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Naphthalene-based periodic nanoporous organosilicas: II. Hydrogen and methane adsorption and physicochemical study

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ABSTRACT

Novel Periodic Nanoporous Organosilicas (PNOs) synthesized by direct co-condensation of tetraethylorthosilicate and triethoxy(naphthalen-1-yl)silane (as described in detail in part I) were evaluated for their hydrogen and methane storage ability. The naphthalene-based PNO materials exhibit regular hexagonal arrangement of uniform pores, high naphthalene content up to 17 wt.%, specific surface areas above 1000 m^2/g and pore size distributions in the microporous/mesoporous boundary. Methane and hydrogen storage properties, at different temperatures, have been investigated for these samples by Sievert-type apparatus. The samples exhibit a reversible methane/hydrogen surface excess adsorption capacity, with measured maximum uptake of up to 5.27 wt.% at 298 K and 3.5 MPa and 2.05 wt.% at 77 K and 4.3 MPa respectively. The analysis of the obtained isotherm curves by Tóth equation shows high grade of surface homogeneity of the samples. Total storage capacities were also estimated. For methane a maximum 41.6 v/v at 298 K and 3.5 MPa was found, while for hydrogen a maximum 15.8 g/L at 77 K and 4.3 MPa was calculated.

1. Introduction

The increasing air pollution from automobile exhaust gas affects every day the environment and our health. Therefore, there is a great need of replacing gasoline and diesel and moreover their harmful emissions, with clean energy. Hydrogen (H_2) and methane (CH_4) are two ideal energy carriers due to their pollutant-free combustion. Particularly, they exhibit higher heating values per mass and produce less (or even no, in the case of hydrogen) carbon dioxide emissions compared to the other fuels [1,2]. The common goal for many researchers is the storage of large amounts of hydrogen and methane at 'safe' pressures. Both these gases can be stored as compressed or liquefied in tanks or adsorbed in solid materials [3,4]. Compressed or liquefied methods require respectively very high pressures and temperatures which make them insufficient for secure gas storage and transfer. On the other hand, adsorption by porous materials seems to bring together many safety advantages, as low pressures are required.

The hydrogen and methane gasses can be adsorbed from solid state either by chemisorption [5,6] or physisorption [7,8]. In the case of chemisorption, the interaction between the gas and the sample can occur within the solid (formation of chemical bonds) and in several cases this mechanism results in an irreversible process. On the other hand, in physisorption the interaction between the solid and the adsorbed gas takes place on the surface of the material [9] and the occurred forces are weak van der Waals type or similar [2]. Finally, the storage in porous materials by physisorption is a promising solution to the reversible high gas uptake [10].

The Department of Energy (DOE) of the United States has set target to develop and verify on-board hydrogen storage systems achieving until 2015 a gravimetric capacity of 0.055 kg H_2 per kg system (5.5 wt.%) or a volumetric capacity of 0.040 kg H_2 per L system (40 kg/m^3), at moderate pressures (10 MPa) and ambient temperatures (233–358 K) [11]. Meanwhile, for methane storage, DOE has set a target only for volumetric capacity at 180 v/v up to 3.5 MPa and 298 K [12].

Among many materials that have been studied for physical adsorption of hydrogen and methane, the MCM-41 family [13] – which are silica-based mesoporous materials with a hexagonal array of cylindrical pores – have been widely explored. For these materials, Sheppard and Buckley [14] reported a maximum hydrogen storage capacity of about 2.0 wt.% at 77 K and 4.5 MPa while Seaton et al. [15] reported a methane storage capacity of about

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3.7 wt.% at 303.15 K and 3.2 MPa. The high specific surface areas of this kind of materials settle them as ideal absorbents. However, these materials lack of active sites that would expand their applicability.

For this reason research was directed towards the synthesis of functionalized periodic mesoporous organosilicas (PMOs). These porous solids based on the organosilicate family of compounds, can be targeted for the development of materials with high and reversible hydrogen/methane adsorption capacity. PMOs are a special class of templated porous materials in which organic groups are located within the channel walls as bridges between Si centers [16–20]. They can be easily obtained by using simple hydrolysis-condensation reactions of a suitable organosilane precursor in the presence of templating molecules arranged in micelles, acting as structure directing agents to provide the necessary porosity (shape, size and topology). These materials combine the high surface area and the narrow and tunable pore size distributions of the traditional templated pure silicate materials (e.g. MCM, SBA family of solids) with the enormous functional variation of organic chemistry [21,22]. In the literature, results are already reported on the hydrogen adsorption for this type of materials. Jung et al. [23] obtained a hydrogen storage capacity of about 0.6 wt.% at 77 K and 0.08 MPa for a mesoporous organic-silica material and a value of about 0.4 wt.% at 77 K and 0.08 MPa for a mesoporous inorganic-silica material.

Additionally, Okubo et al. [24] reported a maximum hydrogen storage capacity of about 0.8 wt.% at 77 K and 0.1 MPa for PMO materials with diverse embedded organic groups. On the contrary, for methane adsorption, only theoretic studies have been done using density functional theory (DFT) calculations on the interaction of methane, with the internal walls of *p*-phenylenesilica, an hybrid mesoporous material derived from 1,4-bis(triethoxysilyl)benzene [25]. In summary, the PMO materials of the above examples have been obtained by the use of bissilylated organic precursors [22] and their hydrogen storage capacity has been analyzed for low pressures only while their methane storage capacity has been studied only theoretically.

In our previous work [26], it has been demonstrated that PMO materials may be obtained not only by the use of bissilylated organic precursors, as their strict definition reports, but also by the use of analogous monosilylated organic precursors. Therefore, it has been shown [26] that PMOs may also be produced even if we substitute the bissilylated with a monosilylated organic precursor, since the final hybrid organic–inorganic products exhibit same properties. It is well know, that the most important factors that influence the hydrogen and methane storage properties of a solid adsorbate are nano-porosity, polarized aromaticity, unsaturated metal sites and point charges [27], it is natural to consider these naphthalene-based porous organosilicates as highly promising materials for this purpose. This is because they are already materials which they fulfill the criteria of nano-porosity and polarized aromaticity. Moreover, these are light solids and therefore one may expect enhanced gravimetric hydrogen and methane storage capacities.

In this work, naphthalene containing Periodic Nanoporous Organosilicas (PNOs) samples with regular hexagonal arrangement of uniform pores, high naphthalene content up to 17 wt.%, specific surface areas above 1000 m^2/g and pore size distributions in the microporous/mesoporous boundary [26] have been studied for the first time for hydrogen and methane storage capacity with Sievert's type apparatus at various temperatures up to 4.3 MPa and 3.5 MPa, respectively. Furthermore, the obtained adsorption isotherms curves have been analyzed by the Tóth [28] equation while the adsorbed molecules per unit surface area and the isosteric heat of adsorption have been evaluated as well.

2. Experimental section

2.1. Materials

Preparation and structural characterization of the PNO materials are described in detail in our previous work [26]. Herein, basic physicochemical parameters, taken from Ref. [26], are summarized in Table 1. In brief, periodic nanoporous organosilicas were synthesized with a typical one step direct co-condensation of tetraethylorthosilicate and triethoxy(naphthalen-1-yl)silane in a 6.33:1 M ratio. Evacuation of the pores from the surfactant was achieved either by treatment with HCl 37 wt.% (sample: Naph-PNO-H^+) or by heat treatment at 623 K (sample: Naph-PNO-350).

2.2. Methods

The PcT (Pressure concentration Temperature) volumetric gas storage apparatus consists of a gas manifold with a series of tubes and valves connecting the sample holder to the gas reservoirs void volume and pressure transducers. The achievement of reliable results on the gas storage isotherms, with high accuracy up to 8 MPa, has been obtained by novel apparatus (*f*-PcT – DeltaE S.r.l) replacing and optimizing different part of a similar apparatus described in the literature (dotted lines in Fig. 1) [29].

The apparatus allows the admittance of different species (He, CH_4, H_2, etc.) from a gas manifold into a calibrated reservoir and the subsequent expansion of that gas in the sample holder volume hold at a fixed temperature. The missing moles after the gas expansion, calculated considering the gas pressure and temperature, are adsorbed into the sample. The gas expansion is repeated at increasing pressures allowing the evaluation of the sorption isotherm in terms of sorbed moles versus equilibrium pressure. The same apparatus is used to evaluate the skeletal density of the sample by using He as inlet gas. Before each adsorption measurement, the samples were treated up to 473 K under high vacuum for 12 h in order to remove water and other possible impurities.

3. Results and discussion

In the following paragraphs will be presented all the results regarding hydrogen and methane adsorption/desorption analysis performed on our samples: Naph-PNO-H^+ and Naph-PNO-350. Both naphthalene-based PNO materials exhibit crystallinity as observed in the X-ray powder diffraction patterns and high naphthalene content up to 17 wt.% as calculated from the thermal analyses [26]. From the nitrogen adsorption/desorption isotherms is concluded that samples have large specific surface areas (both above 1000 m^2/g) and pore size distributions in the microporous/mesoporous boundary as diameters are calculated at about 20 Å. Finally, with helium pycnometry, skeletal densities of both samples were calculated around 2 g/mL. Basic pore parameters obtained from part I [26] are summarized in Table 1. The helium pycnometry measurements were performed in order to evaluate the samples′ skeletal density, while the specific surface area (SSA) and the pore volume were obtained by the Brunauer–Emmett–Teller (BET) method [26]. A higher SSA and pore volume is observed for the Naph-PNO-350 compared to Naph-PNO-H^+ (see Table 1) which in fact is related to the different procedure adopted for the pore evacuation from the surfactant during the synthesis [26].

The adsorption/desorption isotherms of hydrogen and methane were collected by the *f*-PcT apparatus. Particularly, the methane isotherms were obtained at 288 K, 298 K and 315 K, and up to 3.5 MPa, while the hydrogen isotherms at 77 K and up to 4.3 MPa. The experimental data were fitted by the Tóth [28] equation in order to estimate the trend of the samples' adsorption prop-