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Epoxidation of olefins with oxygen/isobutyraldehyde over transition-metal-substituted phosphomolybdic acid on SBA-15

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ABSTRACT

A series of polyoxometalate-based heterogeneous catalysts were prepared by immobilized transition metal mono-substituted phosphomolybdic acids ($PMo_{11}M$, M = Fe, Co or Cu) or unsubstituted phosphomolybdic acid (PMo_{12}) on amino-functionalized SBA-15. A variety of characterization results demonstrated that the $PMo_{11}M$ units are uniformly dispersed on the surface or in the channels of mesoporous SBA-15. The catalytic properties of these hybrid materials (denoted as $PMo_{11}M$/SBA or PMo_{12}/SBA) were investigated in the epoxidation of olefins with molecular oxygen as oxidant and isobutyraldehyde as co-reagent. It has been found that $PMo_{11}Co$/SBA and $PMo_{11}Cu$/SBA are catalytically active for the epoxidation of cyclooctene with acetonitrile as solvent, while $PMo_{11}Fe$/SBA and PMo_{12}/SBA are nearly inactive under the same reaction conditions. Moreover, the relatively active $PMo_{11}Co$/SBA catalyst could also efficiently convert cyclohexene and 1-octene to the corresponding epoxides, and its catalytic activity was solvent dependent. Using suitable solvent like acetonitrile could efficiently inhibit the deactivation of the catalyst, thus bringing excellent stability and recyclability for the $PMo_{11}Co$/SBA catalyst.

1. Introduction

The epoxidation of olefins is an industrially important process since epoxides are widely used as key intermediates in organic synthesis [1–3]. Recently, considerable interests have been drawn on studying the aerobic epoxidation of olefins for developing more efficient and environmentally benign route [4–7]. It was reported that aerobic epoxidation of olefins in solution can be efficiently achieved under quite mild conditions over some transition metal complexes by using molecular oxygen as oxidant and aliphatic aldehyde as co-reactant, which is the so-called "Mukaiyama" procedure [8–13]. Although the usage of co-reactant aldehyde is undesirable, the Mukaiyama method is still worthy of studying for its great advantages, such as very mild operation conditions (low temperatures, atmospheric pressure), high epoxide selectivity, low cost and environmental-friendly nature of the oxidant [11–13].

In general, Mukaiyama epoxidation could be catalyzed by using some homogeneous transition metal complexes like β-diketonate complexes, Schiff's base complexes, metal cyclam complexes and metalloporphyrins complexes [8–13]. For overcoming the separation and recycling problems of the homogeneous catalysts, recent efforts were mainly focused on preparing efficient heterogeneous catalysts [14–23]. Representative catalysts include various transition metal complexes supported on porous materials, Co-containing zeolitic imidazolate framework material, Cu/Ga-based metal-organic framework (MOF) and so on [14–23]. However, in most cases, either the catalytic activity or the selectivity to epoxide of these heterogeneous catalysts is still not very satisfied. Moreover, leaching of active species during the reaction course is commonly occurred. Therefore, it is still an attractive subject to develop more efficient heterogeneous catalysts for Mukaiyama epoxidation.

As an important catalyst system in selective oxidation, polyoxometalate (POM) including various transition metal-substituted phosphomolybdate, has shown numerous advantageous properties, such as thermodynamic stability to oxidation, hydrostability, tunability of redox and acid properties [24–30]. By immobilizing various POMs on different supports like oxides, zeolites, carbons etc., some highly efficient POM-based heterogeneous catalysts have already been obtained for important catalytic oxidation reactions [31–37]. Particularly, it was reported that a few supported POM catalysts can also catalyze the aerobic epoxidation of olefins in the presence of aldehydes. For instance, Johnson and Stein [24] reported amine-modified silica supported Co- and Zn-substituted phosphotungstates or silicotungstates are

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active catalysts for the aerobic epoxidation of cyclohexene in the presence of isobutyraldehyde (IBA). Kholdeeva and coauthors [25] found that amine-modified mesoporous silicate supported $[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ can efficiently catalyze the aerobic oxidation of α-pinene to epoxide with IBA as co-reactant. Concerning the diversity of POM in composition, structure and property, one can expect that there will be very broad space for developing more efficient heterogeneous POM-based catalysts for Mukaiyama epoxidation reactions.

Previously, our group has already carried out some works on preparing various POM-based heterogeneous catalysts for olefin epoxidation with *tert*-butyl hydroperoxide or H_2O_2 as oxidants [38–41]. As a continuation of these works, we here tried to immobilize a series of transition metal-substituted phosphomolybdic acids on to NH_2-modified SBA-15 (denoted as $PMo_{11}M$/SBA, M = Co, Cu, Fe) and to test their catalytic performance for the aerobic epoxidation of olefins in the presence of IBA. It was found that supported Co-substituted phosphomolybdate catalyst can efficiently catalyze a variety of olefins to corresponding epoxides, and can also be easily recycled for a few times without obvious loss in its catalytic activity.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of transition metal mon-substituted phosphomolybdic acids

Transition metal (Fe, Co, Cu) mon-substituted phosphomolybdic acids were prepared according to a literature procedure for the preparation of molybdovanadophosphoric acids [42]. $Na_2HPO_4{\cdot}12H_2O$ (0.01 mol) was dissolved in 20 ml of water and mixed with nitrates of corresponding metal (0.01 mol) that had been dissolved by boiling in 20 ml of water. The mixture was cooled and acidified with 1.0 ml of concentrated sulfuric acid. To this mixture a solution of 0.11 mol of $Na_2MoO_4{\cdot}2H_2O$ dissolved in 40 ml of water was added, large amount of flocculent precipitate appeared. After that, some amount of concentrated sulfuric acid was added slowly with vigorous stirring until it turned to a clear solution. The heteropoly acid was then extracted with 400 ml of ethyl ether after the water solution was cooled. In this extraction, the heteropoly etherate was present as a bottom layer. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The green-yellow solid that remained was dissolved in 50 ml of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. Finally, $H_6PMo_{11}FeO_{40}{\cdot}xH_2O$, $H_7PMo_{11}CoO_{40}{\cdot}xH_2O$ and $H_7PMo_{11}CuO_{40}{\cdot}xH_2O$ were obtained, and denoted as $PMo_{11}M$ (M = Fe, Co, Cu) hereafter. The calculated analytic values (at.%) presented below, all the relative errors were within the scope permitted: $PMo_{11}Fe$ [P (7.19%) Mo (85.39%) Fe (7.42%)]; $PMo_{11}Co$ [P (7.32%) Mo (81.45%) Co (6.98%)]; $PMo_{11}Cu$ [P (8.26%) Mo (85.45%) Cu (7.95%)].

2.1.2. Preparation of amine-functionalized of SBA-15

SBA-15 was prepared according to the literature method [43]. Functionalization of SBA-15 was conducted with schrank techniques [44]. About 1.0 g SBA-15 was treated at 150 °C for 2 h under vacuum. About 30 ml dry toluene was added into the flask quickly, then 2 mmol 3-aminopropyltriethoxysilane (APTES) was added into the suspension under N_2 protection and refluxed at 110 °C for 24 h. Afterwards, the solid was filtered and washed with toluene and anhydrous ethanol for several times. Finally, the solid was extracted using a Soxhlet 24 h with dichloroethane and dried in vacuum overnight. The resulting material was denoted as NH_2-SBA-15.

2.1.3. Immobilization of $PMo_{11}M$ (M = Fe, Co, Cu) on NH_2-SBA-15

A certain quality of NH_2-SBA-15 was added into a 30 ml methanol solution containing some amount of $PMo_{11}M$ (M = Fe, Co, Cu), and refluxed for 6 h. It was then filtered and Soxhleted for 24 h with methanol and dried in vacuum at 80 °C. The resulting product is designated as $PMo_{11}M$/SBA (M = Fe, Co, Cu). For comparison, a reference catalyst of PMo_{12}/SBA was also prepared by immobilizing commercial phosphomolybdic acids (PMo_{12}) on NH_2-SBA-15. The loading of $PMo_{11}M$ (or PMo_{12}) in the supported catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-AES), and the concreted values are given in Table 1.

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA), using Ni-filtered Cu Kα radiation.

FT-IR spectra were recorded on a Nicolet AVATAR 370 DTGS spectrometer in the range 4000–500 cm^{-1}.

N_2 adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 N analyzer. Samples were degassed at 150 °C for 8 h before measurements. Specific surface areas were calculated using BET model. Pore volumes are estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions are evaluated from desorption branches of the nitrogen isotherms using the BJH model.

Transmission electron microscopy (TEM) images were taken with a H8100-IV electron microscope with an energy-dispersive X-ray spectroscopy (EDX) operating at 200 kV. The samples were suspended in ethanol by sonication and then picked up on a Cu grid covered with a carbon film.

XPS measurements were made on a VGESCA LAB MK-II X-ray electron spectrometer using Al Kα radiation.

2.3. Catalyst test

The catalytic oxidation reaction was carried out in a 50 ml three-necked bottle equipped with a stirring bar, reflux condenser, and gas supply. Solvent, olefin, IBA and catalyst were added into the flask respectively, and the whole device was placed in a temperature-controlled oil bath. To commence the reaction, oxygen was passed through the reactor at a flow rate of 10 ml/min^{-1} under atmosphere. The oxidation products of the reaction were analyzed and quantified by Shimadzu GC-8A gas chromatograph with HP-5 capillary column.

Table 1
Texture parameters of SBA-15, PMo_{12}/SBA and $PMo_{11}M$/SBA materials.

Catalyst	$PMo_{11}M$ (mmol/g)	Surface Area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
SBA-15	–	794	1.48	7.2
PMo_{12}/SBA	0.093	265	0.53	5.7
$PMo_{11}Fe$/SBA	0.105	244	0.46	5.2
$PMo_{11}Co$/SBA	0.101	231	0.41	5.8
$PMo_{11}Cu$/SBA	0.066	316	0.64	4.9