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Comparison of commercial and new adsorbent materials for pre-combustion CO_2 capture by pressure swing adsorption

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Abstract

The IGCC technology (Integrated Gasification Combined Cycle) with pre-combustion CO_2 capture is a promising approach for near-zero CO_2 emission power plants to be realized in the near future. A key challenge within this technology is the separation of the CO_2/H_2 gas mixture resulting from the water gas shift reaction that follows the gasification of coal. For the CO_2 stream a purity of about 95% is required; additionally a CO_2 capture rate of 90% is desired, which implies that both streams, H_2 and CO_2, are required at rather high purity (~95%). In contrast to post-combustion capture from power plants, where a large gas stream at low pressure and low CO_2 content has to be treated, in pre-combustion capture a gas mixture at up to 40 bar has to be separated; therefore an adsorption based process, such as pressure swing adsorption (PSA), constitutes a promising method for CO_2 removal from H_2.

In this work, new materials, namely USO-2-Ni MOF, UiO-67/MCM-41 Hybrid and MCM-41, are characterized in terms of equilibrium adsorption isotherms. Excess adsorption isotherms of CO_2 and H_2 on these materials are measured at different temperatures (25°C – 140°C) and in a wide pressure range (up to 150 bar). The experimental data are then described with a suitable isotherm model, in our case Langmuir, Sips and Quadratic. In addition, the cyclic working capacity of CO_2 on each material is computed as a further assessment of the suitability of these materials for pre-combustion capture.

USO-2-Ni; UiO-67/MCM-41 Hybrid; MCM-41; excess adsorption isotherm; cyclic working capacity; PSA

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1. Introduction

Pressure Swing Adsorption (PSA) is one possible option to capture CO_2, i.e. separate CO_2 and H_2, within an IGCC (Integrated Gasification Combined Cycle) power plant. The process and boundary conditions of this separation step, especially a high feed pressure between 30 and 50 bar and a CO_2 mole fraction of about 40% (dry basis), make PSA promising since for the process itself no further compression energy is needed. Moreover, for PSA processes other energy requirements are inherently low. This leads to the situation that the highest energy loss is caused by the CO_2 compression to about 110 bar for transportation and storage that follows the capture. The energy penalty of this step depends mainly on the pressure level of the CO_2 before compression and on its purity, i.e. on the fraction of non-condensable gases present. Apart from a suitable process design, this is defined to a large extent by the adsorbent material. The two characteristics which are most important in this respect are selectivity and cyclic working capacity. The former is, among others, responsible for the obtained purity, whereas the latter gives an indication if desorption at higher pressures is feasible. Therefore, they can be used for a first assessment of the potential of different materials already at the stage when only equilibrium measurements are made.

In this work, three different materials have been synthesized, pelletized and characterized at SINTEF, namely USO-2-Ni metal organic framework (MOF), mesoporous silica MCM-41 and a mixed material consisting of a MOF bound with MCM-41. They are selected because they are believed to be promising for this process. However, to enable their use in a process application, pelletization is a very crucial step. It brings the material in a form suitable for a PSA column and at the same time it can be used to increase the bulk density, which allows reducing the final size of the columns. As for new materials no well-established method of pelletization exists, several possibilities have been tested and the best has been selected.

The synthesized and pelletized materials have been used to determine the equilibrium adsorption isotherms of the two main components, CO_2 and H_2. This was performed at ETH Zürich using a Rubotherm magnetic suspension balance (Rubotherm, Germany). Isotherms at different temperatures in the range between 25 and 140°C and at pressures up to 150 bar were measured and in a further step used to fit the parameters of suitable adsorption isotherms and to determine the isosteric heats of adsorption. The latter is especially important for process design because it influences the temperature behavior in the columns and hence the process performance.

2. Experimental

2.1. Materials

Three different materials are characterized in this study, namely USO-2-Ni MOF, mesoporous silica MCM-41 and a mixed material consisting of UiO-67 metal organic framework bound with MCM-41. All materials have been synthesized and pelletized at SINTEF Materials & Chemistry in Oslo. The preparation procedure is described in more detail in [1, 2, 3, 4]. Before the materials can be characterized they have to be activated [3].

Pure gases are obtained from Pangas (Dagmersellen, Switzerland) at purities of 99.9% for CO_2, 99.999% for H_2 and 99.996% for He.

2.2. Experimental procedure

To evaluate the properties of the adsorbent materials, the equilibrium adsorption isotherms of CO_2 and H_2 are measured on the new tailor-made MOF materials, namely USO-2-Ni MOF and UiO-67/MCM-41 Hybrid and on the mesoporoous silica MCM-41 using a Magnetic Suspension Balance (Rubotherm, Bochum, Germany). Pressures up to 150 bar are applied in these measurements in the temperature ranges from 25 to 140°C (CO_2) and from 25 to 65°C (H_2), respectively. In Table 1 an overview of the conducted experiments is given. The experimental set up used in this study is shown in Figure 1. The details of this set up are discussed elsewhere [5].

Table 1 Experimental overview. The binary measurements are discussed in Schell et al. (2012b).

	CO_2	H_2	CO_2/H_2
MOF	x	x	x
MCM-41	x	x	-
Hybrid	x	x	-

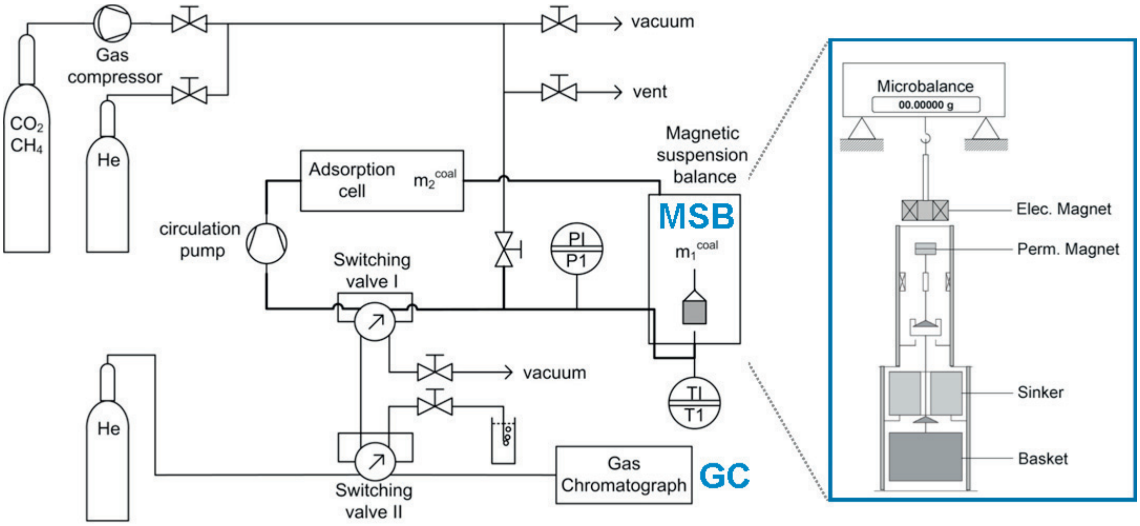

Figure 1 Experimental setup to measure single and binary equilibrium adsorption isotherms.

The measurement procedure is described in more detail in [5, 6], however it is shortly specified in the following for the case of experiments with pure gases. About 0.7 to 1.5 g of adsorbent, depending on the material, is placed in the balance before the system is evacuated at a temperature of 150°C. At these conditions the mass of the metal parts together with the mass of the adsorbent sample, i.e. $m^{\mathrm{met}} + m_0^{\mathrm{ad}}$, is measured:

$$M_1^0 = m^{\mathrm{met}} + m_0^{\mathrm{ad}} \tag{1}$$

To determine the volume of the adsorbent and the metal parts $V_0^{\mathrm{ad}} + V^{\mathrm{met}}$, the system is then filled with the inert helium:

$$V_0^{\mathrm{ad}} + V^{\mathrm{met}} = \frac{M_1^0 - M_1\left(\rho^{\mathrm{b}}, T\right)}{\rho^{\mathrm{b}}} \tag{2}$$

where $M_1\left(\rho^{\mathrm{b}}, T\right)$ is the mass measured at the given experimental conditions, i.e. at density ρ^{b} and temperature T.

After another evacuation step, the system is then filled with the fluid to be adsorbed, in our case CO_2 or H_2. As a direct measurement of the volume of the adsorbed phase is not feasible, generally the so called excess adsorption $\Gamma\left(\rho^{\mathrm{b}}, T\right)$ which is defined according to the first part of equation (3) is considered as the experimental result [7]. It can be calculated from the measurement using the second part of equation (3) at a given pressure and temperature:

$$\begin{aligned} \Gamma\left(\rho^{\mathrm{b}}, T\right) &= m^{\mathrm{ads}} - \rho^{\mathrm{b}} V^{\mathrm{ads}} \\ &= M_1\left(\rho^{\mathrm{b}}, T\right) - M_1^0 + \rho^{\mathrm{b}}\left[V^{\mathrm{met}} + V_0^{\mathrm{ad}}\right] \end{aligned} \tag{3}$$

where m^{ads} and V^{ads} are the mass and the volume of the adsorbed phase, respectively.

The experimental results are then obtained in terms of the molar excess adsorption n^{ex} per unit mass of adsorbent m_0^{ad}, calculated with the molar mass of the adsorbed gas M_{m}, as given in equation (4).

$$n^{\mathrm{ex}} = \frac{\Gamma(\rho^{\mathrm{b}}, T)}{M_{\mathrm{m}} m_0^{\mathrm{ad}}} \tag{4}$$

3. Results

3.1. Equilibrium adsorption isotherms

Experimental excess isotherm data of CO_2 and H_2 on all three adsorbents, as well as the fit with the Quadratic, Sips and Langmuir isotherm model is shown in Figure 2. The excess adsorption is plotted versus the bulk density, whereby the maximum value on the x-axis corresponds approximately to a pressure of 150 bar.

The CO_2 adsorption on the MCM-41 and the UiO-67/MCM-41 Hybrid material can be accurately described with the Sips and the Langmuir isotherm, respectively. The experimental CO_2 adsorption data on USO-2-Ni MOF exhibit an s-shape in the low pressure region and it is therefore best described with the Quadratic isotherm. It is worth noting that the USO-2-Ni MOF has the highest cyclic capacity followed by the MCM-41 and the UiO-67/MCM-41 Hybrid. Moreover, the Henrys constant of the three materials is rather different and this might have an effect on the regeneration step of an adsorption process. All isotherm parameters as well as their temperature dependency are reported in Schell et al. (2012b) where there are also discussed in more detail.

In general, H_2 adsorbs much less than CO_2 on all three investigated materials. This indicates that these materials are well suitable for the separation of CO_2 and H_2. In the case of USO-2-Ni MOF and UiO67-Hybrid the H_2 adsorption can be sufficiently well described with the Langmuir isotherm as shown in Figure 2. We encountered different difficulties while measuring the excess adsorption of H_2 on MCM-41. Given the fact that the material has a very low density the amount of material used for the gravimetric measurement was small. Therefore, the weight change induced by adsorption was very small and below the accuracy limit of the balance. Therefore, the measured data give only a rough estimate of the adsorption and no temperature dependency could be measured. Therefore, we have decided to describe the experimental adsorption data with a straight line. All isotherm parameters as well as their temperature dependency are reported in Schell et al. (2012b)

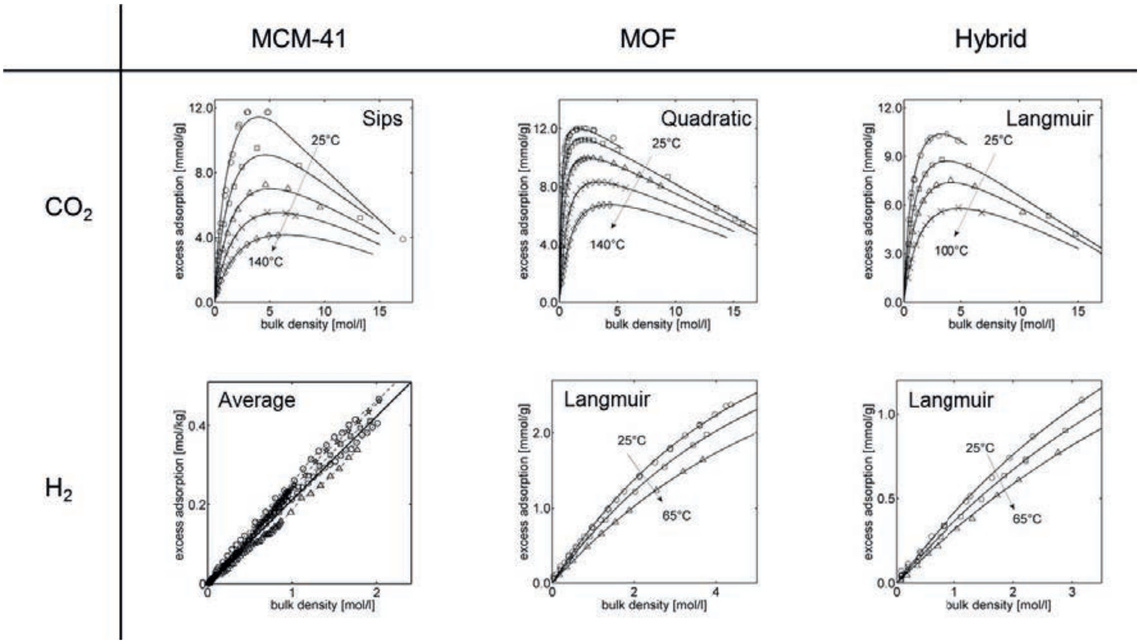

Figure 2 Single component equilibrium adsorption isotherms of CO_2 and H_2 on MCM-41, USO-2-Ni MOF and Uio-67/MCM-41 Hybrid at different temperatures. The symbols represent the experimental data and the lines represent the fit with the Quadratic, Sips and Langmuir isotherm, respectively. These data have been reported in greater detail in an earlier publication [3].

3.2. Cyclic capacities

Besides the adsorption capacity and selectivity also the cyclic working capacity or delta loading gives a good indication if a material is suitable for CO_2 capture by pressure swing adsorption. The cyclic working capacity is the difference between an amount adsorbed at a high pressure (adsorption) and a possible low pressure (regeneration). This is especially important for PSA processes given the fact that the adsorption and the desorption pressure largely influence the energy requirements of the process.

In Figure 3 the cyclic capacities of CO_2 at 25°C on different materials are compared. If for instance a desorption pressure of 0.1 MPa is assumed, the USO-2-Ni MOF shows the highest cyclic capacity followed by the UiO-67/MCM-41 Hybrid and the Activated Carbon and MCM-41, which have basically the same cyclic capacity [3]. It is worth noting that the Zeolite 13X has a very limited cyclic capacity in the range of interest because of the very strong adsorption already at low pressures and it is therefore not suitable for pre-combustion CO_2 capture.

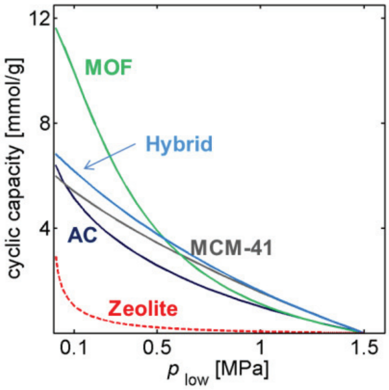

Figure 3 Cyclic capacities of CO_2 at 25°C on USO-2-Ni MOF (green), UiO-67/MCM-41 Hybrid (blue), MCM-41(grey), Activated Carbon (black) and Zeolite 13X (red) assuming an adsorption pressure of 15 bar and different desorption pressures [3].

4. Conclusions

In this study, excess adsorption of CO_2 and H_2 on USO-2-Ni MOF, UiO-67/MCM-41 Hybrid and MCM-41 are presented. The excess adsorption isotherms have been measured at different temperatures (25°C - 140°C) and in a wide pressure range (up to 150 bar) and the experimental data are described with different isotherms, namely Langmuir, Sips and Quadratic, by fitting their parameters to the experimental data. The adsorption capacity and selectivity as well as the cyclic capacity are used to make a first assessment of the potential of a material for pre-combustion CO_2 capture. However, in order to account for all effects, such as e.g. mass transfer and temperature effects proper process design, development and optimization have to be conducted.

Nomenclature

m	mass, [g]
M_1	weight at measuring point 1, [g]
M_1^0	weight at measuring point 1 under vacuum, [g]
M	molar mass, [g/mol]
n	molar adsorption per unit mass of, [mmol/g]
p	Pressure, [MPa]
T	Temperature, [K]
V	Volume, [cm^3]
ρ	molar density, [mol/l]

Sub- and Superscripts:

ad	adsorbent
ads	adsorbed phase
b	bulk phase
ex	excess adsorption
i	component i
m	molar
met	metal parts

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