



Methane storage in zeolite-like carbon materials



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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 Tóth 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.

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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 temperature within the tanks. An interesting alternative is to store NG as an adsorbed phase in porous materials and low pressures resulting in safety advantages. This technology is yet in scientific level and the studies on storage by adsorbed natural gas method are carried out by using methane (CH₄), which is the major component of NG.

The growth attention on the synthesis of suitable materials for physical methane storage is the main aim of many researchers the last years. Many groups of materials have been studied for methane storage, for example the Metal–Organic Frameworks (MOFs) which possess very promising characteristics such as exceptional 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 [1,11–17]. Lozano-Castelló et al. [18] reported a high methane storage

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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 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-templated 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. Hiroto Nishihara et al. reported the synthesis of several types of zeolite-templated 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 distinct structures termed polymorphs A and B, which both possess a three-dimensional network of 12-ring pores, and grow as 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 isolated by centrifugation with PP falcons. Finally, the resulting carbon materials were dried in air in an oven at 393 K. According to the deposition temperature, the CZ samples are denoted as CZ1023, CZ1073 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.

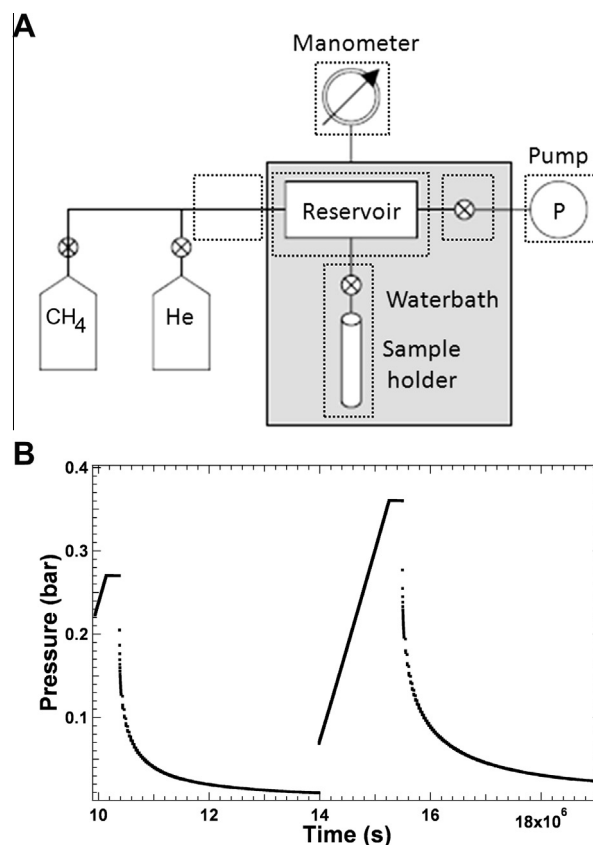


Fig. 1. Schematic representation of the Sieverts' apparatus [38] (a), plot with equilibration kinetics examples (b).

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