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Synthesis and characterization of $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ with its H_2 and CO_2 adsorption

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A 3-D porous metal–organic framework $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ was reported to have high methane storage. The studies about $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ were only related with methane storage but information on detailed synthesis and characterization as well as adsorption properties of $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$, especially the H_2 and CO_2 adsorption properties, was scarce. In this work, $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ has been synthesized by adjusting the molar ratio of the reagents, synthesis temperature, and crystallization time. This method for obtaining $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ at low temperature has not been reported before. Temperature played an important role in synthesis of the sample and low temperature was beneficial for synthesizing bigger sample. Adsorption isotherms for carbon dioxide and hydrogen were measured under high pressure. $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ exhibited H_2 storage up to 2.36 wt% at 18 bar and a high CO_2 capture up to 4.17 mmol g^{-1} at 298 K at 10 bar.

Keywords: Metal–organic framework; $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$; Synthesis; Characterization; H_2 storage; CO_2 capture

1. Introduction

Metal–organic frameworks (MOFs) containing transition metal ions and bridging ligands have been examined by many researchers [1–3]. MOFs having microporous channels are of special interest due to their unique properties such as physical gas adsorption [4, 5] and chemical adsorption [6, 7]. MOFs have an advantage in that they provide not only lightweight materials with high porosity but also highly desirable regular networks. The discovery of new materials with different ligands boosts adsorption applications [8, 9]. MOFs with selectivity have wider application in gas separation [10–12].

Coordination of 4,4'-bpy results in a relatively flexible framework based on the single-site binding of neutral pyridyl groups, and it is an ideal connector between the transition metals for propagation of coordination networks. Because 4,4'-bpy has two potential binding sites which are arranged in a divergent (exo) fashion and a rigid structure that helps us predict the network geometries, the length of the ligand is

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sufficient for creating cavities of molecular dimensions upon formation of networks with metals. In principle, the pyridyl groups of bipyridine can rotate along a central C–C bond. However, the rotation does not affect the mutual orientation of the two lone pairs [13]. Therefore, bipyridine can be regarded as a rigid and prototypical bridging ligand. Networks composed of 4,4'-bpy contain 1-D, 2-D, and 3-D networks. Compared to 1-D and 2-D networks, the 3-D networks are composed of porous structures with high surface area, uniform pore structure, large pore volume, and good gas storage properties. 3-D networks that have only a single 4,4'-bpy ligand are relatively rare [14–23].

In 2000, Shin-ichiro Noro and Susumu Kitagawa used 4,4'-bpy as a ligand to synthesize a 3-D network composed of $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ through solution diffusion. This material had remarkable adsorption capacity for CH_4 which adsorbed 6.5 mmol g^{-1} at 298 K under 36 atm [24]. CH_4 storage capacity for this material was much larger than ZSM-5 and other MOFs [25–29]. Since then, no research has been done on its synthesis and other gas adsorption behaviors. In this work, we synthesized $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ and explored the effects varying synthesis conditions that had on the sample. The sample was characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), Thermogravimetric (TG), and nitrogen adsorption. To show adsorption potential of the material, studies of H_2 storage and CO_2 capture were carried out.

2. Experimental

2.1. Raw chemicals

Copper tetrafluoroborate hexahydrate ($\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, Aldrich, 99%), ammonium fluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$, Aldrich, 98%), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, Aldrich, 99.8%), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Tianjin Chemical, China, 95%) were used in all syntheses without purification. The distilled water used in these experiments was made in our laboratory.

2.2. Synthesis

Following the process outlined by Noro and Kitagawa [24], samples were prepared as follows: add 4,4'-bpy (2 mmol, 0.33 g), $(\text{NH}_4)_2\text{SiF}_6$ (1 mmol, 0.089 g), and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.0234 g) into ethylene glycol and the mixture was thoroughly stirred for 20 min at room temperature in order to dissolve the materials completely. These stirred mixtures were synthesized at room temperature and in refrigerators (Haier LC-162B) that enabled us to vary the temperature. After 7 days, the purple crystals obtained were washed with distilled water and ethanol and dried in air at room temperature.

2.3. Characterization

The crystallinity, phase purity, and identity of the obtained samples were determined by XRD (Rigaku Mini Flex II) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418$) operated at 30 kV

and 15 mA. The scan range was from 5° to 40° (2 θ) at 1° min⁻¹. The crystal morphology and size were observed by SEM (JEOL, JSM-6360LV). The samples were coated with gold to increase their conductivity before scanning. N₂ adsorption was measured on an ASAP 2020 M gas-adsorption apparatus at liquid-nitrogen (77 K) temperature. TG analysis (Netzsch, STA-409-C) was carried out in air (airflow rate 100 mL min⁻¹) at a heating rate of 5 K min⁻¹.

2.4. Gas adsorption measurement

H₂ storage and CO₂ capture adsorption isotherms under high pressure were measured on an Intelligent Gravimetric Analyzer (IGA 001). Prior to measuring the isotherm, a 50 mg sample was pre-dried under reduced pressure, then outgassed at 298 K under high vacuum overnight until no further weight losses were observed. The sample adsorption was then measured at 298 K and 323 K. Each adsorption/desorption step was allowed to approach equilibrium over a period of 15–30 min except for guest molecule, which required 2–8 h to reach equilibrium. All the isotherms for each gas were measured on a single sample.

3. Results and discussion

3.1. Synthesis

A systematic study of [Cu(SiF₆)(4,4'-bpy)₂] in the 4,4'-bpy... (NH₄)₂SiF₆... Cu(BF₄)·6H₂O... ethylene glycol-system was carried out. Powder XRD method was employed to identify the framework structures of the obtained samples. The diffraction peak positions and relative diffraction intensities of our experimental sample of [Cu(SiF₆)(4,4'-bpy)₂] were in good agreement with those previously reported (figure 1) [24]. The molar ratio of the reagents and synthesis temperature in the precursor were first studied and then crystallization time was investigated.

3.1.1. Effect of the mole ratio of 4,4'-bpy/Cu(BF₄)·6H₂O. The effect of the molar of 4,4'-bpy/Cu(BF₄)·6H₂O on the synthesis of the sample is shown in table 1. Experiments were performed at 298 K for 7 days. After fixing the starting molar ratio at Cu(BF₄)·6H₂O:(NH₄)₂SiF₆:2 4,4'-bpy, the starting 4,4'-bpy/Cu(BF₄)·6H₂O molar ratio was varied from 1.6 to 3.0. Pure-phase [Cu(SiF₆)(4,4'-bpy)₂] samples were obtained when the 4,4'-bpy/Cu(BF₄)·6H₂O ratio was 1.8. As the concentration of 4,4'-bpy decreased, the crystallinity of the [Cu(SiF₆)(4,4'-bpy)₂] phase became poor, and an unknown phase crystallized; pure [Cu(SiF₆)(4,4'-bpy)₂] was obtained when the ratio was 1.8 to 2.8. In contrast, when there was an increase in 4,4'-bpy, pure [Cu(SiF₆)(4,4'-bpy)₂] could not be obtained and when the ratio of 4,4'-bpy/Cu(BF₄)·6H₂O was 2.4, the relative crystallinity of the sample was best.

3.1.2. Effect of the mole ratio of (NH₄)₂SiF₆/Cu(BF₄)·6H₂O. The effect of the molar of (NH₄)₂SiF₆/Cu(BF₄)·6H₂O on the synthesis of the sample was listed (table 2). After fixing the starting molar ratio at Cu(BF₄)·6H₂O:(NH₄)₂SiF₆:2.4 4,4'-bpy, and when

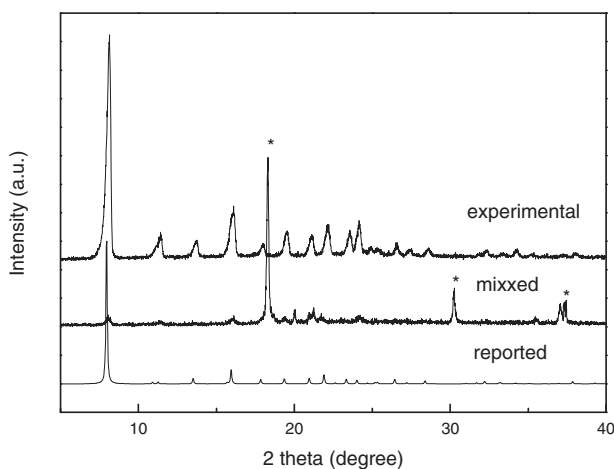


Figure 1. XRD of reported, experimental, and mixed unknown phases of $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$ (*denotes the peaks of an unknown phase).

Table 1. Effect of the mole ratio of $4,4'\text{-bpy}/\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}$.

$4,4'\text{-bpy}/\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}$ (mol mol ⁻¹)	Phase	Relative crystallinity (%)
1.6	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2 + *$	–
2.0	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	65.3
2.4	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	100
2.8	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	82.5
3.0	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2 + *$	–

*Denotes unknown phase.

Table 2. Effect of the mole ratio of $(\text{NH}_4)_2\text{SiF}_6/\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}$.

$(\text{NH}_4)_2\text{SiF}_6/\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}$ (mol mol ⁻¹)	Phase	Relative crystallinity (%)
0.6	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2 + *$	–
0.8	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	88.7
1	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	100
1.2	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2$	90.5
1.4	$\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2 + *$	–

*Denotes unknown phase.

the $(\text{NH}_4)_2\text{SiF}_6/\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}$ ratio is 1, pure product can be formed. A lower or higher $(\text{NH}_4)_2\text{SiF}_6$ content in the mixture usually results in formation of unknown phases. Therefore, the best mole ratio of $\text{Cu}(\text{BF}_4) \cdot 6\text{H}_2\text{O}/(\text{NH}_4)_2\text{SiF}_6/4,4'\text{-bpy}$ was 1 : 1 : 2.4.

Table 3. Effect of the temperature.

Cu(BF ₄)·6H ₂ O/(NH ₄) ₂ SiF ₆ /4,4'-bpy (mol/mol)	Temperature (K)	Phase	Relative crystallinity (%)
1:1:2.4	298	Cu(SiF ₆)(4,4'-bpy) ₂	67.5
1:1:2.4	283	Cu(SiF ₆)(4,4'-bpy) ₂	78.2
1:1:2.4	278	Cu(SiF ₆)(4,4'-bpy) ₂	100
1:1:2.4	276	Cu(SiF ₆)(4,4'-bpy) ₂	69.6
1:1:2.4	273	Cu(SiF ₆)(4,4'-bpy) ₂ +*	

*Denotes unknown phase.

3.1.3. Effect of synthesis temperature. After fixing the molar ratio of the components at Cu(BF₄)·6H₂O:(NH₄)₂SiF₆:2.4 4,4'-bpy in ethylene glycol, experiments were carried out for 7 days at 298 K, 283 K, 278 K, and 276 K, respectively. The experiment data are listed in table 3. This material could be synthesized at room temperature and low temperature, with low temperature more beneficial for synthesizing bigger sample size. When temperature was reduced to freezing, the sample could not be synthesized. There were some unknown phases on the XRD image of the sample synthesized at 273 K (figure 1), which appeared at $2\theta = 17^\circ$, 30° , and 37° .

Morphologies of the crystals synthesized at 298, 283, 278, and 276 K were characterized by SEM. As shown in figure 2, the size of the sample synthesized at 298 K ranged from 1 to 3 μm and its shape was square. When the synthesis temperature was decreased to 283 K, the crystal size was about 5 μm and more regular, and when the synthesis temperature was still reduced further to 278 K, the size of the sample increased to about 10 μm . When the synthesis temperature decreased to 276 K, the sample synthesized was smaller than samples at three previous synthesis temperatures. Low temperature was beneficial for synthesizing good crystal materials, but when the synthesis temperature approached the freezing point, the materials obtained under identical conditions became smaller due to slow diffusion rate of the solution. The XRD and SEM analysis indicated that temperature could influence synthesizing of the sample to a great extent.

3.1.4. Effect of crystallization time. To study the effect of crystallization time, after mixing Cu(BF₄)·6H₂O (1 mmol), (NH₄)₂SiF₆ (1 mmol), and 4,4'-bpy (2.4 mmol) into ethylene glycol, experiments were carried out at 278 K. The XRD patterns of the products that crystallized after 5 days were attributed to [Cu(SiF₆)(4,4'-bpy)₂] (figure 3). However, highly crystallized [Cu(SiF₆)(4,4'-bpy)₂] was not obtained with any change in the crystallization time at the current molar ratio of the components. Figure 3 showed that the phase [Cu(SiF₆)(4,4'-bpy)₂] appeared upon crystallization after 7 days. Well-crystallized, pure-phase [Cu(SiF₆)(4,4'-bpy)₂] was obtained after a crystallization time of 9 days, indicating that long crystallization time preferably led to better 3-D framework [Cu(SiF₆)(4,4'-bpy)₂].

3.2. Characterization

3.2.1. Nitrogen sorption isotherm of [Cu(SiF₆)(4,4'-bpy)₂]. After being dehydrated at 373 K, the pore properties of the sample were analyzed at 77 K. According to N₂

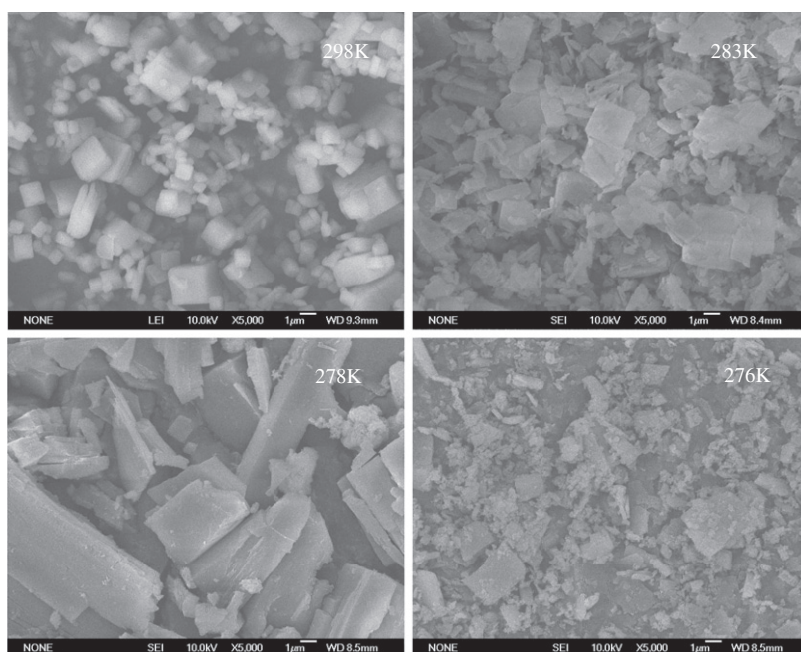


Figure 2. SEM of the sample at 298 K, 283 K, 278 K, and 276 K.

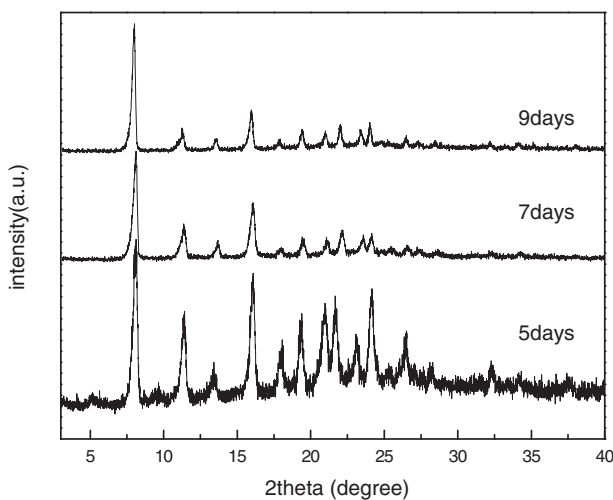


Figure 3. Effect of crystallization on synthesis of the sample.

adsorption–desorption experiments (figure 4) performed at 77 K, the BET surface area was calculated to be $713.4\text{ m}^2\text{ g}^{-1}$. The corresponding Langmuir surface area was $1006.2\text{ m}^2\text{ g}^{-1}$ and the pore volume was calculated to be $0.35\text{ cm}^3\text{ g}^{-1}$.

3.2.2. The TG curve of $[\text{Cu}(\text{SiF}_6)(4,4'\text{-bpy})_2]$. The thermal stability of the sample was tested by TG analysis. As shown in figure 5, two main weight-loss steps were observed.

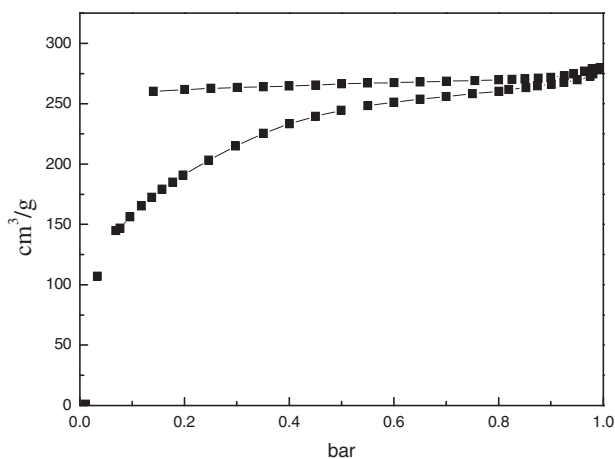


Figure 4. Nitrogen adsorption isotherm of the sample at 77 K.

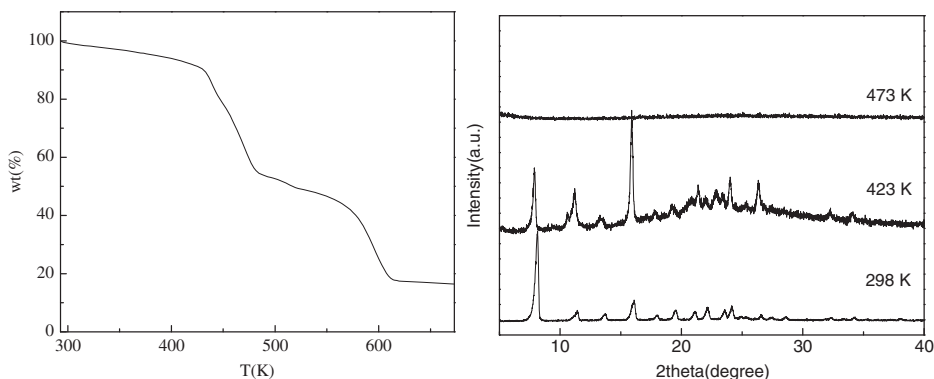


Figure 5. The TG curve of the sample and XRD pattern of the sample activated at different temperatures.

The first (10% of the initial weight) occurred between 298 and 423 K and could be attributed to the loss of guest water and ethanol molecules, and the second (58% of the initial weight) occurred between 423 and 473 K due to decomposition of the framework. It was observed from XRD patterns that when the temperature increased to 423 K, the structure of the sample changed, and as the temperature increased further to 473 K, the material lost its crystal structure, becoming amorphous. The XRD patterns of the sample activated at different temperatures exhibited characteristics identical to those of the thermal curve.

3.3. Gas adsorption

The material had high CH₄ storage, but there was no information available on the adsorption properties of [Cu(SiF₆)(4,4'-bpy)₂], to other gases especially the H₂ and CO₂

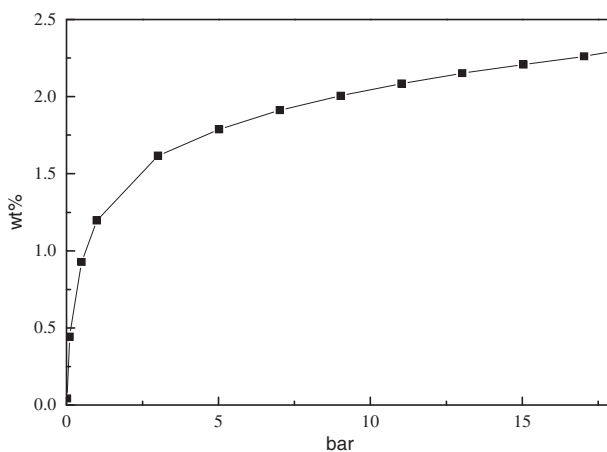


Figure 6. Isotherms for H₂ storage on [Cu(SiF₆)(4,4'-bpy)₂].

adsorption properties. Therefore, H₂ storage and CO₂ capture were done to find the adsorption potential of the material. H₂ and CO₂ adsorption isotherms under high pressure were measured on an IGA 001.

3.3.1. Hydrogen storage. From the adsorption isotherm behavior (figure 6) adsorption capacities of H₂ increased with increase of pressure. When pressure increased to 18 bar, gas adsorption isotherm exhibited the absorption capacity of H₂ at 77 K of 2.36 wt%. At 1 bar and 77 K, [Cu(SiF₆)(4,4'-bpy)₂] adsorbed 1.21 wt% H₂, nearly equivalent to the level of MOF-177 (1.25 wt%) and a bit lower than IRMOF-1 (1.32 wt%) [30–32]. Therefore, this material has good H₂ storage ability.

3.3.2. CO₂ capture. Because the material had a large CH₄ storage, the potential adsorption of gaseous CO₂ was considered. From the adsorption isotherm behavior (figure 7), adsorption capacities of CO₂ increase with increase of pressure. When pressure increased to 10 bar, the sample absorbed 4.17 mmol g⁻¹ CO₂ at 298 K. Adsorption of CO₂ decreased as temperature increased; at 323 K, the absorption capacities of CO₂ at 10 bar decreased to 3.76 mmol g⁻¹. Adsorption of CO₂ is 4.1 mmol g⁻¹ in ZIF-8 [33] and 3.13 mmol g⁻¹ in Cu(dhbc)₂(4,4-bpy) at 298 K at 10 bar [34]. Compared to ZIF-8 and Cu(dhbc)₂(4,4-bpy), the material is a good absorbent to capture CO₂ under the same conditions. According to Clausius–Clapeyron [35–37], the adsorption heat of CO₂ on the sample was calculated to be 22.18 kJ mol⁻¹, higher than ZIF-8 (15.93 kJ mol⁻¹) [38].

4. Conclusions

We have investigated different synthesis conditions on the morphologies and crystallinity of the 3-D material [Cu(SiF₆)(4,4'-bpy)₂]. Low temperature was beneficial for

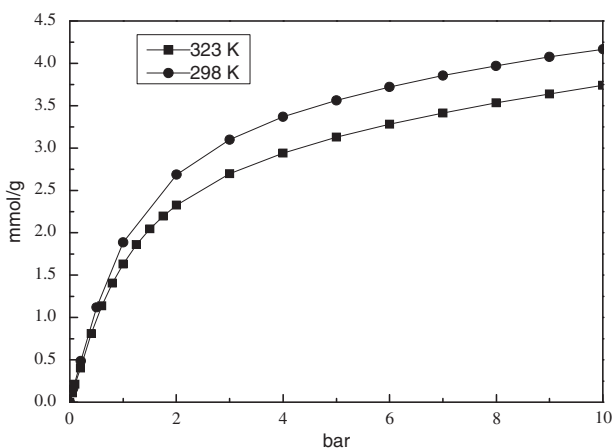


Figure 7. Gas adsorption curve of CO₂ on the sample at 298 K and 323 K.

synthesizing larger crystals, but when the temperature approached the freezing point, the crystalline structure of the materials generated worsened. The material could store 2.36 wt% H₂ at 77 K at 18 bar and capture CO₂ which was 4.17 mmol g⁻¹ at 298 K and 3.72 mmol g⁻¹ at 323 K at 10 bar.

Acknowledgments

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References

- [1] O.M. Yaghi. *Access Nanoporous Mater.*, **111**, 121 (1995).
- [2] M.J. Zaworotko. *Chem. Commun.*, 1 (2001).
- [3] C. Janiak. *Angew. Chem. Int. Ed.*, **36**, 1431 (1997).
- [4] O.M. Yaghi, G. Li, H. Li. *Nature*, **378**, 703 (1995).
- [5] H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi. *J. Am. Chem. Soc.*, **120**, 8571 (1998).
- [6] B.F. Hoskins, R. Robson. *J. Am. Chem. Soc.*, **112**, 1546 (1990).
- [7] H.J. Choi, T.S. Lee, M.P. Uh. *Angew. Chem. Int. Ed.*, **38**, 1405 (1999).
- [8] S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita. *J. Am. Chem. Soc.*, **124**, 2568 (2002).
- [9] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
- [10] D.N. Dytsev, H. Chun, S.H. Yoon, D. Kim, K. Kim. *J. Am. Chem. Soc.*, **126**, 32 (2004).
- [11] J.-R. Li, R.J. Kuppler, H.-C. Zhou. *Chem. Soc. Rev.*, **38**, 1477 (2009).
- [12] Z. Liang, M. Marshall, A.L. Chaffee. *Microporous Mesoporous Mater.*, **132**, 305 (2010).
- [13] B. Kumar, S. Madhushree, R. Lalit. *Chem. Commun.*, 4169 (2006).
- [14] K.N. Power, T.L. Hennigar, M.J. Zaworotko. *New J. Chem.*, **22**, 177 (1998).
- [15] F. Kubel, J. Strahle. *Z. Naturforsch Anorg. Chem. Org. Chem.*, **37**, 272 (1982).
- [16] E.J. Cussen, J.B. Claridge, M.J. Rosseinsky, C.J. Kepert. *J. Am. Chem. Soc.*, **124**, 9574 (2002).

- [17] A.J. Fletcher, E.J. Cussen, D. Bradshaw, M.J. Rosseinsky, K.M. Thomas. *J. Am. Chem. Soc.*, **126**, 9750 (2004).
- [18] G.J. Halder, C.J. Kerpert. *J. Am. Chem. Soc.*, **127**, 7891 (2005).
- [19] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa. *Angew. Chem. Int. Ed.*, **36**, 1725 (1997).
- [20] R.W. Gable, B.F. Hoskins, R. Robson. *J. Chem. Soc., Chem. Commun.*, 1677 (1990).
- [21] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 151 (1994).
- [22] K. Biradha, K.V. Domasevitch, B. Moulton, C. Seward, M.J. Zaworotko. In *Current Challenges on Large Supramolecular Assemblies*, G. Tsoucaris (Ed.), p. 115, Kluwer, Dordrecht (1999).
- [23] K. Biradha, K.V. Domasevitch, B. Moulton, C. Seward, M.J. Zaworotko. *Chem. Commun.*, 1327 (1999).
- [24] S. Noro, S. Kitagawa, M. Kondo, K. Seki. *Angew. Chem. Int. Ed.*, **39**, 2081 (2000).
- [25] S.-Y. Zhang, O. TaLu, D.T. Hayhurst. *J. Phys. Chem.*, **95**, 1722 (1991).
- [26] L. Mantasty, A.M. Woestyn, G. Zgrablich. *Adsorpt. Sci. Technol.*, **11**, 123 (1994).
- [27] Z.H. Xiang, Z. Hu, D.P. Cao, W.T. Yang, J.M. Lu, B.Y. Han, W.C. Wang. *Angew. Chem., Int. Ed.*, **50**, 491 (2011).
- [28] A.R. Millward, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 17998 (2005).
- [29] S.R. Venna, M.A. Carreon. *J. Am. Chem. Soc.*, **132**, 76 (2010).
- [30] H. Furukawa, M.A. Miler, O.M. Yaghi. *J. Mater. Chem.*, **17**, 3197 (2007).
- [31] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi. *J. Am. Chem. Soc.*, **128**, 3497 (2006).
- [32] X. Lin, N.R. Champness, M. Schröder. *Top. Curr. Chem.*, **293**, 35 (2010).
- [33] S.K. Nune, P.K. Thallapally, A. Dohnalkova, C.M. Wang, J. Liu, G.J. Exarhos. *Chem. Commun.*, **46**, 4878 (2010).
- [34] J.-R. Li, Y. Ma, M.C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P.B. Balbuena, H.-C. Zhou. *Coord. Chem. Rev.*, **255**, 1791 (2011).
- [35] D. Ben-Amotz, J.M. Honig. *J. Chem. Phys.*, **118**, 5932 (2003).
- [36] J. Anwar, D. Frenkel, G.M. Noro. *J. Chem. Phys.*, **118**, 728 (2003).
- [37] P. Shamba, J.C. Debnath, R. Zeng, J.L. Wang, S.J. Campbell, S.J. Kennedy, S.X. Dou. *J. Appl. Phys.*, **109**, 07A940/1 (2011).
- [38] J. Pérez-Pellitero, H. Amrouche, F.R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais, A. Simon-Masseron, D. Bazer-Bachi, D. Peralta, N. Bats. *Chem. Eur. J.*, **16**, 1560 (2010).