

Novel Mo-V Oxide Catalysts with Nanospheres as Templates for the Selective Oxidation of Acrolein to Acrylic Acid

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Abstract

Novel Mo-V-PMMA and Mo-V-PS catalysts are prepared by addition of hard polymethyl methacrylate (PMMA) and polystyrene (PS) nanospheres into Mo/V compounds in the preparation process, respectively. The catalytic tests in selective oxidation of acrolein reveal that Mo-V-PMMA catalyst shows very high acrolein conversion (99.1%) and the yield of acrylic acid (90.7%). The BET, DLS, SAXS, XRD, XPS, H₂-TPR and NH₃-TPD measurements reveal that the addition of PMMA and PS nanospheres causes the obvious changes of porous structure, crystal phases composition and chemical properties of catalysts. These differences between Mo-V-PMMA and Mo-V-PS catalysts are attributed to the totally different "real" nano–environment during heat treatment in the high–concentration component mixture. PS nanospheres are in a state of adhesion or agglomeration or not uniformly distributed in the active component solution, while PMMA nanospheres with much better hydrophilicity and monodispersed state promote Mo and V ions more easily and uniformly dispersed in the mixture.

Graphic abstract

Novel Mo-V catalysts are prepared by addition of hard polymethyl methacrylate (PMMA) and polystyrene (PS) nanospheres into Mo/V mixture. Obvious changes of porous structure, crystal phases and chemical properties of catalysts are caused by the nanospheres introduction, showing very high acrolein conversion (99.1%) and the yield of acrylic acid (90.7%) in selective oxidation of acrolein.



Keywords Polymethyl methacrylate · Polystyrene · Mo-V-PMMA catalyst · Mo-V-PS catalyst · Acrolein · Acrylic acid

1 Introduction

Acrylic acid is an important chemical raw material, which is mainly used to manufacture acrylate, superabsorbent resin, water treatment agent and detergent aid. Acrylic

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acid provides very important intermediate for the synthesis and preparation of various fine chemicals due to its excellent polymerization and esterification ability. Acrylic acid catalysts play a very important and irreplaceable role in meeting the increasing demand of acrylic acid in the worldwide. One-step oxidation process of propane or propene to acrylic acid is well-developed [1, 2]. However, at present, a well-developed two-step production process of propene selective oxidation to acrylic acid is mainly used in the industry due to better catalytic activity and higher selectivity of acrylic acid. In the reactions, propene is oxidized with acrolein as the major product and acetone as the main byproduct in the first step. Then acrolein is further re-oxidized to yield acrylic acid and over-oxidized directly to CO and CO₂. Further oxidation of acetone will yield aldehyde, acetic acid and formaldehyde which could be further oxidized to CO and CO_2 in the second step [3]. Direct conversion of propene to acrolein, then to acrylic acid in high efficiency is of great scientific and industrial importance, especially in the current circumstance of cost reduction. The production of acrylic acid at high propene airspeed is an easy and effective method to increase production capacity, but the requirement for catalyst performance also increases significantly.

Over the past several decades, many efforts have been devoted to develop highly active catalysts used for selective oxidation reaction. Composite industrial catalysts with different elements show great differences in catalytic properties. Metallic oxides are the most widely studied and effective catalysts. Mo-V based catalysts for the two-step oxidation reactions have been an active topic of research in recent years [4–18]. Mo and/or V is usually considered to be the basic redox element [4, 5]. In addition, other metal elements, including transition metals (Fe, Co, Ni, Cu) and lone-pair elements (Te, Sb, Bi) play stimulative roles in oxidation-reduction reaction. A series of metal ions participate in the active sites for oxidation reactions, not isolated ions [6]. Mo-V based catalysts added other metal ions have been proposed as efficient catalysts in the oxidation reactions of propane or propene to acrylic acid [7-12]. It is generally believed that Te added to Mo/V based catalyst can better promote the formation of selective partial oxidation catalysts because of the existence of redox couple Te^{6+}/Te^{4+} [13, 14]. Addition of Sb shows the similar role with Te by the redox couple Sb⁵⁺/Sb³⁺ which forms the α -Sb₂O₄ phase as an oxygen inserting element at the surface of the catalysts [15]. Some transition metals such as Fe can decrease the loss of lone-pair elements and stable the catalysts [16]. The presence of Nb improves the selective oxidation reactions which is the result of moderate acid sites and better stability of acrylic acid [17, 18]. A better investigation of the element composition, pore structure and chemical properties of the catalyst is quite necessary for improvement of an efficient catalyst for the oxidation reactions.

In the preparation of catalyst, pore forming agents are often used to change the pore size distribution of catalysts. Most of the pore forming agents are of soft structure, which may cause hole collapse during the calcination of the catalyst, so it is difficult to effectively control the specific pore size. Therefore, selection of a good proppant is beneficial to the formation of specific pore size and even to the improvement of the catalyst performance. The nanospheres of polymethyl methacrylate (PMMA) and polystyrene (PS) are prepared by emulsion polymerization from their respective monomers. The nanospheres can be further used to prepare spherical polyelectrolyte brushes with many functions, such as specific adsorption of proteins [19-21] and nanoreactors for synthesis of magnetic particles [22-24] and metal nanoparticles [25–27]. Therefore, hard nanospheres may be very suitable for pore forming of catalyst.

In this paper, novel acrylic acid catalysts are successfully prepared through employing PMMA and PS nanospheres in the mixture of metal components. Combined with a variety of characterization technologies, we present a comparative investigation on porous structure, crystalline phases and chemical properties of catalysts. The proportion of specific nanopore (50–100 nm) in catalyst is innovatively changed and optimized which shows better catalytic activity under the condition of high loading propene. Small angle X–ray scattering (SAXS) is a powerful tool to analyze the nanoparticles, including metal oxide particles or nano–nanospheres [28–31]. Here, SAXS is used for the first time to "see" the invisible role of nanospheres in the pore size distribution of catalysts.

2 Experimental

2.1 Catalysts Preparation

2.1.1 Materials

All the chemicals and solvents are commercially available and are used without further purification or modification. Ammonium metavanadate (NH_4VO_3 , A111822) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$, A116375) are obtained from Sigma–Aldrich Reagent. Styrene and methyl methacrylate are available from J&K Chemical Ltd. Sodium dodecyl sulfonate (SDS) and potassium persulfate (KPS) are purchased from Shanghai reagent company. The water used in all experiments is purified by reverse osmosis (Shanghai RO Micro Q).

2.1.2 Mo-V Catalyst

50 mmol ammonium metavanadate (NH_4VO_3) are dissolved in 100 ml of distilled water. Varying amounts of ammonium molybdate ((NH₄)₆Mo₇O₂₄.4H₂O) from 14.3 mmol to 57.4 mmol (changing Mo/V) are completed dissolved in 100 ml water. Under vigorous stirring (500 rpm) all the above solutions are mixed in a certain order at room temperature. After stirring for 30 min, the mixed liquids are dried at 100 °C for 24 h. The obtained solids are calcined for 4 h at 410 °C.

2.1.3 Mo-V-PMMA Catalyst/Mo-V-PS Catalyst

Hard nanospheres of PMMA (polymethyl methacrylate) and PS (polystyrene) are applicated in the catalyst preparation process. PMMA and PS nanospheres are prepared by emulsion polymerization. First, 0.5 g sodium dodecyl sulfonate (SDS) are dissolved in 150 ml of water and mixed with 26 g styrene/12 g methyl methacrylate under a constant stirring rate (300 r/min). 1.4 g potassium persulfate (KPS) are dissolved in 50 ml of water and added into the reactor. The polymerization lasts for 2 h at 80 °C under nitrogen atmosphere, and PMMA and PS nanospheres are synthesized.

 $\rm NH_4VO_3$ and $\rm (NH_4)_6Mo_7O_{24}.4H_2O$ are separately dissolved in distilled water and mixed which is the same step as the above preparation method of Mo-V catalyst. Under vigorous stirring (500 rpm), PMMA/PS nanospheres are added into the above mixture at room temperature. After stirring for 0.5 h the mixed liquids are dried for 24 h at 100 °C and the obtained solids are calcined for 4 h at 410 °C in air, formatting Mo-V-PMMA and Mo-V-PS catalysts, respectively.

2.2 Catalysts Characterization

The BET specific surface areas of the catalysts are measured on a Micromeritics Tristar 3000 instrument by N₂ physisorption at -196 °C. The pore size and pore volume of the catalysts are calculated by BJH adsorption curve. The samples are degassed for 3 h at 220 °C.

Thermogravimetric analyzer (TGA) experiments are carried out on a TA Instruments SDT Q600 apparatus. The temperature of 20 mg sample is increased to 600 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min.

Dynamic light scattering (DLS) is used to collect particle size and distribution analysis of nanospheres which is performed on a Malvern Zetasizer Nano ZS 90 instrument with the high resolution of 5 mV and measuring range of particle size $0.6 \text{ nm} \sim 6 \text{ nm}$.

Transmission electron microscopy images (TEM) are obtained on a JEOL 2100F instrument operating at 200 kV.

Small angle X-ray scattering (SAXS) measurements are performed at BL16B1 beamline (Shanghai Synchrotron Radiation Facility, SSRF, China). The sample-to-detector distance is 10 m with MAR 165 CCD detector. Each scattering curve for every sample is an average of 10 measurements to reach better signal-to-noise ratio. After applying detector corrections and azimuthally averaged, two-dimensional scattering patterns are converted to one-dimensional scattering curves and normalized to an absolute scale. The absolute scattering intensity I(q) of sample is obtained after subtracting the normalized background.

X–ray diffraction patterns (XRD) are collected using a Broker ADVANCED 8X diffractometer. CuK α radiation obtained at 40 kV and 40 mA is employed as the X–ray source.

X-ray photoelectron spectroscopy (XPS) analysis is performed using a Shimadzu Kratos Ultra DLD instrument with AlK α radiation (5 mA, 15 kV, 1486.6 eV) as the X-ray source. The photoelectronic signals of C 1 s, O 1 s, Mo 3d and V 2p are analyzed with a multi-channel detector. The samples are submitted to electrons from a W-filament to reduce sample charging effects. The binding energy value of C 1 s is adjusted to 284.8 eV as energy reference.

 H_2 temperature programmed reduction (H_2 -TPR) experiments are carried out on a Micromeritics AutoChem II 2950 apparatus. 50 mg of sample is pre-treated in a mixed flow of O_2 and Ar (50 ml/min, 5% O_2) at 450 °C for 30 min. After cooling to room temperature, the samples are fluxed with a mixed flow of H_2 and Ar (50 ml/min, 5% H_2) for 15 min. Then the temperature is increased to 600 °C at a heating rate of 10 °C/min.

 NH_3 temperature programmed desorption (NH_3 -TPD) experiments are carried out on a PX200 apparatus. 200 mg of sample is pre-treated in a mixed flow of He at 400 °C for 2 h. After cooling to room temperature, the samples are fluxed with a flow of NH_3 for 30 min. Then the temperature is increased to 400 °C at a heating rate of 10 °C/min.

2.3 Catalytic Reaction

The catalytic performance test is carried out at atmospheric pressure in a fixed bed reactor which includes two stainless steel tubular reactors (I.D. 15 mm; length 330 mm) in series. The acrolein as the main product in the first reactor enters the second reactor to provide the feed gas. Commercial catalyst is used in the first reactor, and the studied catalysts with the constant amounts are put into the second reactor. A mixture of $C_3H_6/air/H_2O$ with volume ratio of 1/7.3/1.7 passes through the catalyst bed in the first reactor. The amount of air and water added in the second reactor is one-third that in the first reactor. The temperature of the second reactor is controlled in 240~280 °C. The products are analyzed by an online gas chromatograph (Agilent 7890B) with a HP-FFAP column (50 m) connected to an FID to analyze the organic oxygenates in the products. The other components are separated by Unibeads 1 s 60/80 UM (2 ft), Unibeads 1 s 60/80 UM (4 ft), and HP-A1/S (25 m) columns and analyzed by a TCD.

3 Theory

3.1 Theory Of SAXS Measurement

The measured scattering intensity I(q) of nanospheres as a function of scattering vector (q) contains three independent contributions [29–33]:

$$I(q) = I_{cs}(q) + I_{fluct}(q) + I_{ps}(q)$$
⁽¹⁾

In Eq. 1, $I_{cs}(q)$ is the major contribution to the scattering intensity which is determined by the structure of nanospheres in solution. $I_{cs}(q)$ equals to $B^2(q)$ for the symmetric sphere with radius R, B(q) is the scattering amplitude which is described by Eq. 2 [29–33]:

$$B(q) = 4\pi \int_{0}^{R} \left[\rho^{e}(r) - \rho_{m}^{e}\right] \frac{\sin(qr)}{qr} r^{2} dr$$
(2)

Here, $\rho^e(r)$ is the electron density of nanosphere, ρ^e_m is the electron density of solvent. And $\rho^e(r) - \rho^e_m$ is the electron density difference between nanosphere and the solvent.

The $I_{fluct}(q)$ is caused by the thermal fluctuations of environment in solution which is calculated by Eq. 3 [29–33].

$$I_{fluct}(q) = \frac{I_{fluct}(0)}{1 + \xi^2 q^2}$$
(3)

where ξ is the correlation length determined by the spatial environment fluctuations. The $I_{fluct}(q)$ plays an important role at high q values.

The $I_{ps}(q)$ is resulted from the density differences in nanospheres which is usually neglected.

The fitting scattering intensity of nanospheres is obtained by Eq. 4:

$$I(q) = \left[4\pi \int_0^{\mathsf{R}} \Delta \rho^e(r) \frac{\sin(qr)}{qr} r^2 dr\right]^2 + \frac{I_{fluct}(0)}{1 + \xi^2 q^2} \tag{4}$$

In Eq. 4, $\Delta \rho^e(r) = \rho^e(r) - \rho_m^e$. The $\Delta \rho^e(r)$ is a critical parameter for fitting the SAXS curve shown in Fig. 1.



Fig. 1 Distribution model of excessive electron density of nanosphere vs radius r

4 Results and Discussion

4.1 Catalyst Activity

The commercial catalyst is used in the oxidation of propylene of the first reactor. The Table 1 shows that the yield to acrylic acid and acrolein from the first reactor is 13.3% and 80.9%, respectively. The products from the first reactor enter the second reactor as feed gas. The activities of the Mo-V catalyst, Mo-V-PMMA catalyst and Mo-V-PS catalyst in oxidation of acrolein to acrylic acid are shown in Table 2. Acrylic acid, acrolein, aldehyde, acetic acid and carbon oxides are the main reaction products. The acrolein conversion is 94.9% and the yield to acrylic acid is 88.2% in Mo-V catalyst. Obvious differences in catalytic performance have been observed between Mo-V-PMMA and Mo-V-PS catalysts obtained by introduction of two kinds of different nanospheres. Mo-V-PMMA5% catalyst presents the highest activity in acrolein oxidation, giving a high acrolein conversion of about 99.1% and acrylic acid yield of 90.7%. However, Mo-V-PS5% catalyst has

$$\Delta \rho^{e}(r) = \rho^{e}(r) - \rho^{e}_{m} = \frac{\Delta \rho^{e}_{1}(r \le r_{0}) = 49.6 \text{ e/mn}^{3}(\text{for PMMA}) \text{ or } 6.4 \text{ e/mn}^{3}(\text{for PS})}{\Delta \rho^{e}_{1}(r_{0} < r \le r_{1})}$$
(5)

Where, $\Delta \rho_0^e$ is a constant for PMMA and PS nanospheres in Eq. 5. $\Delta \rho_1^e$ is caused by the adhesion of something else to the surface of nanospheres in solution which is calculated through the fitting curve.

a relatively poor catalytic performance with only 86.3% yield to acrylic acid (acrolein conversion ~ 92.0%) among the studied catalysts. In addition, higher concentration of nanospheres (5%) is slightly beneficial to improve the activity of the catalyst than lower concentration (3%). In

the following, the mass percentage of added nanospheres is 5% in studied Mo-V-PMMA and Mo-V-PS catalysts.

The difference of catalytic performance is directly attributed to the addition of nanospheres. At the condition of thermo-treatment, part of the groups $-CH_2C(CH_3)$ (COOCH₃) on the surface of PMMA nanospheres form -CH₂C(CH₃)COOH and CH₃OH by the hydrolytic reaction in the acidic environment (as seen in Eq. 6) while there is no hydrolysis reaction on the $-CH_2CH(C_6H_5)$ - groups of the PS nanospheres surface. This is one of the most obvious differences between PMMA and PS nanospheres in the preparation process of catalysts. The activity differences in Mo-V-PMMA and Mo-V-PS catalysts may be mainly attributed to porous structure [34], crystal phase composition [35], and chemical property of surface [36]. In the following part, BET, XRD, XPS, TPR and TPD are employed to explore the apparent differences caused by addition of two kinds of nanospheres.

$$(CH_{2} - CH_{3})_{n} \longrightarrow (CH_{2} - CH_{3})_{n} + CH_{3}OH + CH_{3}OH$$

$$(CH_{2} - CH_{3})_{n} + CH_{3}OH + CH_{3}OH$$

$$(CH_{3}) + CH_{3}OH + C$$

4.2 Pore Structure Measurement (BET)

The BET surface area, total pore volume, and average pore size of Mo-V, Mo-V-PMMA and Mo-V-PS catalysts are summarized in Table 3. Compared with Mo-V catalyst, the pore volume of Mo-V-PMMA catalyst increases from $0.019 \text{ cm}^3/\text{g}$ to $0.028 \text{ cm}^3/\text{g}$, and the proportion of nanopores more than 50 nm increases significantly from 36.5% to 57.2%, especially in the range of pore size 50–100 nm. The specific area and pore size also increase in varying degrees. While the addition of PS nanospheres leads to the decrease in specific area, pore volume and pore size of Mo-V-PS catalyst. The proportion of nanopores of Mo-V-PS catalyst more than 50 nm slightly increases from 36.5% to 38.8%,

Table 1 Oxidation of propylene in the first reactor

Catalyst no	Propylene conversion (%)	Yield to products (%)							
		Acrylic acid	Acrolein	Aldehyde	Acetic acid	СО	CO ₂		
Commercial catalyst	99.3%	13.3%	80.9%	1.5%	0.6%	1.3%	1.6%		

Reaction conditions: 2.5 ml of catalyst; gas composition: propene/air/H₂O = 1:7.3:1.7(v/v); C₃H₈ flow: 3.3 ml/min, reaction temperature: 360 °C

Table 2 Activity of the catalysts in oxidation of acrolein to	Catalyst no	Acrolein conversion (%) ^a	Yield to products (%) ^b						
acrylic acid in the second reactor			Acrylic acid (%)	Acrolein (%)	Aldehyde (%)	Acetic acid (%)	CO (%)	CO ₂ (%)	
	Mo-V	94.9	88.2	4.1	0.4	1.9	1.7	2.9	
	Mo-V-PMMA2% ^c	98.8	90.2	1.0	0.3	2.3	2.0	3.4	
	Mo-V-PMMA5%	99.1	90.7	0.7	0.1	2.3	2.1	3.2	
	Mo-V-PS2%	91.8	86.0	6.6	0.3	1.9	1.5	2.8	
	Mo-V-PS5%	92.0	86.3	6.5	0.3	1.8	1.5	2.5	

Reaction conditions: 1 ml of catalyst; raw gas: the products from the first reactor, combining with the added air and H2O (one-third of the first reactor); reaction temperature: 270 °C

^aAcrolein conversion calculated by deducting the acrolein from the first reactor

^bThe data of yield to products from the second reactor

^cThe mass percentage of added nanospheres

Tabl	e 3	Anal	vsis	of	ph	vsical	pro	perties	of	the	catal	ysts
			~									2

Catalyst	Specific area (m ² /g) BET	Pore volume(cm ³ /g) BJH	Pore size (nm) BJH	Pore size distribution (adsorption branch, %)				
				<20 nm	20–50 nm	50–100 nm	>100 nm	
Mo-V	5.3	0.019	16.8	22.5	40.8	27.6	8.9	
Mo-V-PMMA	6.5	0.028	18.6	23.2	19.6	41.3	15.9	
Mo-V-PS	4.1	0.015	16.3	23.5	37.7	23.3	15.5	

but reduces in the range of 50–100 nm. According to references [2, 4, 5, 37], the ratio of pore size in the range of 50–100 nm may be an important factor because it is directly related to the activity of the catalyst. Therefore, it is of great significance to study the effect of the addition of two kinds of nanospheres on the pore size of the catalyst.

4.3 Nanospheres Characterization

In order to study the effect of nanosphere on the pore size of catalyst, the two kinds of nanospheres should satisfy two basic conditions: (1) be completely removed at calcination temperature; (2) be consistent in particle size.

Figure 2 shows the thermogravimetric analyzer (TGA) analysis of PMMA and PS nanospheres. PMMA and PS nanospheres start to decompose at about 310 °C, and completely finish decomposition at about 390 °C. This means that the two nanospheres can be completely removed at calcination temperature (410 °C).

Particle size and distribution analysis of PMMA and PS nanospheres by dynamic light scattering (DLS) are shown in Fig. 3. Both PMMA and PS nanospheres exhibit one narrow and intense peak which means the good dispersion in very diluted condition. The average particle sizes of PMMA and PS nanospheres are both about 75 nm. As shown in the inset of Fig. 3, TEM nano–graphs confirm the regular spherical states with good dispersion in very dilute solution.

The measured particle size of two nanospheres are basically the same (both about 75 nm) from DLS measurement. Combined with the pore size distribution of catalysts in Table 3, the nanopores proportion of Mo-V-PMMA catalyst in the range of 50–100 nm is 41.3% which is much more than 27.6% of Mo-V catalyst. This means that the addition of hard PMMA nanospheres (75 nm) indeed plays an important role in forming precision pore (50~100 nm). However, the



Fig. 2 The TGA analysis of PMMA and PS nanospheres



Fig. 3 The particle size distribution of PMMA and PS nanospheres and TEM micrographs of nanospheres in the inset. The distribution is based on volume distributions

PS nanospheres with the same size (75 nm) doesn't achieve the purpose of pore formation in the range of 50–100 nm, because the nanopores proportion of Mo-V-PS catalyst from 50 nm to 100 nm is only 23.3% which is even smaller than that of Mo-V catalyst.

In the preparation process of catalysts, PMMA and PS nanospheres are added separately to the mixture of Mo/V compound at very high concentration. The aggregation state of nanospheres at high concentration determines the influence on the structure and performance of catalysts. Small angle X–ray scattering (SAXS) is used to study the "real" aggregation state of nanospheres at high concentration during the preparation process of catalysts.

The scattering intensity curves and excess electron density $(\Delta \rho)$ distribution of PMMA and PS nanospheres at different concentration are shown in Fig. 4a, b, c, d. The fitting curves are based on the nanospheres at infinitely low concentrations. The difference between SAXS curve of sample and the fitting line represents the interaction of sample. The greater the difference, the greater the interaction between the particles in sample. SAXS curves of PMMA nanospheres at different concentrations can almost coincide at very small q (scattering vector) range after concentration normalization, while the PS nanosphere curves don't overlap at low q values. This indicates that there is no obvious interaction among PMMA nanospheres, but intense interaction in PS solution. In other words, PMMA nanospheres are in almost independent and monodispersed state, while PS nanospheres may be in a state of adhesion or agglomeration in high concentration solution.

Further structure and chemical formula analysis of PMAA and PS nanosphere, the side–chain group $-C_6H_5$ in PS is completely insoluble in water, and the formed





Fig. 4 SAXS curves of PMMA (**a**) and PS (**c**) nanospheres as a function of concentration; SAXS curves of PMMA (**b**) and PS (**d**) nanospheres after concentration normalization and the radial distribution

hydrophilic groups of -CH₂C(CH₃)COOH and CH₃OH in hydrolytic reaction on the PMMA nanospheres surface are very soluble in water. The hydrophilic groups are beneficial to make PMMA nanospheres distributed more evenly in the mixture of component. Therefore, combining with the aggregation state of nanospheres at high concentration, we may draw a conclusion that PS nanospheres are precipitated or not uniformly distributed in the active component solution in the catalyst preparation, and PMMA nanospheres with much better hydrophilicity and monodispersed state are more easily and evenly dispersed in the active component solution.

4.4 XRD analysis

The X-ray diffractograms of Mo-V catalyst, Mo-V-PMMA catalyst and Mo-V-PS catalyst are presented in Fig. 5. From the detailed comparison of XRD pattern of a, b and c, it can be concluded that the appearance of small reflections at $2\theta = 12.8$, 23.3, 25.7, 27.3, 33.7, 38.9, 45.7 shows the

of excess electron density of PMMA (b) and PS (d) nanosphere in the inset. Solid lines represent fitting curves



Fig. 5 XRD patterns of Mo-V based catalysts: (a) Mo-V catalyst; (b) Mo-V-PMMA catalyst; (c) Mo-V-PS catalyst. ($\textcircled{\bullet}$) MoO₃; (\blacksquare) (V_{0.07}Mo_{0.93})₅O₁₄

existence Mo–oxide–phase MoO₃ [JCPDS, 05–0508]. Similarly, the appearance of peaks at $2\theta = 12.3$, 16.5, 22.3, 23.3, 24.9, 28.2, 31.5, 33.7, 38.9 could be related to the presence of crystalline phase of $(V_{0.07}Mo_{0.93})_5O_{14}$ [JCPDS, 31–1437] in catalysts. The $(V_{0.07}Mo_{0.93})_5O_{14}$ phase has been reported in the Mo/V based oxide catalysts in some literatures [38–40]. Orthorhombic M1 phase and hexagonal M2 phase are not observed, probably because the two phases have been destroyed after calcination in air. This is consistent with the current reports [17, 40, 41].

In the literature, $(V_{0.07}Mo_{0.93})_5O_{14}$ phase is active and helpful to convert the isobutene intermediate to produce methacrolein in the selective oxidation of isobutane [40]. In the oxidation of propane and propene to acrylic acid, $(V_{0.07}Mo_{0.93})_5O_{14}$ phase and MoO₃ phase coexist in the active phases of the catalysts which shows the excellent catalytic performance, however, the catalyst with only a crystal phase of $(V_{0.07}Mo_{0.93})_5O_{14}$ without MoO₃ phase represents relatively poor catalytic activity [39]. In our case,



Fig.6 XRD patterns of Mo-V based catalysts at different ratio of A to B. A and B represent the highest peak intensity height of MoO_3 (A) and $(V_{0.07}Mo_{0.93})_5O_{14}$ (B) crystalline phase

the addition of PMMA and PS nanospheres doesn't lead to the change of crystal types $((V_{0.07}Mo_{0.93})_5O_{14} \text{ and } MoO_3)$, because no additional diffraction peaks have been obviously observed in the XRD patterns of these catalysts. In other words, $(V_{0.07}Mo_{0.93})_5O_{14}$ and MoO₃ phases co-exist in the Mo-V, Mo-V-PMMA and Mo-V-PS catalysts. From the displayed XRD data of Fig. 5, compared with Mo-V catalyst, the peak height of XRD pattern in Mo-V-PMMA and Mo-V-PS catalyst has changed which means the apparent transformation of crystalline phases between MoO₃ and $(V_{0.07}Mo_{0.93})_5O_{14}$.

The XRD patterns of Mo-V based catalyst at different amount of MoO₃ to (V_{0.07}Mo_{0.93})₅O₁₄ crystalline phase are shown in Fig. 6. The crystalline phases in these catalysts are all mainly MoO_3 and $(V_{0.07}Mo_{0.93})_5O_{14}$ but their relative values change obviously. Here, the ratio of the peak intensity of MoO₃ (A, at $2\theta \approx 27.2^{\circ}$) to the peak intensity of $(V_{0.07}Mo_{0.93})_5O_{14}$ (B, at $2\theta \approx 22.2^\circ$) is calculated to study the relationship between crystal phase composition and catalyst activity. Figure 7 shows the dependence of acrolein conversion (Fig. 7a) and selectivity of acrylic acid (Fig. 7b) with the ratio of A to B. Figure 7a shows that with the increase of A/B from 0.32 to 0.80, the conversion rate of acrolein first gradually increases, reaching the maximum above 99.0% at about A/B = 0.7, and then decreases. It appears an obvious asymmetric peak between 0.68 and 0.75 (A/B) which means the excellent conversion of acrolein in this range. While the selectivity of acrylic acid changes little, keeping about 96.5% to 98% (Fig. 7b). Therefore, the A/B of the catalyst with excellent performance should be in the range of 0.68-0.75, most preferred 0.69 to 0.72. According to the XRD data of Mo-V catalyst, Mo-V-PMMA catalyst and Mo-V-PS catalyst, their A/B values are 0.67, 0.69 and 0.37, respectively. The A/B of Mo-V-PMMA catalyst is in the best range $(0.69 \sim 0.72)$ corresponding to excellent catalytic activity.

In the catalyst preparation process, the component compounds are mixed and dried at 100 $^{\circ}$ C, and then calcined at 410 $^{\circ}$ C to form the active components of Mo-V oxide



Fig. 7 Dependence of acrolein conversion (**a**) and acrylic acid selectivity (**b**) on the ratio of A to B

catalyst. During the thermo-treatment process, the type of medium in solution is very important for the formation of crystal phases. The addition of PMMA and PS nanospheres in the component mixture causes the change of the ratio of MoO₃ and $(V_{0.07}Mo_{0.93})_5O_{14}$ which is largely because of the interaction between the nanospheres and the metal compounds. The generated water-soluble -COOH and -OH can form complex ions with vanadium and molybdenum compound which greatly enhances their interaction, and also changes the ratio and distribution of vanadium and molybdenum components, causing the transform between MoO₃ and $(V_{0.07}Mo_{0.93})_5O_{14}$ phases.

4.5 XPS Analysis

Small structure transformation can affect the catalytic activity, especially the important modifications on the surface of catalyst. In order to observe the differences in detail among the different catalysts, the chemical composition and the surface electronic state are characterized by X-ray photoelectron spectroscopy (XPS). The deconvolution results of $V2p_{3/2}$ XPS spectra are shown with short dashed lines in Fig. 8a and the corresponding parameters are listed in Table 4. The high-resolution XPS spectra for $V2p_{3/2}$ can be deconvoluted into three peaks at 517.6 eV, 516.6 eV and 514.5 eV which are assigned to the reported binding energy for V^{5+} , V^{4+} and V^{3+} , respectively [42–44]. As shown in Table 4, the valence state of vanadium in Mo-V catalyst is basically close to 5 with the only high binding energy (517.6 eV). For the Mo-V-PMMA catalyst, the ratio of V^{5+} : V^{4+} is estimated to be 85.6: 14.4, giving an average V valence state of 4.86⁺. A small amount of low valence state V⁴⁺ in catalysts are necessary served as the centers for stabilization of the intermediate compound (acrylate) which may balance the net charge in the crystal structure and facilitate the intercalation and deintercalation of acrylic acid from reactive sites [42-44]. The percentage of V^{5+} species in total vanadium of Mo-V-PS catalyst (28.2%) is significantly less than that in Mo-V-PMMA catalyst (85.6%). In Mo-V-PS catalyst, a new lower V species is formed with the binding energy of 514.5 eV which is undoubtedly ascribable to V^{3+} . The introduction of nanosphere in the catalyst preparation is more likely to cause the coexistence of multiple valence states of vanadium. The most likely reason is that part of vanadium is reduced from V⁵⁺ to low state by the reductive atmosphere caused by the nanosphere's addition. The PMMA and PS nanospheres are all removed (see Fig. 2) producing CO, CO₂ and H₂O in the calcination stage. The redox reaction occurs between CO and part of the high valence vanadium which causes the reduction in vanadium valence.

Figure 8b shows typical spectra in the Mo3d region for the three catalysts. The binding energies at 233.0 eV, 231.9 eV and 229.9 eV for $Mo3d_{5/2}$ signal have been reported in Mo^{6+} ,



Fig.8 XPS spectra (solid lines) and their deconvolution results (short dashed lines) for Mo-V catalyst, Mo-V-PMMA catalyst and Mo-V-PS catalyst. (a) V2p; (b) Mo 3d; (c) O1s

Catalysts	Binding energy of	V ⁵⁺ /V _{total} (%)		
	V ⁵⁺	V ⁴⁺	V ³⁺	
Mo-V	517.6 (100%)	_	_	≈100.0
Mo-V-PMMA	517.6 (85.6%)	516.6 (14.4%)	-	85.6
Mo-V-PS	517.6 (28.2%)	516.6 (62.2%)	514.5 (9.6%)	28.2

 Mo^{5+} , Mo^{4+} , respectively [45, 46]. In the case of Mo-V, Mo-V-PMMA and Mo-V-PS catalysts, the $Mo3d_{5/2}$ core level signal appears at 233.4 eV, 233.2 eV and 233.0 eV and the chemical shift between $Mo3d_{5/2}$ and $Mo3d_{3/2}$ keeps the same value (3.1 eV) shown in Fig. 8b. This implies that the highest oxidation state of molybdenum (Mo^{6+}) is the main valence state present in all studied catalysts. The binding energy shift of main peak from Mo-V catalyst to Mo-V-nanospheres catalyst is also due to the redox reaction with carbon monoxide. Because the amount of molybdenum is relatively high, the surface chemical valence of these catalysts remains above 6.

Table 4 XPS analysis results of

catalysts

The XPS spectra of our samples in the O1s region is shown in Fig. 8c. The binding energy of O1s in metal oxides is considered in the range of 528–531 eV [47]. Compared with Mo-V catalyst (531.2 eV), the O1s binding energy of peak position in Mo-V-PMMA (531.0 eV) and Mo-V-PS catalyst (530.8 eV) variates in the direction of lower value which means the reduction in oxygen valence on the catalyst surface. The partial vanadium and molybdenum converted to lower valence also lowers the valence of oxygen in the oxide catalyst which also causes the reduction in the interaction. A good catalyst should have the property of weak binding ability with acrolein and acrylate [47]. But too weak adsorption may cause acrolein to stay only for a short time or not stay, which is not conducive to the improvement of acrolein conversion. In general, the addition of nanospheres causes the valence change of all elements on the catalyst surface.

4.6 H₂-TPR Analysis

Further comparation of the reduction property of the Mo-V series catalysts, H₂-TPR experiments are performed as shown in Fig. 9. The TPR pattern is generally considered to be affected by operating conditions, such as heating rate and pre-calcination temperature [48]. In our case, the Mo-V catalyst exhibits one main narrow and intense reduction peak around 393 °C, starting at 271 °C which may account for the stoichiometric reduction of V⁵⁺ and Mo⁶⁺ to low valence state [49–53]. The addition of PMMA nanosphere doesn't lead to the obvious shift of reduction peak position (392 °C), but marked change of starting temperature to 232 °C which illustrates the concomitant enhancement of reduction kinetics at lower temperature. On the contrary, the introduction of PS nanosphere in the catalyst causes its position of peak maximum shifted to higher temperature (425 °C) with higher



Fig. 9 H_2 -TPR spectra of differently Mo-V catalyst, Mo-V-PMMA catalyst and Mo-V-PS catalyst

starting temperature (298 °C) which means a low rate of H_2 consumption up to much higher temperature. Overall, the addition of PMMA nanospheres lowers the reduction temperature of the catalyst and increases the amounts of reducible components which is as opposed to the PS nanospheres.

4.7 NH₃-TPD Analysis

The NH₃-TPD profiles of catalysts in the range of 100-380 °C are shown in Fig. 10. The sample Mo-V-PMMA presents the highest number of acid sites, while the fewest number of acid sites appears in the Mo-V-PS catalyst. The centered desorption temperature of Mo-V-PMMA catalyst achieving maximum desorption value is basically consistent with Mo-V catalyst (210 °C) which is much higher than that in Mo-V-PS catalyst (190 °C). This means that the PMMA addition favors a remarkable increase of acid sites on the surface of the catalyst which is probably as a consequence of the interaction between the formed -CH₂C(CH₃)COOH, CH₃OH and the hydroxyl in catalyst, causing the exposure of more acid sites and promote the acid-base properties of center in catalyst. The introduction of PS nanosphere causes not only a drastic elimination of acid sites amount in Mo-V-PS catalyst, but also an obvious decrease in the strength of acid sites. The $-CH_2CH(C_6H_5)$ - groups on the PS nanospheres surface have an obvious steric hindrance



Fig. 10 NH₃-TPD profiles of catalysts Mo-V, Mo-V-PMMA and Mo-V-PS

effect and repulsion with hydroxyl groups which may inhibit the formation of acid sites in Mo-V-PS catalyst. In addition, there is an obvious medium strong acid site around 325 $^{\circ}$ C in Mo-V-PMMA catalyst. More acidic sites of weak or medium strong acids contribute to the conversion of acrylate to acrylic acid [47]. The highest amount and strength of acid sites in Mo-V-PMMA catalyst are much higher than Mo-V and Mo-V-PS catalyst.

4.8 Reaction Mechanism

It is generally accepted that the acrylic acid is produced from acrolein by stepwise redox mechanism [54-56]. The mechanism of acrylic acid formation with Mo-V series as catalysts is shown in previous reports [54-56]. Firstly, acrolein interact with molybdenum in a highly charged state due to the existence of the long electron pair in carbonyl oxygen (I–II). Then the electron pair is transferred to the vacant orbital of Mo-V oxide catalyst (II–III) and $CH_2 = CH - C = O^-$ fragment is rapidly produced. The fragment causes the formation of electrophilic $CH = CH - C = O^+$ by collectivization of carbonyl group electrons (III-IV). At last stage, the acrylic acid is produced from the acrylate decomposition on the surface (IV-V) which is the most time consuming and closely related to the strength of acid anion binding with corresponding stabilization center (V^{4+}) . Lattice oxygen is involved in the reaction and the properties of oxygen in the oxide catalyst have great influence on the activity and selectivity of the catalyst.

The addition of PMMA nanospheres results to more uniform distribution of vanadium and molybdenum compounds, and does play a role in pore formation in the range of 50–100 nm. This leads to the existence of more active centers in the Mo-V-PMMA catalyst. Each active center could be regarded as an independent unit. The active centers with larger pore channels are favorable for the adsorption of acrolein (I-II) and the desorption of acrylate (IV-V). The PMMA nanospheres introduction clearly raises of weak or medium strong acid sites on the catalyst surface, contributing to the adsorption of acrolein to the catalyst surface (I-II). The $(V_{0.07}Mo_{0.93})_5O_{14}$ and MoO₃ phases are the main crystalline phases in all studied catalysts and their optimum ratio probably speed up the transfer the lone electron pair of carbonyl oxygen to the vacant orbital of highly electronegative cation in the oxide catalyst (II-IV). The small amount of V⁴⁺ formed in Mo-V-PMMA catalyst could stabilize the intermediate produce acrylate and facilitate the intercalation and deintercalation of acrylic acid from reactive sites and promotes the formation rate of acrylic acid (IV-V). The lower valence of oxygen in catalyst also reduces the interaction between the catalyst surface and the intermediate product acrylate, promoting the desorption rate of acrylate (IV–V).

In a word, the addition of nanospheres affects the porous structure, crystal phase composition, and chemical property of surface. Furthermore, the efficiency of each step is affected in the production process of acrylic acid from acrolein. Novel Mo-V catalyst with PMMA nanospheres as template obviously improves the catalytic activity for the selective oxidation of acrolein to acrylic acid. More importantly, the hard nanospheres can be extended to the preparation of other similar metal oxide catalysts such as acrylonitrile catalyst.

5 Conclusions

Novel Mo-V-PMMA and Mo-V-PS catalysts with nanospheres as templates are prepared by respectively introducing PMMA and PS nanospheres into Mo/V mixture in the preparation process. The Mo-V-PMMA catalyst shows the very high acrolein conversion 99.1% and acrylic acid yield 90.7% in the selective oxidation of acrolein. Based on the characterization results, the addition of PMMA and PS nanospheres does significantly influence the porous structure, crystalline phases, chemical composition on surface, reduction property and the amount and strength of acid sites. The introduction of PMMA nanospheres obviously increases the proportion of nanopores in the range of pore size 50–100 nm. The ratio of MoO₃ to $(V_{0.07}Mo_{0.93})_5O_{14}$ phase in Mo-V-PMMA catalyst is just in the optimal range of 0.69-0.72 corresponding to excellent catalytic activity. The addition of PMMA nanosphere causes appearance of a small amount of stabilization center V⁴⁺, decrease in reduction temperature and remarkable increase of weak or medium strong acid sites on the catalyst surface, contributing to the conversion of acrylate to acrylic acid.

The obvious difference in activity of Mo-V-PMMA and Mo-V-PS catalysts is ultimately attributed to the "real" micro–environment during heat treatment. On the one hand, the groups of -COOH and -OH can form complex ions with vanadium and molybdenum ions, leading to the ions' distribution more uniform on the surface of Mo-V-PMMA catalyst. On the other hand, PMMA nanospheres in good monodispersed state are more easily and evenly dispersed in the active component solution, while PS nanospheres are in a state of adhesion or agglomeration or not uniformly distributed in the active component solution resulting in the reduction of the catalyst activity.

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