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Determination of the surface area and mesopore volume for lanthanide-incorporated MCM-41 materials by using high resolution thermogravimetry

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Abstract

High-resolution thermogravimetry (HR TGA) was successfully used to study thermodesorption of *n*-butanol from ordered mesoporous materials. The current study was performed for lanthanum and cerium incorporated MCM-41 samples, which were synthesized via liquid crystal templating mechanism. Due to highly ordered structure of mesopores in these materials it was possible to distinguish the characteristic features on the DTG curves, which reflect the starting points for thermodesorption of *n*-butanol from the interior of primary mesopores as well as from their surface. It was demonstrated that *n*-butanol thermodesorption data obtained by HR TGA provide accurate values of the volume of primary mesopores and their specific surface area, which are in a good agreement with those obtained from nitrogen adsorption isotherms. In addition, this study showed that a simple evaluation of the specific surface area and pore volume of nanoporous materials is possible by HR TGA.

Keywords: *n*-Butanol thermodesorption; High-resolution thermogravimetry; Lanthanide-incorporated MCM-41 materials; Specific surface area; Pore volume

1. Introduction

Ordered mesoporous materials (OMM) such as MCM-41, discovered in the beginning of 1990s [1,2], already achieved a great importance and popularity [3]. These materials have been synthesized hydrothermally via liquid crystal templating mechanism [1–3]. Their pore size can be adjusted from 2 to 10 nm by selection of a proper surfactant [1,2], addition of expander molecules during synthesis [2,4] and/or specific post-synthesis treatment [5–7]. Structural and surface properties of OMMs can be evaluated by several methods including adsorption, which plays an important role in their characterization [8,9]. For instance, nitrogen adsorption is commonly used to determine the BET specific surface area, pore volume of primary and secondary mesopores as well as their sizes and distribution [8,9].

A growing interest in the synthesis, modification and applications of OMMs generates a strong demand for development simple and effective methods for characterization of their surface and structural properties. Although X-ray diffraction and electron microscopy are most often used to detect the type of

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ordering of the mesoporous network in these materials, they are insufficient for evaluating the percentage of the ordered structure in the entire material [9]. Because of the porous nature of OMMs, gas adsorption is an attractive technique for characterization their structural and surface properties but accurate adsorption measurements are time consuming and often require special analysis conditions [8,10]. Thus, there is a considerable interest in elaborating new methods to evaluate the surface and structural properties of OMMs. Among various methods thermogravimetry (TGA) seems to be a simple and attractive technique to investigate various inorganic and organic materials [11]. In contrast to adsorption measurements, TGA has much more flexibility with respect to the adsorbate used. Recently, the interest in this field has increased because of introduction of high-resolution thermogravimetric analysis (HR TGA), which is very useful to monitor the stepwise thermodesorption of adsorbed molecules from porous solids [12]. This technique has been employed to characterize surface properties of silicas [13] and microporous carbons [14–17]. The specific surface areas and pore volumes obtained by means of HR TGA were in a good agreement with those obtained from gas adsorption measurements [14–17].

The current work demonstrates the utility of HR TGA to characterize sorption properties of MCM-41 materials, namely, to evaluate their specific surface area and primary mesopore volume. The materials studied in this work were lanthanum and cerium incorporated MCM-41 samples immersed with *n*-butanol. It is shown that their TGA curves, which reflect stepwise thermodesorption of *n*-butanol, exhibit characteristic features, which can be used to evaluate the surface area and mesopore volume.

2. Experimental

2.1. Materials

La- and CeMCM-41 materials were synthesized via hydrothermal method using sodium silicate (Merck), hydrated lanthanum(III) and cerium(III) chlorides (Sigma), distilled water as solvent, cethyltrimethylammonium bromide (CTMABr) as template, and tetramethylammonium hydroxide (TMAOH) as mineralizer. These reactants were mixed according to the following molar composition: $0.26\mathrm{TMAOH} : 0.18\mathrm{CTMABr} : 0.05\mathrm{Ln_2O_3} : 1.0\mathrm{SiO_2} : 0.11\mathrm{Na_2O} : 27.5\mathrm{H_2O}$ (Ln = La or Ce). The procedure used involved the following steps [18]: (i) preparation of a mixture from sodium hydroxide solution and CTMABr, and its aging for 15 min; (ii) preparation of a mixture from sodium silicate and TMAOH, and its aging for more 15 min. The mixture (i) was added to (ii) and homogenized. The resulting gel was divided into two parts: one of them was added to lanthanum chloride, and to the other one, cerium chloride. The gels were aged for 30 min, loaded into PTFE-lined autoclaves, and heated without stirring at 140°C for 48 h. After cooling to room temperature, the resulting solid products were recovered by filtration, washing with deionized water and drying at 100°C for 1 day. The samples were calcined at 500°C for 2 h in nitrogen flowing at 100 ml/min, and later for 4 h in flowing air, at the same flow rate. The calcination temperature was reached at a heating rate of 5°C/min.

Atomic absorption analysis revealed the presence of lanthanides in the chemical composition of the resulting materials. X-ray diffraction (XRD) analysis taken in the 2θ-range from 1 to 12° gave typical pattern for the MCM-41 [18].

2.2. Nitrogen adsorption

Nitrogen adsorption measurements were carried out at −196°C using a model ASAP 2010 volumetric adsorption analyzer Micromeritics (Norcross, GA). The samples (ca. 0.1 g) were loaded into a special sample tube and degassed at 200°C for 2 h using the degas port of the instrument. Adsorption measurements were carried out over a relative pressure range from ca. 10^{-6}–0.995. The specific surface area was determined according to the standard Brunauer–Emmett–Teller (BET) method [19], and total pore volume was evaluated by the single point method [20]. The α_s-plot method was employed to assess microporosity of the samples as well as to estimate the volume of primary mesopores and the surface area of the secondary mesopores [6,8].

2.3. Thermogravimetric measurements

Thermogravimetric experiments were carried out using a Model TGA 2950 high-resolution thermogravimetric analyzer from TA Instruments (New Castle, DE). The HR-TGA instrument is equipped with an open platinum pan and an automatically programmed temperature controller. In order to remove the physically adsorbed species, about 0.01 g of the sample was loaded into the TGA pan and heated in the thermobalance up to 300°C at the maximum heating rate of 5°C/min in flowing nitrogen of 60 ml/min. Next, the furnace was cooled slowly with flowing nitrogen until room temperature was reached and then the sample was immersed with *n*-butanol and quickly loaded to the TGA instrument. After closing the furnace and allowing equilibration of the sample for 15 min the *n*-butanol thermodesorption was measured up to 300°C at the maximum heating rate of 5°C/min and nitrogen flow of 60 ml/min. The sensitivity and resolution parameters were 6 and 4, respectively [14,15].

3. Results and discussion

Nitrogen adsorption isotherms measured on the La- and CeMCM-41 samples studied are shown in Fig. 1. These isotherms exhibit the shape typical for MCM-41 materials. As can be seen in Fig. 1, the hysteresis loop is more pronounced for the CeMCM-41 sample in comparison to that for LaMCM-41. The mesopore volumes and specific surface areas evaluated from nitrogen adsorption isotherms for both samples studied are summarized in Table 1. The specific surface areas are smaller in comparison to those reported for purely siliceous MCM-41 materials [6,8]. It seems that the introduction of a heteroatom into the MCM-41 structure might decrease its surface area. The surface area of the CeMCM-41 sample is higher than that for LaMCM-41. This could be expected if one considers that La seems to be in the state(III) in the MCM-41 framework, while Ce appears to be in the oxidation state(IV) [18]. The ionic radius of La^{3+} (1.15 Å) is higher than that of Ce^{4+} (1.01 Å). Also, the difference in the pore volumes for both materials favors the CeMCM-41 structure.

The HR TGA data for *n*-butanol thermodesorption were recorded in order to evaluate the mesopore volume and specific surface area of the samples studied. The TGA curve plotted as a function of temperature is shown in Fig. 2 for both samples immersed in *n*-butanol. As can be seen in this figure there is a substantial mass loss around 40°C, which reflects the evaporation of the bulk (excess) *n*-butanol, followed by subsequent thermodesorption of *n*-butanol from the interior of mesopores as well as their walls. The TGA curves for both samples are similar and exhibit two steps, which are clearly visible on the DTG curves plotted as a function of time (see Figs. 3 and 4). The first of these steps, located between 40–60°C, reflects thermodesorption of *n*-butanol from the

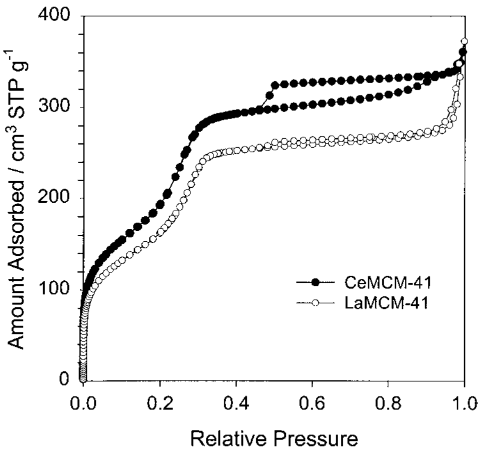

Fig. 1. Nitrogen adsorption isotherms for lanthanide-incorporated MCM-41 materials.

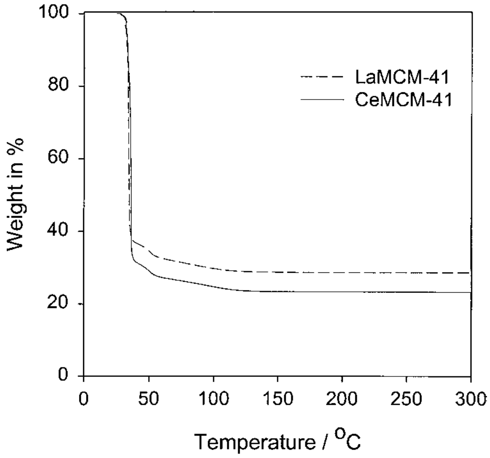

Fig. 2. The TGA curves as functions of temperature for lanthanide-incorporated MCM-41 samples immersed with *n*-butanol. The mass of the *n*-butanol-immersed sample recorded at the starting time of the TGA measurement was assumed as 100%.

Table 1

The volumes of primary mesopores and the specific surface areas obtained from the TGA *n*-butanol thermodesorption and nitrogen adsorption data for the LaMCM-41 and CeMCM-41 samples

Parameter	Method	LaMCM-41	CeMCM-41
Surface area (m^2/g)	N_2 adsorption, BET, 0.04–0.2 p/p_o	590	699
Surface area (m^2/g)	N_2 adsorption, BET, 0.003–0.03 p/p_o	468	550
Surface area (m^2/g)	*n*-butanol, HR TGA	447	545
Pore volume (cm^3/g)	N_2 adsorption, α_s-plot analysis	0.37	0.40
Pore volume (cm^3/g)	*n*-butanol, HR TGA	0.37	0.45

interior of mesopores, which is followed by gradual thermodesorption of this adsorbate from the mesopore walls occurring between ca. 60 and 140°C. Thus, the TGA thermodesorption data recorded in this range can be used to evaluate the mesopore volume and the specific surface area of the samples studied. Since during high-resolution TGA the heating rate is automatically adjusted, i.e., temperature is not a linear function of time, the time-dependent TGA curves are more convenient to identify the characteristic points related to the total adsorption capacity and monolayer capacity, which can be converted to the mesopore volume and specific surface area, respectively.

As can be seen in Figs. 3 and 4, the DTG curves plotted against time show a local minimum (denoted by a) and a shoulder (denoted by b). The projection of this minimum on the TGA curve gives the mass, which after subtraction of the residue value, is equal to the adsorption capacity. This value, after expressing it in moles of thermodesorbed *n*-butanol per gram of the sample and multiplying by the molar volume of liquid *n*-butanol, gives the mesopore volume. The projection of the b-point on the TGA curve gives the monolayer capacity, which can be converted to the specific surface area of the sample assuming that the cross-sectional area of *n*-butanol molecule is known. The molar volume of 98.7 cm^3/mol and the cross-sectional area of 40×10^{-20} m^2/molecule were used for *n*-butanol to calculate the mesopore volume and specific surface area of the samples studied (see Table 1). As can be seen in this table, the volume of primary mesopores evaluated from the TGA thermodesorption data for *n*-butanol and that obtained from nitrogen adsorption data agree very well.

As regards the comparison of the surface areas, the value obtained by the TGA method is close to the BET surface area evaluated from nitrogen adsorption data in the 0.003–0.03 range of relative pressures. The

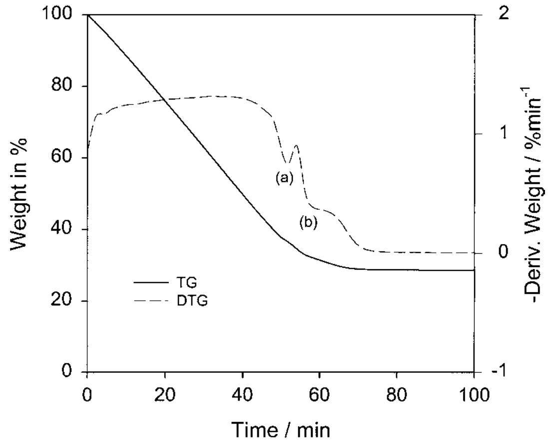

Fig. 3. The TGA and DTG curves as functions of time for the LaMCM-41 sample immersed in *n*-butanol.

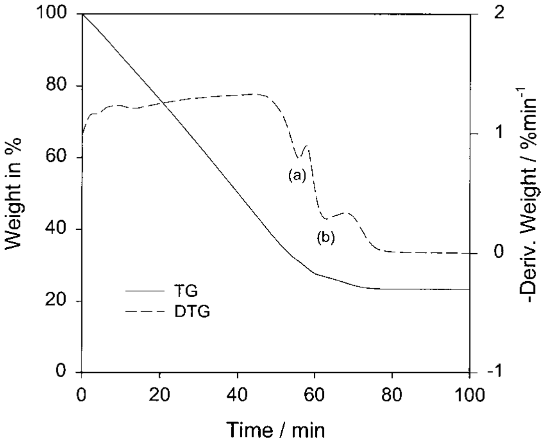

Fig. 4. The TGA and DTG curves as functions of time for the CeMCM-41 sample immersed in *n*-butanol.

agreement is worse for the surface area evaluated from nitrogen adsorption data in the pressure range typical for the standard BET method [21]. Thus, our TGA data indicate that the standard BET method overestimates the specific surface area for mesoporous silicas. A similar conclusion was drawn on the basis of detailed gas adsorption of good quality MCM-41 materials [22].

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