



Effect of vanadyl species in Keggin-type heteropoly catalysts in selective oxidation of methacrolein to methacrylic acid



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ABSTRACT

Three Keggin-type heteropoly catalysts with different vanadyl species, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (V existing in the primary structure), $\text{HVOPMo}_{12}\text{O}_{40}$ (V existing as VO^{2+} in the secondary structure), and $\text{V}_2\text{O}_5/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (V existing in V_2O_5 before calcination), were prepared and studied to identify the preferable vanadyl species for oxidation of methacrolein to methacrylic acid. The catalysts were characterized by FT-IR, Raman, XRD, UV-vis, EPR, and XPS before and after calcination at different temperatures. The calcined catalysts were applied in the selective oxidation of methacrolein. The chemical state and position of the vanadyl species varied with the treatment temperature. Compared with the VO^{2+} species in $\text{HVOPMo}_{12}\text{O}_{40}$, the VO^{2+} species generated in $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and $\text{V}_2\text{O}_5/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ during calcination processes showed very different promotional effects, and the VO^{2+} species that interact with the Keggin structure turned to be the main active vanadyl species in all the catalysts. The active vanadyl species changed from an independent ion form to a squashed square pyramidal on Keggin structure or defect Keggin structure during the oxidation reaction. The optimum conversion of methacrolein and selectivity to methacrylic acid were obtained on the $\text{V}_2\text{O}_5/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst calcined at 350 °C, so a new means of adding vanadium in the Keggin-type heteropoly catalysts to obtain high selectivity to methacrylic acid is proposed.

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1. Introduction

Keggin-type heteropoly compounds are good solid catalysts with strong Brønsted acidity and high redox activity [1,2]. These compounds can be used in both acidic and redox-catalyzed reactions and are typically applied in oxidation of methacrolein (MAL) to methacrylic acid (MAA) on molybdophosphoric or molydovanadylphosphoric compounds for methyl methacrylate (MMA) production [3–11]. Compared with molybdophosphoric compounds, molydovanadylphosphoric compounds exhibit higher catalytic activity, primarily because the addition of vanadyl species can improve MAA selectivity with little influence of MAL conversion [7].

Former research indicates that molydovanadylphosphoric compounds are unstable during calcination and reaction [12–15]. Heteropoly anions are partially decomposed to defective Keggin structures and V migrates from heteropoly anions to the secondary structures [12–14]. Hence, there are at least two kinds of vanadyl species in the catalysts. In particular, some vanadyl species are in

the secondary structure and others are located within the primary Keggin structure. Effective catalysts can be designed and prepared by identifying the active vanadyl species that can promote the oxidation of MAL to MAA.

Some researchers have explored the vanadyl species in heteropoly catalysts for reactions such as isobutene oxidation, oxidation dehydrogenation of isobutyric acid, and methanol oxidation. Brukner et al. utilized different in situ equipments to assess the changes of vanadyl species in $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ during calcination and isobutene oxidation. The results of their investigation revealed that V was partly reduced and migrated from the Keggin structure toward the surface of the heteropoly anion in square pyramidal form. The active sites for this particular reaction are most likely composed of single $\text{O}_4\text{V}^{4+/5+}=\text{O}$ species connected to Mo^{6+} via an oxygen bridge [14]. Marchal-Roch et al. synthesized $\text{H}_{3-x}(\text{VO})_x\text{PMo}_{12}\text{O}_{40}$ and $(\text{NH}_4)_{3-2x}(\text{VO})_x\text{PMo}_{12}\text{O}_{40}$ as catalysts for oxidation dehydrogenation of isobutyric acid to MAA. Vanadyl species act as counterions and can improve isobutyric acid conversion and MAA selectivity [16]. In the work of Bayer et al., vanadyl salts of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ were prepared for oxidation of isobutyric acid. The vanadyl salts of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ showed higher catalytic activity than those of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The reason for this

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condition is that $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ can be reduced and partially decomposed and can supply more active V^{4+} sites during reaction [17]. The above studies, however, did not specify whether V in the Keggin structure is active or not. Molinari et al. tried to use CH_3OH as a chemical probe to discover the relationships of structure–reactivity/selectivity of VO_x species in different structures. Their test results showed that introducing VO_x into catalysts can improve and decrease formaldehyde and dimethyl ether selectivity, respectively. VO_x in the primary Keggin structure unit is more active than the surface VO_x species. Both of these VO_x species are more active than MoO_x species [15]. Compared with methanol, MAL cannot enter the primary Keggin structure, and MAL oxidation has been proved to be a surface reaction [1,2,4]. Li et al. have proved that adding vanadyl species as counterions into the cesium salts of molybdophosphoric acid can improve propane partial oxidation activity [18]. No existing research points out that, in term of catalytic activity, vanadyl species in Keggin structure are more effective than the ones in the secondary structure. To the knowledge of the authors, few studies have explored the influence of different vanadyl species in heteropoly compounds on the oxidation of MAL to MAA. In this study, three kinds of catalysts containing different vanadyl species in primary or secondary structure were designed and prepared to find the preferable active vanadyl species for oxidation of MAL to MAA.

2. Experimental

$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (HPA) was purchased from Sinopharm Chemical Reagent Co., Ltd. It was calcined at 200°C to remove crystalline and absorbed water before using. $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (HPAV) was prepared from MoO_3 (Sinopharm Chemical Reagent Co., Ltd.), V_2O_5 (Tianjin Guangfu fine chemical research institute) and 85% phosphoric acid (Sinopharm Chemical Reagent Co., Ltd.) according to published procedures [19]. A sum of 5 g MoO_3 and 0.287 g V_2O_5 were added to 100 mL of deionized water, which was subsequently heated to reflux. Moreover, 0.364 g of 85% phosphoric acid was added to the mixture, which was refluxed with vigorous stirring for 5 h. A deep orange solution was then formed. The insoluble solid was filtered, and the solution was evaporated at 80°C , obtaining a bright orange solid.

$\text{V}_2\text{O}_5/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (VHPA) was prepared according to the following process. A quantity of 6.0 g of calcined $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was dissolved in 30 mL deionized water and 0.3 g of V_2O_5 was added. After 2 h of vigorous stirring, the mixture was evaporated at 80°C and a yellow solid was obtained.

$\text{HVOPMo}_{12}\text{O}_{40}$ (HVOPA) was prepared from V_2O_5 , $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, and oxalic acid (Sinopharm Chemical Reagent Co., Ltd.) as described elsewhere [15]. Briefly, 2.604 g of oxalic acid was dissolved in 80 mL deionized water, and 0.747 g of V_2O_5 was subsequently added to the solution. The mixture was stirred at 80°C for 2 h, and the suspension was converted to a deep blue solution. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was dissolved in the solution and a dark blue solution formed immediately. After being stirred for 2 h at 80°C , the solution was evaporated at 80°C and a dark blue solid was obtained.

All catalysts were calcined under air at a flow rate of 80 mL/min.

Fourier transform infrared (FT-IR) spectroscopy was performed using an FT-IR spectrometer (Nicolet 380, Thermal Electron Corporation) with anhydrous KBr as standard. Raman spectroscopy was conducted using a laser Raman spectrometer (HR800 UV, Horiba Scientific Co. Ltd.) at a wavelength of 514 nm with a 100 mV laser and CCD detector. Ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy was recorded using a UV–vis spectrophotometer (UV-2550, Shimadzu Corporation). Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer

(Bruker D8 Advance X-ray powder diffractometer). Samples (about 10 mg) were analyzed by thermogravimetry/differential thermal analysis (TG/DTA, DTG-60H, Shimadzu, Japan) using a simultaneous DTA-TG apparatus, which allowed both TGA and DSC curves to be recorded simultaneously. The samples were heated from room temperature to 700°C at a rate of $5^\circ\text{C}/\text{min}$. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos Axis Ultra DLD spectrometer with monochromatic $\text{AlK}\alpha$ radiation. Electron paramagnetic resonance (EPR) measurements (X-band) were performed with a JES-RE-1X (JEOL) at room temperature. The resonance frequency, modulation width, and time constant were 9.79 GHz, 0.5 mT, and 0 s, respectively.

Catalytic oxidation of MAL was performed in a fixed bed reactor at 310°C under atmosphere pressure. A total of 0.6 mL of catalyst was loaded into the fixed bed reactor and the contact time was about 2 s. Before the reaction, the temperature was increased to 310°C , and then a reactant mixture of MAL (4.4 vol.%), O_2 (11.1 vol.%), H_2O (17.8 vol.%), and N_2 (balance) was fed into the reactor to start the reaction. The reaction products were collected and analyzed using a gas chromatograph (SP-7890, Lunan Ruihong Chemical Engineering Instrument Co. Ltd.) equipped with a flame ionization detector and a TDX-01 packed column after the reaction was steady.

3. Results and discussion

3.1. Characterization of catalysts

Catalysts were characterized by FT-IR spectroscopy, Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, XRD, and EPR to fully understand their structures and vanadyl species.

3.1.1. Fourier transform infrared

FT-IR was used to determine the changes in the primary structure of heteropoly compounds after calcination and reaction at 350°C . As depicted in Fig. 1, four main vibration bands emerged around 1064, 961, 874, and 780 cm^{-1} before calcination. These

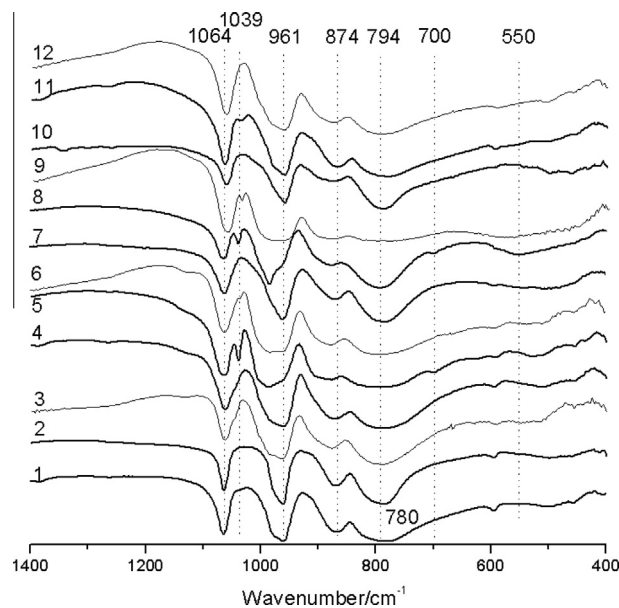


Fig. 1. FT-IR spectra of catalysts precursors, catalysts and catalysts after using (1. HPA; 2. 350HPA-B; 3. 350HPA-A; 4. HPAV; 5. 350HPAV-B; 6. 350HPAV-A; 7. VHPA; 8. 350VHPA-B; 9. 350VHPA-A; 10. HVOPA; 11. 350HVOPA-B; 12. 350HVOPA-A. 350HPA means HPA was calcined at 350°C , so as others. A means used catalysts, B means fresh catalysts.)

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