Thermochimica Acta 511 (2010) 82–88

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Characterization of the porosity and surface chemistry of mesoporous silicas by quasi-equilibrated thermodesorption of 1-butanol and n-nonane

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ARTICLE INFO

Article history:
Received 27 April 2010
Received in revised form 21 July 2010
Accepted 23 July 2010
Available online 3 August 2010

Keywords:
MCM-41
SBA-15
Mesoporous silica
Thermodesorption
QE-TPDA
n-Nonane
1-Butanol
Silanols

ABSTRACT

Mesoporous silicas MCM-41 and SBA-15 were studied using the quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA) of n-nonane and 1-butanol. The QE-TPDA profiles of n-nonane containing one desorption maximum were typical for the mesoporous materials. The pore size distributions from the thermodesorption data were similar to those calculated from N_2 adsorption isotherms. The QE-TPDA profiles of 1-butanol exhibited low temperature maxima (below 70 °C) resulting from desorption of the adsorbate filling the mesopores and high temperature maxima (at ca. 100 °C) attributed to desorption of the molecules specifically adsorbed on the hydrogen-bonded silanols. These findings were confirmed by IR measurements. Hydrothermal treatment of MCM-41 resulted in increase of the H-bonded silanol concentration, while for SBA-15 an inverse effect was observed.

1. Introduction

Methods for studying porous materials are often based on measurements of adsorption/desorption equilibria. Ar or N_2 adsorption isotherms are used for determination of the surface area, the micro- and mesopore volumes as well as the pore size distributions [1,2]. For characterization of porous materials classical volumetric or gravimetric measurements of the adsorption isotherms are most often performed. Alternatively, dynamic flow techniques are used, mainly for determination of the single-point BET surface area [2].

Long time of experiments, relatively large amounts of samples needed and limited choice of the adsorptives are the main drawbacks of the isotherm measurements under static conditions. A novel method for studying meso- and micropore materials which is free from some of those restrictions is quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA) of volatile hydrocarbons [3–6]. The QE-TPDA of n-nonane allows determination of the mesopore size distributions as well as the micro- and mesopore volumes [6]. The possibility of using vapors of various volatile compounds as adsorptives makes this technique a valuable complement of the classical adsorption methods.

Mesoporous micelle-templated silicas (MTS) are interesting materials for many technological applications due to their porous and morphological characteristics. They may be used as stationary phases for liquid chromatography, heterogeneous catalysts or their supports, adsorbents and lately as hard templates in preparation of mesoporous carbons [7]. However, these materials are not thermodynamically stable and tend to lose their porous structure when exposed to high temperature and/or water vapor action. In studies on hydrothermal stability on MTS [8] it has been shown that the mesoporous structure of MCM-41 and MCM-48 is almost totally damaged when they are treated with 100% steam at 100 °C. The main reason for this destruction is a very fast hydroxylation of relatively thin amorphous walls, depending on the kind of silica source used in the synthesis [8–10]. On the other hand, SBA-15 with thicker pore walls can withstand such a hydrothermal treatment without major changes of its structure [8].

Reactivity of the MTS is determined by chemical nature, concentration and accessibility of the silanol groups, which are the main surface active sites [11–13]. They play a key role not only in hydrothermal degradation of the mesoporous structure, but also in functionalization of the surface by grafting of various organic groups [14,15].

The aim of this work was an application of the equilibrated thermodesorption of n-nonane and 1-butanol in studies of the surface of porous silicas with well defined mesoporous structure: MCM-41 and SBA-15. n-Nonane has been found a good probe molecule

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0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.07.028

for characterization of micro- and mesoporous siliceous molecular sieves [5,6]. As 1-butanol has saturation partial pressure similar to that of n-nonane, it is a good adsorptive for the QE-TPDA measurements. Because of its polarity, 1-butanol was expected to be a good probe molecule for characterization of the silanol groups on the silica surface.

2. Experimental

2.1. Studied materials and their characterization

Ordered mesoporous silicas MCM-41 and SBA-15 used in this study were synthesized from tetraethylorthosilicate (TEOS) as a source of silica. The MCM-41 molecular sieve was prepared by mixing 525 mL of distilled water, 45.3 mL of hexadecyldecyltrimethylammonium chloride (CTACl; 25% water solution, Aldrich) and 44.0 mL of ammonia solution (25%, Polish Chemicals Reagents) for 30 min at room temperature, followed by adding 48.6 mL of tetraethylortosilicate (TEOS, 98%, Aldrich). The resulting suspension was stirred for another 1 h. Subsequently, the product was filtered, washed with distilled water and dried at 40 °C.

To obtain the SBA-15 material, 150 mL of 1.6 M HCl (Polish Chemicals Reagents) and 4.0 g of block copolymer of ethylene and propylene oxide (Pluronic P123, Aldrich) was stirred for 1 h at room temperature. Then, the solution was heated up to 45 °C and 9.14 mL of TEOS was instilled. The obtained slurry was stirred for the next 8 h at 45 °C and 15 h at 80 °C (aging of the material). The precipitate was filtered, washed with distilled water and dried at 40 °C.

In order to remove the templates, both synthesized silicas were calcined in air with the heating rate of 1 °C/min to 550 °C followed by 8 h of isothermal period [5].

The calcined mesoporous silicas MCM-41 and SBA-15 were modified by boiling in water. About 200 mg of the material was boiled in 50 ml of distilled water for 1 h with continuous stirring. Then it was filtered, washed with water and methanol and dried at room temperature.

Porosity of the calcined silicas was studied by means of N_2 adsorption at 77 K (Micrometrics ASAP 2010). Before measurement each sample was activated to 300 °C at vacuum during overnight.

IR characterization of the surface silanol groups in the calcined and modified silicas was performed using Bruker Tensor 27 spectrometer with an MCT detector. Samples were studied in the form of self-supporting wafers. Prior to the measurements they were degassed under vacuum at room temperature. The spectra were recorded at room temperature, after heating the sample at the elevated temperature for 20 min and cooling it down. The heating and cooling cycles were repeated several times with gradual increasing of the elevated temperature value (200, 300, 400 and 500 °C).

2.2. The QE-TPDA apparatus and experiments

The QE-TPDA experiments were performed using a TPD setup equipped with a chromatographic thermal conductivity detector. A sample of the adsorbent was placed in a quartz tube (o.d. 6 mm, 15 cm long) which was connected to the detector (Micro Volume TCD, Valco). Helium (5.0, Messer) was used as a carrier gas. There were two independent carrier gas lines controlled by mass flow controllers (Brooks) in the TPD setup. One of the gas lines was equipped with a saturator that was continuously adding a small admixture of the adsorptive to the stream of He. Using a 4-port switching valve the composition of the gas flowing through the sample could be easily changed from pure He to He containing about 0.4% of the adsorptive. The lines were heated in order to avoid any condensation or adsorption of vapors on tubing.

Small samples of the studied materials (about 2–4 mg) were used in the thermodesorption measurements. Before each experiment the sample was activated by heating in the flow of pure He to 200 or 500 °C at 10 °C/min and cooled down to the room temperature. Then the carrier gas was replaced by the He/adsorptive mixture, flowing through the sample tube with the same flow rate. The QE-TPDA experiments were performed by heating the sample with the preadsorbed probe molecules in the flow of He/adsorptive mixture (7.5 cm^3/min) according to a temperature program consisting of several heating and cooling ramps (with the heating and cooling rates of 2 and 4 °C/min). The QE-TPDA experiments and the apparatus were described in more details earlier [3,4].

3. Results

3.1. Porosity characterization by N_2 adsorption and QE-TPDA of n-nonane

The results of the porosity characterization of the studied silicas by low temperature N_2 adsorption and quasi-equilibrated thermodesorption of n-nonane are shown in Fig. 1. The N_2 adsorption/desorption isotherms are typical for the mesoporous materials. Their steep steps resulting from the capillary condensation indicate high uniformity of the cylindrical mesopores.

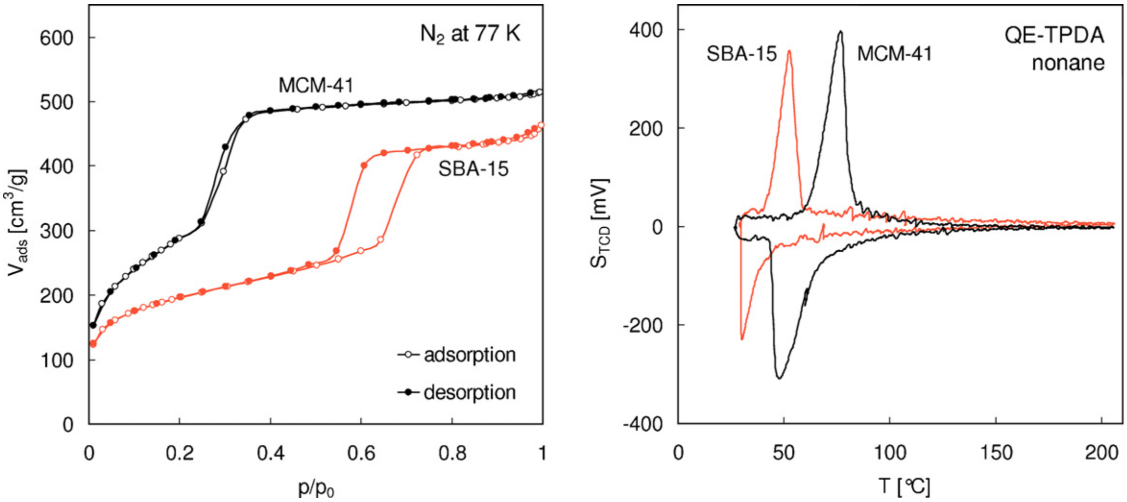

Fig. 1. Low temperature N_2 adsorption isotherms and the QE-TPDA profiles of n-nonane on MCM-41 and SBA-15 silicas, measured at 2 °C/min for partial pressure of nonane of 4.0 and 3.9 mbar, respectively.