Methane storage in zeolite-like carbon materials

Myrsini K. Antoniou a,⁎, Evmorfia K. Diamanti b, Apostolos Enotiadis b, Alfonso Policicchio a, Konstantinos Dimos b, Federica Ciuchi c, Enrico Maccallini a, Dimitrios Gournis b, Raffaele G. Agostino a

⁎ Corresponding author at: CNISM-Dipartimento di Fisica, Università della Calabria, Ponte Bucci, Cubo 33c, I-87036 Arcavacata di Rende (CS), Italy.
E-mail address: antonioum@fis.unical.it (M.K. Antoniou).

Abstract

High specific surface area zeolite-like carbon materials (CZ) were synthesized by combining the hard template method with the Chemical Vapor Deposition (CVD), using zeolite beta as solid template and acetylene as carbon precursor, at different reaction temperatures (1023, 1073 and 1123 K). CZ materials were characterized by X-ray diffraction, Scanning Electron Microscopy and nitrogen adsorption-desorption measurements. The nanoporous CZ materials possess surface areas up to 1130 m²/g and total pore volumes up to 0.75 mL/g while XRD data and SEM images show the successful replication of the structure and morphology of the zeolite particles into the final carbon materials. Methane storage properties at different temperatures (287, 298 and 313 K) have been investigated by Sievert's-type apparatus up to 3.5 MPa. The CZ materials exhibit a high and reversible methane storage capacity, with measured gravimetric uptake up to 8.0 wt% at 298 K and 3.5 MPa, a much higher value compared to the pristine zeolite beta which shows gravimetric methane adsorption capacity up to 1.5 wt% at the same conditions. The analysis of the obtained isotherm curves by Töth model shows the same grade of homogeneity on sample porosity for all probed samples while the evaluation of the adsorption enthalpy at low pressures reveals a similar binding energy between the methane molecules and the samples’ surfaces despite of their different long range order.

1. Introduction

The last two decades the interest in natural gas (NG) as a vehicular fuel has grown rapidly. The most important reason for this growing interest is the fact that among other fossil fuels, NG is the cleanest-burning fuel as its combustion produces less carbon dioxide emissions providing energy security and environmental benefits. However, the big disadvantage of NG is its low energy density (heat of combustion per volume) [1]. In order to avoid this problem liquefied or compressed NG are used but in both cases many safety problems arise such as the need of high pressure-resistance tanks for its storage and the inevitable increase of the specific surface areas and easily tuned pore sizes. These materials exhibit high methane storage capacities [2,3] nevertheless their structure usually collapses after a long period of sorption cycles. Among other adsorbent materials with greater structural stability, the zeolites have been considered as promising candidates for methane storage as well [4–8]. For example, Zhang et al. [9] reported a high methane storage capacity of around 8.2 wt% at 3 MPa and 298 K for zeolite CaX while Rolniak and Kobayashi [10] obtained a methane capacity of around 6.8 wt% at 3 MPa and near ambient temperature for zeolite 13X. On the other hand, the development of carbonaceous porous materials with pre-determined accurately tuned nano-sized reactive chambers and channels (which can have application-tailored surface properties) is of primary importance due to their low cost, light weight, high surface area, high thermal stability, high bulk density and adjustable composition. Such materials have strong potential to achieve among else high and reversible methane adsorption [11–17]. Lozano-Castello et al. [18] reported a high methane storage...
capacity of around 19.2 wt% at 4 MPa and 298 K for activated carbon materials.

Among many methods that have been applied in order to obtain mesoporous carbon carbon materials, the hard template method [19–21] combined with the Chemical Vapor Deposition (CVD) allows controlling the porosity and the structure of the final material by using the appropriate template. Thus, the effective trapping of differently sized gas molecules is enabled by changing the diameter of the channels. Zeolites have been widely explored as hard templates because of their advantages such as high porosity and large accessible surface area. Zeolites Y [22], 13X [23], L [24], ZSM-5 [24] and beta [24,25] have been used as templates to prepare carbon materials, mainly by using acetonitrile as carbon precursor and nitrogen as gas carrier resulting in N-doped carbons. These materials have been tested for hydrogen uptake capacity [23,26,27]. Yang et al. presented hydrogen uptake of up to 6.9 wt% at around 77 K and 2 MPa, using zeolite beta as hard template. Studies on zeolite template carbons have been done for carbon dioxide storage as well [28,29]. Zhou et al. prepared N-doped microporous carbons using zeolite NaY as a hard template with furfuryl alcohol/acetonitrile as carbon precursors, for CO2 adsorption. The maximum CO2 adsorption capacity obtained was 10.4 wt% at 298 K.

Limited literature can be found for methane storage. Guan et al. [30] reported that pyrolysis of carbonaceous precursors resulted to carbon-template materials, by using as template an ammonium-form zeolite Y, which possess around 12.8 wt% methane storage capacity at 4 MPa and 300 K.

In this work, zeolite-like carbon materials, with high specific surface area (SSA), were prepared by CVD using acetylene as carbon precursor and zeolite beta as template. Hiromoto Nishihara et al. reported the synthesis of several types of zeolite-template carbons with different structures depending on the zeolite templates that were used (zeolite Y, zeolite X and zeolite beta), through the acetylene CVD [31]. Acetylene was used as a carbon source since it is more reactive than other hydrocarbons at the same reaction temperature leading to carbon materials of better quality [32–34]. The aim was to develop nitrogen-free zeolite-like carbon materials that will combine the numerous advantages of zeolites and carbons in order to pave the way for the production of novel carbon based materials with high methane adsorption capacity. The choice of zeolite beta as hard template material is due to its peculiar structure: it consists of an intergrowth of two randomly alternating two-dimensional sheets. The intergrowth of the polymorphs does not significantly affect the pores in two of the dimensions, but in the direction of the faulting [26,35]. Zeolite beta has been first used as a hard template by Johnson et al. in order to prepare microporous polymer replicas [36].

2. Experimental section

2.1. Materials

Zeolite beta powder was obtained by Tosoh Corporation (Japan) from the HSZ-900 series with product name 930NHA. The cation type of the particular product is NH4 (containing template) while the Al2O3/SiO2 (mol/mol) ratio is 27.

The porous carbon materials were prepared as follows: a ceramic boat with 0.5 g of zeolite beta (pretreated in air at 923 K for 2 h), was placed in a flow through tube furnace. The sample was then heated up to the desired temperature (1023 K, 1073 K and 1123 K) under argon atmosphere. When the targeted temperature was reached, acetylene as a carbon precursor was admixed (for 15 min) with the carrier gas (argon) at flow rates of 10 cm3/min and 90 cm3/min, respectively. After the completion of acetylene flow, the ceramic boat was cooled down to room temperature under argon atmosphere. The resulting zeolite/carbon composites were recovered and washed with 10 wt% HF for 3 days in order to remove the zeolite framework. Final carbon materials were dried in air in an oven at 393 K. According to the deposition temperature, the CZ samples are denoted as CZ1023, CZ11073 and CZ1123.

2.2. Methods

The methane adsorption isotherms have been obtained by Sieverts’ apparatus at three different temperatures (287 K, 298 K and 313 K) and at pressures up to 3.5 MPa. The samples’ amount used for the methane storage measurements is ~0.07 g. The achievement of reliable results on the gas storage isotherms, with high accuracy up to 8.0 MPa, has been obtained by novel apparatus [37] (F-PcT - DeltaE S.r.l) replacing and optimizing different part of a similar apparatus described in the literature (dotted lines in Fig. 1a).

The maximum error (see Supplementary Data) in the calculation of adsorbed moles ranges from 1.5% to 10% (usually ≤5%) in the 0.0–8.0 MPa, an acceptable value for volumetric measurements on gram-scale samples.

Beside the isotherm curves, the volumetric apparatus can give indication on the equilibration kinetics as well. Pressure versus time graphs are acquired during the measurements. The typical pressure decrease subsequently to the expansion from the calibrated reservoir to the sample holder volume containing the sample is depicted in Fig. 1b. A sufficient equilibration time has been set for each adsorption/desorption step.

Fig. 1. Schematic representation of the Sieverts’ apparatus (a), plot with equilibration kinetics examples (b).
Apparent density was calculated according to Dimos et al. [39] while skeletal density values have been obtained by performing He pycnometry measurements on the Sieverts’ apparatus, by using He as the probe gas in room temperature and in the pressure range of (0.01–0.1) MPa. All skeletal density measurements were repeated eight times to minimize the experimental error.

The nitrogen adsorption–desorption isotherms were measured at 77 K on an Autosorb-MP, Quantachrome instruments porosimeter. Specific surface area (SSA) and porosity were determined with the BET method by taking care that the pertinent consistency criteria are met [40,41]. All samples used for the surface analysis were outgassed at around 523 K for 10 h under high vacuum (10⁻⁵ mbar) before measurement. The carbon pore size distributions were calculated with the slit/cylinder adsorption branch quenched solid density functional theory (QSDFT) kernels for carbon materials [42] while the zeolites isotherm was analyzed with the aid of cylindrical, adsorption, non-local DFT (NLDFT) kernel for silicious materials.

X-ray powder diffraction (XRD) data were collected using Cu Kα radiation of a Bruker AXS Diffractometer/Reflectometer (D8) equipped with a Dynamic Scintillation Detector, NaI and with a Gobel mirror. The measurements are made in transmission: the sample powder is put in special glass capillaries (φ = 1 mm, Hilgenberg GmbH) and the latter in a handmade sample holder. All measurements have been done at room temperature (298 K). The spectra were recorded in the 2θ range from 5° to 40°. The step was 0.03° and the counting time was 1 s/step. The effect of void capillary has been taken into account.

3. Results and discussion

The structure and morphology of the carbon products were studied by powder XRD and SEM. SEM images (Fig. 2a–d) offer an excellent morphological overview of the carbon materials on the sub-micrometer scale. The morphology of the zeolite particles is replicated in the carbon samples produced under the three different temperatures (1023, 1073 and 1123 K). As a matter of fact, all the carbon samples show several hundred nm wide flat particles whose morphology replicates the zeolite one in terms of the overall shape of the particles and their internal texture.

The XRD patterns of pristine material and the final carbon products were compared in order to determine the existing crystalline phases. In Fig. 3 the XRD patterns of zeolite beta and the final CZ samples are presented. When the CVD was performed at 1073 K and 1123 K, the resulting carbon samples exhibit a structural ordering that partly resembles that of zeolite beta as the presence of a broad peak at 2θ = 7° indicates. This feature is, in fact, associated to the ordering on the basal plane and describes the pore ordering. On the other hand, when CVD was performed at 1023 K the structural ordering of zeolite beta seems not to have been readily replicated in the final sample, as the peak at 2θ = 7°
All three carbon samples exhibit a low and broad peak at $2\theta = 25^\circ$ which is similar to the (002) diffraction from turbostratic carbon indicating that a certain degree of local ordering resembling graphite is kept. A peak at $2\theta = 18^\circ$ is observed for all three samples. In the literature, for similar samples, this peak is attributed to the (105) diffraction of zeolite beta or to the possibility that it may arise from other carbon contaminants [26].

The nitrogen adsorption–desorption isotherms of all the samples are shown in Fig. 4a. All the isotherms reveal mesoporosity (IUPAC Type IV shape with hysteresis loops) but also strong signs of microporosity (enhanced uptake at very low pressures). The hysteresis loops have different shapes that can be categorized either as H2 (zeolite) or H4 (CZ1073, CZ1023) or even a combination of the two (CZ1123). The shapes of the hysteresis loops point to complicated partly constricted pore networks where pore blocking and/or cavitation may occur. Especially for the case of CZ1073 desorption hysteresis persists at very low relative pressures ($p/p_0 < 0.4$). This is a purely kinetic effect (diffusion hindrance) and several attempts to use more stringent equilibration criteria (in terms of time) have been carried out. Upon increasing equilibration time the hysteresis loop was generally reduced, however this investigation led to impracticably long total analysis times. The specific surface areas (SSA) of all samples are lying between 700 and 1130 m$^2$/g. The SSA values (calculated using the BET equation), the total pore volume (up to around 40 nm) as well as the pore widths of the samples are listed in Table 1. In comparison with the initial material, the specific surface areas of the final CZ materials have been increased after the CVD method. Particularly, the CZ1073 sample presents the highest specific surface area (1127 m$^2$/g) and micropore volume. Pore size distributions were obtained by means of DFT kernels and are presented in Fig. 4b along with the DFT isotherm fitting curves (log scale, Fig. 4c). Zeolite beta has a pronounced mesopore peak centered at around 6 nm while there are also micropores smaller than 1 nm (1 nm was the lowest size detectable by the zeolites DFT kernel in the pressure range measured). CZ1023 and CZ1073 have an almost identical mesopores size distribution with double peaks centered at 2.3 and 4.3 nm. On the other hand the microporosity of CZ1073 is much more pronounced resulting in a peak centered at ~ 0.9 nm, while the pertinent micropore peak of CZ1023 is located at around 1 nm. CZ1123 has also micropores of around 1 nm however in this case a huge mesopores volume is apparent with local peaks at around 5 and 7 nm. These characteristics have played an important role on the methane adsorption capacity of the samples.

Fig. 5 shows the gravimetric methane surface excess adsorption (close symbols) and desorption (open symbols) isotherms of the investigated samples obtained at 298 K. The overall trend of the curves depicted in Fig. 5a remains similar also at 287 K and 313 K in all samples (see for example Fig. 5b for the CZ1073 sample). However, as expected, there is a clear enhancement in the storage capacity by decreasing the temperature. As observed, the amount of adsorbed methane seems to increase according to the type I IUPAC curve [43]. The desorption isotherm curves (open symbols in Fig. 5a and b) follow the adsorption isotherm indicating that the adsorption process is fully reversible and that the gas can be easily extracted from the material.

In Table 2 are presented all the gravimetric and volumetric surface excess adsorption capacities of methane for all the samples. For the calculation of the volumetric uptakes, the apparent densities of the samples were taken into account (0.8 g/cm$^3$ for zeolite beta and 0.6 g/cm$^3$ for the CZ samples). The sample of zeolite beta presents methane uptake five times lower (1.5 wt% at 3.5 MPa) compared to the three carbon materials while the CZ1073 sample has the highest methane adsorption capacity since it possesses the highest SSA and micropore volume values (Table 1). In particular, its uptake is 8.0 wt% at 3.5 MPa. The sample CZ1123 stores more methane (5.6 wt% at 3.5 MPa) compared to the CZ1023 sample (4 wt% at 3.5 MPa), as expected regarding their SSA values, since their micropore volume values are almost equal (Table 1).

The ability of a material to store molecular species does not depend only on the SSA but also on the micropore volume. The adsorption in microporous materials is dominated by interactions between the adsorbate and the pore walls, thus the micropore volume affects the amount adsorbed and the density of the adsorbed phase. The narrow width of the micropores leads to overlapping forces from opposing pore walls and therefore to increased density. In order to calculate the methane adsorbed density, the amount of adsorbed methane was divided by the micropore volume. In Fig. 6 is demonstrated the adsorbed methane density versus the pressure. It is noticeable that all three CZ samples present higher density values compared to zeolite beta which reaches a plateau at significantly lower pressures. The results are presented in Table 2.

The theoretical asymptotic maximum storage capacity, the equilibrium constant and homogeneity grade of the samples have been evaluated by means of analysis of the adsorption isotherms by means of the Töth [44] model according to the equation:

$$\text{wt}\% = \frac{\text{wt}\%_{\text{max}} K P}{(1 + (K P)\tau) t} T / t$$

where $\text{wt}\%_{\text{max}}$ is the maximum adsorption capacity (theoretical limit reached asymptotically at infinite pressure), $K$ is the equilibrium constant and $\tau$ is a parameter introduced by Töth 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.

Töth model was chosen since it is the most appropriate for the fitting of an adsorption by heterogeneous surfaces compared to those of Langmuir, Freundlich or other models [45,46]. The maximum uptake, $\text{wt}\%_{\text{max}}$ is an extrapolated hypothetical saturation coverage and does not represent a real and plausible uptake value. It is thus presented as one of the three Töth parameters, but is not further analyzed. The value of $K$ for the samples CZ1073 and CZ1123 is the same within the error, while for the samples of
Fig. 4. Nitrogen adsorption–desorption isotherms of zeolite beta, CZ1023, CZ1073 and CZ1123 (a), DFT based pore size distributions of the samples (b) and DFT fitting comparison (c).

Table 1
Structural properties of all samples.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SSA (m²/g)</th>
<th>(V_{\text{tot}}) (mL/g)(^a)</th>
<th>(V_{\text{mDFT}}) (mL/g)(^b)</th>
<th>Pore width (nm)(^c)</th>
<th>Skeleton density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite beta</td>
<td>712</td>
<td>0.51</td>
<td>0.19</td>
<td>1 (6)</td>
<td>1.8</td>
</tr>
<tr>
<td>CZ1023</td>
<td>757</td>
<td>0.58</td>
<td>0.16</td>
<td>1 (2.3 and 4.3)</td>
<td>1.7</td>
</tr>
<tr>
<td>CZ1073</td>
<td>1127</td>
<td>0.75</td>
<td>0.29</td>
<td>0.9 (2.3 and 4.3)</td>
<td>1.5</td>
</tr>
<tr>
<td>CZ1123</td>
<td>808</td>
<td>0.74</td>
<td>0.17</td>
<td>1 (5 and 7)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\(^a\) Calculated at \(p/p_0 = 0.95\) (i.e. pores <40 nm).
\(^b\) Micropore volumes were deduced by DFT calculated integral volume up to 2 nm (\(V_{\text{mDFT}}\)).
\(^c\) Values in parentheses refer to additional peaks in the mesoporous region.
zeolite beta and CZ1032 is higher (Table 3). This can be related to the curvature of the isotherms of these samples (Fig. 5a), indicating a quicker saturation of the adsorption sites for higher $K$. The $t$ values are almost the same within the experimental error and close or even equal to one for all three carbon samples (Table 3), indicating very homogeneous surfaces and low CH4/CH4 interaction while for the zeolite beta sample the $t$ values is lower indicating that its adsorption sites do not show a similar methane affinity.

Finally, the isosteric heat of adsorption was evaluated according to the Clausius–Clapeyron equation:

$$\ln P = -\frac{\Delta H}{RT} + C$$

The formula has been utilized to the isotherm curves obtained on the investigated samples at 286 K, 298 K and 313 K and low pressures (0.01–0.1 MPa).

As it is shown in Table 4 all four samples, within the experimental error, have very close values of isosteric heat of adsorption, indicating a similar bonding energy and affinity of the pore surfaces towards the methane adsorption for low coverages. Plots of heat of adsorption enthalpy as a function of methane uptake are shown in Fig. 7. For the CZ samples the enthalpy values remain nearly constant, suggesting that methane encounters a homogeneous adsorption potential.

4. Conclusions

In conclusion, high surface area zeolite-like carbon materials were developed via a CVD route using zeolite beta as solid template. CVD was performed at three different temperatures.
(1023 K, 1073 K, and 1123 K) using acetylene as carbon precursor. The starting material (zeolite beta) and the final carbon materials (CZ1023, CZ1073 and CZ1123) were evaluated for their capability to store methane at different temperatures (287 K, 298 K and 313 K) using a Sievert-type apparatus up to 3.5 MPa. The sample of zeolite beta has a low methane adsorption capacity, compared to the final carbon samples, up to around 1.5 wt% at 298 K and 3.5 MPa. The sample obtained at 1073 K showed the highest SSA value (1127 m²/g), an appropriate pore width and stores more efficiently the methane molecules reaching a measured uptake of 8.0 wt% at 298 K and 3.5 MPa. All three carbon samples, within the experimental error, show a high grade of surface homogeneity and a similar binding energy between the carbon surface and the gas molecules being the isosteric heat of adsorption close to 13 kJ/mol. The morphology and structure of the CZ samples played the key role in terms of accessible surface: the absence of the pore ordering of the zeolite template in sample CZ1023 determine a high limitation on the accessible surface for CH₄ adsorption.

Acknowledgements

The authors are grateful to Abate Salvatore and Desiderio Giovannini (LICRIL – Liquid Crystal Laboratory INFM-CNR) for precious help during SEM measurements and to DeltaE srl for their helpful technical and economical support. This present study was co-financed by the European Union (European Social Fund e ESF) and Greek National Funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) e Research Funding Programs: Thales. Investing in knowledge society through the European Social Fund.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2013.12.030.

References