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Efficient CO_2 Removal for Ultra-Pure CO Production by Two Hybrid Ultramicroporous Materials

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Abstract: Removal of CO_2 from CO gas mixtures is a necessary but challenging step during production of ultra-pure CO as processed from either steam reforming of hydrocarbons or CO_2 reduction. In this contribution, two hybrid ultramicroporous materials (HUMs), **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i**, which are known to exhibit strong affinity for CO_2, were examined with respect to their performance for this separation. The single-gas CO sorption isotherms of these HUMs were measured for the first time and are indicative of weak affinity for CO and benchmark CO_2/CO selectivity (>4000 for **SIFSIX-3-Ni**). This prompted us to conduct dynamic breakthrough experiments and compare performance with other porous materials. Ultra-pure CO (99.99%) was thereby obtained from CO gas mixtures containing both trace (1%) and bulk (50%) levels of CO_2 in a one-step physisorption-based separation process.

Carbon monoxide, CO, is a valuable reaction intermediate that is utilised for the synthesis of industrially important chemicals such as oxo-alcohols, phosgene, acetic acid and various liquid hydrocarbons.[1] Moreover, high purity CO (i.e. >99.99%) is a certified reference material for calibration service systems, electronics, and semiconductor devices.[2] Currently, CO is produced at industrial scale via steam reforming of a carbon-containing feedstock (e.g. CH_4) and the effluent gas from this process contains CO_2 as an impurity.[3] An alternative to this traditional CO production process, the conversion of CO_2 into valuable carbon-containing products using renewable energy (e.g. solar energy, wind power, geothermal heat), has been proposed as a win-win solution for addressing future energy demands and anthropogenic climate change.[4] The first stage of this process involves reduction of CO_2 into CO in high yield with fast reaction kinetics and has been a subject of interest in the last decade.[5] Utilizing CO_2 resources is also an aspect of NASA's MARS development program.[6] However, all of these processes require removal of CO_2 impurities, including trace level impurities, from CO gas mixtures. The following three methods have thus far been employed for harvesting pure CO from such processes: cryogenic distillation; pressure/vacuum swing adsorption (P/VSA); membrane separation.[7] For example, ultra-pure CO is currently produced by multiple separation plates in cryogenic distillation, two or three membrane separation steps or liquid amine CO_2 capture in a P/VSA process. That there is a significant energy penalty associated with each of these processes reduces the energy efficiency of CO production. An alternative to these traditional separation processes, physisorption, offers promise to reduce the energy footprint by virtue of how facile physisorbents can be recovered after separation. In this context, metal organic materials (MOMs),[8] also known as porous coordination polymers (PCPs)[9] or metal-organic frameworks (MOFs),[10] have emerged as attractive candidates for physisorptive separations because they contain pore structures that can be optimized for a particular application. Indeed, exquisite control over pore size and pore chemistry can be attained if the MOM in question is amenable to crystal-engineering,[11] an aspect that cannot be readily controlled in traditional porous materials such as zeolites, silica, and activated carbons. MOMs, activated carbon and zeolites have been investigated for separating CO_2 from CO but they generally suffer from low adsorption CO_2/CO selectivity (<200).[12] It is therefore unsurprising that there has not to our knowledge been a report which experimentally demonstrates that ultra-pure (>99.99%) CO can be obtained in a one-step physisorption process. We address this matter herein through a studies conducted upon two members of a subclass of MOMs known as hybrid ultramicroporous materials (HUMs).[13]

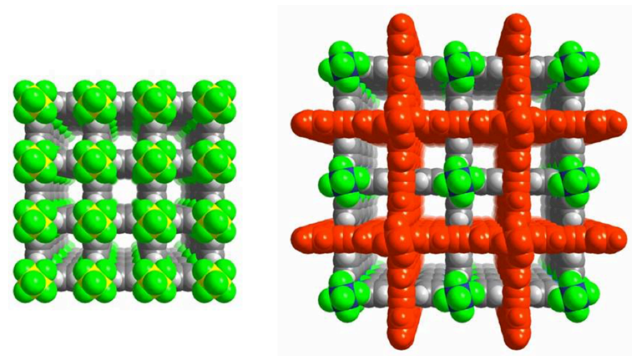

Figure 1. Two hybrid ultramicroporous materials (left: **SIFSIX-3-Ni**; right: **TIFSIX-2-Cu-i**) used in this report, and the second net of two-fold interpenetrated **TIFSIX-2-Cu-i** is highlighted in red. Color code: carbon (grey), hydrogen (white), nickel (purple), nitrogen (blue), silicon (yellow), fluorine (green), copper (maroon) and titanium (navy).

That a wide range of CO_2 concentrations (<1% to >50% CO_2) can exist in CO gas mixtures means that a physisorbent based purification would need to produce high purity CO gas (99.99%) across a range of gas mixture compositions. Herein, we study both trace (1%) and bulk (50%) CO_2 removal from CO using two HUMs **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i**. HUMs are known to exhibit

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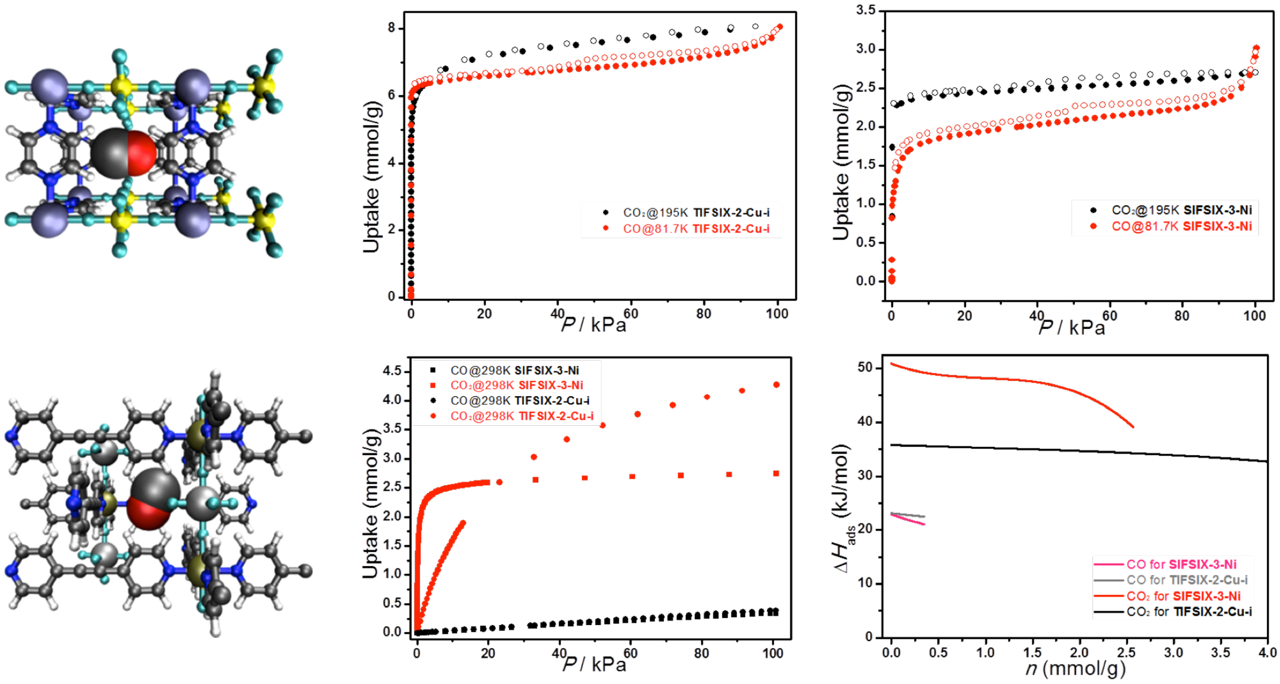

Figure 2. CO binding sites, sorption data and isosteric heat of CO and CO_2 adsorption for **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i**. The location of CO molecules is modeled by density functional theory calculations based upon the crystallographically determined structure of the framework.

benchmark selectivity for CO_2 capture[14] as well as a number of industrially relevant gas mixtures including C_2H_2/C_2H_4[15] and C_2H_2/CO_2.[16] HUMs are highly selective towards CO_2 thanks to a combination of ultramicropores (<0.7 nm) that tightly fit CO_2 and strong electrostatics from inorganic anions such as $Cr_2O_7^{2-}$,[13] SiF_6^{2-},[17] and MoO_4^{2-}[18] that line the pore surface. The two HUMs studied herein belong to the **M'FSIX-L-M** platform (**M'FSIX** = SiF_6^{2-} or TiF_6^{2-}; L = a dipyridyl organic linker; M = divalent transition metal anion), adopt primitive cubic, pcu, topology and exhibit one-dimensional pore channels. In the case of **TIFSIX-2-Cu-i**, i denotes that there is interpenetration of the pcu networks (Figure 1). The rationale for choosing these two HUMs lies in their strong CO_2 interactions, good thermal stability and hydrolytic stability or recyclability.[19] However, their CO sorption performance was unknown until this study.

SIFSIX-3-Ni and **TIFSIX-2-Cu-i** were prepared according to published procedures.[14c,16] Direct-mixing was employed to synthesize the samples used for pure gas sorption and gas mixture breakthrough studies (for details, see experimental section). Experimental powder X-ray diffraction (PXRD) patterns were used to validate bulk purity through comparison with calculated patterns from single-crystal data (Figure S1, supporting information). Porosity was established from 195 K CO_2 sorption experiments (Figure 2) which afforded surface area values for **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i** of 229 and 590 m^2/g, respectively, from Brunauer-Emmett-Teller (BET) theory. These values are consistent with previous reports.[16,20] CO sorption experiments were first conducted at its boiling point of 81.7 K. Typical type-I isotherms were observed for both HUMs, indicating that CO diffuses into these two materials. CO uptakes at P/P_o = 0.95 for **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i** were observed to be 2.5 and 7.6 mmol/g, respectively, which compares well with the respective CO_2 uptakes of 2.7 and 8.0 mmol/g. The higher CO_2 vs CO uptake at the lowest partial pressures at 81.7 K in **SIFSIX-3-Ni** before saturation can be attributed to the larger kinetic diameter of CO (3.76 Å) vs. CO_2 (3.3 Å), which in turn might affect the kinetics of diffusion in the pore channels (3.8 Å) of **SIFSIX-3-Ni**.

CO_2 and CO sorption isotherms were also measured at 273 and 298 K (Figure 2, Figure S2 and S3, supporting information). Interestingly, CO shows much lower uptake (0.34 and 0.38 mmol/g) vs CO_2 (2.74 and 4.27 mmol/g) at 100 kPa and 298 K for **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i**, respectively. The difference in CO_2 and CO uptake at 1 kPa, is larger again, (2.0 vs. 0.004 mmol/g for **SIFSIX-3-Ni** and 0.3 vs. 0.005 mmol/g for **TIFSIX-2-Cu-i**). Notably, the CO_2 uptake of 2.0 mmol/g at 298 K and 1 kPa in **SIFSIX-3-Ni** is above that of materials previously studied for this separation, while the CO_2 uptake of 3.5 mmol/g at 298 K and 50 kPa in **TIFSIX-2-Cu-i** is only below that of **Zeolite 13X** (Table 1). We have attributed the strong affinity of these HUMs towards CO_2 to the tight fit, strong electrostatics and induced polarisation.[14] The situation with respect to CO is very different, presumably because of its larger kinetic diameter (3.76 Å) and smaller quadrupole moment (2.5 X 10^{26} esu cm^2) vs CO_2 (3.3 Å and 4.3 X 10^{26} esu cm^2).[21] To evaluate the energetics of CO_2 and CO interactions with these two HUMs, sorption data at 273 and 298 K were fitted using the virial equation, and the respective isosteric heats of adsorption (Q_{st}) were calculated using the Clausius–Clapeyron equation (Figure S4 and S5, supporting information). Figure 2 reveals that CO (22.9 and 23.1 kJ/mol) exhibits much lower Q_{st} at low loading in **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i**, respectively, than CO_2 (50.9 and 35.8 kJ/mol). This observation is supported by molecular simulations of the corresponding binding sites and interaction energies (Table S1). The simulation experiments reveal that the primary binding site for CO involves multiple $C^{\delta+}\cdots F^{\delta-}$ interactions between CO molecules and the inorganic pillars (SiF_6^{2-} and TiF_6^{2-}, Figure 2). In **SIFSIX-3-Ni**, CO interacts simultaneously with electronegative F atoms from four individual inorganic pillars whereas in **TIFSIX-2-Cu-i** CO exhibits close contact with only one inorganic pillar. For direct comparison, CO_2 was subjected to the same calculations. The preferred binding sites for CO are similar to

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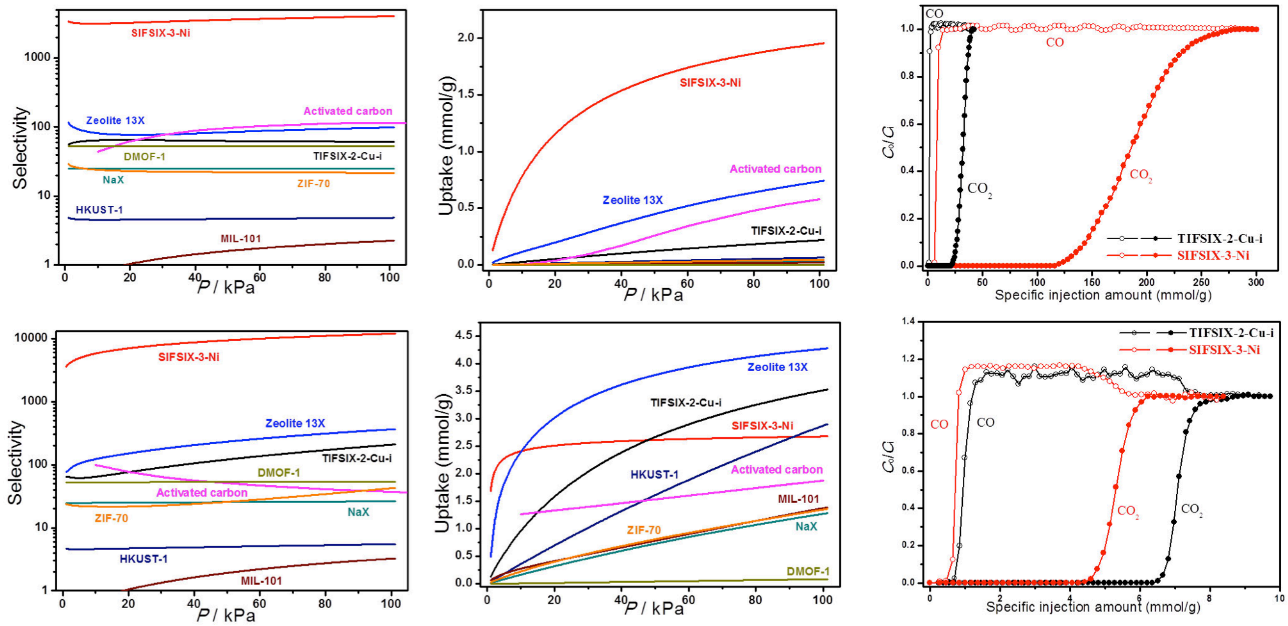

Figure 3. Comparison of **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i** with other porous materials for CO_2/CO separation (top: 1/99; bottom: 50/50): (left) CO_2/CO selectivity; (middle) calculated CO_2 uptake for binary mixture at ambient temperature vs. total pressure (0-1 bar) of gas mixture by IAST calculations; (right) experimental breakthrough curves in a fixed bed under flow (5 cm^3/min for 1/99; 1 cm^3/min for 50/50) of a CO_2/CO gas mixture. CO_2 was not detectable in the effluent gas before breakthrough according to a chromatographic analyzer with a detection limit of <100 ppm.

those for CO_2 but the associated energy is much lower than CO_2, presumably because of lower positive charge on the C atom of CO (Tables S2 and S3). We also note that the calculated C...F distances are longer for CO than CO_2. Specifically, the C...F distances in **SIFSIX-3-Ni** are 3.28 vs 3.23Å for CO and CO_2, respectively, whereas in **TIFSIX-2-Cu-i** they are 2.74 vs 2.59 Å (Figure S18-S21, supporting information). This pore chemistry differs from other high-performing CO_2 capture physisorbents such as metal organic frameworks (e.g. **MOF-74** and **HKUST-1**)[22] and zeolites, the performance of which is related to open metal sites that afford high Q_{st} values for CO_2. However, open metal sites can also exhibit high Q_{st} towards CO from strong M−CO interactions and therefore tend not to result in strong selectivity for CO_2 over CO. Such CO interactions can be attenuated by substitution of the metal ions where possible.[23]

There are two main parameters used to evaluate the performance of a porous material for a given separation at a specific set of conditions: selectivity and capacity (i.e. uptake).[24] Selectivity tends to be more important than uptake for separations, especially trace separations, as pointed out in a recent publication.[25] After fitting single-gas isotherms at 298 K into the dual-site Langmuir-Freundlich equation, the values for CO_2/CO selectivity at 298 K of **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i** were calculated using Ideal Adsorbed Solution Theory (IAST).[26] Fitting details for all the materials listed in Table 1 are presented in Figures S6-S17 and discussed in supporting information. In order to calculate the CO_2/CO selectivity of the two HUMs for trace and bulk purification, two ratios (1/99 and 50/50) of CO_2/CO were used for selectivity calculations at 1 bar total pressure and 298 K. The results indicate that the CO_2/CO selectivity of **SIFSIX-3-Ni** (12000 for 50/50 and 4044 for 1/99) far exceeds all previously reported sorbents by at least one order of magnitude (Figure 3). Even considering the whole pressure range, CO_2/CO selectivity for both gas mixtures is always in excess of 3000 for **SIFSIX-3-Ni**. The nature of the extremely strong interactions between CO_2 and materials exhibited by the **SIFSIX-3-M** platform has been addressed in a number of previous reports.[14] **TIFSIX-2-Cu-i** also exhibits exceptional gas separation performance and only **SIFSIX-3-Ni** and **Zeolite 13X** exhibit higher CO_2/CO selectivity for a 50/50 gas mixture. Conversely, MOFs with open metal sites (i.e. **HKUST-1** and **MIL-101**) exhibit low selectivity (<10) although moderate selectivity has been reported for **DMOF-1**, **ZIF-70**, **activated carbon** and **NaX**.[12] **SIFSIX-3-Ni** not only exhibits the highest CO_2/CO selectivity for a 1/99 gas mixture at 1 bar, its CO_2 uptake of 1.96 mmol/g at 1 kPa is exceptional vs that of the previous benchmark materials examined in this study (<1 mmol/g). **TIFSIX-2-Cu-i** was found to exhibit the second highest CO_2 uptake (3.5 mmol/g) from a 50/50 gas mixture at 1 bar behind **Zeolite 13X** (4.2 mmol/g). The calculated uptakes from IAST calculations are consistent with those of the single-gas isotherms summarized in Table 1. The higher CO_2/CO selectivity for **SIFSIX-3-Ni** compared to **TIFSIX-2-Cu-i** results from much lower Q_{st} for CO than CO_2 in **SIFSIX-3-Ni**. The tight fit for CO_2 results from strong interactions with four SiF_6^{2-} anions simultaneously (Figure S18). It should also be noted that, whereas **Zeolite 13X** exhibits exceptional CO_2 sorption performance, the presence of moisture in gas streams has a detrimental effect on its sorption performance. In addition, **Zeolite 13X** can require excessive heat (>250 °C) and energy to remove adsorbed water molecules and water vapour is present during CO purification.[14d,27]

To directly investigate CO_2 removal from CO by **TIFSIX-2-Cu-i** and **SIFSIX-3-Ni**, dynamic breakthrough experiments using gas mixtures containing 1% and 50% CO_2 in CO were conducted at 298 K. Samples were pre-heated at 50 °C in a flow of He gas for six hours to remove atmospheric impurities before being cooled to room temperature. Evolved gas components were continuously monitored using mass spectrometry (Scheme S1, supporting information). In the breakthrough experiment containing a 50/50 gas mixture with a total pressure of 1 bar, CO and CO_2 were initially co-adsorbed before adsorbed CO was replaced by CO_2. A CO outlet purity of >99.99% was calculated (Figure 3) from the ratio of the integrated

Table 1. Comparison of adsorption data and selectivity in HUMs vs other porous materials.

	SIFSIX-3-Ni	TIFSIX-2-Cu-i	Zeolite 13X[e]	NaX[f]	Activated Carbon[g]	DMOF-1	HKUST-1	MIL-101[h]	ZIF-70[i]
S_{BET}[a]	229	585	742	685	N.A	1863	1663	2674	1730
CO_2 uptake[b]	2.0/2.6	0.3/3.5	1.0/4.2	0.4/4.3	0.6/1.8	0.02/0.88	0.07/3.05	0.14/1.86	0.04/1.4
CO uptake[c]	0.2/0.34	0.2/0.39	0.6/0.95	0.65/1.1	0.16/0.44	0.01/0.03	0.72/1.31	0.73/0.88	0.12/0.22
Selectivity[d]	>4000	209/62	366/99	26/25	35/115	54/53	5/5	3.3/2.3	43/22
Reference	this work	this work	12a	12b	12c	12d	12e	12e	12f

[a] surface area (m^2/g) calculated from Brunauer-Emmett-Teller (BET) theory; [b] gravimetric CO_2 uptake (mmol/g) at 0.01/0.5 bar at 298 K unless noted specifically; [c] gravimetric CO uptake (mmol/g) at 0.5/1 bar at 298 K unless noted specifically; [d] CO_2/CO selectivity with ratio of 50:50 and 1:99 at 298 K and 1 bar of total gas pressure, calculated from IAST theory; [e] at 293 K; [f] at 303 K; [g] at 296 K; [h] at 295 K; [i] at 273 K. Uptake and selectivity for materials except for HUMs were determined from dual-site Langmuir-Freundlich equation after fitting the raw data extracted from corresponding references. More details are presented in supporting information.

area of the CO_2 and CO curves at given times before CO_2 breakthrough occurred. The breakthrough capacities of **SIFSIX-3-Ni** and **TIFSIX-2-Cu-i** are 2.65 and 3.55 mmol/g, respectively, values consistent with the CO_2 uptake of these HUMs (2.57 and 3.52 mmol/g) at a partial pressure of 50 kPa in single component isotherms and the relative surface areas of the two HUMs. For trace (1%) removal of CO_2 from CO, **SIFSIX-3-Ni** performs much better than **TIFSIX-2-Cu-i** in terms of working capacity. We attribute this to the significantly higher uptake of **SIFSIX-3-Ni** at 1 kPa vs that of **TIFSIX-2-Cu-i**.

In conclusion, ultra-pure CO can be generated by energy-efficient removal of trace (1%) and bulk (50%) CO_2 from CO gas mixtures in a one-step physisorption-based separation process by HUMs. The benchmark performance of the two HUMs studied herein, especially **SIFSIX-3-Ni**, can be attributed to new benchmark CO_2/CO selectivity of >4000 that is a consequence of very strong sorbent-sorbate interactions with CO_2 vs weak interactions with CO.

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Keywords: CO_2 capture • gas separation • CO production • trace CO_2 removal • hybrid ultramicroporous materials

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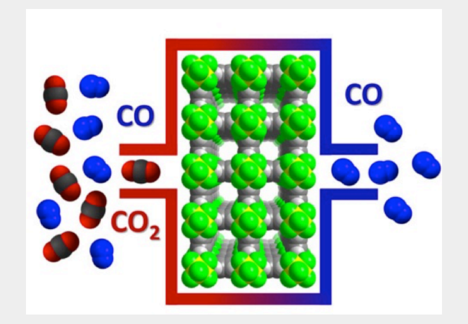
Layout 1:

COMMUNICATION

Benchmark CO_2/CO selectivity under ambient conditions has been observed in two hybrid ultramicroporous materials, thanks to much weaker interactions towards CO vs CO_2. Ultra-pure CO (>99.99%) can thereby be produced efficiently from gas mixtures containing CO_2 impurities (1% and 50%) in a one-step separation process using a fixed bed column of adsorbent.



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Efficient CO_2 Removal for Ultra-Pure CO Production by Two Hybrid Ultramicroporous Materials