

Effect of β -cyclodextrin Attendance on Hexagonal Ordering of MCM-41 Silicas

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(Received 01 July 2014; published online 29 August 2014)

Hydrothermal sol-gel synthesis of hexagonally ordered silicas using a hybrid template system is reported. Hybrid template system was made from ionic surfactant (cetyltrimethylammonium bromide or decyltrimethylammonium bromide) and supramolecular porogen β -cyclodextrin. Tetraethylorthosilicate or its blend with 3-(chloropropyl)triethoxysilane were used as matrix precursors. Synthesized silicas were characterized by IR spectroscopy, X-ray diffraction techniques as well as transmission electron microscopy. It was shown that the hexagonal structure of MCM-41 is not changed despite the addition of β -cyclodextrin.

Keywords: Ordered silica materials, MCM-41, β -Cyclodextrin, Hydrothermal sol-gel synthesis, Template.

PACS numbers: 81.20.Fw, 82.80.Gk, 81.70.Gk

1. INTRODUCTION

Nanomaterials have invariable interest for researchers so far as they possess unique physical and chemical properties, such as the specific optical, electrical, thermal, magnetic, catalysis and adsorption characteristics [1]. Nanoscale effect of porous materials is determined by pores with size in the nanometer range. Among the variety of nanoporous materials, the family of ordered materials gains growing success in scientific works [2]. After the first reports, introducing the M41S family of ordered mesoporous silicas at the beginning of the 1990s, several additional mesoporous materials have been discovered, such as FSM-16, SBA-1,2,3, MSU-1, KIT-1, SBA-11,12,15, and SNU-2 [3]. MCM-41 is the most widely studied M41S material. It has high specific surface area up to 1200 m²/g and well defined uniform pores (diameters between 1,5 and 20 nm), which are hexagonally ordered. MCM-41 materials can be prepared using a variety of surfactants, including quaternary alkylammonium ions [2]. By changing the synthesis conditions and source of reaction materials, it is possible to alter the structure and characteristic of obtained product and therefore create new types of M41S substances. In particular, it was reported the possibility of cyclodextrins (CDs) utilization as template (porogen) in the synthesis of porous substances with regular structure (so-called, nanocasting) [4-9]. Here, "worm-type" pore system is formed with pore sizes exactly resembling the CD diameters (1,5 ~ 2 nm) [4-5, 8]. Amphiphilic nature of CDs and their high water solubility [7] are defining properties for using CDs as porogens.

The purpose of our work was to make MCM-41 porous silicas with ordered pores templated by hybrid porogen system consisting of ionic surfactant and CD. Synthesized silicas were characterized by IR spectroscopy, X-ray diffraction techniques as well as transmission electron microscopy.

2. EXPERIMENTAL

2.1 Synthesis

Silica materials were prepared by basic hydrolysis (NH₄OH) of tetraethylorthosilicate (TEOS) or TEOS/3-(chloropropyl)triethoxysilane (CPTEOS) blend in ethanol-water system in the presence of template. Two series of silicas were synthesized. The first was obtained with cetyltrimethylammonium bromide (CTAB) as template, and the second series was prepared using decyltrimethylammonium bromide (DTAB) as template. In both cases, β -cyclodextrin (β -CD) was used as supramolecular constituent in hybrid template system (ionic surfactant - CTAB or DTAB and supramolecular compound). In brief, ionic surfactant and β -CD were dissolved in ethanol-water solution with stirring at room temperature. Then, appropriate quantity of NH₄OH was added followed by dropwise addition of silica source. The reaction mixture was agitated on magnetic stirrer about 2 h. In order to complete the condensation process, the hydrothermal treatment (HTT) in autoclave at 100 °C during 24 h was carried out. Obtained silicas were washed by small quantities of water and dried at ambient temperature. Then templates were removed by extraction in acid-ethanol solution.

2.2 Analysis

FTIR spectra were collected on a Thermo Nicolet NEXUS FT-IR spectrophotometer (Nicolet, USA). The transmission spectra were registered in the range from 4000 to 400 cm⁻¹ for solid pellets.

TEM experiments were conducted on a JEM JEOL 1230 electron microscope operated at 100kV. Images were obtained with digital camera Gatan. The samples (0,05 g) for TEM measurements were suspended in ethanol (4 ml) and ultrasonically treated for 3 min (ultrasound power 60 W). Obtained suspensions (50 μ L) were supported onto formvar film on a Cu grid, followed by drying at ambient conditions.

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Powder X-ray diffraction patterns were measured on a DRON-4-02 diffractometer (Burevestnik, Russia) equipped with anode using nickel filtered CuK α radiation ($\lambda = 1,54178 \text{ \AA}$).

3. RESULTS AND DISCUSSIONS

β -CD is cyclic oligosaccharide consisting of seven glucopyranose units that are joined together by an $\alpha(1\rightarrow4)$ linkage [10]. It can form inclusion complexes with various organic compounds owing to the molecule construction. Surfactants and β -CD are known to form inclusion complexes in aqueous solutions in which the hydrophobic chain of the surfactant resides in the hydrophobic environment of the interior cavity of cyclodextrin molecule [11]. In the beginning of synthesis micelles of CTAB (or DTAB) and β -CD are formed around which the inorganic precursor can condense. After a stirring period at a certain temperature to allow hydrolysis and pre-condensation of silica source, the temperature was raised and combined with hydrothermal treatment. The IR spectroscopy was applied to analyse synthesized MCM-41 materials. The silanol groups disposed on the silica surface and the presence of remaining water molecules produce the broad stretching band around $3600\text{--}3000 \text{ cm}^{-1}$, followed by a band around 1640 cm^{-1} , attributed to deformation vibration $\delta_{\text{O-H}}$. Functional silica materials with ordered structure were obtained by hydrolysis and polycondensation of TEOS and CPTEOS (silica named Cl-MCM-41). Indication of the presence of functional group on silica is the appearance of specific vibration band of valence vibrations at 2928 cm^{-1} and 2855 cm^{-1} as well as deformation vibrations at 1480 cm^{-1} and 1413 cm^{-1} of the C-H bonds. To control the template removal the band assignments of vibrations of the C-H bonds in the CH and CH₂ groups of template molecules were made. Thus, valence vibrations of the C-H bonds at 2928 cm^{-1} and 2855 cm^{-1} as well as deformation vibrations of the C-H bonds at 1480 cm^{-1} disappears in FTIR spectra of silica materials after template removal.

TEM is important technique to obtain direct structural information at nanometer scale resolution for porous materials. To visualize the ordered pore structure of obtained MCM-41 silicas TEM images were performed (Figure 1). The black strip and the white strip on Figure 1(a) correspond to the silica pore walls and the pores, respectively. As could be seen from the Figure 2(b) the pores are arranged in a honeycomb structure.

Hexagonally ordered structure of obtained silicas was also confirmed via X-ray diffraction analyses. Typically X-ray diffraction patterns of MCM-41 materials contain four main reflection lines at low angles ($2\theta < 10$), which indexed to (100), (110), (200) and (210) Bragg reflections [2]. The presence of the peaks in X-ray diffraction patterns of MCM-41 is not due to a regular periodic arrangement of atoms, but to regular array of pores with diameters in the small nanometer range.

X-ray patterns of ordered silicas, synthesized with using CTAB as template (Figure 2(a)) and DTAB as template ((Figure 2(b)) were obtained. Ordered silica synthesized with using hybrid template named as MCM-41 ^{β -CD}. It was shown that characteristic bands at (100), (110), (200) can be observed for all MCM-41 materials obtained with CTAB template. Then for MCM-41 materials made with DTAB template the

clearest is typical reflection lines at (100).

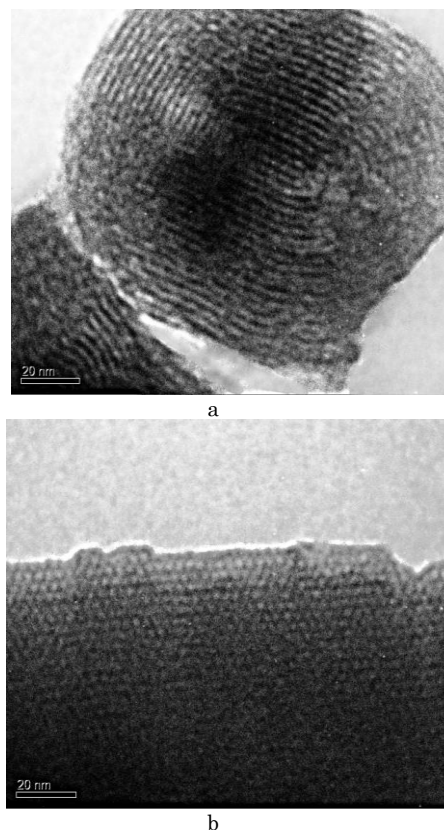


Fig. 1 – TEM images of obtained silicas.

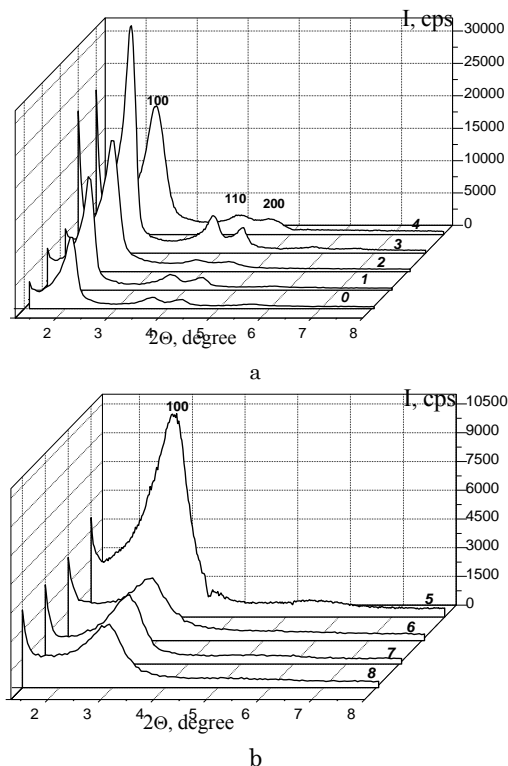


Fig. 2 – X-Ray patterns of ordered silicas obtained with using CTAB as template (a) (0 – MCM-41 (template not removed), 1 – MCM-41, 2 – Cl-MCM-41, 3 – MCM-41 ^{β -CD}, 4 – Cl-MCM-41 ^{β -CD}), and DTAB as template (b) (5 – MCM-41, 6 – Cl-MCM-41, 7 – MCM-41 ^{β -CD}, 8 – Cl-MCM-41 ^{β -CD}).

4. CONCLUSION

Hexagonally ordered silicas were synthesized as a result of sol-gel condensation of structure forming alkoxysilanes TEOS or TEOS/CPTEOS in water-ethanol-ammonia system using hybrid template. The band assignments of FTIR spectra confirm the chemical structure of MCM-41 silicas and complete removing of template. Structural information for obtained ordered silicas was combined by the use of X-ray and

TEM analyses. It was shown, that attendance of small quantities of β -cyclodextrin (5% of the quantity of ionic surfactant in reaction vessel) as additional porogen does not affected on hexagonal structure forming under sol-gel synthesis of ordered silicas. Synthesised ordered siliceous materials could be considered for specific applications in areas as diverse as catalysis, separation, sorption, drug delivery etc.

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