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## Effect of temperature, dilute CO<sub>2</sub> and MEA impregnation on the CO<sub>2</sub> uptake of MIL-53 and HKUST-1 at ambient pressure

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### Abstract

Metal-organic frameworks (MOFs) are promising materials for CO<sub>2</sub> capture. Despite the fact that MOF have been widely investigated for high-pressure pre-combustion capture, their evaluation in post-combustion conditions has received less attention. In this work, the CO<sub>2</sub> uptake of MIL-53 and HKUST-1 was evaluated at 25, 50 and 75°C in presence of 100%, 12% and 5% CO<sub>2</sub> (balanced with N<sub>2</sub>) at atmospheric pressure.

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*Keywords:* CO<sub>2</sub> capture; Li-based sorbents; sorption-enhanced gasification; carbonation; biomass

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### 1. Introduction

Metal-organic frameworks (MOFs) are porous materials that offer a number of advantages for CO<sub>2</sub> capture due to their ordered structures, high thermal stability, adjustable chemical functionality and high porosity [1]. Moreover, adsorption rates in some MOFs are fast, which is essential for practical gas separation applications [2]. For example, basolite A-100 (MIL-53) is a hydrophilic MOF containing 1D diamond shaped channels with pores of diameter close to 0.85 nm and can be used for adsorption applications [3]. Its structure and pore size vary whether the sample is hydrated (ambient temperature) or dehydrated (100°C). At room temperature, the narrow pore phase is the most stable

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form, while at 100°C the structure presents larger pores [3].

Previous work has shown that CO<sub>2</sub> uptake by MIL-53 was between 1.5 and 2 mmol/g at ambient temperature in presence of 100% CO<sub>2</sub>, while a large step-increase in CO<sub>2</sub> uptake occurred at 6 bar with a maximum uptake obtained at 30 bar (10.4 mmol/g) [3].

The increased adsorption of CO<sub>2</sub> at about 6 bar was related to the specific interactions between the gas and the framework which would cause a shrinkage of the structure for low uptake values (<6 bar), while a raise in the adsorption pressure lead to a re-opening of the total porosity and total pore filling [3].

CO<sub>2</sub> adsorption in HKUST-1 extrudates (3x3 mm), (Copper benzene-1,3,5-tricarboxylate or HKUST-1) from 30 to 100°C and up to about 50 bar has been reported for CO<sub>2</sub> pre-combustion capture applications [4].

At low pressures, the adsorbent presents a very high selectivity toward CO<sub>2</sub> compared to CH<sub>4</sub>, with uptake capacity of ~1.8 and 3.6 mmolCO<sub>2</sub>/g sorbent, at 50 and 30°C, respectively [4]. In contrast to zeolites like 5A and NaX, small amounts of H<sub>2</sub>O may actually increase the CO<sub>2</sub> capacity of MOFs and can be easily removed by regeneration [5].

Despite the fact that MOF have been widely investigated for high-pressure pre-combustion capture, their evaluation in post-combustion conditions has received less attention. Therefore, this work wants to evaluate the feasibility of using MOFs MIL-53 and HKUST-1 under post-combustion conditions.

## 2. Methodology

In this work, the CO<sub>2</sub> uptake of MIL-53 and HKUST-1 was evaluated at 25, 50 and 75°C in presence of 100%, 12% and 5% CO<sub>2</sub> (balanced with N<sub>2</sub>) at atmospheric pressure. The CO<sub>2</sub> capture capacity was measured by using a TGA (TA Q500) in a controlled gas flowing environment [6]. As reported by the producer, MIL-53 (688738-10g, BASF) had a particle size of 31.5 µm (D50) and a BET surface of 1100-1500 m<sup>2</sup>/g, while HKUST-1 (688614-10g, BASF) had particles of 15.9 µm (D50) and a BET surface of 1500-2100 m<sup>2</sup>/g.

Ethanolamine (MEA) was used as additive (10 wt%) to promote CO<sub>2</sub> sorption. Prior to CO<sub>2</sub> sorption testing, the samples were dried at 100°C in flowing N<sub>2</sub> (100 mL/min) at 25 C/min for 30 min. The flowing gas was then changed to 100% CO<sub>2</sub> at the desired temperature to determine the CO<sub>2</sub> uptake.

The weight increase due to CO<sub>2</sub> sorption (mg CO<sub>2</sub>/g sorbent) was measured as a function of time at a constant temperature (25, 50, 75 C). Five regeneration cycles were used to ascertain the sorbents stability.

## 3. Results and Discussion

Figures 1 and 2 show the CO<sub>2</sub> sorption and desorption of MIL-53 (Fig.1) and HKUST-1 (Fig.2) at three different temperatures.

The CO<sub>2</sub> sorption experiments show that in presence of pure CO<sub>2</sub>, HKUST-1 has a higher capacity of 15.9wt% (3.6 mmolCO<sub>2</sub>/g sorbent at 25°C) than MIL-53 (8.05wt% or 1.8 mmolCO<sub>2</sub>/g sorbent at 25°C). In addition, the Figures clearly indicate that the CO<sub>2</sub> sorption is favoured at the lowest temperature. This is in agreement with previous work, which found similar CO<sub>2</sub> uptake [4,5]. The rate of the CO<sub>2</sub> sorption and desorption of the two MOFs at the different temperatures was evaluated calculating the derivative of the weight and is presented in Table 1. For both MOFs, the sorption was very fast at 25°C, with 35.7 wt%CO<sub>2</sub>/min and 29 35.7 wt%CO<sub>2</sub>/min, respectively. Inversely, the CO<sub>2</sub> desorption resulted much slower, with 3.14wt% and 1.2wt% CO<sub>2</sub> desorbed per minute. As expected, the sorption and desorption rates resulted lower when the temperature was increased to 50 and 75°C.

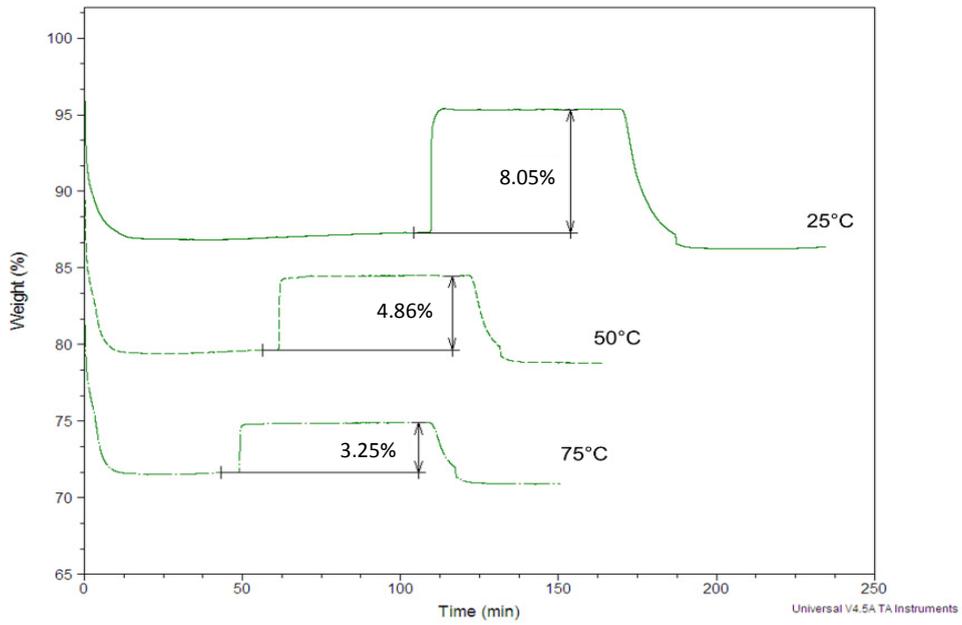


Figure 1. CO<sub>2</sub> capture of MIL-53 at different temperatures in presence of pure CO<sub>2</sub>.

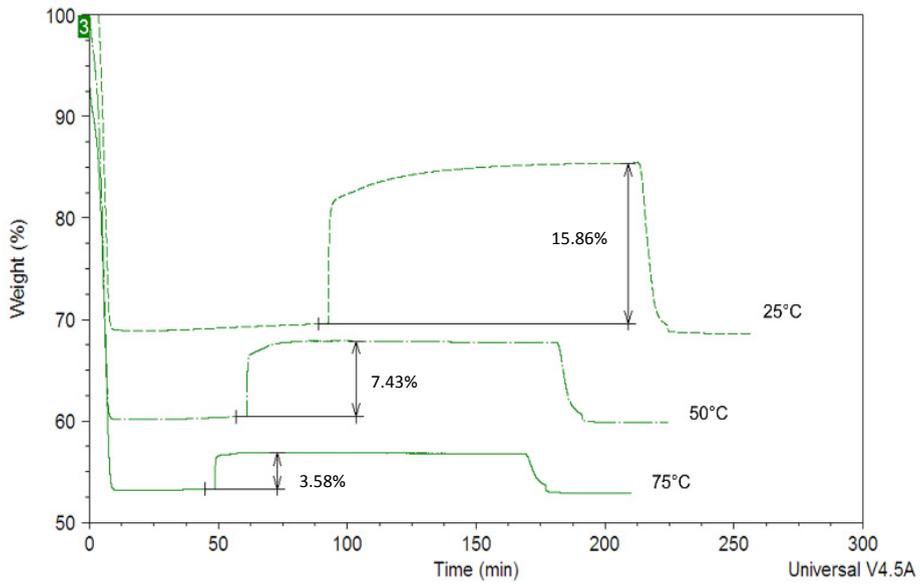


Figure 2. CO<sub>2</sub> capture of HKUST-1 at different temperatures. In presence of pure CO<sub>2</sub>

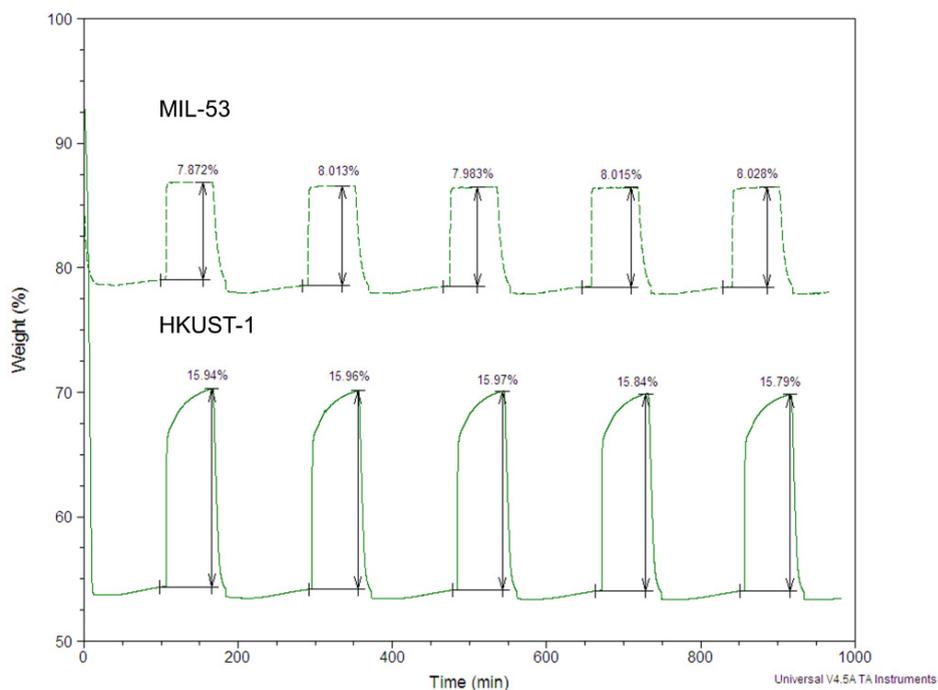
Table 1. Rate of CO sorption/desorption expressed ad derivative weight (wt%/min) at different temperatures.

<b>HKUST-1</b>	<b>CO<sub>2</sub> sorption (wt%/min)</b>	<b>CO<sub>2</sub> desorption (wt%/min)</b>
<b>25°C</b>	35.71	3.14
<b>50°C</b>	22.02	1.63
<b>75°C</b>	12.26	0.72
<b>MIL-53</b>		
<b>25°C</b>	29.02	1.21
<b>50°C</b>	19.09	0.92
<b>75°C</b>	13.50	0.63

The use of diluted CO<sub>2</sub> resulted in a consistent decrease of the CO<sub>2</sub> uptake to ~0.6 mmolCO<sub>2</sub>/g sorbent (using 12% CO<sub>2</sub>/88% N<sub>2</sub>) and 0.25-0.3 mmolCO<sub>2</sub>/g sorbent (using 5% CO<sub>2</sub>/88% N<sub>2</sub>). MIL-53 had the same CO<sub>2</sub> uptake capacity in presence of 12% CO<sub>2</sub>, but performed relatively better (0.31 vs 0.25 mmol CO<sub>2</sub>/g sorbent) than MIL-53 in presence of 5% CO<sub>2</sub>. Therefore, the two MOFs did not performed well under post-combustion conditions.

MIL-53 and HKUST-1 were also doped with 10% Ethanolamine (MEA) in the attempt to boost their CO<sub>2</sub> sorption capacity at ambient pressure. The MEA impregnated MOFs were tested in presence of 12% CO<sub>2</sub> (results not shown) but unfortunately, presence of MEA did not promoted the CO<sub>2</sub> uptake at 25°C probably due to the decrease of available surface.

Finally, the recyclability of MIL-53 and HKUST-1 was tested under pure CO<sub>2</sub>, repeating five CO<sub>2</sub> sorption/desorption cycles as shown in Figure 3. Both MOFs resulted stable and able to capture a constant amount of CO<sub>2</sub>.

Figure 3. Cyclic CO<sub>2</sub> sorption/desorption in presence of pure CO<sub>2</sub>.

#### 4. Conclusions

MIL-53 and HKUST-1 were not effective in capturing CO<sub>2</sub> from diluted flue gas at post-combustion conditions. Further investigations are required to fully understand the potential of MIL-53 and HKUST-1 for CO<sub>2</sub> capture.

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