Phosphomolybdic acid functionalized covalent organic frameworks: Structure characterization and catalytic properties in olefin epoxidation

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ABSTRACT

Novel heteropolyacid-based hybrid composites (denoted as PMA@COF-300) have been obtained by immobilizing 12-phosphomolybdic acid (PMA) onto a covalent organic framework material (COF-300). Structural and spectroscopic studies show that the PMA units are uniformly dispersed on the surface/cavities of COF-300, and relatively stable linkages can be built between the PMA units and the matrix of COF-300 when suitable preparation conditions are adopted. The catalytic properties of the PMA@COF-300 are investigated in the epoxidation of olefins with t-BuOOH as oxidant. The experimental results show that the PMA@COF-300 composites can act as efficient heterogeneous catalysts for the epoxidation of cyclooctene, and can even convert the relatively inert terminal alkene of 1-octene into 1,2-epoxyoctane rapidly at mild conditions. The existence of unique interpenetrated 3-D structure, suitable porous characteristics, and the abundant protonated imine groups in COF-300 play critical role in dispersing and stabilizing the anions of PMA, which is beneficial to the fabrication of highly active and stable heterogeneous PMA functionalized COF-300 catalysts for olefin epoxidation.

1. Introduction

Covalent organic frameworks (COFs) are a series of crystal organic porous materials, which are constructed solely from organic building units via covalent bonds [1]. These new type of porous organic materials have shown superior potential in diverse applications [2–13], such as gas storage [4–7], optoelectronics [8,9], proton conduction [10] and catalysis [11–13]. In view of the application in catalysis, though quite limited, a few kinds of COF materials have already been used as stable and versatile supports for fabricating active and stable heterogeneous catalysts. Wang and co-workers [11] have reported that Pd/COF-LZU1 exhibits excellent catalytic activity in Suzuki-Miyaura coupling reaction. They proposed that the two-dimensional (2-D) layered-sheet structure together with the eclipsed imine bonds render the COF-LZU1 as an ideal scaffold for coordinating metal ions. In another work reported by Thomas and co-workers [12], they found that the presence of N-heterocyclic moieties on the surface of a 2-D covalent triazine-based frameworks (CTFs) can improve the stability of the introduced Pd nanoparticles for the liquid phase glycerol oxidation.

Recently, research interest in the immobilization of hetero-polyacid (HPA) onto solid supports has been growing for the purpose to obtain highly active and stable heterogeneous HPA-based catalysts [14–30]. Different porous materials, such as silica [19–21], mesoporous molecular sieves [22–24], porous carbon [25–27] and metal organic frameworks [28–30] have been widely used as supports in this respect. However, it is not easy to get truly heterogeneous supported HPA catalysts, since the relatively large size of the HPA clusters brings serious difficulty to formation of stable linkages between the solid support and the HPA. A common solution for improving the stability of the supported HPA catalysts is the introduction of functional groups on the surface of the supports. For instance, Mizuno and coworkers [20] have reported that immobilization of $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ on dihydroimidazolium cation

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modified SiO_2 can form a truly heterogeneous catalyst for oxidizing a broad range of olefins and sulfides with H_2O_2. Halligudi and co-workers [24] immobilized molybdovanadophosphoric acids onto amine-functionalized mesoporous silicas (MCM-41, MCM-48 and SBA-15), and obtained truly heterogeneous catalysts for the selective oxidation of anthracene with tert-butyl hydroperoxide (t-BuOOH). Our recent work [31] has shown that 12-phosphomolybdic acid (PMA) can be electrostatically immobilized on the periodic mesoporous organosilicas containing imidazolium groups, and the resultant catalysts are active and stable in the epoxidation of olefins with t-BuOOH. At present, it is still an attractive subject to prepare novel HPA-based heterogeneous catalysts with high activity and stability for selective oxidation/epoxidation reactions.

In this work, we make an attempt to use a 3-D structure COF material, named COF-300 [32], as support to immobilize 12-phosphomolybdic acid (PMA) for getting novel hybrid PMA-based solid catalysts (PMA@COF-300). As a representative 3-D COF material constructed from C—C and C=N covalent linkages, COF-300 possesses multiply interpenetrated diamond structures, abundant imine groups and permanent porosity [32]. Furthermore, COF-300 is insoluble in water and other common organic solvents, and has a good chemical stability and thermal stability [32]. Despite all of these promising features, there is no report till now to use COF-300 as catalyst or catalyst support. Here, three PMA@COF-300 composites containing different contents PMA or thermal treated at different temperatures are prepared by wetness impregnation method. The physicochemical properties of these composites are studied by a variety of characterization means, and their catalytic properties are investigated in the epoxidation of olefins with t-BuOOH as oxidant.

2. Experimental

2.1. Materials preparation

Tetra-(4-anilyl)-methane was synthesized and purified following a published procedure [33]. Other starting materials and solvents were purchased and purified according to standard procedures.

COF-300 was synthesized by a literature reported method [32]. Typically, terephthaldehyde (120 mg, 0.89 mmol), tetra-(4-anilyl)-methane (200 mg, 0.52 mmol), anhydrous dioxane (10 mL) and aqueous acetic acid (3 M, 2 mL) were added to the special ampoule (volume ca. 100 mL). The ampoule was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 20 Pa and flame sealed. Upon warming to room temperature, the ampoule was placed in an oven at 120 °C and left undisturbed for 72 h, yielding a yellow solid at the bottom of the tube which was isolated either by filtration and washed with anhydrous dioxane and anhydrous THF. The resulting powder was immersed in anhydrous THF for 24 h and dried at room temperature and 1.33×10^{-3} Pa for 12 h and 100 °C,

1.33×10^{-3} Pa for 2 h to afford a yellow powder of COF-300. Yield: 90 mg, 56% based on tetra-(4-anilyl)-methane. Elemental analysis: Calcd. for $C_{41}H_{28}N_4 \cdot 2H_2O$: C, 80.37; H, 5.26; N, 9.14%. Found: C, 78.93; H, 5.25; N, 8.92%.

The supported PMA@COF-300 composites were prepared by wetness impregnation method. A certain amount of PMA (100 mg or 500 mg) was dissolved in 50 mL deionized water, and the solution mixed with 1.0 g of COF-300. This mixture was stirred for 24 h at a desired temperature (20 or 80 °C). After that, the suspension was filtered, washed with abundant hot deionized water and vacuum dried to get the final product. The preparation process of PMA@COF-300 is shown in Scheme 1. By changing the contents of PMA and the preparation temperatures (20 or 80 °C), three PMA@COF-300 composites, denoted as PMA@COF-300a, PMA@COF-300b and PMA@COF-300c, respectively, were obtained. The preparation conditions and the PMA contents of the three samples are present in Table 1.

2.2. Characterization techniques

X-ray powder diffraction (XRD) patterns were collected with a Bruker D8 Advance X-ray powder diffractometer in reflectance Bragg-Brentano geometry employing Ni filtered Cu Kα line focused radiation at 1600 W (40 kV, 40 mA) power. The morphology of the composite materials was investigated by an XL-30 ESEM FEG Scanning Electron Microscope (FE-SEM) coupled with energy dispersive spectroscopy (EDS), operating at an acceleration voltage of 20 kV. The sample was dispersed onto sticky carbon surface and chromium coated. The photographs were taken in the regime of secondary electrons SEI. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy observations (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging were performed on a Philips TF-F20 transmission electron microscope open rationing at 200 kV. Line-scan was performed using EDS in STEM mode. The sample was prepared by dropping an ethanol dispersion of the nanosheets onto copper grids coated with a thin carbon film and drying at room temperature. N_2 adsorption—desorption isotherms were measured at the liquid nitrogen temperature, using the Micromeritics ASAP 2020 automated adsorption analyzer. All samples were degassed at 393 K for 12 h before the measurements. The surface areas were calculated using the BET (Brunauer—Emmett—Teller) method on the adsorption data in the relative pressure range of 0.05—0.2. The total pore volumes were derived at the relative pressure of $P/P_0 = 0.99$, assuming full surface saturation with nitrogen. The pore size distributions were calculated from N_2 adsorption isotherms by the Non Linear Density Functional Theory (NLDFT) methods. The Fourier transformation infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer in the range of 4000 to 500 cm^{-1}. The ^{31}P CP-MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB
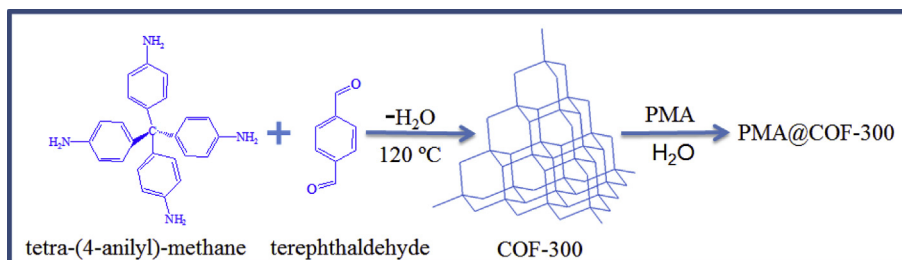
Scheme 1. Preparation process of PMA@COF-300 composites.