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Fine-regulation of gradient gate-opening in nanoporous crystals for sieving separation of ternary C₃ hydrocarbons†

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The adsorptive separation of ternary propyne (C₃H₄)/propylene (C₃H₆)/propane (C₃H₈) mixtures is of significant importance due to its energy efficiency. However, achieving this process using an adsorbent has not yet been accomplished. To tackle such a challenge, herein, we present a novel approach of fine-regulation of the gradient of gate-opening in soft nanoporous crystals. Through node substitution, an exclusive gate-opening to C₃H₄ (17.1 kPa) in NTU-65-FeZr has been tailored into a sequential response of C₃H₄ (1.6 kPa), C₃H₆ (19.4 kPa), and finally C₃H₈ (57.2 kPa) in NTU-65-CoTi, of which the gradient framework changes have been validated by *in situ* powder X-ray diffractions and modeling calculations. Such a significant breakthrough enables NTU-65-CoTi to sieve the ternary mixtures of C₃H₄/C₃H₆/C₃H₈ under ambient conditions, particularly, highly pure C₃H₈ (99.9%) and C₃H₆ (99.5%) can be obtained from the vacuum PSA scheme. In addition, the fully reversible structural change ensures no loss in performance during the cycling dynamic separations. Moving forward, regulating gradient gate-opening can be conveniently extended to other families of soft nanoporous crystals, making it a powerful tool to optimize these materials for more complex applications.

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Introduction

Efficient separation of the ternary C₃ hydrocarbons is crucial for the petrochemical industry as C₃H₆ is an essential feedstock for valuable commodities.¹ Currently, the separation process involves energy-intensive catalytic hydrogenation and cryogenic distillation, which accounts for nearly 3% of all separation energy.^{1–3} Therefore, there is a need for a more energy-efficient technology for this task. Adsorption separation using porous materials, specifically porous coordination polymers (PCPs), shows great promise due to their finely designed pore chemistry.^{4–13} In this regard, recent progress has been made in binary separations using strategies such as π -complexation,

sieving strategies and kinetic diffusion.^{14–23} However, the similar molecular sizes and kinetic diameters exacerbate the challenge of C₃H₄/C₃H₆/C₃H₈ separation, particularly by one material.

Recent research has shown that the purification of ethylene from a complex mixture of C₂ hydrocarbons and carbon dioxide can be achieved using sequentially packed sorbents, where the three impurities were captured by three PCPs.²⁴ Although this strategy requires overcoming the difficulties of preparation of the three materials, and also their rational packing, it enables us to believe that integrating gradient sorbent–sorbate interactions may address the challenge of C₃H₄/C₃H₆/C₃H₈ separation in a single domain, as well as the precise understanding of hierarchical sites or gradient gate-openings.

The concept of hierarchical sites holds certain theoretical feasibility, but its implementation is hindered by the significant limitations in rational assembly of these sites in a confined nanospace. Comparably, the strategy of gradient gate-openings shows promising prospects. Since the early reports of soft crystals,^{25,26} the soft nature of these materials has been gradually understood, that is, the stronger the interaction, the earlier the gate-opening.^{27,28} In addition, soft frameworks can exhibit sensitive responses to even extremely small stimuli.^{29–31} Given these advantages, significant efforts have been dedicated to the construction of soft PCPs;^{27,29,32–35} however, neither the fine pre-design nor function-oriented synthesis of such a material,

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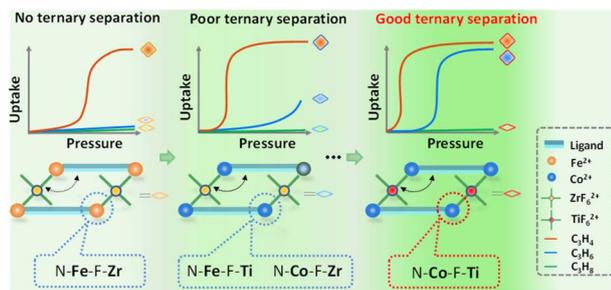
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Scheme 1 Illustration of fine-regulation of gradient gate-opening in soft NTU-65-series via node substitution for sieving separation of C₃ hydrocarbons in a single domain.

whose framework can sequentially recognize these similar molecules, has yet been reported.

During our investigation of porous materials,^{20,36,37} we have reported a soft crystal, NTU-65, [Cu(L)₂(SiF₆)] (L = 1,4-di(1*H*-imidazolyl)benzene). The temperature dependent gate-opening allows it to show a sieving separation of C₂H₄/C₂H₂/CO₂ mixtures.

However, this framework cannot separate the equimolar C₃H₆/C₃H₈ due to a small difference in uptake at this ratio caused by the gate-opening effect which either occurs too early or too late (Fig. S2†). Inspired by reticular chemistry³⁸ and NTU-65, herein, we report a fine tuning of the framework softness *via* node substitution in a series of PCPs (NTU-65-series: NTU-65-FeZr, NTU-65-FeTi, NTU-65-CoZr and NTU-65-CoTi, Scheme 1), as the metal nodes may alter the transformation characteristics of soft structures. As expected, a sole gate-opening toward C₃H₄ in NTU-65-FeZr evolves into a gradient response to C₃H₄ and C₃H₆ in NTU-65-CoTi, yielding an unprecedented breakthrough of sieving separation of C₃H₄/C₃H₆/C₃H₈.

Results and discussion

Solvothermal reactions of L and the corresponding metal salt provide NTU-65-series (Fig. S3†). They crystallize in the monoclinic system (Table S1†) and adopt the same coordination configurations. The M1 centres (M1: Fe²⁺ or Co²⁺) of NTU-65-series are connected by four imidazole N atoms in a planar configuration from four L and two F atoms in the axial vertex from two M₂F₆²⁻ (M₂: Zr⁴⁺ or Ti⁴⁺) ions. As a result, cross-linked 2D channels are observed in the packed frameworks, although the window apertures undergo minimal changes (Fig. 1a, b and S4–S8†), along with similar accessible volumes (43.5%, 44.8%, 42.4% and 44.8%).³⁹ To reach the adjacent nodes, the dihedral angle between the benzene and imidazole rings in L in NTU-65-series shows significant changes. For example, the angle of the L_{Cis} in NTU-65-FeZr is as large as 14.81°, while this angle decreases to 3.45° in NTU-65-FeTi (Fig. 1c). Additionally, the dihedral angle in L_{Trans} in NTU-65-CoTi is up to 22.69°. Therefore, different degrees of softness are expected in the NTU-65-series. Phase purity of the four crystals has been confirmed by X-ray powder diffraction measurement (Fig. S9†). In addition, all samples are thermally stable, up to 350 °C (Fig. S10†).

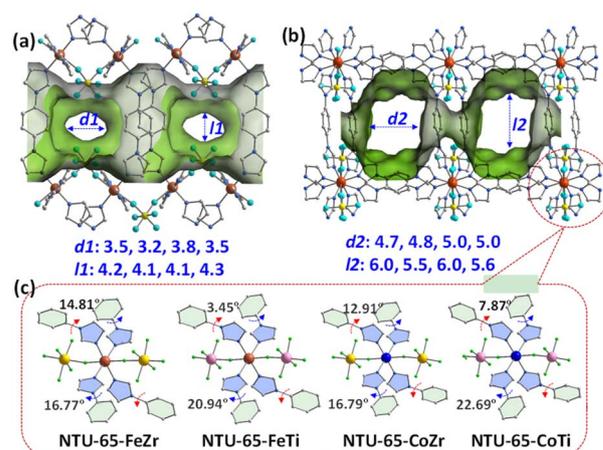


Fig. 1 Crystal structure of NTU-65-series along the *a*-axis (a) and *b*-axis (b). Comparison of the dihedral angle in L in NTU-65 series (c).

Permanent porosity of the activated NTU-65-series was evaluated using N₂ adsorption measurements at 77 K (Fig. S12†). Initially, all samples show minimal N₂ uptake until reaching $P/P_0 = 0.61, 0.26, 0.27$ and 0.24 . However, a peculiar ‘kink’ phenomenon occurred in all of them. This is due to the rapid increase in adsorption capacity of the crystals after instantaneous gate-opening under this condition, accompanied by a rapid decrease in system pressure, to $P/P_0 = 0.10, 0.07, 0.05$ and 0.04 , respectively. Subsequently, N₂ uptake increases with increased pressure in NTU-65-FeZr, while type-I adsorption isotherms were observed in NTU-65-FeTi and NTU-65-CoTi. Differently, NTU-65-CoZr exhibits a second adsorption platform before reaching $P/P_0 = 0.6$, followed by pressure-dependent uptake. Despite these differences, all four crystals demonstrated a similar maximum N₂ capacity (219.5 to 236.2 cm³ g⁻¹). Evaluated by using these isotherms, the crystals exhibit comparable surface areas (540–610 m² g⁻¹) and pore volumes (0.34–0.36 cm³ g⁻¹) (Fig. S13, S14 and Table S2†). Additionally, all isotherms display desorption hysteresis, confirming the filling effect of the soft frameworks.^{40,41}

To further investigate structural softness, CO₂ isotherms were collected at 195 K, as CO₂ may interact differently with the frameworks compared to N₂.^{42,43} Unlike the ‘kink’ phenomenon in the above N₂ isotherms, all CO₂ uptakes of the NTU-65-series increase with elevated pressure. Meanwhile, gradient adsorption platforms indicating sequential gate-openings were clearly observed in NTU-65-series. For NTU-65-FeZr, the first gate-opening occurs at 2.1 kPa, followed by the second and third gate-opening at 22.8 and 56.3 kPa, respectively (Fig. 2a). However, NTU-65-FeTi shows an earlier first gate-opening pressure (OP) of 1.7 kPa. The second and third gate-openings in NTU-65-FeZr merge into one in NTU-65-FeTi, at 31.4 kPa (Fig. 2b). Notably, three gate-openings appear again in NTU-65-CoZr (starting at 0.8, 14.6 and 45.8 kPa), whose responsive pressures are all lower than that of NTU-65-FeZr, and the first OP is also lower than that of NTU-65-FeTi (Fig. 2c). Remarkably, NTU-65-CoTi exhibits an advancement of the first OP at 0.5 kPa, followed by a second quick uptake at 18.8 kPa (Fig. 2d). Therefore, these isotherms



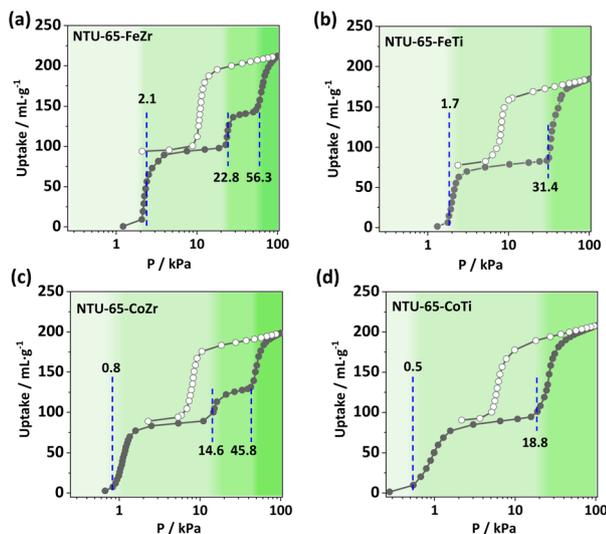


Fig. 2 CO₂ adsorption isotherms of NTU-65-series (a)–(d) at 195 K.

indicate that the four activated crystals possess non-porous characteristics and can be opened by N₂ or CO₂ once the stimuli exceed the energy barrier controlling the framework closure. Meanwhile, the gradually decreased pressure (2.1 to 0.5 kPa) for the first gate-opening reflects the fact that the four frameworks show different sensitivities to external stimuli. Additionally, the difference in multi-step gate-openings in them validates the effectiveness of the node substitution strategy in regulation of the framework with gradient softness, which may provide a promising platform for sequential recognition of gases with extremely small differences.

To investigate the function of gradient and sensitive gate-openings, adsorption isotherms of C₃H₄, C₃H₆ and C₃H₈ were collected on NTU-65-series (Fig. 3 and S15–S18[†]). NTU-65-FeZr

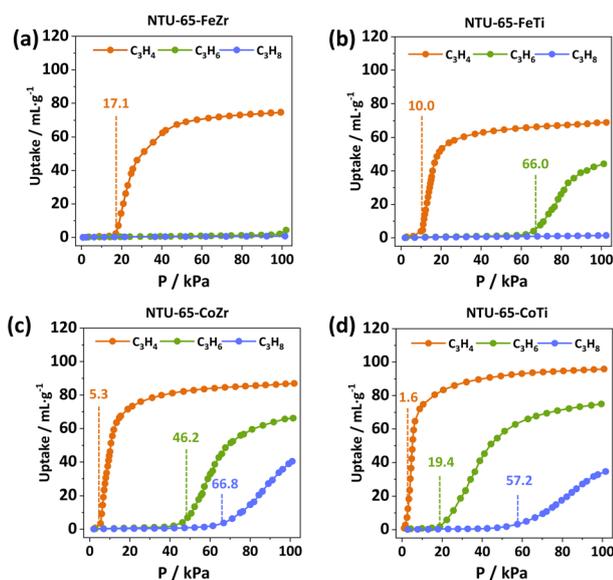


Fig. 3 C₃H₄, C₃H₆ and C₃H₈ adsorption isotherms of NTU-65-series (a)–(d) at 273 K.

exhibits minimal uptake of C₃H₆ and C₃H₈ at the threshold pressure, whereas C₃H₄ adsorption begins at 17.1 kPa with a maximum capacity of 74.7 cm³ g⁻¹ (Fig. 3a). Meanwhile, the starting OP is advanced to 10.0 kPa in NTU-65-FeTi, along with nearly the same C₃H₄ capacity (69.0 cm³ g⁻¹) (Fig. 3b). Unlike NTU-65-FeZr, C₃H₆ molecules open the framework of NTU-65-FeTi at 66.0 kPa with a capacity of 44.2 cm³ g⁻¹ at 100 kPa (Fig. 3c). Interestingly, the OP of the three gases (C₃H₄: 5.3 kPa, C₃H₆: 46.2 kPa and C₃H₈: 66.8 kPa) exhibit a forward movement again in NTU-65-CoZr (Fig. 3d). However, the isotherms indicate two crucial issues that may arise during the dynamic separation of such ternary mixtures: (1) insufficient partial pressure for C₃H₄ adsorption (far larger than 1 kPa); and (2) lower separation performance between C₃H₆ and C₃H₈ (small uptake difference of only 7.6 cm³ g⁻¹ at around 50 kPa). Remarkably, these issues may be solved by using NTU-65-CoTi, which exhibits rapid uptake of C₃H₄ at 1.6 kPa and a significantly improved uptake difference between C₃H₆ and C₃H₈, reaching as high as 55.9 cm³ g⁻¹ at 50 kPa. Additionally, the total C₃H₄ capacity is increased to 95.9 cm³ g⁻¹. Moreover, the uptake ratios of binary mixtures (C₃H₄/C₃H₆, C₃H₆/C₃H₈ and C₃H₄/C₃H₈) were significantly and simultaneously improved compared to that of other benchmark materials (Table 1 and S3[†]).

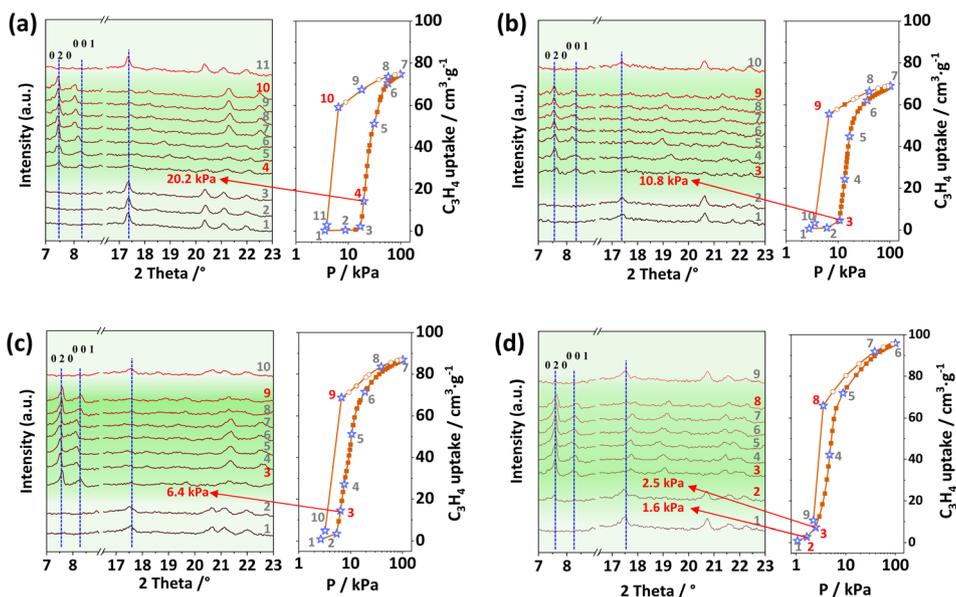
To confirm the systemic structural changes, *in situ* powder X-ray diffraction patterns/sorption measurements were performed (Fig. 4). The characteristic peaks corresponding to crystal faces of [0 2 0] and [0 0 1] in the as-synthesized phases (at about 6.5 and 7.2°) become weaker and shift to a higher-angle region in the activated crystals, indicative of structural contraction commonly observed in flexible PCPs. However, these two peaks reappear at similar positions to those obtained from their as-synthesized phases after an increase in pressure. Additionally, these open structures transform back into the closed state when the pressure decreases to a very low value, showing reversible sorption and structural changes in NTU-65-series. In addition, gas-loaded crystallographic analysis has also been attempted to explore the detailed structural changes. However, the small crystal size and crack after activation results in extremely weak or no diffraction. To understand the trend in softness of these PCPs, we conducted density functional theory (DFT) calculations taking C₃H₄ as the probe molecule (Fig. S20[†]). Previously, we have shown that the gate-opening pressure of PCPs induced by gas adsorption is dependent on the binding energy of the gas molecule with the PCP.⁴⁴ We therefore calculated the binding energies of C₃H₄ with the NTU-65-series. The binding energy increases (becomes more negative) in the following order: NTU-65-FeZr (-7.8 kcal mol⁻¹) < NTU-65-FeTi (-8.1 kcal mol⁻¹) < NTU-65-CoZr (-8.5 kcal mol⁻¹) < NTU-65-CoTi (-9.1 kcal mol⁻¹). This is consistent with the order of gate-opening pressure of these PCPs in response to C₃H₄ adsorption for these PCPs (Fig. 3).

The sequential recognition of C3 hydrocarbons encouraged us to perform dynamic separations. Given the commonly encountered ratio of C3 hydrocarbons in industry, a simulated feed-gas of C₃H₄/C₃H₆/C₃H₈ (0.5/49.75/49.75, v/v/v) was used for breakthrough experiments at 273 K. Consistent with the single-component gas isotherms, C₃H₆ and C₃H₈ elute simultaneously



Table 1 Summarized capacities ($\text{cm}^3 \text{g}^{-1}$) and uptake ratios of C3 hydrocarbons for NTU-65-series at 273 K

PCPs	C_3H_4	C_3H_6	C_3H_8	Uptake ratios		
	0.1 bar	0.5 bar	0.5 bar	$\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$ (0.1/0.5)	$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ (0.5/0.5)	$\text{C}_3\text{H}_4/\text{C}_3\text{H}_8$ (0.1/0.5)
NTU-65-CoTi	73.93	57.44	1.55	1.28	37.05	47.70
NTU-65-CoZr	46.24	8.55	0.96	5.41	8.91	48.17
NTU-65-FeTi	3.93	1.27	0.73	3.01	1.74	5.34
NTU-65-FeZr	0.59	0.74	0.51	0.80	1.45	1.16

Fig. 4 *In situ* PXRD patterns of NTU-65-FeZr (a), NTU-65-FeTi (b), NTU-65-CoZr (c) and NTU-65-CoTi (d) during C_3H_4 adsorption/desorption at 273 K.

from the NTU-65-FeZr sample bed, while C_3H_4 was captured until 85.8 min g^{-1} , showing impossible ternary separation (Fig. 5a). For NTU-65-CoZr, C_3H_8 was detected as the first elution at 19.3 min g^{-1} , followed by C_3H_6 at 27.8 min g^{-1} . Additionally, C_3H_4 passes through the column at 106.3 min g^{-1} (Fig. 5b). Considering the OP of C_3H_6 (46.2 kPa) and the small uptake difference ($7.6 \text{ cm}^3 \text{ g}^{-1}$) of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ in NTU-65-CoZr, the observable separation time of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ should be attributed to the slight pore opening, caused by accumulated C_3H_6 adsorption. This phenomenon is similar to the selective C_3H_4 or C_2H_2 capture in GeFSIX-dps-Zn⁴⁵ and Co(4-DPDS)₂MoO₄,⁴⁶ respectively, where the partial pressures of C_3H_4 (10 kPa) or C_2H_2 (1 kPa) in the feed-gas for breakthrough separations are lower than that of the corresponding OPs ($\sim 16 \text{ kPa}$ and $\sim 17 \text{ kPa}$) of the frameworks at the same temperature. In addition, a similar and insufficient ternary separation was also observed in NTU-65-FeTi. Remarkably, NTU-65-CoTi exhibits a significant separation of the ternary mixture of $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$, in which highly pure C_3H_8 elutes out at 17.0 min g^{-1} , while the outflows of C_3H_6 and C_3H_4 from the sample bed are around 41.1 min g^{-1} and 132.9 min g^{-1} (Fig. 5c). Additionally, the further extended retention time of C_3H_4 (from 85.8 min g^{-1} in NTU-65-FeZr to 132.9 min g^{-1} in NTU-65-CoTi) reflects the increased

cumulative effect in NTU-65-series, as structural deformation becomes easier. To the best of our knowledge, the PCPs, including rigid and soft frameworks, have been widely explored for gas separations; however, this is the first example that can separate C3 hydrocarbons in one-step in a single domain. Furthermore, this promising separation was also confirmed at increased velocity (5 and 10 mL min^{-1}) of such ternary mixtures, as well as the binary mixtures (Fig. S21–S27 and Tables S4–S7†). More importantly, due to the reversible structural changes, there is almost no performance loss during the cycling measurements on NTU-65-CoTi (Fig. 5d and S28†), a critical factor in evaluating the feasibility of the adsorbents.

Based on these breakthrough results, how the NTU-65-CoTi might be possible to procure pure C_3H_6 and C_3H_8 are mostly expected. As shown in Fig. 5e, two beds are needed, Bed A and B, both packed with NTU-65-CoTi.^{47,48} During the adsorption cycle, the two beds A and B operate sequentially. The operation of Bed A and B should last for at least 130 min g^{-1} and 35 min g^{-1} , respectively. Highly pure C_3H_8 (99.9%, GC limitation) is recovered from Bed B at the end of the adsorption cycle. After termination of the adsorption cycle, both Bed A and B are subjected to counter-current vacuum desorption. From Bed A, the product C_3H_4 with improved concentration (from 0.5% to



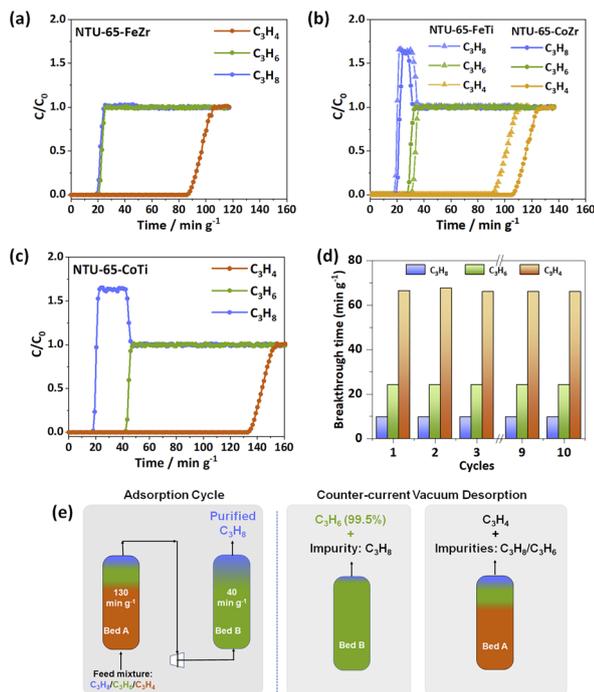


Fig. 5 Breakthrough curves of NTU-65-series (a)–(d) for $C_3H_4/C_3H_6/C_3H_8$ (0.5/49.75/49.75, v/v/v, 2 mL min^{-1}) at 273 K. Cycling performance of NTU-65-CoTi (5 mL min^{-1}) (d). Schematic representation of the separation of C3 ternary mixtures using two packed beds of NTU-65-CoTi in a vacuum swing adsorption process (e).

6.3%) can be obtained, while from Bed B, the product C_3H_6 can be harvested with a purity approaching 99.5%.

Conclusions

In summary, due to the demand for energy-efficient separation of C3 hydrocarbons, we here report a gradient regulation of framework softness *via* the node substitution approach. The exclusive response to C_3H_4 in NTU-65-FeZr has been tailored into a sequential capture of C_3H_4 and C_3H_6 in NTU-65-CoTi. This breakthrough enables an unprecedented ability for sieving separation of the ternary $C_3H_4/C_3H_6/C_3H_8$ mixtures in a single domain. By following designed procedures, highly pure C_3H_8 (99.9%) and C_3H_6 (99.5%) can be obtained. Moving forward, given that the conditions for feasible gas separation vary significantly, the precise understanding and ability to tune the gate-openings of soft PCPs are particularly important, potentially indicating a path to other challenging multi-component systems.

Data availability

The data supporting the findings of this study are available within the article and/or its ESI.†

Author contributions

J. D. conceived the research idea and designed the experiments. S. L. and Y. H. conducted the experiments. S. L., Y. H., J. W.,

Y. L., and J. T. analysed and discussed the data. J. Z. and K. R. performed the calculations. J. D. and K. G. wrote the paper. All authors offered constructive comments on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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