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Vanadium-substituted heteropolyacids immobilized on amine-functionalized mesoporous MCM-41: A recyclable catalyst for selective oxidation of alcohols with H_2O_2

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New hybrid materials of vanadium-substituted phosphotungstic acids (VHPW) immobilized on amine-functionalized mesoporous MCM-41 (VHPW/MCM-41/NH_2) are prepared and characterized by FT-IR, XRD, N_2 adsorption, elemental analysis, SEM and TEM for their structural integrity and physicochemical properties. It is found that the structure of the heteropolyacids is retained upon immobilization over mesoporous materials. The catalytic activities of these hybrid materials are tested in the selective oxidation of alcohols to the carbonyl products with 30% aqueous H_2O_2 as oxidant in toluene. The catalytic activities of different number of vanadium-substituted phosphotungstic acid are investigated, and among the catalysts, $H_5[PV_2W_{10}O_{40}]$ immobilized on amine-functionalized MCM-41 exhibits the highest activity with 97% conversion and 99% selectivity in the oxidation of benzyl alcohol to benzaldehyde. The hybrid catalyst is proved to be a highly efficient recyclable solid catalyst for the selective oxidation of aromatic alcohols to the corresponding aldehydes with H_2O_2.

1. Introduction

The selective oxidation of alcohols to their corresponding aldehydes and ketones without over-oxidized product is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing [1a,b]. In some catalytic systems, it was difficult to control the producing of benzaldehyde in the oxidation of benzyl alcohol, and often benzoic acid was obtained instead of benzaldehyde. The traditional oxidation procedures are carried out with stoichiometric inorganic oxidants, such as potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$) in the strong acid condition. Unfortunately, these oxidants reagents often have low atomic efficiency and low selectivity, producing large amounts of unwanted toxic waste and by-product [2a,b]. Therefore, they should be replaced with green oxidants, such as molecular oxygen or aqueous H_2O_2, only water as co-product, from both economic and environmental viewpoints. However, this requires highly active, selective, and recyclable heterogeneous catalysts [3] usually containing noble metals for these transformations [4a,b], and the main drawbacks associated with these systems are very expensive chemical reagent, long reaction time, and in majority of cases an elevated temperature for effective catalytic activity [5]. Thus, development of oxidation systems which are readily accessible, stable, inexpensive and environmentally acceptable, and can promote selective oxidation under mild reaction conditions remains a challenge.

Polyoxometalates (POMs) or heteropolyacids (HPAs) are a class of well-defined transition metal oxygen clusters with structural diversity, showing many applications in catalysis, electronics, optics, medicine, biology, etc. [6]. Among the numerous HPAs, heteropolymolybdates and heteropolytungstates related to the Keggin structure have received much attention because of their strong acid and the rich redox chemistry [7a,b], and have been widely used as the catalysts in both oxidative and acid-catalyzed reactions as homogeneous and heterogeneous catalysts for the oxidation of different organic molecules, such as alcohols [8a],

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thioethers [8b], alkenes [8c] and esterification [8d]. Their strong acid and appropriate redox properties can be controlled at the molecular or atomic level [7a,9a,b]. The catalytic activity of HPAs can be improved by partial substitution of redox metal ions in Keggin structure, among which the introduction of vanadium into the Keggin framework has been demonstrated to be beneficial for redox catalysis [10], shifting its reactivity from acid-dominated to redox-dominated, as by the selective oxidation of methanol to either dimethyl ether or formaldehyde [11], and by other selective oxidations of alkanes and aldehydes [12a–d]. Quantum chemistry calculations have been carried out to study the structures and properties of the α-Keggin-type vanadium-substituted heteropolyanions $[PV_nMo_{12-n}O_{40}]^{(3+n)-}$ ($n = 0–3$) and found that the d-orbital contribution of vanadium atom to the LUMO of the vanadium-substituted heteropolymolybdates is a key factor in their catalytic performances [13]. However, HPAs still suffer from some shortcomings, such as the low surface area, the high solubility, and the environmental problems. These homogeneous catalytic systems also have difficulties in catalyst separation from the reaction solution and repeated utilization. In order to overcome these disadvantages, the dispersion of them on suitable carriers is full of urgency. Therefore, many kinds of heterogeneous catalysts based on HPAs immobilized on various supports, such as metal oxides [14a], silica [14b], metal nanocatalysts [14c] and activated carbon [14d], have been reported. Specially, the silica materials used in this study, such as MCM-41 and SBA-15, exhibit a narrow pore size distribution within the mesoporous range and a high surface area [15a–e]. It was found that immobilizing HPAs into molecular sieves not only improved the surface acidity of molecular sieves but also greatly increased the selectivity of molecular sieves in catalytic reactions [16a–c]. Khdera et al. reported acid catalyzed organic transformations by $H_3PW_{12}O_{40}$ immobilized onto MCM-41, and the results indicate that both the surface acidity and the catalytic activity for the Pechmann, esterification reaction and Friedel–Crafts acylation reactions sharply increase with the modification of MCM-41 by HPAs [17]. In order to preventing the leaching of HPAs in the polar medium, Amini and co-workers immobilized the Keggin tungsten heteropolyacids on the inner surface of mesoporous MCM-41 by chemical bonding to aminosilane groups [18].

To date, catalytic oxidation by the mixed-addenda vanadium atom into molybdenum polyoxometalates, such as Keggin $H_{3+x}[PMo_{12-x}V_xO_{40}]$ and Wells Dawson-type $H_{3+x}[P_2Mo_{18-x}V_xO_{40}]$ vanadium-substituted heteropolyoxometalates, have been widely investigated [19a–e], while the investigation of different vanadium substituted Keggin-type tungsten heteropolyacids and their catalytic oxidation activities is very limited. Kumar et al. fabricated the silica supported $H_4PW_{11}VO_{40}$ catalyst used to nitration of phenol taking 1,2-dichloroethane as solvent [20]. Trakarnpruk et al. reported the immobilized acidic and cesium salts of $[PVW_{11}O_{40}]^{4+}$ and ($[PW_{12}O_{40}]^{3+}$) supported on MCM-41 as catalysts for oxidation of cyclohexane [21]. Sumimoto et al. investigated the performance of Zn powder as a reducing reagent for the liquid-phase oxidation of benzene in an aqueous acetic acid solvent into phenol over V-supported HPA catalysts [22]. Herein we report the full details of preparation of a new series of vanadium-substituted phosphotungstates (VHPW) immobilized on amine-functionalized mesoporous MCM-41 (denoted as VHPW/MCM-41/NH_2) and their catalytic performance in selective oxidation of various alcohols with H_2O_2, and the catalytic performance of different vanadium substituted VHPW/MCM-41/NH_2 are compared. Among the catalysts, the divanadium-substituted V_2HPW/MCM-41/NH_2 is proved to be a highly efficient solid catalyst for the selective oxidation of aromatic alcohols to the corresponding aldehydes with H_2O_2, featured by the high conversion and selectivity, easy recovery, and quite steady reuse.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of phosphotungstate acid $H_3[PW_{12}O_{40}]$ and three vanadium-substituted heteropolyacids

All materials used were of analytical reagent grade and used without further purification unless otherwise stated. The preparation of $H_3[PW_{12}O_{40}]\cdot 6H_2O$ was described elsewhere [23]. $H_4[PVW_{11}O_{40}]\cdot 15H_2O$, $H_5[PV_2W_{10}O_{40}]\cdot 23H_2O$ and $H_6[PV_3W_9O_{40}]\cdot 24H_2O$, designated as neat V_1HPW, V_2HPW, and V_3HPW, respectively, were prepared as described previously [24]. In the synthesis of $H_4[PVW_{11}O_{40}]\cdot 15H_2O$, $NaVO_3$ (0.89 g, 7.3 mmol) dissolved in 15 ml of deionized water at 80 °C was mixed with Na_2HPO_4 aqueous solution (1.04 g, 7.3 mmol in 20 ml of water) and cooled to room temperature. The mixture was acidified with 5 ml of concentrated sulfuric acid. $Na_2WO_4\cdot 2H_2O$ aqueous solution (26.16 g, 79.3 mmol dissolved in 50 ml of water) was then added to the above solution dropwise with vigorous stirring, followed by slow addition of 80 ml concentrated H_2SO_4. $H_4[PVW_{11}O_{40}]\cdot 15H_2O$ was obtained with ether extraction followed by evaporation and recrystallization. Synthesis of the other two vanadium substituted heteropolyacids is similar to that of $H_4[PVW_{11}O_{40}]\cdot 15H_2O$, but appropriate amount of $NaVO_3$ and $Na_2WO_4\cdot 2H_2O$ was added. The composition of the materials was confirmed by elemental analysis and FT-IR.

2.1.2. Preparation of MCM-41

The mesoporous silica MCM-41 was synthesized by hydrothermal method described by Cai et al. [25]. The procedure was as follows: about 2.0 g of hexadecyl trimethyl ammonium bromide (CTAB) used as structure directing agent was dissolved in 1000 ml of deionized water and 7 ml of 2 M sodium hydroxide solution was added to the solution. Then 10 ml of tetraethoxysilane (TEOS) used as silica sources was added into the mixture solution by dropwise. After stirring for half an hour, the gel was transferred into a stainless steel autoclave and hydrothermalized at 100 °C for 10 h. The solid product was recovered by filtered, washed with hot water and dried at room temperature. The dry material was calcined by heating to 550 °C for 5 h to remove the template from the interior of the pores.

2.1.3. Functionalization of MCM-41 silica using 3-aminopropyltriethoxysilane (APTES)

Modification of the mesoporous materials with amino-groups [16c] was accomplished by mixing 10 ml 3-aminopropyl-triethoxysilane (APTES) in anhydrous toluene with 1 g of MCM-41 molecular sieve in 60 °C for 24 h. After the reaction, the materials were washed exhaustively with several portions of toluene, followed by methanol and finally water. After each wash, the solid was separated from the solvent by centrifugation (20 min, 12,000 rpm). The amino-modified materials were finally dried in a vacuum a few hours for subsequent application (denoted as MCM-41/NH_2). For modified MCM-41/NH_2, the functional group ($-SiNH_2$) promotes immobilization of polyanion VHPW by taking advantage of electrostatic interactions, producing ($-SiNH_3^+$) (VHPW) (Scheme 1). Besides, stronger hydrogen interactions are produced with aminopropyl functionalized support compared to the nonfunctionalized one. Hence, a more stable heterogeneous catalyst is produced with higher amount of heteropolyacids molecules retained within the support.

2.1.4. Preparation of VHPW/MCM-41/NH_2 catalysts

MCM-41 supported catalysts were prepared by wet impregnation method. In a typical process, 1.0 g MCM-41/NH_2 was dispersed into a solution of VHPW, prepared by dissolving the required amount (0.35 g) of VHPA in 20 ml distilled water. The mixture was stirred for 24 h at room temperature. The product was separated by