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Authors	Zaworotko, Michael J.;Mukherjee, Soumya;Kumar, Naveen;Bezrukov, Andrey A.;Tan, Kui;Pham, Tony;Forrest, Katherine A.;Oyekan, Kolade;Qazvini, Omid T.;Madden, David G.;Space, Brian
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Autoren: Michael Zaworotko, Soumya Mukherjee, Naveen Kumar, Andrey A. Bezrukov, Kui Tan, Tony Pham, Katherine A. Forrest, Kolade Oyekan, Omid T. Qazvini, David G. Madden, and Brian Space

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Amino functionalised hybrid ultramicroporous materials that enable single-step ethylene purification from a ternary mixture

Soumya Mukherjee,^{†,*[a,b]} Naveen Kumar,^{†[a]} Andrey A. Bezrukov,^[a] Kui Tan,^[c] Tony Pham,^[d] Katherine A. Forrest,^[d] Kolade A. Oyekan,^[c] Omid T. Qazvini,^[e] David G. Madden,^[a] Brian Space,^[c,f] and Michael J. Zaworotko^{*[a]}

- [a] Dr. S. Mukherjee, N. Kumar, Dr. A. A. Bezrukov, Dr. D. G. Madden, Prof. M. J. Zaworotko
Bernal Institute, Department of Chemical Sciences, University of Limerick, Limerick V94 T9PX, Republic of Ireland. E-mail: xtal@ul.ie
- [b] Dr. S. Mukherjee
Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching b. München, Germany. E-mail: soumya.mukherjee@tum.de
- [c] Dr. K. Tan, K. A. Oyekan
Department of Materials Science & Engineering, University of Texas at Dallas, Richardson, Texas 75080, USA.
- [d] Dr. T. Pham, Dr. K. A. Forrest, Prof. B. Space
Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE205, Tampa, Florida 33620-5250, USA.
- [e] Dr. O. T. Qazvini
Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom.
- [f] Prof. B. Space
Department of Chemistry, North Carolina State University, USA.
S.M. and N.K. contributed equally.

Supporting information (SI) for this article is given via a link at the end of the document. Supplementary crystallographic data has been deposited at the Cambridge Crystallographic Data Centre as CCDC 2050185, <https://www.ccdc.cam.ac.uk/structures/>

Abstract: Pyrazine-linked hybrid ultramicroporous (pore size <7 Å) materials (HUMs) offer benchmark performance for trace carbon capture thanks to strong selectivity for CO₂ over small gas molecules, including light hydrocarbons. That the prototypal pyrazine-linked HUMs are amenable to crystal engineering has enabled second generation HUMs to supersede the performance of the parent HUM, **SIFSIX-3-Zn**, mainly through substitution of the metal and/or the inorganic pillar. Herein, we report that two isostructural aminopyrazine-linked HUMs, **MFSIX-17-Ni** (17 = aminopyrazine; M = Si, Ti), which we had anticipated would offer even stronger affinity for CO₂ than their pyrazine analogs, unexpectedly exhibit reduced CO₂ affinity but enhanced C₂H₂ affinity. **MFSIX-17-Ni** are consequently the first physisorbents that enable single-step production of polymer-grade (>99.95% for **SIFSIX-17-Ni**) ethylene from a ternary equimolar mixture of ethylene, acetylene and CO₂ thanks to coadsorption of the latter two gases. We attribute this performance to the very different binding sites in **MFSIX-17-Ni** versus **SIFSIX-3-Zn**.

Introduction

The chemical industry accounts for around 7% of World GDP with revenue of \$5.7 trillion/annum.^[1] Its energy footprint, which is driven by downstream purification of commodity chemicals, is even larger, representing ca. 15% of global energy consumption.^[2] Overall, separation/purification of commodity chemicals alone represents ca. 40% of the industrially consumed energy.^[3] Forecasts have indicated that by 2050 there will be a three-fold increase in demand for commodity chemicals, demanding more energy-efficient approaches to commodity purification.^[3] As the basic feedstock for the production of plastics, detergents and coatings, ethylene (C₂H₄) is the highest volume product of the global chemical industry.^[4] The production of C₂H₄ and propylene alone account for 0.3% of global energy.^[5] The energy-intensive state-of-the-art for production of polymer-grade (> 99.95% purity) C₂H₄ involves steam cracking of hydrocarbons.^[5-6] Alternatively, oxidative coupling of methane

(CH₄) results in gas mixtures that include acetylene (C₂H₂) and carbon dioxide (CO₂) in addition to C₂H₄.^[7] Production of polymer-grade C₂H₄ therefore involves removal of these two impurities from C₂H₄/C₂H₂/CO₂ ternary mixtures. Presently, C₂H₂ is removed *via* one of two processes: catalytic hydrogenation (using expensive noble-metal catalysts at high temperature/pressure); solvent extraction (causing solvent waste with the need for large operating units). CO₂ is also removed chemically, using caustic soda.^[5] Physisorbents offer potential to greatly reduce the energy footprint of separation processes.^[3, 8] Nevertheless, despite advances in gas purification from binary mixtures using physisorbents under ambient pressure and temperature,^[9] including C₂H₄,^[10] C₂H₄ purification from ternary C₂-CO₂ mixtures remains an unmet challenge.^[11] This is largely a consequence of the similar physicochemical properties (molecular sizes and boiling points, Scheme S1) of the three components^[11a, 12] and the absence of physisorbents that selectively exclude C₂H₄. One approach to address this challenge is the use of multiple ultramicroporous physisorbents using synergistic sorbent separation technology, SSST.^[13] Another approach would be to exploit a single sorbent^[14] that is highly selective for both CO₂ and C₂H₂ over C₂H₄ under ambient conditions, the first example of which is reported herein.

Metal-organic materials (MOMs),^[15] including metal-organic frameworks (MOFs)^[16] and hybrid ultramicroporous materials (HUMs),^[17] are attractive candidates for sorbent design since they are modular.^[18] HUMs, which can generally be described as 2D square lattice (**sql**) metal-organic networks pillared by inorganic anions (e.g. SiF₆²⁻, TiF₆²⁻, NbOF₅²⁻) with **pcu** topology (Figure 1a), can combine the right pore chemistry (strong electrostatics) and pore size (high density of tight binding sites). The resulting energetic 'sweet spots' have enabled HUMs to be the current selectivity benchmarks for several industrially relevant binary gas separations, including C₂H₂ over C₂H₄ (S_{AE})^[19] and CO₂ over N₂ (S_{CN}).^[20] Unfortunately, these benchmark HUMs are unsuited for ternary C₂-CO₂ separations because, whereas they are highly selective for one of the two impurities over C₂H₄, they are not

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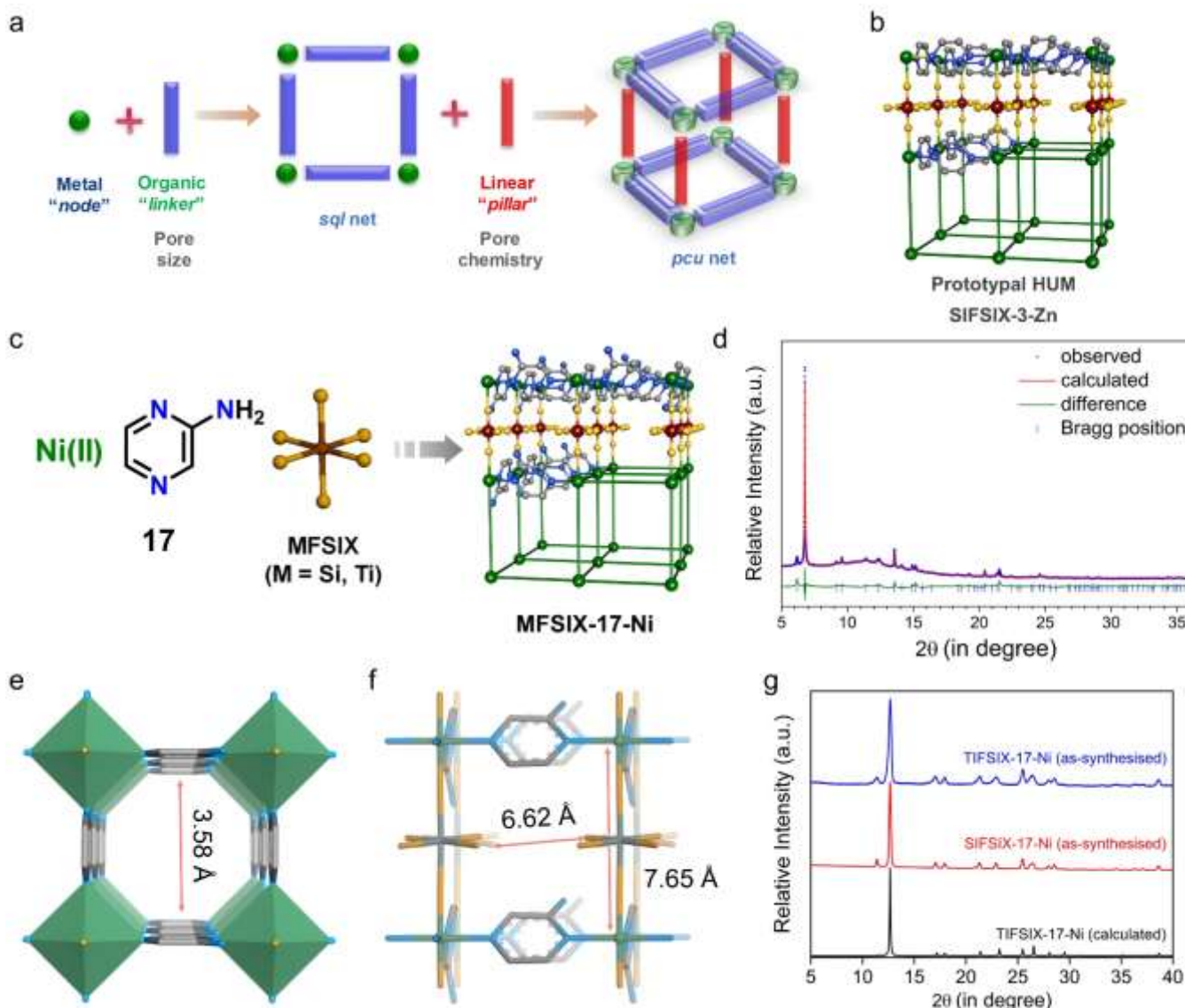


Figure 1. a) Schematic illustration of the modularity of pillared square grids that form **pcu** topology HUMs, enabling exquisite control of both pore size and pore chemistry; b) The prototypical pyrazine (pyz) linked HUM $[\text{Zn}(\text{pyz})_2(\text{SiF}_6)]_n$, **SIFSIX-3-Zn**, is formed from $\text{Zn}(\text{II})$ -pyz cationic **sqf** nets and inorganic SiF_6^{2-} (**SIFSIX**) pillars; c) Schematic illustration of the building blocks ($\text{Ni}(\text{II})$, pyz- NH_2 linker ligand (**17**), **SIFSIX**/**TIFSIX** inorganic pillars) and the **pcu** network topology of **MFSIX-17-Ni**; d) Rietveld refinement plot for desolvated **TIFSIX-17-Ni** (dynamic vacuum, 298 K), $R_{\text{wp}} = 4.69\%$. Powder X-ray diffraction, PXRD, data was collected using synchrotron radiation, $\lambda = 0.82455(2)$ Å; e) Cross-sectional channel view of the desolvated crystal structure of **TIFSIX-17-Ni** along the crystallographic *c* axis; 3.59×3.59 Å ultramicropores are formed; f) crystal structure of desolvated **TIFSIX-17-Ni** viewed along the *a*- and *b*-axes; $\text{Ni}(\text{II})$ - NH_2 -pyz **sqf** layers are pillared by TiF_6^{2-} anions; g) Comparison of as-synthesised PXRD patterns ($\text{CuK}\alpha$ radiation, $\lambda = 1.54056$ Å) of the **MFSIX-17-Ni** phases with the calculated pattern of **TIFSIX-17-Ni**. Colour codes: grey, C; blue, N; red, O; orange, F; green (polyhedra and sphere in Figures 1e and 1f respectively), Ni; greenish grey, Ti.

selective enough to address the other impurity. Herein, we report on the unexpected outcome of our study on the sorption properties of an amine functionalised variant of the **SIFSIX-3-Zn** (Figure 1b) family of HUMs,^[20a] **MFSIX-17-Ni** ($M = \text{Si}, \text{Ti}$; **17** = pyz- NH_2).

Results and Discussion

Solvothermal reaction of pyz- NH_2 with nickel hexafluorotitanate afforded the previously unreported HUM, $[\text{Ni}(\text{pyz-NH}_2)_2(\text{TiF}_6)]_n$ (pyz- NH_2 = 2-aminopyrazine), **TIFSIX-17-Ni** (Figures 1c, S1), as a dark green microcrystalline powder. **TIFSIX-17-Ni** is an analogue of the previously reported sorbent **ZJUT-1** (**ZJUT** = Zhejiang University of Technology).^[21] **ZJUT-1** (termed **SIFSIX-17-Ni** herein) was reported in 2018 and studied in the context of

propyne/propylene separation but remains unexplored with respect to C_2 and CO_2 gas sorption. The structure of desolvated **TIFSIX-17-Ni** was determined from *in situ* synchrotron powder X-ray diffraction (PXRD) data obtained from beamline i11^[22] at the Diamond Light Source at 298 K (Figure 1d, see Supporting Information Table S1 for details). **TIFSIX-17-Ni** has the same **pcu** network connectivity and is isostructural with its pyz based analogue, $[\text{Ni}(\text{pyz})_2(\text{SiF}_6)]_n$, **SIFSIX-3-Ni**.^[20b, 23] The *c* distance is slightly greater in **TIFSIX-17-Ni** (Figure S6) than **SIFSIX-3-Ni** (~7.65 Å versus ~7.5 Å, respectively) (Figures 1f, S7). The *a* distances, 6.98 Å (**TIFSIX-17-Ni**) versus 7.01 Å (**SIFSIX-3-Ni**), are comparable. The pore shape/chemistry, however, is profoundly affected by the amino group in **TIFSIX-17-Ni**. Specifically, axial F atoms in SiF_6^{2-} orient towards the pore at 45° to the crystallographic *a* axis in desolvated **SIFSIX-3-Ni**, whereas the F atoms in desolvated **TIFSIX-17-Ni** orient at 35° , meaning that pyz

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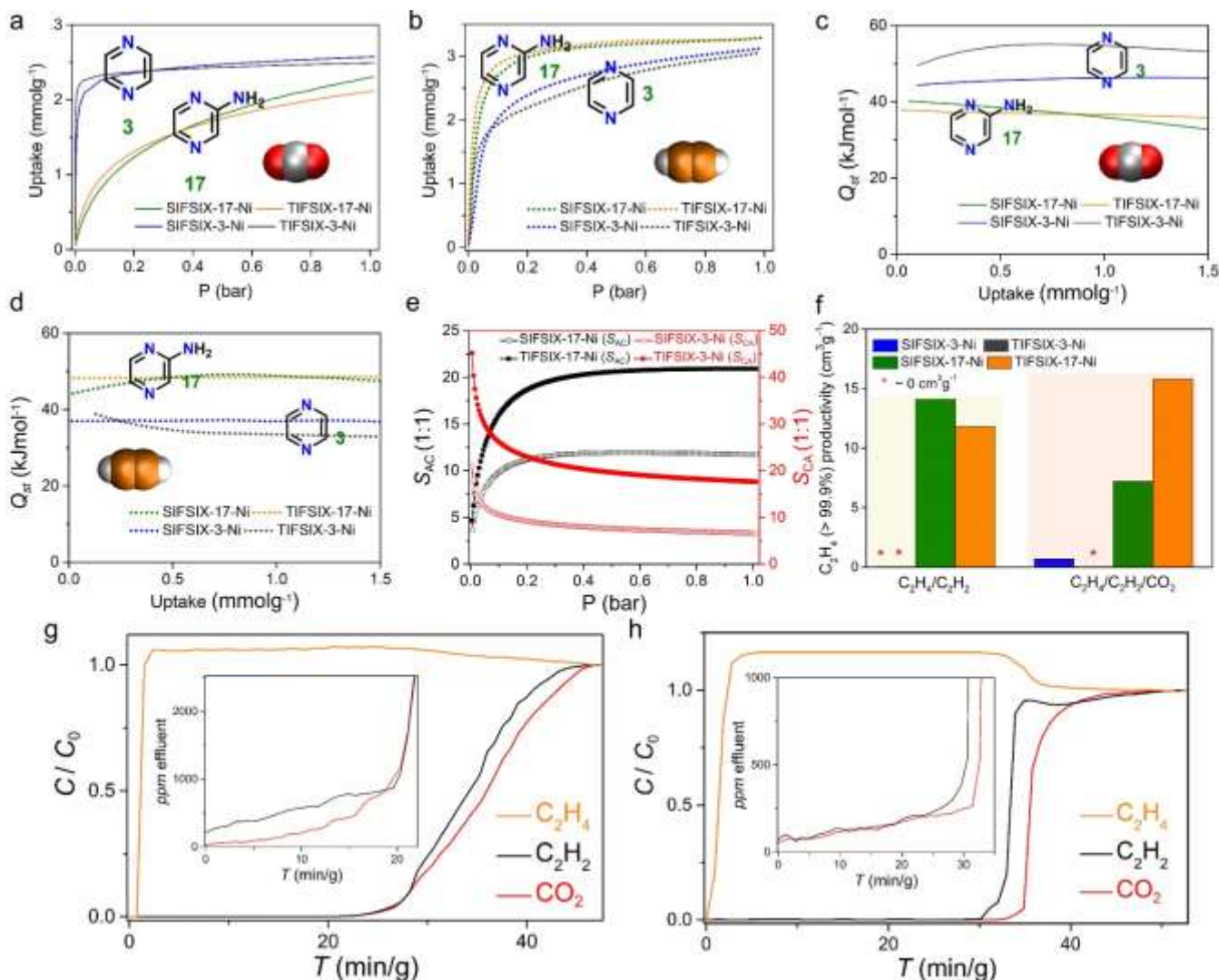


Figure 2. a) CO₂ and b) C₂H₂ sorption isotherms at 298 K for **MFSIX-3-Ni** and **MFSIX-17-Ni**; the isosteric enthalpies of adsorption for c) CO₂ and d) C₂H₄ for **MFSIX-3-Ni** and **MFSIX-17-Ni**; e) Ideal adsorbed solution theory, IAST selectivity (at 298 K until 1 bar) trends for C₂H₂ over CO₂, S_{AC} and for CO₂ over C₂H₂, S_{CA} (1:1, v/v gas mixtures); f) Dynamic column breakthrough, DCB experiments derived comparison of high-grade (99.9%) C₂H₄ productivity (cm³ g⁻¹) for binary C₂H₄/C₂H₂ and ternary C₂H₄/C₂H₂/CO₂ (volumetric ratios of 1:1 and 1:1:1, respectively) mixtures; Ambient temperature (298 K) and pressure (1 bar) experimental DCB curves for C₂H₄/C₂H₂/CO₂ (1:1:1, v/v) ratio by a sorbent bed filled with g) **SIFSIX-17-Ni** and h) **TIFSIX-17-Ni** (total gas flow: 2.1 cm³ min⁻¹). Insets of g) and h) present the C₂H₂ and CO₂ effluent concentrations for **SIFSIX-17-Ni** and **TIFSIX-17-Ni**, respectively in the above-mentioned DCB experiments.

rings are disordered between two positions and amino groups are disordered over eight positions (Figure S8). This structural difference can be attributed to F...NH₂ H-bonding interactions and, as discussed below, importantly results in a longer F...F diagonal distance across the pore (Figure 1f; Figures S7, S8). After confirming bulk phase purity (Figure 1g; Figures S2, S3), thermogravimetric analysis (TGA) profiles (Figure S9) indicated that activated **SIFSIX-17-Ni** and **TIFSIX-17-Ni** are stable to 493 K and 533 K respectively. *In situ* synchrotron PXRD experiments confirmed rigidity of the frameworks upon desolvation; only minor decreases in unit cell volumes of 2.9 % and 1.8 % were observed for **SIFSIX-17-Ni** and **TIFSIX-17-Ni**, respectively (Figures S4, S5). Contraction mainly occurred along the *c* axis: 2.0 % along *c* versus 0.4% along *a* for **SIFSIX-17-Ni**; 1.2 % along *c* versus 0.3% along *a* for **TIFSIX-17-Ni**. The stability of **MFSIX-17-Ni** to humidity was confirmed using an accelerated stability protocol adopted by the pharmaceutical industry (storage at 313 K and 75% RH) (Figures S10-S12).^[24]

The sorption properties of **MFSIX-17-Ni** were first examined using single-component isotherms (Figures S13-S26). Type I cryogenic

(195 K) CO₂ isotherms (Figures S13, S14) for both pyz-NH₂ HUMs revealed Brunauer–Emmett–Teller (BET) surface areas of 229.2 (**SIFSIX-17-Ni**) and 237.6 m² g⁻¹ (**TIFSIX-17-Ni**). The 298 K and 273 K isotherms indicated affinity for sorbates as follows: CO₂ over nitrogen (N₂) and CH₄; C₂H₂ over C₂H₄ and ethane (C₂H₆) (Figures S15-S22). These affinities contrast to the isostructural pyz linked HUMs, **MFSIX-3-Ni**. Specifically, amine introduction resulted in enhanced C₂H₂ affinity and, unexpectedly given the presence of amino groups, reduced CO₂ affinity (Figures 2a, 2b). These trends are most pronounced in the low pressure region (< 10,000 ppm or 0.01 bar) which is so critical for trace separations. Uptakes at 0.01 bar (mmol g⁻¹) for CO₂ were as follows: **SIFSIX-17-Ni** (0.20) < **TIFSIX-17-Ni** (0.32) < **SIFSIX-3-Ni** (1.76) < **TIFSIX-3-Ni** (2.16). The corresponding trend for C₂H₂ was **SIFSIX-3-Ni** (0.29) < **TIFSIX-3-Ni** (0.55) < **SIFSIX-17-Ni** (0.91) < **TIFSIX-17-Ni** (1.38).

Low-coverage isosteric enthalpy of adsorption (Q_{st}) values were determined from the CO₂ and C₂H₂ adsorption isotherms recorded at 273 and 298 K (Figures S23-S26) by fitting them to a virial-type expression (methods section, Supporting Information;

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Figures S27-S30 and Tables S4-S7). **MFSIX-3-Ni** was found to exhibit higher $Q_{st}(\text{CO}_2)$ values at low loading than the **MFSIX-17-Ni** HUMs: **TIFSIX-17-Ni** (37.8 kJ mol⁻¹) < **SIFSIX-17-Ni** (40.2 kJ mol⁻¹) < **SIFSIX-3-Ni** (44.4 kJ mol⁻¹) < **TIFSIX-3-Ni** (49.5 kJ mol⁻¹). The reverse trend was observed for $Q_{st}(\text{C}_2\text{H}_2)$: **TIFSIX-3-Ni** (38.8 kJ mol⁻¹) < **SIFSIX-3-Ni** (37.0 kJ mol⁻¹) < **SIFSIX-17-Ni** (44.2 kJ mol⁻¹) < **TIFSIX-17-Ni** (48.3 kJ mol⁻¹). The Q_{st} values were determined to be consistent across CO₂ and C₂H₂ loading. This is supported by the rigid nature of both pyz-NH₂ HUMs as evident from *in situ* PXRD analyses (Figures S4, S5). These studies suggest single site CO₂/C₂H₂ binding in **MFSIX-17-Ni**. Ideal adsorbed solution theory, IAST^[25] selectivities were calculated by fitting the single-component C₂H₂, CO₂ and C₂H₄ isotherms to the dual-site Langmuir-Freundlich DSLF equation (see Supporting Information for details, Table S8) for binary gas mixtures of C₂H₂/C₂H₄ and C₂H₂/CO₂ (both 1:1, v/v) at 1 bar and 298 K. High C₂H₂/C₂H₄ selectivities (S_{AE}) were obtained for both **SIFSIX-17-Ni** (506.4) and **TIFSIX-17-Ni** (670.9) (Figure S31, values in parenthesis denote S_{AE} at 1 bar and 298 K). Figure 2e reveals C₂H₂/CO₂ selectivities (S_{AC}) for **SIFSIX-17-Ni** and **TIFSIX-17-Ni** of 11.7 and 20.9 respectively at 1 bar and 298 K, whereas CO₂/C₂H₂ selectivities (S_{CA}) for **SIFSIX-3-Ni** and **TIFSIX-3-Ni** of 6.6 and 17.6, respectively, were determined. To our knowledge, this is only the second occurrence of “inverted” C₂H₂ versus CO₂ sorption within a family of physisorbents.^[26]

The similarity in $Q_{st}(\text{CO}_2)$ and $Q_{st}(\text{C}_2\text{H}_2)$ values for **MFSIX-17-Ni** HUMs implies that coadsorption of CO₂ and C₂H₂ could occur under dynamic conditions such as dynamic column breakthrough (DCB) experiments. Ambient temperature (298 K) and pressure (1 bar) DCB experiments were conducted using fixed-bed columns of each of the four HUM adsorbents with three inlet gas mixtures of fixed composition (v/v): two binary mixtures, C₂H₄/C₂H₂ (1:1), CO₂/C₂H₂ (1:1); one ternary mixture C₂H₄/C₂H₂/CO₂ (1:1:1) (Figures 2g, 2h; Figures S32-S34; for experimental details, see Supporting Information). For the **MFSIX-3-Ni** HUMs, the respective breakthrough times confirmed effective separation for each of the three gas mixtures (Figures S32, S34) with C₂H₂ eluting last in each case except for the CO₂/C₂H₂ (1:1) DCB experiment with **TIFSIX-3-Ni** (Figure S32d), for which coadsorption resulted in no separation. For the **MFSIX-17-Ni** HUMs, each DCB experiment was successful in terms of separating the three gas mixtures by eluting pure C₂H₄ or CO₂ as the effluent (Figures 2g, 2h; Figure S33). Unlike the **MFSIX-3-Ni** HUMs, which suffer from C₂H₄/C₂H₂ coadsorption (Figure S32),^[26] the binary C₂H₄/C₂H₂ DCB experiments with **MFSIX-17-Ni** HUMs led to negligible C₂H₄ uptakes (Figure S33) and elution of high-purity (> 99.95%) C₂H₄ for a relatively long time as supported by monitoring of C₂H₄ effluent purity levels during DCB experiments (Table S9). Perhaps our most significant observations concern the ternary C₂H₄/C₂H₂/CO₂ (1:1:1) breakthrough experiments (Figures 2g, 2h; Figure S34). Whereas **MFSIX-3-Ni** separated the C₂-CO₂ stream, coadsorption of CO₂ and C₂H₂ was found to occur only for a relatively short duration before CO₂ adsorption dominated. The breakthrough sequence was C₂H₄ (1/1 min/g) < C₂H₂ (20/22.5 min/g) < CO₂ (32/32 min/g) for the **SIFSIX-3-Ni/TIFSIX-3-Ni** packed sorbent beds (Figure S34). This resulted in low ethylene productivity and compromised ethylene purity in the effluent stream (Figure 2f; Table S9). Conversely, for the **MFSIX-17-Ni** sorbent beds, the breakthrough sequence was C₂H₄ (0.7/0.5 min/g) < C₂H₂ (25/30 min/g) < CO₂ (25.8/32 min/g) for **SIFSIX-17-Ni/TIFSIX-17-Ni**, respectively (Figures 2g, 2h). C₂H₄

effluent streams from the **SIFSIX-17-Ni** and **TIFSIX-17-Ni** fixed beds revealed C₂H₄ purity as high as 99.958% and 99.912% with high-purity ethylene productivities of 7.2 and 15.8 cm³ g⁻¹, respectively (Figure 2f; Table S9). We attribute the similar elution times of CO₂ and C₂H₂ to coadsorption driven by the similar affinities for these sorbents when exposed to C₂-CO₂ ternary mixtures.

In situ infrared (IR) spectroscopy was employed to elucidate the mechanism of the sorbent-sorbate interactions. **TIFSIX-3-Ni** and **TIFSIX-17-Ni** were first heated in high vacuum for activation and then cooled to room temperature for recording the IR spectra of activated samples and to monitor the loading of CO₂ and C₂H₂ (Figure 3). We first established the assignment of HUMs vibrational bands by comparing with the reported spectrum of matrix isolated (monomeric) pyz,^[27] and by conducting density functional theory (DFT) calculation on the vibrational frequency of pyz-NH₂ linker. Table S10 summarises the detailed assignment of observed bands in Figure 3. 1 bar CO₂ was then introduced into the activated samples for ~ 5 min to ensure adsorption saturation. We note that the IR absorption of gas phase CO₂ is prohibitively high at this pressure, precluding the observation of adsorbed CO₂. We then evacuated the chamber and recorded spectra as a function of time during desorption. Within ~ 5 seconds of evacuation, the pressure of gas-phase CO₂ drops below ~ 0.7 mbar (negligible gas-phase IR absorption). The adsorbed CO₂ within **TIFSIX-3-Ni** is initially detected by its characteristic peak at 2342 and 3699 cm⁻¹ in the difference spectra of Figure 3a, which corresponds to the asymmetric stretching band $\nu_{as}(\text{CO}_2)$ and combination band $\nu_a + \nu_s(\text{CO}_2)$.^[28] The desorption of CO₂ from **TIFSIX-3-Ni** was relatively slow, intensity of the $\nu_{as}(\text{CO}_2)$ band decreasing by only ~ 35% after ~ 100 min of evacuation at room temperature (Figure S35). This is in agreement with the pure CO₂ isotherm based strong binding of CO₂ to **TIFSIX-3-Ni**.^[29] The peak width of $\nu_{as}(\text{CO}_2)$ band, determined by Voigt profile fitting, is 7.7 cm⁻¹ and the initial $\nu_{as}(\text{CO}_2)$ spectrum in **TIFSIX-3-Ni** exhibits an asymmetric line shape (Figure S36). Desorption of CO₂ is facilitated upon heating the sample to 423 K for ~ 20 min in vacuum. After evacuation of most of the adsorbed CO₂ molecules from **TIFSIX-3-Ni** (Figure S36), the remaining $\nu_{as}(\text{CO}_2)$ band narrows and red-shifts to 2339 cm⁻¹, the same position as the adsorbed CO₂ in **TIFSIX-17-Ni**. Meanwhile, the spectral line becomes more symmetric. The broadening and asymmetric line shape of the $\nu_{as}(\text{CO}_2)$ band in **TIFSIX-3-Ni** suggests strong vibrational dynamic coupling between adsorbed CO₂ molecules and the pyz linked ultramicropores under high loading.^[30] Our previous reports on **MFSIX-3-Ni** have identified binding sites *via* molecular modelling^[26] and PXRD derived structural solution.^[23] These studies revealed that CO₂ interacts primarily with four electronegative F atoms from surrounding SiF₆²⁻ anions and are key to its benchmark CO₂ selectivity.^[20b] However, the interactions between CO₂ and TiF₆²⁻ anions in **TIFSIX-3-Ni** and **TIFSIX-17-Ni** cannot be directly characterised by IR spectroscopy since the vibrations of TiF₆²⁻ occur below 650 cm⁻¹, beyond the detection range of an infrared MCT-A detector. Nevertheless, difference spectra offer additional evidence that CO₂ interacts with the pyz linker in **TIFSIX-3-Ni**, as suggested by the strong perturbation of characteristic bands including $\nu(\text{CH})$, $\nu(\text{CC})_{\text{phenyl}}$, $\delta(\text{CH})_{\text{ip}}$ and $\delta(\text{CH})_{\text{oop}}$. In comparison with **TIFSIX-3-Ni**, the spectra for **TIFSIX-17-Ni** exhibit marked differences in both CO₂ and perturbed phenyl ring bands. For $\nu_{as}(\text{CO}_2)$ band at 2139 cm⁻¹ in **TIFSIX-17-Ni**, its peak width is 5.5 cm⁻¹, narrower compared to that in

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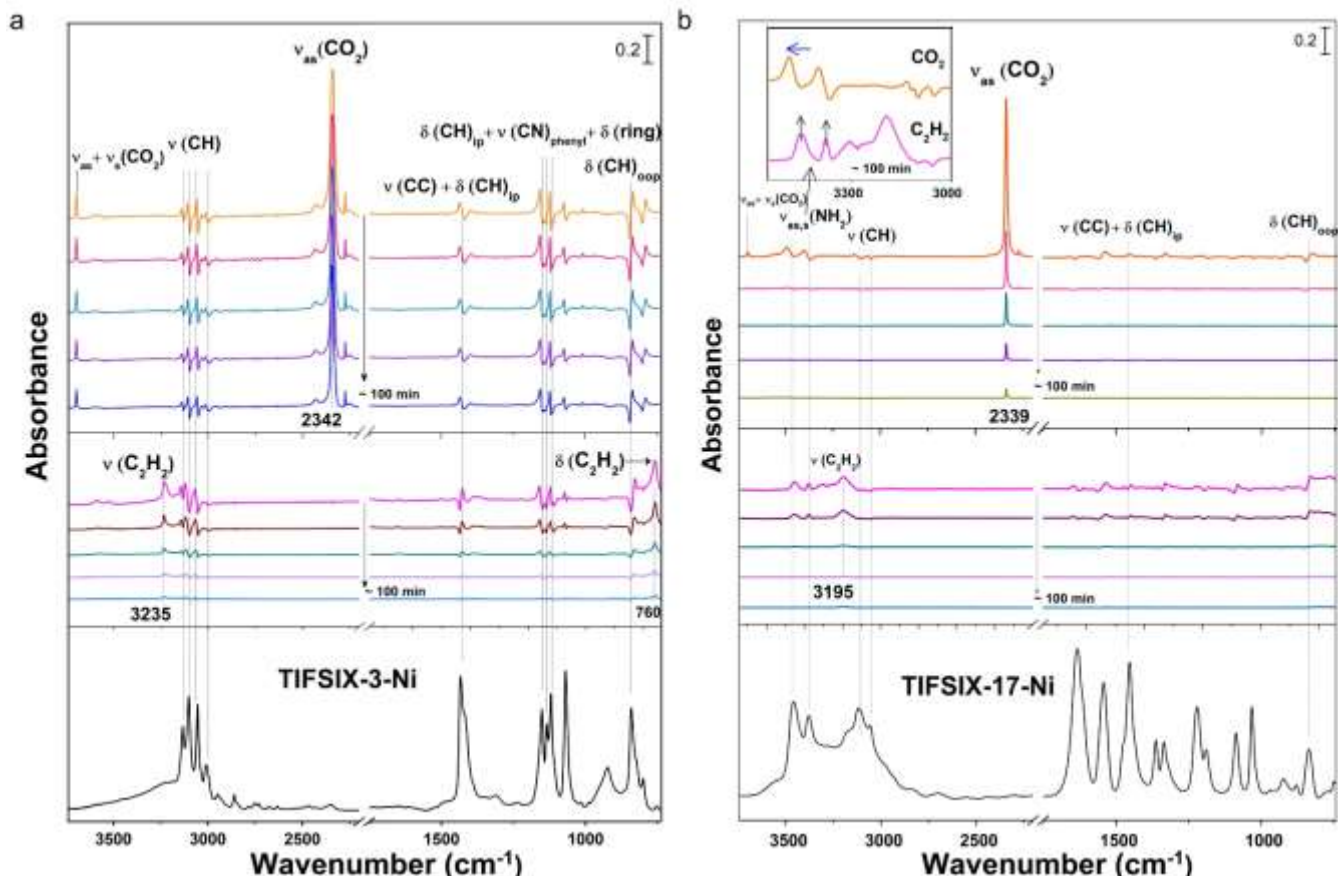


Figure 3. IR spectra showing adsorbed CO₂ and C₂H₂ in **TIFSIX-3-Ni**(a) and **TIFSIX-17-Ni**(b), respectively. Top and middle panels: difference spectra of unloading CO₂ (top) and C₂H₂ (middle) process from two HUMs under vacuum, each spectrum is referenced to the spectra of activated **TIFSIX-3-Ni** and **TIFSIX-17-Ni** sample. The orange and pink spectra are recorded after subsequent evacuation of ~1 bar gas phase CO₂ and C₂H₂ within ~5 sec. Bottom panel: IR spectra of activated **TIFSIX-3-Ni** and **TIFSIX-17-Ni**, referenced to pure KBr pellet in vacuum (< 0.027 mbar base pressure).

TIFSIX-3-Ni. The band decreases quickly upon evacuation and within ~100 min only < 5% of its initial intensity remained (Figure S35). A fast reduction of the combination band $\nu_{as} + \nu_s$ at 3696 cm⁻¹ is also evident in Figure 3b. Perturbation of the phenyl ring bands is also much weaker compared to **TIFSIX-3-Ni**, thus supporting the sorption experiments which indicate that introduction of the NH₂ group reduces CO₂ affinity in **TIFSIX-17-Ni**. This behaviour can be attributed to two effects. First, the presence of NH₂ within the channel isolates the adsorbed CO₂ molecules and prevents their dynamic coupling as indicated by the narrowing of $\nu_{as}(\text{CO}_2)$ band in **TIFSIX-17-Ni**. Secondly, CO₂ interactions with pyz cause the degree of phenyl ring modes' perturbation to decrease when the hydrogen atoms of the pyz linker are substituted by -NH₂. Chemisorption driven carbamate formation,^[31] as encountered in amine-grafted physisorbents, did not occur according to the difference spectra for **TIFSIX-17-Ni** in the region 1000-1800 cm⁻¹. No peaks associated with the $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{N})$ bands of carbamate were observed.^[32] Furthermore, we found that the $\nu(\text{N}-\text{H})$ bands exhibited an unusual blue shift upon loading of CO₂. This observation suggests that adsorbed CO₂ molecules did not form H-bonding interactions with the -NH₂ group, which would have shifted the $\nu(\text{N}-\text{H})$ frequency downwards.^[33] Rather, this result is indicative that the N-H bond is strengthened by encountering a repulsive force from the adsorbed CO₂.

The samples were *in-situ* regenerated in vacuum at 383 K and cooled back to 298 K for the corresponding C₂H₂ experiments. Upon adsorbing C₂H₂, the perturbations of phenyl modes behaved similarly to CO₂ loading, *i.e.*, they are more significant in

TIFSIX-3-Ni than in **TIFSIX-17-Ni**. However, we noted that the $\nu(\text{N}-\text{H})$ bands respond differently from loading of CO₂. The two $\nu(\text{N}-\text{H})$ bands increase in intensity upon increased dosing of C₂H₂ (Inset, Figure 3b). The intensity of $\nu(\text{N}-\text{H})$ bands is usually correlated with the basicity of the amine group. As the basicity decreases when -NH₂ bind with an acidic group, the $\nu(\text{N}-\text{H})$ bands grow stronger.^[34] C₂H₂ is well-known to show acidity and can form HC≡CH...N complexes through strong hydrogen bonding according to *ab initio* calculations.^[35] It was determined by GCMC simulations that the C₂H₂ binding site in **SIFSIX-3-Ni** involves multiple C-H...F interactions.^[13] We infer that the adsorbed C₂H₂ forms C-H...N hydrogen bonds with -NH₂ in **TIFSIX-17-Ni**. This is supported by the observation that the stretching band $\nu(\text{C}-\text{H})$ of adsorbed C₂H₂ within **TIFSIX-17-Ni** appears at a lower frequency of 3195 cm⁻¹ and displays broader line-shape when compared with the corresponding peak in **TIFSIX-3-Ni**.

Insights into the nature of the binding sites for C₂H₂, CO₂, and C₂H₄ in **TIFSIX-17-Ni** were revealed through classical molecular simulations (for full details, see Supporting Information). Figures 4d, 4e and 4f show a comparison of the modelled binding sites for each adsorbate in **TIFSIX-17-Ni** versus those in **SIFSIX-3-Ni** (Figures 4a, 4b and 4c).^[13] It was observed that all three molecules are oriented vertically along the *c*-axis in the channels of **SIFSIX-3-Ni**, where they interact with equatorial F atoms of the SiF₆²⁻ groups. On the other hand, the tilt of the pyz rings, longer F...F diagonal distance across the unit cell, and presence of the -NH₂ groups on the linkers in **TIFSIX-17-Ni** cause the C₂H₂

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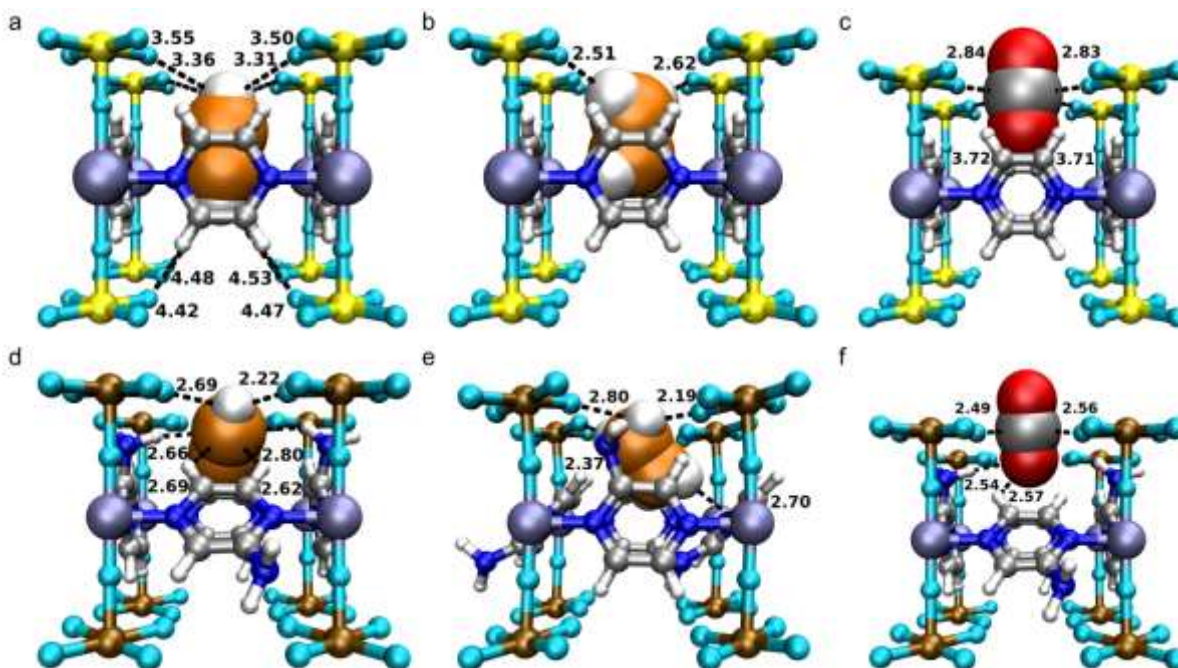


Figure 4. C_2H_2 (a, d), C_2H_4 (b, e) and CO_2 (c, f) binding sites in **SIFSIX-3-Ni** (top) and **TIFSIX-17-Ni** (bottom). Closest contacts between HUM atoms and the gas molecules are defined by the distances (in Å) between the H atom of hydrocarbons and the closest framework atoms. Adsorbed C2 and CO_2 molecules are presented in space-filling mode (C, grey; H, white; O, red; N, blue; F, cyan; Si, yellow; Ni, lavender; Ti, gold).

molecules to align within the pores at an angle with respect to the square grid. This results in shorter H...F interactions between the C_2H_2 and the inorganic pillars compared to those in **SIFSIX-3-Ni**. The C_2H_2 molecules also interact favourably with the $-NH_2$ groups on the linkers as it adsorbs near the TiF_6^{2-} pillars. Both types of HUM-adsorbate interactions contribute to a high calculated binding energy for C_2H_2 in **TIFSIX-17-Ni**, especially compared to that in **SIFSIX-3-Ni**.

C_2H_4 exhibits a similar orientation within the channels of **TIFSIX-17-Ni** to that of C_2H_2 but makes fewer contacts with the framework, resulting in lower affinity and selectivity for C_2H_4 . The calculated binding energy for C_2H_4 in **TIFSIX-17-Ni** was determined to be lower than both C_2H_2 and CO_2 , consistent with the results obtained for **SIFSIX-3-Ni**.^[13] The orientation of CO_2 molecules around the TiF_6^{2-} pillars in **TIFSIX-17-Ni** is similar to that observed in **SIFSIX-3-Ni** as well as to other members of the **SIFSIX-3-M** series.^[20a, 23, 36] However, the CO_2 molecule exhibits O...N repulsion with the surrounding $-NH_2$ groups on the linker, thereby decreasing its interaction energy relative to that of **SIFSIX-3-Ni**. The trend in the calculated binding energy for the different adsorbates localised in **TIFSIX-17-Ni** is $C_2H_2 > CO_2 > C_2H_4$ (see Supporting Information, Figures S38-40), which is consistent with the trend in the experimental low-coverage Q_{st} values.

Conclusion

MFSIX-17-Ni are the first physisorbents that enable single-step production of polymer-grade (> 99.95%) ethylene from a ternary equimolar mixture of ethylene, acetylene and CO_2 under ambient conditions. We attribute these results to the binding sites in **MFSIX-17-Ni**, which are very different to those in the isostructural family of HUMs based upon **SIFSIX-3-Zn**. These binding sites are impacted by the presence of amino groups and enable coadsorption of CO_2 and C_2H_2 , thanks to high affinity towards both gases. This study once again illustrates how apparently subtle

changes in pore size,^[37] shape^[38] and chemistry^[39] in ultramicroporous materials can profoundly impact selectivity and separation performances,^[11a, 17] in this case enabling single-step production of polymer grade C_2H_4 by removing both C_2H_2 and CO_2 from a ternary C_2-CO_2 gas mixture.

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Keywords: porous materials • crystal engineering • coordination networks • physisorption • ethylene purification

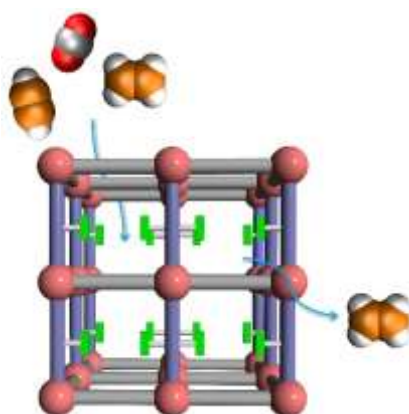
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Hybrid ultramicroporous materials in which aminopyrazine ligands substitute pyrazine ligands are the first physisorbents that enable polymer-grade (> 99.95%) ethylene production from ternary C₂-CO₂ gas mixtures under ambient conditions thanks to coadsorption of both C₂H₂ and CO₂.

Bernal Institute, Department of Chemical Sciences, University of Limerick, Limerick V94 T9PX, Republic of Ireland; Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching b. München, Germany; Department of Materials Science & Engineering, University of Texas at Dallas, Richardson, Texas 75080, USA; Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE205, Tampa, Florida 33620-5250, USA; Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom; Department of Chemistry, North Carolina State University, USA.

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