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

Maria Mańko, Barbara Gil, Rafał Janus, Piotr Kuśtrowski, Wacław Makowski*

Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

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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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* Corresponding author. Tel.: +48 12 6632245; fax: +48 12 6340515.
E-mail address: makowski@chemia.uj.edu.pl (W. Makowski).

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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.

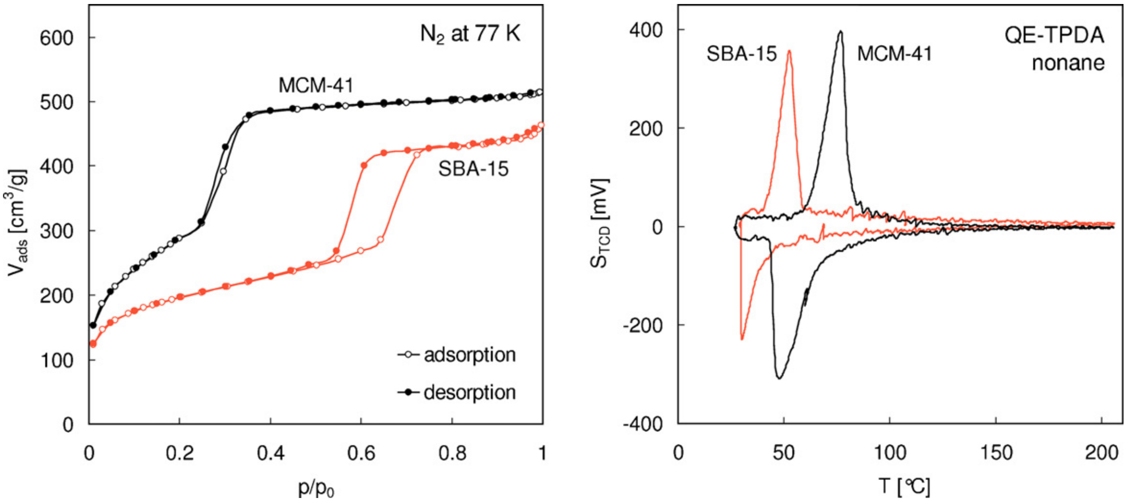

Fig. 1. Low temperature N_2 adsorption isotherms and the QE-TPDA profiles of n-nonane on MCM-41 and SBA-15 silicas, measured at 2 °C/min for partial pressure of nonane of 4.0 and 3.9 mbar, respectively.

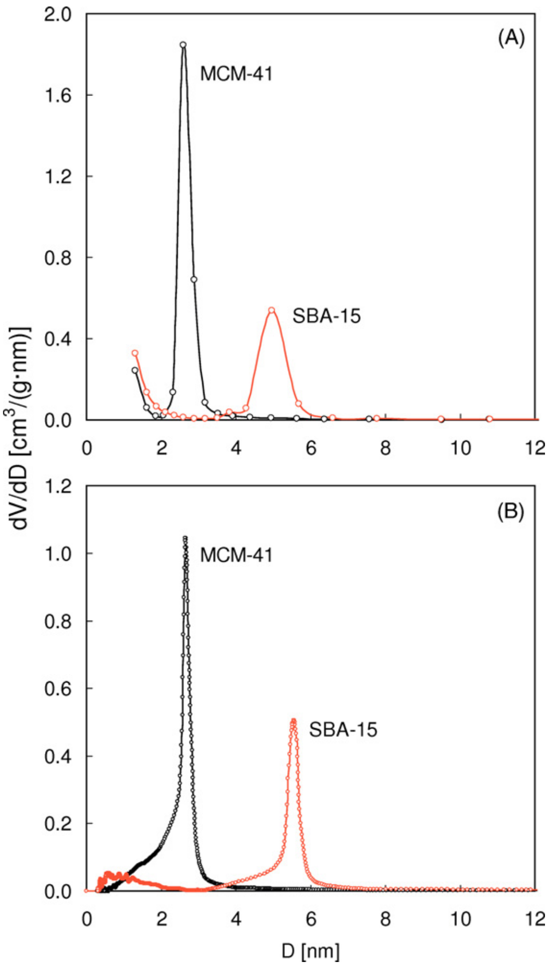

Fig. 2. Comparison of the pore size distributions determined from the N_2 desorption isotherms (A) and the QE-TPDA profiles of n-nonane (B).

Moreover, the isotherm with no hysteresis loop for the narrow pore MCM-41 material confirms that the pores in this silica are perfectly cylindrically shaped [16]. The QE-TPDA profiles of n-nonane are also representative for the mesoporous silicas [5,6]. The maxima observed in these profiles correspond to desorption of n-nonane from the mesopores during heating, and the minima – to its adsorption while cooling. A saw-tooth shape of the desorption peaks, with almost straight leading edge, confirm uniform size of the mesopores. Different positions of the desorption maxima (53 °C for SBA-15 and 77 °C for MCM-41) result form differences in the mesopore size of the studied silicas – the lower the pore size, the higher the desorption temperature.

In Fig. 2 the BJH pore size distributions (PSDs), calculated from the N_2 desorption isotherms, are compared with the PSDs obtained from the thermodesorption profiles of n-nonane, using the modified BJH approach [6]. As far as their shape, intensity and positions of the maxima are concerned, the corresponding PSDs show quite good agreement. The sizes found using both methods for MCM-41 (cf. Table 1) are practically the same (2.6 nm). The mesopore size of 5.6 nm found for SBA-15 from n-nonane thermodesorption data seems slightly overestimated. However, the value of 5 nm calculated form the N_2 isotherm is not very precise, as the pressure increments/decrements used in the adsorption measurements were not very small. The PSDs obtained from the thermodesorption profiles are more precise, since they are calculated from numerous experimental data points recorded in one measurement. This high precision is reflected by lower width of the peaks present in these PSDs.

3.2. QE-TPDA of butanol

The QE-TPDA profiles of 1-butanol on MCM-41 and SBA-15 are presented in Fig. 3A. The profiles observed for the alcohol slightly differ from those obtained for n-nonane. They are dominated by the low temperature maxima (for SBA-15 at 48 °C and for MCM-41 at 59 °C) that should be attributed to desorption from the mesopores. However, an additional broad peak or shoulder above 70 °C may be noticed. This part of the thermodesorption profile corresponds to desorption of the molecules adsorbed on the silica surface. Presence of the maximum in this range of the QE-TPDA profile indicates special stabilization of the adsorbed 1-butanol molecules, most probably resulting from their specific interactions with the OH groups on the silica surface.

As the silanol groups are not stable at high temperatures and may be changed upon thermal activation, the fresh silica samples were also studied. The mesoporous silicas MCM-41 and SBA-15 are quite hydrophobic, so it is possible to remove most of the physisorbed water from their surface just by purging with He at room temperature. The QE-TPDA profiles of 1-butanol for a fresh sample of MCM-41 obtained in consecutive cycles reveal changes of the studied material upon heating (Fig. 3B). Differences in the shape of the desorption–adsorption profiles between the subsequent cycles were observed. The profile observed in the last (10th) cycle is quite similar to the QE-TPDA profile of n-nonane. With every desorption–adsorption cycle an increase in the intensity of the low temperature desorption peak is observed, indicating gradual increase of the mesopores' core volume. On the other hand, the intensity of the broad maximum above 70 °C, which corresponds to desorption of the molecules specifically adsorbed on the silica surface, is decreasing with following adsorption–desorption cycles, most probably due to thermal degradation of the surface silanols.

3.3. Effect of the hydrothermal treatment on the porosity of the studied silicas

In order to find out if the high temperature desorption peaks observed in the QE-TPDA profiles of 1-butanol may be attributed to interactions of the adsorbed molecules with the surface silanol groups, both mesoporous silicas modified by 1 h boiling in distilled water were studied. Such hydrothermal treatment should lead to partial hydrolysis of the siloxane bridges and formation of the silanol groups on the silica surface.

Table 1
Values of the porosity parameters determined from N_2 adsorption isotherms and the QE-TPDA profiles of n-nonane and 1-butanol. All the pore volumes were calculated assuming density of the adsorbate equal to that of the liquid.

Material	S_{BET} (m²/g)	D_{meso} (nm)		V_{meso} (cm³/g)	V_{core} (cm³/g)		V_{film} (cm³/g)	
	N_2	N_2	C_9H_{20}	N_2	C_9H_{20}	BuOH	C_9H_{20}	BuOH
MCM-41	1051	2.59	2.65	0.66	0.53	0.35	0.043	0.11
MCM-41-M	–	–	2.39	–	0.37	0.23	0.071	0.28
SBA-15	693	4.96	5.55	0.58	0.34	0.43	0.13	0.18
SBA-15-M	457	5.51	5.97	0.70	0.44	0.21	0.065	0.14

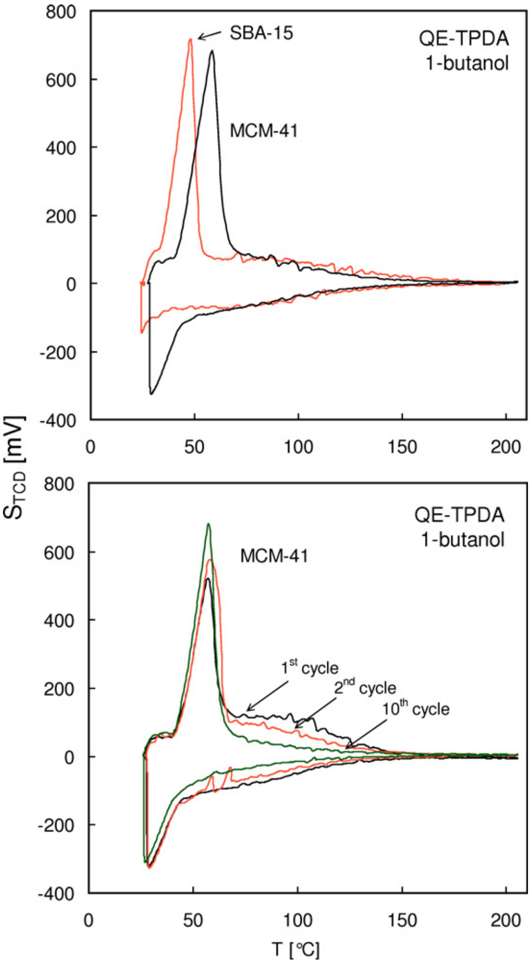

Fig. 3. The QE-TPDA profiles of 1-butanol on MCM-41 and SBA-15, measured at 4 °C/min for partial pressure of 1-butanol of 6.3 and 4.5 mbar, respectively (A). Evolution of the QE-TPDA profiles of 1-butanol obtained in consecutive cycles for MCM-41, without its previous activation, measured at 4 °C/min and partial pressure of 1-butanol of 5.6 mbar (B).

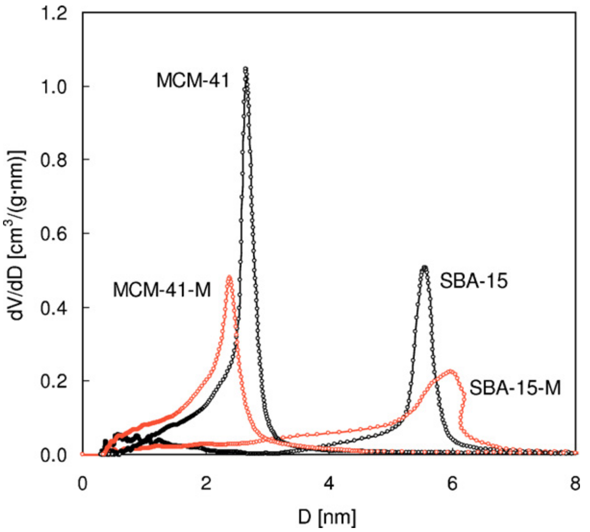

Fig. 5. Comparison of the pore size distributions of the non-modified and modified silicas determined from the QE-TPDA profiles of n-nonane.

Porosity of the modified silicas MCM-41-M and SBA-15-M was characterized by QE-TPDA of n-nonane. The resulting thermodesorption profiles are similar in shape to those found for the non-modified materials (Fig. 4). For MCM-41 a considerable decrease in the mesopore volume upon boiling may be noticed, indicated by lower intensity of the profile found for MCM-41-M. The result of hydroxylation is an increase of the silica density and decrease of sorption capability [17]. For SBA-15 practically no change of the intensity of the main peak was observed, but the high temperature part of the profile of the modified sample approached faster the baseline level.

The pore size distributions calculated from QE-TPDA profiles of n-nonane for the modified and non-modified silicas are compared in Fig. 5. It may be noticed that the hydrothermal treatment resulted in deterioration of the mesoporous structure, since the peaks in the PSDs obtained for the modified materials became broader and less intensive. However, the mesopore diameters were only slightly changed – for SBA-15 it increased from 5.6 to 6.0 nm, while for MCM-41 it decreased from 2.7 to 2.3 nm.

3.4. Effect of the hydrothermal treatment on the QE-TPDA profiles of 1-butanol

The QE-TPDA profiles of 1-butanol obtained for the modified and non-modified silicas are compared in Fig. 6. Major differences may

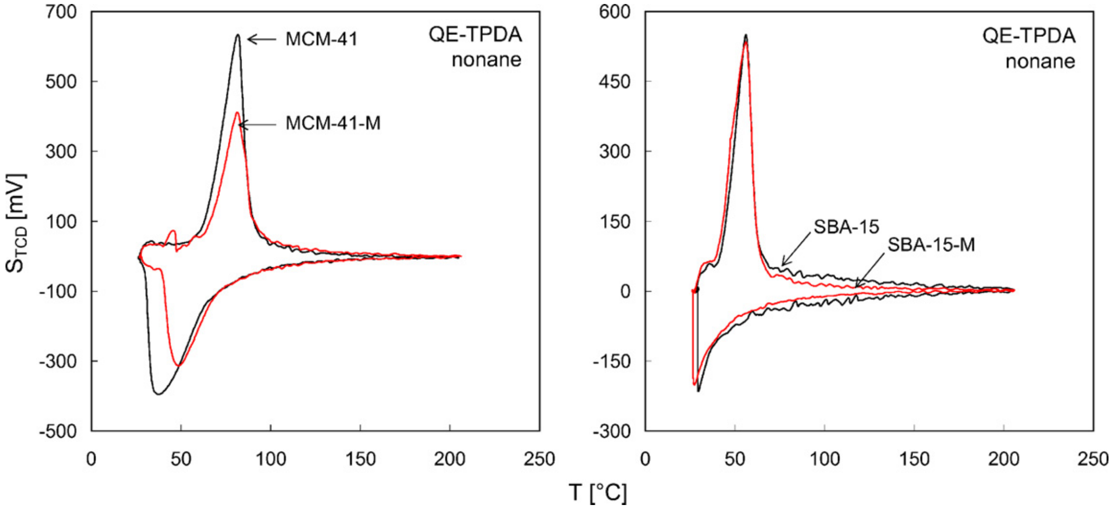

Fig. 4. Comparison of he QE-TPDA profiles of n-nonane for the modified and non-modified silicas, measured at 4 °C/min for partial pressure of nonane equal to 4.0 mbar (MCM-41), 3.8 mbar (MCM-41-M), 3.9 mbar (SBA-15) and 3.7 mbar (SBA-15-M).

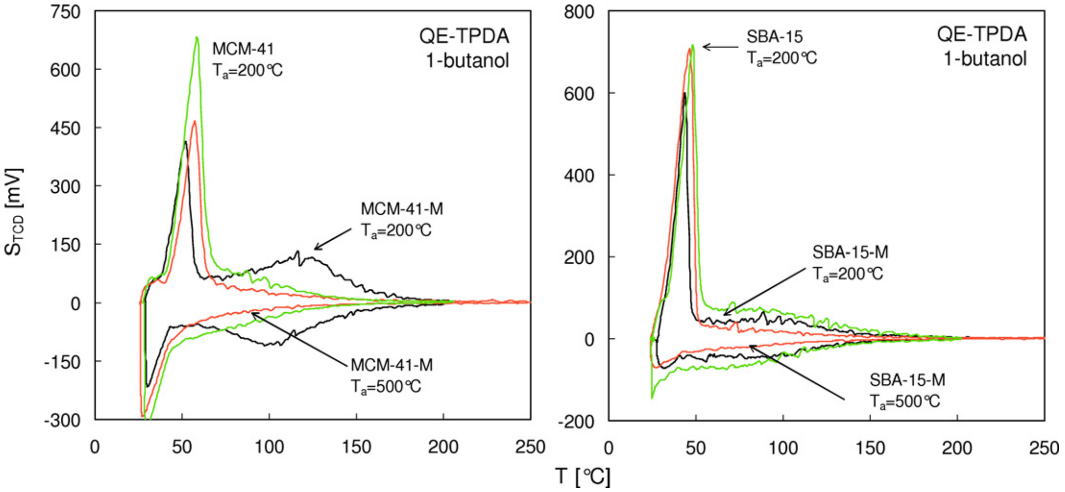

Fig. 6. Comparison of the QE-TPDA profiles of 1-butanol on the non-modified silicas after activation at 200 °C and the modified ones after activation at 200 and 500 °C, measured at 4 °C/min for partial pressures of 1-butanol equal to 6.3 mbar (MCM-41, 200 °C), 5.5 mbar (MCM-41-M, 200 °C), 6.4 mbar (MCM-41-M, 500 °C), 4.5 mbar (SBA-15, 200 °C), 6.6 mbar (SBA-15-M, 200 °C) and 5.0 mbar (SBA-15-M, 500 °C).

be noticed for the modified materials activated at different temperatures. For MCM-41-M after activation at 200 °C additional high temperature desorption maximum and adsorption minimum are present at about 117 and 98 °C, respectively. These peaks disappear completely after activation of the modified sample at 500 °C. The QE-TPDA profile of 1-butanol becomes then very similar to that of n-nonane. Lower intensity of the main peak observed at 51–57 °C for the modified MCM-41 confirms decrease of the mesopore volume upon the hydrothermal treatment.

For SBA-15-M activated at 200 °C the additional desorption peak (with the maximum at 90 °C) is also present, but its intensity is lower than in the case of MCM-41-M. It is even lower than for the non-modified material. High temperature activation of SBA-15-M results in further decrease of the QE-TPDA profile in the temperature range of 70–200 °C.

3.5. IR studies of the silanol groups in the modified and non-modified silicas

The IR spectra of O-H stretching vibration recorded after activation of the silica samples at different temperatures are show in Fig. 7. Prior to the measurements the samples were formed into self-supporting pellets and dehydrated under vacuum at room temperature. The spectra were measured, after heating the sample at different temperatures for 20 min and cooling down to 100 °C, so all the spectra are recorded at the same temperature. The spectra contain a broad band at 3500 cm^{-1}, related to the silanol groups interacting by the hydrogen bonds, and the sharp band at 3750 cm^{-1}, which should be attributed to the isolated terminal silanols [11]. As the activation temperature increases, the band of the H-bonded silanols gradually decreases while the band of the terminal silanols increases. The IR results indicate that it is the H-bonded –OH groups that are responsible for the enhanced high temperature thermodesorption of 1-butanol. Comparison of the spectra obtained for the modified and non-modified silicas corroborates this conclusion. After the hydrothermal treatment of the content of the hydrogen-bonded silanols increases considerably for MCM-41, but slightly decreases for SBA-15. Similar effect was observed in thermodesorption of 1-butanol.

4. Discussion

The parameters characterizing porosity of the studied silicas, determined from N_2 adsorption isotherms as well as the thermodesorption profiles of n-nonane and 1-butanol, are compared in Table 1. V_{meso} was calculated from N_2 adsorption data as the cumulative desorption BJH volume (1.7–30 nm). V_{core} and V_{film} were obtained by integrating the low and high temperature peaks (or shoulders) in the desorption part of the QE-TPDA profiles, respectively.

Values of the parameters obtained from the QE-TPDA profiles of n-nonane reproduce well the trends reported earlier [6]: the pore sizes are slightly larger and the pore volumes are somewhat smaller that the corresponding parameters calculated form the N_2 adsorption data. However, relatively low accuracy in determination of the sample mass in the QE-TPDA measurement is a major contribution of the uncertainty of the pore volume. Additional source of the experimental error is the calibration constant, reflecting proportionality of the detector signal to the concentration of the adsorptive in the carrier gas. Judging by reproducibility of the results, the overall relative uncertainty of the pore volume may be estimated at about 5–10%.

Changes of the porosity parameters resulting from the hydrothermal treatment are in agreement with data reported earlier by Galarneau et al. [18]. Decrease of the mesopore size and volume observed for MCM-41 may be explained by dissolution of silica at the pore openings and its deposition in an amorphous form on the inner surface, accompanied by shortening of the mesopores. In the case of SBA-15 the opposite effect was observed – both the mesopore size and volume increased upon the hydrothermal treatment. For this type of mesoporous silica, characterized by thicker walls and rougher surface comprising micropores, another mechanism of interaction with water was proposed [18]. Dissolution of the surface irregularities and deposition of silica within the pores leads to smoothing of the mesopore surface, which is evidenced by decrease of the high temperature part of the QE-TPDA profile of n-nonane for SBA-15-M.

Although values of the pore core volume determined from the QE-TPDA profiles of 1-butanol are similar to those calculated from n-nonane thermodesorption, there are some significant differences between them. It is surprising that the core volume obtained from thermodesorption of 1-butanol is clearly larger for SBA-15 than for MCM-41. This may indicate differences in packing of the molecules of n-nonane and 1-butanol confined in the mesopores, depending on their size.

Considerably higher volumes quantifying the molecules adsorbed on the silica surface (V_{film}), obtained form thermodesorption profiles of 1-butanol, reflect specific interactions of the polar

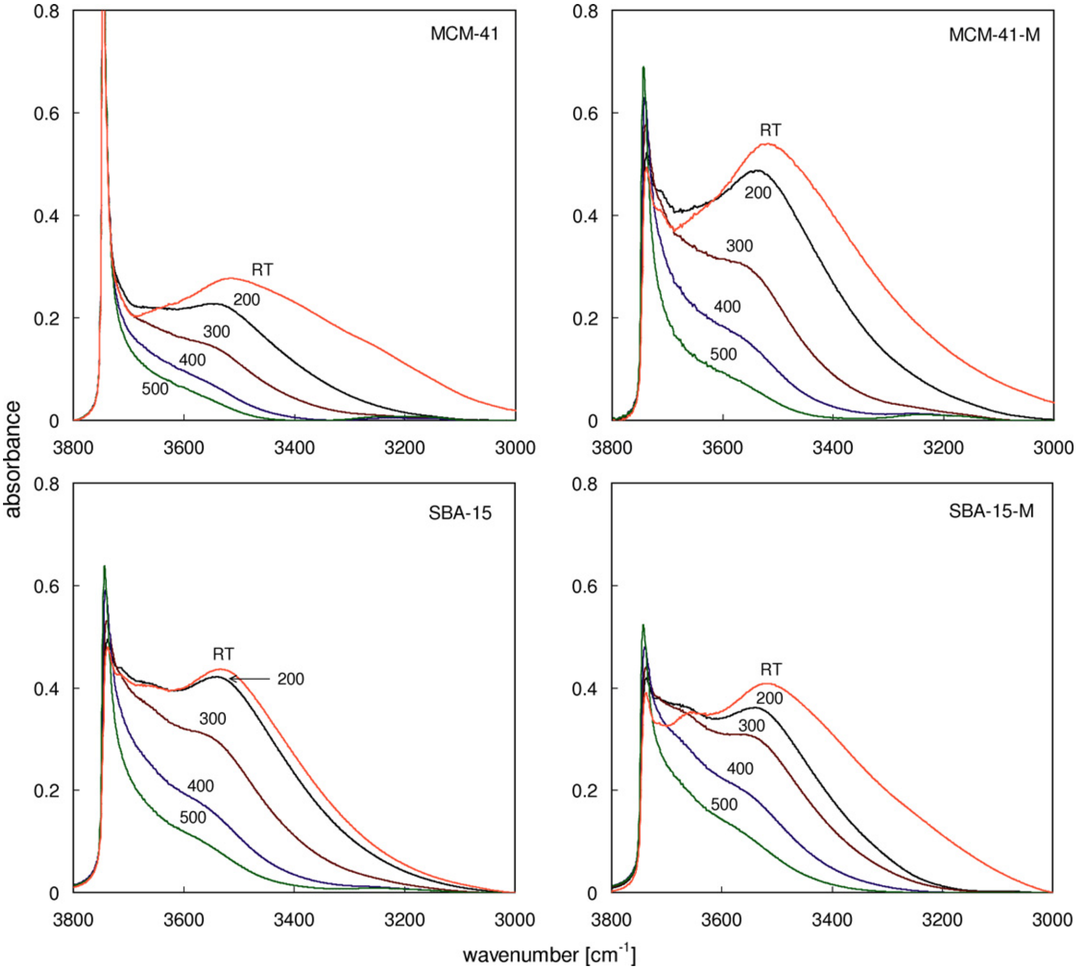

Fig. 7. Temperature evolution of the IR spectra of the non-modified and modified silicas in the 3800–3000 cm^{-1} silanol group range. The first spectrum in each series (RT) was measured at room temperature after 20 min evacuation. All the other spectra were recorded at room temperature, after heating the sample under vacuum at the indicated temperature for 20 min, and cooling it down.

molecules with the H-bonded surface silanols. The fact that the adsorbed alcohol molecules are more strongly retained on the surface of MCM-41-M indicates differences between the silanol groups in the studied silicas after the hydrothermal treatment. It is possible that in MCM-41-M they are located on the surface of the amorphous silica formed by partial degradation of the porous structure, while in SBA-15-M they are present on the inner surface of the mesopores. It is worth noticing that these differences were not observed by IR spectroscopy.

5. Conclusions

The results obtained in this work indicate that the quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA) of 1-butanol is a good method for studying the surface of mesoporous silicas and it completes well the QE-TPDA of n-nonane, developed earlier for characterization of their porosity. Apart from determination of the mesopore volume, it reveals presence of the hydrogen-bonded silanols on the silica surface, formed by its interaction with water molecules. Such interpretation of the high temperature desorption peaks of 1-butanol was confirmed by the IR measurements of the OH stretching vibrations.

It has been shown that modification of MCM-41 silica by the hydrothermal treatment resulted in partial hydroxylation of siloxane bridges leading to formation of the surface silanols. This treatment also brought about degradation of its porous system by changes of the mesopore size and volume. For SBA-15 smaller changes of the surface and porosity upon the hydrothermal treatment were observed.

This work has confirmed that the QE-TPDA technique is a good method for characterization of the porous materials. By monitoring of physisorption of non-polar molecules of n-alkanes it allows detection and characterization of the micropores and mesopores, giving results similar to those obtained from the standard low temperature N_2 or Ar adsorption isotherm measurements. Unlike the latter method, the QE-TPDA offers broader range of the substances to be used as the probe molecules. Thus polar compounds like 1-butanol may be applied for characterization of the surface functional groups, while bulky molecules of branched alkanes or substituted aromatic hydrocarbons may be used for probing size and shape of the micropores. Additional information concerning the pore morphology may be obtained from differences in packing of the adsorbed molecules, resulting from the balance of their lateral interactions and their interactions with the surface. Therefore, further work on development of this technique aimed at all these issues is planned.

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References

[1] F. Rouquerol, J. Rouquerol, K.W. Sing, in: F. Schüth, et al. (Eds.), Handbook of Porous Solids, Vol. 1, Wiley–VCH, Weinheim, 2002, pp. 236–275.
[2] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of porous solids and powders: surface area, pore size and density, Springer, Dordrecht, The Netherlands, 2006.
[3] W. Makowski, Thermochim. Acta 454 (2007) 26.
[4] W. Makowski, Ł. Ogorzałek, Thermochim. Acta 465 (2007) 30.
[5] W. Makowski, P. Kuśtrowski, Micropor. Mesopor. Mater. 102 (2007) 283–289.
[6] W. Makowski, L. Chmielarz, P. Kuśtrowski, Micropor. Mesopor. Mater. 120 (2009) 257.
[7] L.F. Giraldo, B.L. Lopez, L. Perez, S. Urrego, L. Sierra, M. Mesa, Macromol. Symp. 258 (2009) 129.
[8] K. Cassiers, T. Linssen, M. Mathieu, M. Benjelloun, K. Schrijnemakers, P. Van Der Voort, P. Cool, E.F. Vansant, Chem. Mater. 14 (2002) 2317–2324.
[9] F. Zhang, Y. Yan, H. Yang, Y. Meng, C. Yu, B. Tu, D. Zhao, J. Phys. Chem. B 109 (2005) 8723–8732.
[10] P. Smirnov, T. Yamaguchi, S. Kittaka, S. Takahara, Y. Kuroda, J. Phys. Chem. B 104 (2000) 5498–5504.
[11] J.P. Gallas, J.M. Goupil, A. Vimont, J.C. Lavalley, B. Gil, J.P. Gilson, O. Miserque, Langmuir 25 (2009) 5825.
[12] F. Di Renzo, A. Galarneau, P. Trens, F. Fajula, in: F. Schüth, et al. (Eds.), Handbook of Porous Solids, Vol. 3, Wiley–VCH, Weinheim, 2002, pp. 1311–1394.
[13] C. Setzer, G. van Essche, N. Pryor, in: F. Schüth, et al. (Eds.), Handbook of Porous Solids, Vol. 3, Wiley–VCH, Weinheim, 2002, pp. 1543–1585.
[14] P. Kumar, V.V. Guliants, Micropor. Mesopor. Mater. 132 (2010) 1–14.
[15] P. Kuśtrowski, L. Chmielarz, R. Dziembaj, P. Cool, E.F. Vansant, J. Phys. Chem. B 109 (2005) 11552–11558.
[16] C.G. Sonwane, S.K. Bhatia, N. Calos, Ind. Eng. Chem. Res. 37 (1998) 2271–2283, and the references therein.
[17] V. Kocherbitov, V. Alfredsson, J. Phys. Chem. C 111 (2007) 12906–12913.
[18] A. Galarneau, M. Nader, F. Guenneau, F. Di Renzo, A. Gedeon, J. Phys. Chem. C 111 (2007) 8268.