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Size effect on SBA-15 microporosity

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Abstract

The experimental published data on SBA-15 microporosity was interpreted using a size effect approach. This approach regards the wall micropores of SBA-15 material as stress-induced defects in its pores walls. It was shown that the microporosity is the function of the ratio of the pore wall thickness to pore diameter—the characteristic parameter representing the size of nanotubular silica pores. This suggests that the size effect plays an important role in the microporosity formation and supplements the template-induced microporosity related to the partial occlusion of the PEO chains in silica matrix.

Keywords: Microporosity; SBA-15; Size effect

1. Introduction

For more than a decade, since the first publications of the MCM materials [1,2], ordered mesoporous silicas (OMS) were the subject of intensive fundamental and applied research. OMS were employed in preparation of advanced materials applied as catalysts, chemical sensors, optical and magnetic devices [3–7], performed as hard templates for preparation of other ordered mesoporous solids [8,9] and for drug release [10]. SBA-15 silica [11,12] displayed significantly higher stability under various conditions (steaming, high temperature) compared with MCM-41 silica. Therefore, it is frequently used for synthesis of various advanced materials.

SBA-15, unlike MCM-41, contains micropores within the walls of primary mesopores forming 3-D connected pore network with connections between mesopores [13–15]. First, increasing microporosity enhanced hydrothermal stability in steam [16]. Furthermore, micropores in SBA-15 are apparently critical for preparation of ordered nanostructures, like carbon and platinum replicas [17,18]. The porosity of the walls may also promote molecular transport in catalysis and adsorption. The SBA-15 affinity for ethylene weakened as microporosity decreased thus affecting ethane/ethylene separation [19].

SBA-15 preparation includes four main steps: (1) synthesis of silica–organic polymer nanocomposite using silica source (for example TEOS) and amphiphilic triblock copolymers as a structure-directing agent (template), (2) ageing the composite at elevated temperature, (3) filtration (and optionally washing) the obtained solid and (4) removing copolymer by extraction and/or calcination [11,12]. Several studies indicated that the micro- to mesopores ratio depends on the SBA-15 synthesis parameters:

- silica source [15,20,29] and length of the EO_n block [21],
- silica/template ratio [20–23],
- aging period and temperature level [16,22–27,29],
- pH of mixture [15,28].
- presence of inorganic salt [16,19].

Generation of SBA-15 walls microporosity was proposed to involve a corona [24,27] created by partial occlusion

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of the hydrophilic poly(ethylene oxide) (PEO) chains into silica matrix transformed to micropores upon calcinations. However, this model does not seem to explain effects of all preparation parameters. In this paper, a different approach was proposed and the experimental published data was reinterpret and compared. The wall micropores of SBA-15 material are regarded as stress-induced defects of its solid phase structure.

2. Effect of silica source/template ratio

The silica source/template ratio was found to have a significant effect on microporosity of SBA-15 [20–23]. The SBA-15 microporosity may arise, as already mentioned, from the partial occlusion of the PEO chains in silica matrix. It leads to the conclusion that at constant amount of EO and increasing content of silica source, the fraction of corona would decrease, thus decreasing the micropore volume fraction in the total pore volume. The data plotted in Fig. 1 indicate the opposite, namely, the micropore volume fraction increases with increasing silica/template ratio. One data set [23] was not included since the total pore volume is not reported, although, the absolute micropore volume increased with increasing the silica/template ratio. The micropore volume fraction was selected since it provides a basis for comparison of the results from different sources. This dependence of micropore volume fraction on the silica/template ratio implies that occlusion of the PEO chains in silica matrix may not be the only reason of the micropores formation.

3. Stress-induced SBA-15 microporosity

Polymers may experience mechanical forces such as pressing, tension and bending during the self-assembling and post-synthesis steps. The wall micropores of final product, i.e. hexagonally packed silica nanotubes, may be considered as stress-induced defects in solid pore walls. The larger an object—the more defects it accumulates during preparation—phenomenon known as size effect [30]. Size effects is widely applied in the investigations of the materials of macroscopic (mm) [31,32] and nanoscopic [33] scales. We suggest that this law would act in SBA-15 material so the thicker the nanotube wall the more defects (micropores) it contains. Indeed, MCM-41 with very small wall thickness of 0.5–2.0 nm [34] is micropore-free, as was mentioned above.

The pore wall thickness increases with increasing the silica/template ratio (Fig. 2) similarly to the behavior of the micropore volume in Fig. 1. Thus, the increase of the micropore volume (Fig. 1) could be a result of increased amount of stress-induced defects in the thicker wall (Fig. 2).

SBA-15 material synthesized at high silica/template ratio was reported to display hexagonal structure with microporous silica nanocapsules sticking on the walls of the mesoporous channels forming plugged hexagonal templated silica [22]. The formation of the micropores in the plugs was attributed to the templating effect of the impurities such as diblock copolymers and free PO chains [22]. Kruk et al. [21] proposed that during the assembling process, the PEO blocks interact only with a limited amount of TEOS. The remaining TEOS preferably solubilized in the copolymer micelles and condensed to form the microporous plugs. Bao et al. [20] assumed the same mechanism, pointing out that the condensed amorphous silica is microporous. Using successive removal of the surfactant by ethanol, Miyazawa et al. [23] proved that micropores exist within the mesopores walls and the OMS is not a physical mixture of mesoporous and microporous materials. They proposed that silica/template ratio affects the siloxane network structure in the pore walls that results in changes of microporosity. Therefore, the formation of microporous plugs in the silica nanotubes may explain the increase of

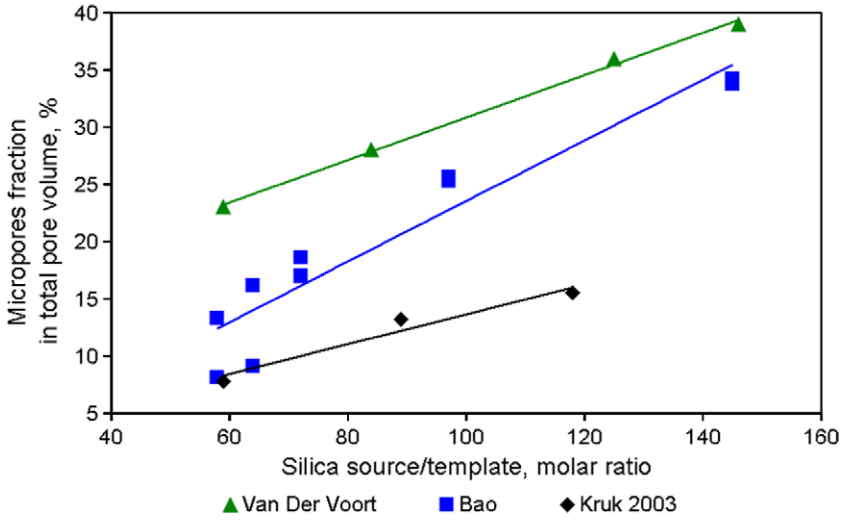

Fig. 1. Effect of the silica source/template ratio on the fraction of micropore volume in the OMS.