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Research Briefing template

TITLE: Separating molecules by their shapes can purify natural gas.

This is a summary of: Sheng Zhou, Mohamed Eddaoudi, S. Z., M. E. *et al*. Asymmetric pore windows in MOF membranes for natural gas valorization. *Nature* https://doi.org/10.1038/xxxx (2021)

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STANDFIRST:

Membranes made from metal-organic frameworks contain tiny (modular) pores that can separate mixtures of gases. Editing the shape of these pore-apertures offers a new approach to improving molecular separation, enabling researchers to fabricate a membrane that can remove nitrogen and carbon dioxide from natural gas in an energy-efficient and cost-effective way.

SECTION 1: The mission

Natural gas is an abundant energy source poised to play a major role in the global transition to net-zero emissions[1-3]. But the methane in natural gas reservoirs is usually contaminated with nitrogen and carbon dioxide. Nitrogen dilutes the heating value of natural gas, and must be removed in order to fully valorize this resource[4].

Separating nitrogen from methane remains a major challenge, though, in part because their boiling points, polarizability and kinetic sizes are all similar. Expensive cryogenic distillation is currently the only technology deployed at large scale to tease the two apart.

Gas separation membranes could offer a more economical method to purify natural gas. These membranes work by selectively allowing one component from a mixture of gases to pass through their pores. But the minor differences between methane and nitrogen means that even state-of-the-art membranes offer poor selectivity between these molecules. Narrowing a membrane's pores can improve its selectivity, but this often slows the flow of molecules through the membrane and reduces its productivity.

SECTION 2: The solution

We have designed a porous membrane that can separate nitrogen from methane by exploiting one significant difference between the molecules: their shapes. Nitrogen is a linear molecule, while methane is tetrahedral, offering a trefoil-shaped profile. Our membrane is built from a metal-organic framework (MOF), a crystalline lattice of metal-based nodes linked by organic molecules that act as struts.

For example, a MOF called Zr-*fum*-**fcu**-MOF contains zirconium-based nodes and fumarate (*fum*) linkers, and has face-centered cubic (**fcu**) topology. Its narrow pore-apertures have a characteristic trefoil shape[5] (Fig. 1a), which a methane tetrahedron can just fit through. We hoped that methane penetration could be blocked by subtly editing these pore-apertures, transforming their trefoil shape into an irregular shape (Fig. 1b).

To that end, we created a new MOF containing two different linkers, fumarate and mesaconate (*mes*), in a 2:1 ratio. The Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membrane has a precisely edited pore-aperture shape, where two fumarates and one mesaconate form an asymmetric triangular window that blocks methane transport but allows nitrogen to pass through. This MOF enabled a shape-mismatch-induced separation process to selectively remove nitrogen from nitrogen/methane mixtures.

The membrane exhibits a record-breaking nitrogen permeance greater than 3000 gas permeation units (GPU, which measures the rate of molecular flow through a membrane at a given pressure). It also shows a 15-fold greater selectivity for nitrogen over methane. This performance is maintained under practical pressures of 50 bar.

Furthermore, the membranes can simultaneously remove both carbon dioxide and nitrogen from natural gas, with a permeance of >5300 GPU and selectivity of >24. Techno-economic analysis shows that our membranes have the potential to reduce methane purification costs by ~66% for nitrogen, and by ~73% for simultaneous removal of carbon dioxide and nitrogen, relative to cryogenic distillation and amine-based carbon dioxide capture.

SECTION 3: The implications

These fabricated membranes could be an energy-efficient and cost-effective alternative to the current methods for natural gas valorization. The shape-mismatch-induced separation process, realized by precise pore-aperture editing, could be applied to other complex and challenging separation systems that cannot be addressed using conventional approaches.

We have shown that the membrane is stable to traces of water and corrosive hydrogen sulfide found in natural gas. But these contaminants could decrease the permeance of the membrane — their strong affinities to the MOF means these molecules could clog pore-apertures, and block the diffusion of nitrogen. As a result, a dehydration/desulfurization process might be needed before natural gas is passed through the membrane unit, in order to maintain its high productivity.

We now plan to translate the designed membranes onto hollow fiber supports, which have a higher surface-to-volume ratio, packing density and excellent processability for large-scale industrial applications. We have already shown that these membranes can be fabricated on stainless-steel nets, proving the viability of using such inexpensive supports.

SIGNING OFF

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SECTION 4: Behind the paper

When researchers aim to fabricate a gas-separation membrane, they usually check the kinetic size of each gas component and then look for a material with a suitable pore-aperture size. This routine logic makes sense in most scenarios, but not every time — as evinced by the problem of nitrogen/methane separation. Facing this challenge, we decided to think outside the box. Prof. Eddaoudi's focus on structural details, and our research group's ethos of being meticulous about structures, inspired my pursuit of a ‘nose’ that relied on the shape difference between nitrogen and methane. After many brainstorming discussion with Prof. Eddaoudi, we envisioned and conceptualized a pore-aperture editing strategy to make the best use of this shape difference. Thanks to the highly tunable nature of the structure of MOFs, and our group’s well-established platform for the electrochemical synthesis of MOF membranes[5], we were able to realize this exciting new concept of shape-mismatch-induced separation. **S.Z.**

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FIGURE

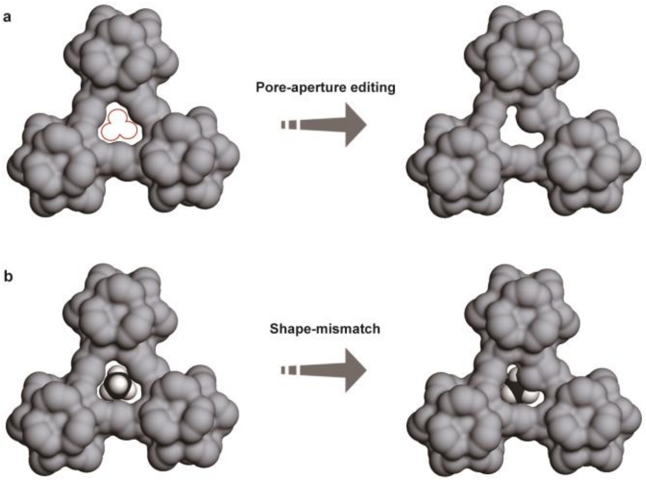

FIGURE 1 LEGEND

Pore-aperture editing enables shape-mismatch-induced separation.

Pore-aperture editing can transform a MOF’s regular trefoil-shaped pore entrance so that it has an irregular shape (a). Although a methane molecule could fit into the original pore-aperture, it cannot pass through the edited pore-aperture, due to shape mismatch (b). This strategy allows nitrogen to be separated efficiently from a nitrogen/methane mixture.

EXPERT OPINION

Three aspects of this work are especially notable: the rational approach for pore engineering; the testing of the membranes under conditions relevant to real-world practices; and the techno-economic analysis for the separation of nitrogen and methane. The idea of creating a mismatch between the pore-aperture shape and the molecular configurations of a gas mixture could be a model for further membrane development.
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FROM THE EDITOR

This work stands out because, although using metal–organic framework materials for gas separations is a busy and productive research area, it is rare to read a paper on the topic which combines materials design with excellent performance as well as technoeconomic analysis to suggest that real-world applications are a realistic prospect, rather than far-off dream.
Claire Hansell, Senior Editor and Team Manager, Nature