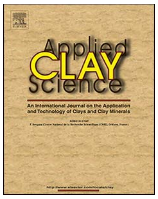
Applied Clay Science 150 (2017) 210–216

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

Comparative study of Keggin-type polyoxometalate pillared layered double hydroxides via two synthetic routes: Characterization and catalytic behavior in green epoxidation of cyclohexene

Juanjuan Ma[a,b,*], Min Yang[a], Qian Chen[a], Shusu Zhang[a], Han Cheng[a], Shiyue Wang[a], Lin Liu[a,*], Chengyan Zhang[a], Zhiwei Tong[a,c], Zhong Chen[b]

[a] *Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, China*
[b] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*
[c] *SORST, Japan Science and Technology (JST), Japan*

ARTICLE INFO

Keywords:
Keggin-type polyoxometalate
Layered double hydroxides (LDH)
Exfoliation/restacking
Intercalation
Cyclohexene epoxidation

ABSTRACT

Mg–Al LDH pillared by Keggin-type polyoxometalate $[PW_{12}O_{40}]^{3-}$ (PW_{12}) have been fabricated by the ion-exchange and exfoliation/restacking methods respectively (denoted as PW_{12}/LDH_{Ex} and PW_{12}/LDH_{Re}). X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR) spectroscopy and N_2 adsorption-desorption were used to characterize the structure and morphology of the intercalated compounds. PW_{12}/LDH_{Re} can be obtained without the formation of the impurity phase, which is unavoidable for the ion-exchange product PW_{12}/LDH_{Ex}. XRD results showed that the C3 axis of the PW_{12} anions is perpendicularly oriented to the surface of LDH layers. The catalytic properties of these hybrid materials were investigated in the green epoxidation of cyclohexene with oxygen as oxidant and isobutyraldehyde as co-reagent. Both hybrids were demonstrated to be efficient heterogeneous catalysts and can be recycled five times without obvious loss of catalytic activity. By comparison, PW_{12}/LDH_{Re} shows relatively higher catalytic activity and the conversion can reach 100% after 1.5 h at 60 °C.

1. Introduction

The epoxidation of olefins is an important reaction in the laboratory as well as in chemical industry, because epoxides are widely used as raw materials for epoxy resins, paints, surfactants, and are valuable intermediates in organic synthesis (Mizuno et al., 2005). Among various catalyst systems for epoxidation reactions, polyoxometalates (POMs) have received much interest due to their unique properties like thermal and oxidative stability, chemical tunability and high ionic conductivity (Omwoma et al., 2015; Tang et al., 2010). However, the application of POM-based homogeneous catalytic systems has been restricted by the poor solubility of POMs in a few solvent media particularly useful in promoting catalytic reactions, due to their crystalline nature, high negative charge, low energy lattice, contamination/separation, and decomposition issues (Qi et al., 2010). Consequently, numerous attempts have been made to immobilize POM clusters on solid supports (such as ZrO_2 (Farhadi and Zaidi, 2009), magnetic nanoparticles (Kooti and Afshari, 2012), mesoporous-silica (Cai et al., 2013; Inumaru et al., 2007), MCM-41 (Trakarnpruk, 2016; Wang et al., 2008), zirconia-alumina mixed oxides (Parida and Mallick, 2009)) to overcome the above limitations.

Hydrotalcite-like layered double hydroxides (LDH) are known to possess interlayer anion-exchange capability. The general formula of LDH is $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, with M^{II} and M^{III} representing the metal cations octahedrally coordinated by hydroxyl groups and A^{n-} representing a hydrated counterion situated between the layers (Allmann, 1968, 1970; Taylor, 1973). It has been demonstrated that LDH are ideal inorganic supports for immobilizing bulky POM catalysts, as the interlayer spaces are very flexible to accommodate guest molecules of different sizes (Rives and Ulibarri, 1999). Over the past few decades, a variety of POM/LDH compounds have been synthesized by the conventional methods such as co-precipitation, ion-exchange and show excellent catalytic performance including selective oxidation of sulfide (Liu et al., 2015; Zhang et al., 2015), alkenes (Carriazo et al., 2007; Liu et al., 2008) and alcohols (Hasannia and Yadollahi, 2015). However, the relevant intercalation hybrids face two serious challenges: 1) it is almost impossible to obtain POM/LDH compounds with no impurity; (2) the oxidants generally are strong ones

---

* Corresponding authors at: Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, China.
E-mail addresses: majj0518@hotmail.com (J. Ma), liulin@hhit.edu.cn (L. Liu).

http://dx.doi.org/10.1016/j.clay.2017.09.030
Received 29 June 2017; Received in revised form 22 September 2017; Accepted 26 September 2017
0169-1317/ © 2017 Elsevier B.V. All rights reserved.

like H_2O_2, tert-butyl hydroperoxide. In this context, the development of pure and environmental friendly POM/LDH nanohybrid catalysts is highly desirable.

Recently, we have reported a simple and rapid exfoliation/restacking synthetic route for preparing the intercalation compounds of LDH with metalloporphyrin (Ma et al., 2014). The obtained functional organic-inorganic intercalation compounds based on the exfoliated LDH platelets have been proven to be promising catalysts for cyclohexene epoxidation. To extend the application scope of exfoliation/restacking method, we have applied it to explore the intercalation of the classical Keggin-type $[PW_{12}O_{40}]^{3-}$ (PW_{12}) into Mg_2Al-LDH. For comparison, the corresponding intercalation product by the ion-exchange method was also prepared. Both nanohybrids were characterized by a variety of techniques including XRD, FTIR, SEM and HRTEM, and their catalytic performances for the epoxidation of cyclohexene with molecular oxygen as oxidant were investigated.

2. Experimental

2.1. Chemical materials

Sodium phosphotungstate ($Na_3PW_{12}O_{40}\cdot H_2O$), cyclohexene (99%) and naphthalene were purchased from Sinopharm Chemical Reagent Co., Ltd. Isobutyraldehyde (98%) was purchased from Alladdin. All other chemicals were commercial products (AR grade) and used as received.

2.2. Synthesis of LDH-NO_3 support

Mg-Al-CO_3 LDH was obtained by hydrothermally treating 75 mL of an aqueous solution containing $Mg(NO_3)_2\cdot 6H_2O$ (0.1 mol/L), $Al(NO_3)_3\cdot 9H_2O$ (0.05 mol/L) and urea (0.245 mol/L) at 140 °C for 24 h. The resulting precipitate was collected by centrifugation, washed with deionized water and anhydrous ethanol several times. Then Mg-Al-CO_3 LDH was converted into its NO_3^- form by a HNO_3-$NaNO_3$ treatment as described in previous literature (Han et al., 2008).

2.3. Synthesis of PW_{12}/LDH

Ion-exchange route: 0.1 g Mg-Al-NO_3 LDH powder was dispersed into 100 mL of distilled water containing 10 mmol/L $Na_3PW_{12}O_{40}\cdot H_2O$ along with maintaining the pH at 2.5 using diluted HNO_3. The amount of PW_{12} anion was about 8-fold excess of the anionic exchange capacity (AEC) of the MgAl-NO_3 dispersion. Then the mixed slurry was agitated vigorously for 3 h at 60 °C under a nitrogen atmosphere. PW_{12} anions were incorporated into Mg—Al LDH to form PW_{12}/LDH_{Ex} catalyst.

Exfoliation/restacking route: To achieve the exfoliation of LDH, 0.1 g Mg-Al-NO_3 LDH were mixed with 100 mL of formamide and agitated vigorously for 2 days under a nitrogen atmosphere. The resulting translucent colloidal dispersion of exfoliated LDH particles was purged with nitrogen for the elimination of atmospheric carbon dioxide and then centrifuged at 2000 rpm for 10 min to separate the unexfoliated component. The PW_{12}/LDH_{Re} was synthesized by adding the solution of 10 mmol/L $Na_3PW_{12}O_{40}$ aqueous solution (pH ≈ 2.5) into the exfoliated LDH particles dispersion with stirring for 1 day under N_2 atmosphere.

2.4. Characterization

X-ray diffraction patterns were recorded by a Philips diffractometer (model X'pert Pro) using Cu Kα radiation ($\lambda = 0.154$ nm) operated at 40 kV and 20 mA. The morphology of the samples was evaluated by scanning electron microscope (SEM, JEOL JSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, voltage of 200 kV). Samples for HRTEM measurements were prepared by sonicating the products in ethanol for 30 min and evaporating a drop of the resulting suspension onto a copper grid. Fourier transform infrared (FTIR) spectra were recorded on a Tensor-27 spectrometer using KBr pellet technique (sample/KBr = 1 / 100 weight ratio) in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans for each spectrum. X-ray photoelectron spectroscopy (XPS) analysis was performed with ESCALAB 250Xi electron spectrometer with a monochromatized Al-Kα X-ray source (1486.6 eV). ^{31}P NMR spectra were acquired using a Bruker Avance III 400 MHz NMR spectrometer. N_2 adsorption-desorption isotherms were measured at − 196 °C using a BeiShiDe Specific Surface & Pore Size Analyzer (3H-2000PM2). The BET surface areas and pore size distributions were determined by the nonlocal density function theory (NLDFT) method based on the adsorption data (Ravikovitch et al., 1997). Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out simultaneously in air using Netzsch STA449F3 apparatus at a heating rate of 10 °C min^{-1}. Elemental analyses were performed by inductively coupled plasma (ICP) emission spectroscopy on a Shimadzu ICPS-7500 instrument after microwave assisted acid digestion. The operating conditions for measurement were as follows: power, 1.2 kW; carrier gas flow rate, 0.7 L/min; plasma gas flow rate 1.2 L/min; cooling gas flow rate, 14.0 L/min.

2.5. Catalytic reaction

Catalytic tests were performed in a two-necked 10 mL round-bottomed flask equipped with a reflux condenser. The reaction system contains 2 mmol of cyclohexene, catalyst (0.15 mol% with respect to the substrate based on PW_{12}), 6 mmol of isobutyraldehyde (IBA), 0.2 mmol of naphthalene as the internal standard and 4 mL of acetonitrile. The mixture was stirred with O_2 as the oxidant (flowing rate: 5.0 mL/min). At different time intervals, aliquots of the reaction mixture (100 μL) were withdrawn and mixed with 300 μL of acetonitrile. The mixture was separated by centrifugation and the liquid products were analyzed by Agilent 7820A gas chromatography system (GC). For the recycling experiments, the catalyst was exhaustively washed with acetonitrile to remove the occluded reactants and products, and dried overnight under vacuum at 60 °C. Then the recovered catalyst was used under the same experimental conditions as described above.

3. Results and discussion

3.1. Catalysts characterization

XRD patterns of the products in each stage were shown in Fig. 1. As we can see, the d(003) basal spacing enlarges from 0.75 nm to 0.88 nm after salt-acid treatment. In comparison with the precursor, the (00*l*) diffraction peaks of both PW_{12}/LDH compounds shift to lower angles,

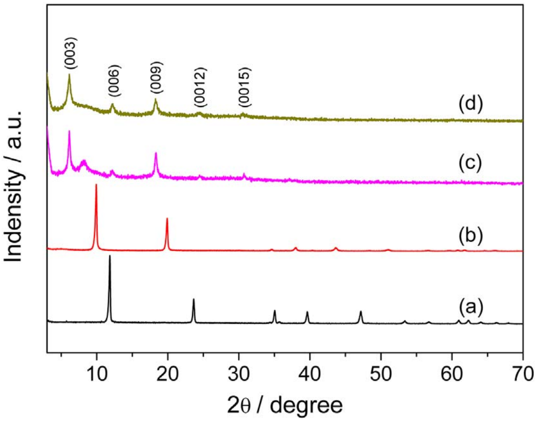


Fig. 1. XRD patterns of (a) Mg-Al-CO_3 LDH, (b) Mg-Al-NO_3 LDH, (c) PW_{12}/LDH_{Ex}, (d) PW_{12}/LDH_{Re}.

Download English Version:

https://daneshyari.com/en/article/5468501

Download Persian Version:

https://daneshyari.com/article/5468501

Daneshyari.com