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Selective oxidation of styrene to 1,2-epoxyethylbenzene by hydrogen peroxide over heterogeneous phosphomolybdic acid supported on ionic liquid modified MCM-41

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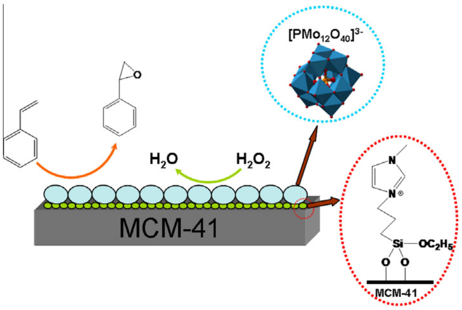
HIGHLIGHTS

- The solvent-free heterogeneous oxidation system is environmentally friendly.
- PMo/ILMCM-41 prepared by grafting shows outstanding reusability in reaction.
- Heterogeneous catalyst can easily separate by centrifugation after reaction.
- PMo/ILMCM-41 possesses hydrophilic and hydrophobic properties.
- PMo/ILMCM-41 can adsorb H_2O_2 and styrene simultaneously to improve the oxidation.

GRAPHICAL ABSTRACT

The heterogeneous catalyst PMo/ILMCM-41 prepared by the grafting method shows outstanding reusability in the selective oxidation of styrene to 1,2-epoxyethylbenzene catalyzed by PMo/ILMCM-41 using H_2O_2 as oxidant. The amphiphilic catalyst can adsorb H_2O_2 and styrene from aqueous and organic phase simultaneously to solve the disadvantage of mass interface transfer limitation.



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ABSTRACT

Styrene was selectively oxidized to 1,2-epoxyethylbenzene catalyzed by phosphomolybdic acid supported on ionic liquid modified MCM-41 using hydrogen peroxide as oxidant. The synthesized catalyst was characterized by XRD, FT-IR, and N_2 adsorption–desorption analyses, and the results indicate that the sample retained mesoporous structure after ionic liquid-modified and immobilization of phosphomolybdic acid. Maximum activity was observed at a loading of 30 wt.% phosphomolybdic acid on ionic liquid modified MCM-41. Reaction conditions such as reaction time, temperature, amount of catalyst, and H_2O_2/styrene molar ratio were systematically optimized to obtain a maximum styrene conversion of 95.4%. 1,2-Epoxyethylbenzene selectivity of 90.2% when the reaction conditions were set to 3 h reaction time, 50 °C, 100 mg catalyst, and a H_2O_2/styrene molar ratio of 1.2. The heterogeneous catalyst is easily separated by centrifugation and was reused without deactivation after six runs.

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1. Introduction

Epoxide olefin compounds are valuable materials for the synthesis of a wide variety of chemical products, such as drugs, agrochemicals, and food additives, placing the epoxidation reaction among the important reactions in organic synthesis. The oxidant carries an indispensable role in epoxide reactions of olefin, and oxidants including molecular oxygen [1,2], organic hydroperoxides [3,4], hydrogen peroxide [5–10], have been reported. Among these oxidants, hydrogen peroxide has been widely investigated because it is highly reactive, inexpensive, and environment friendly features. Epoxide reactions of olefin with hydrogen peroxide as the oxidant generally requires the presence of a catalyst, of which tungsten [11], manganese [12], rhenium [13], and molybdenum [14] based catalysts, molecular sieve catalysts including TS-1 [5], Ti-zeolites [15], Ti-silicas [16], and polyoxometalate catalysts [17–19] have been reported. Of these catalysts, polyoxometalates catalysts are considered to be the most promising catalysts for epoxidation, and have been widely researched in the last three decades. In 1983, Venturello et al. [17,18] reported a catalytic system consisting of tungstate and phosphate which was used in olefin epoxidation with hydrogen peroxide as the oxidant. In 1988, Ishii and his group [19] discovered that olefin epoxidation could be catalyzed by $H_3PW_{12}O_{40}$ and cetylpyridinium chloride using hydrogen peroxide solution as the oxidant. In the epoxidation of organic olefin compounds catalyzed by polyoxometalates with H_2O_2 as the oxidant, olefin and H_2O_2 are in the organic phase and aqueous phase, respectively, so the mass transfer across the interface between the two phases is the rate-limiting step. In order to enhance the rate of mass transfer, organic solvents, such as dichloromethane [20], chlorobenzene [21,22], acetonitrile [23] methanol [24] and cetylpyridinium chloride (Phase Transfer Agents, PTA) [19], are usually added to the reaction system, but are facing several issues such as environmental pollution, high cost, and difficulties in separation.

In the present work, phosphomolybdic acid was grafted onto ionic liquid modified MCM-41 to prepare an organic–inorganic hybrid material catalyst which was used to selectively oxidize styrene to 1,2-epoxyethylbenzene in the presence of H_2O_2. The catalyst can adsorb styrene and H_2O_2 simultaneously from the aqueous and oil phases to solve the limitation of transfer across the interface of aqueous and oil phases without any solvent. This catalyst system was used to create an environmentally friendly heterogeneous system and special attention was given to the stability and recoverability of this catalyst. The influence of reaction parameters on styrene oxidation was also investigated.

2. Experimental

2.1. General

Phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 6H_2O$, AR grade), hydrogen peroxide (30 wt.%, AR grade), N-methyl imidazolium (AR grade), 3-chloropropyltriethoxysilan (AR grade), chloroform (AR grade), and diethyl ether (AR grade) were purchased from Sinopharm Chemical Reagents Co., Ltd. (China).

2.2. Synthesis of 1-triethoxysilylpropyl-3-methylimidazoliumchloride ionic liquid

3.36 g of N-methyl imidazolium and 9.63 g of 3-chloropropyltriethoxysilan were added to a three-neck glass flask and the mixture was refluxed for 24 h at 95 °C. 1-Triethoxysilylpropyl-3-methylimidazoliumchloride ionic liquid was obtained.

2.3. Synthesis of ionic liquid modified MCM-41

The pure siliceous MCM-41 was synthesized using sodium silicate hydrate as the SiO_2 source and cetyltrimethylammonium bromide as the template, according to the procedure in the literature [25]. 1.4 g of the as-prepared ionic liquid and 50 mL of chloroform were added into a three-neck glass flask, followed by addition of 2 g of MCM-41. The mixture was dried under vacuum at 150 °C for 24 h, and then refluxed for 24 h with constant stirring. The product was obtained after cooling to room temperature, washing with chloroform and diethyl ether, and drying, and is denoted as ILMCM-41 (Scheme 1).

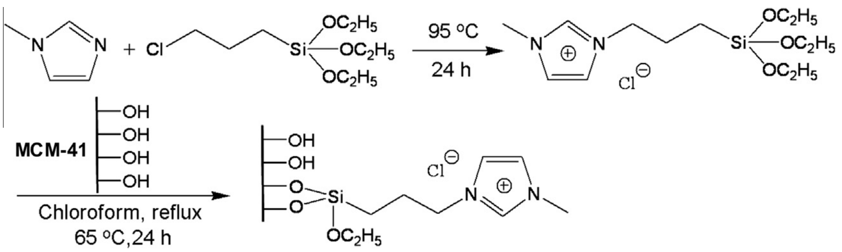
2.4. Synthesis of supported catalysis

ILMCM-41 supported phosphomolybdic acid catalyst was prepared using the following method: 1 g of ILMCM-41 was dispersed into 50 mL of deionized water, followed by dripping the aqueous phosphomolybdic acid solution into the ILMCM-41 solution until the proper loading was achieved (10–40 wt.%), $AgNO_3$ is used to test the existence of Cl^-. The PMo/ILMCM-41 catalyst was achieved with the washed solid being dried at 100 °C for 12 h.

The PMo/MCM-41 catalyst was prepared through impregnation. Briefly, an aqueous solution of phosphomolybdic acid was mixed with 1 g of MCM-41 under constant stirring, and held for 8 h at room temperature. A product containing 30 wt.% phosphomolybdic acid was obtained after drying at 100 °C for 4 h and calcination at 300 °C for 5 h.

2.5. A typical procedure for the selective oxidation of styrene to 1,2-epoxyethylbenzene

In a typical styrene oxidation, hydrogen peroxide and styrene were added to a three-neck flask, which is then heated to the reaction temperature in an oil bath. The catalyst was added into the flask to obtain a suspension to start the oxidation reaction. Liquid samples were taken to determine the concentration variation of the 1,2-epoxyethylbenzene. The feed and products were analyzed on an Agilent-6890 plus gas chromatograph equipped with an FID using an HP-5 capillary column. The oxidation products of styrene were identified by means of LC–MS (HP1100LC/MSD).



Scheme 1. Preparation of ionic liquid-modified MCM-41.