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# Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants

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MIL-101(Cr) has drawn much attention due to its high stability compared with other metal-organic frameworks. In this study, three trace flue gas contaminants (H<sub>2</sub>O, NO, SO<sub>2</sub>) were each added to a 10 vol% CO<sub>2</sub>/N<sub>2</sub> feed flow and found to have a minimal impact on the adsorption capacity of CO<sub>2</sub>. In dynamic CO<sub>2</sub> regeneration experiments, complete regeneration occurred in 10 min at 328 K for temperature swing adsorption-N<sub>2</sub>-stripping under a 50 cm<sup>3</sup>/min N<sub>2</sub> flow and at 348 K for vacuum-temperature swing adsorption at 20 KPa. Almost 99% of the pre-regeneration adsorption capacity was preserved after 5 cycles of adsorption/desorption under a gas flow of 10 vol% CO<sub>2</sub>, 100 ppm SO<sub>2</sub>, 100 ppm NO, and 10% RH, respectively. Strong resistance to flue gas contaminants, mild recovery conditions, and excellent recycling efficiency make MIL-101(Cr) an attractive adsorbent support for CO<sub>2</sub> capture.

The development of efficient technologies for the capture and sequestration of carbon dioxide produced by existing point sources, such as fossil-fuel power plants and blast furnaces, will prove vital in controlling the environmental impact of anthropogenic emissions. In order for these technologies to be economically viable, carbon capture and sequestration (CCS) systems must curb the energy penalty associated with CO<sub>2</sub> capture and sorbent regeneration, and operate effectively in realistic conditions. The search for materials that fulfill the criteria of an efficient CO<sub>2</sub> sorbent has been proceeding with urgency<sup>1</sup>.

Processes based on aqueous amine absorbents represent the best, currently available, and practically applied technology for CO<sub>2</sub> capture. They include an energy penalty of roughly 30% on top of the power generation of the plant<sup>2</sup>. An alternative approach to reduce the energy penalty is by using solid sorbents since the desorption processes consume comparatively less energy.

Metal-organic frameworks (MOFs) is one of the major families of sorbents capable of capturing CO<sub>2</sub><sup>3-5</sup>. Their properties of highly tunable pore surfaces<sup>6-9</sup> and exceptional surface areas<sup>10</sup> are well-suited for CO<sub>2</sub> capture. Many studies have reported outstanding capacities for MOFs at high pressures. Recently, more researches have focused on understanding the performance of MOFs materials at the lower pressures relevant to the majority of CO<sub>2</sub> capture processes. Yazaydin et al<sup>11</sup> performed a screening of a diverse collection of 14 MOFs for CO<sub>2</sub> capture from flue gas at 0.1 bar. They found that the best-performing MOFs in regards to CO<sub>2</sub> adsorption at the test pressure of 0.1 bar were of the M<sub>2</sub>(dobdc) class (M = Zn, Ni, Co, Mg; dobdc = 2,5-dioxido-1,4-benzenedicarboxylate), likely due to their higher density of open metal sites. Despite of these progresses in knowledge, essential elements of applying MOFs in many large scale processes, namely contaminant influence on CO<sub>2</sub> capture and adsorbent regeneration, call for more in-depth examination.

A thorough investigation of MOFs for CO<sub>2</sub> capture requires consideration of the stability of the framework to humidity as well as the impact of humidity on CO<sub>2</sub>/N<sub>2</sub> separation<sup>12,13</sup>. Liu et al<sup>14,15</sup> examined the adsorption equilibria of CO<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O for two MOFs, HKUST-1 and Ni/dobdc. HKUST-1 experienced a significant decrease in CO<sub>2</sub> uptake to about 75% of its original value and a concomitant loss of partial crystallinity after exposure to 30% relative humidity (RH). Ni/dobdc, on the other hand, retained substantial CO<sub>2</sub> capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity with moderate H<sub>2</sub>O loadings, though CO<sub>2</sub> capacity could not be fully recovered after water adsorption. The effect of humidity on the M<sub>2</sub>(dobdc) series of MOFs was also studied by Kizzie et al<sup>16</sup>. Mg<sub>2</sub>(dobdc), which displayed the highest capacity for CO<sub>2</sub> at low pressures, performed the worst out of the series with a recovery of only 16% of its initial CO<sub>2</sub> capacity after regeneration, while Co<sub>2</sub>(dobdc) performed the best with a recovery of 85%.



Despite water's status as a very common, high concentration contaminant, other gaseous substances (e.g.  $\text{SO}_x$  and  $\text{NO}_x$ ) often have a considerable impact on adsorption processes. A modeling-based analysis of several contaminants on Mg/MOF-74 by Yu et al. suggests that  $\text{SO}_x$  and its hydrates could corrupt  $\text{CO}_2$  adsorption ability to a major extent.  $\text{NO}_x$  on the other hand was predicted to have a significantly smaller effect on limiting  $\text{CO}_2$  adsorption<sup>17</sup>. However, experimental evaluations of trace gas impacts on MOFs appear to be untested.

Another area of research regarding MOFs that could use further investigation is the regeneration of the frameworks, which must be carried out after each adsorption cycle. Regeneration of a solid adsorbent can be achieved by temperature swing adsorption (TSA), pressure swing adsorption (PSA), vacuum swing adsorption (VSA), vacuum temperature swing adsorption (VTSA), or steam stripping. Regenerated under a variation of steam stripping, He purge, Ni/dobdc was found to adsorb  $\text{CO}_2$  reversibly, with more than 94% of  $\text{CO}_2$  capacity recovered at room temperature. That translates to a  $\text{CO}_2$  capacity of 3.52 mmol/g after regeneration compared to an initial capacity of 3.74 mmol/g, which was obtained for a dry  $\text{CO}_2/\text{N}_2$  (15 : 85) mixture under ambient conditions<sup>15</sup>.

In order to research the regeneration conditions as well as the influence of flue gas contaminants, a particularly promising MOFs, chromium(III) terephthalate MIL-101(Cr), was selected as the focal point of this study. MIL-101(Cr) is an exceptionally porous material in the MOFs family that harbors active metal sites of unsaturated Cr(III) capable of capturing  $\text{CO}_2$  by Lewis acid-base interactions between the O of  $\text{CO}_2$  and Cr(III)<sup>18,19</sup>. It exhibits a  $\text{CO}_2$  adsorption capacity of approximately 40 mmol/g at 298 K and 5 MPa. MIL-101(Cr) also displays superb hydrothermal stability, especially compared to other MOFs<sup>20,21</sup>. The framework remains chemically and structurally intact even after immersion in boiling water and exposure at elevated temperatures to a number of organic solvents. In spite of the ample studies on the adsorption properties of MIL-101(Cr), including after modifications such as with various amines (tetraethylenepentamine<sup>22</sup>, pentaethylenehexamine<sup>23</sup>, polyethyleneimine<sup>24</sup>, eg.), more research is needed with respect to the nature of  $\text{CO}_2$  adsorption on MIL-101(Cr) in the realistic operating conditions of contaminant-filled, multi-component gas flows and multiple cycles of regeneration.

Herein, MIL-101(Cr) was synthesized by the hydrothermal method, and then characterized with various experimental methods including  $\text{N}_2$  adsorption/desorption isotherms, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and thermogravimetric analysis (TGA). The effects of adsorption temperature on MIL-101(Cr) were evaluated by analyzing breakthrough curves at different temperatures. A deactivation model was then applied to better understand the breakthrough curves. Next, we detailed the influence of three contaminants ( $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{SO}_2$ ) on  $\text{CO}_2$  adsorption of MIL-101(Cr). Lastly, this study sought to clarify the regeneration conditions under a mixed  $\text{CO}_2/\text{N}_2$  flow, in order to further ascertain the suitability of MIL-101(Cr) for  $\text{CO}_2$  separation and storage.

## Results

**Characteristics of MIL-101(Cr).** The adsorbent structure was analyzed by XRD to verify its identity. The diffraction peak patterns (Supplementary Figure S1) are consistent with the peak locations and relative intensities reported for MIL-101(Cr)<sup>25,26</sup>, suggesting that the synthesized product exhibits the MIL-101(Cr) structure.

The nitrogen adsorption isotherm and total pore volume of the dehydrated MIL-101(Cr) are shown in Supplementary Figure S2. The specific surface area of MIL-101(Cr), calculated by the BET and the Langmuir methods, is about 3314 and 4842  $\text{m}^2/\text{g}$ , respectively. These values are close to the reported values for MIL-101(Cr)<sup>25</sup>. The total pore volume of MIL-101(Cr) is estimated to be 1.68  $\text{cm}^3/\text{g}$  at a relative pressure of  $P/P_0 = 0.99$ . The pore diameter distribution

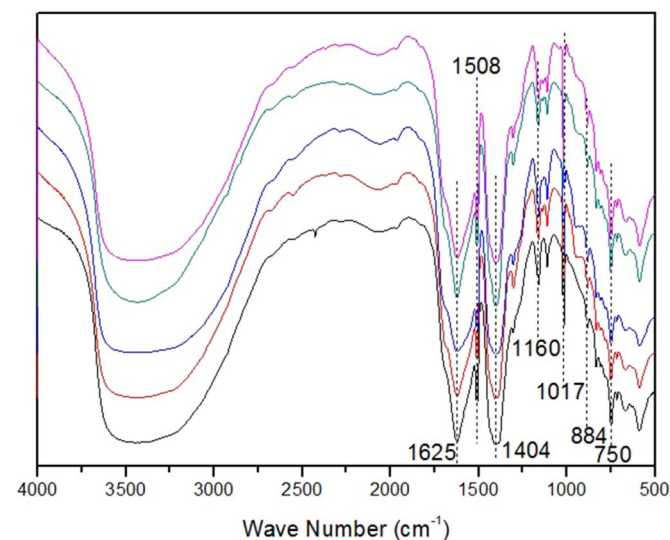
of MIL-101(Cr) confirms two domains of pore sizes (i.e., 18 and 23 Å), which is similar to those estimated from the crystal structure<sup>25</sup>.

TGA and DSC were employed to analyze the MIL-101(Cr) sample (Supplementary Figure S3). Exhibited are three distinct weight loss stages. The first stage, in the range from 303 to 423 K, corresponds to the loss of guest water molecules in the large cages (internal diameter of 34 Å)<sup>26</sup>. The second weight loss step (423–573 K) is also due to the loss of guest water molecules, but in the middle-sized cages (internal diameter of 29 Å)<sup>26</sup>. The third weight loss stage (>573 K) may result from the elimination of OH/F groups, leading to the decomposition of the frameworks<sup>25</sup>.

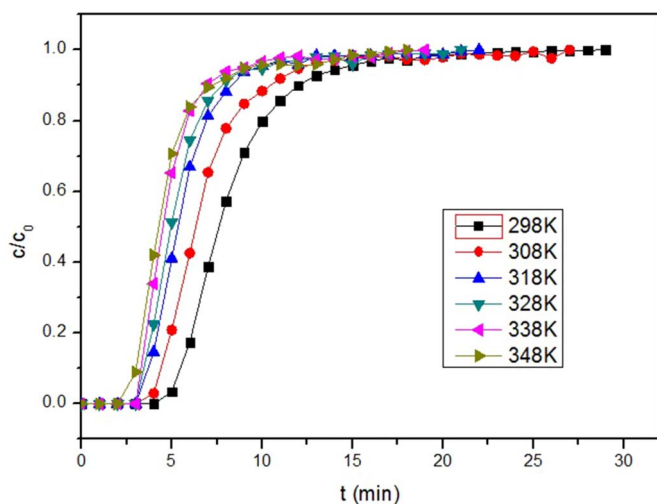
FT-IR characterization was conducted to detect the identity of the MIL-101(Cr) functional groups and their status after being exposed to contaminant-containing flows. The patterns of FT-IR are shown in Figure 1. For MIL-101(Cr), the band at 1625  $\text{cm}^{-1}$  indicates the presence of adsorbed water. The bands at 1404  $\text{cm}^{-1}$  correspond to the symmetric (O–C–O) vibrations, implying the presence of dicarboxylate within the MIL-101(Cr) framework<sup>27,28</sup>. The other bands between 600 and 1600  $\text{cm}^{-1}$  are attributed to benzene, including the stretching vibration (C=C) at 1508  $\text{cm}^{-1}$  and deformation vibration (C–H) at 1160, 1017, 884, and 750  $\text{cm}^{-1}$ . These results confirm that the MIL-101(Cr) framework did not transform after  $\text{CO}_2$  adsorption under contaminant-containing  $\text{CO}_2/\text{N}_2$  flows.

**Adsorption behavior. Effects of temperature.** The effects of adsorption temperature on MIL-101(Cr) were evaluated by analyzing breakthrough curves at different temperatures, as shown in Figure 2. The breakthrough time was found to decrease with increasing temperature. The adsorption capacity of MIL-101(Cr) at various temperatures is given in Figure 3. The adsorption capacity of MIL-101(Cr) decreases with increasing temperature from 0.495 mmol/g at 298 K to 0.279 mmol/g at 348 K. Capacity decreases sharply from 298 K to 318 K but more gradually from 318 K to 348 K. This adsorption behavior is typical of physical adsorption, which was verified by FT-IR. Note that after  $\text{CO}_2$  adsorption there were no obvious shifts in the locations of the bands. The discrepancy between the two  $\text{CO}_2$  capacities for MIL-101(Cr) given in Table 1 can be explained by the lower gas flow rate employed in this work.

To better understand the effect of temperature on the breakthrough curves, a deactivation model with two rate constants was selected to simulate the experimental data. The application of the deactivation model requires the following basic assumptions: 1) an



**Figure 1 | FT-IR spectra of MIL-101(Cr) before and after gas adsorption.** From bottom to top: MIL-101(Cr), MIL-101(Cr)- $\text{CO}_2$ , MIL-101(Cr)- $\text{H}_2\text{O}$ , MIL-101(Cr)- $\text{NO}$ , and MIL-101(Cr)- $\text{SO}_2$ .



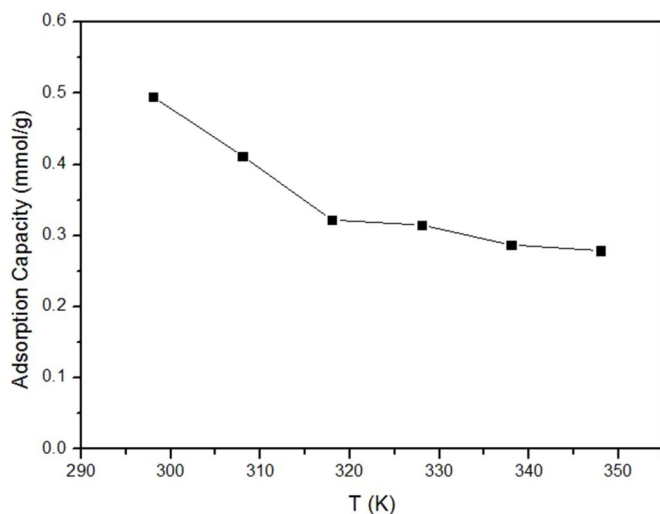
**Figure 2** | Breakthrough curves of 10 vol% CO<sub>2</sub> adsorption on MIL-101(Cr) at different temperatures.

isothermal absorber; 2) pseudo-steady-state; 3) negligible axial dispersion in the fixed-bed column; and 4) negligible mass-transfer resistances. The initial adsorption rate constant (mL/min·g), parameter  $a$ , and the deactivation rate constant (min<sup>-1</sup>), parameter  $b$ , were calculated by equation (1)<sup>29</sup>.

$$\frac{c}{c_0} = \exp\left(\frac{1 - \exp\left(\frac{aW}{Q}(1 - \exp(-bt))\right)}{1 - \exp(-bt)} \exp(-bt)\right) \quad (1)$$

where  $W$  is the mass of adsorbent (g), and  $Q$  is the gas flow rate (cm<sup>3</sup>/min). In this model, the effects of the overall factors on the diminishing rate of CO<sub>2</sub> capture are reflected in terms of the deactivation rate.

The increase in the initial adsorption and deactivation rate constants  $a$  and  $b$  with increasing temperature (Table 2) indicates that the adsorption and desorption processes of MIL-101(Cr) were enhanced. The shift in breakthrough curves toward the left can be contributed to the stronger desorption than adsorption process, where the growth rate of  $b$  is greater than that of  $a$ . (Supplementary Figure S4).



**Figure 3** | The adsorption capacity of MIL-101(Cr) at various temperatures.

**Table 1** | Dynamic CO<sub>2</sub> Adsorption Capacity of Sorbents at 0.1 atm

Sorbent	Temperature, T (K)	Capacity (mmol/g)	Ref
AC	298	0.57	32
ZSM-5	313	0.32	33
MIL-101(Cr)	303	0.31	34
MIL-101(Cr)	298	0.49	This work

**Effects of H<sub>2</sub>O, NO, and SO<sub>2</sub>.** The importance of testing the impact of humidity lies in ascertaining the stability of the framework structure and retention of adsorption capacity after exposure to water in gas flows. Figure 4(a) depicts the relationship between adsorption capacity and relative humidity (RH). Results show that adsorption capacity increases slightly to 0.509 mmol/g at 10% RH, but decreases from 10% RH to 100% RH. The increased CO<sub>2</sub> capacity may be attributed to electrostatic interactions between water bound to Cr<sup>3+</sup> sites and the quadrupole moment of CO<sub>2</sub><sup>30</sup>. The slightly decreased CO<sub>2</sub> capacity above 10% RH is due to the competitive adsorption of water and CO<sub>2</sub>. Unlike other MOFs such as HKUST-1 that lost about 25% of its adsorption capacity after exposure to a 30% RH gas flow or Mg<sub>2</sub>(dobdc) that experienced a 84% decrease in capacity, MIL-101(Cr) performed much better in humidified environments<sup>16,30</sup>.

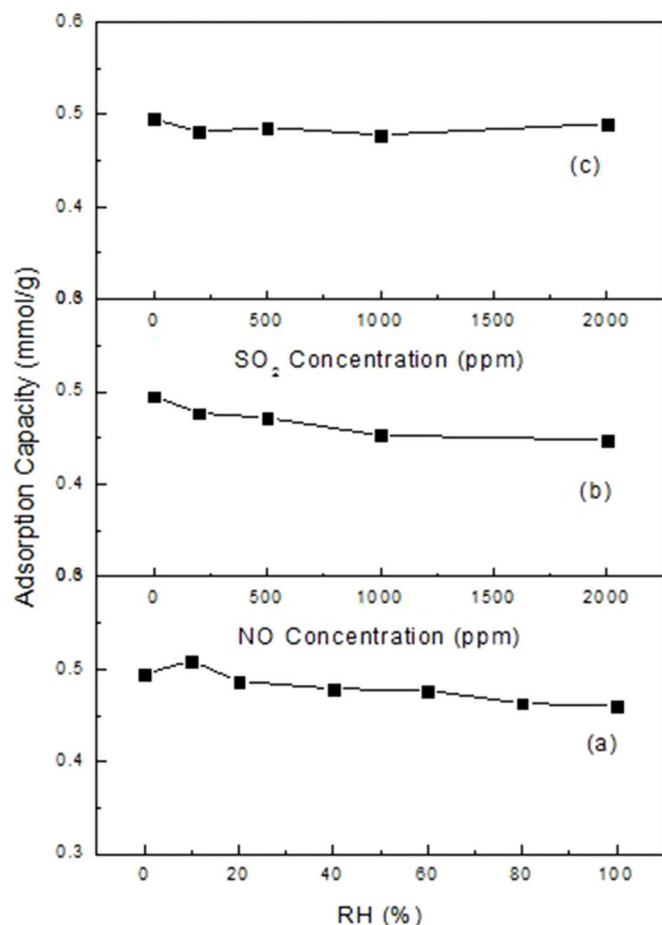
Besides the gases H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> that constitute 95% or more of typical flue gas, the more minor components like SO<sub>2</sub> and NO can play a major role in affecting adsorption processes<sup>1</sup>. The effect of NO on adsorption capacity is shown in Figure 4(b). Capacity follows a gradually declining trend when the concentration of NO rises from 0 to 2000 ppm. The adsorption stability of MIL-101(Cr) in the presence of SO<sub>2</sub> is illustrated in Figure 4(c). Results show that adsorption capacity changes very little when the concentration of SO<sub>2</sub> rises from 0 to 2000 ppm. At SO<sub>2</sub> concentrations of 0, 200, 500, 1000 and 2000 ppm, MIL-101(Cr) adsorption capacities are 0.495, 0.481, 0.486, 0.478 and 0.49 mmol/g.

The experimental results for the impact of SO<sub>2</sub> and NO on MIL-101 are supported by the results of a simulation study. However, the influence of H<sub>2</sub>O determined here differs from the conclusion of that study, where the models predicted H<sub>2</sub>O would completely occupy the coordinatively unsaturated “open metal” sites<sup>17</sup>. A possible explanation for the relatively small effect of trace contaminants on CO<sub>2</sub> adsorption may be as follows. Gas adsorption onto MIL-101(Cr) is a physical adsorption process; thus MIL-101(Cr) lacks the reactive functional groups to chemically adsorb the flue gas contaminants. Secondly, because concentrations of contaminants are always significantly less than that of CO<sub>2</sub> in flue gas, trace gases that do adsorb onto the framework will be largely substituted by the much higher-concentrated CO<sub>2</sub>.

**Desorption of CO<sub>2</sub>.** The results of the regeneration experiment are shown in Figure 5. For both TSA-N<sub>2</sub>-stripping and VTSA regeneration methods, desorption efficiency increases with the increasing temperature. Desorption attains 100% efficiency when temperature reaches 328 K for TSA-N<sub>2</sub>-stripping and 348 K at 20 KPa for VTSA. Full regeneration temperatures of different MOFs are presented in Table 3. The milder desorption temperature, corresponding to the

**Table 2** | Parameters of the Deactivation Model for CO<sub>2</sub> Adsorption on MIL-101(Cr) at Different Temperatures

Temperature (K)	$a$ (mL/min·g)	$b$ (min <sup>-1</sup> )	R <sup>2</sup>
298	48.2425	0.5361	0.9974
318	48.5590	0.7777	0.9976
338	52.1053	0.9834	0.9948



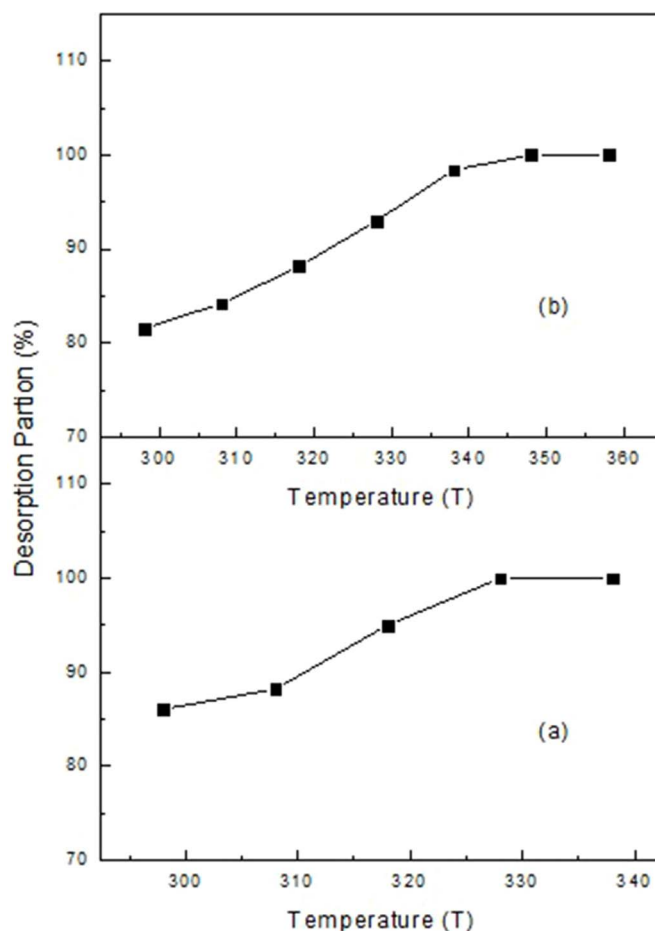
**Figure 4** | Effects of (a) moisture, (b) NO, and (c) SO<sub>2</sub> on 10 vol% CO<sub>2</sub> adsorption on MIL-101(Cr) at 298 K.

low enthalpy of CO<sub>2</sub> adsorption of MIL-101(Cr)<sup>16</sup>, suggests that the regenerative heat can come from the waste heat of the power plant, thus enhance the economic feasibility of the process.

**Cyclic adsorption/regeneration behavior of MIL-101(Cr).** Durable cyclic adsorption/regeneration behavior of sorbents is essential for long-term operation. Figure 6 depicts the CO<sub>2</sub> adsorption of MIL-101(Cr) during repetitive cycles (5 cycles) in the presence of moisture (RH 10%), SO<sub>2</sub> (100 ppm), and NO (100 ppm) at 298 K, with regenerations under flowing N<sub>2</sub> at a temperature of 328 K and pressure of 20 KPa at 348 K for 10 min. The cyclical data reveal that the adsorption performance of MIL-101(Cr) is fairly stable, with <5% drop in CO<sub>2</sub> adsorption capacity after 5 adsorption/regeneration cycles.

## Discussion

This study revealed that the CO<sub>2</sub> adsorption capacity of MIL-101(Cr) was able to maintain a high level of performance in trace gas-contaminated environments as well as after multiple cycles of adsorption and mild-condition regeneration. The addition of H<sub>2</sub>O, SO<sub>2</sub>, and NO to a 10 vol% CO<sub>2</sub>/N<sub>2</sub> feed flow was found to have only a minor effect on adsorption capacity. Furthermore, complete regeneration was observed at 328K after 10 min for TSA-N<sub>2</sub>-stripping and at 348 K and 20 KPa for VTSA. At the above temperatures and under feed flow conditions of 10 vol% CO<sub>2</sub>, 100 ppm SO<sub>2</sub>, 100 ppm NO, and 10% RH, MIL-101(Cr) preserved greater than 95% of its adsorption capacity after 5 cycles of adsorption/desorption. The deactivation model applied to express CO<sub>2</sub> uptake fit well with the breakthrough curves under various temperatures. The findings of this study



**Figure 5** | Results of the regeneration experiment. (a) TSA-N<sub>2</sub>-stripping regeneration, a nitrogen flow of 50 cm<sup>3</sup>/min for 10 min. (b) VTSA regeneration, a pressure of 20 KPa for 10 min.

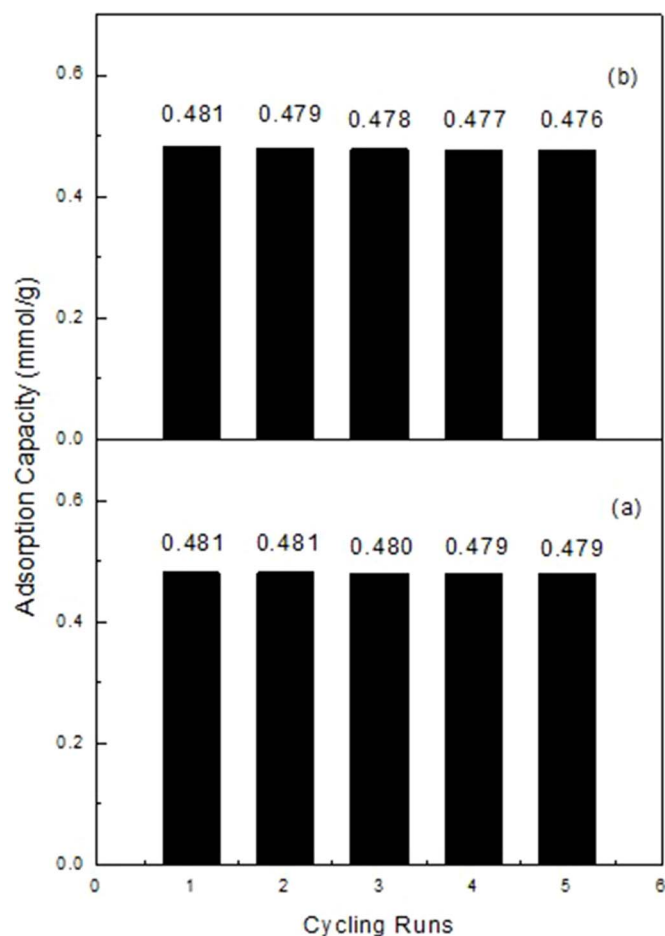
provide evidence for MIL-101(Cr)'s resistance to gaseous contaminants and its viability as an easily-regenerated material in gas adsorption processes.

## Methods

**Adsorbent preparation.** MIL-101(Cr), the highly crystallized green powder of chromium terephthalate, was synthesized according to the method described in the literature<sup>25</sup>. Briefly, 8.0 g of chromium nitrate nonahydrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, ≥99.0%; Sinopharm Chemical Reagent Co., Ltd.), 3.28 g of terephthalic acid (HOOC-C<sub>6</sub>H<sub>4</sub>-COOH, ≥99.0%; Sinopharm Chemical Reagent Co., Ltd.), 250 μL hydrofluoric acid (HF, ≥40.0%; Sinopharm Chemical Reagent Co., Ltd.) and 140 mL of ultrapure water were transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, heated up to 220°C for 8 h, and then slowly cooled to room temperature. The purification of MIL-101(Cr) was conducted following a previously reported method<sup>31</sup>. The green suspension of MIL-101(Cr) was filtered by using a stainless steel meshwork (with a diameter of 0.061 mm) to remove the re-crystallized needle-shaped, colorless terephthalic acid, which retained on the meshwork while the

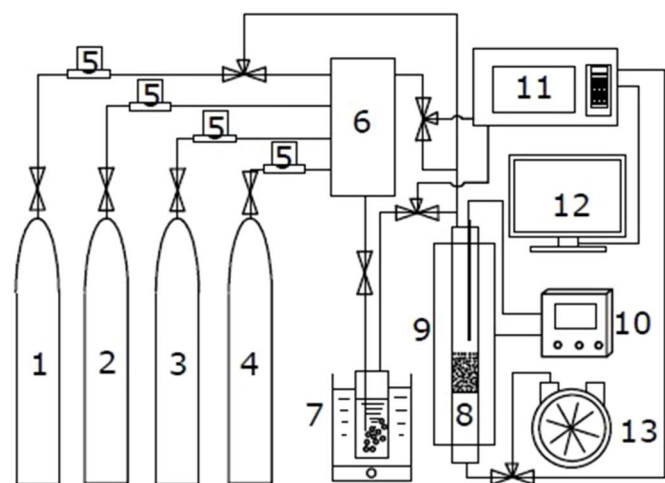
**Table 3** | The Full Regeneration Temperature of Purge Flow with Different MOFs

Material	Full regeneration temperature of purge flow (K)	Ref
Mg-MOF-74	353	35
Amino-MIL-53	432	36
Co-MOF-74	373	37
mmen-2	393	38
Mg-MOF-74(S)	323	39
MIL-101(Cr)	328	This work



**Figure 6** | Cycling adsorption/regeneration runs of MIL-101(Cr) (adsorption at 298 K; CO<sub>2</sub>, 10 vol%; SO<sub>2</sub>, 100 ppm; NO, 100 ppm; RH, 10%; gas flow rate, 50 cm<sup>3</sup>/min; (a) regeneration at 328 K; N<sub>2</sub> flow rate, 50 cm<sup>3</sup>/min; (b) regeneration at 348 K; pressure at 20 KPa).

MIL-101(Cr) suspension passed through it. The filtrated MIL-101(Cr) suspension was subsequently centrifuged at 8000 rpm (for 15 min to collect the precipitates of MIL-101(Cr)) and 3500 rpm twice (for 10 min to collect the suspension of



**Figure 7** | Schematic for the experimental system. 1) Nitrogen; 2) Carbon dioxide; 3) Sulfur dioxide; 4) Nitric oxide; 5) Mass flow meters; 6) Mixing tank; 7) Saturator; 8) Adsorbent; 9) Tubular furnace; 10) Temperature controller; 11) Gas chromatograph; 12) Data recording system; 13) Vacuum pump.

MIL-101(Cr)). Lastly, the suspension of MIL-101(Cr) was washed several times with ultrapure water and dried at 378 K for 24 h in a hot air oven for the usage of adsorption experiments.

**Characterization of synthesized MIL-101(Cr).** The surface area and pore volume were measured with a static volume adsorption system (Model-ASAP 2020, Micromeritics Inc., USA) by obtaining the N<sub>2</sub> adsorption/desorption isotherms at 77.4 K. Prior to the adsorption measurement, the samples were out-gassed at 473 K for 24 h. The N<sub>2</sub> adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K) and then used to determine the surface areas with the Brunauer–Emmett–Teller equation. The pore size distributions were calculated by the Barrett–Joyner–Halenda method. The total pore volume was calculated from the amount of adsorbed N<sub>2</sub> at P/P<sub>0</sub> = 0.99. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was carried out with a thermogravimetric analyzer (SDT Q600, TA Instruments, Inc., New Castle, DE) under a dynamic N<sub>2</sub> atmosphere from 303 to 873 K with a heating rate of 10 K/min. The crystal phase and the surface functional groups of sorbents were characterized by a powder X-ray diffractometer (XRD, Rigaku D/Max 2550/PC, Rigaku Co., Ltd., Japan) using Cu K $\alpha$  radiation (40 kV, 30 mA) and by a Fourier transform infrared spectrometer (FT-IR, NICOLET 6700, Thermal Scientific, USA), respectively.

**Adsorption/desorption experiments.** The experiment flowchart is shown in Figure 7. The procedure for the CO<sub>2</sub> adsorption experiment, similar to a previously reported method, is given in detail in the Supplementary Information. In this work, the adsorbent MIL-101(Cr) was regenerated using TSA–N<sub>2</sub>-stripping and VTSA. The mass of the adsorbent measured before adsorption. As the adsorption process reached equilibrium, the mass of the adsorbent was quickly measured and the influent gas valve closed. The adsorption column was then heated to the desired temperature. For steam stripping regeneration, the inlet of the adsorption column was switched to a nitrogen flow of 50 cm<sup>3</sup>/min. For VTSA regeneration, the outlet of the adsorption column was connected to a vacuum pump system, which can be operated at a given pressure. The mass of adsorbent was measured after 10 min. The adsorbents were completely regenerated when the mass of regenerated adsorbent equaled the mass of the initial sample of pure adsorbent. The total mass loss equals the amount of desorbed CO<sub>2</sub>.

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## Author contributions

Y.S., Y.H. and Q.L. designed the project; Q.L. carried out the experiment with help from L.N., S.Z. and M.T.; Q.L. and L.N. wrote the manuscript. All authors discussed the results and commented on the manuscript.

## Additional information

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