Rapid temperature-assisted synthesis of nanoporous γ-cyclodextrin-based metal–organic framework for selective CO2 adsorption

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Short Communication

Rapid Temperature-Assisted Synthesis of Nanoporous γ-Cyclodextrin-based Metal–Organic Framework (CD-MOF) for Selective CO_2 Adsorption

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Abstract

We present a rapid temperature-assisted synthesis route to synthesize cyclodextrin-based metal-organic frameworks (CD-MOFs) surfactant freely in a short time. The cubic crystals of CD-MOF with an average edge length of 10-15 μm, specific surface area 775 m^2 g^{-1} and total pore volume 0.229 cm^3 g^{-1} were synthesized in much shorter time rather than conventional CD-MOFs. To show the efficiency of the synthesized CF-MOF as adsorbent of gas, the uptake of CO_2 at different temperature and pressure demonstrated. It is shown that the CO_2 uptake increases with increasing pressure and decreasing temperature. Further microgravimetric investigation on gas adsorption at low pressures demonstrated superior gas uptake (147 mg g^{-1} c.a.) than previous reports. At the maximum equilibrium pressure, the uptake amounts of CO_2 were found to be about the 326 and 268 mg g^{-1} at 303 and 323 K, respectively. The synthesized CD-MOF particles have great potential to be used in gas storage and separation applications.

Keywords: Metal-organic framework; cyclodextrin; synthesis; CO_2 adsorption.

1. Introduction

The emissions of greenhouse gases from human activities such as fossil fuels combustion, has led to the climate change and global warming [1]–[3]. Carbon dioxide (CO_2), considered as a major components of greenhouse gases, has become one of the most serious environmental concern affecting human health [4]. This leads to increasing demands for CO_2 adsorption, storages and separation. In this regard, adsorptive separation based on porous materials such as traditional zeolites [5], carbons [6], [7], metal-organic frameworks (MOFs) [8], covalent organic polymers [9] etc. has been investigated. MOFs represent a new class of highly porous crystalline materials, which gain considerable attentions thanks to their simple synthesis method, large specific surface area, high porosity, controllable pore structure, and functional surface chemistry [10]–[14]. These characteristics have made them promising candidates for a wide range of application including adsorption [15]–[17], gas storage [18], separation [13], catalysis [19], ion exchange [20], sensing [21], drug delivery [22], [23], and health care [24].

Cyclodextrin-based MOFs (CD-MOFs), as environmentally friendly and biocompatible MOFs, have recently been demonstrated. The internal cavities od cyclodextrins provides suitable accommodation site for quest molecules [25]. Generally, CD-MOFs are synthesized from naturally available cyclic oligosaccharide ligand (cyclodextrin) and metal ions by vapor diffusion method [26]. γ-cyclodextrin (γ-CD) is a symmetrical cyclic oligosaccharide that is mass-produced enzymatically from starch and comprised of eight asymmetric a-1,4-linked dglucopyranosyl residues. Advantageously, γ-CD-MOF non-toxicity and biocompatibility features offer a unique opportunity to use in a variety of applications like gas adsorption and separation [27]. For instance, Yan et al. [28] utilized thermogravimetric approach to study the adsorption and desorption of CO_2 over CD-MOF. The γ-CD-MOF has been synthesized from γ-

CD and potassium ions within 7 days at ambient temperature for the first time [29]. However, the long synthesis time restricts its mass production and industrial uses. In this regard, several approaches have been reported in open literature to decrease the synthesis time. For instance, Liu et al. [30] synthesized micron-sized CD-MOF crystals through microwave irradiation technique for drug delivery applications. Polyethylene glycol 20000 (PEG 20000) was added to form crystals. In another study, they modified the conventional vapor diffusion method by using surfactant (CTAB), which lead to decrease the synthesis time to 6 hours [31].

we report a strategy to form γ-CD-MOF using γ-cyclodextrin and potassium ions. These γ-CD building units are then adjoined by potassium ions, in aqueous media at higher temperature and pressure than ambient temperature and pressure (using an autoclave), to form a body-centered cubic structure with the empirical formula $[(C_{48}H_{80}O_{40})(KOH)_2]_n$. Herein, we considered a rapid surfactant free temperature-assisted synthesis of γ-CD-MOF within few hours. In this work, only an autoclave was used to accelerate crystal formation from seven days to 15 hours and no surfactant or other substance was used to speed up the reaction. As a result, it is more economical to use this method and there is no additional cost for the preparation of surfactant.

The structural and morphological characterization of synthesized product as well as their CO_2 adsorption were thoroughly investigated.

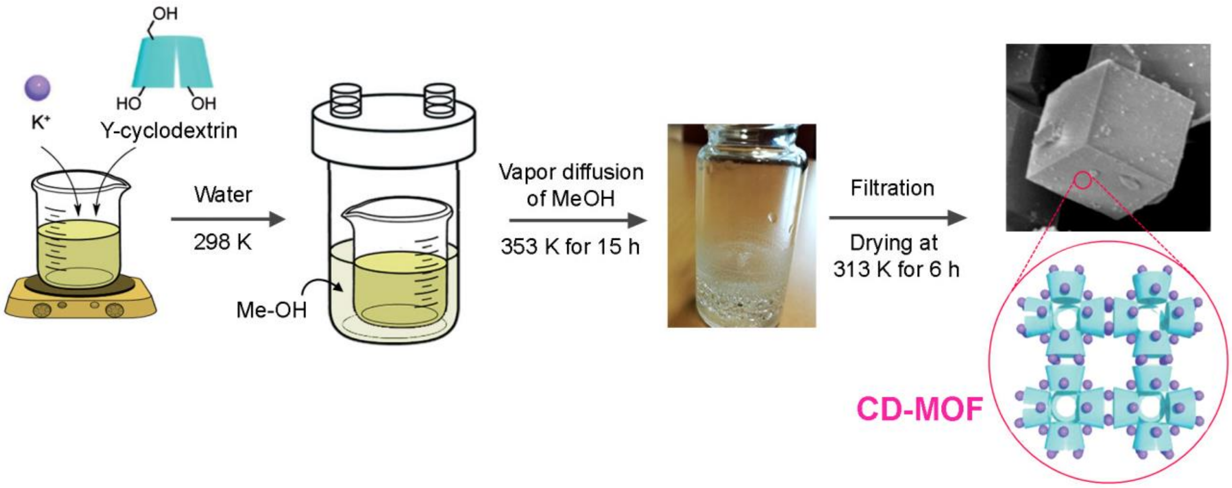
2. Experimental procedure

2.1. Materials

γ-cyclodextrin (γ-CD) was obtained from Sigma-Aldrich (Germany). Potassium hydroxide (KOH) and methanol (MeOH) were obtained from Merck Co. (Germany) and used directly without additional purification. Aqueous solutions were prepared by using deionized water (Millipore Milli-Q™).

2.2. Synthesis of CD-MOF

γ-CD-MOF was synthesized by a facile vapor diffusion method according to the procedure reported in literature [29] with some major modifications. Briefly, 1.0 mmol of γ-CD and 8.0 mmol of the KOH were dissolved in 20 mL of H_2O at ambient temperature. Then, the product was filtered and transferred into Teflon autoclave containing methanol (MeOH). The vapor diffusion of MeOH into the aqueous solution was performed at 353 K for 15 h. Then, the autoclave was slowly cooled and the resulted crystals were collected on a filter paper, washed with MeOH and dried at 313 K in an oven for 6 h. A schematic representation for the synthesis procedure is shown in Scheme 1.



Scheme 1. Schematic representation of CD-MOF synthesis procedure.

2.3. Characterization

The surface morphology of synthesized CD-MOF was studied after gold coating of sample by scanning electron microscopy (SEM, TESCAN, Czech Republic). Fourier transformed infrared

(FTIR) spectra of sample from 500 to 4000 cm^{-1} was recorded on Bruker Vector 22 instrument to study the functional group analysis and possible reactions. Powder X-ray diffraction (PXRD) was collected using a Philips PW 3040/60 X'pert diffractometer with Cu Kα radiation to evaluate the crystalline structure of CD-MOF. The specific surface area and pore size distributions of CD-MOF were obtained according to the Brunauer-Emmett-Teller (BET) method from the N_2 adsorption/desorption isotherms at 77 K using Micrometrics ASAP 2020. Thermogravimetric analysis (TGA) was carried out using TGA-TA Instruments, models Q600 at a heating rate of 10 K min^{-1} in air.

2.4. CO_2 adsorption isotherm measurement

For testing the capability of CD-MOF in CO_2 uptake, two different techniques have been applied. The first is a microcalorimetric method that allows to measure simultaneously the quantity adsorbed and the heat of adsorption. Briefly, a microcalorimeter (Tian-Calvet) consists in an adsorption instrument for volumetric analysis, which is coupled to calorimeter that records the heat develops during the adsorption. It works with a twin cells system immersed inside an insulated cylinder in which the temperature is fixed and controlled at 303 K The pressure changes are monitored with two high precision pressure transducers. Regarding the second technique, a microbalance has been used. The IGA 002 (Hiden) is a very sensitive balance mounted in a thermostatic heatsink. It allows to control and measure the mass change, the pressure and the temperature in order to determinate the reproducibly of the isotherms in different analysis conditions. The set up was in the range of 0-20 bar and 303-323 K.

3. Results and discussion

3.1. Structural analysis

The SEM micrographs of the synthesized CD-MOF particles are shown in Figure 1. To study the effect of reaction time on morphology and crystal structure of the prepared particles, CD-MOF synthesized after 5 h and 15 h were considered by SEM. It is obvious that after 5 h, the MOF crystal growth was not completed and the time was not sufficient for MeOH vapor diffusion. However, after 15 h, the CD-MOF with uniform morphology and cubic structure were completely grown. The results exhibited CD-MOF crystals with edge lengths in the range of 10-15 μm and uniform size distribution (Figure 1d). The cubic crystal size of our CD-MOF is significantly smaller than the CD-MOF synthesized by Smaldone et al. [29] through MeOH vapor diffusion at ambient temperature within one week (40-500 μm). In this study, we shorten the synthesis time from 7 days to 15 h, while the CD-MOF particles retain their crystal structure and porosity. Recently, Liu et al. [31] proposed a modified method in which the CD-MOF size was tuned with the addition of surfactants and elevating the temperature. They reported the crystal size of 5-10 μm, which is fairly close to the value of our surfactant-free synthesized CD-MOF samples.

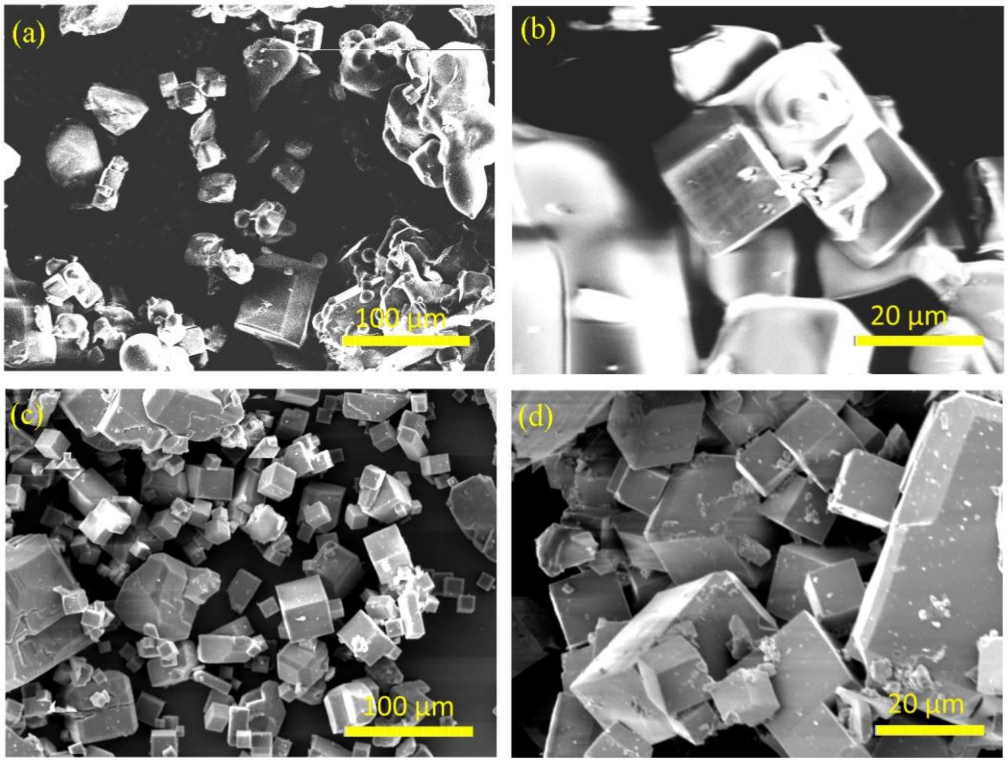


Figure 1: SEM micrographs of CD-MOF synthesized after: (a,b) 5 h, and (b,c) 15 h at different.

The FTIR spectrum of synthesized CD-MOF is shown in Figure 2. For comparison, the FTIR of the γ-CD is also reported. The broad band located around 3400 cm^{-1} is related to the OH stretching vibration of glucose units of cyclodextrin [32]. The stretching vibrations of C-H bonds are located at peak at 2930 cm^{-1}. The other vibrations at 1658, 1420 and 1159 cm^{-1} are attributed to bending vibrations of hydroxyl group. The bands appeared at 1028 cm^{-1} and 860 cm^{-1} are also related to C-O and C-C stretching vibrations [33]. It does not reveal any important differences in chemical structure of the two samples. The temperature-assisted vapor diffusion synthesis seems to not modify or damage in structure of the bare cyclodextrins. Figure 2b shows the PXRD patterns of CD-MOF particles synthesized after 5 h and 15 h. As can be seen, the CD-MOF synthesized after 5 h exhibits weak peak indicating that the reaction did not completed. On the contrary, the diffraction pattern for CD-MOF synthesized after 15 h reveals the crystallinity and successful synthesis under the temperature-assisted vapor diffusion condition. The diffraction peaks were found at 2θ values of 4.2, 5.9, 7.3, 14.1 and 17.5º, which matched well with previous published works [6], [29], [31].

BET measurements were carried out to determine the specific surface area and porous structure of the synthesized CD-MOF. Figure 2c shows the nitrogen adsorption/desorption isotherms at 77 K, which is in good agreement with literature [29]. The specific surface area and total pore volume were found to be 775 m^2 g^{-1} and 0.229 cm^3 g^{-1}, respectively.

Thermogravimetric analysis (TGA) was also used to elucidate the thermal stability of synthesized CD-MOF at high temperatures and heat. The TGA curve of CD-MOF particles (Figure 2d) shows three steps of weight loss from 25 to 700 ºC. In the first step, significant weight loss did not occur up to 270 ºC, corresponding to the full evacuation of pores and thermal stability of frameworks. A small weight loss at approximately 100 °C is also corresponds to the loss of H_2O molecules and the residual solvent [29]. The second step of weight loss starts around 270 ºC which is related to the thermal degradation of CD-MOF. In this step, the degradation gradient was swift and detectable. The third step of weight loss occurs in temperature ranges over 340 ºC, which is associated with the decomposition continuation. The obtained results demonstrate that the synthesized CD-MOF particles have higher thermal stability than those reported in literature [29], [32].

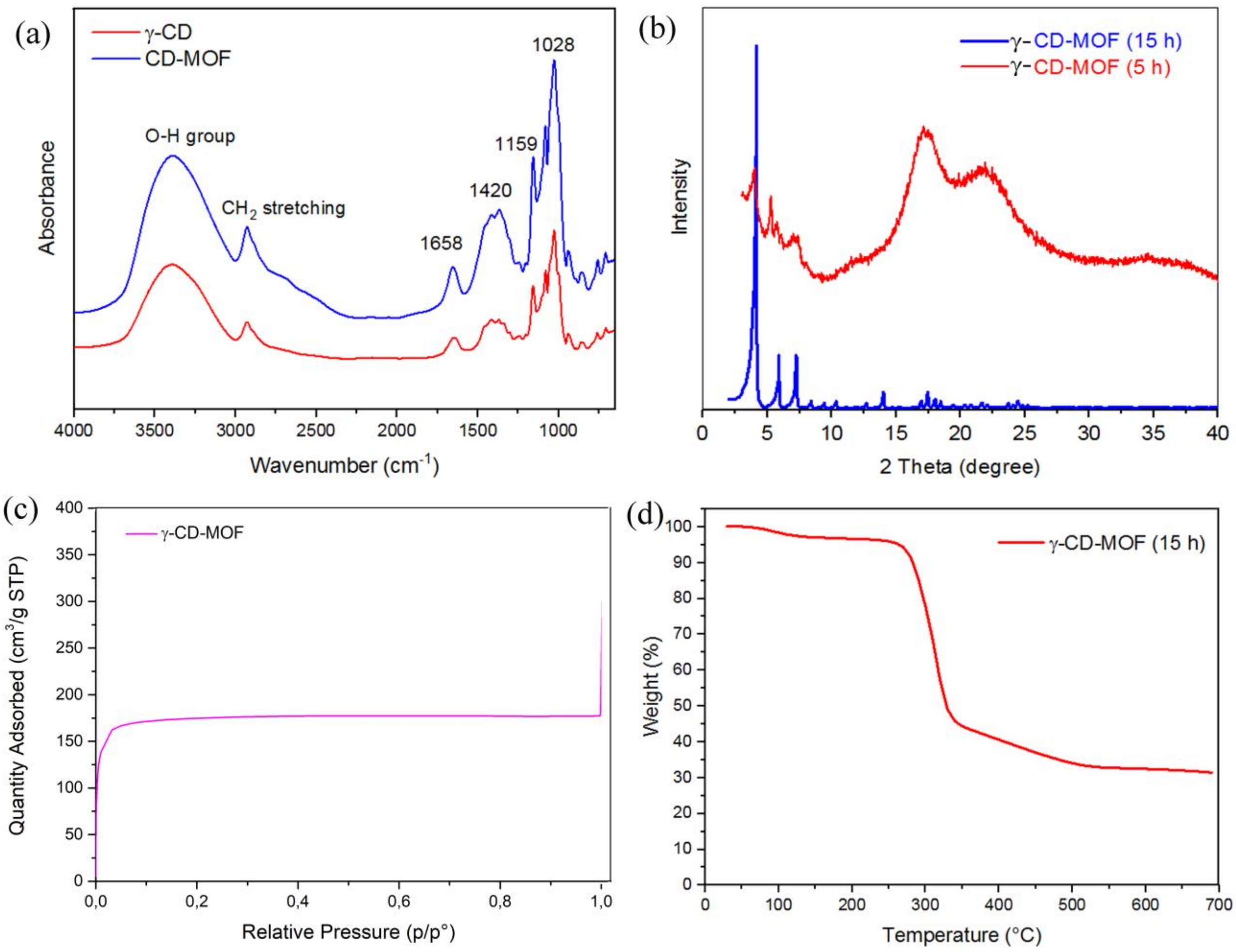


Figure 2: (a) FTIR spectrum, (b) PXRD patterns, (c) N_2 adsorption/desorption isotherms and (d) TGA curve of synthesized CD-MOF.

3.2. CO_2 adsorption

The CO_2 adsorption capability was evaluated using two different techniques: microcalorimetric and microgravimetric approaches. The microcalorimeter allows the energetic study of the adsorption process and so it is an important tool to understand the behavior of an absorbent in cyclical processes of gas-mixture separation. Furthermore, it is also useful for evaluate the quantity of gas adsorbed. It allows to build the adsorption isotherms and so it is possible to evaluate the reversibility of the adsorption process. In other words, appropriate doses of gas are admitted onto the adsorbent and each dose is left to reach the equilibrium. The heat and the pressure at the equilibrium point is recorded till the first adsorption run is performed. Then, the system is evacuated and a second run with the similar doses is carried out. The results obtained are depicted in Figure 3. Particularly, Figure 3a shows the first and the second adsorption isotherms, whereas Figure 3b represents the plot of the differential heat of adsorption.

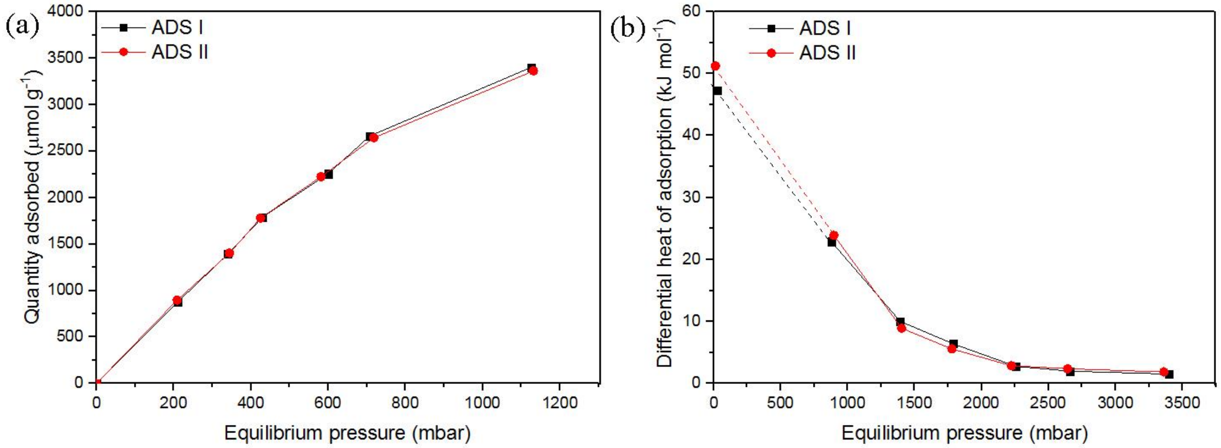


Figure 3: (a) Adsorption isotherms, (b) differential heat of adsorption plot: first run (black line) and second run (red line).

As shown in Figure 3a, the CO_2 adsorption phenomenon is perfectly reversable, because the first and the second run are overlapped. Furthermore, the adsorption process does not reach a plateau, so the CD-MOF is able to entrap more CO_2, increasing the pressure. The maximum adsorption recorded is 3360 μmol g^{-1} (147 mg g^{-1} c.a.) at the pressure of about 1 bar. Saha et al. [34] found out that for MOF-5 and MOF-77 the ability of CO_2 capture is about 0.3 and 0.5 mg g^{-1}, respectively. Smaldone and co-workers [29] synthesized CD-MOF-2 made of γ-cyclodextrins and rubidium hydroxide and performing some solid-state NMR experiments. They demonstrate that the free hydroxyl group of the γ-CD can interact with the CO_2, increasing the CO_2 uptake capacity (44 mg g^{-1}) at less than 1.32 mbar and between 273 and 298 K. They also found out that when the crystals of CD-MOF are pulverized, the powder turn into an amorphous state, decreasing the capability of the CD-MOF to adsorb the CO_2. Thus, this result highlights the importance of the crystallinity in MOF for reaching the adsorption target. Moreover Hu et al. [35] demonstrated that the presence of alkali hydroxides, such as LiOH, NaOH and KOH inside the structure of the MOF leads to a higher selectivity and adsorption capacity. Indeed, the use of alkali solution for the CO_2 capture and storage is a well-known strategy. Strong basic solutions are able to adsorb high amount of CO_2 via carbonate precipitation [36]. Thus, the presence of KOH in γ-CD-MOF could increase the amount of carbon dioxide captured. The microcalorimeter allows to directly determinate the heat develops during the adsorption. Thus, it is possible to evaluate the differential heat of adsorption, Q_{diff}, that is obtained by the direct calorimetric Q values by carrying out the operation specified in following equation:

$$Q_{diff} = \left(\partial Q / \partial n_a\right)_{T,A} \tag{1}$$

where Q depends on some parameters of the instrument, n_a is the amount of carbon dioxide adsorbed at fixed temperature, A is the specific surface area of the sample and T is the temperature of the measurement.

Interestingly, it is possible to plot the differential heat of adsorption versus the coverage. This plot allows to determinate the site energy distribution. The initial heat value (q_0), corresponding to the highest energy of interaction of the CO_2 with the strongest sites, was evaluated by extrapolating the heat when the coverage is 0. For the primary adsorption the estimated q_0 is 52 kJ mol^{-1} for the second 48 kJ mol^{-1}. These values show that the adsorption on these materials could be considered like a physisorption. These results are important because the interaction between the CO_2 and the surface is not strong in order of the chemical bond, which would facilitate the regeneration of the materials in possible industrial application [37]. Furthermore, the heats of adsorption have been considered as an indicator of the heterogeneity of the surface. In the case CD-MOF, the heat of adsorption changes during the adsorption, hence all the sites of the surface are heterogeneous. This energetic heterogeneity of the surface depends on the distribution of micro- and mesopore and also on the shape and size of them and of the amount of crystallinity present [38].

The CO_2 adsorption capacity of CD-MOF was assessed at different temperatures (303 and 323 K) and in the range of 0-14 bar using the microbalance. Figure 4 shows the equilibrium adsorption isotherms of CO_2 over synthesized CD-MOF. Apparently, CO_2 uptake increases with increasing pressure and decreasing temperature. The shape of the isotherms reveals the physisorption of adsorbate (CO_2) on CD-MOF, suggesting its possibility to use in pressure- or temperature-swing adsorption (TSA and PSA) process [39]. Furthermore, it showed high uptake of CO_2 at low pressures (up to 1 bar), corresponding to the preferential interaction between the CO_2 molecules and partial positive charges of potassium ions [8]. At 1 bar, the uptake amounts of CO_2 are 126.4 and 93.7 mg g^{-1} at 303 and 323 K, respectively. At high pressures, the CO_2 adsorption increases gradually as a function of available surface area and pore volume of CD-MOF. At the maximum equilibrium pressure, CD-MOF took up 326 and 268 mg g^{-1} CO_2 at 303 and 323 K, respectively.

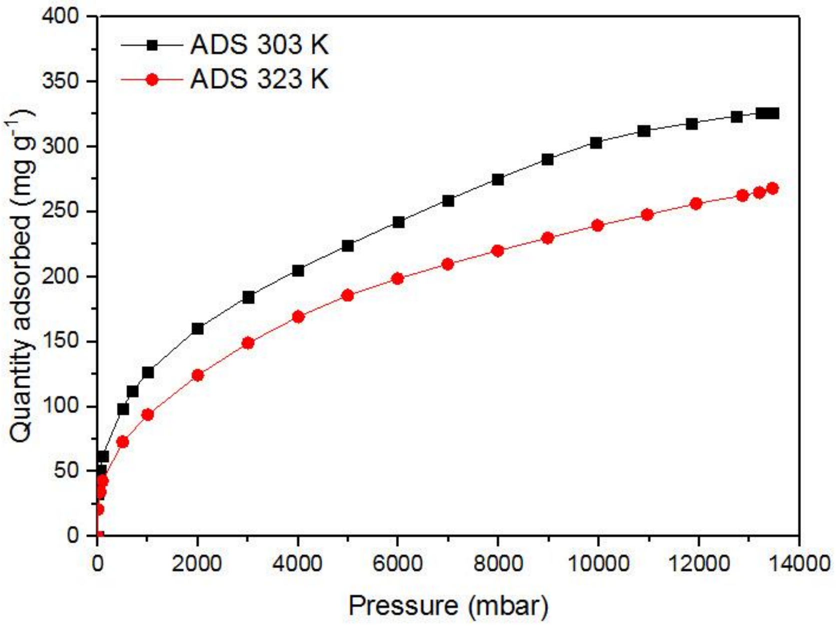


Figure 4: Adsorption isotherms: 303 K (black line) and 323 K (red line).

4. Conclusion

In summary, CD-MOF was successfully synthesized by rapid temperature-assisted approach and used as gas adsorbent. The most important findings are summarized below.

- The CD-MOF crystals showed uniform morphology with cubic structure which is consistent with literature, although the reaction time was shortened from 7 days to few hours.
- The synthesized CD-MOF structure with high surface area was provided high CO_2 adsorption capacity at ambient temperature.
- The CO_2 uptake was about the 326 and 268 mg g^{-1} at 303 and 323 K, respectively at maximum equilibrium pressure.
- The shape of the adsorption isotherms reveals the physisorption of CO_2 on CD-MOF.
- The developed product had superior CO_2 uptake specially at low pressure, which may be used as a potential gas adsorbent and separator.

References

[1] Y. Abdoli, M. Razavian, and S. Fatemi, “Bimetallic Ni–Co-based metal–organic framework: An open metal site adsorbent for enhancing CO2 capture,” *Appl. Organomet. Chem.*, vol. 33, no. 8, pp. 1–14, 2019.

[2] C. E. Bien *et al.*, “Bioinspired Metal-Organic Framework for Trace CO2 Capture,” *J. Am. Chem. Soc.*, vol. 140, no. 40, pp. 12662–12666, 2018.

[3] Z. Hu, Y. Wang, B. B. Shah, and D. Zhao, “CO2 Capture in Metal-Organic Framework Adsorbents: An Engineering Perspective,” *Adv. Sustain. Syst.*, vol. 3, no. 1, p. 1800080, 2019.

[4] A. Ö. Yazaydin *et al.*, “Enhanced CO2 adsorption in metal-organic frameworks via occupation of open-metal sites by coordinated water molecules,” *Chem. Mater.*, vol. 21, no. 8, pp. 1425–1430, 2009.

[5] R. Girimonte, B. Formisani, and F. Testa, “CO2 adsorption in a confined fluidized bed of zeolite pellets: Influence of operating velocity,” *Particuology*, vol. 46, no. 2018, pp. 67–74, 2019.

[6] Y. Furukawa, T. Ishiwata, K. Sugikawa, K. Kokado, and K. Sada, “Nano- and microsized cubic gel particles from cyclodextrin metal-organic frameworks,” *Angew. Chemie - Int. Ed.*, vol. 51, no. 42, pp. 10566–10569, 2012.

[7] A. Anceschi, G. Magnacca, F. Trotta, and M. Zanetti, “Preparation and characterization of microporous carbon spheres from high amylose pea maltodextrin,” *RSC Adv.*, vol. 7, no. 57, pp. 36117–36123, 2017.

[8] R. A. Agarwal, A. K. Gupta, and D. De, “Flexible Zn-MOF Exhibiting Selective CO2 Adsorption and Efficient Lewis Acidic Catalytic Activity,” *Cryst. Growth Des.*, vol. 19,

no. 3, pp. 2010–2018, 2019.

[9] H. A. Maitlo *et al.*, “Competitive adsorption of gaseous aromatic hydrocarbons in a binary mixture on nanoporous covalent organic polymers at various partial pressures,” *Environ. Res.*, vol. 173, no. February, pp. 1–11, 2019.

[10] M. Hasanzadeh, A. Simchia, and H. Shahriyari Far, “Nanoporous composites of activated carbon-metal organic frameworks for organic dye adsorption: Synthesis, adsorption mechanism and kinetics studies,” *J. Ind. Eng. Chem.*, vol. 81, pp. 405–414, 2020.

[11] M. Hasanzadeh, A. Simchi, and H. S. Far, “Kinetics and adsorptive study of organic dye removal using water-stable nanoscale metal organic frameworks,” *Mater. Chem. Phys.*, vol. 233, no. October 2018, pp. 267–275, 2019.

[12] K. Wang, C. Li, Y. Liang, T. Han, H. Huang, and Q. Yang, “Rational Construction of Defects in a Metal-Organic Framework for Highly Efficient Adsorption and Separation of Dyes,” *Chem. Eng. J.*, vol. 289, pp. 486–493, 2016.

[13] H. Ren, J. Jin, J. Hu, and H. Liu, “Affinity between Metal–Organic Frameworks and Polyimides in Asymmetric Mixed Matrix Membranes for Gas Separations,” *Ind. Eng. Chem. Res.*, vol. 51, no. 30, pp. 10156–10164, 2012.

[14] H. Zhang, J. Nai, L. Yu, and X. W. (David) Lou, “Metal-Organic-Framework-Based Materials as Platforms for Renewable Energy and Environmental Applications,” *Joule*, vol. 1, no. 1, pp. 77–107, 2017.

[15] N. A. Khan, Z. Hasan, and S. H. Jhung, “Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): A review,” *J. Hazard. Mater.*, vol. 244–245, pp. 444–456, 2013.

[16] A. Hamedi *et al.*, “In situ synthesis of MIL-100(Fe) at the surface of fe3o4@ac as highly

efficient dye adsorbing nanocomposite," *Int. J. Mol. Sci.*, vol. 20, no. 22, Nov. 2019.

[17] A. Hamedi, M. B. Zarandi, and M. R. Nateghi, "Highly efficient removal of dye pollutants by MIL-101(Fe) metal-organic framework loaded magnetic particles mediated by Poly L-Dopa," *J. Environ. Chem. Eng.*, vol. 7, no. 1, Feb. 2019.

[18] L. Wang, Y. Han, X. Feng, J. Zhou, P. Qi, and B. Wang, "Metal-organic frameworks for energy storage: Batteries and supercapacitors," *Coord. Chem. Rev.*, vol. 307, pp. 361–381, 2016.

[19] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, and J. T. Hupp, "Metal – organic frameworks issue Metal – organic framework materials as catalysts," *Chem. Soc. Rev.*, vol. 38, pp. 1450–1459, 2009.

[20] J. An and N. L. Rosi, "Tuning MOF CO2 Adsorption Properties via Cation Exchange," *J. Am. Chem. Soc.*, vol. 132, no. 16, pp. 5578–5579, 2010.

[21] G. W. Peterson *et al.*, "Multifunctional purification and sensing of toxic hydride gases by CuBTC metal-organic framework," *Ind. Eng. Chem. Res.*, vol. 54, no. 14, pp. 3626–3633, 2015.

[22] S. Beg *et al.*, "Nanoporous metal organic frameworks as hybrid polymer–metal composites for drug delivery and biomedical applications," *Drug Discov. Today*, vol. 22, no. 4, pp. 625–637, 2017.

[23] A. Hamedi *et al.*, "Metal Organic Frameworks in Medicine," 2019.

[24] A. C. Mckinlay *et al.*, "BioMOFs : Metal – Organic Frameworks for Biological and Medical Applications," *Angew. Chemie Int. Ed.*, vol. 49, no. 36, pp. 6260–6266, 2010.

[25] A. R. Pedrazzo *et al.*, "Eco-friendly ß-cyclodextrin and linecaps polymers for the removal of heavy metals," *Polymers (Basel).*, vol. 11, no. 10, Oct. 2019.

[26] X. Li *et al.*, “Cyclodextrin-based metal-organic frameworks particles as efficient carriers for lansoprazole: Study of morphology and chemical composition of individual particles,” *Int. J. Pharm.*, vol. 531, no. 2, pp. 424–432, 2017.

[27] Krūkle-Bērziņa, Belyakov, Mishnev, and Shubin, “Stability and Phase Transitions of Nontoxic γ-Cyclodextrin-K+ Metal-Organic Framework in Various Solvents,” *Crystals*, vol. 10, no. 1, p. 37, Jan. 2020.

[28] T. K. Yan, A. Nagai, W. Michida, K. Kusakabe, and S. B. Yusup, “Crystal Growth of Cyclodextrin-based Metal-organic Framework for Carbon Dioxide Capture and Separation,” *Procedia Eng.*, vol. 148, pp. 30–34, 2016.

[29] R. A. Smaldone *et al.*, “Metalorganic frameworks from edible natural products,” *Angew. Chemie - Int. Ed.*, vol. 49, no. 46, pp. 8630–8634, 2010.

[30] B. Liu *et al.*, “Microwave-Assisted Rapid Synthesis of γ-Cyclodextrin Metal-Organic Frameworks for Size Control and Efficient Drug Loading,” *Cryst. Growth Des.*, vol. 17, no. 4, pp. 1654–1660, 2017.

[31] B. Liu *et al.*, “Optimized synthesis and crystalline stability of γ-cyclodextrin metal-organic frameworks for drug adsorption,” *Int. J. Pharm.*, vol. 514, no. 1, pp. 212–219, 2016.

[32] I. Kritskiy, T. Volkova, A. Surov, and I. Terekhova, “γ-Cyclodextrin-metal organic frameworks as efficient microcontainers for encapsulation of leflunomide and acceleration of its transformation into teriflunomide,” *Carbohydr. Polym.*, vol. 216, no. January, pp. 224–230, 2019.

[33] P. Lampman, K. Vyvyan, D. L. Pavia, and G. S. Kriz, *Introduction to spectroscopy*. Cengage Learning, 2008.

[34] D. Saha, Z. Bao, F. Jia, and S. Deng, “Adsorption of CO2, CH4, N2O, and N 2 on MOF-5, MOF-177, and zeolite 5A,” *Environ. Sci. Technol.*, vol. 44, no. 5, pp. 1820–1826, Mar. 2010.

[35] Z. Hu, S. Faucher, Y. Zhuo, Y. Un, S. Wang, and D. Zhao, “Combination of Optimization and Metalated-Ligand Exchange:An Effective Approach to Functionalize UiO-66(Zr) MOFs for CO_2 Separation,” 2015.

[36] E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, and C. W. Jones, “Direct Capture of CO2 from Ambient Air,” *Chemical Reviews*, vol. 116, no. 19. American Chemical Society, pp. 11840–11876, 12-Oct-2016.

[37] D. P. Vargas, L. Giraldo, and J. C. Moreno-Piraján, “Calorimetric study of the CO2 adsorption on carbon materials,” *J. Therm. Anal. Calorim.*, vol. 117, no. 3, pp. 1299–1309, 2014.

[38] Z. Zhao, X. Cui, J. Ma, and R. Li, “Adsorption of carbon dioxide on alkali-modified zeolite 13X adsorbents,” *Int. J. Greenh. Gas Control*, vol. 1, no. 3, pp. 355–359, Jul. 2007.

[39] Z. Liang, M. Marshall, and A. L. Chaffee, “CO2 adsorption-based separation by metal organic framework (Cu-BTC) versus zeolite (13X),” *Energy and Fuels*, vol. 23, no. 5, pp. 2785–2789, 2009.