An efficient nano-sieve

A rigid and easily scalable metal organic framework is shown to be among the most efficient materials for separating ethylene from ethane.

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Energy supply, consumption and generation are among the biggest challenges humankind faces nowadays. Depletion of natural resources and the undeniable relationship between energy generation and global warming call for immediate action. In the long term, green energy sources, such as solar energy will inevitably take over from current technologies, but this will take a number of decades.¹ In addition to decreasing emissions of greenhouse gases, energy efficiency will play a significant role in enabling sustainable development.² The energy used in manufacturing accounts for circa 55 % of overall energy consumption, and the production of base chemicals is one of the most energy intensive industries. This is because separation units require large energy inputs, accounting for 10-15% of the world's energy consumption and therefore responsible for millions of tonnes of CO₂ emitted every year.³ Separating molecules that differ in size by less than 10% is not easy: imagine how much time (hence energy) it would take to separate, by hand, millions of marbles of 10 and 9 mm diameter. Now imagine only making one mistake every 200 marbles (if a purity of 99.5% is targeted). It would be much easier to have a sieve with a regular size of 9.5 mm through which only the smaller marbles would pass. On page XXX of this issue, Chen, Zhou and co-workers describe a molecular sieve that efficiently discriminates ethane from ethylene, two molecules that differ in size by 0.01 nm.⁴ This is a remarkable scientific achievement (to date only a few materials with this specific pore size are known)⁵⁻⁷ that may have important technological implications.

Ethylene, mostly used for the production of polyethylene and ethylene oxide, is the olefin most in demand, with over 150 million tonnes utilised in 2017. Ethane is a common byproduct during ethylene manufacture that needs to be separated to achieve the high purity of ethylene required to meet polymerization grade (99.9%). Because of the small difference in size and boiling points between olefin (0.38 nm, -103.7 °C) and paraffin (0.39 nm, -88.5 °C), this separation is industrially carried out by cryogenic distillation (-160 °C) at high pressures and high reflux ratios.³ The development of energy efficient and effective ethane/ethylene separation methods able to deliver high purity ethylene is one of the biggest challenges for the materials' and engineering communities. For an adsorbent to be considered promising, it has to display high selectivity and high capacity in combination with stability and easy scalability. A shape selective adsorbent that allowed the adsorption of only one component of the mixture while still offering fast adsorption kinetics would offer tremendous advantages in simplifying the separation scheme. In addition, if such an adsorbent possessed moderate adsorption enthalpies, the regeneration step to recover the olefin would require a low energy input and heat effects during adsorption and desorption would be minimized. When exploring potential metal organic framework (MOF) candidates with pore apertures between 0.34 and 0.44 nm, Chen et al. have found a calcium based material that ticks all these boxes.⁴

MOFs are fascinating materials, formed from the combination of organic ligands and metal nodes or clusters, allowing for a large degree of design by synthesis that has led to tens of thousands of structures. In many of these solids, host-guest interactions and linker rotation lead to structural flexibility such as breathing or swelling,⁸ with sharp molecular sieving only rarely demonstrated.^{9,10} UTSA-280 (see Figure 1), the material reported by Chen et al.,⁴ with squaric acid as a linker and with molecular formula [Ca(C₄O₄)(H₂O)], displays one dimensional cylindrical pore channels and a modest BET surface area of 330 m²/g. However, single component adsorption isotherms demonstrate a large uptake of ethylene of 1.86 mol/kg, and a negligible uptake of ethane, as further confirmed by breakthrough experiments that show sharp separation of olefin from paraffin and suggest the absence of diffusion limitations. Experiments performed in the presence of common contaminants further demonstrate the promise of this adsorbent. The high rigidity of the squaric acid linker along with pore size seem to be the reasons behind this outstanding performance. Furthermore, the material can be easily scaled up under green synthesis conditions.

The performance here seems impressive, however, we should realise that these results are only the first step in the development of a new separation technology. We would like to encourage the authors and other researchers to go beyond the proof of concept and to look at the potential separation process. This would be, most likely, based on a Vacuum Pressure Swing Adsorption process, but exploration of other technologies such as Simulated Moving Bed¹⁴ technology where, i.e. CO₂ could be used as desorbing gas, should not be discarded. Finally, the long-term stability of the MOF and the absence of deactivation due to olefin polymerization in the pores should be demonstrated under realistic process conditions.

In addition to demonstrating the potential of MOFs for gas separations, we believe that these results also highlight the fact that there is still a lot to discover about the thousands of MOF structures already reported. This work is not an example of rational design, but of rational thinking. These results should trigger the curiosity of researchers to further explore data mining strategies to help identify promising structures for current challenges, and not only gas separations. In this sense, recent developments in the area of artificial intelligence for materials discovery will be instrumental.^{12,13} In

addition, it is of the utmost importance to continue building MOF databases containing as many structures as possible.¹⁴ What also is of the utmost importance is to reduce CO₂ emissions, if this and similarly selective ethane/ethylene separation materials can be industrially implemented, such processes could help save circa 0.1% of the energy consumed in the world. This is a not inconsiderate amount.

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Figure 1 | Schematic representation of the separation of ethane/ethylene mixtures. A column is packed with UTSA-280 in its empty form (left), but after exposure to mixed gases is saturated with ethylene (right), the ethylene residing in the pores of the MOF. Green, red, dark grey and light grey colours represent Ca, O, C and H atoms.