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CO_2 - Reinforced nanoporous carbon potential energy field during CO_2/CH_4 mixture adsorption. A comprehensive volumetric, *in-situ* IR, and thermodynamic insight

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ABSTRACT

CO_2/CH_4 mixture adsorption is very important in different fields like, for example, a biogas purification. Using a comprehensive experimental approach based on volumetric and *in-situ* FTIR measurements the new results of CO_2/CH_4 mixture separation on a carbon film are reported. The application of this experimental approach makes it possible to elaborate the effect of enhanced CH_4 adsorption at low CO_2 concentrations in the adsorbed phase. The presence of this effect is proved experimentally for the first time. This effect is responsible for the deviation of Ideal Adsorption Solution model from the experimental data. To discuss separation mechanism the activity coefficients at constant spreading pressure values are calculated. At low spreading pressure, CO_2 activity coefficient is strongly disturbed by the presence of CH_4 molecules in the surface mixture. In contrast, the CH_4 activity coefficients are remarkably influenced by adsorbed CO_2 only at higher CO_2 surface concentrations. The obtained activity coefficients are successfully described by a new modification of the Redlich-Kister equation. This modification takes into account the interaction between binary mixture components and an adsorbent. Finally we show that the studied carbon possesses very good CO_2/CH_4 mixture separation properties, comparable to those reported for other adsorbents.

1. Introduction

CO_2/CH_4 mixture has been considered as very important because it is a major biogas component [1] produced by bacteria from anaerobic fermentation of a biodegradable waste. A biogas is currently one of the most important renewable energy sources. However, before a biogas is used, CO_2 should be removed [2] since this component lowers the gas heating value. Among more or less advanced procedures of a biogas purification, adsorption-based methods (for example the Pressure Swing Adsorption [3]) play an important role, and activated carbons (and carbonaceous materials) are still considered as the most promising adsorbents [4]. This is caused by energy-efficiency and cost effectiveness of the adsorption-based methods and generally, by a relatively low cost of activated carbons. However, the major difficulty with activated carbons application is relatively low selectivity to CO_2 [5], thus the experimental as well as simulation studies of CO_2/CH_4 mixture have been reported, to optimize properties of the “best possible” carbon material. Among carbon materials, studied in the molecular simulations of CO_2/CH_4 mixture adsorption, one can mention a model carbon slit-like micropores, triply periodic carbon minimal surfaces, and Virtual Porous Carbons (VPC) [6].

Mentioned above theoretical studies are important not only in the field of a biogas purification, but simulations have shed a new light on the mechanism of the so-called “enhanced coal bed

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methane recovery process". This process is important in the reduction of anthropogenic CO_2. Considering CO_2/CH_4 mixture adsorption, a two-stage mechanism of the process has been reported, and the influence of pore sizes and surface oxidation on this mechanism has been studied theoretically. It is suggested that in very narrow micropores and at low mixture pressures, adsorbed CO_2 molecules can enlarge the potential field in pores, and drag some methane molecules from the gas phase. In this way, CH_4 adsorption (*via* dispersive interactions) can be increased in micropores [7]. This effect can be caused by the permanent quadrupole moment of CO_2 molecule, and in general, by larger tendency of CO_2 to intermolecular interactions. Thus, adsorbed CO_2 molecules can induce permanent electric moments in adsorbed CH_4 molecules. However, at larger CO_2 pore concentrations, the dominant CO_2-CO_2 interactions can lead to the displacement of CH_4 molecules from small pores. It is interesting that similar effect was reported for some Metal Organic Framework (MOF) materials. It was shown that water preadsorption should increase adsorption of CO_2 [8]. Summing up, molecular simulations suggest the occurrence of this enhancement effect at low pressures, however, (up to our knowledge) the experimental data confirming this effect do not exist.

Using adsorption measurements reinforced by the *in-situ* Fourier Transform Infra Red (FTIR) spectroscopy results, we are able to get deeper insight into the mechanism of CO_2/CH_4 mixture adsorption and separation. Special attention has been paid to the enhancement of CH_4 storage due to preadsorbed CO_2 (as it is described above). By the application of adsorption thermodynamics we discuss the mechanism of adsorption and separation in narrow carbon micropores. Unexpected plots of CO_2 activity coefficients are reported. It is shown that in narrow carbon nanopores the interaction between the adsorbent, CO_2 and CH_4 is more complicated as it has been proposed till now. Finally we show that studied nanoporous carbon is a potential candidate for CO_2/CH_4 mixture separation, and that the IAS based separation coefficients should be treated with a care.

2. Experimental methods

A carbon film used in this study was prepared from a pure cellulose. The charring experiments were described in detail elsewhere [9–11]. The cellulose film heated at 573 K in air for 1 h was outgassed at 873 K for 1 h under the dynamic vacuum ($1.3\ 10^{-6}$ bar) to remove surface oxygen. The full structural characteristics of the tested adsorbent have been described previously [12]. Briefly, based on the results of low-temperature Ar and N_2 adsorption, the tested carbon film can be regarded as a strictly microporous solid with the BET surface area equal to 478.3 m^2/g (carbon labeled C_{873} in [12]). It is important that the pore size distribution (calculated using the Density Functional Theory method) shows mainly the presence of very narrow micropores with the diameter equal to 0.62 nm (and the volume equal to 0.19 cm^3/g). Our previous simulation studies showed [6] that the most effective carbon for CO_2/CH_4 mixture separation should possess pores with diameters smaller than c.a. 1 nm, thus the studied carbon is a perfect candidate for this purpose.

The *in-situ* FTIR studies were carried out in a vacuum cell described previously [9,10,13]. The application of this technique makes it possible to determine in what extent physical or chemical adsorption occurs. Moreover, we can easily determine the absence of any surface oxygen compounds formed by chemisorption. We can also, based on the spectra of carbon, check in what extent a carbon material changes its structure during adsorption and in what extent a sample is affected by possible impurities.

The construction of the *in-situ* FTIR cell enables the thermal treatment of the carbon film up to 1200 K in any controlled atmosphere or in a vacuum. The CO_2 and CH_4 adsorption was performed under isothermal conditions (T = 298 K). For each run (see Table 1) after adsorption of CH_4, the CO_2 partial pressure was changed by addition of the next portion of the gas. The spectra for the samples were recorded using the Mattson Genesis II FTIR spectrophotometer. Spectral changes accompanying adsorption of gases were used, after calibration, to describe quantitatively observed phenomena. The respective gas phase was a background for each carbon film spectrum, enabling the observation of spectral changes of a sample surface, without perturbation from the gas phase. A period of at least 5 h (monitoring continuously) at each gas composition was held in order to be sure that the equilibrium was achieved.

Additionally, the adsorption isotherms of separate gases were measured volumetrically (T = 298 K).

All experiments were repeated at least three times and qualitatively similar results were obtained. The presented results are representative for three tested series of experiments.

Fig. 1 shows the FTIR spectra obtained after exposing the studied carbon sample to CH_4/CO_2 gas mixture at increasing partial CO_2 pressure. To the best of our knowledge there is a lack of *in-situ* FTIR studies using carbonaceous materials as molecular sieves in the CO_2/CH_4 separation process. What is important, adsorption of the gas mixture on carbon surface does not cause the appearance of any oxygen-containing surface compounds, particularly carbonate or carbonyl groups. It means that adsorption of both compounds is physical and fully reversible.

At 298 K the increase in the CO_2 pressure causes first the increase, and then the decrease in the intensities of the bands observed for physically adsorbed CH_4 (at 3016 cm^{-1}). The occurrence of this maximum during physical adsorption of CH_4 stays in an excellent agreement with the results of previous theoretical reports [7], and is the major subject of this work.

3. Results and discussion

The experimental adsorption data for pure gases are shown in Fig. 2. As in the case of "ordinary" microporous activated carbons, the adsorption of CO_2 is larger than the adsorption of CH_4 (see for example [15–17]). This is mainly caused by larger potential energy of C-CO_2 interactions in very narrow micropores [7]. This also causes that the equilibrium CO_2/CH_4 selectivity at "zero" coverage is enhanced in very narrow micropores.

As it has been often proposed [18], adsorption data were fitted using the Dubinin and Astakhov (DA) [19] adsorption isotherm equation (Fig. 2). Both studied gases are supercritical at the measurement temperature, therefore the "pseudo saturated vapour pressure" should be calculated. To do this the method proposed by Amankwah and Schwarz (AS) [20] was applied. As it was shown recently [18] application of the AS approach leads to the best fit of the DA model to simulated CO_2 and CH_4 adsorption isotherms [18]. As it is seen from Fig. 2 the DA model fits our experimental data very well (Fig. 2). The determination coefficient (showing the fit of

Table 1
The parameters of experimental runs; p is the sum of pCH_4 and pCO_2 at the end of experiment, yCO_2 is the equilibrium mole fraction of CO_2 in the gas phase.

Run number	pCH_4 [bar]	p [bar]	yCO_2
1	0.065	0.20	0.68
2	0.13	0.40	0.67
3	0.20	0.47	0.58
4	0.26	0.53	0.52
5	0.34	0.67	0.49
6	0.41	0.78	0.48