ELSEVIER

Current Opinion in Colloid & Interface Science 10 (2005) 94 – 101

Current Opinion in COLLOID and INTERFACE SCIENCE

www.elsevier.com/locate/cocis

Ordered mesoporous silica-based materials templated from fluorocarbon–hydrocarbon surfactant mixtures and semi-fluorinated surfactants

Feng-Shou Xiao *

College of Chemistry and State Key Laboratory for Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China

Available online 22 June 2005

Abstract

Ordered mesoporous silica-based materials with various mesostructures are generally synthesized from hydrocarbon surfactants. In this review, I have briefly summarized recent developments of syntheses of ordered mesoporous silica-based materials templated from fluorocarbon–hydrocarbon surfactant mixtures and semi-fluorinated surfactants. The novel templates of fluorocarbon–hydrocarbon surfactant mixtures, semi-fluorinated, and fluorinated surfactants offer a good opportunity to synthesize ordered mesoporous silica-based materials with improved stability, highly catalytic activity, tailorable pore sizes, and novel mesostructures.

Keywords: Ordered mesoporous materials; Template synthesis; Fluorocarbon–hydrocarbon surfactant mixture; Semi-fluorinated surfactant

1. Introduction

Since the first discovery of ordered mesoporous materials [1••], a series of novel ordered mesoporous materials have been successfully synthesized by using hydrocarbon surfactants [2–5]. These mesoporous materials exhibit high surface area (600–1300 m^2/g) and large pore size (2–30 nm), compared with microporous crystals of zeolites [1••]. But unfortunately, these mesoporous materials have relatively low stabilities of mesostructures and active sites, which severely hinders their practical applications in catalysis [2]. The relatively low stability of mesoporous materials such as MCM-41, as compared to microporous crystals of zeolites, can be mainly attributed to the imperfectly condensed mesoporous walls with large amounts of terminal hydroxyl groups in amorphous nature [1••,2]. Moreover, ordered porous materials with pore sizes ranging from 1.0 to 2.5 nm are relatively scarce, although these porous materials are important for shape-selectivity in catalysis because the most common substrates in organic reactions are less than 2.5 nm [2].

In this review, I have briefly summarized recent developments of syntheses of ordered mesoporous silica-based materials with improved stability, highly catalytic activity, tailorable pore sizes, and novel mesostructures, by using advantages of fluorocarbon–hydrocarbon surfactant mixtures, semi-fluorinated, and fluorinated surfactants.

2. Templated synthesis of ultrastable ordered mesoporous silica materials by fluorocarbon–hydrocarbon surfactant mixtures

A number of successful examples of mesoporous materials with good hydrothermal stability have been reported recently [6–8], but their hydrothermal stability is still much lower than that of zeolites. Notably, the mesostructured materials are generally prepared at room temperature or relatively low temperatures (80–150 °C) due to unfavorable conditions for micelle formation at the higher temperatures (>150 °C). Possibly, the level of silica

* Tel.: +86 431 5168590; fax: +86 431 5168624.
E-mail address: fsxiao@mail.jlu.edu.cn.

1359-0294/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cocis.2005.05.006

condensation in mesoporous walls will be enhanced by increasing the crystallization temperature. Fluorocarbon surfactants are a kind of stable surfactants which are widely used at high temperatures (>200 °C). However, due to the rigidity and strong hydrophobicity of the fluorocarbon chains [9], fluorocarbon surfactants cannot form ordered surfactant micelle quickly, and therefore these fluorocarbon surfactants are not suitable as templates for the preparation of well-ordered mesoporous materials. Very interestingly, when a fluorocarbon surfactant ($C_3F_7O(CFCF_3CF_2O)_2CFCF_3CONH(CH_2)_3N^+(C_2H_5)_2CH_3I^-$, FC-4) is mixed with a triblock copolymer surfactant ($EO_{20}PO_{70}EO_{20}$, P123) to form a surfactant mixture and this mixture is used as the template, highly ordered mesoporous silica-based materials with unusual hydrothermal stability, designated JLU-20, are successfully synthesized in strong acidic media at high temperatures (160–220 °C) [10••].

The X-ray diffraction (XRD) pattern of calcined JLU-20 (Fig. 1aB) shows four clearly well-resolved peaks that can be indexed as the (100), (110), (200), (210) diffractions associated with the *p6mm* hexagonal symmetry. Notably, JLU-20 exhibits much higher hydrothermal stability than SBA-15 (ordered hexagonal silica templated from polymer surfactant of P123 in strongly acidic media) [3]. After treatment in boiling water for 80 h, JLU-20 still remains well-ordered (Fig. 1aC), whereas SBA-15 loses most of its mesostructure (Table 1). Fig. 1aA and aB shows that the unit cell of JLU-20 does not contract during calcination at 650 °C for 2 h, demonstrating its excellent thermal stability (Table 1).

TEM images (Fig. 1b) of calcined JLU-20 show well-ordered hexagonal arrays of mesopores with one-dimensional channels and further confirm that JLU-20 has a 2-D hexagonal (*P6mm*) mesostructure. Particularly, JLU-20 has continuous zigzag mesoporous channels (Fig. 1c), indicat-

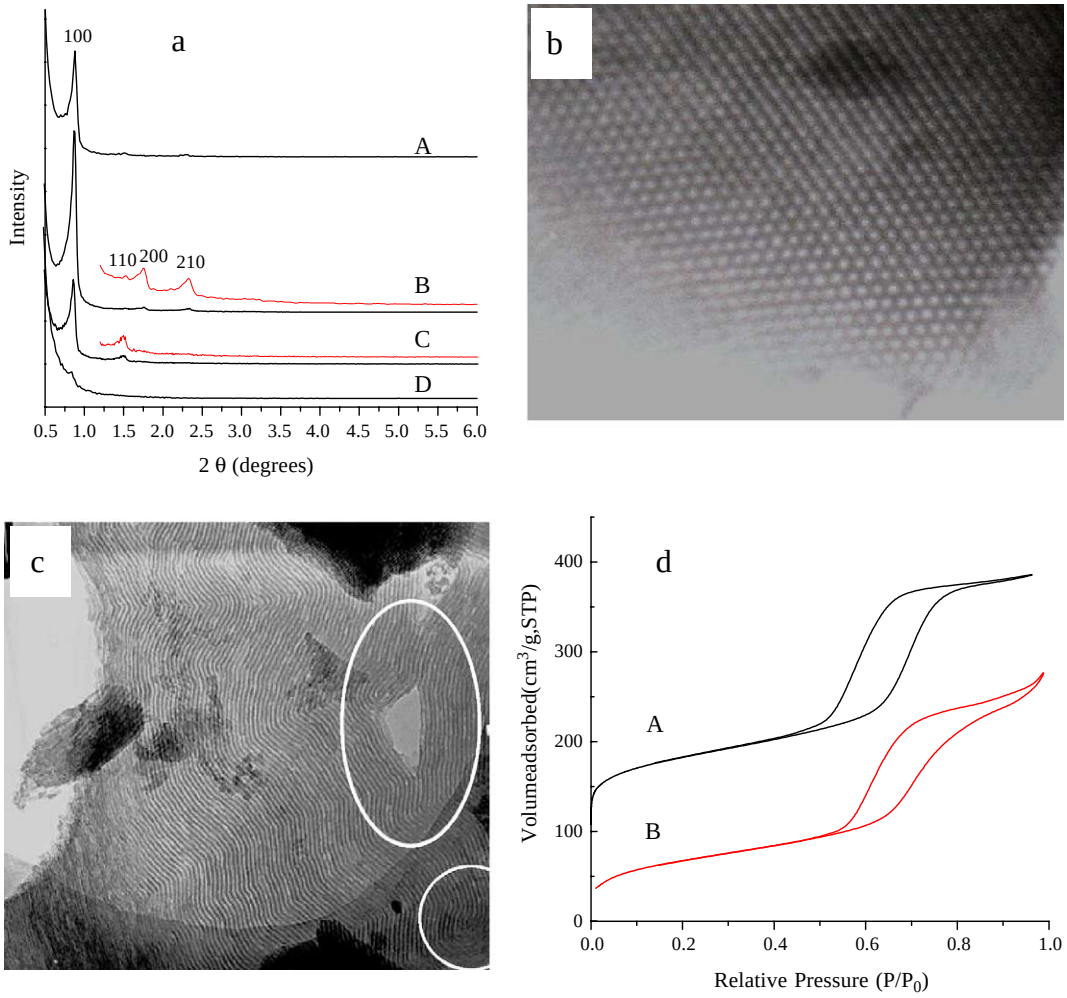

Fig. 1. a) XRD patterns of as-synthesized JLU-20 (curve A), calcined JLU-20 (B), JLU-20 treated in boiling water for 80 h (C), and as-synthesized sample prepared with the same procedure as JLU-20 except for the absence of FC-4 in the initial reaction mixture (D). b) TEM image of calcined JLU-20 taken in the [100] direction. c) TEM image of calcined JLU-20 taken in the [110] direction. d) N_2 adsorption/desorption isotherms of calcined JLU-20 (A) and treated in boiling water for 80 h (B). Isotherms B have been offset by 100 cm3/g along the vertical axis for clarity (Reproduced from Ref. [10••]).