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Hydrolysis reaction on the characterization of wormhole-like mesoporous tungsten oxide

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Abstract

Wormhole-like mesostructures have promising applications in heterogeneous catalysis because channel branching within the wormhole-like mesostructures can facilitate access to active sites on the framework walls. We adopt the poly(alkylene oxide) triblock copolymer of L62 (BASF Pluronic $EO_8PO_{30}EO_8$) as a template to form wormhole-like mesoporous tungsten oxide. In the hydrolysis experiment, 10 or 20% anhydrous ethanol was replaced with distilled deionized water (H_2O). The crystallinity of wormhole-like mesoporous tungsten oxide decreases when the anhydrous ethanol solvent is replaced with H_2O. Such a decrease in the relative strength of O–W–O binding attributes to the hydrolysis of the wormhole-like mesoporous tungsten oxide from Raman spectra. Specific surface area and average pore size of wormhole-like mesoporous tungsten oxide decrease with the amount of H_2O replacement. The phenomenon can also be confirmed by nitrogen adsorption–desorption isotherms. These results show that the hydrolysis reactions have great significance and application for the development of wormhole-like mesoporous tungsten oxide in the future.

Keywords: Nanostructure materials; Sol–gel process; Microstructure; Transmission electron microscopy; X-ray diffraction

1. Introduction

Due to its high potential for photoconductive behavior, tungsten oxide is the most promising candidate for use in electrochromic materials, dye sensitized solar cells, and gas sensors [1–3]. The improved properties of nanostructured materials usually result from their enormous surface area, which provides large quantities of active area to react with, e.g. photochromism, where coloration and bleaching steps are enhanced quickly by irradiating the bare tungsten oxide thin film with light [4,5]. The pore size and distribution can be designed for specific practical applications which have been proposed for these nanostructures [1–3].

It is well known that water plays an important role in the formation of a mesostructured framework. The quantity of water inside the hybrid coating can control the final mesophase. This effect has also been observed in mesoporous silica-based systems [6–8]. In base media, the hydrolysis of silicon alkoxides and their further condensation follows a particles dynamic that leads to a distribution of silicate species in solution with oligomeric species of various degrees of polymerization [9]. Most of the related works are about the preparation of silica, but the references concerning the preparations or characteristics of non-silica-based materials are deficient. Kim et al. [10] developed mesoporous alumina through a post-hydrolysis method to induce the hydrolysis and condensation reactions as the terminal reaction step. Mecheri et al. [11] reported the addition of hydrated tungsten oxide ($WO_3{\cdot}2H_2O$) resulted in a higher proton conductivity, improved heat resistance and lower water solubility for fuel cell applications.

Furthermore, wormhole-like mesostructures have promising applications in heterogeneous catalysis because channel branching within the wormhole-like mesostructures can facilitate access to active sites on the framework walls [12–17]. However, there are few reports of wormhole-like mesoporous tungsten oxide that discuss the influence of hydrolysis reaction. In this work, we adjust the addition of water to investigate the hydrolyzed effect on the characterization of wormhole-like

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mesoporous tungsten oxide by microstructure analyses. We also report on the possible hydrolysis reaction that governs or suppresses the growth of wormhole-like mesoporous tungsten oxide.

2. Experimental

We adopt nonionic surfactants that possess dipolar or zwitterionic headgroups and exhibit substantially lower critical micelle concentrations (CMCs) than the corresponding ionic surfactants. The samples were prepared by a kind of sol–gel process, using colloidal solution of tungstic chloride stabilized by addition of selected organic poly(alkylene oxide) triblock copolymer. 0.5 g of poly(alkylene oxide) triblock copolymers of L62 (BASF Pluronic $EO_8PO_{30}EO_8$) were dissolved in 5 g of ethanol solvent (purity: 99.8%). To this solution, 2.5 mmol of the anhydrous inorganic chloride precursor, WCl_6 (Aldrich), was slowly added and vigorously stirred for 48 h. In the hydrolysis experiment, 10 or 20% anhydrous ethanol was replaced with distilled deionized water (H_2O). The resulting solutions were gelled in an open Petri dish at 60 °C in air and calcined at 250 °C for 12 h to remove the residual triblock copolymer.

Wormhole-like mesoporous tungsten oxide synthesized by sol–gel and incorporating triblock copolymer to generate liquid crystal template was characterized by a variety of analyses. The mesostructure of tungsten oxide obtained was then investigated by X-ray powder diffractometry (Rigaku D/max-IV, using Cu Kα radiation), transmission electron microscopy (Hitachi Model HF-2000, 200 keV), and Raman spectrometer (LabRAM HR, Jobin Yvon). The structure and bonding type of wormhole-like mesoporous tungsten oxide was evaluated by Raman spectra that obtained from the excitation of a 525 nm argon laser focused with a spot diameter of 1 Am. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2010 system after the samples were vacuum-dried at 150 °C for 12 h in a N_2 atmosphere. Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P_0) ranging from 0 to 1.0.

3. Results and discussion

The synthesized factors of wormhole-like mesoporous tungsten oxide precursor solution, including surfactant concentration, pH, and temperature, are important in promoting the stability of liquid-crystal micelles as a mesostructure director. It has been demonstrated [18] that the triblock copolymers of L62 are completely are removed and form wormhole-like mesoporous tungsten oxide upon calcination at 250 °C. However, the recent studies of the mesostructured crystallinity of tungsten oxide do not have detailed discussion of this. Fig. 1 shows X-ray powder diffraction patterns of wormhole-like mesoporous tungsten oxide samples prepared by (a) full anhydrous ethanol, (b) 10%, and (c) 20% replaced with H_2O and calcined at 250 °C. The crystalline structure in Fig. 1a is the cubic type of nanocrystals (JCPDS-ICDD 41-0905, $a = b = c = 3.714$ Å). Three peaks can be identified at 2θ values of 24.08°, 34.01° and 55.41° by a spectral deconvolution analysis of the X-ray spectra. These peaks are consistent with the cubic crystalline structure and correspond to 100, 110 and 210 diffractions, respectively. Tungsten oxide exists in many polymorphic modifications, but monoclinic γ-WO_3 is the only polymorph from 290 to 600 K [19,20]. Furthermore, the crystal phases which were replaced with 10% (Fig. 1b) and 20% H_2O (Fig. 1c) are both monoclinic crystalline, as seen from the position of the peak and the broadness of the peak. The crystallinity of wormhole-like mesoporous tungsten oxide decreases when the anhydrous ethanol solvent was replaced with H_2O due to the full-width at half-maximum (FWHM).

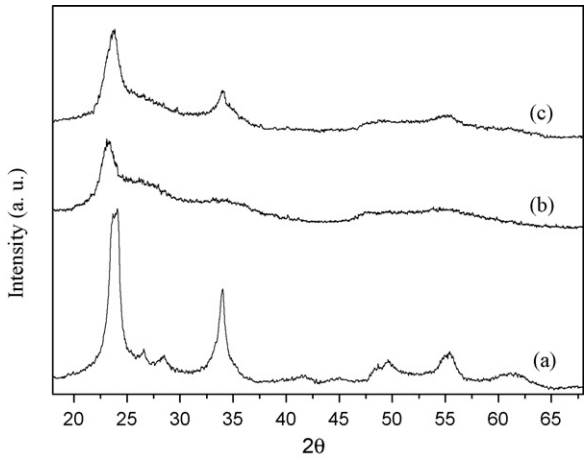

Fig. 1. XRD patterns of wormhole-like mesoporous tungsten oxide samples prepared with (a) full anhydrous ethanol, (b) 10%, and (c) 20% replaced with H_2O and calcined at 250 °C.

Raman spectroscopy is a powerful tool to investigate the bonding structure of wormhole-like mesoporous tungsten oxide. The Raman spectra of wormhole-like mesoporous tungsten oxide are presented in Fig. 2. The spectra yield information concerning the existence of different phases and bonds of the wormhole-like mesoporous tungsten oxide crystals. The wormhole-like mesoporous tungsten oxide synthesized with full anhydrous ethanol (Fig. 2a) has a better crystallinity than that of the 10% (Fig. 2b) or 20% H_2O replacement (Fig. 2c) as shown in Raman spectra. The degree of crystallinity of wormhole-like mesoporous tungsten oxide powder with the cubic phase prepared with full anhydrous ethanol is in agreement with the confirmed results of XRD (Figs. 1a and 2a). However, the broad profile of the samples synthesized with 10% H_2O replacement (Fig. 2b) is indicative of the defects of mesopores that are abundant in n-type semiconductors. The Raman spectra of wormhole-like mesoporous tungsten oxide samples in Fig. 2a and b show

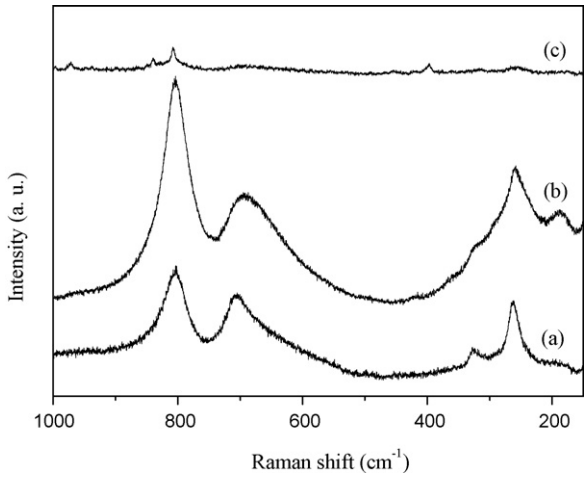

Fig. 2. Raman spectra of wormhole-like mesoporous tungsten oxide samples prepared with (a) full anhydrous ethanol, (b) 10%, and (c) 20% replaced with H_2O and calcined at 250 °C.