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Article

Synthesis of dicationic alkyl imidazolium peroxopolyoxotungsten-based phase transfer catalyst and its catalytic activity for olefin epoxidation

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ABSTRACT

Peroxopolyoxotungsten-based hybrid catalysts modified by dicationic long-chain alkyl imidazolium cations have been synthesized and characterized. The catalytic activity of the catalysts was measured for the epoxidation of olefins with H_2O_2 . These catalysts proved to be high catalytic activity phase transfer catalysts. In particular, for the catalyst $[D_{12}min]_{1.5}PW_4O_{24}$ modified by the dodecyl dicationic imidazolium cation, the conversion of cyclohexene and selectivity for epoxycyclohexane were 97.7% and 96.3%, respectively. After the reaction, the catalyst could be recovered simply by filtration and reused four times. The conversion of cyclohexene and selectivity for epoxycyclohexane were still 72.4% and 97.2%, respectively, after recycling the catalyst four times. In addition, this phase transfer catalyst can be applied to the epoxidation of a wide range of olefins.

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1. Introduction

Epoxides are valuable organic raw materials and intermediates for fine chemical and pharmaceutical synthesis [1–3]. H_2O_2 -based catalytic epoxidation efficiency and reusability under mild conditions have received much attention from an economic and environmental point of view [4]. A wide range of catalysts for olefin epoxidation have been described, such as heteroatomic molecular sieves, transition metal (Mo, W, Mn, and V) compounds, and polyoxometalates (POMs) [5–11]. Tungsten-based POM catalysts show high efficiency of hydrogen peroxide use and high selectivity towards epoxides, typically the Venturello-Ishii ($\{PO_4[WO(O_2)_2]_4\}^{3-}$) species, and have attracted considerable attention as effective catalysts for the H_2O_2 -based epoxidation of olefins [12,13]. Since Xi et al. [14] reported that quaternary ammonium POMs can be used as

reaction-controlled phase-separation catalysts for olefin epoxidation, considerable effort has been focused on modifying POMs with organic species to obtain phase transfer POM-based hybrid catalysts with improved catalytic activity, selectivity, and convenient catalyst recovery and recycling that combine the advantages of both homogeneous and heterogeneous catalysts [15–19].

In this work, we synthesized a series of POM-based ionic hybrid catalysts by combining dicationic long-chain alkyl imidazolium cations with Venturello-Ishii anions. Characterization was performed using Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), 1H NMR, and CHN elemental analysis. The obtained hybrid catalysts were used for the solid-liquid-solid phase transfer catalytic epoxidation of olefins with aqueous H_2O_2 in different solvents.

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2. Experimental

2.1. Preparation of catalysts

The procedure for the synthesis of the catalysts is shown in Scheme 1. The preparation of $[D_{12}mim]_{1.5}PW_4O_{24}$ is used as an example.

2.1.1. Synthesis of *N*-alkylimidazole

The synthesis of *N*-dodecylimidazole was used as an example. *N*-dodecyl bromide (7 g, 28 mmol) was dissolved in dimethyl formamide (DMF, 25 mL) and then added to a solution of the sodium salt of imidazole, which was formed by the reaction of imidazole (2.3 g, 33.9 mmol) with sodium hydride (1.4 g, 62 mmol) in DMF (25 mL). The mixture was heated at 60 °C for 6 h, cooled, and then filtered. The filtrate was washed with brine and water, and then dried with sodium sulfate. The solvent was separated by reduced pressure distillation and *N*-alkylimidazole was obtained as a pale yellow oily product. 1H NMR (400 MHz, $CDCl_3$) δ = 7.45 (s, 1H, CH), 7.04 (s, 1H, CH), 6.90 (s, 1H, CH), 3.91 (t, J = 7.1 Hz, 2H, CH_2), 1.77 (m, J = 13.5 Hz, 2H, CH_2), 1.27 (m, J = 13.1 Hz, 18H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3).

2.1.2. Synthesis of dicationic imidazolium ionic liquids

Dicationic imidazolium ionic liquids were prepared by refluxing *N*-dodecylimidazole (4.72 g, 20 mmol) and 1,4-dibromobutane (2.16 g, 10 mmol) in isopropanol (25 mL) at 80 °C for 24 h. Then, the products were washed with diethyl ether four times under vacuum. 1H NMR (400 MHz, $CDCl_3$) δ = 10.18 (s, 2H, CH_2), 8.12 (s, 2H, CH), 7.29 (s, 2H, CH), 4.58 (s, 4H, CH_2), 4.27 (t, J = 7.5 Hz, 4H, CH_2), 2.19 (s, 4H, CH_2), 1.90 (d, J = 6.4 Hz, 4H, CH_2), 1.25 (m, 36H, CH_2), 0.88 (t, J = 6.8 Hz, 6H, CH_3).

2.1.3. Synthesis of dicationic alkyl imidazolium peroxopolyoxotungsten-based catalyst [20]

A suspension of tungstic acid (2.50 g, 10 mmol) in 7.93 g (70 mmol) of 30% aqueous H_2O_2 was stirred and heated at 60 °C until a colorless solution was obtained. After filtering and cooling the solution at room temperature, 40 wt% H_3PO_4 (0.62 g, 2.5 mmol) was added, and the solution was diluted with 30 mL of water and then stirred for 30 min. Dicationic imidazolium ionic liquid (3.75 mmol) in dichloromethane (40 mL) was added dropwise to the resultant solution with strong stirring over a period of more than 2 min. Stirring was continued for an additional 60 min. The organic phase was then separated, dried over Na_2SO_4 , filtered, and gently evaporated by reduced pres-

sure distillation on a rotary evaporator under reduced pressure at 40–50 °C, which gave a yellow powder. This catalyst was $[D_{12}mim]_{1.5}PW_4O_{24}$.

2.2. Characterization of catalyst structure

FT-IR spectra were recorded on an ABB FTLA2000 FT-IR spectrometer (Canada) (KBr discs, 4000–500 cm^{-1}). TGA was carried out with a METTLER-TOLEDO TGA/1100SF instrument (Switzerland) in N_2 at a heating rate of 10 °C/min. Elemental analyses (C, H, and N) were performed on a CHN elemental analyzer (Elementar Vario EL III, Germany). The 1H NMR spectra were recorded on an AVANCE III 400 MHz digital NMR spectrometer (Bruker, Germany) using a $CDCl_3$ solvent.

2.3. Epoxidation procedure

Cyclohexene (9 mmol), CH_3CN (10 mL), and catalyst (0.1 g) were added to a 25 mL flask. The reaction started after the addition of aqueous H_2O_2 (30 wt%, 3 mmol) at 60 °C within 10 min under vigorous stirring. After the reaction, the product mixture was analyzed by gas chromatography (GC). The catalyst was recovered by filtration immediately after the reaction ready for the next reaction (run). The conversion (X) and selectivity (S) were calculated as follows:

$$X = (\text{mol epoxide product} + \text{mol byproducts}) / (\text{mol initial } H_2O_2) \times 100\%$$

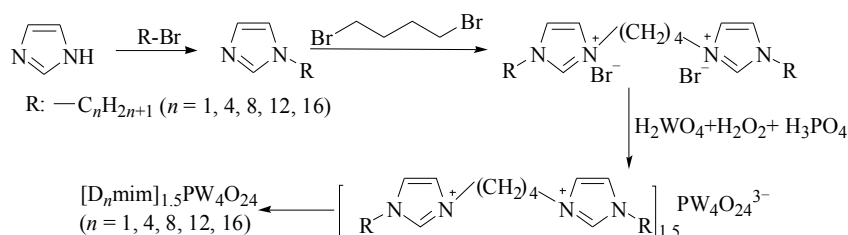
$$S = (\text{mol epoxide product}) / (\text{mol epoxide product} + \text{mol byproducts}) \times 100\%$$

All of the olefin substrates were tested using the same procedure.

3. Results and discussion

3.1. Catalyst structure and thermal stability

The TGA curves of the catalysts are shown in Fig. 1. The hybrid catalysts were stable up to 200 °C (region I), indicating that these catalysts are thermally stable. The slight mass loss is due to the removal of the combination water. The mass loss between 250 and 600 °C is due to decomposition of the organic components in the catalyst (region II), which is consistent with the CHN elemental analysis (Table 1). Thus, these results confirm that the molar of cation and polyanion of the catalysts is 1.5:1, and the hybrids have the chemical formulas shown in Scheme 1.



Scheme 1. Typical preparation procedure of the catalysts.

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