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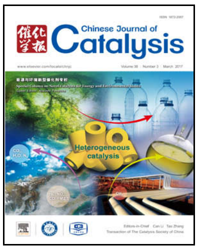

Article

One-pot synthesis of ordered mesoporous Cu-KIT-6 and its improved catalytic behavior for the epoxidation of styrene: Effects of the pH value of the initial gel

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ABSTRACT

The heterogeneously copper-catalyzed oxidative cleavage of styrene was studied using copper-doped mesoporous KIT-6 (Cu-KIT-6$_x$) prepared via pH adjustment (where x is the pH: 1.43, 2.27, 3.78, 3.97, 4.24 or 6.62). Variations in the catalyst structure and morphology with pH values were characterized by X-ray power diffraction, nitrogen adsorption-desorption analysis, transmission electron microscopy and X-ray photoelectron spectroscopy. As the pH value applied during the initial synthesis, the resulting Cu-KIT-6$_x$ exhibited different structural, textural and surface characteristics, especially in terms of specific copper species and copper content. At a pH value of 3.78, approximately 4.6 wt% copper(II) was successfully incorporated into the framework of the initial KIT-6, in the form of –Cu–O–Si– groups. The catalytic performance of each catalyst was evaluated by following the epoxidation of styrene, employing *tert*-butyl hydroperoxide as the oxidant and CH_3CN as the solvent. A significant styrene conversion of 43.5% with 86.6% selectivity for the desired styrene epoxide was obtained over the Cu-KIT-6$_{3.78}$. A higher Cu content, an ordered cubic *Ia*3*d* mesoporous architecture and various specific textural characteristics all combined to endow the Cu-KIT-6$_{3.78}$ with high catalytic activity and good stability.

1. Introduction

The epoxidation of styrene is an extremely important industrial process, because the resulting styrene oxide (SO) is used in the manufacture of epoxy resins, paints, surfactants and pharmaceuticals. Despite this, the electrophilic addition of an oxidant to the styrene double bond is one of the most challenging steps in oxidation catalysis. Over the past several decades, considerable efforts has been devoted to designing appropriate and effective catalysts for the epoxidation of styrene [1]. Homogeneous catalysts, including polyoxometalate salts [2] and transition metals coordinated with porphyrins [3,4] or salen [5], have been used to improve the conversion of olefins. However, these catalysts are difficult to separate from the product mixture and impossible to recycle. Thus, the immobilization of catalytically active metals on alumina [6], zeolites [7] or silica [8,9] as heterogeneous catalysts would be useful.

KIT-6, developed by the Korea Advanced Institute of Science

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and Technology, is a cubic *Ia*3*d* mesoporous silica with a bi-continuous structure, tunable pores, thick pore walls and high hydrothermal stability [10,11]. Unlike the two dimensional (2D) pore arrays in MCM-41 and SBA-15, KIT-6 incorporates unique 3D interpenetrating channels that facilitate the direct and open access of guest molecules without pore blockage. Thus, KIT-6 shows significant promise as a support for large molecule conversion reactions. Recently, numerous transition metals (such as V [12], Fe [13], Ni [14] and Ti [15]) have been anchored on KIT-6 to catalyze organic reactions, including styrene epoxidation, methylcyclopentane conversion, fuel desulfurization and photocatalytic reduction.

So-called direct synthesis [16–19] is the main route to incorporating heteroatoms into the framework of mesoporous silicas. This process is time-efficient and simple, although only a small fraction of the metal in the initial synthetic system can be incorporated into the template matrix without reducing the structural periodicity. This is because the metal precursors are typically highly soluble and are primarily present in the synthesis solution as cations under highly acidic conditions, which reduces the formation of –O–M–O–Si–O– bonds (where M is the metal) during the condensation process. Several strategies have been developed to mitigate the difficulties associated with heteroatom grafting in acidic media. Xiao and co-workers [20] reported that Al^{3+} and Ti^{4+} can be substituted into SBA-15 at a pH of 7.5 using their so-called pH adjustment method, and that the finished products display highly ordered mesopores with large surface areas and uniform pore diameter distributions. Subsequently, Fe- [21], Cr- [22], Sn- [23], Ag- [24] and Ni-loaded [25] mesoporous SBA-15 materials were synthesized at pH values above 2. Inspired by this method, some groups incorporated Ga [26] and Cu [27] into silica frameworks in dilute acids. These heteroatom-containing mesoporous silicas were found to be effective catalysts for styrene oxidation. As an example, La-doped KIT-6 (with a La in Si mole fraction of 0.02) synthesized at a pH of 8 yielded a styrene conversion of 20.6% and a selectivity for benzaldehyde of 74.6% during the oxidation of styrene with hydrogen peroxide [28]. Similarly, our research group determined an optimal pH value of 7.5 for the introduction of Co into the framework of SBA-15, resulting in a styrene conversion of 22% and a benzaldehyde selectivity of 92% in the same reaction process [29].

Copper oxide, a simple and inexpensive transition metal oxide, exhibits excellent catalytic activity for styrene epoxidation due to its high selectivity for SO [30–33]. However, there have been few reports of the addition of Cu to KIT-6 by the pH adjustment method, and the effects of pH on the associated variations in structure and morphology remain unknown. A better understanding of the impact of structural properties on catalytic applications would enable the design of more efficient Cu-KIT-6 catalysts. In the present work, mesoporous Cu-KIT-6 materials were prepared using the pH adjustment method (with pH values from 1.43 to 6.62). The results demonstrate that the formation of different Cu species in the KIT-6 is very sensitive to the pH value. A detailed characterization and discussion of the varying catalytic behavior during the epoxidation of styrene are provided herein.

2. Experimental

2.1. Materials

Pluronic P123 (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer, $EO_{20}PO_{70}EO_{20}$, molecular weight = 5800, Aldrich) was used as a structure-directing agent. $Cu(NO_3)_2·2.5H_2O$ (Alfa Aesar) was employed as the Cu precursor. *n*-Butanol (*n*-BuOH), ethyl silicate (TEOS), concentrated HCl (37.0 wt%), NaOH and CH_3CN used in the synthesis as well as in catalytic experiments were all analytical reagent grade. Styrene (99.5%) and *tert*-butyl hydroperoxide (TBHP, 70 wt% aqueous solution) were supplied by Alfa Aesar. All chemicals were used as received without further purification.

2.2. Preparation of Cu-KIT-6 mesoporous materials

Ordered mesoporous Cu-KIT-6 was synthesized via the pH-adjustment method. Briefly, 2.50 g of Pluronic P123 was added to 90 g of distilled water and 4.9 g of HCl with stirring at room temperature. After the P123 was completely dissolved, 2.5 g of *n*-BuOH was added to the solution and the mixture was allowed to stir for 1 h. Subsequently, 5.4 g of TEOS was added slowly in a dropwise manner and the solution was stirred for another 2 h, followed by the dropwise addition of a defined amount of NaOH solution (10 mol/L) to adjust the pH of the mixture (Table 1). Following this, 1.45 g of solid $Cu(NO_3)_2·2.5H_2O$ was added to the solution and the resulting light green mixture was stirred vigorously for 22 h. In the final step, the mixture was transferred into a polypropylene bottle that was then sealed and heated for 24 h at 100 °C under static conditions. The TEOS:P123:HCl:H_2O:BuOH:Cu molar ratio in the synthesis gel mixture was 1:0.017:1.93:193:1.31:0.25. The final solid material was filtered off, washed several times with distilled water and dried at 100 °C for 6 h. Calcination was carried out at 550 °C in air with a ramp rate of 2 °C/min and an isothermal period of 6 h to obtain a template-free mesoporous catalyst. The samples are denoted herein as Cu-KIT-6_x, where x indicates the pH value of the synthesis mixture. As a control, a Cu-KIT-6 catalyst was prepared without pH adjustment, following the above procedure, and a cubic mesoporous KIT-6 support was synthesized according to a standard procedure [10].

2.3. Catalyst characterization

The mesoporous structures and crystalline phases of the catalysts were characterized by X-ray powder diffraction (XRD) using a D8 Advance diffractometer (Bruker) fitted with a LynxEye detector. Cu K_α radiation (λ = 0.154 nm) was used and the X-ray tube was operated at 40 kV and 40 mA. The small-angle XRD patterns were acquired between 0.6° and 3° with a step width of 0.02° at a count time of 0.4 s per step, and

Table 1
Dosage of 10 mol/L NaOH for the desired pH values.

V/mL	4.5	4.8	4.9	5.2	5.5	6.0
pH	1.43	2.27	3.78	3.97	4.24	6.62