Solid State Sciences 13 (2011) 2105–2112

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Tailoring the nano-channel of ZrO_2/SBA-15 mesoporous materials for efficiently trapping and degradation volatile nitrosamines

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ARTICLE INFO

Article history:
Received 5 April 2011
Received in revised form
3 June 2011
Accepted 4 August 2011
Available online 11 August 2011

Keywords:
Mesoporous materials
Functionalization
Zirconia
Nitrosamine
Degradation

ABSTRACT

This article reports a bifunctionalized mesoporous ZrO_2/SBA-15 materials prepared through a simplified one-pot synthesis, in which the aged sample was evaporated with mother solution under the self-adjusted pH condition. The results of low-angle XRD, HRTEM, nitrogen adsorption-desorption, in-situ ^1H NMR and NH_3-TPD tests confirmed the well-ordered hexagonal structure and large pore size of these composites along with the newly formed acidity and basicity. Temperature programmed surface reaction (TPSR) was employed to assess the catalytic function of ZrO_2/SBA-15 composites on the degradation of carcinogenic volatile nitrosamines such as *N*-nitrosopyrrolidine (NPYR). Due to the special interaction between the N–NO group of nitrosamines and the acidic site of mesoporous composite, NPYR could be efficiently trapped and then catalytic degraded at lower temperature, which enables this functional composite to be a new candidate for environment protection.

1. Introduction

SBA-15 mesoporous silica has attracted much attention due to its tunable mono-dimension ordered structure, high surface area and large pore size [1]. However, lack of adequacy active sites limited its application therefore many efforts have been devoted to functionalize this material, for instance, incorporating heteroatom such as Al, Ti and Zr into the framework of SBA-15 by "post grafting" or "direct synthesis" [2–5]. Among these heteroatom-containing composites, Zr-incorporated silica samples has been proved possessing strong acidic and redox sites generated from different coordination states of adjacent cations [6,7], and its catalytic activity is highly dependent on the amount of loaded zirconium [8,9], so that many innovative strategies are tried to synthesize the mesoporous silica with higher zirconium loading amount. Wong et al had prepared Zr-substituted SBA-15 by using high Zr/Si molar ratio of 1.0 that was correspond to 49.8 wt% Zr in the initial gel, however, the zirconium content in final solid sample was 4.8 wt% [8]. The lower doping capacity of zirconium in SBA-15 was attributed to the strong acidic synthesis system, in which the zirconium precursors only existed in the ionic form and most of them were leached in following filter and wash steps. Consequently, some low acidic synthesis strategies, say, nonuse of mineral acid in initial gel or "pH-adjusting" method have been tried, by which higher content of zirconium was doped in the mesoporous silica [10,11]. However, the pore volume of resulting Zr-substituted mesoporous material was usually smaller than that of parent SBA-15 due to the incomplete condensation of silica wall or the pore blockage. Therefore, it is necessary to seek new method fabricating the high Zr-incorporated SBA-15 mesoporous material with original large pore volume and high surface area.

Herein, we prepared a series of Zr-incorporated SBA-15 mesoporous materials with high zirconia content by using $ZrOCl_2$ as precursor and nonionic surfactant P123 (EO20PO70EO20) as template via a synthesis route of in-situ condensation combined thermal evaporation. In this process, the initial strong acidity of system ensures complete hydrolysis of silica precursor, and evaporation of the aged sample in mother solution can adjust the acidity of synthesis system by gradual removal of dissociative acid, which facilitate the incorporation of zirconium into framework of SBA-15 and result in the higher zirconium content in final samples. To evaluate the acidity and basicity of resulting composites, TPD (temperature program desorption) of NH_3 and CO_2, along with 1H magic-angle-spinning (MAS) NMR techniques were employed.

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doi:10.1016/j.solidstatesciences.2011.08.007

N-nitrosopyrrolidine (NPYR), one of the volatile nitrosamines, was selected as the probe to assess the adsorptive and catalytic functions of the ZrO_2/SBA-15 materials.

Volatile nitrosamines are well known to be carcinogens, but it is difficult to eliminate them because of their volatility and trace content in environment [12,13]. Zeolites can selectively adsorb volatile nitrosamines [14–17], but their micropores resulted in large diffusion resistance of nitrosamine molecules in channels. Consequently, mesoporous molecular sieves such as SBA-15 become the candidates of adsorbents and thus their modification is necessary as aforementioned. To elevate the efficiency of SBA-15 in removing nitrosamines, new attempt is tried here to establish a suitable chemical micro-environment in the channel of mesoporous silica, in which both acidic and basic sites exist to have synergy in adsorbing nitrosamines that also possess both weak acidity and basicity [18]. As an amphoteric modifier, zirconia was selected to prepare a functionalized mesoporous SBA-15 for elimination of nitrosamines.

2. Experimental

2.1. Samples preparation

NPYR and zirconyl chloride were the products of Sigma. Triblock copolymer P123 (EO20PO70EO20) was purchased from Aldrich. A typical synthesis of mesoporous sample xZrO2/SBA-15, where x stands for the weigh percent of ZrO2 in samples, was performed as follows: two grams of P123 along with a calculated amount of zirconyl chloride were dissolved in 75 g of 1.6 M HCl, then 4.25 g of tetraethyl orthosilicate (TEOS) was added under stirring at 313 K. The molar ratio of TEOS: P123: $ZrOCl_2 \cdot 8H_2O$: HCl: H_2O was 1: 0.02: y: 6: 192, where y represents the molar ratios of $ZrOCl_2$ $8H_2O$ to TEOS and it is 0.025, 0.084 and 0.159 for the preparation of samples containing ZrO_2 of 5%, 15% and 25% in total oxides, respectively. The mixture was stirred at 313 K for 24 h and then hydrothermally treated at 373 K for another 24 h under static condition. Finally, the slurry was evaporated with stirring at 353 K until it was dried, omitting the conventional pH-adjusting and thermal re-treatment along with filtering and washing [10], finally the solid was calcined at 823 K for 6 h to remove the template.

2.2. Characterization

The XRD patterns of samples were acquired on an ARL XTRA diffractometer using Cu Kα radiation in the range of 2-theta from 0.5° to 8° or from 10° to 70°, respectively. UV–Vis Diffuse reflectance (DR) spectra were recorded on an UV-2401 (Shimadzu) spectrophotometer adapted with a praying mantis accessory using $BaSO_4$ as standard. In the test of transmission electron microscopes (TEM), the sample was dispersed in ethanol and placed on holey copper grids for measurement.

The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometritics ASAP2000 system. The pore size distribution (PSD) curves were calculated from the analysis of the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm.

The experimental processes of NH_3-TPD, CO_2-TPD experiments and *In situ* FTIR measurement were described in the supporting information. Experiment of gaseous adsorption and Temperature programmed surface reaction (TPSR) test of NPYR was refer to the literature [16,19].

The ^1H magic-angle-spinning (MAS) NMR spectra of samples were recorded with a Bruker MSL400 spectrometer operating at frequencies of 400.13 and 104.26 MHz, respectively. A Bruker MAS probe head was used with a zirconia rotor of 4 mm in diameter and measured with an ordinary single pulse sequence. All measurements were performed at room temperature with a spinning rate of 10 kHz. The flip angle of the pulse and the recycle delay were about $\pi/4$ and 1 s, respectively, for ^1H single. The ^1H chemical shifts were expressed with respect to neat tetramethylsilane (TMS).

3. Results and discussion

3.1. The textural structure of the functionalized materials

Fig. 1 illustrates the small-angle and wide–angle XRD patterns of Zr-incorporated SBA-15 materials. The samples doped with low amount of zirconium exhibited the well resolved diffraction peaks identical to that of SBA-15, indexing to (1 0 0), (1 1 0), and (2 0 0) diffractions characteristic of the typical two dimensional hexagonal pore ordering of *p*6 *mm* space group. This indicates the existence of highly ordered mesoporous hexagonal structure in these functionalized materials. Moreover, 5ZrO_2/SBA-15 composite had a slightly stronger peak of (1 0 0) than SBA-15, but 25ZrO_2/SBA-15 had a weaker peak (1 0 0) than the parent and the peaks of (1 1 0), (2 0 0) absent. Adding small amount of Zr^{4+} into the initial synthetic system increases the long range ordered structure of mesoporous material, owing to the stabilization of Zr on the framework of SBA-15 [10], but overfull Zr^{4+} is harmful for the long range order inversely. Meanwhile the peak (100) on the XRD patterns of Zr-incorporated samples shifted to lower angle, and its d value rose from 10.02 (SBA-15), 10.17 (5ZrO_2/SBA-15), 10.47 (15ZrO_2/SBA-15)

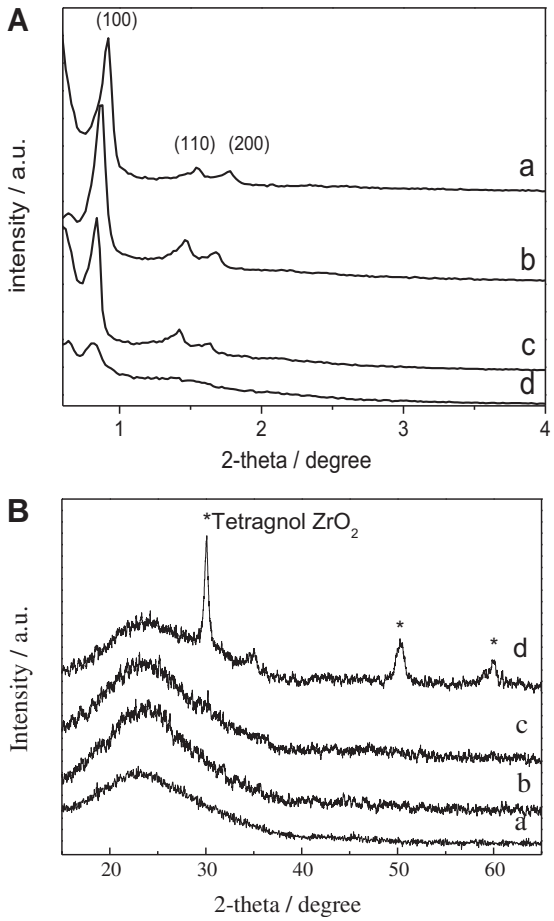

Fig. 1. (A) Low-angle and (B) wide–angle XRD patterns of (a) SBA-15 (b) 5ZrO_2/SBA-15 (c) 15ZrO_2/SBA-15 (d) 25ZrO_2/SBA-15 samples.