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Enhanced catalytic performances by surface silylation of Cu(II) Schiff base-containing SBA-15 in epoxidation of styrene with H_2O_2

Ying Yang, Jingqi Guan, Pengpeng Qiu, Qiubin Kan *

College of Chemistry, Jilin University, Jiefang Road 2519, Changchun 130023, Jilin, PR China

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ABSTRACT

Schiff base functionalized SBA-15 mesoporous materials were synthesized by post-grafting of salicylaldehyde onto silylated and non-silylated amino-modified SBA-15 and followed by the introduction of Cu(II) ions via a ligand exchange reaction. Both hybrid materials prepared were characterized by XRD, FT-IR, UV–vis spectroscopy, N_2 adsorption/desorption, TG/DTA and ICP-AES techniques and comparatively examined as catalysts in epoxidation of styrene with 30 wt.% aqueous hydrogen peroxide as oxidant. It was found that the silylated material was more active and selective to styrene oxide than the non-silylated one in CH_3CN. The considerably improved activity (86.1%) and styrene oxide selectivity (95.2%) were achieved after 30 min when adding sodium hydroxide to maintain a pH of 7.5–8.0 in reaction medium. Moreover, the silylated catalyst showed good recoverability and relatively high stability against leaching of active copper species. These superior effects were attributed to the high hydrophobic character of the solid surface produced by the silanol neutralization.

1. Introduction

The epoxidation of olefins is of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1,2]. Previously, much attention has been drawn on developing novel catalytic processes based on titanosilicalite (TS-1) and Al-free Ti-beta catalysts [3]. Along with the Ti-containing mesoporous molecular sieves (i.e. Ti-MCM-41, Ti-MCM-48), these Ti-based catalysts are active for aqueous H_2O_2 oxidation of alkanes and alkenes [4,5]. However, the yields of epoxide are relatively low as a consequence of the lower H_2O_2 selectivities. It is assumed that the low epoxide selectivity and severe deactivation of Ti-containing catalysts are caused by the poison of catalytically active Ti species by H_2O adsorbed on the surface with relatively high hydrophilicity derived from a large number of silanol groups. Therefore, a lot of researches have been pursued into the trimethylsilylation of silica materials to increase the surface hydrophobicity. For example, Cagnoli et al. [6] reported that silylation of Ti-MCM-41 could improve the catalytic activity and selectivity in the limonene oxidation with H_2O_2. Tatsumi and coworkers [7] also pointed out that the silylated Ti-MCM-41 (48) showed remarkably higher catalytic activity in the oxidation of substrates with various molecule sizes (from C_6 to C_{12}) with H_2O_2 compared to non-silylated samples. Recently, silylation of metal complex-containing mesoporous materials also seems to be effective. In this field, worthy of special mention is the work of Jia et al. [8] silylating oxodiperoxo molybdenum complex-containing MCM-41 by trimethylsilyl chlorine (TMCS) and the catalytic activity was improved in cyclooctene epoxidation with TBHP.

Schiff base transition metal complexes have been extensively studied because of their remarkable electronic tunability and potential use as catalysts in a wide range of epoxidation reactions. However, most heterogenized metal Schiff base complexes showed low selectivity to epoxides and poor stability in liquid-phase oxidations [9,10]. A typical e.g. is Cu(II) Schiff base-containing MCM-41 (Cu-MCM-41) material, which was highly efficient for epoxidation of olefins, reaching 97% conversion of styrene and 86% yield of epoxide after 24 h with TBHP. However, only 34% conversion and 6% yield were reached when using H_2O_2 as the oxidant and rapid deactivation was observed in recycled runs [11]. The question is the same as the originally stated Ti-containing catalyst in epoxidation of olefins by H_2O_2. Thus, some strategies, such as tunability of the electronic properties of Schiff bases [12], using TBHP or O_2 instead of H_2O_2 in reaction medium [8,13], have been adopted to improve epoxide selectivity and catalyst stability. As far as we know, there has been no report on improving the catalytic performance of heterogenized metal Schiff base complex by surface silylation of support in epoxidation of styrene with H_2O_2.

Herein, we first report a Cu(II) Schiff base-containing silylated SBA-15 hybrid material synthesized by a post-grafting route.

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* Corresponding author. Tel.: +86 431 88499140; fax: +86 431 88499140.
E-mail address: qkan@mail.jlu.edu.cn (Q. Kan).

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Considering the required more severe conditions and, in the case of chloride, resulted in loss of copper from the complex, the silylation procedure was carried out by hexamethyldisilazane (HMDS) instead of commonly used TMCS. Both the silylated and the non-silylated catalysts were examined as catalysts in epoxidation of styrene with 30 wt.% aqueous hydrogen peroxide as oxidant.

2. Experimental

2.1. Silylated Cu-SBA-15 synthesis

The mesoporous support SBA-15 (1.0 g), prepared by a literature method [14], was activated by heating at 120 °C for 2 h and used to prepare amino-functionalized SBA-15 using a procedure described in our early work [15]. Analysis found for APS-SBA-15: C, 5.37; H, 1.41; N, 1.39. FTIR (KBr pellets, cm^{-1}): 1510 (NH_2), 1000–1130 (Si–O–Si), 960 (Si–OH), 687 (N–H).

Silylated APS-SBA-15 was prepared by a post-grafting method. In a typical synthesis, 4.0 g of HMDS was added dropwise to a suspension of 2.0 g APS-SBA-15 in anhydrous hexane. The mixture was stirred under N_2 atmosphere at room temperature for 24 h. The resulting solid was filtered, washed with hexane and dried under vacuum. This solid (0.3 g) was then refluxed with salicylaldehyde (6.9 mmol, 0.84 g) in ethanol under N_2 atmosphere at 80 °C for 3 h. The resulting yellowish solid was then collected by filtration and was dried under vacuum. Finally, the silylated Cu-SBA-15 was prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ (0.17 mmol) in methanol and by stirring the above said yellowish solid (0.122 g) in suspension at room temperature for 12 h. The green solid thus formed during stirring was filtered, washed with methanol using Soxhlet and dried under vacuum (Scheme 1). ICP-AES result showed copper content in silylated Cu-SBA-15 is ca. 0.122 mmol/g.

2.2. Cu-SBA-15 synthesis

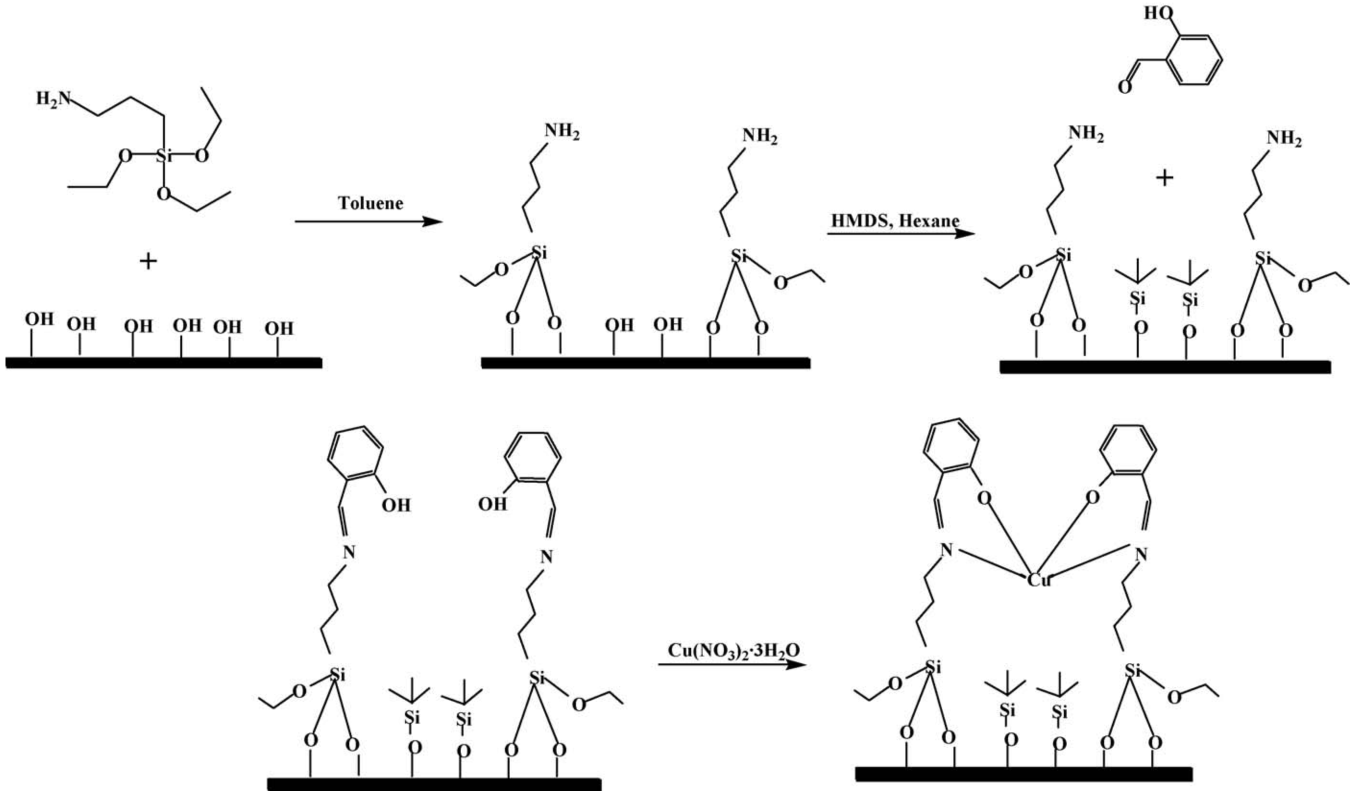
Cu-SBA-15 was synthesized according to the procedure reported by the literature [11] for comparison. ICP-AES result showed copper content in Cu-SBA-15 catalyst is ca. 0.130 mmol/g.

2.3. Characterization

Powder XRD was collected with a Rigaku X-ray diffractometer with nickel filtered CuKα radiation (λ = 1.5418 Å). The samples were scanned in the range 2θ = 0.4–5.0° and in steps of 2°/min. N_2 adsorption/desorption isotherms were recorded at −196 °C with a Micromeritics ASAP 2020. Before measurements, the samples were outgassed at 120 °C for 12 h. The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) method and the pore size distributions were measured by using Barrett–Joyner–Halenda (BJH) analyse from the desorption branch of the isotherms. The infrared spectra (IR) of samples were recorded in KBr disks using a NICOLET impact 410 spectrometer. UV–vis spectra were recorded on a Perkin Elmer UV-vis spectrophotometer Lambda 20 using barium sulfate as the standard. TG/DTA was carried out on Shimadzu DTG-60 instrument. Microanalyses for C, H, N were performed at the Perkin Elmer 2400. Metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a Perkin Elmer emission spectrometer.

2.4. Catalytic reactions

The catalytic reactions were carried out in a glass batch reactor supplied with a magnetic stirrer and backflow condenser. Typically, 5 mmol of styrene along with 5 ml of solvent (CH_3CN) and 25 mg of catalyst were added to the flask. The reaction was started by adding 30% H_2O_2 (15 mmol, 3 equiv.) at reaction



Scheme 1. Preparation of Cu(II) Schiff base complex on silylated SBA-15.