Competitive adsorption equilibrium of binary mixture on porous materials

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The capture of carbon dioxide produced by combustion of fossil fuels is largely studied to reduce the greenhouse gas emission to an acceptable level. In this aim, various methods are considered including membrane separation or molecular sieves adsorption… In addition, to minimize CO_2 emissions, renewable energy resources could be converted first in hydrogen gas. For an efficient and clean use, hydrogen gas must be pure. So, the purification processes play an essential role in these schemes of energy production (Weinberger, 2005). For instance hydrogen extraction from gas mixtures where the main components are H_2, CH_4 and CO_2 can be realized by competitive adsorption under pressure in carbon porous structures.

In this work, we report a study by Grand Canonical Monte Carlo (GCMC) simulations of the adsorption process. The Monte Carlo simulation is used to predict the adsorption of gases on carbonaceous porous materials. In the GCMC ensemble where the temperature, volume and chemical potential are kept constant, the gas adsorbed amount is determined as an average on the fluctuation of the number of adsorbed molecules. The realization of accurate GCMC simulations requires the knowledge of the adsorbent structure and a detailed description of the interactions between the adsorbed molecules (H_2 or/and CO_2) and carbon atoms.

Interactions between the gas molecules are described by pair potentials and electrical multipoles, assuming that each molecule H_2 or CO_2 is the source of van der Waals interactions and, possibly, electrical quadrupoles. The van der Waals interactions are represented by Lennard-Jones (LJ) potentials and electrical quadrupoles by adequate distributions of effective charges (Stubbs and Siepmann, 2004). The crossed van der Waals interactions between carbon materials and gas molecules are obtained from the Lorentz-Berthelot's rules (Darkrim and Levesque, 2000). We used the following LJ potential parameters for H_2 : ε_{H2}=36.7K and σ_{H2}=2.958Å (located at mass centre), for CO_2 : ε_C=27.0K, ε_o=79.0K, $\sigma_C = 2.80$Å and σ_O=3.05Å (located on C and O atoms). The structure of the carbon nanofiber adsorbent was modelled by an array of slit-shaped pores characterized by an unique nanopore width of 25Å.

The adsorption uptakes are computed following the Gibbs definition. We interpret the adsorption selectivity both for pure gases and mixtures on the basis of the partial density profiles of adsorbed gases in nanopores as shown in fig. 1. The large selectivity of CO_2 relative to H_2 results from the dominant adsorption of CO_2 near the pore walls. So, H_2 molecules are almost excluded by CO_2 molecules from this part of the adsorption domain. For the considered pressure and temperature, in the central part of slits, the densities of adsorbed H_2 and CO_2 molecules are equal to their bulk densities (blue and red dashed lines in fig. 1). The comparison between pure and mixture density profiles shows that CO_2 adsorption is practically not

modified by the presence of H_2 molecules enabling a large adsorption selectivity in favour of the adsorption of CO_2 which allows an efficient H_2 purification.

These results show that the optimisation of the purification process is feasible by GCMC simulations which can help to design adequate adsorbent materials and to define optimal thermodynamic conditions.

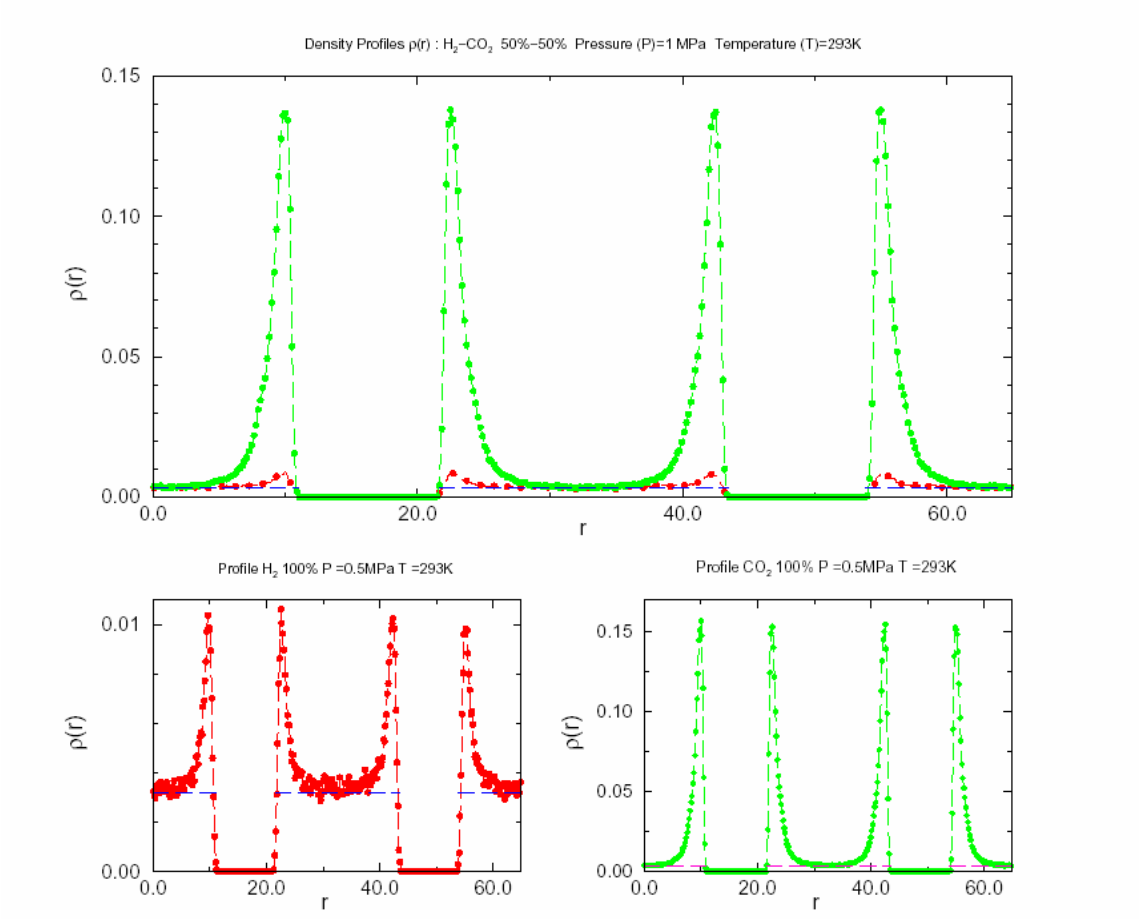

Figure 1: Top : density profiles of H_2-CO_2 equimolar mixture adsorbed on carbon porous materials at 1MPa and 293K : dashed dotted green line CO_2, dashed dotted red line H_2. Bottom : density profiles of pure H_2 and CO_2 at 0.5MPa and 293K : the blue and red dashed lines indicate the value of H_2 and CO_2 bulk densities.

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