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 m²/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 Töth 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.

Keywords:
Naphthalene
Periodic Mesoporous Organosilicas
Hydrogen storage
Methane storage
Sievert-type apparatus

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 (H₂) and methane (CH₄) 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 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 as compressed or liquefied in tanks or adsorbed in solid materials [3,4].

The hydrogen and methane gases 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 H₂ per kg system (5.5 wt.%) or a volumetric capacity of 0.040 kg H₂ per L system (40 kg/m³), 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
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((trimethoxysilyl)benzene [25]. In summary, the PMO materials of the above examples have been obtained by the use of bisilylated 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 bisilylated 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 bisilylated with a monosilylated organic precursor, since the final hybrid organic–inorganic products exhibit same properties. It is well known, 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 m²/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 Töth [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 tetraethyl-orthosilicate and triethoxy(naphthalen-1-yl)silane in a 6.3:1 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, CH₄, H₂, 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 m²/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 1 [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, 290 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 Töth [28] equation in order to estimate the trend of the samples’ adsorption prop-
properties. Tóth model was chosen since it is the most appropriate for the fitting of an adsorption by heterogeneous surfaces compared to Langmuir, Freundlich or other adsorption models [30,31]. The information obtained by the Tóth analysis includes the theoretic maximum gas storage capacity, the equilibrium constant and the homogeneity grade of the samples. The maximum uptake parameter (wt.%max) is the extrapolated hypothetical saturation coverage. Its real counterpart is the uptake value when the saturation coverage takes place, which is not the present case. For this reason, the theoretic maximum uptake is presented since it is one of the three Tóth parameters, but is not further analyzed. The possible formation of one monolayer of adsorbed molecules per nm² has been evaluated while the isosteric heat of adsorption has been studied as well, indicating the bonding energy between the adsorbant and the adsorbent.

As already mentioned in the introduction, DOE has set a target only for volumetric capacity for methane adsorption (180 v/v) and such an expression is preferable in the relevant publications. Regardless of the storage pressure (3.5 MPa), since the delivery pressure is 0.1 MPa, the methane volume is referred to standard temperature and pressure (STP, 0.1 MPa and 273 K), so DOE’s target for methane volumetric capacity is 180 (STP) v/v (i.e. 180 L of STP methane per L of system). Though, this expression exhibits a significant problem as the ratio of methane to absorbent, where both are expressed in the same volume unit i.e. L or mL, requires the correct calculation of the absorbent’s real volume [32]. Similar problem occurs in the volumetric storage capacity of H₂ (DOE’s 2015 target: 40 kg/m³). Unfortunately, even though DOE clearly refers to total system’s volume for both CH₄ and H₂, the latter is frequently miscalculated. It is common phenomenon, depending on the nature of the material, that various forms for density or other expressions for the calculation of volume are used [32–38]. This confusion leads in a state where materials even from the same family may not be properly compared due to the different volume’s calculation approach.

Since all measurements in this work were performed with powders, the apparent densities (d_appar, 0.13 g/mL for both samples) were used for the conversion of gravimetric to volumetric storage capacities. Here presented experimental data concern the surface excess adsorption of methane and hydrogen. However, for real applications the total storage capacity is more essential [38–40]. Total storage capacity takes into account also the compressed quantity of the gas in the system’s volume and can be fairly estimated as the density (mol/L) of methane and hydrogen at their storage pressure is known [41]. For the later evaluation, first the void space in a specific volume of a system should be estimated since this is the real volume where compression occurs. Void space fraction (V_space) of a system can be calculated from the following formula:

\[ V_{\text{space}} = 1 - \frac{d_{\text{appar}}}{d_{\text{skelet}}} \]

where d_appar and d_skelet are the apparent and skeletal densities of the absorbent [39].

3.1. Methane adsorption

Fig. 2 shows the gravimetric methane surface excess adsorption (closed symbols) and desorption (open symbols) isotherms of the investigated samples obtained up to 3.5 MPa and at 298 K. As it is shown, the isotherm curves are in agreement with the type I IU-PAC [9] curve: the desorption isotherms follow the adsorption isothers (no large hysteresis loop is observed) proving the fully reversibility of the methane adsorption and consequently the fact that methane can be easily extracted from the material.

Considering the two samples, Naph-PNO-350 has higher methane uptake reaching up to 5.27 wt.% at 3.5 MPa, as expected taking into account its higher SSA and pore volume values (Table 1). Gravimetric storage capacity of sample Naph-PNO-H⁺ reaches 4.33 wt.%, while the corresponding volumetric capacities using d_appar are 8.35 and 10.26 (STP) v/v for samples Naph-PNO-H⁺ and Naph-PNO-350, respectively. These gravimetric capacities are higher than relevant reported on MCM-41 materials [15], while in MOFs, which are frequently studied on gas storage adsorption, the percentages are in some cases comparable or higher because of their unique structure [42]. The better adsorptive characteristics of Naph-PNO-350 are observed for the whole range of pressures (Fig. 2). However, the ability of this sample to store higher values

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m²/g)</th>
<th>V_bre (mL/g)</th>
<th>d_skelet (Å)</th>
<th>a_s (Å)</th>
<th>d_appar (g/mL)</th>
<th>d_skelet (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naph-PNO-H⁺</td>
<td>1076</td>
<td>0.43</td>
<td>20.4</td>
<td>48.9</td>
<td>2.068</td>
<td>0.13</td>
</tr>
<tr>
<td>Naph-PNO-350</td>
<td>1076</td>
<td>0.57</td>
<td>22.0</td>
<td>44.0</td>
<td>1.96</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Data taken from Ref. [26].
of methane compared to Naph-PNO-H⁺, may not only depend on the SSA but also to the possibility to form more than one monolayer of adsorbed methane molecules.

For this reason, the evaluation of the adsorbed methane molecules per nm² \( (N_{molec}/nm^2) \) could be useful to indicate the efficacy of the sample to create more than one monolayer and it can be easily evaluated by using the following formula:

\[
N_{molec}/nm^2 = N_A \times \text{wt.\%}/(10^{20} \times MW_{\text{gas}} \times SSA)
\]

where \( N_A \) is the Avogadro’s number, \( MW_{\text{gas}} \) the molecular weight of the adsorbed gas and SSA the specific surface area obtained by the BET method.

Regarding methane storage in porous materials, the formation of one monolayer is reached when roughly 3 molecules per nm² are adsorbed (since the area occupied by a methane molecule is about 0.3 nm²). As shown in Fig. 3, one monolayer coverage of CH₄ is not reached for none of the samples at room temperature. The Naph-PNO-350 sample adsorbs more molecules per nm² (1.8 molec/nm² at 3.5 MPa, 12% more than the Naph-PNO-H⁺ in the same conditions) showing a higher affinity of its pore walls towards the methane adsorption.

The theoretic maximum methane storage capacity, the equilibrium constant and homogeneity grade of the samples have been evaluated by means of analysis of the adsorption isotherms by using the Tóth [28] model according to the equation:

\[
\text{wt.\%} = \text{wt.\%}_{\text{max}} \times K \times P/(1 + (K \times P)^t)^{1/t}
\]

where \( \text{wt.\%}_{\text{max}} \) is the asymptotic storage capacity, \( K \) is the equilibrium constant and \( t \) is a parameter introduced from Tóth in order to consider the homogeneity grade of the sample. The \( K \) constant is determined by the energetic interaction between the adsorbent and the adsorbate. In terms of energy, a high \( K \)-value means high adsorption enthalpy. In consequence of the above, the higher \( K \)-value of the sample Naph-PNO-350 (Table 2) confirms its ability to attract more efficiently the methane molecules. \( K \)-values of both samples are approximately tenfold higher compared to pure hexagonal mesoporous silica (MCM-41, \( K = 0.04 \)) which was prepared with the same synthetic procedure and it has been studied for methane storage for comparison reasons (data not shown). No saturation is reached in the probed pressure range (Fig. 4), as plots have not reached a plateau. Finally, we obtained the same \( t \)-value, for both samples, which is close to unity (within the error) indicating a high grade of surface homogeneity with respect to the methane adsorption process (Table 2) and very low dependence of the CH₄/surface interaction on the coverage.

A direct evaluation of the CH₄ isosteric heat of adsorption (\( \Delta H \)) for the investigated materials is evaluated according to the Clau- sius–Clapeyron equation:

\[
\ln P = -(\Delta H/RT) + C
\]

and it is determined from a plot of \( \ln P \) vs. \( 1/T \) (Fig. 5). The formula has been utilized using the data of the isotherm curves obtained on the investigated samples at 288 K, 298 K and 315 K and low pressures (0.01–0.1 MPa).

In Fig. 5 we show the linear fitting of the adsorption data for both samples while Table 3 reports the isosteric heat results. As expected, the value for the Naph-PNO-350 is slightly higher corroborating the previous results on the higher affinity of its pore surfaces towards the methane adsorption. Estimated isosteric heat of adsorption values for both samples are in agreement with previously reported values for various materials where the range is approximately between 10 and 20 kJ/mol [15,42,43]. The higher binding energy between the methane molecules and the pore walls in sample Naph-PNO-350 settle it as more efficient to attract methane molecules. This, together with its higher SSA (5%) and pore volume values, explain the observed increase of +20% for the methane uptake of this samples. This could result from the different methods used for the template removal. As an outcome, it can be assumed that the lower SSA and consequently gas uptake of the Naph-PNO-H⁺ sample probably originates by the surfactant’s residual (5.6 wt.%) in this sample after the cation exchange reactions as observed in the DTA/TG analysis in Ref. [26]. However, the latter is rather a scenario which is not and could not be confirmed by any used technique.
Table 3
Calculated isosteric heat of adsorption and its error for Naph-PNO-H\(^+\) and Naph-PNO-350 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Delta H) (kJ/mol) low coverages</th>
<th>Error (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naph-PNO-H(^+)</td>
<td>14.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Naph-PNO-350</td>
<td>18.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

For completion of the results, the total methane storage capacities of both samples were estimated. For this evaluation, it is essential that according to Eq. (1) the void space for 1 L of a system is calculated [39]. The adsorbed, compressed and total volumetric (v/v) capacities for samples Naph-PNO-H\(^+\) and Naph-PNO-350 are shown in Figs. 6 and 7, respectively. As observed for both samples, the compressed methane amounts are higher than the adsorbed. However, the contribution of the adsorbed quantity to the total capacity of the system is significant since the powder in fact occupies minimum volume in the system leaving nearly the whole 1 L as void space for additionally compression.

3.2. Hydrogen adsorption

Fig. 8 shows the hydrogen surface excess adsorption (closed symbols) and desorption (open symbols) isotherms of the investigated samples obtained up to 4.3 MPa and at 77 K. As already shown before in the case of the methane adsorption isotherms, the amount of adsorbed hydrogen seems to increase according to the type I IUPAC [9] curve, while desorption isotherms follow the adsorption isotherms which indicates the full reversibility of the hydrogen adsorption. From the data presented in Fig. 8, it is clear that both samples exhibit a very similar hydrogen storage uptake of about 2 wt.% at 77 K and 4.3 MPa.

More specifically, the gravimetric storage capacity of sample Naph-PNO-H\(^+\) reaches 1.91 wt.%, while sample Naph-PNO-350 reaches 2.05 wt.%. Compared with similar materials these percentages are higher [14,23,24], while in MOFs these values vary significantly and there are analogous reported values but also high uptakes up to 7.6 wt.% [40,42,44]. The corresponding volumetric capacities using \(d_{\text{appar}}\) are 2.53 and 2.72 g/L for samples Naph-PNO-H\(^+\) and Naph-PNO-350, respectively. Gravimetric and volumetric surface excess adsorption (using \(d_{\text{appar}}\)) of methane (3.5 MPa at 298 K) and hydrogen (4.3 MPa at 77 K) for samples Naph-PNO-H\(^+\) and Naph-PNO-350 are summarized in Table 4.

The obtained hydrogen isotherms were analyzed by the Toth [28] Eq. (3). As shown in Table 5, we obtained a high K-value for both samples, which reveals a strong interaction between the hydrogen molecules and the samples’ surface and an enhanced adsorption in low pressures (Fig. 8). Compared to MCM-41 (\(K=0.2\)), these K-values were at least 10-fold higher, indicating that both PNO’s exhibit enhanced binding energy. Finally, we observed the same relative high t-value for both samples which demonstrates a high grade of homogeneity for the interaction of hydrogen with the surface. Though, the t-values in the case of hydrogen are 0.2 less than for methane. This suggests that naphthyl groups interact with hydrogen but not with methane, so the same samples appear homogeneous for methane and least homogeneous for hydrogen. This does not necessarily mean that the surface is homogeneous but that the adsorption sites have same methane and nearly similar hydrogen affinity.

As already discussed for methane, also in this case the evaluation of the adsorbed molecules per nm\(^2\) could indicate the efficacy of the samples to create more than one monolayer. The calculation can be easily done using Eq. (2). Regarding hydrogen storage in porous materials, the formation of one monolayer is reached when ca. 6.95–8.55 molecules per nm\(^2\) are adsorbed. The area occupied by H\(_2\) molecule is 0.117 nm\(^2\) in the solid phase and 0.144 nm\(^2\) in the liquid phase. While being adsorbed and forms a monolayer, hydrogen can be considered as a bi-dimensional liquid where hydrogen’s binding to surface is not directional but permits molecules mobility into the adsorbed phase.

In Fig. 9 we report the number of hydrogen molecules per surface’s nm\(^2\) for Naph-PNO-H\(^+\) and Naph-PNO-350 samples up to 4.3 MPa and at 77 K. It is clear that none of the samples form one monolayer at liquid nitrogen temperature, nevertheless, both of them adsorb the same value of 5.6 molecules per nm\(^2\) i.e. we have a coverage of about 0.72 monolayers. As a consequence, we observed that Naph-PNO-H\(^+\) and Naph-PNO-350 samples show the
same capacity in storing hydrogen molecules and that, in this case, the different pore structure of the samples did not play an important role.

As in the case of methane, for completion of the results, the total hydrogen storage capacities of both samples were estimated. The adsorbed, compressed and total volumetric (g/L) capacities for samples Naph-PNO-H+ and Naph-PNO-350 are shown in Figs. 10 and 11, respectively. Again the compressed hydrogen amounts are higher than the adsorbed. However, for the same reason mentioned for methane, the contribution of the adsorbed quantity to the total capacity of the system is significant. The total volumetric storage capacities at maximum pressure are summarized in Table 4.

4. Conclusions

In conclusion novel naphthalene-based Periodic Nanoporous Organosilicas (PNOs), exhibiting regular hexagonal arrangement of uniform pores, high naphthalene content up to 17 wt.%, specific surface areas above 1000 m²/g and pore size distributions in the microporous/mesoporous boundary were evaluated for their hydrogen and methane storage capacity. The different procedure adopted for the pore evacuation resulted in two samples, Naph-PNO-H+ and Naph-PNO-350, with slightly different pore characteristics and specific surface area. Hydrogen and methane surface excess adsorption measurements were performed by using a Sieverts type apparatus at different temperatures and pressure up to 4.3 MPa and 3.5 MPa respectively. We found a methane uptake value of 4.33 wt.% and 5.27 wt.% for Naph-PNO-H+ and Naph-PNO-350 samples respectively at 298 K, while about 2 wt.% uptake for hydrogen at liquid nitrogen temperature (77 K) for both samples. The analysis of the adsorption isotherms with the Tóth model, have shown a stronger interaction between the gas molecules and the samples' surface with respect to the MCM-41 reference sample. Furthermore, we observed high t-values indicating very homogeneous surfaces with respect to the gas adsorption processes particularly in the case of methane. The most likely scenario is that naphthyl groups interact with hydrogen but not with methane, so the same samples appear homogeneous for methane and least homogeneous for hydrogen. This does not necessarily mean that the surface is homogeneous but that the adsorption sites have similar methane affinity.

In the case of methane, the pore characteristics (SSA and pore volume) of the samples appear to have played an important role in terms of adsorption. In fact, the observed differences of the methane uptake properties of the samples could be attributed to

Table 4
Gravimetric and volumetric surface excess adsorption and total volumetric storage capacities of methane (3.5 MPa at 298 K) and hydrogen (4.3 MPa at 77 K) for samples Naph-PNO-H+ and Naph-PNO-350.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grav. CH₄ (wt.%)</th>
<th>Vol. CH₄ (v/v) a</th>
<th>Vol. CH₄ (v/v) b</th>
<th>Grav. H₂ (wt.%)</th>
<th>Vol. H₂ (g/L) c</th>
<th>Vol. H₂ (g/L) d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naph-PNO-H+</td>
<td>4.33</td>
<td>8.35</td>
<td>39.86</td>
<td>1.91</td>
<td>2.53</td>
<td>15.66</td>
</tr>
<tr>
<td>Naph-PNO-350</td>
<td>5.27</td>
<td>10.26</td>
<td>41.60</td>
<td>2.05</td>
<td>2.72</td>
<td>15.77</td>
</tr>
</tbody>
</table>

a Apparent densities and ideal gas law for equivalent CH₄ volume at standard temperature and pressure (STP) used for calculations.

b STP total capacity, compressed quantities were estimated for void space in 1 L of system and density was obtained by NIST [41].

b Apparent densities used for calculations.

d Total capacity, compressed quantities calculated as for methane.

Table 5
Theoretic maximum hydrogen gravimetric storage capacity, equilibrium constant and homogeneity grade for Naph-PNO-H+ and Naph-PNO-350 samples obtained as Tóth equation fitting parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% max</th>
<th>K (bar⁻¹)</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naph-PNO-H+</td>
<td>2.20 ± 0.10</td>
<td>3.60 ± 0.05</td>
<td>0.80 ± 0.20</td>
</tr>
<tr>
<td>Naph-PNO-350</td>
<td>3.30 ± 0.04</td>
<td>5.90 ± 0.90</td>
<td>0.80 ± 0.20</td>
</tr>
</tbody>
</table>

Fig. 9. Number of hydrogen molecules per surface's nm² for Naph-PNO-H+ and Naph-PNO-350 samples up to 4.3 MPa and at 77 K. Lines between points represent the data fitting procedure based on the Tóth model.

Fig. 10. Total, compressed and adsorbed hydrogen volumetric (g/L) storage capacity of sample Naph-PNO-350 on a basis of 1 L container up to 4.3 MPa and at 77 K.

Fig. 11. Total, compressed and adsorbed hydrogen volumetric (g/L) storage capacity of sample Naph-PNO-350 on a basis of 1 L container up to 4.3 MPa at 77 K.
the higher SSA and pore volume values of the Naph-PNO-350 sample. On the other hand, these characteristics appear not to have affected the hydrogen storage capacity of the samples.

Acknowledgements

The authors are grateful to Desiderio Giovanni and Abate Salvatore (IPCF-CNR) and to DeltaE srl for their technical and economical support.

References