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Original article

Design and synthesis of hybrid solids based on the tetravanadate core toward improved catalytic properties

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ABSTRACT

Five inorganic–organic hybrid vanadates based on tetravanadate cores, transition metals and N-donor ligands have been designed and synthesized under hydrothermal conditions, namely, $[Zn(eIM)_3]_2V_4O_{12}$ (**1**), $[Zn(pIM)_3]_2V_4O_{12}\cdot H_2O$ (**2**), $[Zn(ipIM)_3]_2V_4O_{12}$ (**3**), $[Co(eIM)_3]_2V_4O_{12}\cdot H_2O$ (**4**), $[Cu(eIM)_2(H_2O)]_2V_4O_{12}$ (**5**) (eIM = 1-ethylimidazole, pIM = 1-propylimidazole, ipIM = isopropylimidazole). All compounds were fully characterized by single-crystal XRD, powder XRD, elemental analysis, TGA, and FT-IR spectroscopy. The hybrid zinc vanadates (**1–3**) and cobalt vanadate (**4**) exhibit interesting 2D folded structures and the hybrid copper vanadate (**5**) presents a 1D chain configuration. All compounds can catalyze olefin epoxidation reactions when using TBHP (TBHP = *tert*-butyl hydroperoxide) as an oxidant in acetonitrile. The introduction of transition metal ions into tetravanadate cores not only improved the catalytic activity but also fulfilled the heterogeneous catalytic behavior. **1–5** all exhibit extraordinary efficiency in converting olefins to the corresponding epoxides with high conversion and selectivity (particularly, conv. up to 97.1%, sele. up to 100% for **1**). Leaching test was also carried out to prove the heterogeneous behavior.

1. Introduction

Oxidation reactions, such as the oxidation of C–H bonds, hydroxylation, epoxidation, and oxidation of heteroatom-based substrates, are very valuable processes in biology, chemistry, and industry [1–4]. Among them, the epoxidation of alkenes attracts continuing interest owing to the importance of epoxides as key chemical intermediates for a wide variety of industrial and chemical applications [5–8]. Up to now a large number of efficient methods for the epoxidation of alkenes with transition-metal catalysts, such as Ti, V, Mn, Te, W, Re, Pt, have been developed [9]. However, most of them are homogeneous and require tedious separation of the expensive catalyst [10]. Therefore, developing highly active, widely applicable heterogeneous and easily recycled catalysts for epoxidation is still desirable.

As a new generation of solid-state materials, polyoxovanadates (POVs) have been developed not only for their various fascinating framework topologies, but also for their potential application in the fields of magnetism, electrical conductivity, catalysis and photochemistry [11–13]. Recently our group has reported three new organic functionalized POVs with imidazole ligands, $V^{V}_{6}O_{15}(mIM)_8$, $V^{IV}_{2}V^{V}_{4}O_{14}(mIM)_8$, $V^{IV}_{2}V^{V}_{4}O_{14}(mIM)_8$ (mIM: 1-methylimidazole, eIM: 1-ethylimidazole), which are highly efficient and selective catalysts for the oxidation of benzyl alcohols [14]. To further promote the catalytic activity of POV complexes and guarantee the heterogeneity during the catalytic process, transition-metal species have been introduced into the POVs system and led to a variety of novel heterogenous catalysts [15–20]. For example, Arriortua et al. reported three isostructural vanadate compounds of $M(HAep)_2(VO_3)_4$ (M═Co, Ni, Cu; Aep = 1-(2-aminoethl) piperazine) compounds, which display efficient catalytic activity for alkyl and aryl sulfides [15]. Recently, our group prepared three inorganic–organic hybrid vanadates $[Co_2(mIM)_5(H_2O)_2]V_4O_{12}$, $[Ni_2(mIM)_7(H_2O)]$-$V_4O_{12}\cdot H_2O$ and $[Cd(eIM)_2(H_2O)]V_2O_6$ with chiral 3D framework, 2D folded network and 1D ladder chain architectures using a hydrothermal synthetic approach under different conditions [21], and another study of Cu-vanadate showed much better catalytic activity for the selective oxidation of sulfides and alcohols than the vanadate alone [22]. Such strategy is also adopted in the catalytic epoxidation reactions [23–26]. Palaniandavar reported a family of Mn(III) complexes [Mn(L)Cl] of

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linear bis(phenolate) ligands, which displays selective catalytic activity for the epoxidation of olefins [26]. Inspired by these work, we tried to introduce transition metal ions into the title tetravanadate cores to obtain hybrid vanadates, which might be a feasible way to improve the catalytic property in the epoxidation of olefins.

Herein, using similar hydrothermal synthetic approach, we successfully grafted different transition metal ions into POVs to synthesize a series of organic-inorganic hybrid vanadates $[Zn(eIM)_3]_2V_4O_{12}$ (**1**), $[Zn(pIM)_3]_2V_4O_{12}{\cdot}H_2O$ (**2**), $[Zn(ipIM)_3]_2V_4O_{12}$ (**3**), $[Co(eIM)_3]_2V_4O_{12}{\cdot}H_2O$ (**4**), $[Cu(eIM)_2(H_2O)]_2V_4O_{12}$ (**5**), (eIM = 1-ethylimidazole, pIM = 1-propylimidazole, ipIM = isopropylimidazole). By introducing Co^{2+}, Cu^{2+} and Zn^{2+} as structural connection nodes, the polyhedral fragments of tetravanadate $[V_4O_{12}]^{4-}$ units were linked together to create 2D network architectures and 1D chain structures, respectively. All compounds were fully characterized by single-crystal X-ray diffraction (SXRD), powder X-ray diffraction (PXRD), elemental analyses, TGA and FT-IR spectroscopy. Further, not only the catalytic activity of these compounds in the olefin epoxidation proved to be improved greatly, but also the catalysts can be reused without losing their activity after three circles and can function as heterogeneous catalysts, which may have potential applications in the industry. To our knowledge, this is the first time that inorganic–organic hybrid vanadates were used as catalysts in the olefin epoxidation.

2. Experimental

2.1. Materials and general methods

All chemicals and reagents were commercially obtained and used without further purification. All syntheses were carried out in 20 mL Teflon-lined stainless steel containers under autogenous pressure. The mixed reactants were stirred at room temperature for 120 min before heating. The FT-IR spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. The X-ray powder diffraction (XPRD) of samples was collected on a Bruker D8 X-ray diffractometer equipped with a graphite monochromatized Cu $K\alpha$ radiator ($\lambda = 0.15418$ Å). The TGA was performed on a DTG-60 AH instrument under a N_2 atmosphere with a heating rate of 10 °C/min. Elemental (C, H and N) analyses were performed on a PerkinElmer 2400 II analyzer. The metal contents of the compounds **1**–**5** were measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. After the catalytic reaction was completed, the resulting mixture was analyzed by GC–MS and GC using naphthalene as an internal standard substrate. The GC analyses were performed on a Shimadzu GC-2014C with an FID detector equipped with an Rtx-1701 Sil capillary column. The GC–MS spectra were recorded on an Agilent 7890A-5975C at an ionization voltage of 1200 V. Atomic absorption analysis were measured by an inductively coupled plasma spectrometer (ICP) on an ICP-6000 analyzer.

2.2. Synthesis of $[Zn(eIM)_3]_2V_4O_{12}$ (**1**)

A mixture of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.1705 g, 0.8 mmol), NH_4VO_3 (0.1404 g, 0.8 mmol), eIM (0.3 mL), and H_2O (8 mL) was heated at about 120 °C for 72 h. After the mixture was cooled to room temperature, yellow crystals were isolated from the mixture. Yield: 76% (based on NH_4VO_3); Anal. Calcd. for $C_{30}H_{48}Zn_2N_{12}V_4O_{12}$ (%): C, 32.63; H, 4.35; N, 15.23. Found: C, 32.76; H, 4.41; N, 15.21.

2.3. Synthesis of $[Zn(pIM)_3]_2V_4O_{12}{\cdot}H_2O$ (**2**)

Compound **2** was synthesized by almost the same procedure as compound **1** except eIM was replaced by ipIM, and the amount was reduced to 0.2 mL. After the mixture was cooled to room temperature, yellow crystals were isolated from the mixture. Yield: 68% (based on NH_4VO_3); Anal. Calcd. for $C_{36}H_{64}{\cdot}Zn_2N_{12}O_{14}V_4$ (%): C, 35.3; H, 5.23; N, 13.73. Found: C, 35.36; H, 5.26; N, 13.61.

2.4. Synthesis of $[Zn(ipIM)_3]_2V_4O_{12}$ (**3**)

Compound **3** was synthesized by almost the same procedure as compound **1** except the amount of eIM was reduced from 0.3 mL to 0.2 mL. After the mixture was cooled to room temperature, yellow crystals were isolated from the mixture. Yield: 70% (based on NH_4VO_3); Anal. Calcd. for $C_{36}H_{60}Zn_2N_{12}O_{12}V_4$ (%): C, 36.38; H, 5.05; N, 14.14. Found: C, 36.52; H, 5.07; N, 14.19.

2.5. Synthesis of $[Co(eIM)_3]_2V_4O_{12}{\cdot}H_2O$ (**4**)

A mixture of $CoCl_2{\cdot}6H_2O$ (0.1705 g, 0.8 mmol), NH_4VO_3 (0.1404 g, 0.8 mmol), eIM (0.8 mL), and H_2O (8 mL) was heated at about 120 °C for 72 h. After the mixture was cooled to room temperature, dark purple crystals were isolated from the mixture. Yield: 62% (based on NH_4VO_3); Anal. Calcd. for $C_{30}H_{52}Co_2N_{12}O_{14}V_4$ (%): C, 31.96; H, 4.61; N, 14.91. Found: C, 31.71; H, 4.42; N, 14.58.

2.6. Synthesis of $[Cu(eIM)_2(H_2O)]_2V_4O_{12}$ (**5**)

A mixture of $CuCl_2{\cdot}2H_2O$ (0.1705 g, 0.8 mmol), NH_4VO_3 (0.1404 g, 0.8 mmol), eIM (0.7 mL), and H_2O (8 mL) was heated at about 120 °C for 72 h. After the mixture was cooled to room temperature, green crystals were isolated from the mixture. Yield: 68% (based on NH_4VO_3); Anal. Calcd. for $C_{20}H_{36}Cu_2N_8O_{14}V_4$ (%): C, 25.44; H, 3.82; N, 11.87. Found: C, 25.65; H, 3.74; N, 11.75.

2.7. Catalyzed epoxidation of olefin

Compound **1** (0.01 mmol, 5.0 mg), olefin (1 mmol), TBHP (*tert*-butyl hydroperoxide, 2 mmol), acetonitrile (2 mL) were added to a glass tube, then the catalytic reaction was performed on a Wattecs Parallel Reactor at 75 °C for 24 h. After the reaction was completed, the resulting mixture was analyzed by GC–MS and GC.

2.8. X-ray crystallography

The single-crystal XRD data of all compounds were collected on a Bruker APEX-II CCD detector with graphite mobochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Crystals were mounted on a glass fiber and coated with oil. All absorption corrections were performed using a multiscan technique. The reflections collected were integrated and scaled using the APEX 2 software package [27,28]. All crystal structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL program package (Bruker) [27,28]. All of the non-hydrogen atoms were located by the direct methods and were refined anisotropically. All hydrogen atoms were fixed at calculated position and refined as riding models. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC-1058623 (**1**), CCDC-1058590 (**2**), CCDC-1058657 (**3**), CCDC-1404876 (**4**), CCDC-1404877 (**5**). The crystallographic details of **1–5** are summarized in Table S1 (Supporting information).

3. Results and discussion

3.1. Synthesis

At present, many inorganic–organic hybrid vanadates with a variety of structures have been synthesized using the hydrother-