



Feature Article

Metallophthalocyanine intercalated layered double hydroxides as an efficient catalyst for the selective epoxidation of olefin with oxygen



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ABSTRACT

Varied metallophthalocyanine intercalated layered double hydroxides (LDHs) as bifunctional hybrid catalysts for selective epoxidation have been prepared and characterized. Systematic characterizations suggested the successful intercalation of the metallophthalocyanines into the interlayer of ZnAl LDHs. The synthesized hybrid exhibited excellent catalytic activity in the selective epoxidation of various olefins through O₂/isobutaldehyde system. The basicity of the hybrid benefits to the selectivity of epoxide, and the bifunctional roles of the catalyst in the reaction have been discussed and verified by a series of controlled experiments. On the basis of obtained results, a probable mechanism of the epoxidation by the hybrid has been proposed and detailedly investigated. Under the catalysis of metallophthalocyanines intercalated LDHs in the presence of O₂/isobutaldehyde, the production of epoxide undergoes two reaction paths. And two types of intermediates, namely acylperoxy radical and peroxyacid, are formed in the reaction, and the former is predominant.

1. Introduction

The selective and efficient epoxidation of olefinic compounds is one of the most important industrial processes, because the epoxide is useful intermediate in the production of varied pharmaceuticals, flavor & fragrance and fine chemicals [1,2]. Traditionally, expensive peracids are always applied in the direct epoxidation of alkenes to produce the corresponding epoxides, but with a formation of large amounts of effluents [3,4]. Although varied approaches have been developed for the transformation [5–8], from the view of economic and sustainable chemistry, heterogeneous catalytic process employing oxygen or H₂O₂ as the ultimate oxygen is quite attractive. Many kinds of catalysts based on supported complex [9–11], metal oxide [12,13], transition metal substituted heteropolyanions (TMS-HPAs) [14,15], and supported catalysts [16,17] have been introduced into the oxidation. However, some drawbacks exist in these catalytic systems, for example, complex synthesis procedure for catalysts, harsh reaction conditions, and low catalytic activity and the selectivity of the products. Development of efficient, stable and recyclable catalyst with high selectivity of the corresponding epoxide is still desirable.

Transition-metal complexes of corrole, salen, porphyrins, and phthalocyanines have been extensively used to resemble the functionality of cytochrome P450 [18–21]. Compared with the other catalysts,

phthalocyanine counterparts are cheap and readily accessible on an industrial scale: their worldwide production is about 80 000 t/year, making them very attractive as potential industrial catalysts [22,23]. To avoid the drawback of homogeneous metallophthalocyanines, such as self oxidation and formation of inactive di-oxo [24–26], the stabilization of the metallophthalocyanines molecular in a support is imperative for further developments in the field. Some supported metallophthalocyanines have been designed for the epoxidation of alkenes. Copper (II) phthalocyanine encapsulated in zeolite Y has been prepared by Seelan, et al. and introduced into the styrene oxidation by TBHP [27], however, the selectivity was only 39.1% with benzaldehyde as the main by-product. Manna, et al. reported a hybrid by encapsulating a copper-phthalocyanine complex in silica-nanoparticle-assembled microcapsules (CuPcS@MC) [28]. The epoxide was the only product when the conversion of styrene was 50% with TBHP as the oxidant. Except the drawback of the low yield, a 3 equivalent of Na₂CO₃ was required, making the process complexed. Rezaeifard, et al. have prepared the Cu (II) phthalocyanine-tetrasulfonic acid tetrasodium complex (CuPcS) immobilized on the silica coated magnetic nanoparticles (Fe₃O₄@SiO₂, SMNP) via the amine functionality and investigated the catalytic performance in the epoxidation of olefins [29]. A high 93% yield of cyclohexane oxide was obtained with the tetra-*n*-butylammonium peroxomonosulfate (*n*-Bu₄NHSO₅, TBAOX) as the oxidant.

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Copperperchlorophthalocyanine has been successfully immobilized in the channels of HSI-MCM-41 molecular sieves through a post-synthesis method (Cu-AM(PS)) [30], which gave full conversion of styrene with the highest selectivity of 74.4%. The authors found that the basicity of the prepared catalyst originated from 3-aminopropyl group benefited to the enhancement of the initial rate of epoxidation by O₂/isobutyraldehyde; furthermore, the base could also accelerate the cleavage of O–O bond to produce the high oxo intermediates, which could react directly with the alkene to give epoxide.

Layered double hydroxides (LDHs), whose anions in the interlayers can be modified, is a representative basic material and has been widely applied as basic catalysts or supports in varied reactions [31–33]. In this context, we envisioned that intercalation of metallophthalocyanine anions into LDHs might provide an efficient biomimetic catalyst for the alkene epoxidation. The obtained hybrid would not only present the high activity of metallophthalocyanine, but also lead to a supported metallophthalocyanine, making the catalyst stable and recyclable. Moreover, according to the reported results [30], the surface basicity of the hybrid might improve the catalytic activity and the selectivity of epoxide.

In the study, four tetrasulfonic metallophthalocyanine (MPcTs, M = Co, Cu, Mn and Fe) intercalated LDHs have been prepared and investigated in the aerobic epoxidation of alkene in the presence of isobutaldehyde. The effects of reaction conditions on the oxidation have been systematically studied. Under the optimized conditions, the relation of structure-activity and the probable mechanism have also been discussed.

2. Experimental

All the chemicals used in the experiments were of analytical grade and were purchased from Energy-chemical.

2.1. Synthesis of MPcTs(NH₄)₄

Tetra-sulfonic cobalt phthalocyanine tetra-ammonium was prepared and purified according to the reported method [34]. Triammonium 4-sulfophthalate (3.0 g, 0.01 mol), urea (7.5 g, 0.125 mol), ammonium molybdate (0.03 g, 0.025 mol) and anhydrous cobalt(II) chloride (0.32, 2.5 mmol) were ground together in a 100 mL flask until homogeneous. After stirring for 2 h at 240 °C, blue black solid was obtained. The crude product was washed alternately with ethanol and acetone for 5 times. The obtained solid was then dissolved in water, and insoluble impurities were separated by filtration. The solution was distilled under vacuum to remove the water. After drying overnight at 80 °C, the blue black, pure product CoPcTs(NH₄)₄ was obtained in a yield of about 68%. MPcTs(NH₄)₄ (M = Cu, Mn and Fe) were prepared and purified by the similar procedure.

2.2. Synthesis of MPcTs-Zn₂Al-LDH

The hybrid catalysts were obtained through the coprecipitation method. A typical procedure for the CoPcTs intercalated Zn₂Al LDH (CoPcTs-Zn₂Al-LDH) would be as follows: a solution of Zn(NO₃)₂·6H₂O (1.67 g, 0.0056 mol) and Al(NO₃)₃·9H₂O (1.05 g, 0.0028 mol) in 50 mL of deionized water was slowly added to 10 mL of distilled water dissolved with sodium CoPcTs(NH₄)₄ (1.36 g, 1.54 × 10⁻³ mol) with mechanic stirring under 25 °C. 0.1 mol L⁻¹ NaOH was then added into the solution continuously and a pH ≈ 7.5 was maintained. Then the suspension was stirred for another 24 h at 80 °C under N₂ atmosphere. After filtration, the product was washed with distilled water and finally dried at room temperature under vacuum. A black solid CoPcTs-Zn₂Al-LDH was obtained. MPcTs-Zn₂Al-LDHs (M = Cu, Mn and Fe) were obtained by the similar procedure.

2.3. Characterization of catalysts

The XRD patterns were obtained on a Rigaku D/max 2500 PC X-ray generator with Cu-Kα (1.5402 Å) radiation. FTIR spectra of the prepared catalyst were collected on a Nicolet PROTÉGÉ 460 FTIR spectrometer using KBr disks. SEM images were recorded on a JEOL JSM-6360LA scanning electron microscope. A Perkin-Elmer Instruments Lambda 35 was used to analyze the diffuse reflectance ultraviolet visible spectroscopy (DR UV-vis). Thermogravimetric measurements of these compounds were performed in a Seiko Instrument TG/DTA model 32, in the temperature range 323–1173 K at a heating rate of 10 K/min under an N₂ atmosphere. The metal compositions of samples were measured via inductively coupled plasma optical emission spectrometry (ICP-OES) method on a Varian Vista-AX device, and the samples were prepared by wet-digestion method.

2.4. Catalytic epoxidation of styrene over O₂/IBA system

In a typical procedure, styrene (2 mmol), catalyst (6 mg), acetonitrile (10 mL), IBA (isobutyraldehyde, 5 mmol), and chlorobenzene (inert internal standard, 0.5 mmol) were first introduced into a 25 mL round-bottom flask equipped with condenser and magnetic stirrer. Dioxygen was bubbled through the solution at a volume rate of 15 mL min⁻¹. Then the mixture was stirred at 60 °C and sampled at different intervals during the reaction. Qualitative and quantitative analysis of all the products were performed on GC-MS (Shimadzu GCMS-2010) and GC-FID (Shimadzu GC-2010AF), respectively. The TOF (turnover frequency) was calculated by following formula: TOF = mol of converted styrene/mol of MPcTs in the catalyst/reaction time.

2.5. ¹⁸O-labeled H₂¹⁸O experiments

To a mixture of styrene (104 mg, 1 mmol), CoPcTs-Zn₂Al-LDHs (3 mg), IBA (180 mg, 2.5 mmol), and H₂¹⁸O [90 mg (5 mmol), 97% ¹⁸O enriched, Aladdin Chemical Co.] in a dried solvent mixture (5 mL) of CH₃CN was bubbled dioxygen (15 mL/min). The reaction mixture was stirred for 1.5 h at 60 °C and then directly analyzed by GC-MS through calculation of the mass peaks.

3. Results and discussion

3.1. Characterization of MPcTs-Zn₂Al-LDH

In order to probe the formation and location of macrocyclic MPc molecules in the hydrotalcites, XRD was used to identify the structure of LDHs. Compared with CO₃²⁻-Zn₂Al-LDH, XRD patterns of MPcTs-Zn₂Al-LDH depicted in Fig. 1 show common features with reflections typical of a intercalated hydrotalcite-like phase [35,36]. Sharp and

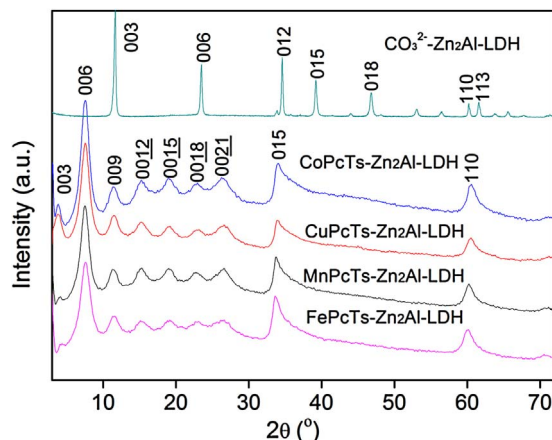


Fig. 1. XRD patterns of MPcTs-Zn₂Al-LDHs (M = Co, Cu, Mn and Fe).

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