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ScienceDirect
Microporous and Mesoporous Materials 98 (2007) 242–248
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Isothermal template removal from MCM-41 in hydrogen flow

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Received 25 May 2006; received in revised form 12 September 2006; accepted 14 September 2006
Available online 27 October 2006

Abstract

Thermal evacuation of template surfactant from MCM-41 in hydrogen atmosphere was investigated. Micelle templated silica was prepared using hexadecyltrimethylammonium bromide. The mechanism of template removal appears to be completely different in hydrogen as compared to calcination in air. It seems that moderate heating of as-synthesized MCM-41 (up to about 250 °C) in hydrogen stream for about 15 h is effective and simple method of template removal leaving no pure carbon residues on silica surface. Adsorption properties of partially evacuated MCM-41 samples were tested using gas chromatography. Products of template degradation were analyzed using GC–MS technique. The main products of template degradation at 250 °C in hydrogen flow are hexadecene and hexadecane-*N*,*N*-dimethylamine. Concentration of surface silanols for MCM-41 calcined and thermally treated in hydrogen flow was investigated by NMR technique.

Keywords: MCM-41 silica; Template removal; GC–MS; CHN; NMR; Adsorption

1. Introduction

Mesoporous silica materials of MCM-41 type are synthesized from the surfactant micellar template addition of an inorganic silica source [1,2]. Quaternary alkylammonium chlorides or bromides are most commonly used as a template. The cylindrical micelles of surfactant at the presence of, e.g., ammonium as catalyst becomes covered in the solution with silica layer about 1 nm thick. Thus, the surfactant micelles are encapsulated in silica skeleton. The micellar core is after synthesis removed and porous honeycomb like structure is created. Two main methods are used for template removal. One consists of thermal degradation of template by heating up to 600 °C in air for 8 h. However, after calcination further processing in high temperature is required to remove carbon deposits and to obtain final colorless (white) siliceous material [3]. High temperature treatment influences among others the chemistry of silica surface and partial condensation of surface silanols [4]. The remaining part of surfactant molecules which forms the core of micellar template is eliminated at higher temperatures by combustion in oxygen atmosphere. Degradation of template against temperature is usually monitored in dynamic conditions with linear heating rate. Investigations of surfactant removal presented in many papers have shown that degradation of the surfactant at higher temperature occurs by a stepwise mechanism [5,6]. At first stage of calcination within the temperature range 120–250 °C the Hoffman degradation of surfactant molecules takes place. At this stage of process trimethylamine is evolved. Complete degradation consist of several stages starting from elimination of head amine group in temperature range 120–250 °C. Next steps are strongly exothermic and take place above 250 °C. The exothermic processes are related with cracking reactions of hydrocarbon chains and their conversion to carbon dioxide and water. Substantial template removal requires long-term heating at 550 °C in oxidation atmosphere.

Recently, we have stated that thermal treatment of an as-synthesized sample in vacuum at lower temperature

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1387-1811/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2006.09.011

~200 °C is suitable for removal of main part of organic template. However, silica sample prepared under these conditions still contains some amount of carbon species [7–9].

Another method of pore emptying is extraction by use various solvents. The extraction is a convenient method because silica material is not treated with high temperature. However, for some samples we observed that after extraction part of template is present in pores of MCM-41 silica samples.

It is not yet clear what will occur when as-synthesized MCM-41 material is retained at constant temperature and if at a given temperature some equilibrium state of partially decomposed template may be attained. As it was mentioned above pore emptying is realized usually by calcination in 550 °C. At so high temperature some amounts of silanols present on silica surface condense forming siloxane bridges. Hence, silica surface becomes more hydrophobic in comparison to silica gel surface obtained by classical sol–gel method.

The channel arrangement and structure of the silicate in bulk material as well as surface character affect the catalytic and adsorptive properties of the material. Therefore, it is interesting to study the mechanisms of template degradation under different conditions. Our earlier investigations of template removal in inert argon atmosphere indicate that during thermal processing of MCM-41 sample, template transformations are accompanied by very small exothermic effects as comparing to calcination in air. Moreover, final siliceous product possesses identical structural parameters as calcinated sample [9]. In the present paper the new approach for preparation of siliceous MCM-41 material free of surfactant molecules is discussed. The properties of mixed organo-silica complexes of MCM-41 type at various temperatures in hydrogen stream were investigated. The samples were treated at relatively low temperatures to avoid the rapid degradation of template and strong exothermic processes.

2. Experimental

2.1. Sample preparation

MCM-41 raw materials were synthesized using hexadecyltrimethylammonium bromide (C16TMAB, 96%, Fluka) as surfactant. The preparation procedure followed the method described in literature [10]. Tetraethoxysilane (TEOS, 98% Fluka) was used as a silica source. The initial sample was dried at 100 °C and used without further thermal treatment, thus the micellar filling was entirely preserved. Prior to the experiments a part of raw MCM-41 sample was calcinated at 550 °C for 8 h and next processed at 550 °C for 5 h in an oxygen stream in order to eliminate the carbon deposits left after calcination in static condition. Finally white (colorless) silica sample was obtained. The initial sample dried at 100 °C is denoted as MCM-41-1, calcinated sample processed in oxygen stream is designated as MCM-41-OX.

Next sample was prepared using extraction method. The part of as-synthesized MCM-41 sample was placed into Soxhlet apparatus and extracted with acidified methanol. This sample is denoted as MCM-41-EX. The extraction of the template was carried out using the mixture of 170 cm^3 of methanol and 17 cm^3 of concentrated HCl under reflux for 10 h.

Next four samples of MCM-41 silicas were prepared by heating of as-synthesized sample at 110, 150, 200 and 250 °C in hydrogen stream. The flow of hydrogen was 30 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The initial sample was placed in stainless steel column of 50 cm length and 2 mm in the diameter. Prior to experiments small particles of as-synthesized material with diameter 0.1 mm were separated. The heating in hydrogen flow was performed using gas chromatograph HP 5890 with thermal conductivity detector. Thermally treated samples in hydrogen flow are denoted indicating temperature of treatment, i.e. MCM-41(110), MCM-41(150), MCM-41(200) and MCM-41(250).

2.2. Methods

Nitrogen adsorption measurements were carried out using a volumetric adsorption analyzer ASAP 2405 (Micrometrics, Norcros, GA). The specific surface areas S_{BET}, were calculated using the BET method for the adsorption data in a relatively pressure range p/p_0 from 0.05 to 0.25. Pore size and pore size distribution were determined using the BJH procedure [11].

GC/MS analysis was performed using gas chromatograph combined with mass spectrometer GCQ (Thermo-Finningan, USA) equipped with capillary column RT-5 (Resteck) of 0.18 mm ID and 50 cm length. Heating rate was 10 °C/min. MS analysis was realized using electron ionization 70 V, within 35–400m/z.

X-ray powder diffraction (XRD) patterns were measured on Dyfractometer HZG 4AZ (Germany) using Cu Kα radiation. X-ray patterns were obtained by measuring the number of impulse within a given angle over 10 s. The measurements were taken for every 0.02°.

Elemental analysis of the investigated samples was performed using a CHN analyzer (Perkin–Elmer CHN 2400).

Table 1
Elemental analysis of investigated MCM-41 samples (content in % by weight)

Samples	Elemental analysis		
	% C	% H	% N
MCM-41-1	31.86	6.63	1.94
MCM-41(110)	28.44	5.72	1.74
MCM-41(150)	22.25	4.55	1.49
MCM-41(200)	6.52	1.69	0.32
MCM-41(250)	3.89	1.25	0.12
MCM-41-EX	3.19	1.21	0.21
MCM-41-OX	0.19 (2.78[a])	0.27 (1.20[a])	0.18 (0.11[a])

[a] C, H, N contamination for calcined MCM-41 silica at 550 °C for 8 h.