

## ZEOLITE CATALYSIS

## Torn between two sites

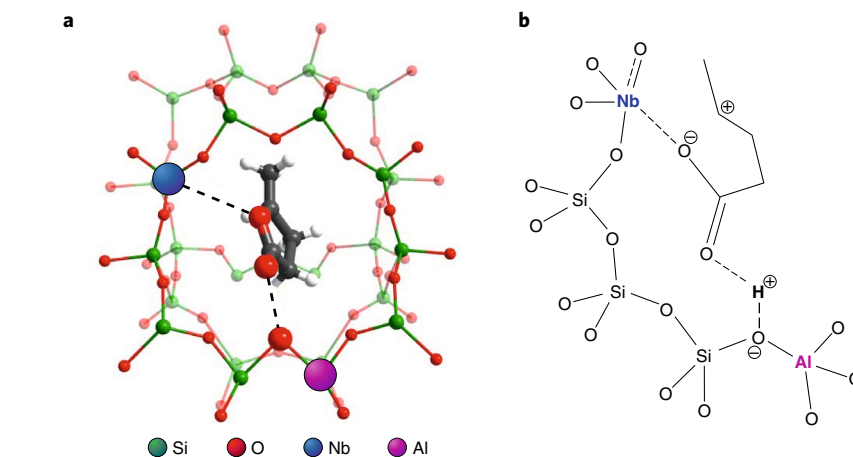
Mild Lewis and Brønsted acid sites within the confined porous structure of a Nb–Al-containing zeolite work in co-operation to efficiently break down bio-based  $\gamma$ -valerolactone to butenes.

Baira Donoeva and Krijn P. de Jong

Today, about 10% of oil and gas goes to the production of chemicals ('petrochemicals'), mainly light alkenes and aromatics, which are primarily used as building blocks for plastics. Current growth in demand for petrochemicals is estimated at 4% per annum<sup>1</sup> and, therefore, it is expected that when demand for liquid transportation fuels softens at the end of the century, the majority of fossil oil and gas resources will be used for chemical manufacturing. This would make the petrochemicals sector one of the main CO<sub>2</sub> emitters. Using biomass may offer a more sustainable way to produce chemicals and materials in the future, therefore pathways for biomass conversion are being developed<sup>2</sup>, for which the design of efficient catalysts is crucial<sup>3</sup>.

Butenes are commodity petrochemicals, currently produced on a scale of ~130 million metric tonnes per year by the cracking of oil fractions and used to produce fuels, polymers and chemicals<sup>1</sup>. In 2010, Dumesic et al. reported an approach to produce butenes via decarboxylation of biomass-derived  $\gamma$ -valerolactone (GVL) over a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst with butene yields up to 96% at 36 bar using 80% GVL feedstock<sup>4</sup>. Stable performance of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was challenged by coke formation when the catalysis was run in the presence of water, resulting in reduction of butene yield over a period of 100 hours.

Now, writing in *Nature Materials*, Lin and co-workers report the synthesis of a hetero-atomic zeolite NbAIS-1, and its activity and stability for conversion of GVL into butenes<sup>5</sup>. This microporous material consists of silica that simultaneously incorporates niobium and aluminium atoms within its framework. NbAIS-1 possesses unique acid properties, that is, mild Lewis acid sites due to the presence of Nb (V) and mild Brønsted acid sites due to the presence of Al (III). By simultaneous incorporation of Nb and Al in the zeolite, fine-tuning of acidity, and hence catalytic properties, is possible. Using practically relevant 30% GVL solution in water, a nearly quantitative molar yield of butenes was achieved over



**Fig. 1 | Structure of  $\gamma$ -valerolactone bound between the Lewis and Brønsted sites in NbAIS-1 to form butene and CO<sub>2</sub>.** **a**, The structure of  $\gamma$ -valerolactone within zeolite pores as obtained using in situ X-ray diffraction data. **b**, A corresponding chemical structure of one of the intermediates of  $\gamma$ -valerolactone cleavage, chosen for illustrative purposes. This clearly shows the co-operative binding between Lewis and Brønsted sites is optimal for formation of a C4 butene. Panel **a** reproduced with permission from ref. <sup>5</sup>, Springer Nature Ltd.

NbAIS-1 at 320 °C and ambient pressure. No coke or by-product formation was observed under optimized conditions and so the catalyst showed remarkable stability in the presence of water, with butene yield remaining over 99%, over a period of 180 h due to the absence of strong acid sites in NbAIS-1. Strong acid sites, present in conventional zeolites, bind reactants and products strongly; causing condensation reactions and thus coke formation that deactivates the catalyst.

In order to understand the catalytic properties, Lin and coworkers used a range of techniques to characterize NbAIS-1 and to study the adsorption and activation of GVL within the pores. Synchrotron X-ray powder diffraction showed that in the case of Al-only and Nb-only zeolites, GVL binds to acid sites via a single bond. In contrast, in NbAIS-1, two bonds simultaneously form between the oxygen atoms of GVL and the Lewis and Brønsted acid sites. This co-operative binding allows for optimal activation of GVL thus optimizing catalysis (Fig. 1a). Next, the team performed in situ

inelastic neutron scattering coupled with density functional theory calculations to follow GVL bond activation and conversion within NbAIS-1, allowing a detailed reaction mechanism to be constructed (Fig. 1b). Lin and co-workers conclude that the specific structure of the active site in NbAIS-1, comprised of two types of acid sites located in close proximity and working in co-operation, is the reason for the high activity and selectivity. Interestingly, similar complex catalytic active sites with multiple catalyst-substrate binding points within a confined environment are well known in biological catalysis. Enzymes, that is, catalysts driving chemical processes in the living world, have highly specific chemical and spatial configuration of the active sites that are responsible for their extremely high activity and selectivity, similar to the heterogeneous catalyst reported here.

One of the main challenges for butene production from GVL is the access to cheap feedstock. Production of GVL from biomass is a complex multi-step process

requiring hydrogen and noble metal catalysts, with the current production scale not nearly comparable with that of butenes. The conversion of GVL to butenes leads to a concentrated CO<sub>2</sub> stream as a by-product which is, however, suitable for carbon capture and storage. Given the bio-based nature of the feedstock for this transformation, a process with overall negative CO<sub>2</sub> emissions may be envisaged. Further research stemming from this work might focus on controlling the precise location of Al and Nb atoms, because the intimacy between different types of active sites can be critical in catalysis<sup>6</sup>. In NbAlS-1 with an optimized composition, there is only 1 Nb per 37 Si atoms and 1 Al per 25 Si atoms, not all Nb sites might have an Al site located sufficiently close to activate GVL via 'chelation'. Incorporation of Nb atoms into the zeolite seems to introduce some mesoporosity, which can have a positive effect on performance.

It would be interesting to disentangle the chemical and textural effects, or to explore Nb,Al-containing materials with controlled mesoporosity. Importantly, for an optimal process design, an industrial catalyst must be efficient at high pressures. Conversion of GVL to butenes is accompanied by the formation of CO<sub>2</sub>; hence the activity of NbAlS-1 is expected to be lower at higher pressures. Further catalytic studies and catalyst optimization at high pressures are therefore encouraged.

The work of Lin and co-workers represents a nice example of designing catalysts with complex active sites that have potential, for instance, in tandem transformations of small molecules over Lewis and Brønsted acid sites, where the proximity between the two acid sites and the possibility of controlling their strength can result in highly selective transformations. We envisage that there will be future work to get to industrial

application of this catalyst, with the need for higher pressures, mesoporosity and active site location control. □

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Published online: 16 December 2019  
<https://doi.org/10.1038/s41563-019-0568-0>

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## SOFT PHOTONICS

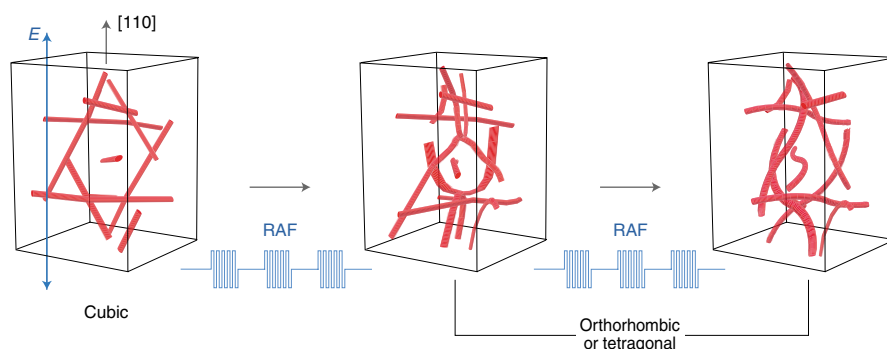
# Electroshock tuning of photonic crystals

Photonic crystals with optical bandgaps across the entire visible spectrum are generated by reconfiguring three-dimensional blue phase liquid crystalline lattices into long-lived metastable non-cubic structures using sequences of electric pulses.

Slobodan Žumer

Photonic crystals are materials capable of fascinating and extensive control over the flow of light — including full and partial refraction, reflection and guiding — using the interaction of the electromagnetic waves of light with their regular material lattice structures<sup>1</sup>. These materials are nowadays crucial light-controlling elements in photonics, a fast-growing field with numerous engineering and biological applications. Methods to dynamically control the photonic bandgaps of such crystals, that is, the intensity and wavelength of light that is reflected by the crystal lattice, are thus in high demand. Now writing in *Nature Materials*, Khoo and co-workers describe how arrays of electrical pulse sequences can be used to dynamically reconfigure the lattice of three-dimensional (3D) soft photonic crystals into metastable structures with photonic bandgaps across the entire visible spectrum<sup>2</sup>.

Photonic crystals occur naturally in opals and in some living organisms, such



**Fig. 1 | Lattice reconfiguration of a cubic blue-phase liquid crystal using the repetitively-applied-field technique.** Specific sequences of RAF with a.c. electric field,  $E$ , aligned along the [110] direction of a cubic BP liquid crystal induces the reconfiguration of the crystal lattice into long-lived metastable orthorhombic or tetragonal structures. Red cylinders and spaghetti-like objects represent defect lines. Adapted with permission from ref. <sup>2</sup>, Springer Nature Ltd.

as in the coloured feathers of certain birds and highly iridescent exoskeletons of some beetles. Synthetically, photonic crystals

can be produced by various procedures: solid-state systems are formed by material depositing, etching, drilling or 3D printing;