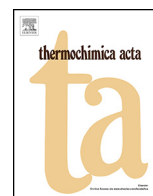




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Optimisation of thermoporometry measurements to evaluate mesoporous organic and carbon xero-, cryo- and aerogels

Petra Veselá^{a,b,*}, Joakim Riikonen^a, Tuomo Nissinen^a, Vesa-Pekka Lehto^a, Václav Slovák^b

^a Department of Applied Physics, Faculty of Wood and Forestry, University of Eastern Finland, Yliopistoranta 1F, Kuopio, Finland

^b Department of Chemistry, Faculty of Science, University of Ostrava, 30 dubna 22, Ostrava, 701 03, Czech Republic

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ABSTRACT

Thermoporometry (TPM) was used for characterisation of porous structure of organic and carbon materials (based on melamine or cellulose acetate) by examining melting behaviour of water inside the pores. Due to specific porous features (low pore volumes, broad distribution of mesopores and small macropores), an optimisation of TPM measurements by a sample pretreatment and adjustment of experimental parameters was necessary. Removing the soluble impurities before a TPM measurement was required as the impurities affected melting of water in the pores and thus also the calculated pore size distribution (PSD). Heating rate of $1\text{ }^{\circ}\text{C min}^{-1}$ was optimal for resolution and separation of the peaks originating from melting in the pores and in the bulk. The best ratio of water to a sample mass ranged from 4:14 for the samples with lower mesopore volumes ($\approx 0.1\text{ cm}^3\text{ g}^{-1}$) to 12:12 for the samples with higher volumes ($\approx 0.4\text{ cm}^3\text{ g}^{-1}$). A simple procedure without separation of the overlapping peaks was used for the assessment of pore volumes and PSDs. The results of TPM measurements are reasonably in agreement with the findings from nitrogen adsorption and SEM. Only supercritically dried organic aerogel was not measurable by TPM due to shrinkage of its porous structure after wetting.

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1. Introduction

TPM is a method which enables characterisation of the porous nanostructured materials. It is based on depression of melting/freezing temperature of a liquid entrapped in the pores, which is caused by the small size of crystals formed inside the pores. TPM provides some benefits in comparison with the methods commonly used for porosity characterisation, e.g., gas sorption (GS) or mercury intrusion porosimetry (MIP). TPM enables to study wet and soft materials (e.g., [1–3]), no extra pretreatment of a sample is usually needed, analysis is neither time nor money consuming and it can be performed with a common differential scanning calorimeter (DSC) without a need for a specific instrument. Moreover, TPM is known to be applicable both for mesopores and small macropores [4,5]. The lower limit of measurable pore sizes arises from the

temperature limit where solid–liquid transition disappears ($\approx 2\text{ nm}$ [5–7]), while the upper limit results from the temperature resolution that enables to distinguish the transitions that take place in the pores and in the bulk. For example, average pore diameter of a material with ca. 500 nm pores was determined using o-xylene, but PSD could not be obtained because of the overlapping peaks [5,8].

Many kinds of porous materials have been studied with TPM such as: mesoporous silica [6,9–12], controlled-pore glasses [4,13], porous alumina [7], polymeric materials [1,2,7], cellulose-based materials [3,14], cement-based materials [15] etc. TPM is often applied to samples with pore volumes over $0.4\text{ cm}^3\text{ g}^{-1}$ (e.g., [4,7,10,16]) while samples with lower volumes are not frequently studied. Furthermore, the samples typically studied by TPM technique, such as ordered mesoporous silica, have smaller pores with narrow PSD ($\approx 2\text{–}15\text{ nm}$ [6,9–12]). There are also studies of the controlled-pore glasses with very large pores (up to diameter $\approx 200\text{ nm}$) but those also have very narrow PSDs [4,13]. Only a few publications about TPM report studies on samples having broad PSD (e.g., [15,17]).

Materials with high pore volume, small pore size and narrow PSD are ideal for TPM. However, an analysis of materials with low

* Corresponding author at: University of Ostrava, 30 dubna 22, 701 03 Ostrava, Czech Republic. Tel.: +420 597 092 188.

E-mail addresses: petra.vesela@osu.cz (P. Veselá), joakim.riikonen@uef.fi (J. Riikonen), tuomo.nissinen@uef.fi (T. Nissinen), vesa-pekka.lehto@uef.fi (V.-P. Lehto), vaclav.slovak@osu.cz (V. Slovák).

pore volume, large pore size and/or wide pore size distribution is more complicated because it is often difficult to define the correct baseline for the melting/freezing peak and to separate the peak arising from the transition in the pores from the one arising from the transition in the bulk.

Organic and carbonaceous xerogels/cryogels/aerogels are a diverse group of the materials with various porous properties that strongly depend on conditions of polycondensation, drying and pyrolysis steps in their preparation. Polycondensation conditions and used precursors determine the initial character of the formed porous structure [18–23]. Subsequent drying can, in some cases, cause a collapse of the previously developed porosity [19,24]. Pyrolysis of the porous organic materials into the carbonaceous materials can either only maintain the already developed pores or also create new ones; moreover, it usually introduces micropores in the material [19,22,24].

Various pore structures of organic and carbonaceous xerogels/cryogels/aerogels have been reported. Some of them exhibit a narrow PSD with pore diameters from few nanometres to approximately 10 nm [16,20,21], but mostly they possess a wider PSD with larger pores (e.g., ≈ 10 –100 nm or even larger) [20–22]. The mesopore volumes of these materials, calculated from nitrogen GS measurements, range from almost negligible (e.g., $0.03 \text{ cm}^3 \text{ g}^{-1}$), up to very large volumes around $3 \text{ cm}^3 \text{ g}^{-1}$ [18,23,24]. TPM is not frequently used for organic and carbonaceous xerogels, cryogels or aerogels in the literature. To our best knowledge, there are only two articles in which TPM has been used for studying the analogous resorcinol and formaldehyde based materials: hydrogels [16] and organic/carbon aerogels [22].

The novelty of this article lies in the optimisation of the thermoporometry measurements for organic and carbonaceous xero-, cryo- and aerogels—materials which are typically not reported in the thermoporometry literature. The aim was to show how to determine reliable PSDs for these materials with large pore size (up to 100 nm in diameter) and low pore volume. The optimisation was done by adjusting sample pretreatment and experimental conditions. In addition, we describe a specific approach to TPM calculations which does not need a separation of the overlapping peaks.

2. Experimental

2.1. Preparation of the samples

Two different types of materials were prepared. The first group was based on a reaction among melamine, resorcinol and formaldehyde in an aqueous solution at 90°C using Na_2CO_3 as a catalyst. The mixture was held at 70°C for 24 h in an oven for polycondensation and aging to produce wet organic gels. Drying was performed in three ways to obtain different kinds of materials. Subcritical drying (70°C for 24 h) led to organic xerogel (M–X–O), while organic cryogel (M–C–O) was obtained after freeze-drying (52 Pa, 48 h). The third type of drying was supercritical drying with CO_2 . The wet organic gel was first washed with fresh acetone every 24 h at least for one week, then with liquid CO_2 several times during 24 h and finally dried supercritically to produce organic aerogel (M–A–O). The dried samples were pyrolysed under nitrogen flow (0.5 h at 100°C , $10^\circ\text{C min}^{-1}$ ramp to 800°C , and 1 h at 800°C) to obtain carbon xerogel, cryogel and aerogel (M–X–X, M–C–X and M–A–X, respectively).

The second type of a material was based on cellulose acetate, which was dissolved in acetone. Triethylenediamine was added as a catalyst and polymethylpolyphenyldiisocyanate as a crosslinking agent. The gel was aged for 1 week at room temperature and then washed with water to remove the unreacted components. Freeze-drying (52 Pa, 48 h) was proceeded to obtain a dry sample

(CA–C–O) and pyrolysis (1 h at 100°C , $10^\circ\text{C min}^{-1}$ ramp to 500°C , 1 h at 500°C) led to a carbonaceous sample CA–C–X.

2.2. SEM

Microscopic observations of the pyrolysed samples were carried out on SEM (Zeiss Sigma HD VP). The samples were dried in a vacuum oven (1 h at 65°C) before imaging to remove moisture. No sputtering was used. The experiments were realised using in-lens detector and acceleration voltage of 3 kV.

2.3. Thermoporometry experiments

TPM measurements were performed with Discovery DSC 144 instrument (TA instruments) using water as a probe liquid. Water is typically used as a probe liquid due to its high heat of fusion which increases the sensitivity of an experiment (e.g., [1,3,9,14]). The high sensitivity was especially desirable due to low pore volumes of the samples.

The instrument was calibrated both for temperature and enthalpy using dodecane, water and indium as calibration standards. Proper amount of sample was weighed (with accuracy of 0.001 mg) in an aluminium pan and gently compressed. After that, desired amount of water was added, the pan was hermetically sealed and let to stabilise for at least 1 h before each measurement (1 h was determined as an adequate period based on the preliminary experiments). After inserting a sample into the DSC instrument the following prefreezing programme was used: cooling to -60°C (5°C min^{-1}), 2 min at -60°C , heating to -3°C (5°C min^{-1}), heating to -0.3°C ($0.3^\circ\text{C min}^{-1}$), 10 min at -0.3°C . This procedure was applied at the beginning of the actual measurement so that water in the pores would be in a liquid state, while bulk water would be frozen and can thus act as a nucleation centre for water inside the pores. The actual measurement was performed by cooling to -60°C (5 , 1 or $0.5^\circ\text{C min}^{-1}$) to record freezing of water in the pores. The sample was let to equilibrate at -60°C for 10 min and it was then heated to 20°C (5 , 1 or $0.5^\circ\text{C min}^{-1}$) to record both melting in the pores and melting of bulk water. After each measurement, a hermetically sealed pan was weighed (affirmation of sealability), pierced, dried in a vacuum oven (4 h at 120°C) and reweighed to obtain mass of the dry sample.

Several parameters were varied to obtain the optimal TPM results. In sample preparation, the effect of impurities was studied by comparing the unwashed and washed samples. The following washing procedure was used: 15 h in a contact with water, removing water with the possible dissolved impurities, 2 h in a contact with water, removing of the excessive water and a drying in a vacuum oven (65°C , 1 h).

Also wettability of the samples was assessed to find the optimal way of a sample preparation. A small mass of a previously washed organic or carbon sample was first added in an excess of water. The following procedures were used afterwards: boiling of a sample for 10 min (“boiling”), exposing a sample to vacuum ($10 \times 10 \text{ s}$) (“vacuum”) or sonicating a sample for 1 min (“sonication”), adding a small amount of ethanol to a sample before water to improve wetting and subsequent repetitive washing of a sample with water to remove ethanol (“EtOH”). Also a simple addition of excess water to a sample without further treatment was used (“control”). A sample was kept in a contact with water for the next 5 h for stabilisation after each process. Then the excess of water was removed by pressing the sample with a paper tissue. The sample was then measured with DSC.

For obtaining an optimal DSC signal, different heating rates ($5/1/0.5^\circ\text{C min}^{-1}$) as well as an ideal ratio of added water to sample mass were examined.

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