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Direct synthesis of thiol-ligands-functionalized SBA-15: Effect of 3-mercaptopropyltrimethoxysilane concentration on pore structure

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Abstract

Mesoporous thiol-functionalized SBA-15 silicas have been directly synthesized by co-condensation of tetraethyl orthosilicate and 3-mercaptopropyltrimethoxysilane with triblock copolymer poly(ethylene glycol)-B-poly(propylene glycol)-B-Poly(ethylene glycol) as structure-directing agent under hydrothermal condition. Mesoporous structure was obtained after the surfactant removal by Soxhlet ethanol extraction. These materials have been characterized by means of powder X-ray diffraction, nitrogen sorption, transmission electron microscopy, thermogravimetry analysis, elemental analysis and solid state ^{29}Si nuclear magnetic resonance. The effect of 3-mercaptopropyltrimethoxysilane concentration in the initial mixture on the pore structure of functionalized SBA-15, including pore ordering, surface area, pore size and pore volume, is investigated in detail. In order to functionalize the SBA-15 silicas without a significant change of pore structure, the molar concentration of 3-mercaptopropyltrimethoxysilane should be limited to less than 20%.

Keywords: Mesoporous; Thiol groups; Functionalized SBA-15; Pore ordering; Pore structure

1. Introduction

Ordered mesoporous silica-based materials have attracted much attention due to their large surface area and well-defined pore size easily tuned by choosing different supramolecular surfactants as structure-directing agents. These materials may find promising application in catalysis, sensing and separation, as well as environmental remediation. Recently, considerable efforts have been devoted on the application of mesoporous silicas as adsorbents to remove toxic heavy metal cations or organic pollutants from wastewater [1–5]. Thiol ligands, acting as biting sites for heavy metal cations, have been incorporated into mesoporous silica by either postsynthesis grafting or co-condensation of functional organosilane with tetraethyl orthosilicate (TEOS) [6–9]. It is proved that thiolated mesoprous silicas exhibit high complexation affinity to mercury and other metal cations. Liu et al. reported that the mercury concentration in aqueous solution could be reduced by thiol monolayers on MCM-41 to below U.S. Environmental Protection Agency elemental limits for hazardous wastes [6]. Similar results for functionalized HMS, MSU have also been achieved by Mercier et al. [1,7,10,11] and Corrius et al. [12]. In contrast to the extensive investigation on functionalized HMS, MSU and MCM-41, less attention has been paid, to the best of our knowledge, to the surface modification of SBA-15 with nonionic surfactant as template, although SBA-15 is more hydrothermally stable because of its more regular structure and much thicker pore wall. Among the limited literature related to surface modification of SBA-15 [8,9,13], most of them have concentrated on the interaction between the heavy metal ions and the functional groups. For example, Liu et al. functionalized SBA-15 with thiol and amino groups by postsynthesis route and tested them for Hg^{2+}, Zn^{2+} and other metal cations adsorption [9]. The thiol-grafted SBA-15 exhibited high complexation affinity to mercury, while the aminated SBA-15 showed a high binding ability to copper,

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zinc, chromium, and nickel cations. Unfortunately, little attention has been focused on the parameters that may affect the pore structure of SBA-15 during direct surface modification. In the present paper, thiol-ligands-functionalized SBA-15 was prepared by co-condensation of 3-mercaptopropyltrimethoxysilane (MPTMS) and TEOS under suitable condition. The evolution of the pore structure with the concentration of functional organosilane in initial mixture was investigated in detail by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption, thermogravimetry (TGA) and solid state ^{29}Si nuclear magnetic resonance (NMR).

2. Experimental

2.1. Materials synthesis

The synthesis of SBA-15 material was performed according to the following procedure with a molar ratio of

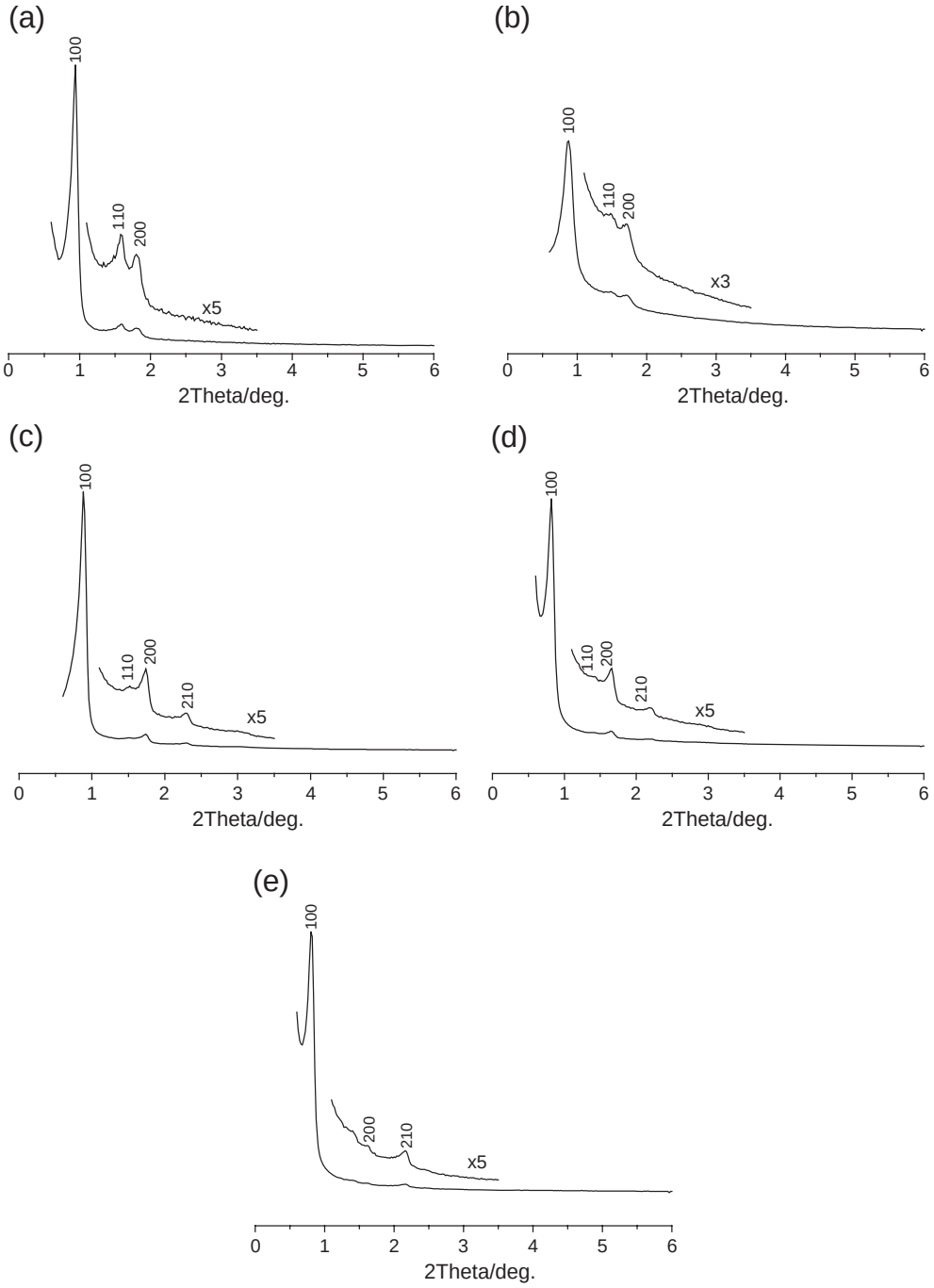

Fig. 1. XRD spectra of the thiol-functionalized SBA-15 with different molar ratios of MPTMS/(MPTMS+TEOS): (a) 0%, (b) 5%, (c) 10%, (d) 15%, and (e) 20%. The region where (110), (200) and (210) peaks appear is scaled 3 or 5 times.