku D/Max-B diffractometer using Cu K α radiation. The working conditions were 40 kV, 40 mA, and a scanning range from 4° to 90°. The data were analyzed using JADE 5.0 software.

X-ray photoelectron spectroscopy (XPS) was performed

with a Thermo ESCALAB 250 system using Al K α radiation (1486.6 eV). Binding energies were corrected using the C 1s line as a standard (284.6 eV).

H₂ temperature-programmed reduction (H₂-TPR) experiments were carried out in a flow reactor system using 30 mg of catalyst. The catalysts were pre-treated in Ar at 300 °C for 30 min to remove adsorbed water and CO₂, and then cooled to 100 °C. The samples were reduced in a 10% H₂/Ar stream (30 mL/min) at a heating rate of 10 °C/min from 100 to 700 °C. H₂ consumption was measured using a TCD.

The oxygen mobilities of the catalysts were evaluated from the results of temperature-programmed desorption of O₂ (O₂-TPD). The catalysts were pre-treated in Ar at 400 °C for 30 min and then cooled to 50 °C prior to desorption of O₂ for 30 min. After purging the reactor with Ar for 40 min to a flat baseline, the temperature was raised to 650 °C at a rate of 10 °C/min. The effluent gas was analyzed for O₂ using a TCD.

The acid characteristics of the catalysts were studied by temperature-programmed desorption of NH₃ (NH₃-TPD) using 0.1 g of catalyst. All the catalysts were pre-treated in He at 400 °C for 30 min, and NH₃ was chemisorbed for 40 min in a 10% NH₃/He stream (30 mL/min) after cooling to 50 °C. After purging the reactor with He to a flat baseline, the experiments were carried out at a heating rate of 10 °C/min to 600 °C. The desorption of NH₃ was determined using a TCD.

The oxidation of 2-propanol was carried out in a tubular fixed-bed quartz reactor. The molar fractions of 2-propanol, O₂, N₂, and H₂O were 0.08, 0.21, 0.33, and 0.38, respectively. The reaction was carried out at 250 °C because propanol oxidation proceeded very rapidly at 350–400 °C, and differences among the rates for different samples could not be observed. The reaction products were detected by on-line GC.

3. Results and discussion

3.1. Catalytic performance

Table 1 lists the performance of MoVTeNbO_x catalysts with different amounts of Cr in the selective oxidation of propane to AA. It can be seen that the conversion of propane increases firstly and then, decreases when the amount of Cr is larger than 0.006. The selectivity for AA also increases significantly with increasing Cr doping. The best performance (48.7% yield) was obtained when y = 0.002. The results show that doping the

Table 1

Performance of MoVTeNbCr_yO_x catalyst with different Cr contents for selective oxidation of propane to acrylic acid.

Cr content (y)	Conversion of propane (%)	Selectivity for products (%)				Yield of AA (%)
		AA	CO _x	ACA	Others	
0	33.2	41.8	18.8	22.6	16.8	13.9
0.002	74.8	65.1	7.1	22.0	5.8	48.7
0.006	77.0	50.8	11.8	33.0	4.4	39.1
0.008	55.0	57.2	17.3	16.9	8.6	31.5
0.01	45.9	28.9	41.9	28.8	0.4	13.3

Reaction conditions: 390 °C, C₃H₈:O₂:H₂O = 1:2:1.56 (molar ratio), 2560 mL/(g·h).

AA: acrylic acid; CO_x: CO + CO₂; ACA: acetic acid; Others: CH₄ + C₂H₄ + propanol + formaldehyde + acetaldehyde + acetone.

MoVTenbO_x system with a small amount of Cr has a great influence on the catalytic performance in the reaction.

Figure 1 shows the distribution of AA, CO_x (CO and CO₂), ACA (acetic acid), and other by-products (CH₄ + C₂H₄ + propanol + formaldehyde + acetaldehyde + acetone) obtained using catalysts with $y = 0$ and 0.002 under different gas hourly space velocities (GHSVs). The results show that the selectivity for AA increases with increasing space velocity of the reaction stream. They also show that increasing the space velocity reduces the contact time between AA and the catalyst, which could prevent the products cracking or deep oxidation occurring. A comparison of the AA selectivities of Cr-doped and undoped catalysts under each space velocity shows that the selectivity of the Cr-doped catalyst is significantly higher than that of the undoped one. This may be because the Cr-doped catalysts prevent cracking or further oxidation of the products.

The catalytic performance of MoVTenbCr_{0.002}O_x at different GHSVs, water volumes, and propane:oxygen ratios was investigated to study the effects of the reaction conditions (Fig. 2). Water vapor was treated as an ideal gas when calculating GHSV. Figure 2(a) shows that a high GHSV leads to high selectivity, but the activity first increases and then decreases with increasing GHSV. When GHSV is 3197 mL/(g·h), the activity and selectivity are close to the highest values, and the yield of AA is maximum. We explored the influence of the reaction temperature on the catalytic performance at 390, 400, 410, and 420 °C. The catalyst gave the best performance at 400 °C. Figure 2(b) and (c) also show that the catalyst gave a good performance at low water flow rate and high propane/oxygen ratios. To summarize, a GHSV of 3197 mL/(g·h), a reaction temperature of 400 °C, a propane/oxygen molar ratio of 1:2, and a water flow rate of 0.5 mL/h are the best reaction conditions, and the maximum conversion of propane and selectivity for AA are 64.8% and 78.3%, respectively. The yield of AA (50.7%) exceeded the highest yield of AA (48%) previously reported.

3.2. Bulk structural characterization of catalysts

According to the XRD patterns shown in Fig. 3, the catalysts doped with different amounts of Cr consisted mainly of three

Fig. 1. Product distribution in selective oxidation of propane using Cr-doped and undoped MoVTenbO_x catalysts at different GHSVs. (1) $y = 0$; (2) $y = 0.002$.

phases: Mo_{5-x}(V/Nb)_xO₁₄ ($2\theta = 7.78^\circ, 8.78^\circ, 14.08^\circ, 22.18^\circ, 23.38^\circ, 24.98^\circ, 29.78^\circ, 31.58^\circ, 32.48^\circ, \text{ and } 33.58^\circ$), an M2 phase (Te_{0.33}Mo_{3.33}) ($2\theta = 22.18^\circ, 28.28^\circ, 36.28^\circ, 45.28^\circ, \text{ and } 50.08^\circ$), and an M1 phase (Te₂M₂₀O₅₇) ($2\theta = 7.78^\circ, 9.08^\circ, 22.18^\circ, 26.28^\circ, 26.88^\circ, 27.38^\circ, 29.28^\circ, \text{ and } 35.48^\circ$), where M represents either Mo, V, or Nb [14–16]. The XRD results for catalysts with different Cr contents were the same, and peaks representing the crystalline phase of CrO_x were not observed, probably because the amount of added Cr was small or the Cr species were highly dispersed in the catalyst.

3.3. Surface structural characterization of catalysts

The XPS results and specific surface area of the catalysts are listed in Table 2. Because the differences in specific surface areas among the catalyst are very small, their effect on the catalytic performance can be ignored. However, Cr doping significantly changes the amounts of Mo⁶⁺, V⁵⁺, and Te⁴⁺ species on the catalyst surface. Although the changes are not regular, two points can be noted. One is that the amounts of Mo⁶⁺, V⁵⁺, and Te⁴⁺ species on the surface increase significantly when a small

Fig. 2. Catalytic performance of MoVTenbCr_{0.002}O_x as a function of GHSV (a), water content (b), and O₂:propane molar ratio (c). Reaction conditions: (a) O₂:propane = 2:1, 390 °C; (b) O₂:propane = 2:1, 400 °C; (c) GHSV = 3197 mL/(g·h), water flow rate: 0.5 mL/h, 400 °C.

Fig. 3. XRD patterns of MoVTenbCrO_x catalysts.

Table 2

XPS results and surface area of MoVTenbCrO_x catalysts with different Cr contents.

Cr content (<i>y</i>)	Mo ⁶⁺ / (Mo ⁶⁺ +Mo ⁵⁺)	V ⁵⁺ / (V ⁵⁺ +V ⁴⁺)	Te ⁴⁺ / (Te ⁶⁺ +Te ⁴⁺)	Cr ³⁺ / (Cr ³⁺ +Cr ²⁺)	Surface area (m ² /g)
0	0.79	0.42	0.60	0	2.89
0.002	0.96	0.47	0.86	0.75	2.65
0.006	0.91	0.48	0.85	0.82	—
0.01	0.93	0.43	0.91	0.96	3.07

amount of Cr is added. The other is that the contents of Cr³⁺ and Te⁴⁺ on the surface also increase with increasing Cr content. The XPS results show that the valence state changes of these species may be the result of a redox reaction taking place between Cr and Mo, V, and Te species on the catalyst surface. In the M1 phase in particular, Te in the pore spaces can more easily maintain the redox cycle, Te⁶⁺ + Cr²⁺ ⇌ Te⁴⁺ + Cr³⁺, than Mo and V in the frame structure can, which may result in a significant increase in the Te⁴⁺ content. However, further study is needed to determine whether the Cr in the catalyst is located on the catalyst surface or in the bulk.

V⁵⁺ and Cr³⁺ species are active sites for the activation of propane, and an increase in the numbers of these two species will lead to high propane conversion. Te⁴⁺ sites are closely related to the AA selectivity, as they are the active sites that produce allyl radicals by α-H abstraction from propylene. Furthermore, the reaction intermediates are mainly adsorbed on Mo sites, and Mo⁶⁺ favors oxygen insertion into intermediates to obtain the product. The number of Mo⁶⁺ species is therefore also related to the catalytic performance [6,17]. The experimental results show that the trend in changes in the V⁵⁺ species on the catalyst surface caused by Cr doping corresponds to the trend in changes in propane conversion, but there is no obvious relationship with changes in the Cr³⁺ content, which suggests that the number of V⁵⁺ species on the surface is an important factor determining the conversion of propane. For the catalyst with *y* = 0.002, the numbers of V⁵⁺, Mo⁶⁺, and Te⁴⁺ species on the surface are all close to the highest, which could be one reason for high catalytic activity and AA yield of the catalyst. When the Cr content increases, the content of V⁵⁺ on the surface decreases, that of Mo⁶⁺ remains almost the same, and that of Te⁴⁺

Fig. 4. H₂-TPR profiles of MoVTenbCrO_x catalysts.

increases. The conversions and selectivities all significantly decrease. This indicates that a high content of Cr³⁺ is unfavorable to the reaction, and for the best performance, the catalysts need to have appropriate proportions of V⁵⁺, Mo⁶⁺, and Te⁴⁺ species. An appropriate Cr content may play an important role in adjusting the proportions of V⁵⁺, Mo⁶⁺, and Te⁴⁺ species on the catalyst surface.

H₂-TPR profiles of the catalysts are presented in Fig. 4. A reduction peak is observed for the MoVTenbCrO_x catalysts at about 600 °C [18, 19]. A comparison of the H₂ consumptions and reduction temperatures of all the catalysts shows that appropriate Cr doping can make the active species easier to reduce, and the reducibility trend for each catalyst is consistent with that of propane conversion. In particular, the catalyst with *y* = 0.002, which gives the highest H₂ consumption and lowest reduction temperature, has the best catalytic performance. The H₂-TPR and XPS results confirmed that Cr promoted the oxidation abilities of the catalysts, which is beneficial to the reaction.

The selective oxidation of propane follows a redox mechanism, in which gas-phase O₂ can adsorb on the catalyst surface to oxidize the reduced catalyst. We therefore studied the O₂ desorption abilities of catalysts with different amounts of Cr. As can be seen from Fig. 5, both the peak area and the temperature of O₂ desorption change with increasing Cr content. The O₂ desorption temperatures of the *y* = 0 and 0.01 catalysts are

Fig. 5. O₂-TPD profiles of MoVTenbCrO_x catalysts.

relatively low, about 430–450 °C, with big peak areas, and these shift to higher temperatures of about 490 °C for the $y = 0.002$ and 0.006 catalysts, with smaller peak areas. The desorption properties and reactivities of the lattice oxygens are different for different oxygen species on the catalysts as they are present in different environments. It has been reported that O^- , which is more stable, showed higher olefin selectivity than other oxygen species did in reactions with C_2 or C_4 hydrocarbons [20]. In contrast, O^{2-} , with poor stability, was more likely to give products such as acetic acid and formate. Furthermore, this oxygen species was quite active, highly reactive, and beneficial to the deep oxidation of hydrocarbons because it combines relatively loosely with metal ions [21]. Compared with the $y = 0.002$ and 0.006 catalysts, the $y = 0$ and 0.01 catalysts had lower desorption temperatures and higher amounts of O_2 were desorbed; this could be one reason for more carbon oxide and acetic acid obtained with these two catalysts.

The NH_3 -TPD profiles of the catalysts are shown in Figs. 6 and 7. It can be seen that the desorption temperatures and the desorption peak areas of the Cr-doped catalysts were lower than those of the undoped catalyst. The $y = 0.002$ catalyst had the lowest desorption temperature and the lowest amount of acid sites, but gave the best catalytic performance. As we know, the catalyst used for selective oxidation of propane to AA needs an appropriate amount of acid sites of appropriate strengths on the catalyst surface. Otherwise, it can promote cleavage of propane C–C bonds or complete oxidation of intermediates. Ac-

cording to the NH_3 -TPD results, the catalysts with $y = 0$ and 0.01 have larger numbers of acid sites, and the acid strengths of the sites are higher than in the other catalysts. A combination of these results and the O_2 -TPD results suggests that both the catalysts have strong oxidation abilities, which may make it easier for propane and the products to adsorb on the catalyst surface, resulting in bond cleavage or deep oxidation of intermediates. In contrast, the catalyst with $y = 0.002$ has the smallest number of acid sites, the weakest acid strength, and the weakest oxidation ability, so it gives the highest AA selectivity.

3.4. 2-Propanol oxidation

Scheme 1 shows a possible reaction pathway in the selective oxidation of propane [5,22,23]. Path I comprises conversion of propane to propylene, which is further oxidized to AA via acrolein. Path II involves oxidation of propane to 1-propanol, and 1-propanol is subsequently either converted to propylene by dehydration or to propionic acid by further oxidation via propionaldehyde. Path III is similar to Path II except that propane is oxidized to 2-propanol, and then 2-propanol either dehydrates to propylene or further oxidizes to acetone or acetic acid. According to previous research, the conversion of propane to propylene is the RDS during propane oxidation. Therefore, the conversion of propane and the AA yield should have some connection with the RDS. As shown in Table 3, the main products of 2-propanol oxidation are propylene and acetone. The selectivity for propylene changes little, but first increased and then decreased with increasing Cr content. The change in 2-propanol conversion is obvious, with a similar trend. Two points can be observed from the results. One is that the addition of Cr species promoted the dehydration step, but the effect is not significant. The other is that after Cr doping, the improvement in AA selectivity in selective oxidation of propane is much higher than the increase in propylene selectivity in 2-propanol oxidation. It is therefore suggested that the selec-

Fig. 6. NH_3 -TPD profiles of $MoVTeNbCr_yO_x$ catalysts.

Fig. 7. NH_3 -TPD peak areas for $MoVTeNbCr_yO_x$ catalysts.

Scheme 1. Reaction pathways in propane oxidation.

Table 3

Oxidation of 2-propanol over $MoVTeNbCr_yO_x$ catalysts.

Cr content (y)	2-Propanol conversion (%)	Propylene selectivity (%)	Acetone selectivity (%)
0	27.8	53.04	46.96
0.002	72.48	59.81	40.19
0.006	78.07	58.52	41.48
0.01	28.55	55.71	44.29

Graphical Abstract

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An outstanding Cr-doped catalyst for selective oxidation of propane to acrylic acid

Aixin Xu, Yang Wang, Hanqing Ge, Shu Chen, Yanhua Li, Weimin Lu*

Zhejiang University; Lanzhou Chemical Research Center of Petrochemical Research Institute, China Petroleum

An active MoVTenbO_x catalyst doped with the optimal amount of Cr gave an acrylic acid yield of 50.7%, exceeding the highest acrylic acid yield reported to date.

tive oxidation of propane to AA mainly occurs by path I, and Cr doping facilitates the RDS. This hypothesis needs further experimental confirmation.

4. Conclusions

We report a series of MoVTenbCr_yO_x catalysts for the selective oxidation of propane to AA. An AA yield of 50.7% was achieved, exceeding the highest AA yield reported to date. The effect of Cr doping of MoVTenbO_x catalysts on selective oxidation of propane was also investigated. The results show that Cr doping significantly changes the surface and bulk properties. Although Cr doping did not significantly change the phase structures and specific surface areas of the catalysts, it regulated the contents of different metal ions with different valences on the catalyst surface. The contents of Mo⁶⁺, V⁵⁺, and Te⁴⁺ species on the catalyst surface are in appropriate ranges as a result of Cr doping, so the oxidation capacity of the catalyst is enhanced, resulting in a significant increase in propane conversion. An appropriate amount of Cr doping reduces the strength and number of acid sites on the catalyst surface, inhibiting C–C bond cleavage in the intermediates and further oxidation of AA; this increases the AA selectivity. The results might be useful in studies of doping with other elements to improve the redox or acid properties of catalysts and will help to establish the basis for exploiting catalysts that have independent intellectual property rights, and are highly efficient for the selective oxidation of propane to AA.

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Cr掺杂的丙烷选择氧化制丙烯酸高效催化剂

徐爱新^a, 王 阳^a, 葛汉青^b, 陈 淑^a, 李彦花^a, 陆维敏^{a,*}

^a浙江大学催化研究所, 浙江省应用化学重点实验室, 浙江杭州310028^b中国石油石油化工研究院兰州化工研究中心, 甘肃兰州730000

摘要: 在丙烷选择氧化制丙烯酸催化剂 MoVTenbO_x 的活性相M1基础上掺杂一定量的Cr, 当Cr/Nb摩尔比为0.002时, 催化剂具有很高的丙烯酸选择性(78.3%)和收率(50.7%); 并采用X射线衍射、X射线光电子能谱、程序升温还原、 O_2 程序升温脱附、 NH_3 程序升温脱附和异丙醇氧化等手段对催化剂的构效关系进行了探讨. 结果表明, 适量Cr的添加可调节催化剂表面 Mo^{6+} 、 V^{5+} 和 Te^{4+} 等物种含量, 提高催化剂的氧化能力, 使丙烷转化率增加. 同时, 适量Cr的添加使得催化剂表面酸强度下降, 酸性位点数量减少, 从而抑制丙烯酸的深度氧化, 提高了丙烯酸选择性.

关键词: 丙烷; 选择氧化; 丙烯酸; MoVTenbO_x 催化剂; 铬掺杂

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*通讯联系人. 电话: 13777462563; 电子信箱: luweimin@zju.edu.cn

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1. 前言

近年来, 随着塑料、聚合物、纤维和有机橡胶在新兴市场中需求的快速增长, 丙烯酸的需求也大幅提高^[1]. 目前, 工业上丙烯酸主要是通过丙烯的部分氧化制取. 但由于丙烯的需求量不断增加, 其价格大幅提高, 而储量丰富、价格低廉的丙烷却尚未被充分利用^[2]. 因此采用丙烷代替丙烯, 通过一步法制取丙烯酸引起了人们的广泛关注^[3,4]. 研究发现, 拥有M1和M2相的 Mo-V-Te(Sb)-Nb-O 催化剂对于丙烷选择氧化制备丙烯酸的反应最具应用前景^[5,6]. 日本Mitsubishi公司将该催化剂用于丙烷选择氧化反应中, 丙烯酸收率为48%, 初步具备了作为工业应用的条件^[7]. 因此研发一种具有我国自主知识产权的高效催化剂具有重要意义.

从反应路径来看, 丙烷选择氧化制丙烯酸过程可分两步. 首先是丙烷活化并脱氢生成丙烯, 此步为整个反应的速控步; 然后是丙烯选择氧化经丙烯醛得到丙烯酸^[5,8,9]. 可见在此反应中, 催化剂的氧化还原性能提高和速控步的反应速率非常关键.

在 MoVTenbO_x 体系中添加一定量的W和Pd可以提高反应速控步的速率, 使催化剂性能有所改善, 但最终丙烯酸收率增加不大^[10,11]. 在丙烷氧化脱氢制备丙烯的催化剂中, 在 $\text{CrO}_x/\text{Al}_2\text{O}_3$ 表面负载一定量的 VO_x 比 $\text{VO}_x/\text{Al}_2\text{O}_3$ 催化剂有着更高的反应性能和丙烯选择性, 原因是表面的V-O-Cr取代了V-O-Al或V-O-V^[12]. 另外 $\text{CrO}_x/\text{TiO}_2$ 等催化剂也可用于丙烷脱氢制备丙烯的反应中^[13].

基于Cr具有较强的催化丙烷脱氢功能, 及其与V物种结合可能起到的作用, 本文将Cr掺杂在 MoVTenbO_x 催化剂中, 并用于丙烷选择氧化制备丙烯酸的反应中, 初步讨论催化剂构效关系.

2. 实验部分

2.1. 催化剂制备

采用共沉淀法制备催化剂 MoVTenbO_x ($\text{Mo/V/Te/Nb} = 7.82/1.18/0.94/1$). 将一定量的钼酸铵、偏钒酸铵和碲酸的混合物加到20 mL蒸馏水中, 在80 °C搅拌溶解, 再加入20 mL草酸铌溶液, 然后在80 °C搅拌直至蒸干, 并在空气中80 °C干燥12 h. 该粉末样品在 N_2 下分别在150和600 °C焙烧2 h, 即得催化剂. 在上述溶液蒸干前, 加入Cr/Nb摩尔比(y)为0.002, 0.006, 0.008和0.01的硝酸铬溶液, 其它步骤不变, 即制得掺Cr的催化剂 $\text{MoVTenbCr}_y\text{O}_x$. 实验所用药品均为分析纯(国药).

2.2. 催化剂评价

催化剂的评价在常压、连续流动的固定床石英管式反应器中进行(内径 = 7.4 mm), 催化剂用量0.6 g. 为防止产物冷凝, 与气相色谱相连的外部气体管路保持在140 °C. Porapak Qs (4.0 m×3.2 mm)填充柱主要用于分离烃类物质, FID检测器; TDX-01 (2.0 m×3.2 mm)填充柱主要分离氧气和碳氧化物, TCD检测器. 用碳归一法处理色谱数据.

2.3. 催化剂的表征

催化剂的物相鉴定在Rigaku D/Max-B型X射线粉末衍射(XRD)仪上进行, $\text{Cu K}\alpha$ 射线源($\lambda = 0.15406 \text{ nm}$), 管电压40 kV, 管电流40 mA, 扫描范围 $2\theta = 4^\circ - 90^\circ$. 数据用JADE 5.0软件进行分析处理.

X射线光电子能谱(XPS)实验在Thermo ESCALAB 250型X射线扫描能谱仪上进行. $\text{Al K}\alpha$ (1486.6 eV)为辐射源. 以表面污染碳的C 1s结合能($E_b = 284.6 \text{ eV}$)为内标.

氢气程序升温还原(H_2 -TPR)实验在自建的反应装置上进行. 催化剂用量为30 mg, 首先在Ar气氛下升到

300 °C 维持 30 min 以脱除吸附的 H_2O 和 CO_2 等, 降至 100 °C 后, 切换为 10% H_2/Ar 混合气体 (30 mL/min), 以 10 °C/min 升至 700 °C, 尾气用 TCD 检测。

程序升温脱附氧 (O_2 -TPD) 检测催化剂的氧流动性。催化剂首先在 Ar 保护下 400 °C 预处理 30 min, 然后降温至 50 °C 吸附氧气 30 min, 吸附完后利用 Ar 吹扫石英管 40 min 至基线走平, 然后以 10 °C/min 升至 650 °C, O_2 的脱附量用 TCD 检测。

程序升温脱附氨 (NH_3 -TPD) 用于表征催化剂表面酸性, 催化剂用量为 0.1 g。催化剂先在 He 气氛下 400 °C 预处理 30 min, 降至 50 °C。然后在 10% NH_3/He 混合气体 (30 mL/min) 下吸附 40 min, 然后利用 He 吹扫催化剂至基线走平; 之后以 10 °C/min 升至 600 °C, NH_3 的脱附量通过 TCD 检测。

异丙醇氧化反应用于研究对反应速控步的影响。实验在流动的固定床装置中进行, 反应气的组成包括异丙醇、水、氧气和氮气, 其摩尔分数分别为 0.08, 0.21, 0.33 和 0.38。由于醇的氧化在 350–400 °C 反应极其迅速, 以至于无法获取各催化剂性能差异, 所以反应在 250 °C 进行, 产物通过在线色谱检测。

3. 结果与讨论

3.1. 催化剂的催化性能

表 1 为不同 Cr 掺杂量的 MoVTenbO_x 催化剂上丙烷选择氧化制备丙烯酸反应性能。由表可见, 随着 Cr 加入量的增多, 丙烷转化率先明显增大后又减少, 丙烯酸选择性也有一定程度的提高; 当 Cr/Nb 摩尔比 $y = 0.002$ 时, 丙烷转化率接近最高, 丙烯酸的收率也达最高, 为 48.7%。结果表明, 在 MoVTenbO_x 催化剂中掺入少量的 Cr 对该反应的催化性能有很大影响。

图 1 为 $y = 0$ 与 0.002 时, $\text{MoVTenbCr}_y\text{O}_x$ 催化剂在不同空速时丙烷选择氧化产物丙烯酸、乙酸、碳氧化物 (CO 与 CO_2) 和其它副产物 (甲烷、乙烷、甲醛、乙醛、丙烯醛、丙酮) 选择性的对比图。可以看出, 两种催化剂上丙烯酸选择性均随空速的增大而增大, 说明空速的增大减少了丙烯酸与催化剂的接触时间, 从而不利于丙烯酸的裂解或深度氧化。还可以看出, 在相同空速条件下, 掺 Cr 催化剂上丙烯酸选择性明显高于未掺杂 Cr 的, 可能是由于 Cr 的掺入抑制了丙烯酸的深度氧化。

图 2 为不同反应条件下 (空速、水量和烷氧比) $\text{MoVTenbCr}_{0.002}\text{O}_x$ 催化剂的性能, 在计算空速时, 将水蒸气视为理想气体。由图可见, 随着空速的增加, 催化剂

活性先增大后减小, 而丙烯酸选择性一直增大; 至 3197 mL/(g·h) 时, 丙烷转化率和丙烯酸选择性最高。因此在空速为 3197 mL/(g·h) 及其它反应条件不变时考察了温度对催化剂性能的影响, 发现 400 °C 时丙烯酸的选择性和收率最高。另外, 丙烷转化率随着水量的增大而降低, 但随着氧气与丙烷比例的增加而增大。因此, $\text{MoVTenbCr}_{0.002}\text{O}_x$ 催化剂适宜的反应条件为 400 °C, 空速 3197 mL/(g·h), 水量 0.5 mL/h, 氧气与丙烷比 2:1, 此时丙烷转化率和丙烯酸选择性分别为 64.8% 和 78.3%, 丙烯酸收率为 50.7%, 超过文献报道值 (48%)。

3.2. 催化剂的体相性质

图 3 为各催化剂的 XRD 谱。可以看出, 不同 Cr 掺杂量的催化剂主要包括三种晶相: $\text{Mo}_{5-x}(\text{V/Nb})_x\text{O}_{14}$ ($2\theta = 7.78^\circ, 8.78^\circ, 14.08^\circ, 22.18^\circ, 23.38^\circ, 24.98^\circ, 29.78^\circ, 31.58^\circ, 32.48^\circ$ 和 33.58°), M2 相 ($\text{Te}_{0.33}\text{MO}_{3.33}$) ($2\theta = 22.18^\circ, 28.28^\circ, 36.28^\circ, 45.28^\circ$ 和 50.08°) 和 M1 相 ($\text{Te}_2\text{M}_{20}\text{O}_{57}$) ($2\theta = 7.78^\circ, 9.08^\circ, 22.18^\circ, 26.28^\circ, 26.88^\circ, 27.38^\circ, 29.28^\circ$ 和 35.48°), 其中 M 为 Mo, V 或 Nb^[14–16]。由于这三种物相的部分衍射峰位置重叠, 因而很难计算各物相的相对含量。另外少量 Cr 的掺杂并未使催化剂的相组成发生明显的变化, 且未出现氧化铬相。这可能是由于 Cr 的掺杂量较少或高度分散所致。

3.3. 催化剂的表面性质

表 2 为不同 Cr 掺杂量催化剂的 XPS 数据和比表面积。可以看出, 掺入 Cr 后催化剂的比表面积变化很小, 其对催化性能的影响基本可以忽略; 但却使催化剂表面 Mo^{6+} , V^{5+} 和 Te^{4+} 等物种的含量发生明显变化。虽然 Mo^{6+} 和 V^{5+} 物种在表面含量的变化趋势不具有规律性, 但少量 Cr 的加入即可使催化剂表面 Mo^{6+} , V^{5+} 和 Te^{4+} 等物种的量均明显增加; 随着 Cr 掺入量的提高, 催化剂表面 Te^{4+} 与 Cr^{3+} 的含量不断增加。XPS 结果表明, 掺入的 Cr 很有可能与催化剂表面 Mo, V 和 Te 物种发生了一定的氧化还原作用, 使后者价态发生了变化。特别是在 M1 相中, 相比处于骨架结构中的 Mo 和 V 物种, 位于孔道位置的 Te 较易发生 $\text{Te}^{6+} + \text{Cr}^{2+} \rightleftharpoons \text{Te}^{4+} + \text{Cr}^{3+}$, 从而导致 Te^{4+} 含量明显变大。但 Cr 在催化剂中的具体存在状态尚需进一步的研究。

V^{5+} 和 Cr^{3+} 均具有活化丙烷的作用, 对催化剂活性的影响很大, 其含量的增大有利于提高丙烷转化率。而 Te^{4+} 是丙烯脱去 α 氢产生烯丙基自由基的活性位, 与丙烯酸选择性密切相关。由于丙烷反应的中间体主要吸附在 Mo 位点上, 并通过 Mo^{6+} 对中间产物进行插氧, 因此 Mo^{6+}

数量也与催化性能密切相关^[6,17]。结果表明, Cr的掺入引起催化剂表面 V^{5+} 物种含量的变化趋势正好与丙烷转化率的吻合, 而 Cr^{3+} 含量却与丙烷转化率和产物选择性并不存在明显的关联, 因此催化剂表面 V^{5+} 含量是影响丙烷转化率的主要原因之一。当 $y = 0.002$ 时, 催化剂中 V^{5+} 物种比例接近最高, 同时其 Mo^{6+} 和 Te^{4+} 也具有较高含量, 这可能是该催化剂具有较高活性和选择性的原因之一。随着Cr含量继续增大, 表面 V^{5+} 的含量有所降低, Mo^{6+} 的含量变化不大, 而 Te^{4+} 的含量明显提高, 此时丙烷转化率和丙烯酸选择性均明显下降。这表明 Cr^{3+} 含量过高不利于该反应, 而且 $MoVTNbO_x$ 催化剂表面 Mo^{6+} , V^{5+} 和 Te^{4+} 含量适宜时, 催化性能最佳; 而Cr的掺入恰好调节了催化剂表面 Mo^{6+} , V^{5+} 和 Te^{4+} 含量。

H_2 -TPR结果(图4)表明, 所有催化剂均在600 °C左右出现一个耗氢峰^[18,19]; 从还原温度和耗氢量看, 适量Cr的添加提高了催化剂的可还原性, 其还原温度和耗氢量顺序与丙烷转化率变化基本一致。当 $y = 0.002$ 时, 催化剂耗氢量最大, 还原温度最低, 其催化性能最好。由此可见, 适量Cr的加入使得催化剂的氧化能力提高, 有利于反应进行。

丙烷选择氧化过程遵循氧化还原机理, 催化剂的晶格氧还原后, 气相氧通过吸附在催化剂表面使其氧化。因此, 借助 O_2 -TPD实验可了解不同Cr掺杂量催化剂的相对氧脱附能力, 结果如图5所示。

当 $y = 0$ 和0.01时, 催化剂在相对较低的温度(430–450 °C)出现较大的氧脱附峰; 而 $y = 0.002$ 和0.006时, 催化剂在较高的温度(480–500 °C)出现较小的氧脱附峰。由于表面各氧物种和晶格氧所处的环境差别极大, 因此它们的脱附和反应性能也不尽相同: 热稳定性较好的氧物种(如 O^-)在与 C_2 – C_4 烃类反应时, 往往主要形成烯烃^[20]; 热稳定性较差的氧物种(如 O^{2-}), 易得到诸如乙酸和甲酸盐类化合物, 并且这些表面氧物种与金属离子结合较弱, 因而活泼性较高、反应性较强, 在催化反应中都会促进深度氧化^[21]。因此, 相对而言, $y = 0$ 和0.01时, 催化剂具有较低的脱附温度和较多的氧脱附量可能是其在反应中产生大量的碳氧化物和乙酸的原因之一。

图6和图7为各催化剂的 NH_3 -TPD谱。由图可见, Cr的添加使得催化剂上 NH_3 脱附温度降低, 脱附量减少; 当 $y = 0.002$ 时, 催化剂的 NH_3 脱附温度和脱附量均最低, 而此时的催化性能最好。对于丙烷选择氧化制丙烯酸反应, 要求催化剂具有一定的酸性。但是酸性太强或酸量太多将促进丙烷碳-碳键的断裂和中间物的完全氧化,

因而不利于丙烯酸选择性提高。结果表明, 对于 $y = 0$ 和0.01的催化剂, 表面酸性较强和酸量较多, 同时结合 O_2 -TPD结果, 这两种催化剂的氧化能力也比较强。这可能导致反应原料或产物很容易吸附在催化剂表面, 发生断键和深度氧化反应。相反, 当 $y = 0.002$ 时催化剂酸量最少, 酸强度低, 氧化能力也比较弱, 这可能是其具有最高选择性的原因之一。

3.4. 异丙醇氧化

丙烷部分氧化的反应过程涉及3条路径(图式1)^[5,22,23]。路径1中, 丙烷分子氧化脱氢产生丙烯, 然后进一步氧化生成丙烯醛和丙烯酸。路径2涉及丙烷氧化为正丙醇, 然后通过脱水再转化为丙烯, 或者进一步氧化生成丙醛或丙酸。路径3与路径2类似, 丙烷氧化成异丙醇, 再进一步脱水生成丙烯, 或者进一步氧化生成丙酮或乙酸。在丙烷的氧化过程中, 丙烷氧化生成丙烯是速控步, 其反应速率的提高将增加丙烷反应速率和丙烯酸收率。

表3为不同Cr含量的催化剂上异丙醇氧化性能的变化趋势。可以看出, 该反应主要产物仍为丙烯和丙酮。随着Cr掺杂量的增加, 丙烯的选择性先增加后降低, 但变化幅度较小, 而异丙醇的转化率却变化明显。由此可见, Cr的掺入有利于异丙醇脱水生成丙烯, 但是其作用并不是很明显; Cr掺入后丙烯酸选择性增幅远高于异丙醇氧化产物丙烯选择性。因此, 我们初步认为, 丙烷选择氧化制丙烯酸主要按照路径1进行; 而Cr的掺入有利于路径1中速控步的进行, 但尚需进一步的实验验证。

4. 结论

制备了丙烷选择氧化制丙烯酸催化剂 $MoVTNbCr_yO_x$, 其丙烯酸收率高达50.7%, 为文献报道最高值。同时, 讨论了Cr掺杂对 $MoVTNbO_x$ 催化剂上丙烷选择氧化反应性能的影响。结果表明, 虽然适量Cr的掺杂并没有明显改变 $MoVTNbO_x$ 催化剂的相结构和比表面积, 但起到了调节催化剂表面不同价态金属含量的作用, 使得催化剂表面 Mo^{6+} , V^{5+} 和 Te^{4+} 物种的含量处于一种合适的范围内, 从而提高了催化剂的氧化能力, 导致丙烷转化率明显增加。同时少量Cr的掺杂致使催化剂表面酸强度下降, 酸位点数量减少, 抑制了反应中间物的深度氧化反应, 从而提高了丙烯酸选择性。该结果对采用其它元素掺杂, 进一步改善催化剂的氧化还原性能或酸性提供了依据, 为开发具有自主知识产权的丙烷选择氧化制丙烯酸高效催化剂奠定了实验基础。