Available online at www.sciencedirect.com
ScienceDirect
Microporous and Mesoporous Materials 106 (2007) 262–267
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Organic-functionalized sodalite nanocrystals and their dispersion in solvents

Dan Li [a], Jianfeng Yao [a], Huanting Wang [a,*], Na Hao [a], Dongyuan Zhao [a], Kyle R. Ratinac [b], Simon P. Ringer [b]

[a] *Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia*
[b] *Australian Key Center for Microscopy and Microanalysis, The University of Sydney, Sydney, NSW 2006, Australia*

Received 30 January 2007; received in revised form 2 March 2007; accepted 5 March 2007
Available online 13 March 2007

Abstract

Hydroxy-sodalite nanocrystals with organic functional groups (i.e., $=\mathrm{Si}\text{–}(\mathrm{CH_3})(\mathrm{CH_2})_3\mathrm{NH_2}$, denoted Sod-N, or $\equiv\mathrm{Si}\text{–}\mathrm{CH_3}$, denoted Sod-C) were synthesized by the direct transformation of organic-functionalized silicalite nanocrystals. The chemical structure of organic-functionalized sodalite nanocrystals was confirmed by ^{29}Si MAS NMR spectroscopy. Gas sorption results showed that the sodalite nanocrystals contained uniform pore channels that were accessible to hydrogen, but inaccessible to nitrogen, as expected. The BET surface areas are calculated to be 22.8, 19.6 and 19.1 m^2/g for plain sodalite nanocrystals (Sod), Sod-N, and Sod-C, respectively; similarly, Sod-N and Sod-C exhibited slightly lower hydrogen adsorption than Sod. The dispersion of Sod-N and Sod-C in organic solvents was favored by the presence of organic functional groups. Therefore, the organic-functionalized sodalite nanocrystals prepared in this work may be very useful for fabricating zeolite nanostructures and sodalite-polymer nanocomposite membranes.

Keywords: Sodalite; Silicalite; Organic functionalized; Nanocrystals; Dispersion

1. Introduction

Sodalite is a small-pore zeolite whose framework consists of a six-membered ring aperture with a pore size of 2.8 Å. Because of its small pore size and high ion exchange capacity, sodalite has been considered as a good candidate material for a wide range of applications such as optical materials, waste management, hydrogen storage, and hydrogen separation [1]. The active research into efficient storage and separation of hydrogen has been driven by its potential as an essential component of future energy economies. Consequently, we are interested in developing high-selectivity, high-flux membranes for the separation and purification of hydrogen gas. Among the various possible membranes, polymeric ones have been extensively studied for hydrogen separation because they are of low-cost and can be easily fabricated into compact hollow fibers and flat sheets with a high separation-area-to-volume ratio [2–4]. Although some polymer membranes exhibit good hydrogen selectivity and permeability, there is still plenty of room for development of membranes with improved performance [2]. Previous studies by a number of groups have suggested that the incorporation of zeolites into the polymer matrix can significantly increase gas separation selectivity by enhancing selective gas adsorption and diffusion through the membranes [3–6]. Therefore, the addition of sodalite into polymers promises to yield sodalite-polymer composite membranes with superior selectivity for hydrogen separation. It has been suggested that template-free sodalite nanocrystals with good interfacial compatibility with the chosen polymer are needed to effectively fabricate sodalite-polymer composite membranes [3]. As

---

[*] Corresponding author. Tel.: +61 3 9905 3449; fax: +61 3 9905 5686.
E-mail address: huanting.wang@eng.monash.edu.au (H. Wang).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.03.006

part of our project aiming to design such membranes, the focus of this paper is the synthesis of template-free sodalite nanocrystals with suitably tailored surface properties.

Our newly developed method for synthesizing colloidal hydroxy-sodalite nanocrystals by the transformation of silicalite nanocrystals is used in this study [1], since there is no other method for the synthesis of colloidal structure-directing agent free hydroxy-sodalite nanocrystals available. The hydroxy-sodalite nanocrystals obtained have a sodalite structure whose framework charges are balanced by hydroxide ions, and they do not enclose template molecules within their pore channels. The strategy of attaching organic functional groups to zeolites is adopted to achieve suitable surface properties of the hydroxy-sodalite nanocrystals because it is one of the most effective ways for modifying surface properties or adding surface reactivity to zeolite crystals [7–12]. Two kinds of organic groups including methyl and amino moieties are introduced into the sodalite nanocrystals by adding controlled amounts of 3-aminopropyl(diethoxy) methylsilane and methyltrimethoxysilane during the growth of silicalite nanocrystals. The sodalite nanocrystals are thus expected to be made more hydrophobic ($-CH_3$) or reactive ($-NH_2$). The preparation and characterization of organic-functionalized sodalite nanocrystals and their dispersion in solvents are detailed in this paper.

2. Experimental section

2.1. Synthesis of organic-functionalized silicalite nanocrystals

Clear synthesis solutions were prepared by dropwise addition of 20 g of 1 M tetrapropylammonium hydroxide (TPAOH, Sigma–Aldrich) solution into the mixture of 17.8 g of tetraethyl orthosilicate (TEOS, 99%, Sigma–Aldrich) and 1.8 g of 3-aminopropyl(diethoxy) methylsilane (ADMS, 97%, Sigma–Aldrich) or 1.3 g of methyltrimethoxysilane (MTMS, 98%, Sigma–Aldrich) under vigorous stirring, followed by continued stirring at room temperature for 3 h. The molar composition of final solution was 1 TPAOH:4.32 SiO_2:0.48 ADMS (or MTMS): 44 H_2O. Crystallization was carried out at 80 °C for 12–15 days. The milky silicalite suspensions obtained were dried at 90–100 °C leading to solid silicalites (denoted Sil-N and Sil-C for silicalites prepared with ADMS and MTMS, respectively). To observe their morphologies by scanning electron microscopy, the samples were prepared by repeated cycles of washing with deionized water and centrifuging, followed by drying at 90–100 °C overnight.

2.2. Synthesis of organic-functionalized sodalite nanocrystals

An alkaline solution with a molar composition of 6.07 Na_2O:1 Al_2O_3:66 H_2O was prepared by mixing 20 g of sodium hydroxide (99%, Merck), 9.2 g of sodium aluminates (anhydrous, Sigma–Aldrich), and 60 g of deionized water at room temperature for 1–2 h. 1 g of the dried silicalite sample (i.e. Sil-N and Sil-C) was added to 11 g of the alkaline solution during 2–3 min of stirring, and then aged at room temperature for 4 h without further stirring. The transformation was carried out at 80 °C for 0–4 h. The samples obtained were cooled to room temperature and collected by repeated cycles of washing with deionized water and centrifuging, followed by drying at 90–100 °C overnight. The samples were denoted Sod-N and Sod-C, respectively, when Sil-N and Sil-C were used as silica source, respectively. For comparison, hydroxy-sodalite nanocrystals (denoted Sod) were also prepared from silicalite nanocrystals according to our previous paper [1].

2.3. Characterization

Scanning electron microscopy (SEM) images were taken with a JSM-6300F microscope (JEOL). The particle size distributions for Sil-N, Sil-C, Sod-N and Sod-C were determined by manual measurement of 300 nanocrystals each in SEM images with a Photoshop software. X-ray diffraction (XRD) patterns were measured on a Philips PW1140/90 diffractometer with Cu Kα radiation (25 mA and 40 kV) at a scan rate of 1°/min with a step size of 0.02°. Thermogravimetric analysis (TGA, Perkin Elmer, Pyris 1 analyzer) was performed in air at a heating rate of 5 °C/min to 600 °C. ^{29}Si solid-state nuclear magnetic resonance (NMR) was conducted on a Bruker DSX300 spectrometer (Germany) under conditions of cross polarization (CP) and magic angle spinning (MAS). ^{29}Si solid-state MAS NMR spectra were collected at room temperature with a frequency of 59.6 MHz, a recycling delay of 600 s, a radiation frequency intensity of 62.5 kHz, and a reference sample of $Q_8M_8([(CH_3)_3SiO]_8Si_8O_{12}])$. Nitrogen and hydrogen adsorption–desorption experiments were performed at 77 K with a Micrometritics ASAP 2020MC analyzer and a Micrometritics ASAP 2010MC analyzer, respectively. The samples were degassed at 473 K before analysis. The surface areas were determined by the Brunauer–Emmett–Teller (BET) method. Suspended particle size distributions were quantified by light scattering with a Malvern Mastersizer 2000 analyzer. Different solvents-deionized water, isopropanol (97%, Sigma–Aldrich), dichloromethane (DCM, Sigma–Aldrich) and dimethylformamide (DMF, Sigma–Aldrich) – were used for sample dispersion. Approximately 12–15 ml of suspension was prepared by dispersing 50 mg of sample into 50 ml of solvent under ultrasonication before injection into the Mastersizer for size distribution analysis.

3. Results and discussion

3.1. Transformation of silicalite

The XRD patterns (Fig. 1) show the transformation of organic-functionalized silicalites (Sil-N and Sil-C) under hydrothermal treatment at 80 °C. The organic-functionalized silicalites (Sil-N and Sil-C) became amorphous