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Direct Air Capture of CO_2 by Physisorbent Materials

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Abstract: *Sequestration of CO_2, either from gas mixtures or directly from air (direct air capture, DAC), could mitigate carbon emissions. Here five materials are investigated for their ability to adsorb CO_2 directly from air and other gas mixtures. The sorbents studied are benchmark materials that encompass four types of porous material, one chemisorbent,* ***TEPA-SBA-15*** *(amine-modified mesoporous silica) and four physisorbents:* ***Zeolite 13X*** *(inorganic);* ***HKUST-1*** *and* ***Mg-MOF-74/Mg-dobdc*** *(metal–organic frameworks, MOFs);* ***SIFSIX-3-Ni****, (hybrid ultramicroporous material). Temperature-programmed desorption (TPD) experiments afforded information about the contents of each sorbent under equilibrium conditions and their ease of recycling. Accelerated stability tests addressed projected shelf-life of the five sorbents. The four physisorbents were found to be capable of carbon capture from CO_2-rich gas mixtures, but competition and reaction with atmospheric moisture significantly reduced their DAC performance.*

The development of a new generation of porous materials is key to enabling the "age of gas", wherein new technologies develop around the use of gases.[1] Carbon dioxide (CO_2) represents a topical challenge in this context: anthropogenic emissions of CO_2 are accepted as a significant risk to global climate; CO_2 is an undesirable component of commodities such as natural gas and biogas. The level of atmospheric CO_2 surpassed 400 ppm in 2013, which represents an increase of over 120 ppm since pre-industrial levels.[2] Human activity is currently adding an additional 24 Gt of CO_2 per year to the atmosphere, of which, 14 Gt is from anthropogenic CO_2 point sources.[3] While over half the CO_2 emissions are from large, industrial point sources, the remainder of these emissions are from small, mobile sources such as cars, trucks, and aircraft. It is becoming critical to develop economical pathways to reduce levels of CO_2 in the atmosphere and two approaches are being actively considered: 1) CO_2 removal from post-combustion industrial point sources (i.e. flue-gas capture) and 2) atmospheric CO_2 removal by direct air capture (DAC).[4] Post-combustion CO_2 capture would reduce emissions from large-scale sources of CO_2 such as coal-burning power stations; however, this technology may not be practical for application in mobile sources and fails to address the question of what to do with captured CO_2. Geological sequestration or use of the captured CO_2 as a commodity is feasible, but capture, purification, pressurization, and transportation must each be addressed in order to enable this carbon capture solution. DAC could mitigate CO_2 emissions from all sources and in turn enable onsite technologies that require CO_2 as a feedstock, thereby eliminating the need for storage and transport infrastructure. Examples of such technologies include "fuel from air" conversion of CO_2 into alcohols by algae and more efficient greenhouse growth of plants. Further, solving the challenge DAC would provide materials to facilitate other carbon capture needs such as pre-combustion removal of CO_2 from natural gas, biogas and other fuel gases.

However, implementation of DAC necessitates a low cost sorbent that combines optimum uptake, kinetics, energetics, physical/chemical stability and selectivity for CO_2 over competing gases and vapors at atmospheric CO_2 concentrations. To date, DAC systems have typically employed solid organo-amine based chemisorbents, wherein amine functional groups are either physically or chemically anchored to the surface of cellulose,[5] porous silicas[6] or porous polymer networks.[7] However, these sorbents require elevated temperatures (> 100 °C) for regeneration. DAC using physisorption is an attractive proposition, but has so far been handicapped by the lack of suitable physisorbents that are highly selective towards CO_2 and stable in the presence of competing gases and vapors. Nevertheless, physisorbents that can capture CO_2 with high selectivity are attractive since they would likely require much less energy for recycling. Porous metal–organic materials (MOMs)[8] and the newly described subclass of coordination polymer called hybrid ultramicroporous materials (HUMs),[9] show potential for use in sorbent-based applications such as gas purification,[10] gas storage,[11] and small-molecule separations.[11d,12] Further, their benchmark selectivity towards CO_2[9a,b] means they could serve as physisorbents for DAC. However, whereas the most selective MOMs and HUMs have received attention for the flue-gas capture of CO_2,[10a,11c,13] to the best of our knowledge no work has yet been reported for these types of physisorbents in the context of DAC. Here, we use temperature-programmed desorption (TPD), thermogravimetric analysis (TGA), and mass spectrometry (MS) to evaluate five sorbents, **SIFSIX-3-Ni**,[9e] **HKUST-1**,[14] **Mg-MOF-74/Mg-dobdc**,[13c] **Zeolite 13X**[15] and **TEPA-SBA-15**,[16] in the context of DAC and five other gas mixtures. We also address the stability of these

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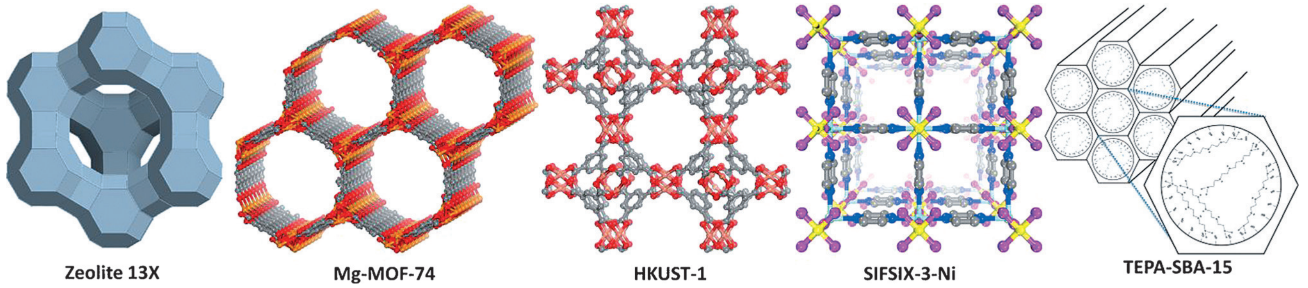

Zeolite 13X Mg-MOF-74 HKUST-1 SIFSIX-3-Ni TEPA-SBA-15

Figure 1. The five sorbent materials investigated in this study. The colors of the atoms are as follows: orange, Mg; red, O; gray, C; salmon, Cu; blue, N; yellow, Si; pink, F; turquoise, Ni.

sorbents to atmospheric water vapor via accelerated stability tests that simulate long-term storage or "shelf-life".[17]

The five sorbents studied herein represent four classes of porous materials that have been widely investigated in the context of carbon capture (Figure 1). **SIFSIX-3-Ni**[9e] is a recently reported variant of a class of sorbents we call HUMs,[9a–d] because they combine ultramicropores (<0.7 nm) in a material comprised of transition metals linked by two types of linker: organic ligands and inorganic anions.

The relatively high electrostatic contribution from the inorganic anions combined with tight binding sites affords strong interactions between adsorbent and adsorbate (large Q_{st}) and extra-high selectivity for polarizable gases (e.g. CO_2). **HKUST-1**[14] (marketed as Basolite C300) and **Mg-MOF-74**[13c] are prototypical examples of physisorbent metal–organic materials, also known as MOFs[18] or porous coordination polymers, PCPs.[19] **Zeolite 13X**[15] is a well-studied inorganic physisorbent that is already used in liquid bulk separations and fuel desulfurization.[20] **TEPA-SBA-15**,[16] an amine-modified mesoporous silicate, is a chemisorbent that belongs to the general class of sorbents known as amine-functionalized silica. These sorbents were synthesized following literature methods (see Supporting Information, SI), except for **Zeolite 13X**, which was used as received from commercial sources. Each of the sorbents was characterized by powder X-ray diffraction (PXRD; Figure S6–S12), thermogravimetric analysis (TGA; Figure S13–S18), and infrared spectroscopy (FT-IR; Figure S19–S23). Where required (e.g. **HKUST-1**, **Mg-MOF-74**, and **SIFSIX-3-Ni**), the sorbents were subjected to solvent exchange and activation using published procedures; details for the exchange process and activation protocols are given in the SI. After activation, each sorbent was subjected to sorption experiments to verify that they met specifications according to the literature.

The DAC performance of each sorbent was evaluated using pristine, activated samples exposed to a specific gas mixture for a prescribed time period before being subjected to temperature-programmed desorption (TPD). In a typical TPD experiment, a sample was placed in a quartz reactor cell positioned within a tube furnace. This cell was heated to a temperature that guarantees the full evacuation of the host in the presence of He carrier gas while the exhaust gas was continuously monitored using a mass spectrometer (MS). These experiments provide the identity and relative quantity of gas(es) or vapor(s) desorbed by the sample as a function of temperature, or, if temperature is held constant, as a function of time. They also afford an understanding of the energy required for recycling the adsorbent material, although the TPD experiments we conducted do not provide information about the kinetics of CO_2 adsorption/desorption. Kinetics, along with recyclability and cost, are important aspects of DAC that will need to be carefully investigated in future experiments. In short, TPD experiments, address relative H_2O/CO_2 uptake, and afford a qualitative indication of the ease with which the sorbent can be recycled.

In conjunction with the DAC experiments, the five sorbents were also subjected to TPD-TGA experiments in which each sorbent was placed in a TGA, heated to the temperature required for its activation and held for a prescribed period of time before being cooled to ca. 30 °C. Upon cooling, the sample was then exposed to the conditions described below until the uptake remained constant. The mass gain for each sorbent was measured as a function of time. These conditions, including duration of exposure, were replicated for each sample using the TPD apparatus. The quantity and identity of adsorbed species in each sorbent was thereby determined (see Figure 2 for DAC plots; all TPD plots are in the SI). Each sorbent was exposed to six gas mixtures, each designed to address a different aspect of the sorbent's performance with respect to CO_2 sorption:

- DAC: Each sorbent was activated and then exposed to the laboratory atmosphere (avg. 23.4 °C; 49 % relative humidity, RH) for 12 h (see the SI). This experiment tests the equilibrium contents of the sorbent following atmospheric exposure.
- Dry CO_2 (1 atm): To establish the CO_2 mass uptake for each sorbent, a dry 1 atm stream of CO_2 was passed over the sorbent.
- Moist CO_2 (1 atm): A 1 atm stream of CO_2 that had been bubbled through deionized water was flowed over the sorbent. The relative ability of each sorbent to capture CO_2 from a humid, high concentration CO_2 source was thereby determined.
- Dry CO_2 (0.15 atm): A 15 % CO_2, 85 % N_2 mix derived from pure gases mixed using a mass flow controller was used to simulate dry flue-gas conditions.
- Moist CO_2 (0.15 atm): The same mix as above, but bubbled through deionized water, was used to simulate realistic flue-gas conditions.

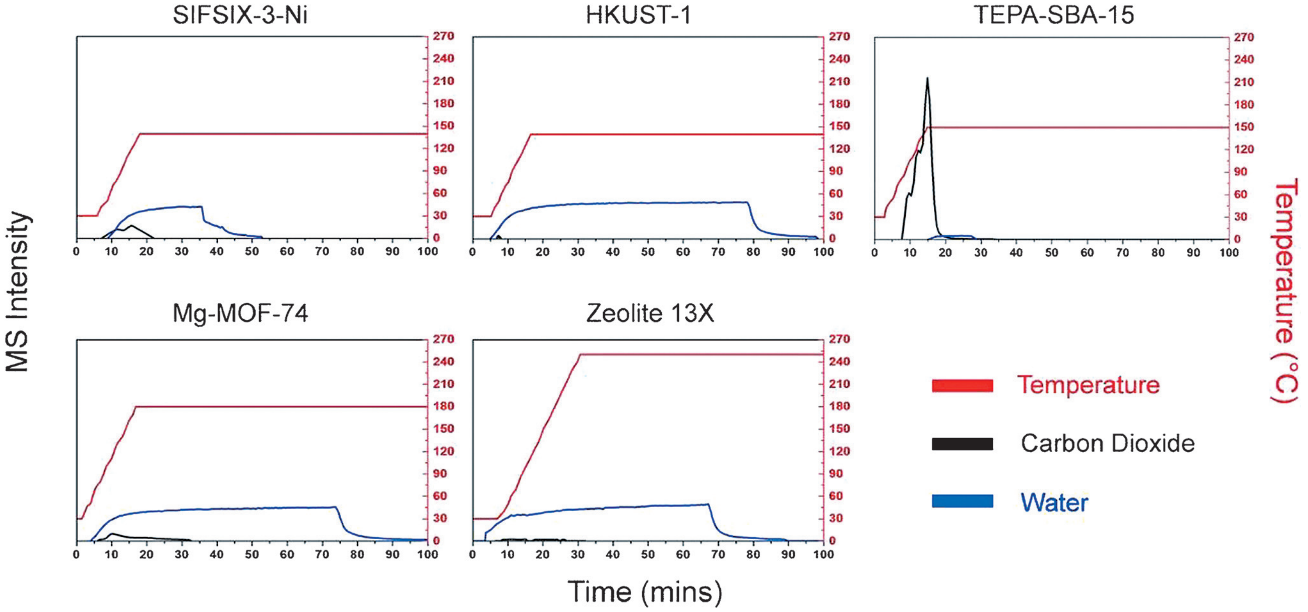

Figure 2. TPD plots of direct air capture of CO_2 experiments for the five sorbents studied herein. The red curve is the temperature ramp profile used for desorption. The MS signals for CO_2 and H_2O are given by the black and blue curves, respectively.

- Moist N_2 (1 atm): This gas mixture was produced by bubbling pure nitrogen gas through deionized water and estimates capacity of each sorbent for water in the absence of CO_2.

Data for TPD experiments are presented in Table 1. The chemisorbent **TEPA-SBA-15** exhibits far superior DAC performance when compared to each of the physisorbents, adsorbing the most CO_2 and the least H_2O after 12 h of exposure. Of the physisorbents, **SIFSIX-3-Ni** performed best, followed by **Mg-MOF-74**, **HKUST-1**, and **Zeolite 13X**.

When exposed to simulated flue-gas (moist 0.15 atm CO_2/0.85 atm N_2), **TEPA-SBA-15** and **SIFSIX-3-Ni** were again the top two performers, followed by **Mg-MOF-74. Zeolite 13X** performed somewhat better than **HKUST-1**, however, both sorbents performed significantly worse under these conditions than either **TEPA-SBA-15** or **SIFSIX-3-Ni**. TPD experiments also provide an estimate of the relative ease of regeneration of the sorbent. The DAC plots in Figure 2 indicate that **SIFSIX-3-Ni** is the easiest sorbent to regenerate, needing the lowest temperature and the shortest time to remove adsorbed CO_2. **TEPA-SBA-15** required a slightly higher temperature to release CO_2 in about the same amount of time as **SIFSIX-3-Ni**. The significantly lower quantity of H_2O adsorbed by **TEPA-SBA-15** made for quicker regeneration than any of the other materials studied. However,

Table 1: TPD coupled with mass spectrometry.[a]

Sorbent	DAC (1 atm; 49% RH)[b]		Moist CO_2 (1 atm)[c]		Moist CO_2 (0.15 atm)[c]		Moist N_2 (1 atm)[c]	Dry CO_2 (1 atm)	Dry CO_2 (0.15 atm)
	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O	H_2O	CO_2	CO_2
SIFSIX-3-Ni	< 8% (8.0)	> 92% (93)	> 93% (109.5)	< 7% (7)	62% (76)	38% (46)	100% (120)	100% (110)	100% (109)
HKUST-1	1% (2.1)	99% (178)	> 44% (51.3)	< 56% (65)	8.5% (12.8)	> 91% (137)	100% (370)	100% (110)	100% (70)
Mg-MOF-74	< 4% (6.3)	> 96% (171)	39% (100.5)	61% (157)	51% (68)	49% (65)	100% (360)	100% (250)	100% (235)
Zeolite 13X	1% (1.5)	99% (146)	> 45% (53.6)	< 55% (66)	22% (26.3)	78% (93)	100% (270)	100% (170)	100% (140)
TEPA-SBA-15[d]	93% (158)	7% (12)	98% (148.8)	2% (3)	92% (130.3)	8% (11)	100% (120)	100% (160)	100% (152)

[a] Mass of analyte is given in parenthesis, expressed as $mg\,g^{-1}$. [b] Relative humidity and temperature where measured using thermometer-hygrometer. [c] Water-saturated gas feeds were obtained by bubbling each pure gas through deionized water. [d] TEPA-SBA-15 is an amine-modified mesoporous chemisorbent material.

chemisorbents can suffer from issues such as sorbent degradation over repeated cycling and amine deactivation in the presence of NO_x, SO_x, O_2 and CO_2.[21] **HKUST-1** required a similar temperature to that of **SIFSIX-3-Ni**, but a much longer time was needed to remove adsorbed water. **Mg-MOF-74** also requires a higher temperature and longer time than **SIFSIX-3-Ni** to remove CO_2 and H_2O. In both **HKUST-1** and **Mg-MOF-74**, H_2O coordinates unsaturated metal sites, making removal of adsorbed water difficult.[22] **Zeolite 13X**, which contains surface hydroxy groups and Na^+ ions that can bind H_2O molecules, required the highest temperature and longest regeneration time.

Performance in these TPD experiments correlates well with ideal selectivity[23] for CO_2 over N_2 (S_{CN}) and the isosteric heat of adsorption (Q_{st}), both of which were determined from pure CO_2 adsorption isotherms. Amine-modified adsorbents exhibit Q_{st} values of 50–100 kJ mol^{-1} and extra-high S_{CN} as N_2 gas does not chemically react with the amine groups.[24] **SIFSIX-3-Ni** ($S_{CN} \approx 1874$) exhibits much higher S_{CN} than either **HKUST-1** ($S_{CN} \approx 101$)[25] or **Mg-MOF-74** ($S_{CN} \approx 148$).[13b] However, whereas ideal adsorbed solution theory (IAST)[23] can be used as an indicator of a material's likely ability to selectively adsorb CO_2 over competing gases such as N_2, pure gas isotherms are not necessarily indicative concerning how a sorbent will behave when exposed to gas mixtures, especially those involving water vapor, hence the need to perform the TPD experiments detailed herein.

The TPD experiments revealed that the physisorbents adsorb large quantities of H_2O. This not only mitigates against CO_2 uptake, but recent studies suggest that MOMs can be susceptible to degradation when exposed to water or water vapor.[10a,22a,26] In this context, Walton and co-workers have presented guidelines to rank the water stability of MOMs.[27] However, to our knowledge there have been no reports concerning stability tests of the type regulated for the pharmaceutical industry where six months of storage under "accelerated" conditions are accepted as being representative of two years of long-term storage or shelf-life.[17,28] We exposed pristine samples of each of the five sorbents studied herein to 40 °C and 75 % humidity and removed aliquots for analysis (PXRD, TGA, and gas sorption, see SI for full details) after 1, 7, and 14 days.

TEPA-SBA-15 and **Zeolite 13X** were both found to remain stable after 14 days of testing. The surface area of **TEPA-SBA-15** was not measured as it is a chemisorbent and degassing under vacuum can degrade the amine grafts (see Figure S17). However, its capacity to adsorb CO_2 at 293 K was unchanged after exposure to the humidity chamber for 1, 7, and 14 days (Figure 3). The surface area calculated for a pristine sample of **Zeolite 13X**, ca. 832 m^2 g^{-1}, agrees well with previously reported values.[15a] After exposure to the humidity chamber for 1, 7, and 14 days, **Zeolite 13X** exhibited BET surface areas of ca. 816 m^2 g^{-1}, 867 m^2 g^{-1}, and 865 m^2 g^{-1}, respectively. The amount of CO_2 adsorbed (293 K, 1 atm) by **Zeolite 13X** was also unaffected by stability tests (ca. 136 cm^3 g^{-1}). **SIFSIX-3-Ni** also maintained its adsorption performance after accelerated stability tests. Pristine **SIFSIX-3-Ni** exhibited a BET surface area of ca. 223 m^2 g^{-1}, agreeing with values reported for its Zn and Cu variants.[9a,b]

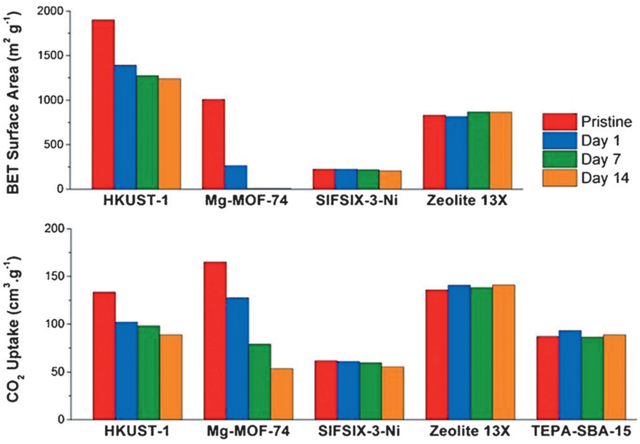

Figure 3. Bar graphs depict BET surface area (top) and CO_2 uptake at 293 K and 1 atm (bottom) for each sorbent in pristine condition (red) and after 1 (blue), 7 (green), and 14 days (orange) exposure in a controlled humidity chamber (40 °C; 75 % RH).

After 1, 7, and 14 days, the BET surface areas for **SIFSIX-3-Ni** were measured to be ca. 222 m^2 g^{-1}, 218 m^2 g^{-1}, and 208 m^2 g^{-1}, respectively (Figure 3). In terms of CO_2 uptake at 293 K and 1 atm, a pristine activated sample of **SIFSIX-3-Ni** adsorbs ca. 60 cm^3 g^{-1}. This value was little changed after accelerated stability tests.

Conversely, **HKUST-1** and **Mg-MOF-74** were degraded by exposure to humidity. The BET surface area measured for pristine activated **HKUST-1**, ca. 1900 m^2 g^{-1}, matches the best values reported.[29] After exposure to the humidity chamber, the BET surface area of **HKUST-1** decreased to 1370 m^2 g^{-1}, 1270 m^2 g^{-1} and 1240 m^2 g^{-1} after 1, 7 and 14 days, respectively. The observed decrease in BET surface area for **HKUST-1** is consistent with previous reports on its stability in the presence of water.[26b] The amount of CO_2 **HKUST-1** adsorbs at 293 K and 1 atm also diminished following exposure to humidity. The pristine activated sample can adsorb as much as 134 cm^3 g^{-1}, larger than **SIFSIX-3-Ni** and about the same as **Zeolite-13X**. However, after just 1 day the value dropped to 102 cm^3 g^{-1} (Figure 3). 7 days and 14 days uptakes of CO_2 dropped to 98 cm^3 g^{-1} and 89 cm^3 g^{-1}, respectively.

The sorption performance of **Mg-MOF-74** after accelerated stability testing was the worst of the five sorbents studied. After just 1 day of exposure, the BET surface area decreased by 74 % (Figure 3), and after 7 or 14 days exposure only negligible N_2 uptake at 77 K was measured (BET surface area 6 m^2 g^{-1}). These observations are consistent with earlier studies concerning the stability of **Mg-MOF-74** to water.[22,26b] CO_2 uptake was likewise diminished following exposure to humidity: pristine **Mg-MOF-74** adsorbs 165 cm^3 g^{-1} CO_2 at 1 atm and 293 K. One day of exposure in the humidity chamber reduced uptake to ca. 127 cm^3 g^{-1} CO_2; 7 days to ca. 79 cm^3 g^{-1} (−52 %); 14 days to 53 cm^3 g^{-1}.

In addition to measuring adsorption performance, PXRD and TGA measurements were collected during the accelerated stability tests. TGA experiments for all sorbents showed little evidence of change in the thermal stability profile; there were only small changes in the thermal decomposition temperature and the weight loss (presumably water) for days 1, 7, and 14. PXRD patterns also remained largely unchanged after exposure to humidity. However, **SIFSIX-3-Ni**, exhibited a different PXRD pattern from the pristine activated sample, that is, it matches an as yet unidentified precursor to **SIFSIX-3-Ni** (see Figure S10 and S11). However, heating at 110 °C for 10 min resulted in a PXRD pattern that closely matches pristine activated **SIFSIX-3-Ni**. In each case (1, 7, and 14 days), the material obtained from the humidity chamber was activated and retained the surface area and CO_2 uptake of a pristine, activated sample of **SIFSIX-3-Ni**.

Interestingly, **HKUST-1** and **Mg-MOF-74** showed no discernible changes in their respective PXRD patterns after exposure to humidity yet, as discussed earlier, adsorption performance diminished. Such an effect has been observed by several other research groups that have studied the effect of water and/or water vapor upon MOMs. One hypothesis offered is that the presence of water leads to partial pore blocking or pore collapse. If degradation of adsorption performance is associated with surface adulteration, then particle size should be addressed in future experimental protocols.

DAC remains a challenging but potentially fruitful approach to reduce the impact of anthropogenic emissions of CO_2. In this contribution, we address how water vapor impacts two important practical considerations with respect to DAC, in particular, and carbon capture, in general: competition between water vapor and CO_2 in gas mixtures including air and simulated flue gas; shelf-life of sorbents following exposure to atmospheric stability. With respect to the former, all four physisorbents studied exhibit strong S_{CN} but their performance with respect to CO_2 uptake was diminished in the presence of water vapor. The chemisorbent was unaffected by water vapor, but its energetics are not as favorable for recycling as **SIFSIX-3-Ni**. With respect to stability, the use of a relatively simple and standard stability test suggests that even short-term exposure to humidity can result in significant degradation of performance. In conclusion, there are two take-home messages: a standard stability test, perhaps of the type described herein, should be adopted and applied to candidate sorbents; physisorbents can compete with chemisorbents with respect to S_{CN} but DAC performance is mitigated because of competition with water vapor. The strong performance of **SIFSIX-3-Ni** highlights how controlling pore size and pore chemistry to improve DAC performance and stability in the presence of water vapor must be further addressed if physisorbents are to compete with chemisorbents.

Acknowledgements

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[1] S. Kitagawa, *Angew. Chem. Int. Ed.* **2015**, *54*, 10686–10687; *Angew. Chem.* **2015**, *127*, 10834–10835.

[2] R. Monastersky, *Nature* **2013**, *497*, 13–14.

[3] IPCC, Carbon Dioxide Capture and Storage: A Special Report of Working Group III of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA, 2005.

[4] A. Goeppert, M. Czaun, G. K. S. Prakash, G. A. Olah, *Energy Environ. Sci.* **2012**, *5*, 7833–7853.

[5] a) H. Sehaqui, M. E. Gálvez, V. Becatinni, Y.-C. Ng, A. Steinfeld, T. Zimmermann, P. Tingaut, *Environ. Sci. Technol.* **2015**, *49*, 3167–3174; b) C. Gebald, J. A. Wurzbacher, P. Tingaut, A. Steinfeld, *Environ. Sci. Technol.* **2013**, *47*, 10063–10070.

[6] a) Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, *Ind. Eng. Chem. Res.* **2010**, *49*, 359–365; b) A. Goeppert, H. Zhang, M. Czaun, R. B. May, G. K. S. Prakash, G. A. Olah, S. R. Narayanan, *ChemSusChem* **2014**, *7*, 1386–1397; c) A. R. Kulkarni, D. S. Sholl, *Ind. Eng. Chem. Res.* **2012**, *51*, 8631–8645.

[7] a) W. Lu, J. P. Sculley, D. Yuan, R. Krishna, H.-C. Zhou, *J. Phys. Chem. C* **2013**, *117*, 20037–20042; b) J. Wang, M. Wang, W. Li, W. Qiao, D. Long, L. Ling, *AIChE J.* **2015**, *61*, 972–980.

[8] J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417.

[9] a) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature* **2013**, *495*, 80–84; b) O. Shekhah, Y. Belmabkhout, Z. J. Chen, V. Guillerm, A. Cairns, K. Adil, M. Eddaoudi, *Nat. Commun.* **2014**, *5*, 7; c) M. H. Mohamed, S. K. Elsaidi, T. Pham, K. A. Forrest, B. Tudor, L. Wojtas, B. Space, M. J. Zaworotko, *Chem. Commun.* **2013**, *49*, 9809–9811; d) M. H. Mohamed, S. K. Elsaidi, L. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space, M. J. Zaworotko, *J. Am. Chem. Soc.* **2012**, *134*, 19556–19559; e) O. Shekhah, Y. Belmabkhout, K. Adil, P. Bhatt, A. Cairns, M. Eddaoudi, *Chem. Commun.* **2015**, *51*, 13595–13598; f) H. S. Scott, A. Bajpai, K.-J. Chen, T. Pham, B. Space, J. J. Perry IV, M. J. Zaworotko, *Chem. Commun.* **2015**, *51*, 14832–14835.

[10] a) Z. J. Zhang, Z. Z. Yao, S. C. Xiang, B. L. Chen, *Energy Environ. Sci.* **2014**, *7*, 2868–2899; b) E. Barea, C. Montoro, J. A. R. Navarro, *Chem. Soc. Rev.* **2014**, *43*, 5419–5430.

[11] a) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657–5678; b) M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, *Chem. Rev.* **2012**, *112*, 782–835; c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781; d) J.-R. Li, Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H. K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **2011**, *255*, 1791–1823.

[12] a) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869–932; b) K. A. Cychosz, R. Ahmad, A. J. Matzger, *Chem. Sci.* **2010**, *1*, 293–302; c) B. Van de Voorde, B. Bueken, J. Denayer, D. De Vos, *Chem. Soc. Rev.* **2014**, *43*, 5766–5788; d) S. Qiu, M. Xue, G. Zhu, *Chem. Soc. Rev.* **2014**, *43*, 6116–6140.

[13] a) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308–2322; b) J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, J. R. Long, *Energy Environ. Sci.* **2011**, *4*, 3030–3040; c) S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871; d) J. A. Mason, T. M. McDonald, T.-H. Bae, J. E. Bachman, K. Sumida, J. J. Dutton, S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* **2015**, *137*, 4787–4803.

[14] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148 – 1150.

[15] a) F. Su, C. Lu, *Energy Environ. Sci.* **2012**, *5*, 9021 – 9027; b) F. B. Cortés, F. Chejne, F. Carrasco-Marín, C. Moreno-Castilla, A. F. Pérez-Cadenas, *Adsorption* **2010**, *16*, 141 – 146; c) J.-S. Lee, J.-H. Kim, J.-T. Kim, J.-K. Suh, J.-M. Lee, C.-H. Lee, *J. Chem. Eng. Data* **2002**, *47*, 1237 – 1242.

[16] A. Zhao, A. Samanta, P. Sarkar, R. Gupta, *Ind. Eng. Chem. Res.* **2013**, *52*, 6480 – 6491.

[17] International Conference on Harmonization, Q1A(R2): Stability testing of new drug substances and products, 2003.

[18] a) D. Farrusseng, *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*, Wiley-VCH, Weinheim, **2011**; b) L. R. MacGillivray, *Metal-Organic Frameworks: Design and Applications*, Wiley, Hoboken, **2010**.

[19] a) M. L. Foo, R. Matsuda, S. Kitagawa, *Chem. Mater.* **2014**, *26*, 310 – 322; b) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109 – 119; c) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375; *Angew. Chem.* **2004**, *116*, 2388 – 2430.

[20] a) R. T. Yang, *Gas Separation by Adsorption Processes*, Imperial College Press, London, **2008**; b) http://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-1430/molecular-sieves.html.

[21] a) A. Sayari, A. Heydari-Gorji, Y. Yang, *J. Am. Chem. Soc.* **2012**, *134*, 13834 – 13842; b) A. P. Hallenbeck, J. R. Kitchin, *Ind. Eng. Chem. Res.* **2013**, *52*, 10788 – 10794.

[22] a) K. Tan, N. Nijem, Y. Z. Gao, S. Zuluaga, J. Li, T. Thonhauser, Y. J. Chabal, *CrystEngComm* **2015**, *17*, 247 – 260; b) K. Tan, S. Zuluaga, Q. H. Gong, P. Canepa, H. Wang, J. Li, Y. J. Chabal, T. Thonhauser, *Chem. Mater.* **2014**, *26*, 6886 – 6895.

[23] A. L. Myers, J. M. Prausnitz, *AIChE J.* **1965**, *11*, 121 – 127.

[24] C. W. Jones, *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 31 – 52.

[25] P. Aprea, D. Caputo, N. Gargiulo, F. Iucolano, F. Pepe, *J. Chem. Eng. Data* **2010**, *55*, 3655 – 3661.

[26] a) J. Canivet, A. Fateeva, Y. M. Guo, B. Coasne, D. Farrusseng, *Chem. Soc. Rev.* **2014**, *43*, 5594 – 5617; b) P. M. Schoenecker, C. G. Carson, H. Jasuja, C. J. J. Flemming, K. S. Walton, *Ind. Eng. Chem. Res.* **2012**, *51*, 6513 – 6519.

[27] N. C. Burtch, H. Jasuja, K. S. Walton, *Chem. Rev.* **2014**, *114*, 10575 – 10612.

[28] a) K. C. Waterman in *Handbook of Stability Testing in Pharmaceutical Development* (Ed.: K. Huynh-Ba), Springer, New York, **2009**, pp. 116 – 135; b) S. W. Baertschi, P. J. Jansen, K. M. Alsante in *Pharmaceutical Stress Testing: Predicting Drug Degradation*, 2nd. ed. (Eds.: S. W. Baertschi, K. M. Alsante, R. A. Reed), Informa Healthcare, London, **2011**.

[29] Y. Yang, P. Shukla, S. Wang, V. Rudolph, X.-M. Chen, Z. Zhu, *RSC Adv.* **2013**, *3*, 17065 – 17072.

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