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DOI:

[10.1126/science.aay8447](https://doi.org/10.1126/science.aay8447)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Chai, Y., Han, X., Li, W., Liu, S., Yao, S., Wang, C., Shi, W., Da-silva, I., Manuel, P., Cheng, Y., Daemen, L. D., Ramirez-cuesta, A. J., Tang, C. C., Jiang, L., Yang, S., Guan, N., & Li, L. (2020). Control of zeolite pore interior for chemoselective alkyne/olefin separations. *Science*, 368(6494), 1002-1006.
<https://doi.org/10.1126/science.aay8447>

Published in:

Science

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Control of zeolite pore interior for chemoselective alkyne/olefin separations

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Abstract: Efficient removal of alkyne impurities for the production of polymer-grade lower olefins remains an important and challenging target for many industries. We report a strategy to control the pore interior of faujasite (FAU) zeolites by confinement of isolated open Ni(II) sites in their six-membered rings. Under ambient conditions, Ni@FAU showed exceptional adsorption of alkynes and efficient separations of acetylene/ethylene, propyne/propylene and butyne/1,3-butadiene mixtures with

unprecedented dynamic separation selectivities of 100, 92 and 83, respectively. *In situ* neutron diffraction and inelastic neutron scattering revealed confined Ni(II) sites that enabled chemoselective and reversible binding to acetylene through formation of meta-stable $[\text{Ni(II)(C}_2\text{H}_2)_3]$ complexes. Control of pore interior chemistry of easy-scalable zeolites has unlocked their potentials in challenging industrial separations.

One Sentence Summary: The reversible, chemoselective binding of alkynes on open Ni(II) sites confined in FAU zeolites enables the efficient production of polymer-grade lower olefins under ambient conditions.

Greater than 350 million tonnes of lower olefins (ethylene, propylene, and 1,3-butadiene) are produced each year through steam cracking of hydrocarbons. Separating large quantities of chemical mixtures into purer form accounts for an enormous amount of global energy consumption (1). To obtain polymer-grade olefins, the by-products of alkynes (acetylene, propyne, and butyne) in the stream must be reduced to <5 ppm because these alkynes irreversibly poison the catalysts for polymerization (2). State-of-the-art techniques to purify olefins are based upon partial hydrogenation of alkynes over supported Pd-catalysts, which however suffers from poor selectivity and high costs (3). Emerging porous sorbents, notably metal-organic frameworks (MOFs), show preferential adsorption of alkynes over olefins, promoting alternative adsorption-based purification processes for ethylene (4-8) and propylene (9-11).

However, this increasing interest has yet to be commercialized because of the inherently limited stability and high production costs of MOFs. In addition, the primary physisorption mechanism in MOFs driving separations results in a trade-off between adsorption selectivity and capacity. Possessing structural robustness and low-cost production, zeolites are widely used for industrial separations based upon their molecular sieving property (12), but are not effective for alkyne/olefin separations because these molecules have similar molecular sizes and volatilities (13). Zeolites can act as excellent scaffolds to stabilize active metal sites to uncover new function and properties. Here we confine isolated Ni(II) sites into FAU zeolite to achieve exceptional adsorption of alkynes from a range of alkyne-olefin mixtures. The strong yet fully reversible binding between alkyne and the open Ni(II) sites resulted in the formation of meta-stable $[\text{Ni(alkyne)}_3]$ complexes under dynamic conditions and enabled the complete removal of alkynes from olefins (alkynes < 1 ppm). The facile production and high stability of Ni@FAU

reinforce its potential in industrial purification of lower olefins.

M@FAU zeolites [M= Ni(II), Cu(II), Zn(II)] were synthesized from hydrothermal reactions of mixed gels {molar ratio of SiO₂:Al₂O₃:Na₂O:M-TAPTS:H₂O=7.8:1.0:2.2:0.6:174; TAPTS=3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane} and subsequent processing (yield = 77-85%). The TAPTS ligand was used to complex Ni(II) ions for their inclusion in the zeolite pore structure at locations that can be difficult to access during conventional postsynthesis ion-exchange. Similar approaches based upon (3-mercaptopropyl)trimethoxysilane ligand have been reported to introduce metal sites or clusters into desirable sites of various zeolites, showing excellent catalytic activities (14, 15). Synchrotron x-ray powder diffraction data confirmed that M@FAU crystallize in the cubic space group, *Fd-3m*, adopting the FAU-topology and there is an absence of bulk phase of metal oxides (Fig. S1, Table S1).

The homogenous distribution of transition-metal cations throughout the M@FAU crystals (3 to 5 μ m) were confirmed by electron microscopic studies (Figs. S2-3). Under ambient conditions, the pores of M@FAU samples were filled with water molecules that could be removed completely by heating at 623 K (Fig. S4). The divalent oxidation state of the confined metal ions was confirmed by x-ray photoelectron spectroscopy (XPS) (Fig. S5) and the primary location of confined Ni(II) sites in FAU zeolite has been studied by density functional theory (DFT) calculations (Fig. S6) and by *in situ* neutron powder diffraction (NPD) studies (see below).

The adsorption capacities of desolvated M@FAU and the parent Na-FAU were first evaluated by measuring the adsorption isotherms of C₂H₂ and C₂H₄ (Fig. 1A, Figs. S7-8). At 1 bar and 298 K, Ni@FAU, [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)], showed overall lower uptakes of C₂H₂ (3.48 mmol/g; equivalent to ~3.7 C₂H₂ per Ni(II) site) and C₂H₄ (2.36 mmol/g) than that of Na-FAU (5.15 and 4.06 mmol/g, respectively) because of the moderate decrease of Brunauer-Emmett-Teller (BET) surface areas on incorporation of Ni(II) sites (from 710 to 531 m²/g, Fig. S9). Interestingly, 2.0 mmol/g of C₂H₂ uptake was recorded in Ni@FAU at 0.02 bar, a pressure that is relevant to the partial pressure of C₂H₂ impurity in industrial C₂H₄ streams. The steep C₂H₂ uptake of Ni@FAU at low pressure was consistent with its higher heat of adsorption (48.6 kJ/mol) than that of Na-FAU (21.7 kJ/mol) and of C₂H₄ uptake in Ni@FAU (25.8 kJ/mol), which were determined by differential scanning calorimetry (Figs. S10-21, Table S2, Supplementary Text).

Temperature-programmed desorption (TPD) profiles of C₂H₂- and C₂H₄-loaded Ni@FAU revealed higher adsorption of C₂H₂ (1.75 mmol/g) than C₂H₄ (0.51 mmol/g), and showed desorption peaks centred

at 363 and 329 K, respectively. When co-adsorbed with an equimolar mixture of C_2H_2/C_2H_4 , the TPD profile resembled that of C_2H_2 -loaded Ni@FAU and little desorption of C_2H_4 was observed. Moreover, the preadsorbed C_2H_4 molecules in Ni@FAU could be readily displaced by C_2H_2 under dynamic conditions (Fig. 1B). The presence of strongly bound C_2H_2 molecules in Ni@FAU is also confirmed by in situ Fourier-transform infrared (FTIR) studies at 298 K (Fig. 1C). Upon adsorption in Ni@FAU, $\nu_s(CH)$ and $\nu_{as}(CH)$ bands of C_2H_2 red-shifted to 2925 and 3010 cm^{-1} , respectively, comparing to gaseous or physisorbed C_2H_2 (3100~3400 cm^{-1}) (16, 17), whereas no shift was observed for adsorbed C_2H_4 molecules. Infrared bands of bound C_2H_2 molecules were observed in the equimolar C_2H_2/C_2H_4 co-adsorbed Ni@FAU, demonstrating the selective uptake of C_2H_2 under competitive adsorption.

The adsorption species in C_2H_2 - and C_2H_4 -loaded Ni@FAU were identified by mass spectrometry (18). The pulsed laser vaporization of Ni@FAU target in He produced a series of fragments, and Ni-containing fragments can be distinguished by the characteristic isotope ratio of nickel ($^{58}Ni:^{60}Ni = 68\%:26\%$). Based upon the control experiment of metallic Ni and Na-FAU (Figs. S22-23), fragments corresponding to $Ni(C_2H_2)_3$ species were identified as a key species in C_2H_2 -adsorbed Ni@FAU (Fig. 1D), whereas no $Ni(C_2H_4)_n$ ($n = 1$ to 4) species were observed for C_2H_4 -adsorbed Ni@FAU. These results demonstrated the highly selective adsorption of C_2H_2 in Ni@FAU and its high capability to remove trace C_2H_2 from the C_2H_4 stream.

The ability of M@FAU (M=Ni, Cu, Zn) to separate C_2H_2/C_2H_4 mixtures under dynamic conditions were evaluated by breakthrough experiments. All of the samples showed sufficient dynamic adsorption of C_2H_2 and could produce ultra-pure C_2H_4 ($C_2H_2 < 1$ ppm) streams at the outlet of the fixed-beds at 298 K (Fig. 2A, Fig. S24-25). The dynamic C_2H_2 uptakes calculated from column breakthrough curves (2% C_2H_2 :2% C_2H_4) were 0.91, 1.26 and 1.72 mmol/g for Zn@FAU, Cu@FAU and Ni@FAU, respectively. The dynamic C_2H_2 uptake of Ni@FAU remained the same when the C_2H_4 concentration was increased to 50 % or the C_2H_2 concentration decreased to 1% (Fig. 2B). This capability is distinct to the porous sorbents functioning solely through physisorption (6), which show rapid reductions of dynamic uptakes with decreasing gas concentrations.

Furthermore, this dynamic uptake compared favorably to the leading MOFs, for example, 1.70 mmol/g of JCM-1 (19), 1.18 mmol/g of UTSA-200a (20), 1.23 mmol/g of NbU (21) and 0.73 mmol/g of SIFSIX-2-Cu-i (4). Additionally, Ni@FAU showed a higher overall acetylene productivity (116.8 mmol/g) compared with leading MOFs, such as NKMOF-1-Ni (96.0 mmol/g) (8), UTSA-200a (85.7 mmol/g) (20), and SIFSIX-2-Cu-i (53.3 mmol/g) (4). Also, Ni@FAU exhibited a very low dynamic uptake of

C₂H₄ (0.02 mmol/g) under the same conditions, and an exceptional C₂H₂/C₂H₄ dynamic selectivity of ~100 was achieved, compared with reported state-of-the-art sorbents (Table S3). A comparison of experimentally-determined C₂H₂/C₂H₄ dynamic selectivity against the dynamic uptake of C₂H₂ demonstrated the exceptional performance of Ni@FAU for C₂H₂/C₂H₄ separation (Fig. 2C).

We observed similar separation capability with Ni@FAU after increasing the column temperature from 298 to 308 K (Fig. S26) or adding CO₂ or H₂O into the gas stream (Fig. S27), while an ~25% decrease in the adsorption capability of C₂H₂ was observed for Ni@FAU sample that has been pre-adsorbed with H₂O (Fig. S28). The performance of Ni@FAU was further evaluated at 5 bar, where excellent C₂H₂/C₂H₄ separations were observed, and the dynamic uptakes of C₂H₂ and C₂H₄ increased to 2.25 and 0.39 mmol/g, respectively (Fig. S29). Moreover, Ni@FAU could be used to separate mixtures of propyne/propylene, butyne/1,3-butadiene and acetylene/propylene with high dynamic alkyne uptakes of 1.58~1.80 mmol/g and exceptional breakthrough selectivities of 92, 83 and 109, respectively, under ambient conditions (Fig. 2 E to G).

These results signal the potential of Ni@FAU for the adsorptive removal of alkynes from industrial olefin streams. Practical sorbents must be recyclable. After 10 cycles of C₂H₂/C₂H₄ separations with Ni@FAU, we observed no decline in the retention time, and full sorbent regeneration at 373 K between each cycle. (Fig. 2D). In contrast, Cu@FAU exhibited poor reversibility for C₂H₂/C₂H₄ separations because the formation of oligomers on Cu(II) sites blocking the pores (Fig. S30). To understand the role of Ni(II) in Ni@FAU, we introduced the metal ions into the FAU zeolites by different methods, such as ion-exchange (denoted as Ni-FAU) or wet impregnation (denoted as NiO/FAU) (Figs. S31-32). These two samples exhibited very poor separation of C₂H₂/C₂H₄ (Fig. 2A), suggesting that the excellent performance of Ni@FAU originates from its binding environment of the confined Ni(II) sites within the pores.

In situ NPD studies enabled the locations of the confined Ni(II) sites and the adsorbed gas (C₂D₂, C₂D₄, C₃D₄, and C₃D₆) molecules within Ni@FAU (Figs. S33-38, Table S4). Fourier difference map analysis of the desolvated Ni@FAU [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)] confirmed the structural integrity and the absence of residual nuclear density in the supercage. In-depth analysis revealed apparent residual nuclear density near the six-membered ring of the sodalite cage, which we assigned as Ni(II) ions stabilized by framework oxygen centres (Fig. S39). This assignment is consistent with DFT calculations (Fig. S6). By contrast, Ni(II) sites within Ni-FAU were primarily hexagonal prism sites, which were sterically hindered by the highly confined void (diameter of ~2.5 Å) for gas binding. This finding was consistent with its

poor separation performance (Fig. S40, Supplementary Text).

Upon gas loading, variations in Bragg peak intensities were observed and the binding domains of gases were successfully interpreted by Fourier difference map analysis and Rietveld refinements (Fig. 3 A to E). At low loading in $[\text{Ni}_{12}\text{Na}_{20}(\text{Al}_{44}\text{Si}_{148}\text{O}_{384})] \cdot (\text{C}_2\text{D}_2)_{12}$ (equivalent to ~ 1 mmol/g C_2D_2 uptake), all adsorbed C_2D_2 molecules were located at a single site, which is distributed over six equivalent positions in the supercage and exhibited a side-on interaction to the Ni(II) sites [$\text{C} \cdots \text{Ni} = 3.87\text{-}4.08$ Å, $\angle \text{C} \equiv \text{C} \cdots \text{Ni} = 91.1^\circ$], suggesting the binding interaction between the $\text{C} \equiv \text{C}$ bond and Ni(II) centres (Fig. S41). In addition, supplementary hydrogen bonds between $\text{D}_{\text{C}_2\text{D}_2}$ and framework oxygen were observed [$\text{D} \cdots \text{O} = 2.99$ Å, $\angle \text{C-D} \cdots \text{O} = 161^\circ$] (Fig. 3B). A similar host-guest binding mechanism [$\text{C} \cdots \text{Ni} = 3.83\text{-}4.05$ Å, $\angle \text{C} \equiv \text{C} \cdots \text{Ni} = 91.9^\circ$] was observed in $[\text{Ni}_{12}\text{Na}_{20}(\text{Al}_{44}\text{Si}_{148}\text{O}_{384})] \cdot (\text{C}_2\text{D}_2)_{26}$ (equivalent to ~ 2.3 mmol/g C_2D_2 uptake) with weaker hydrogen bonds to the framework oxygen [$\text{D} \cdots \text{O} = 3.27$ Å, $\angle \text{C-D} \cdots \text{O} = 151^\circ$]. The overall binding geometry is in excellent agreement with cation-acetylene π complexation (13, 22). X-ray absorption near edge structure (XANES) analysis confirmed the retention of divalent oxidation state of Ni(II) sites on acetylene binding (Fig. S42), and no elongation of C-C distance in bound C_2D_2 was found in the NPD analysis. These results were consistent with the selective yet reversible sorption.

However, $[\text{Ni}_{12}\text{Na}_{20}(\text{Al}_{44}\text{Si}_{148}\text{O}_{384})] \cdot (\text{C}_2\text{D}_4)_{17}$ (equivalent to ~ 1.5 mmol/g C_2D_4 uptake) exhibited a different binding geometry with two distinct sites (**1** and **2**) in the supercage (Fig. S41). C_2D_4 (**1**) molecules (accounting for $\sim 40\%$ of adsorbed C_2D_4) interact with Ni(II) [$\text{C} \cdots \text{Ni} = 3.11$ Å, $\angle \text{C}=\text{C} \cdots \text{Ni} = 77.8^\circ$] in a similar side-on manner to that of C_2D_2 , whereas C_2D_4 (**2**) (accounting for $\sim 60\%$ of adsorbed C_2D_4) showed no interaction with Ni(II), but multiple hydrogen bonds to the framework oxygen [$\text{D} \cdots \text{O} = 2.46\text{-}3.36$ Å, $\angle \text{C-D} \cdots \text{O} = 124\text{-}178^\circ$]. These NPD studies revealed the explicit difference between C_2D_2 and C_2D_4 upon adsorption in Ni@FAU. Additional π electrons in C_2D_2 and its linear geometry (and thus low spatial hindrance) enabled the formation of meta-stable $[\text{Ni}(\text{II})(\text{C}_2\text{D}_2)_3]$ complexes in the supercage of FAU, fully consistent with the mass spectrometry results. In contrast, the Ni(II) sites were heavily blocked by the bulky C_2D_4 by the formation of a dynamic 1:1 adduct, which led to the majority of adsorbed C_2D_4 being stabilized through weak hydrogen bonding and intermolecular guest-guest interactions. Similar host-guest binding interactions were observed in the structure models of $[\text{Ni}_{12}\text{Na}_{20}(\text{Al}_{44}\text{Si}_{148}\text{O}_{384})] \cdot (\text{C}_3\text{D}_4)_{20}$ and $[\text{Ni}_{12}\text{Na}_{20}(\text{Al}_{44}\text{Si}_{148}\text{O}_{384})] \cdot (\text{C}_3\text{D}_6)_{26}$ with $\text{C} \cdots \text{Ni}$ distances of 3.96 Å and 4.56 Å, respectively (only one binding site observed in each model; Fig. 3 D and E). Thus, the distinct nature of sorbent-gas interaction construed the high selectivity of Ni@FAU towards alkyne adsorption.

To visualize the binding dynamics of adsorbed C_2H_2 and C_2H_4 molecules, inelastic neutron scattering (INS) were conducted with Ni@FAU as a function of gas loading at 5 K (Figs. 43-48). Comparing to the INS spectra of solid C_2H_2 and C_2H_4 , the difference INS spectra (i.e., signals of adsorbed gas molecules) had differences in the low-energy region (<30 meV) that were correlated to the translation and libration modes of molecular vibration. In the solid state, molecules interact with adjacent ones in all three dimensions (Figs. 49-54, Table S5), resulting in coupling and dispersion of the modes (23). When adsorbed onto Ni(II) sites, gas molecules become isolated and restricted in an anisotropic environment, resulting in distinct INS features. The peak frequencies and (anisotropic) amplitude were directly dictated by the Ni(II)-gas interactions and the local environment.

We assigned the sharp and intense INS peaks at 3.8 meV for bound C_2H_2 (Peak I) and 2.5-3.8 meV for adsorbed C_2H_4 (Peak I' and II') to the motion of gas molecules within the plane perpendicular to the Ni(II)-gas axis, because these molecules are the least hindered and had the lowest frequencies and largest displacement. These INS spectra were in excellent agreement with the binding sites elucidated by NPD, in terms of Peak I correlating to the sole binding site of C_2H_2 , whereas Peaks I' and II' resulting from the two C_2H_4 sites with the former being the major adsorption site. Peak I for bound C_2H_2 occurred at a higher average energy, which confirmed the stronger interaction between Ni@FAU and C_2H_2 than that of C_2H_4 .

In addition, adsorbed gas molecules may rotate or twist around an axis perpendicular to the Ni(II)-gas axis and move toward or away from the Ni(II) sites, contributing to the peaks at 10 to 15 meV and at 15 to 30 meV, respectively. Moreover, the asymmetric and symmetric C-H bending modes for bound C_2H_2 at 81.5 and 99 meV, respectively, were blue-shifted comparing to that of solid C_2H_2 (80 and 95 meV, respectively; Fig. 4A), indicating these internal modes were strongly hindered upon binding on the Ni(II) sites. In contrast, no apparent shift was observed for the in-plane C-H rocking mode of C_2H_4 at 102 meV upon adsorption (Fig. 4B). Overall, the INS study showed excellent agreement with NPD, adsorption and breakthrough results and identified the crucial role of confined Ni(II) sites on the chemoselective binding of C_2H_2 in Ni@FAU.

Solid-sorbent-based techniques hold increasing promise to improve the operational efficiency of existing separation processes in petrochemical industries, and the separation of alkyne impurities from olefins can only be realised by exploiting the differences in their properties, such as dimensions (24, 25), shapes (26), conformation (27), polarisabilities (4), coordination abilities (28), binding affinity (29), and the geometry-matching with the sorbent pores (30). Zeolites with well-defined channels are considered

as viable candidates for gas separation for decades, primarily based upon their molecular sieving property (12). By confining atomically dispersed Ni(II) sites into the FAU zeolite channels, the discrimination between alkyne and olefin binding was amplified in Ni@FAU, which enabled the production of polymer-grade olefins under conditions relevant to practical processes. Combining its facile synthesis at large scale and excellent stability, the Ni@FAU sorbent offers a potential practical solution to the challenging alkyne/olefin separations.

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ACKNOWLEDGEMENTS

We thank Prof. Chuanming Wang from SINOPEC for helpful discussions. **Funding:** Supported by the National

Natural Science Fund of China (21722303, 21421001, 21688102), the Municipal Natural Science Fund of Tianjin (18JCQJC47400, 18JCZDJC37400), 111 Project (B12015, B18030), UK EPSRC (EP/P011632/1), the University of Manchester and Newton Advanced Fellowship by the Royal Society (W.S. and S.Y.). Beamlines WISH and I11 accessed through the STFC/ISIS Facility and Diamond Light Source, respectively. Inelastic neutron scattering experiments were conducted at the VISION beamline at ORNL's Spallation Neutron Source, which is supported by the Scientific User Facilities Division, Office of Basic Energy Sciences (BES), U.S. Department of Energy (DOE), under Contract No. DE-AC0500OR22725 with UT Battelle, LLC. The computing resources were made available through the VirtuES and the ICEMAN projects, funded by Laboratory Directed Research and Development program at ORNL. **Authors contributions:** Y.C. conducted zeolite syntheses and performance tests. S.L. and S.Yao participated in sample characterization. C.W. and L.J. performed mass spectrometry analyses. W.S. and N.G. analyzed the data and provided helpful discussions. X.H., W.L., I.S., P.M., Y.C., L.D.D., A.J.R.C. and C.C.T. collected and analysed synchrotron X-ray diffraction, neutron diffraction and inelastic neutron scattering data. S.Yang and L.L. directed and supervised the project. Y.C., X.H., S.Yang, and L.L. prepared the manuscript. **Competing interests:** Authors from Nankai University are inventors of a patent (CN202010177858.0) on materials reported in this work. **Data and materials availability:** Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 1939577-1939585. Copies of the data can be obtained free of charge from <https://www.ccdc.cam.ac.uk/structures/>. Other data needed to evaluate the conclusions in the Report are present in the Report or the Supplementary Materials.

SUPPLEMENTARY MATERIALS

Materials and Methods

Supplementary Text

Figs S1 to S55

Tables S1 to S5

Reference (31-55)

Figures and legends

Figure 1. Adsorption data of C_2H_2 and C_2H_4 for Ni@FAU. (A) Adsorption isotherms of C_2H_2 and C_2H_4 for Ni@FAU at 298 K; (B) TPD profiles of C_2H_2 - and C_2H_4 -adsorbed Ni@FAU after their individual adsorption, co-adsorption and successive adsorption (first C_2H_4 and then switched to C_2H_2) at 298 K; (C) In situ FTIR spectra of Ni@FAU on adsorption of C_2H_2 and C_2H_4 followed by He purging (dotted lines) at 298 K; (D) Mass spectra of species produced by pulsed laser vaporisation of the Ni@FAU target in the presence of carrier gas He, C_2H_2 (2%)/He and C_2H_4 (2%)/He.

Figure 2. Column breakthrough studies for alkyne/olefin separations. (A) Column breakthrough curves for a C_2H_2/C_2H_4 (2%/2%) mixture using various zeolite samples at 298 K. C_2H_2 and C_2H_4 are shown in purple and orange, respectively. (B) Effects of feed gas composition on C_2H_2/C_2H_4 separation over Ni@FAU at 298 K. (C) Plot of C_2H_2/C_2H_4 dynamic selectivity against C_2H_2 dynamic uptake under ambient conditions with state-of-the-art sorbent materials. (D) View of recyclability of Ni@FAU for the separation of C_2H_2/C_2H_4 (2%/2%) at 298 K. Sample regeneration was achieved by treatment in He at 423 K for 30 min. (E-G) Column breakthrough curves for propylene/propyne (2%/2%), butyne/1,3-butadiene (2%/2%) and acetylene/propylene (2%/2%) over fixed-beds packed with Ni@FAU at 298 K. Total gas flow: 6.0 mL/min, sample weight: 0.2 g.

Figure 3. Views of crystal structures for the Ni@FAU zeolite as a function of gas loading. All structures were derived from Rietveld refinements of neutron powder diffraction data at 7 K [Si/Al: yellow; O: red; Ni: green. C: grey; D: white; C₂D₄ (**1**) is highlighted in blue for clarity]. The host-guest interactions are highlighted in dash lines and the estimated standard deviation values for binding distances are typically within 0.02-0.08 Å. Views of binding sites for adsorbed gas molecules in [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)]·(C₂D₂)₁₂ (**A**), [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)]·(C₂D₂)₂₆ (**B**), [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)]·(C₂D₄)₁₇ (**C**), [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)]·(C₃D₄)₂₀ (**D**), and [Ni₁₂Na₂₀(Al₄₄Si₁₄₈O₃₈₄)]·(C₃D₆)₂₆ (**E**).

Figure 4. Inelastic neutron scattering (INS) spectra for Ni@FAU as a function of gas loading. (A) Comparison of INS spectra of C_2H_2 -loaded Ni@FAU and that of solid C_2H_2 . **(B)** Comparison of INS spectra of C_2H_4 -loaded Ni@FAU and that of solid C_2H_4 . Enlarged details showing the translational/librational and the internal vibrational modes of adsorbed C_2H_2 and C_2H_4 molecules. Difference spectra were produced by removing signals of the bare zeolite and sample holder. Raw spectra are shown in the Supplementary Materials.