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A novel approach towards solvent-free epoxidation of cyclohexene by Ti(IV)–Schiff base complex-intercalated LDH using H_2O_2 as oxidant

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ABSTRACT

A novel heterogeneous catalyst has been developed by immobilizing Ti(IV)–Schiff base complex in Zn–Al/LDH by an ion-exchange method. Powder X-ray diffraction, Fourier transform infrared spectroscopy, diffuse reflectance UV–Visible spectroscopy, N_2-adsorption and thermal studies confirm the successful intercalation of the Ti-complex within the LDH structure. The supported catalyst shows an excellent catalytic activity in cyclohexene epoxidation reaction. In this paper, we report an environmentally benign reaction pathway in a solvent-free condition, taking H_2O_2 as oxidant. As high as 95% conversion of cyclohexene took place at 70 °C in 6 h. The heterogeneous catalyst can be recovered easily and reused multiple times without significant loss in catalytic activity and selectivity, which is a better green alternative for practical applications.

1. Introduction

One of the challenges facing chemists this century is to develop new transformations that are not only efficient, selective and high-yielding but are also environmentally benign [1,2]. The utilization of nontoxic chemicals, renewable materials and solvent-free conditions are the key issues in the green synthetic strategy. Solvent-free methods are of great interest in order to replace classical procedures making them profitable, cleaner, safer and operationally easier. Hydrogen peroxide is probably the preferred terminal oxidant after dioxygen due to environmental and economic considerations [3–6]. Indeed in certain circumstances, it is better than oxygen insofar as O_2/organic mixtures may sometimes be spontaneously ignited. So, epoxidation systems that use hydrogen peroxide as oxidant in a solvent-free condition in conjunction with recyclable and reusable heterogeneous catalysts are potentially viable for large-scale production.

The epoxidation of alkenes by the electrophilic addition of oxygen to a carbon–carbon double bond remains one of the most significant challenges in synthetic chemistry. The formed epoxides are the building block intermediates that can be converted to a variety of products [7,8]. The titanium(IV)-catalyzed reactions with a variety of different alkenes ranging from low molecular weight alkenes to large molecules are well known [4]. Titanium(IV) alkoxides catalyze the epoxidation of a variety of alkenes with an alkyl hydroperoxide as the oxygen donor [9–14]. Propene can be efficiently epoxidized using hydrogen peroxide in an activated form of oxygen using the titanium silicalite TS-1 as catalyst [15]. But the reactions are relatively slow, and formation of by-products by the addition of tert. butyl hydroperoxide radical to the substrate is often observed [12]. These problems have been overcome by the development of a heterogeneous titanium catalyst [13].

Insertion of organic or organometallic species into inorganic solids offers an attractive route to nanohybrids in which complementary properties of the two components are expressed in a single material. Layered solids in which guest species can access interlamellar space via the intercalation process provide some of the best-studied examples of such systems [16]. Layered double hydroxides (LDH), also known as anionic clay, constitute a class of host–guest materials that have gained great attention recently. LDHs are brucite-like solids that are constituted by two metals typically having 2 + (M^{II}) and 3 + (M^{III}) oxidation states, octahedrally surrounded by oxo bridges and hydroxyl groups. The structure is organized forming layers that bear an excess of positive charge equivalent to the number of trivalent metals. This excess of positive charge requires the presence of charge compensating anions that are located in the interlayer spaces [17–22]. Sandra Gago et al. have reported immobilization of oxomolybdenum species in a LDH pillared by 2,2′-Bipyridine-5,5′-dicarboxylate anions for liquid-phase epoxidation of cis-cyclooctene, 1-octene and trans-2-octene using tert-butyl hydroperoxide as oxygen source [23]. LDH containing metal complexes of chelating ligands namely NTA (nitriloacetate) and EDTA (ethylenediamine tetraacetate) have also been prepared either by direct intercalation of metal

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complexes or indirectly by forming metal complexes between the host layers following intercalation of the ligands [24].

In the present work, we describe a new protocol for immobilization of Ti(IV)-complex in the interlayer of LDH by replacing the interlayer gallery anions in an ion-exchange method. The heterogeneous Ti-complex so formed is found to be an excellent catalyst for epoxidation of cyclohexene in a solvent-free condition using H_2O_2 as oxidant.

2. Experimental

2.1. Materials

3-Amino-2-pyrazine carboxylic acid, 2-pyridine carboxaldehyde, titanium tetra-isopropoxide (Aldrich), $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (CDS) were used without further purification. Ethanol was dried using molecular sieve 5A prior to its use in the reaction.

2.2. Preparation of the catalysts

2.2.1. Preparation of LDH

The layered double hydroxide containing Zn:Al molar ratio 2:1 was prepared by the co-precipitation method at a constant pH of 11 [25]. The synthesis was carried out by dropwise addition of mixed metal nitrate solution [$Zn(NO_3)_2{\cdot}6H_2O$ (0.133 M) and $Al(NO_3)_3{\cdot}9H_2O$ (0.066 M)] to 2 M NaOH solution taken in a flask containing 100 ml of deionized water under magnetic stirring, and nitrogen atmosphere was maintained throughout the addition. The resulting slurry was kept stirring for 1 h at room temperature. Then, it was filtered, washed thoroughly with deionized water till the washings were neutral to litmus and dried at 100 °C overnight [26,27]. Elemental analysis showed the following composition. Found/calcd (%). For $Zn_{0.68}{\cdot}Al_{0.32}$ $(OH)_2$ $(NO_3^-)_{0.32}$ 0.38 H_2O (Zn, Al–LDH–NO_3): Zn, 38.87/39.07; Al, 7.53/7.63; N, 3.86/3.93; H, 2.19/2.26. IR (KBr) 3450, 1620, 1384, 675, 445 cm^{-1}.

2.2.2. Synthesis of the metal complex

3-Amino-2-pyrazine carboxylic acid treated with Na_2CO_3 in ethanolic medium produces the sodium salt of 3-amino-2-pyrazine carboxylic acid. In 30 ml of ethanol, 10 mmol of sodium salt of 3-amino-2-pyrazine carboxylic acid was refluxed with 10 mmol of 2-pyridine carboxaldehyde. The whole mixture was kept on water bath at 60 °C for 2 h to produce the Schiff base ligand. Ti-complex was formed by refluxing 0.456 g (1.8 mmol) of sodium salt of Schiff base ligand and 0.29 ml (1 mmol) of titanium tetra-isopropoxide ($C_{12}H_{28}O_4Ti$) in ethanolic medium at 60 °C for 2 h. The final product was filtered, washed several times with ethanol to get rid of nonreacted ligand and recrystalized from diethyl ether. Finally, the metal complex was dried in vacuum and kept in a desiccator. Anal. Found/calcd (%). For ligand: C, 52.43/52.8; H, 2.57/2.8; N, 21.9/22.4. For Ti-complex: C, 47.98/48.17; H, 2.32/2.55; N, 20.02/20.43. IR (KBr) 3300, 1725, 1640 cm^{-1}. For Schiff base ligand: ^1H NMR ($CDCl_3$, room temp., 200 MHz): δ = (7.15, t), (7.63, t), (7.7, d), (8.41, d), (8.59, s), (8.86, d), (8.71, d). ^{13}C CP MAS NMR (100.62 MHz, $CDCl_3$): δ = 130.1, 130.9, 131.4, 133.9, 134.1, 134.7, 138.7, 139.0, 148.2, 167.0, 167.7. For Ti-complex: ^1H NMR ($CDCl_3$, room temp., 200 MHz): δ = (7.18, t), (7.67, t), (7.9, d), (8.23, d), (8.34, s), (8.89, d), (8.76, d). ^{13}C CP MAS NMR (100.62 MHz, $CDCl_3$): δ = 131.1, 131.4, 132.2, 132.8, 135.1, 135.4, 137.4, 138.2, 147.2, 166.1, 166.5.

2.2.3. LDH/Ti(IV)-complex

One gram of Zn–Al/LDH was used after drying under reduced pressure at 100 °C. Thirty milliliter of ethanol was added to 1 g dried LDH and stirred for 1 h. To an ethanolic suspension of LDH, 0.5 mmol (0.274 g) of metal complex was transferred and refluxed at 60 °C for 24 h with constant stirring. The final product was isolated by filtration, washed with ethanol and kept overnight in vacuum at 70 °C. The schematic representation of the total synthesis pathway is depicted in Scheme 1. Anal. Found/calcd(%). For $[Zn_2Al(OH)_6NO_3^-]$(Ti-complex)$_{0.33}$ 0.63H_2O(Zn, Al–LDH/Ti-complex): Zn, 24.76/25.15; Al, 4.91/5.19; C, 16.48/16.75; N, 6.92/7.10; H, 2.08/2.28. IR (KBr) 3450, 3300, 1725, 1640, 1384, 675, 445 cm^{-1}.

Elemental analysis of LDH/Ti(IV)-complex gave 9.2 wt.% Ti. Hence, the uptake of metal complex is in the same proportion as the amount of Ti present. The ratio of Ti/Zn + Al in the final product is found to be 0.3.

2.3. Physico-chemical characterization of the catalyst

Powder XRD measurements were performed on a Rigaku D/MAX2500 diffractometer, using Cu Kα radiation at 40 kV, 30 mA, a scanning rate of 5 °/min and a 2θ angle ranging from 3° to 80°. The FT-IR spectra of the samples were recorded using a Varian 800-FT-IR in KBr matrix in the range of 4000–400 cm^{-1}. The coordination environments of the samples were examined by diffuse reflectance UV–Vis spectroscopy. The spectra were recorded in a Varian-100 spectrophotometer in the wavelength range of 200–800 nm in $BaSO_4$ phase. Surface area was determined by N_2 adsorption–desorption at liquid nitrogen temperature (77 K) using ASAP 2020 (Micromeritics). Prior to adsorption–desorption measurement, the samples were equilibrated by degassing at 120 °C for 6 h. SEM images were obtained using HITACHI 3400N microscope. Thermogravimetric/differential thermal analysis (TG/DTA) was performed under air with a Shimadzu TGA-50 system at a heating rate of 5 °C min^{-1}. The chemical composition of the products was confirmed quantitatively and qualitatively by energy-dispersive X-ray (EDX) using a HITACHI 3400N microscope. The Ti loading in the catalyst and in the leaching solution was determined by using atomic absorption spectroscopy (Perkin-Elmer AAS 300 with acetylene (C_2H_2) flame). ^1H and ^{13}C CP MAS NMR spectra were recorded on 200 and 100.62 MHz, respectively, using a Bruker Avance 400 MHz spectrometer.

2.4. Catalytic reaction

Catalytic test of the prepared catalyst was carried out in a 100-ml two-necked round-bottom flask fitted with a reflux condenser. In a solvent-free condition, 10 mmol of cyclohexene and 0.05 g of catalyst were taken. To this, 30% H_2O_2 (30 mmol) was added dropwise. Reaction was carried out at 70 °C for 6 h (Scheme 2). The reaction products were analyzed by offline GC (Shimadzu GC-2010) equipped with a capillary column (ZB-1, 30 m length, 0.53 mm I.D. and 3.0 μ film thickness) using a flame ionization detector (FID). The selectivity of the epoxide (cyclohexene oxide) is a measure of the reactivity of the catalyst. The percentage of conversion of the substrate and the percentage of selectivity of the products in the epoxidation reaction are calculated as:

$$\text{Substrate conversion }(\%) = [\text{substrate converted (moles)}/\text{substrate used (moles)}] \times 100$$

$$\text{Product selectivity }(\%) = [\text{product formed (moles)}/\text{substrate converted (moles)}] \times 100$$

The decomposition of H_2O_2 was followed by measuring the volume of oxygen liberated at atmospheric pressure by conventional gasometric method [28].