Colloids and Surfaces A: Physicochem. Eng. Aspects 474 (2015) 76–84

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Adsorption of CO_2/CH_4 and CO_2/N_2 mixtures in SBA-15 and CMK-5 in the presence of water: A computer simulation study

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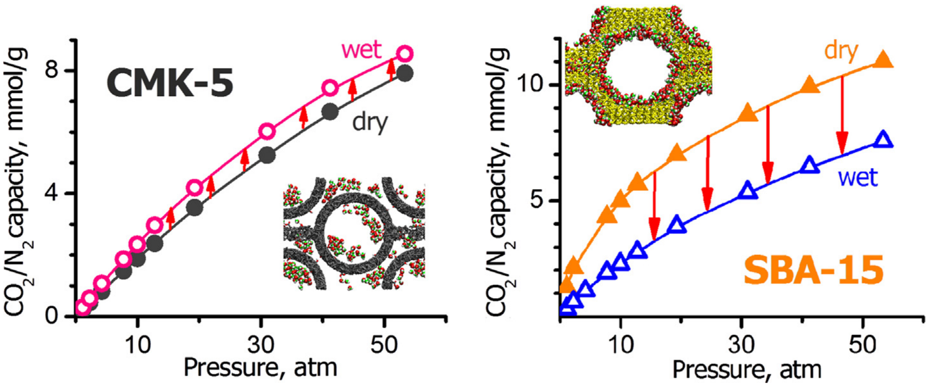
HIGHLIGHTS

- Adsorption of gas mixtures in wet adsorbents is studied by Monte Carlo simulations.
- Mechanisms of adsorption in hydrophilic SBA-15 and hydrophobic CMK-5 are compared.
- The decrease of gas capacity and selectivity to CO_2 is found for wet SBA-15.
- The increase of gas capacity and selectivity to CO_2 is found for wet CMK-5.
- The effect of humidity is governed by interactions of CO_2 with adsorbent and H_2O.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 January 2015
Received in revised form 10 March 2015
Accepted 12 March 2015
Available online 21 March 2015

Keywords:
Monte Carlo simulation
Gas adsorption
Preadsorbed water
SBA-15
CMK-5

ABSTRACT

Adsorption of CO_2/CH_4 and CO_2/N_2 gas mixtures in SBA-15 and CMK-5 is studied by Grand Canonical Monte Carlo. Simulations are carried out at 298 K for pressures up to 50 atm in dry adsorbents and in the presence of preadsorbed water (3.5 or 11.1 mmol/g). Effects of preadsorbed water on adsorption of gas mixtures are different for hydrophilic and hydrophobic porous materials. For SBA-15 the presence of water has a negative effect on adsorption, significantly reducing both the adsorption capacity and selectivity to carbon dioxide. By contrast, in CMK-5 the capacity and selectivity increase with increasing content of preadsorbed water. The behavior of gas capacities in moist adsorbents is largely determined by adsorption in the mesoporous regions of the pore space, while the selectivities can be affected by adsorption in micropores of SBA-15 and in inter-pore spaces of CMK-5.

1. Introduction

Removal of carbon dioxide from gas mixtures is an important component of different industrial and environmental processes, such as biogas purification and carbon capture from flue gas. Separation methods based on physical adsorption (e.g., pressure swing adsorption) are viewed as promising techniques for these applications [1–3]. At present, the inventory of candidate materials for adsorptive separation of CO_2-containing mixtures includes various carbonaceous materials, siliceous porous adsorbents and their derivatives, and metal-organic frameworks [4].

The presence of water, which is frequently found either in the gas mixtures or in the adsorbent itself, has a pronounced effect on adsorptive separation. This effect is typically quantified through the observed changes in gas adsorption capacity of the wet adsorbent as compared to the dry material. The gas capacity of wet adsorbents

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http://dx.doi.org/10.1016/j.colsurfa.2015.03.008
0927-7757/

can decrease or increase, depending on the type of the adsorbent used for separation. The changes in gas capacity are often associated with processes other than physical adsorption. For example, a sharp increase of gas capacity observed at relatively low temperatures and high pressure can be related to the formation of gas hydrates in porous media [5–7]. Under ambient conditions for moist natural coals the gas capacities are normally lower than for dry ones [8–11]. However, it was shown [12–14] that gas adsorption in coals (especially in the presence of water) is accompanied by significant deformation of the solid, so the immediate cause of the changes in gas adsorption properties cannot be readily determined. The effects of water on adsorption in metal-organic frameworks may also be different, leading either to an increase or decrease of gas capacity, but the extremely wide variety of such materials hinders the determination of the general mechanism of gas adsorption in MOFs in the presence of water [15]. Examples of purely physical adsorption are provided by zeolites and carbon nanotubes. For the former materials the presence of water leads to a decrease of gas adsorption [16,17], while for the latter an increase of adsorption capacity can occur at low water content [18]. It is obvious that the effects of water on gas adsorption should be closely connected to the hydrophilic or hydrophobic nature of the adsorbent. However, the exact mechanisms of the influence of water on gas adsorption are not known.

Computer simulation is an efficient instrument for resolving such problems, since it is capable of modeling the processes of interest at the required level of detail in a controllable environment, while providing the necessary tools for establishing the connections between the observed phenomena and their molecular-level physical background. In the last few years several Monte Carlo computational studies of adsorption in the presence of preadsorbed water have been published [19–25]. Most of these studies [19–24] focused on the simulation of adsorption of pure carbon dioxide and methane, as well as their mixtures in carbon pores of different shapes. The adsorbent capacity for methane was shown to decrease in the presence of water [19–23]. For carbon dioxide the adsorption in wet carbons appears to be a more complex process than for methane. While in the presence of water the adsorption capacity for CO_2 was frequently lower than in dry adsorbents, under certain conditions (e.g., at low pressure) the amount of adsorbed CO_2 remained constant or even increased when water was added to the simulated system [21–24]. This behavior of the adsorbent was explained by the competition of two important factors: CO_2–water interactions (carbon dioxide adsorption becomes energetically more favorable; capacity increases) and diminishing accessible volume (less space available to gas molecules; capacity decreases). The influence of preadsorbed water on gas adsorption in siliceous materials can be illustrated by the simulation study carried out by Joos et al. [25]. It was shown that the addition of water to zeolite 13X leads to a decrease of CO_2 adsorption, which can even be manifested on the order of magnitude scale under certain conditions.

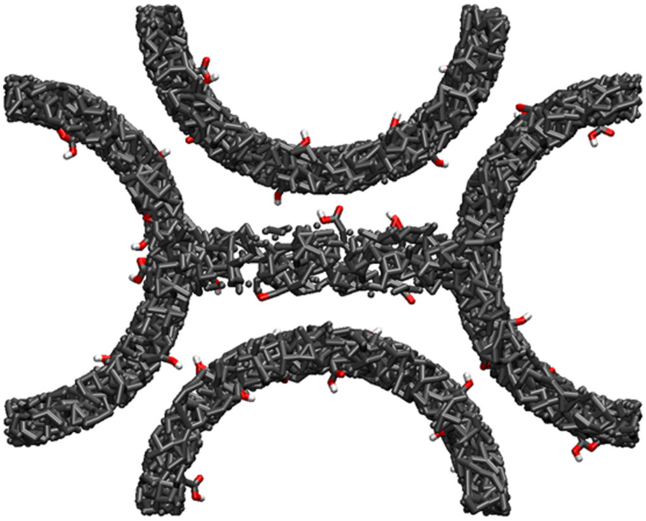

Fig. 2. Structure of CMK-5 (view along *z* axis).

In the present work the Grand Canonical Monte Carlo method is used to investigate the mechanisms of moisture effects on the adsorption of CO_2/CH_4 and CO_2/N_2 equimolar gas mixtures in SBA-15 mesoporous silica [26,27] and its carbon replica, CMK-5 [28,29]. These materials represent two important classes – siliceous and carbonaceous adsorbents, which are classical examples of hydrophilic and hydrophobic systems. Both adsorbents have complex porous structures comprised of mesopores and micropores (SBA-15) or inter-pore spaces between carbon nanopipes (CMK-5). The contributions of different parts of porous space to total gas adsorption will be studied in detail.

2. Simulation details

2.1. Adsorbent structures

The structures of adsorbents are shown in Figs. 1 and 2. The structure of SBA-15 siliceous adsorbent was obtained following a procedure similar to the one used in simulation studies of silica materials (see, for example [30–34]). β-cristobalite was chosen as the starting material since its density is close to the desired density of the amorphous silica (2.2 g/cm^3). Porous space was created by cutting out four semi-cylinders with a radius of 19.5 Å from a 71.7 Å × 57.3 Å × 64.5 Å β-cristobalite crystalline matrix.

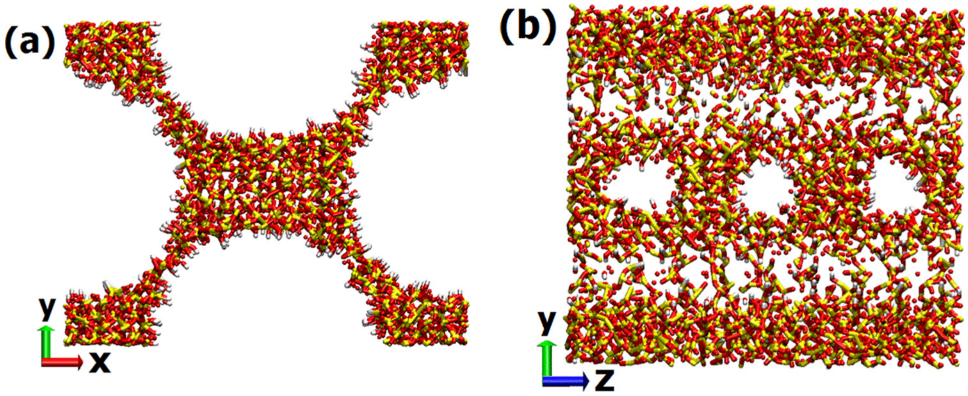

Fig. 1. Structure of SBA-15: (a) view along *z* axis, (b) view along *x* axis.