Thermoporosimetry of n-alkanes for characterization of mesoporous SBA-15 silicas – Towards deeper understanding the effect of the probe liquid nature

D. Majda [a, *], K. Tarach [a], K. Góra-Marek [a], A. Michalik-Zym [b], B.D. Napruszewska [b], M. Zimowska [b], E.M. Serwicka [b]

[a] Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland
[b] Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Niezapominajek 8, 30-239 Kraków, Poland

ABSTRACT

Thermoporosimetry (TPM), based on DSC measure melting point depression of n-alkane confined in mesopores, can provide very useful information about the porous properties of studied material as long as the obtained results are well understand and described. In this paper we reported original and detailed results concerning the nature of the alkanes confined inside the channels of a series of mesoporous SBA-15 silicas, differing by size of the unit cell. The complex character of pore size distribution profiles, known from our earlier works, was investigated and finally evaluated. For the first time the impact of such factors as solid to liquid mass ratio, the degree of pore cover and freezing time on the n-alkane TPM results was explained. Additionally, the even-odd effect on alkane TPM was evaluated. Based on FT-IR investigations the interactions between the probe molecules and the pore walls were found to be negligible.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

A comprehensive characterization of nanoporous materials, with regards to porosity, pore size distribution, surface area and pore volume, is important because these materials offer a wide range of potential application (e.g. catalysis [1], adsorbents [2], electronics [3], drug delivery [4,5] or medical diagnostics [6]). Although development of various experimental techniques, such as gas sorption, X-ray diffraction, neutron scattering, mercury porosimetry or electron microscopy allows performing pore size analysis over the micro/mesopore size range [7 and references therein], none of these approaches can be considered the absolute one and used without reflection on the hypotheses and assumptions hidden in its background. Even the quite recently developed method based on Non-Local Density Functional Theory (NLDFT) is not free of disadvantages. It is a reliable tool for characterization of ordered materials, but not for ones with chemically functionalized surfaces, because it does not take into account the chemical and geometrical

heterogeneity of pore walls. Moreover, the application of NLDFT is useful and leads to accurate results only if the given experimental system is compatible with the one chosen for NLDFT kernel [7].

A promising alternative method for studying porosity is known as thermoporosimetry (TPM). TPM has been known since the works of Thomson [8,9], but it is still not well recognized and developed. It is based on the fact that a fluid confined in the pores of a solid material experiences an important shift of its liquid to solid transition temperature (ΔT) and this shift is related to the size of the pores, in which the liquid is trapped [10], according to the Gibbs–Thomson equation. Differential Scanning Calorimetry (DSC) is a technique proposed in 1955 by Kuhn et al. [11,12] to measure ΔT. He discovered that soaking the porous material in the liquid and measuring the melting or crystallization profiles by DSC is enough to perform the porosity characterization. Moreover, it turned out that application of this technique is very simple, fast, inexpensive and nondestructive.

Although several liquids have been used to probe porous properties (e.g. benzene [13], acetonitrile [14], carbon tetrachloride [15], acetone [16]), it is water and n-alkanes that appear to carry a particular potential. Water, with large heat of fusion enhances the sensitivity of the DSC technique and allows decreasing the size of

* Corresponding author. Tel.: +48 12 663 22 03.
 E-mail address: majda@chemia.uj.edu.pl (D. Majda).

studied samples [17]. Moreover, it is the unique liquid for examining the hydrated materials which can collapse during drying. On the other hand the effect of specific interaction between polar molecules of water and the porous solid remains unknown and may lead to erroneous interpretation of DSC signals. Alkanes, with non-polar molecules which, in inorganic solids, should mitigate surface–fluid interactions, seem to be very attractive alternative to water-TPM. In addition, they may also reveal differences in surface chemistry of the porous materials thanks to the variation in their molecular size [18,19]. In our past work we repeatedly appreciated the advantages of various alkanes for study porosity of zeolites [20–22] or of mesoporous silicas [23]. In the particular we reported important differences in the behaviour of odd and even-numbered alkanes in TPM experiments carried out on a series of ordered mesoporous SBA-15 silicas, differing by the hexagonal unit cell parameter *a*. Those phenomena were tentatively attributed to different packing of alkane molecules in the solidified state [24]. However, to get deeper insight into these effects the further refinement of the n-alkane TPM method was needed first. Thus, in our previous paper [25] we focused on examining the influence of various parameters on the TPM results, which led to the optimization of experimental protocols and allowed establishing reliable calibration equations. We selected short-length alkanes, n-hexane, n-heptane and n-octane, for practical reasons: it is impossible to use n-pentane because its melting temperature is beyond the temperature range of typical DSC instrument, and n-nonane displays complex phase transition behaviour due to the formation of so-called "rotator" state [26]. Our experiments revealed that the value of pore diameter obtained from n-hexane and n-octane -TPM strongly depend on the liquid to solid mass ratio (l/m) and only for n-heptane-TPM the PSD profiles are relatively narrow, uniform, and almost independent of the l/m. Moreover, the peak positions of PSDs derived from nC6 or nC8-TPM were shifted toward higher pore size values when l/m decreases and sometimes exhibits complex character, with two well separated maxima. We concluded that n-heptane is the most proper for alkane-TPM but the questions of the reasons making the other hydrocarbons inadvisable remained unanswered.

The aim of current work was a detailed study on the physicochemical properties of the alkanes confined inside the channels of a series of mesoporous SBA-15 silicas, differing by size of the unit cell, in order to provide a wider overview of the effects observed previously and responsible for n-alkane-TPM results. Thus, this work should be treated as "part 2" of the results published recently under title: "Thermoporosimetry of n-alkanes for characterization of mesoporous SBA-15 silicas – refinement of methodology" [25].

2. Experimental

The sample preparation was described in detail in our previous paper [25]. Herein, we focused on five SBA-15 silicas (M1, M4, M5, M6 and M7) for which the differences in pore size were the most significant. In order to keep this report compatible with the previous one the samples names were left unchanged.

Prior to the TPM measurements, the SBA-15 silicas were characterized by small angle X-ray diffraction, electron microscopy (SEM/TEM) and low temperature N_2 adsorption, also described previously. Additionally, in current study FT-IR technique was used to check the influence of the silanol groups presented in internal surface of SBA-15 on the TPM results.

The FT-IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a MCT detector with the spectral resolution of 1 cm^{-1}. Prior to FT-IR studies, all studied materials had been pressed into the form of self-supporting discs (ca. 4–7 mg/cm^2), weighted and pre-treated in situ in a home-made quartz IR

cell at 350 °C under vacuum conditions for 30 min. All the spectra presented in this work were normalized to 10 mg of sample.

Interaction of hydrocarbons with siliceous SBA-15 materials was tracked by the recording the spectra at room temperature. After reaction of all silanol groups with probe molecules, evidenced as vanishing of ca. 3750 cm^{-1} band, the IR cell with hydrocarbon gas phase (20 Trr) were gradually cooled down. The FT-IR spectra were taken in temperature scale, down to −170 °C with the step of 5 °C.

3. Results and discussion

The XRD patterns, SEM/TEM images and the low temperature N_2 adsorption–desorption isotherms (type IV with H1-type hysteresis loops, with exception to M1 with H1/H2) as well as the pore size distribution profiles obtained from NLDFT model were already published in our previous papers [24,25] and are additionally available as Supplementary materials. Briefly, XRD and SEM/TEM experiments confirmed the presence of well-ordered hexagonal symmetry in all studied samples. Moreover, TEM images show parallel channels of dimensions increasing when passing from M1 to M7 samples. The pore size distributions as well as other porosity parameters obtained from N_2 isotherms are in agreement with typical characteristics expected for SBA-15 silicas. In Table 1 porosity parameters of studied materials derived from N_2 adsorption and XRD patterns were collected. Most of the results presented therein were already reported [25]. The exceptions are the values of surface area now based on NLDFT calculations and lattice constant.

DSC profiles of solid to liquid phase transition of n-hexane, n-heptane and n-octane confined in one of the studied SBA-15 silicas (M7) are shown in Fig. 1a. The first endothermic peaks correspond to the melting of the solid confined in the pores (p) while the second ones result from the melting of the probe outside the pores (b). It was impossible to measure the melting enthalpy of n-hexane frozen inside the pores of M1 because of the DSC apparatus limitation.

The shift in the melting point of a solid confined in the pores is inversely proportional to the radius of the pore in which it is confined. The biggest ΔT reflect smallest pore size. It is clearly seen from Fig. 1b–d that pore dimensions increase from M1 to M7 samples. The sample defined as M6 seem to have almost the same pore diameter as M7. The same tendency is observed independently on the nature of alkane confined inside the pores of studied silicas. Noteworthy, while the DSC profiles of n-hexane and n-heptane phase transition are characterized by single maxima for all studied systems, one of n-octane, recorded for sample M4, exhibit slightly bimodal character.

In our recent paper [25] we concluded that n-heptane is the most proper for alkane-TPM, because the data obtained from n-hexane and n-octane -TPM strongly depend on the experimental conditions. In order to understand what factors make the alkane advisable or inadvisable for TPM experiments, in the present work we compare the PSD profiles obtained for C_6, C_7 and C_8 n-alkanes

Table 1
Structural (XRD) and textural (N_2 adsorption–desorption isotherm) parameters of investigated SBA-15 samples. S - specific surface area, V_{cum} – cumulative pore volume, V_{mic} – micropore volume, D – pore diameter, d_{100} - basal spacing, a – lattice constant.

Sample	N2				XRD	
	t plot	NL-DFT				
	V_{mic} [cm^3/g]	S [m^2/g]	V_{cum} [cm^3/g]	D [nm]	d_{100} [nm]	a [nm]
M1	0.065	787	0.58	5.1	8.8	10.2
M4	0.048	876	1.01	8.1	10.5	12.1
M5	0.005	781	1.22	9.1	11.1	12.8
M6	0.000	416	1.15	10.5	11.3	13.0
M7	0.000	396	1.14	11.3	11.3	13.0