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Commentary

Ultrafast-adsorption-kinetics molecular sieving of propylene from propane

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The separation of propylene (C_3H_6) and propane (C_3H_8) is very costly due to similar physical-chemical properties and has been listed as one of the seven chemical separations to change the world [1]. High-purity C_3H_6 is an important raw material to produce polypropylene and acrylonitrile [2]. However, C_3H_8 is produced as a by-product in the production process of C_3H_6, which has a similar structure and boiling point as those of C_3H_6 [3]. Traditionally, the separation of C_3H_6 and C_3H_8 by distillation has high energy consumption and an unremarkable separation effect [4]. Therefore, there is an urgent need to develop more energy-saving and efficient methods for the separation of C_3H_6 and C_3H_8.

A molecular sieve is a kind of porous material that can selectively adsorb molecules with specific sizes and shapes and is often used for substance purification [5,6]. In the past few decades, due to the contradiction between simultaneous molecular sieving and diffusion within their restricted nanopores, molecular sieves have been impeded by slow adsorption kinetics [7]. Therefore, designing molecular sieves with appropriate pore sizes to separate C_3H_6 and C_3H_8 with low energy consumption and high separation efficiency has remained a challenging task.

Recently, Cui et al. published their latest research on C_3H_6 purification in *Science* [8]. They developed a molecular sieve designated as ZU-609, which comprised organic linkers and copper metal nodes and was modified rationally by incorporating sulfonic acid anions based on the two-dimensional structure of ZU-609 (**Figure 1(A)**). This design successfully controlled the pore size and shape of the molecular sieve, resulting in the formation of molecular-sieving gates and rapid diffusion channels in ZU-609. As shown in **Figure 1(B)** and **Figure 1(C)**, the cross-sectional size of the molecular sieving gate in ZU-609 was 4.2 Å × 5.1 Å, which was between the molecule sizes of C_3H_6 (4.1 Å × 5.1 Å) and C_3H_8 (5.3 Å × 5.1 Å). This precise cross-sectional cut-off size of the sieving gate allowed C_3H_8 to be excluded from C_3H_6. The equilibrium adsorption isotherms indicated an uptake ratio of 22.3 for C_3H_6 and C_3H_8 at 298 K, which proved that ZU-609 has excellent C_3H_6-sieving performance (**Figure 1(D)**).

For porous materials, adsorption kinetics is an important index for measuring gas adsorption efficiency [9–11]. Cui et al. compared ZU-609 with previously reported molecular sieves, such as Zeolite-4A, Co-gallate, and KAUST-7 [8]. It was found that the co-existed large channels composed of sulfonic anions and helically arranged metal-organic structures resulted in the diffusion coefficient of C_3H_6 in ZU-609 that was one to two orders of magnitude higher than in other molecular sieves (**Figure 1(E)**). The simulation analysis of ZU-609 after adsorbing C_3H_6 demonstrated that the adsorption configuration of C_3H_6 molecules was mainly distributed around the anions

in ZU-609 (**Figure 1(F)**). Furthermore, the minimum energy path profile simulated using the dispersion-corrected density functional theory (DFT-D) clearly showed the local diffusion energy barriers as propylene molecules diffused through the channel of ZU-609 (**Figure 1(G)**). These computational studies provided molecular-level insights into the confined adsorption and adsorption kinetics of C_3H_6 in ZU-609.

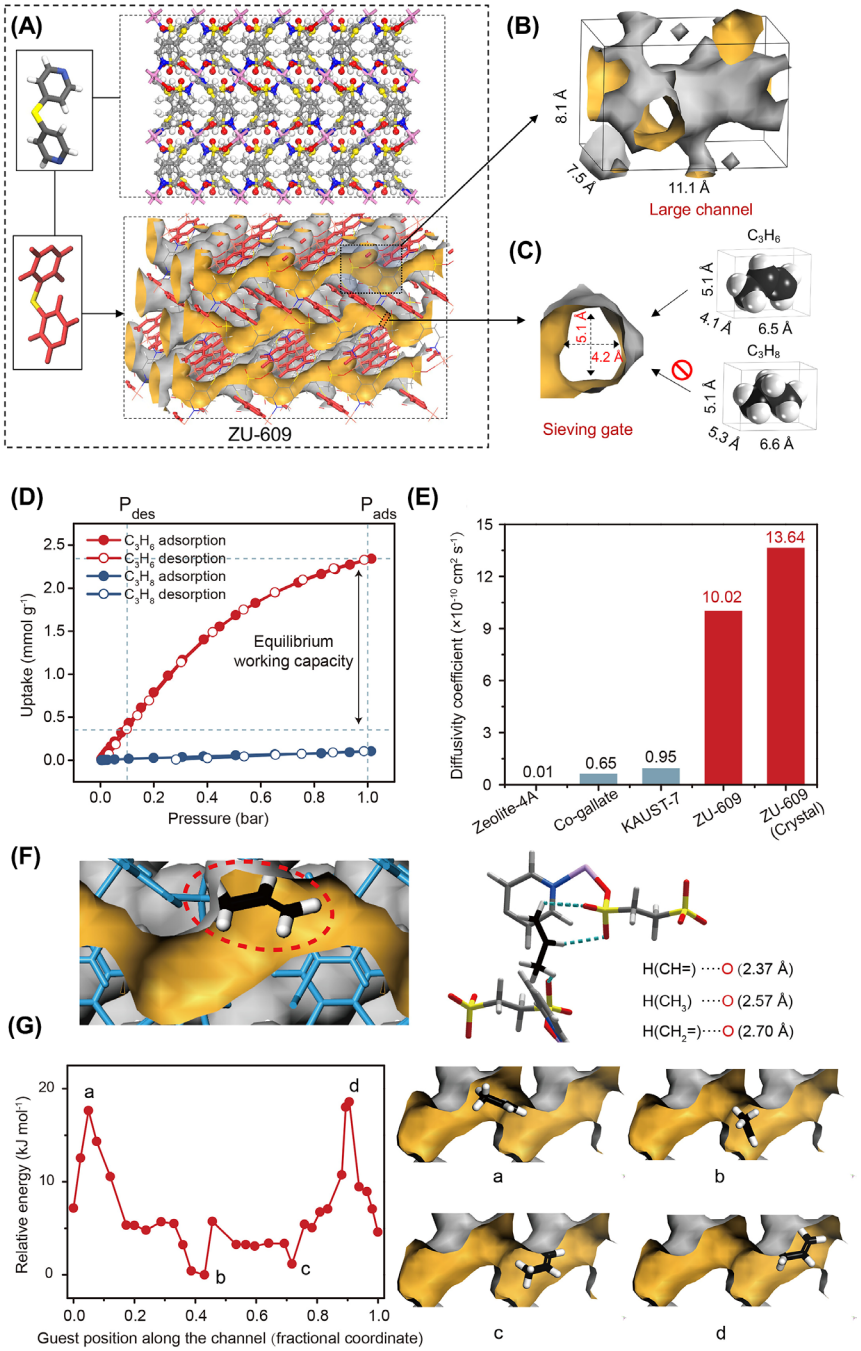

Figure 1. (A) Structure of ZU-609. **(B)** Structure of large channel. **(C)** Structure and size of sieving gate, C_3H_6, and C_3H_8. **(D)** Gas sorption isotherms of C_3H_6 and C_3H_8 by ZU-609. **(E)** Comparison of C_3H_6 diffusivity coefficient of ZU-609 with those of reported porous materials. **(F)** Adsorption configuration of C_3H_6 in ZU-609. **(G)** Simulated minimum energy path profile and images for C_3H_6 in ZU-609. Reproduced with permission from Cui et al. [8]. Copyright 2024 AAAS.

Notably, breakthrough experiments indicated that ZU-609 had a remarkable sieving effect on an equimolar C_3H_6/C_3H_8 mixture (**Figure 2(A)**). Compared with Co-gallate, KAUST-7, Y-abtc, and ZU-609 exhibited excellent capture ability for C_3H_6, and the corresponding C_3H_6 productivity was about 32.2 $L.kg^{-1}$ (**Figure 2(B)**). Surprisingly, even at a gas flow rate of 9 $NmL.min^{-1}$, the separation purity of C_3H_6 reached 99.97% and the dynamic capacity of C_3H_6 in ZU-609 maintained an equilibrium capacity of 94.1% (**Figure 2(C)** and **Figure 2 (D)**).

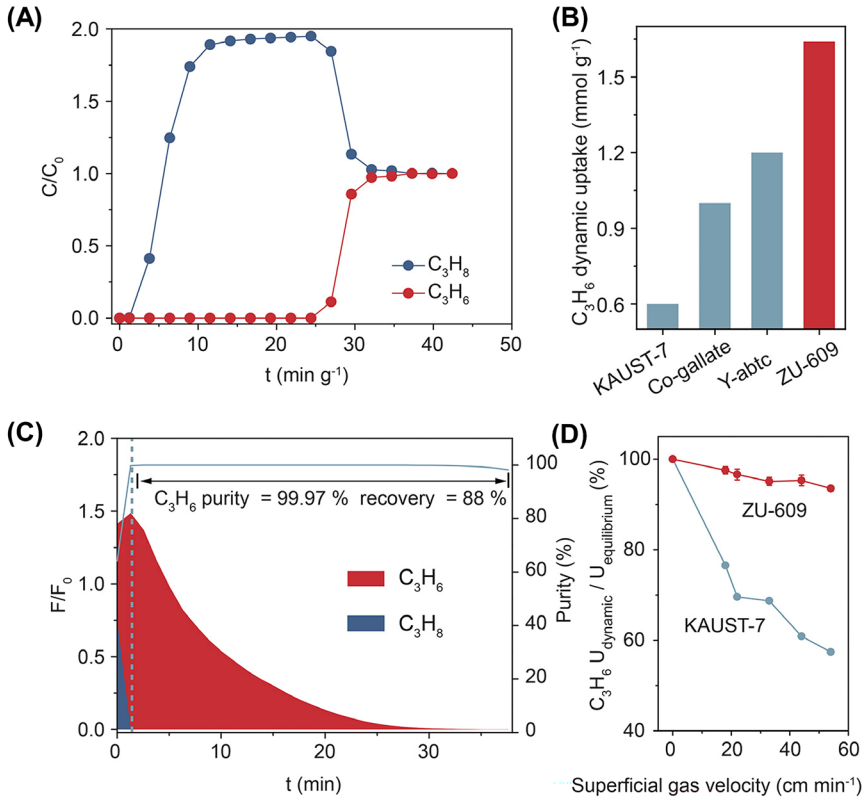

Figure 2. (A) Breakthrough curves of ZU-609 for mixture of equimolar C_3H_6/C_3H_8. **(B)** Comparison between dynamic uptake of C_3H_6 by ZU-609 and those of other reported materials. **(C)** Purity of eluted C_3H_6 and flow rate curve of desorbed C_3H_6 and C_3H_8 by ZU-609. **(D)** Ratios of C_3H_6 dynamic absorption to equilibrium absorption of ZU-609 and KAUST-7 at varying superficial gas velocities for equimolar C_3H_6/C_3H_8 mixture. Reproduced with permission from Cui et al. [8]. Copyright 2024 AAAS.

In summary, Cui et al. [8] developed a new type of molecular sieve of ZU-609 with excellent C_3H_6/C_3H_8 propane-separation performance. The gate cross-sectional size of ZU-609 was precisely controlled at 4.2 Å × 5.1 Å, which was between the molecular sizes of C_3H_6 and C_3H_8, successfully achieving effective molecular sieving. The unique combination of anionic sites and helical metal-organic motifs enabled the diffusion coefficient of C_3H_6 within ZU-609, which was one to two orders of magnitude higher than those of other molecular sieves. ZU-609 exhibited excellent dynamic adsorption performance for the C_3H_6/C_3H_8 mixture, with a yield of 32.2 L kg^{-1} and a separation purity of 99.97%, which was significantly superior to those of

other molecular sieves. These exceptional results highlight the tremendous potential of rapid-adsorption molecular sieves for industrial-scale separation.

Furthermore, increasing stability and recyclability under industrial operating environments remains an important priority. Integrating rapid-kinetic molecular sieves with membrane separation, adsorption methods, and other technologies allows for more cost-effective and efficient gas separation. With pioneering rapid-adsorption molecular sieving, this work lays the foundation for the design of next-generation materials and provides key insights toward enhancing energy efficiency and enabling sustainable technologies.

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Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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