

Adaptive alkyne trap purifies crude ethylene

Yi Xie & Banglin Chen

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Removing trace alkyne contaminants in crude ethylene is challenging by traditional catalytic hydrogenation. Now, adsorptive separation through advanced materials design selectively sequesters alkynes in a single-step pathway to produce high-purity ethylene from complex mixtures.

Ethylene is one of the most largely produced chemical feedstocks in the petrochemical industry. The importance of ethylene to human society is manifested by a wide range of downstream chemical manufacturing, such as polyethylene, one of the most produced plastics in the world. Industrial ethylene plants produce crude ethylene by hydrocarbon steam cracking with a series of undesired impurities, including ethane, propylene and alkynes¹. Considering the scale of ethylene production and the similarity of the physicochemical properties of the impurities, industrial ethylene purification is one of the most energy-intensive processes. Although substantial effort has been devoted to optimizing the catalytic hydrogenation reaction to minimize alkyne contamination, it is still challenging to realize high alkene selectivity over alkanes and full conversion².

Adsorptive separation offers an energy-efficient solution to mitigate this problem. The energy consumption of obtaining high-purity ethylene by selective impurity removal using porous materials is estimated to be much lower than conventional methods³. Given the similarities between alkene and alkyne molecules, high selectivity toward the alkyne over the alkene requires atomically precise pore engineering for specific molecular recognition. Metal–organic frameworks (MOFs), a class of organic–inorganic hybrid reticular materials, have been widely explored and commercialized for large-scale gas separations in industry for such applications⁴.

Over the past decade, scientists have advanced pore engineering through reticular chemistry, pushing the limits of gas separation. Notable advancements in separating alkynes from alkenes in binary mixtures such as C_2H_2/C_2H_4 and C_3H_4/C_3H_6 have been achieved by synergistically engineering the pore surface with robust binding sites and tuning the pore size to minimize alkene coadsorption⁵. However, alkene purification is far from a binary mixture separation in real-world scenarios. Selective separation of the desired product in a dynamic, multicomponent adsorption process and enabling single-step collection is of great interest.

Now, writing in *Nature Chemical Engineering*, Dan Li, Weigang Lu and co-workers report a microporous MOF named JNU-3, featuring a one-dimensional (1D) pore channel orthogonally decorated by a unique array of dynamic pockets⁶ (Fig. 1). These pockets demonstrate high selectivity in recognizing alkynes over ethylene. The unique desymmetrized ligand geometry contributed to a balance between robustness and flexibility originating from local linker motion. The overall molecular scaffold of the MOF remains rigid in the

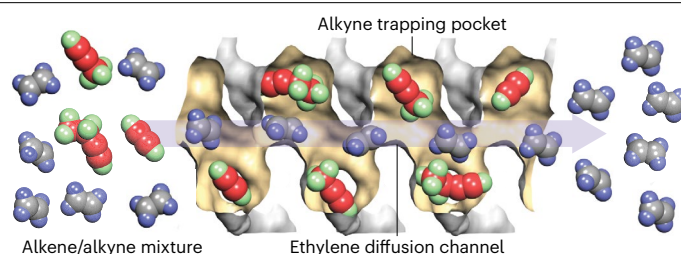


Fig. 1 | An adaptive pocket array in a porous material serving as alkyne traps for one-step ethylene purification. A schematic depiction of a mixture of ethylene and alkynes diffusing through the pore channel where the alkyne impurities are selectively captured at the side pockets that are orthogonal to the 1D channel. High-purity intermediate-sized ethylene is produced spontaneously with large capacity. The carbon and hydrogen atoms of alkyne molecules are shown as red and green while those of ethylene molecules are shown in gray and blue.

desolvated state, termed as JNU-3a, featuring 1D channels and coexisting cavities interconnected to the channel, enabling the transport of hydrocarbon molecules. The gourd-like opening of the cavity is stretchable due to the surrounding locally flexible motifs, previously demonstrated to enable highly selective propylene capture from propane⁷.

The authors showed that the activated JNU-3a exhibited more than four times higher adsorption uptake for key alkyne molecules relevant to the ethylene purification industry (C_2H_2 , C_3H_4 and 1- C_4H_6) compared with C_2H_4 at elevated temperature. The large drop of ethylene uptake and high preservation of alkyne highlight the thermoregulatory gating effect induced by the flexible–robust framework⁸. Remarkably, the isotherms indicated that the MOF is able to capture alkynes at very low pressure, which is highly desirable for practical separations considering the trace amount of alkynes present in the feed ethylene stream. As a result, the excellent selectivity of alkynes over ethylene renders this material a top-performing candidate for simultaneous multicomponent alkyne capture.

The binding affinity for various gases was quantified experimentally, confirming that the binding strength toward alkynes is nearly double that of ethylene within the molecular trap of this MOF. The host–guest binding mechanism was further elucidated by in situ single-crystal X-ray diffraction with gas molecules encapsulated inside the crystal lattice. A guest-dependent pocket-opening deformation is clearly shown by the crystal structures where it can be expanded by 1 Å in the presence of the largest 1- C_4H_6 . The alkynes are stabilized inside the cavity via hydrogen bonds with host linkers and the weak van der Waals contacts on the carbon–carbon triple bond, while the ethylene experiences much weaker interactions, as supported by additional theoretical calculations. The absence of gas molecules in the 1D pore channel corroborates the pocket-binding-dominated mechanism.

The authors demonstrated the capability of JNU-3a for the practical separation of alkynes from ethylene by a series of column breakthrough experiments at different conditions and scales.

The dynamic separation at the laboratory scale showed that all alkynes are simultaneously retained in the fixed-bed column and break through at almost the same time, indicating that the alkynes are captured in a non-competitive manner, which is rarely observed in other porous materials and is challenging to achieve. In a single cycle of a breakthrough experiment, more than 800 ml g^{-1} of high-purity C_2H_4 ($\geq 99.9995\%$) is produced at various flow rates and even in the presence of water vapor. Surprisingly, this material can be feasibly regenerated at room temperature in vacuo. More importantly, the authors successfully realized the implementation of a pilot-scale set-up and collected high-quality ethylene in a gas cylinder, showcasing the promise of JNU-3a for future ethylene purification.

This work highlights how a flexible-robust porous material can tackle energy-intensive separations of complex multicomponent mixtures. Its adaptability acts as a 'lock-key' switch, enabling precise discrimination between different gases. While undesired impurities are contemporaneously captured in the molecular traps, the valuable product can be efficiently generated in one single adsorption cycle without being desorbed. This promising method might potentially be extended to the purification of other important chemicals, such as propylene and styrene. However, challenges remain in the rational design of the adaptiveness of porous materials and predicting multicomponent competitive adsorption-separation behavior. These currently elusive mechanisms are envisioned to be decoded by virtue

of advanced characterizations, simulations and machine learning. More insights are highly desired for customizing new framework materials with well-defined flexibility for various chemical separations in the future.

Yi Xie¹✉ & Banglin Chen²✉

¹Department of Chemistry, Northwestern University, Evanston, IL, USA.

²College of Chemistry & Materials Science, Fujian Normal University, Fuzhou, China.

✉ e-mail: yi.xie@northwestern.edu; banglin.chen@fjnu.edu.cn

Published online: 11 January 2024

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Competing interests

The authors declare no competing interests.