



# Shaping metal–organic framework (MOF) powder materials for CO<sub>2</sub> capture applications—a thermogravimetric study

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## Abstract

The paper presents the effect of the tableting pressure and time on the chemical structure and crystallinity of the CuBTC and MIL-53(Al) metal–organic framework tablets. For MOFs, the no-binder tableting method was employed using a pressure of 3.7, 7.4, 29.6 and 59.2 kN m<sup>−2</sup>, respectively, for a duration of 0.5, 1 and 2 min. The obtained tablets were crushed and sieved to obtain the desired fraction from 500 to 650 μm. In this study, the thermogravimetric test has been used for the assessment of the effect of shaping metal–organic frameworks on the CO<sub>2</sub> adsorption properties. The examination of the CO<sub>2</sub> sorption capacity of metal–organic frameworks was carried out using a Mettler TGA/SDTA 851e thermobalance and TG-Vacuum. The results indicate a significant effect of compression on the crystal structure and CO<sub>2</sub> sorption capacity of MOFs.

**Keywords** CO<sub>2</sub> capture · MOFS · Thermogravimetric study · TG-Vacuum

## Introduction

The issues of atmospheric air protection due to greenhouse gas (GHG) emissions have become a worldwide problem, because increased atmospheric greenhouse gas concentrations cause global warming. Carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and fluorinated gases (HFC, PFC, SF<sub>6</sub>) are all greenhouse gases, among which CO<sub>2</sub> plays an increasingly important role due to its levels in the atmosphere. To achieve the goals and objectives set at the Climate Summit in Paris (COP 2015) toward the reduction in the emissions of greenhouse gases, including CO<sub>2</sub>, decisive actions to reduce the CO<sub>2</sub> emission must be taken by all sectors of the economy [1]. The CCS technology (carbon capture and storage) is proposed as one of the ways of stabilizing the concentrations of CO<sub>2</sub> in the air, apart from reducing the energy intensity of processes and the intensity of carbon dioxide emission [2]. Among the

proposed CO<sub>2</sub> separation technologies, the absorption technology is most developed now; however, the adsorption technology, especially VPSA, is gaining importance [2]. Zeolites, activated carbon, molecular sieves and amine-modified microporous adsorbents are among the most used adsorbents for VPSA separation process [3–5]. Besides these adsorbents, metal–organic frameworks (MOFs) are being developed as promising materials for CO<sub>2</sub> separation. Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCP), have been disseminated by the team of Omar Yaghi from the University of California, Berkeley [6]. Metal–organic frameworks, MOFs, are composed of metal atoms or complexes combined with organic bridging ligands, which are summarized in the three-dimensional structure mainly by strong coordination bonds [6–9]. Due to very high sorption capacity of some MOFs compared to zeolites, these compounds are mentioned as potentially the best adsorbents for CO<sub>2</sub> capture VPSA systems [10]. MOFs can also be adsorbents suitable for flue gas cleaning from SO<sub>2</sub> and NO<sub>x</sub> in view of the need for removing these impurities down to an appropriate level prior to CO<sub>2</sub> separation in the pre-treatment section of the VPSA installation. Classic methods of metal–organic framework synthesis result in MOF crystalline powders with sizes ranging from

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nanometers to hundreds of microns. The powder material is not industrially favorable due to the difficulties in processing such as pressure drop for fluid flow through a packed bed or dustiness [11]. In real VPSA carbon dioxide adsorption installation, MOFs may only be used in pelletized forms. Adsorption columns should be filled with MOF pellets or granules with appropriate thermal stability, which will allow large pressure drops to be avoided during the CO<sub>2</sub> capture on the adsorbent bed. Therefore, shaping of MOF powders into a tailorable form is a primary step to achieve the industrialization for MOFs [12]. The development of shaping MOF powder materials is crucial to using metal–organic frameworks on a large scale. The knowledge of the granulation of MOFs to prepare them for being used in real CO<sub>2</sub> capture VPSA adsorption units is scarce [11, 13–16]. Unfortunately, there have not been enough tests that would verify CO<sub>2</sub> adsorption on such shaping MOFs. Preliminary investigations have shown that the method of pelletization and its conditions (pressure, time) should be selected individually for individual MOF types. In contrast to zeolites, this procedure can be complex for some types of MOFs. For MOF granulation, two methods are proposed [11, 13–16]: pelletization using a binder, during which material properties such as porosity or density change, and treating the powder directly with pressure, without using a binder. Both methods were used, e.g., for making pellets based on powdered CuBTC [11, 13–16]. It is important to note that pressure used during pelletizing affects the physical and chemical properties of the material, including in particular the crystalline structure of MOFs. Pelletization tests carried out for individual types of MOFs, such as UiO-66, CuBTC, MIL-47, MIL-53, reported in the literature, have shown that both the binder type and applied pressure must be selected individually to suit a particular type [14]. Finsy et al. [14] propose the pelletization of MIL-47 and MIL-53(Al) with and without the use of a PVA binder. The solution without the binder has turned out to be successful only for MIL-47 with an applied pressure of 500 bar. In the case of MIL-53(Al), due to moisture, among other factors, the use of a binder has become necessary [14]. Due to the fact that the binder reduces the sorption capacity of the obtained pellet, as it blocks pores (thus reducing their volume) and becomes an inactive part in the adsorbent, it is essential to look for ways of pelletizing without its use. In this work, the impact of the tabletization, pressure and time on the structure and CO<sub>2</sub> adsorption properties of two types of MOFs (CuBTC and MIL-53(Al)) has been investigated. The MOFs are characterized in detail in both powder and tablet forms, and the CO<sub>2</sub> adsorption characteristics are carried out using a TG and TG-Vacuum analysis.

## Methods and materials

### Materials characterization

Two types of commercially available metal–organic frameworks: CuBTC (Basolite™ C300 produced by BASF) and MIL-53(Al) (Basolite™ A100 produced by BASF) were chosen for the tests. The MOF material Basolite™ C300 (copper benzene-1,3,5-tricarboxylate) Cu<sub>3</sub>(BTC)<sub>2</sub> consists of Cu–Cu dimers connected by 1,3,5-tricarboxylate linkers to form a three-dimensional network with micropores in the range of 0.7–0.9 nm. The MOF material Basolite™ A100 (aluminum terephthalate) Al<sub>2</sub>(-BDC)<sub>3</sub> consists of octahedral AlO<sub>4</sub>(OH)<sub>2</sub> units connected through 1,4-benzenedicarboxylate ligands [17].

The crystal structure for all samples before and after mechanical compression was confirmed by powder X-ray diffraction (XRD). XRD patterns were recorded on a Bruker AXS D8 Advance diffractometer using CuK $\alpha$  radiation of wavelength 0.15405 nm. Diffraction data were recorded between 1° and 50° 2 $\theta$  at an interval of 0.02° 2 $\theta$ . The Fourier transform infrared (FTIR) spectra of the MOF materials were recorded at room temperature on a Nicolet 6700 spectrometer using KBr pellet technique.

### Pellet preparation

For MOFs (CuBTC and MIL-53(Al)), the no-binder pelletizing method was employed using a pressure of 3.7, 7.4, 29.6 and 59.2 kN m<sup>-2</sup>, respectively, for a duration of 2 and 0.5 min. A Specac press was used to prepare tablets based on powder MOFs. The obtained tablets have a thickness between 0.5 and 1.0 mm. Tablets of MOFs were crushed and sieved to obtain the desired tablet fraction from 500 to 650  $\mu$ m.

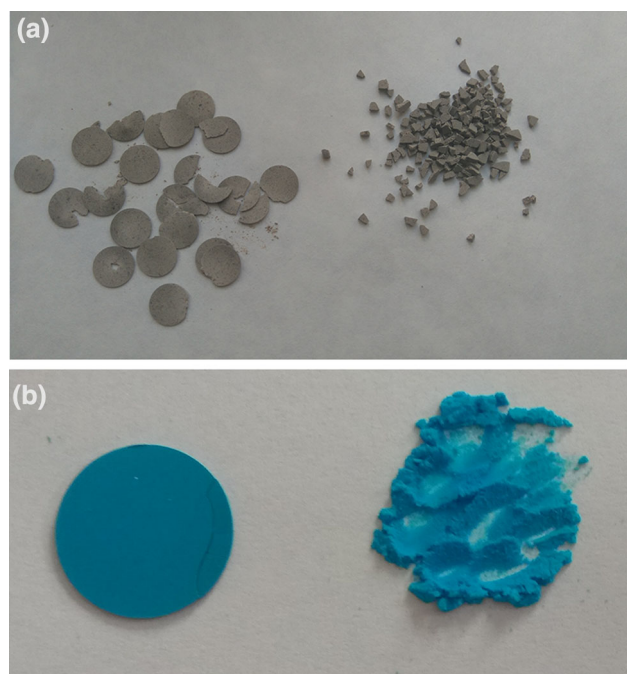
### Thermogravimetric study

The Mettler TGA/SDTA 851e thermobalance and TG-Vacuum system were employed to examine the CO<sub>2</sub> adsorption performance of the powdered and pelletized adsorbents. For the examination of the CO<sub>2</sub> adsorption process, the isothermal test was used. In the isothermal test, adsorbent samples (10 mg) were heated from 25 to 100 °C in a nitrogen atmosphere (with a heating rate of 10 °C min<sup>-1</sup>) and held at this temperature for 30 min (until a constant sample mass was achieved). Then the CO<sub>2</sub> adsorption process was conducted isothermally (at a temperature of 30 °C), being held at that temperature until an equilibrium state was attained, under atmospheric pressure, using 100% CO<sub>2</sub> at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. The comparison of the CO<sub>2</sub> desorption between the powdered

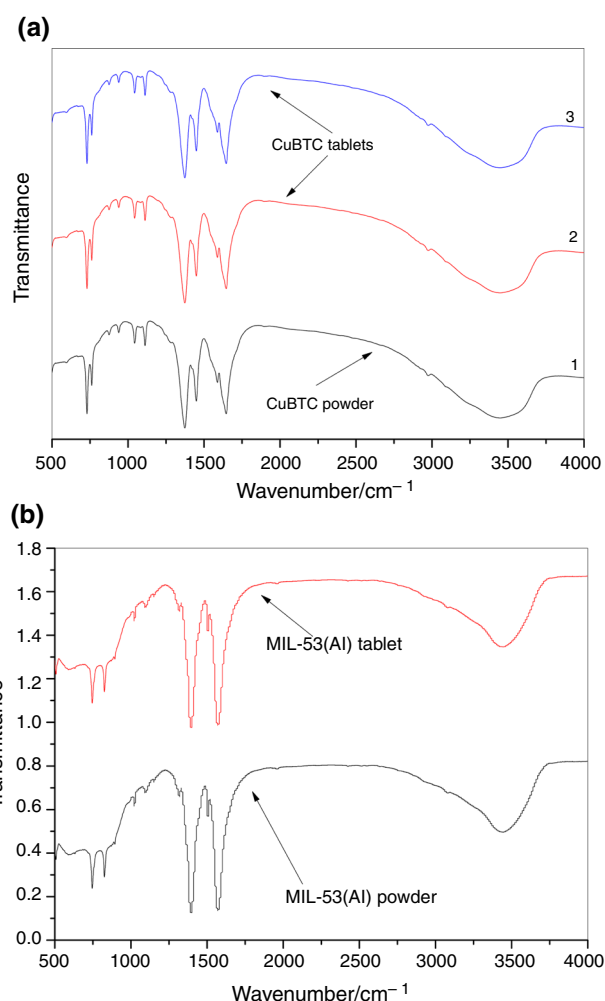
and pelletized adsorbents was also made. The cyclic adsorption/desorption test using the TG-Vacuum was carried out. In the regeneration of the MOFs, the pressure was reduced below atmospheric pressure (a vacuum was employed). The adsorption stage pressure was equal to atmospheric pressure, while in the desorption stage it was 10 kPa abs. The duration of a single-cycle adsorption/desorption was 30 min. The adsorption/desorption cycles were repeated five times in a continuous manner. The gas flow rate was set at 50 cm<sup>3</sup> min<sup>−1</sup>. The tests were conducted using 100% CO<sub>2</sub> at a constant temperature of 30 °C. The tests were carried out for pure CO<sub>2</sub>.

## Results and discussion

Figure 1 shows powder (Fig. 1b) and pelletized CuBTC (tablet, Fig. 1b) and MIL-53(Al) (tablets, Fig. 1a). After mechanical compression, MOFs were crushed into small sizes (500–650 μm). Figure 1a illustrates also the crushed particles of MIL-53(Al). The FTIR spectra of the powdered and tablet CuBTC and MIL-53(Al) are shown in Fig. 2. The figure illustrates the effect of the applied pressure on the chemical structure of the obtained CuBTC and MIL-53(Al) tablet. As indicated by Fig. 2, all the major FTIR peaks in the powder spectra are essentially replicated in the spectra of the tablets (pressures of 3.7 kN m<sup>−2</sup> and 7.4 kN m<sup>−2</sup>) and all FTIR spectra clearly reveal no distinct changes in the chemical structure of the materials before

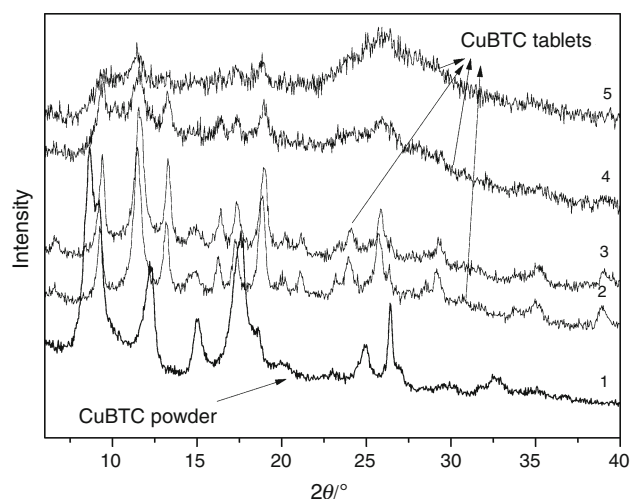


**Fig. 1** Powder and pelletized **a** MIL-53(Al) (tablets, crushed tablets); **b** CuBTC (tablet, powder)



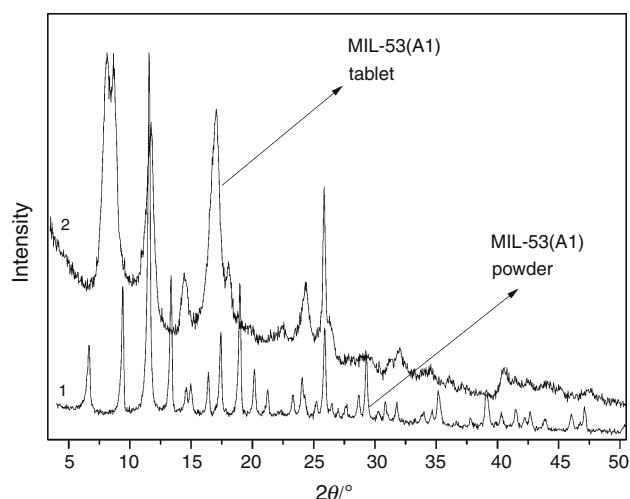
**Fig. 2** FTIR spectra of the powdered and tablet: **a** CuBTC (pressures of 3.7 kN m<sup>−2</sup> and 7.4 kN m<sup>−2</sup>), **b** MIL-53(Al) (pressures of 3.7 kN m<sup>−2</sup>)

and after mechanical compression. The FTIR spectra of CuBTC (Fig. 2a) before and after compression show a characteristic absorption bands at 3500, 1720, 1450, 1300, 1100, 1200, 750, 760 cm<sup>−1</sup>. The absorption peak at 1720 cm<sup>−1</sup> is from the carboxylic acid C=O stretching vibrations. The aromatic C=C bond appeared at 1450 cm<sup>−1</sup>, and the C–O bond in carboxylic acid group appeared at 1300 cm<sup>−1</sup>. The peak at 3500 cm<sup>−1</sup> coming from the hydroxyl groups (O–H bond) indicates that some water molecules occupy in pores of samples [18]. The FTIR spectra of MIL-53(Al) powder and MIL-53(Al) tablet (Fig. 2b) exhibit the same vibrational bands in the usual region of 1400–1700 cm<sup>−1</sup> for the carboxylic function. The absorption peaks at 1600 cm<sup>−1</sup> and 1500 cm<sup>−1</sup> can be assigned to –CO<sub>2</sub> asymmetric stretchings, whereas band at 1400 cm<sup>−1</sup> can be assigned to –CO<sub>2</sub> symmetric stretchings. The band in the region 3500–3600 cm<sup>−1</sup> corresponds to the bending and stretching modes of water [19, 20]. Figure 3



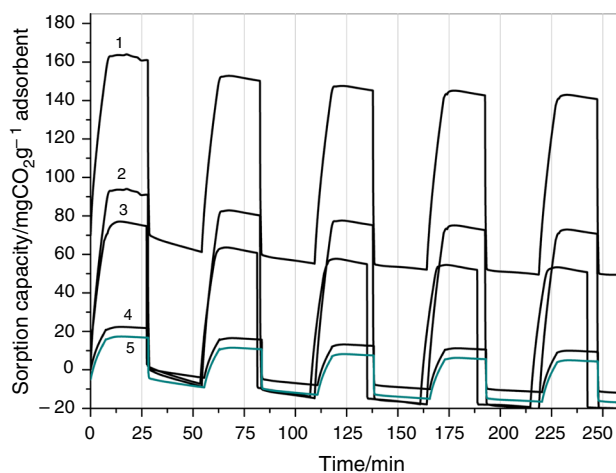
**Fig. 3** XRD diffraction patterns of the CuBTC metal-organic framework: (1) powder; (2) tablet at a pressure of  $3.7 \text{ kN m}^{-2}$ ; (3) tablet at a pressure of  $7.4 \text{ kN m}^{-2}$ ; (4) tablet at a pressure of  $29.6 \text{ kN m}^{-2}$ ; (5) tablet at a pressure of  $59.2 \text{ kN m}^{-2}$

illustrates the effect of the applied pressure on the crystallinity of the obtained CuBTC tablets. In the X-ray diffraction pattern of the crystalline CuBTC powder, lattice planes of [200], [102], [202] and [302] correspond to the four major peaks [18]. In the case of the pressures of  $3.7 \text{ kN m}^{-2}$  and  $7.4 \text{ kN m}^{-2}$ , the crystallinity of the obtained tablet was retained. This meant that no destruction of the CuBTC structure occurred due to mechanical compression [18]. In the case of the pressures of  $29.6 \text{ kN m}^{-2}$  and  $59.2 \text{ kN m}^{-2}$ , the crystalline structure was destroyed, as is shown by the obtained XRD diffraction patterns, in which the disappearance of the well-developed XRD peaks characteristic of the crystalline structure of these compounds is observed. Contrary to the information available in the literature [14] regarding the pelletization of MIL-53(Al), pellets were obtained by pelletizing with no binder, using a pressure of  $3.7 \text{ kN m}^{-2}$ . As shown in Fig. 4, the applied pressure of  $3.7 \text{ kN m}^{-2}$ , which yielded MIL-53(Al) tablets with adequate hardness, did not destroy the MOF crystalline structure. This is confirmed by the XRD diffraction patterns shown in Fig. 4, on which well-developed XRD reflections can be observed for MIL-53(Al) before and after mechanical compression. The intensity of the four main peaks, however, decreased slightly due to mechanical compression of MIL-53(Al) powder and their position slightly shifted on the  $2\theta$ -axis. The peaks in the XRD of the MIL-53(Al) tablet are broader than in MIL-53(Al) powder, and some of them disappeared after mechanical compression. The results show a significant effect of pelletizing pressure on the crystal structure of the obtained CuBTC and MIL-53(Al) metal-organic framework tablets. The effect of the applied pelletizing pressure



**Fig. 4** XRD diffraction patterns of the MIL-53(Al): (1) powder; (2) tablet at a pressure of  $3.7 \text{ kN m}^{-2}$

is also visible in the results for the sorption capacity of CuBTC and MIL-53(Al) with respect to  $\text{CO}_2$ . Figure 5 shows the effect of the applied pressure on the  $\text{CO}_2$  sorption capacity of CuBTC metal-organic framework. In the case of the pressure of  $3.7 \text{ kN m}^{-2}$  (the minimum pressure needed for producing a tablet), the sorption capacity was  $95 \text{ mg CO}_2 \text{ g}^{-1}$  CuBTC, which decreased to  $77 \text{ mg CO}_2 \text{ g}^{-1}$  CuBTC for a tablet prepared under the pressure of  $7.4 \text{ kN m}^{-2}$ , then to  $22 \text{ mg CO}_2 \text{ g}^{-1}$  CuBTC for a tablet prepared under the pressure of  $29.6 \text{ kN m}^{-2}$  and finally to  $17 \text{ mg CO}_2 \text{ g}^{-1}$  CuBTC for a tablet prepared under the pressure of  $59.2 \text{ kN m}^{-2}$ . For comparison, the sorption capacity of CuBTC in the powder form is about

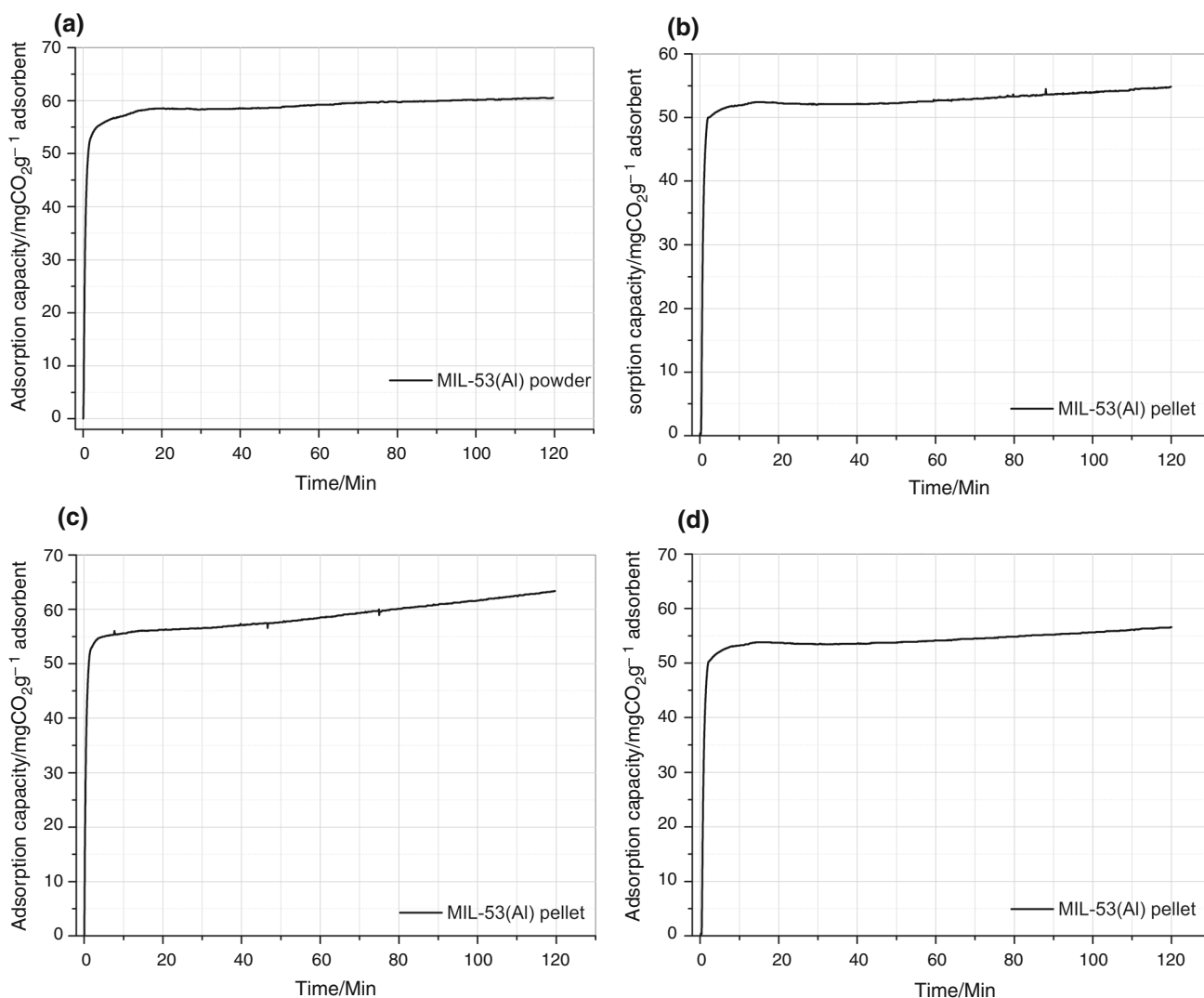


**Fig. 5** Effect of palletizing pressure on the  $\text{CO}_2$  sorption capacity of CuBTC in multi-stage adsorption/desorption cycles in a vacuum system (TG-Vacuum simulation, a desorption pressure of  $10 \text{ kPa abs}$ ) (CuBTC: 1—powder, 2—tablet at a pressure of  $3.7 \text{ kN m}^{-2}$ , 3—tablet at a pressure of  $7.4 \text{ kN m}^{-2}$ , 4—tablet at a pressure of  $29.6 \text{ kN m}^{-2}$ , 5—tablet at a pressure of  $59.2 \text{ kN m}^{-2}$ )



160 mg CO<sub>2</sub> g<sup>−1</sup> adsorbent. So, even applying the minimum pressure required for producing a pellet resulted in a reduction in sorption capacity by 40.7%. The CO<sub>2</sub> adsorption capacity of the CuBTC particles is significantly influenced by the mechanical compression shaping procedure. The applied pressure is particularly important. Bazer-Bachi et al. [13] proposed the pelletization of ZIF-8 and CuBTC metal–organic frameworks using a pressure of 5, 10 and 17 kN, and by analyzing the structure prior to and after pelletizing, they also found that higher pressure caused a lower sorption capacity and a lower crystallinity degree of obtained pellets. For the MIL-53(Al) metal–organic framework, the most advantageous pelletizing pressure is also 3.7 kN m<sup>−2</sup>. The obtained pellet retains its crystallinity in the highest degree. Figure 6 shows the effect of pelletizing duration and pellet thickness on the

CO<sub>2</sub> sorption capacity of MIL-53(Al). It is interesting to note that in the case of this MOF, no reduction in CO<sub>2</sub> sorption capacity occurs when applying the pelletizing pressure of 3.7 kN m<sup>−2</sup> and time=2 min (60 mg CO<sub>2</sub> g<sup>−1</sup> adsorbent), compared to the powder form of this MOF (60 mg CO<sub>2</sub> g<sup>−1</sup> adsorbent). The CO<sub>2</sub> adsorption capacity of the MIL-53(Al) is slightly influenced by the mechanical compression procedure. As shown in Fig. 6, the CO<sub>2</sub> sorption capacity of MIL-53(Al) has been influenced neither by the pelletizing time used (0.5 min, 2 min) nor by the thickness of the prepared tablet. These data demonstrate that after mechanical compression, the CO<sub>2</sub> adsorption capacity of the MIL-53(Al) tablets was unchanged. It is important, because the shape of tablets is more applicable for different industrial conditions.



**Fig. 6** Effect of pelletizing duration and pellet thickness on the sorption capacity of MIL-53 (Al) in a single adsorption cycle (TG simulation): **a** powder; **b** pellet at a pressure of 3.7 kN m<sup>−2</sup>, time—

0.5 min, thickness—1 mm; **c** pellet at a pressure of 3.7 kN m<sup>−2</sup>, time—2 min, thickness—1 mm; **d** pellet at a pressure of 3.7 kN m<sup>−2</sup>, time—0.5 min, thickness—0.5 mm

## Conclusions

The investigation carried out has demonstrated that the metal–organic frameworks such as CuBTC and MIL-53(Al) can be effectively pelletized without losing its sorption properties, and can be used as a bed in the process of carbon dioxide separation from combustion gas by the vacuum pressure swing adsorption (V-PSA) method. On the basis of XRD and FTIR spectroscopy results, no significant chemical changes were found and the crystal structure of the MOFs remained unchanged after pressing at the appropriate pressure. Results from the study indicate that indeed both CuBTC and MIL-53(Al) can be engineered into forms suitable for CO<sub>2</sub> capture from flue gases.

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