

est potential tetrapod trackways suggest a mode of locomotion more similar to that of salamanders (5). If the locomotion seen in mudskippers is a more adequate model, it needs to be shown how alternating, hindlimb-driven (salamander-like) locomotion evolved later on (6, 7). More intermediate fossils are needed (8), but alternative modern analogs should also be considered (9). Moreover, the mostly aquatic Late Devonian stem tetrapods with highly limited terrestrial capabilities probably encountered challenging inclined sandy or muddy banks when moving onto land. This is the issue that McNroe *et al.* address in their interdisciplinary study. Drawing from diverse lines of argumentation and using the crutching



Coordinated tail use. Mudskippers use their fins and tail to navigate difficult terrain while out of the water. McNroe *et al.* use biomechanical analysis of mudskipper motion, mathematical modeling, drag measurements in granular media, and bioinspired robots to investigate whether early land vertebrates also relied on their tails to move on land.

model as their starting point, the authors propose that stem tetrapod tails may have improved the robustness of locomotion on challenging substrates, in a similar fashion as seen in mudskippers.

Both in robots and mathematical models, parameter combinations can systematically be varied to access the sensitivity of the result to variation in individual parameters (2, 10)—something that is not possible when only living organisms are used as analogs. Bioinspired robots are increasingly used as heuristic tools to investigate animal adaptive behavior (11). Similarly, computer animation has great power for generating hypotheses on motion using digital models (10). However, both approaches face the same problem: how to decide which of the many possible modes of locomotion is the most realistic (10). To validate a model,

it needs to be shown that its predictions closely match experimental data of the biomechanics measured in modern analogs. Only if this is achieved should the model be used to infer characteristics of a fossil (12).

Using bioinspired robotics as well as animations or even sophisticated musculoskeletal modeling (13) to elucidate function in extinct organisms has further advantages. Optimization criteria can be used to find plausible parameter combinations without user interference (10, 11). The results become less dependent on subjective opinion, and future insights can more readily be incorporated into existing models. It is this integrative methodology, exemplified by McNroe *et al.*'s study, that fosters increasingly interdisciplinary analyses of function in fossils.

Whether or not mudskippers' tail use is an adequate modern analog for stem tetrapods remains debatable. It can only be confirmed by identifying morphological correlates that are present both in modern analogs and in fossils. McNroe *et al.* do not resolve this issue, but rather contribute to a more general understanding of the mechanism of coordinated tail use during crutching locomotion on soft substrates. The authors were interested in the overarching principle of tail use, and their models serve as templates. In contrast, attempts to reconstruct the function of a structure of a specific fossil should use its anatomical details as anchors for the model (3, 14).

McNroe *et al.*'s study shows that recruiting expertise from different fields facilitates integrated modeling approaches to problems of form and function in extinct organisms.

This enables new hypotheses to be generated and existing ones to be tested in a transparent and reproducible manner. ■

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CHEMISTRY

Molecular sieves for gas separation

Metal-organic framework materials enable efficient separation of similar gases

By Jerry Y. S. Lin

Separation and purification are critical industrial processes for separating components of chemical mixtures, and these processes account for about half of industrial energy usage (1). Gas mixtures of compounds with very similar physical properties are particularly difficult to separate. On pages 137 and 141 of this issue, Cadiau *et al.* (2) and Cui *et al.* (3), respectively, show that microporous materials can be designed to have high adsorption capacity and selectivity for particular hydrocarbons, enabling energy-efficient separation.

Traditional gas separation technologies use distillation, requiring repeated evaporation and condensation of the mixture, or absorption with a liquid medium that requires cooling and heating a large amount of nonactive solvent to complete a separation cycle. Both technologies are energy intensive. Newer technologies use solid separation media and are generally more energy efficient. For example, membrane-based separation can require 90% less energy than distillation to separate propylene-propane mixtures (1, 4). The cornerstone of these newer separation processes is a solid adsorbent or membrane, often made of a microporous material with a pore size smaller than 0.5 nm and a large internal pore surface area (>300 m²/g).

In many microporous solid media used as adsorbents or membranes (5), there is a trade-off between adsorption capacity (or permeability) and selectivity for separating challenging gas mixtures, making it difficult for the adsorption or membrane process to achieve high separation efficiency. To improve adsorption capacity while also maintaining selectivity, scientists have modified the internal surface properties of porous media to enhance interaction of the adsorbent surface with a specific component and thus increase the adsorption capacity for that component. For example, the crystalline microporous zeolite LiX provides good adsorption capacity for nitrogen over oxygen due to Li cation-

nitrogen interactions (6). Selectivity can also be achieved by varying the pore size of the solid media to provide molecular sieving, as in carbon molecular sieve (CMS) materials (6). However, zeolites have a limited number of crystal structures and CMS materials have amorphous pore structures, making it hard to generalize these approaches.

Metal-organic frameworks (MOFs) are microporous crystalline materials constructed from transition-metal ions and bridging organic ligands (7). These materials can form a vast variety of ordered structures, pore sizes, porosity, and functional groups. MOFs can be made into effective adsorbents or membranes for gas separation by introducing

separation, the ultramicroporous mixed metal-organic framework (M²MOF) family has high selectivity but low acetylene adsorption capacity (11). The two studies in this issue overcome this trade-off problem through crystal engineering that controls both surface chemistry and pore size of the MOF materials. The resulting MOF materials have high adsorption capacity and selectivity for separation of acetylene-ethylene mixtures, as reported by Cui *et al.*, and propylene-propane mixtures, as shown by Cadiau *et al.*

The materials are based on a group of MOF materials with a pillared square-grid structure (see the figure) (12). The unit cell consists of eight metal nodes, joined by an

action. These interactions are much weaker for ethylene because it is far less acidic than acetylene. They identify MOFs with very high acetylene adsorption capacity and acetylene-ethylene selectivity (2.1 mmol/g and ~44.8 at 0.025 bar, both higher than for previously reported materials). Variation in the MOF pore size does not influence the kinetics of acetylene and ethylene adsorption. Rather, it influences the host-guest and guest-guest interactions and hence the equilibrium adsorption capacity and selectivity.

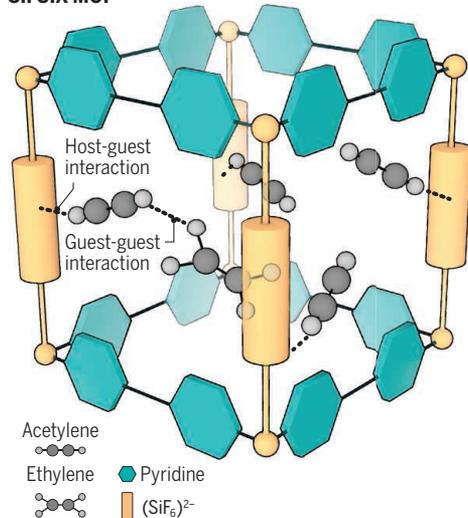
Cadieu *et al.* study the same class of MOFs but take a different approach, designing an adsorbent for propylene-propane separation based on the molecular exclusion principle. They focus on the pillar-structured MOF with the smallest cage, using an organic linker containing only one pyrazine (see the figure). Furthermore, they replace the (SiF₆)²⁻ pillars in the cage with somewhat bulkier (NbOF₅)²⁻ pillars (called NbOFFIVE). This causes tilting of the pyrazine molecule on the linker, effectively reducing the aperture opening from 0.50 nm [with (SiF₆)²⁻ pillars] to 0.30 nm. With strong host-guest and guest-guest interactions for propylene, the small aperture permits transport of the smaller propylene molecules into and out of the MOF cage, but excludes the slightly bulkier propane. Thus, this MOF shows high propylene adsorption capacity and unprecedented (essentially infinite) propylene-propane selectivity.

The two studies present a novel direction for the design and synthesis of MOF-based adsorbents for challenging gas separations. The authors report some stability data, but it remains to be shown whether the adsorbents are stable under industrially relevant conditions. The adsorption kinetics should also be studied, especially the kinetic effects of MOF framework flexibility at high adsorbate loading. Industrial application requires pelleting, which might affect the adsorption characteristics. Future studies should also aim to integrate these MOFs into membranes for continuous gas separation processes. ■

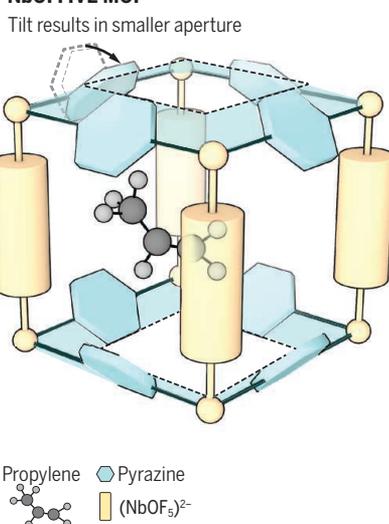
Highly selective

In this issue, Cadieu *et al.* report a pillared square-grid-structured MOF with a controlled aperture opening for molecular sieving of propylene over propane (right). Cui *et al.* have designed similar structured MOFs with optimized surface functionalities and cage sizes for preferential adsorption of acetylene over ethylene (left).

SIFSIX MOF



NbOFFIVE MOF



surface functionalities, such as exposed metal centers (8) or amines (9), in MOF-74 families to enhance CO₂ adsorption capacity and selectivity over N₂. Alternatively, their molecular sieving characteristics can be exploited, as has been shown for the MOF material ZIF-8 for propylene-propane separation (10).

These MOF materials have improved separation characteristics compared to classical materials, but they still suffer from the adsorption capacity versus selectivity trade-off for gas separations. For example, for acetylene-ethylene separation, the MOF-74 family with a high density of open metal sites shows high acetylene adsorption capacity but low separation selectivity (8). For the same

organic linker containing one or two pyridines or pyrazines, that form the upper and bottom squares. The squares are pillared apart via (SiF₆)²⁻ anions (called SIFSIX). The pore aperture size on the squares can be controlled by varying the length and/or orientation of the organic linker. The surface chemistry is determined by the pillar ions, metals, and organic linker molecules.

Cui *et al.* synthesized four (SiF₆)²⁻-pillared MOF materials with different pore sizes by changing the length of the organic linker or creating an interpenetrated polymorph structure. They obtained high acetylene adsorption capacity on MOFs of appropriate pore size by optimizing hydrogen-bond interactions between acetylene molecules and strongly basic (SiF₆)²⁻, van der Waals interactions between acetylene molecules and the organic linker, and the guest-guest molecule inter-

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