Porous Solids for Biogas Upgrading

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ABSTRACT

The sorption CO_2 and CH_4 in binderless beads of 13X zeolite and MOF-508 has been investigated between 303 and 473 K and total pressure up to 5 atm through fixed bed adsorption experiments. The amount adsorbed of CO_2 and CH_4 in zeolite 13X is around 4.7 mmol/gads and 0.4 mmol/gads, respectively, at 313 K and 3.7 atm in a 50/50 equimolar mixture. In a 25(CO_2)/75(CH_4) mixture the amount adsorbed is 4.0 and 0.84 mmol/g at the same temperature and pressure. MOF-508b exhibits highly selective adsorption to CO_2 with the adsorption capacity of 6 mmol/g at 303 K and 4.5 bar. Experimental CO_2/CH_4 selectivities in zeolite 13X range from 37 at a low pressure of 0.667 atm to approximately 5 at the high temperature of 423 K. In MOF-508b the selectivities are moderately high at low temperatures of 303 K in the range of 3-6, while their selectivity significantly decreases as the temperature increases. The breakthrough curves measured show a plateau of pure CH_4 of approximately 6 minutes in zeolite 13X depending of the operating conditions chosen.

Keywords: Biogas Upgrading; Porous Solids; Pressure Swing Adsorption, Zeolite 13X, MOF 508b

INTRODUCTION

The reduction of CO_2 and CH_4 emissions to atmosphere is a matter of great concern nowadays since both gases can contribute significantly to the so-called greenhouse effect that describes the trapping of heat near earth´s surface by gases in the atmosphere. At the same time CO_2/CH_4 separations are of interest in treating gas streams like landfill gas, biogas and coal-bed methane. Accordingly, there is a need to investigate on this topic and that can be done with improved efficient technologies to separate or remove CO_2 and CH_4 from exhaust gases. Two recent reviews discuss this matter with great detail concerning the use of adsorbents (porous solids) based technologies to handle CO_2 capture and CO_2/CH_4 separations [1,2].

Biogas is mainly composed by CH_4 (60 to 70%) and CO_2 (30 to 40%) and to obtain a high energy content CO_2 needs to be separated from CH_4. For this purpose a variety of solid physical adsorbents have been considered including molecular sieve zeolites and a new class of adsorbents named Metal-Organic Frameworks (MOFs). The technology for biogas upgrading using adsorbents is called Pressure Swing Adsorption (PSA). With this technique, carbon dioxide is separated from the biogas by adsorption under elevated pressure. The adsorbing material, is regenerated by a sequential decrease in pressure before the column is reloaded again, hence the name of the technique.

In this work, we will present breakthrough experiments and selectivity data of CO_2 and CH_4 in MOF-508b and zeolite 13X at 303, 313, 323, 343, 373 and 423 K and partial pressures up to 4.5 bar. This data could be used in the design (simulation) of a cyclic adsorption processes (PSA) for the purification of biogas and CO_2 sequestration.

EXPERIMENTAL SECTION

Adsorbates and Adsorbent

The adsorbates under investigation were CO_2 and CH_4. The gases containing purity higher than 99.5% were supplied by Air Liquide. The microporous MOF-508b Zn(BDC)(4,4'-Bipy)0.5 (1) (4,4'-Bipy = 4,4'-bipyridine) was synthesized according to the procedure given in ref. [3] by Prof Banglin Chen of the University of Texas San Antonio, USA and zeolite 13X was kindly furnished by the company Chemiewerk Bad Köstritz GmbH, Heinrichshall 2, 07586 Bad Köstritz, Germany.

Equipment and procedure

Adsorption equilibrium data were obtained from breakthrough experiments in a laboratorial unit existing at LSRE. Figure 1 shows a schematic representation of the apparatus used to measure single and multicomponent breakthrough curves. A detailed description of the apparatus set-up is given in a previous work [3].

The experimental procedure follows: An adsorption column packed with crystals of MOF-508b dispersed in glass wool was operated by introducing a constant flowrate of adsorbate gas mixture with known composition in a helium stream at a fixed total pressure. The analysis of the system consists in measuring continuously the mass flow at the outlet of the packed bed with a thermal conductivity detector (TCD). In multicomponent experiments, samples are collected from the column output during the breakthrough curve for further analysis in a silica-gel chromatographic column.

Prior to each run, the packed bed is regenerated for at least 2 hr at 423 K under helium flow up to 50ml/min. The next experiment can start as soon as the TCD signal is stable again. In our experimental procedure first experiments were not taking into account. The reversibility is evaluated by repeating some experiments occasionally and verifying the amount adsorbed which generally agree well. In this work, two columns with different internal diameter were used for single and multicomponent experiments. The characteristics of these adsorption units are reported in Table 2.

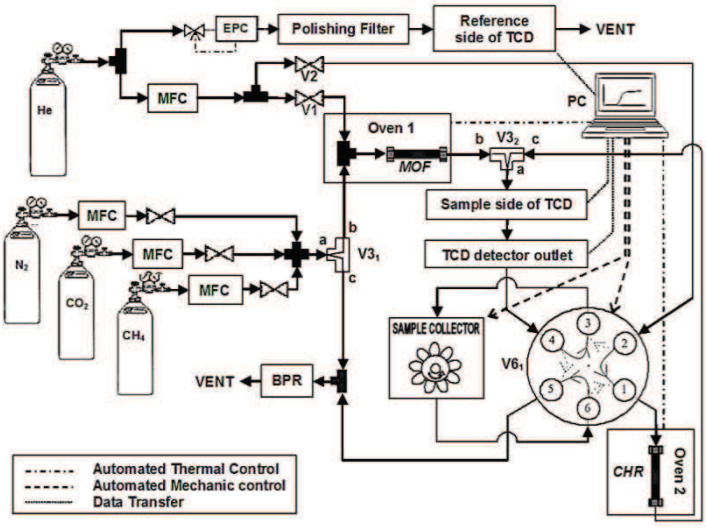

Figure 1. Schematic diagram of the apparatus used to measure adsorption equilibrium for mono- and multi-component systems: (BPR) back pressure regulator; (Sample collector) 10 sample-loops; (CHR)

chromatographic silica gel column; (MOF) packed column containing MOF; (EPC) electronic pressure controller; (MFC) mass flow controller; (PC) Computer; (TCD) thermal conductivity detector; (V1, V2) valves; (V31, V32) 3-ways valves; (V6) 6-ways crossover valve; (①,②,③,④,⑤,⑥) streams.

RESULTS AND DISCUSSION

The design of a Pressure Swing Adsorption process for biogas upgrading using porous solids requires the measurement of thermodynamic data such as the adsorption equilibrium data and selectivities between CO_2 and CH_4 based in the ratio of the amount adsorbed of the compounds at a certain temperature and pressure. Such data can be obtained from breakthrough experiments. The following sections show such data measured at LSRE for a new binderless zeolite 13X and a new metal-organic framework named MOF 508b.

Zeolite 13X

In this section we give an overview of the binary breakthrough curves obtained from where the amounts adsorbed and the selectivities of CO_2 and CH_4 were calculated. In Figure 2 the breakthrough curves for a 50/50 (a) 25/75 (b) CO_2/CH_4 mixtures are shown at the temperature of 313 K to show the influence of total pressure in the column: 5 atm (a1,b1), 3 atm (a2,b2) and 1 atm (a3,b3). We plot the breakthrough curves in terms of the normalized mole flow of the adsorptive species F_i/F_{0i}, as a function of time.

Figure 2 shows that at the low temperature of 313 K the separation between CO_2 and CH_4 is significant given rise to long plateaus of pure CH_4. For example Figure b1) shows a plateau of almost 6 min of pure CH_4 for the mixture 25/75 at the total pressure of 5 atm, with CH_4 breaking practically at 1 min. Another interesting feature observed in Figure 4 is that the mass transfer zone for CH_4 is very steep being much more dispersive for CO_2. This could be attributed to the higher mass transfer resistance of CO_2 in 13X zeolite when compared to CH_4. As the pressure decreases it is clear that the plateaus of pure CH_4 are reduced. Figure 2b3) shows that at 313 K and 1 atm total pressure the plateau of pure CH4 is around 3 min. Another interesting feature is that for 50/50 mixtures the roll-up is more significant than for the 25/75 mixtures.

The separation efficiency of the binderless beads of zeolite 13X for binary mixtures CH_4/CO_2 can be rationalized in terms of the sorption selectivity, S, defined on a molar basis by $S = (q_1/p_1)/(q_2/p_2)$, where component 1 (CO_2) is the more adsorbed component. Figure 3 shows the temperature-dependent sorption selectivity for the 50/50 and 25/75 CO_2/CH_4 mixtures as function of total pressure of the adsorbed species. The $S_{CO2/CH4}$ is very high at the low temperature of 313 K and total pressure of sorbates of 0.666 atm being 36.3 and 21.1 for the 25/75 and 50/50 mixtures, respectively. As the pressure increases the selectivities decreases but the values are still considerable high at 313 K and total pressure of 3.34 atm ranging from 14.4 to 10.4 for the 25/75 and 50/50 mixtures, respectively. When temperature increases the selectivities decreases being the lowest value observed 5.4 at 423 K, partial pressure, 3.34 atm in a 50/50 mixture. These results show that the binderless beads o 13X zeolite can be considered an excellent separator of mixtures CO_2/CH_4 when appropriate operating conditions are chosen.

MOF 508b

A similar study was performed in MOF 508b where breakthrough fixed-bed adsorption of binary mixtures CO_2/CH_4 has been examined in details at different conditions. The typical breakthrough curves at 303 K are shown in Figure 4**.** Both breakthrough curves clearly indicate that MOF 508b is also a efficient for the removal of CO_2 from its binary CH_4/CO_2 mixtures.

The separation efficiency of MOF 508b for the separation of binary CH_4/CO_2 mixture can be also rationalized and compared in terms of the sorption selectivity. Figure 5 shows the temperature-dependent sorption selectivity as function of the mixture partial pressure. $S_{CO2/CH4}$ are moderately high at low temperature of 303 K in the range of 3-6, while their selectivity significantly decreases as the temperature increases. This values of selectivity are no so high as in the case of zeolite 13X but represent a good indications how this new MOFs materials can be exploited to improve the separation of compounds do the partially unlimited combinations of metal clusters and organic linkers which are the base for the synthesis if this new frameworks.

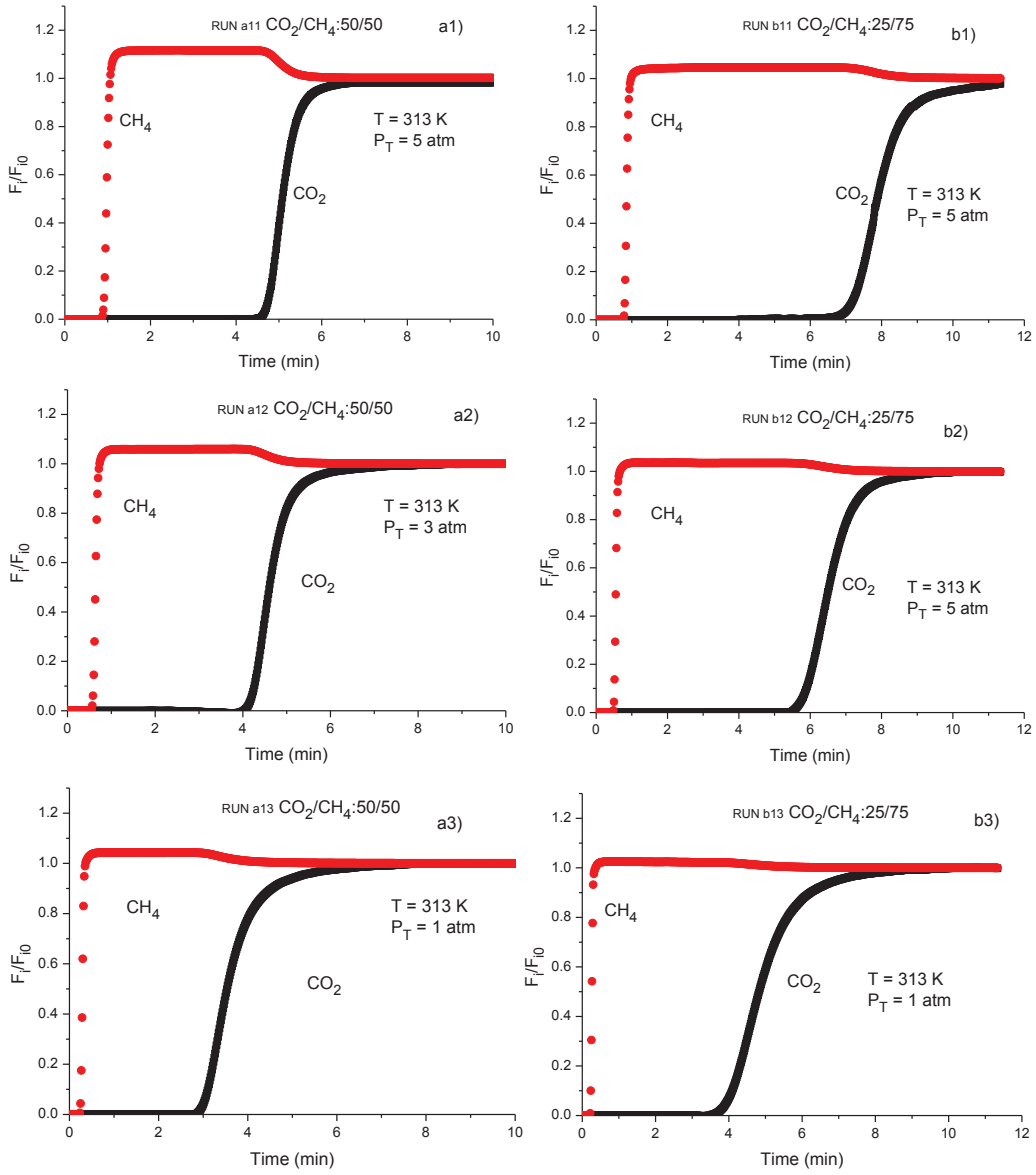

Figure 2. Experimental breakthrough curves for sorption of binary mixtures $CO_2(1)/CH_4(2)$ at 313 K in zeolite 13X. a1) Run a11, 50/50 mixture, Total pressure = 5 atm; a2) Run a12, 50/50 mixture, Total pressure = 3 atm; a3) Run a13, 50/50 mixture, Total pressure = 1 atm; b1) Run b11, 25(1)/75(2) mixture, Total pressure = 5 atm; b2) Run b12, 25(1)/75(2) mixture, Total pressure = 3 atm; b1) Run b13, 25(1)/75(2) mixture, Total pressure = 1 atm.

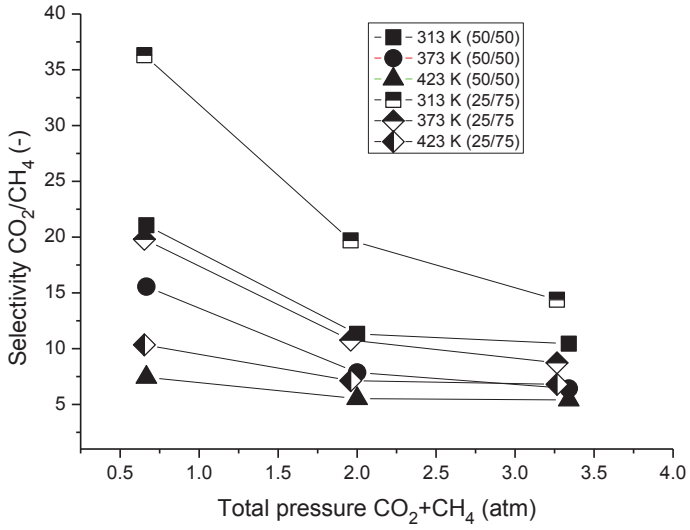

Figure 3 Selectivities in zeolite 13 X as function of total mixture pressure of adsorbable species for all runs performed.

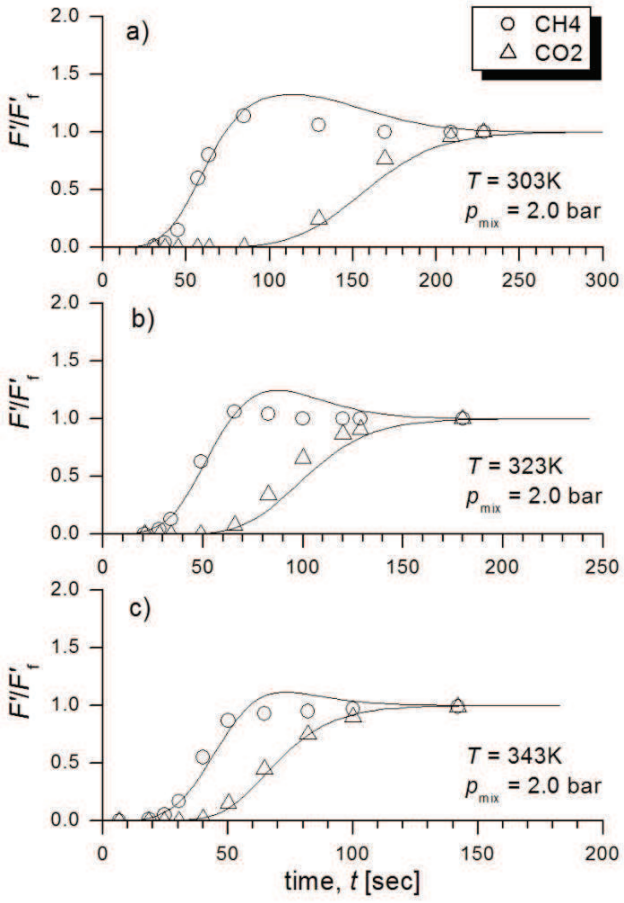

Figure 4. Effect of temperature on binary breakthrough curves for equimolar mixtures of CH_4–CO_2 in MOF 508b at a) T = 303 K, b) T = 323 K and c) T = 343 K at a total mixture pressure around 2 bar. Total system pressure was fixed at 5 bar.

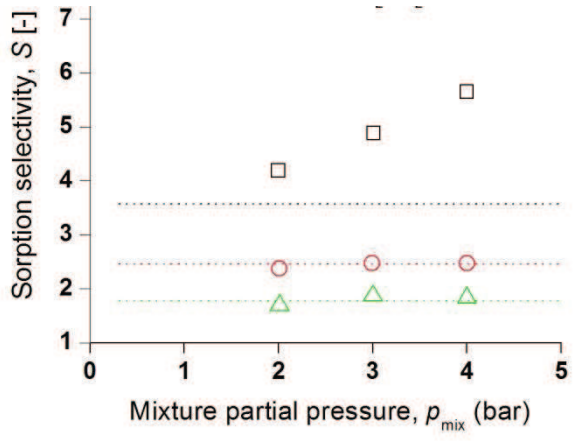

Figure 5. Temperature-dependent sorption selectivity for CO_2/CH_4 in MOF 508b as function of the mixture partial pressure (□, T=303K; ○, T=323K; △, T=343K).

CONCLUSIONS

Among the several technologies available for CO_2 removal Pressure Swing Adsorption (PSA) using a porous solid has been proved to be a efficient one. The discovery of new porous solids can increase the competitiveness of PSA technology. In this work it is shown through experimental data that the new 13X zeolite binderless beads zeolite can improve significantly the PSA technologies for BIOGAS upgrading with selectivities CO_2/CH_4 that can reach the value 34 and amounts adsorbed of CO_2 around 5.2 mmol/g. It also shown that metal organic frameworks such as the class of MOF-508b can also be an alternative in future for the separation of mixtures CO_2/CH_4 in biogas upgrading strategies.

References

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