

POROUS CATALYSTS

The platinum rush

Ultra-stable and catalytic platinum atoms and clusters have been obtained by entrapment within a zeolite framework during its formation.

Krijn P. de Jong and Jovana Zečević

Approximately half of the world's platinum usage is in catalytic applications such as exhaust gas treatment, industrial chemical production and oil refining¹. Since the chemical transformations catalysed by platinum take place at the metal's surface, maximal activity calls for a high surface-to-volume ratio and thereby a small particle size. This has prompted a recent 'rush' to obtain catalytic-metal particles smaller than 1 nm (referred to hereafter as 'clusters') or even single atoms stabilized on or in host materials^{2,3}, sometimes with surprising structure sensitivities⁴. In view of the lower thermodynamic stability of atoms at the surface compared with those in the bulk of a metal, controlling and preserving the size of metal particles, clusters and atoms, during both synthesis and catalysis, is a challenge. In particular for high-temperature catalysis, the use of a support or host material to stabilize small particles is essential. Zeolites are microporous crystalline materials with well-defined pores and cavities that can act as host materials, and attempts have been made to synthesize metal atoms or clusters in zeolites, with varying levels of success⁵⁻⁷.

In this issue of *Nature Materials*, Liu and co-workers report the entrapment of platinum clusters and atoms during the synthesis of a siliceous zeolite framework (MCM-22) to enhance their catalytic performance and thermal stability⁸. Unlike most synthesis attempts in the past that start from molecular Pt precursors (Fig. 1a), the authors added premade Pt clusters to a layered 2D zeolite precursor that was treated with cetyl trimethyl ammonium bromide. Subsequent pyrolysis and oxidation in air at 540 °C gave rise to the 3D MCM-22 structure with entrapped Pt (Pt@MCM-22) (Fig. 1b). Using high-resolution electron microscopy, they detected both single Pt atoms and Pt clusters of 0.2–0.7 nm, which they validated by extended X-ray absorption fine structure (EXAFS), infrared and ultraviolet–visible spectroscopic analyses. EXAFS provided a Pt–Pt coordination number of 4.7, which indicates an average Pt-cluster size of less than 1 nm.

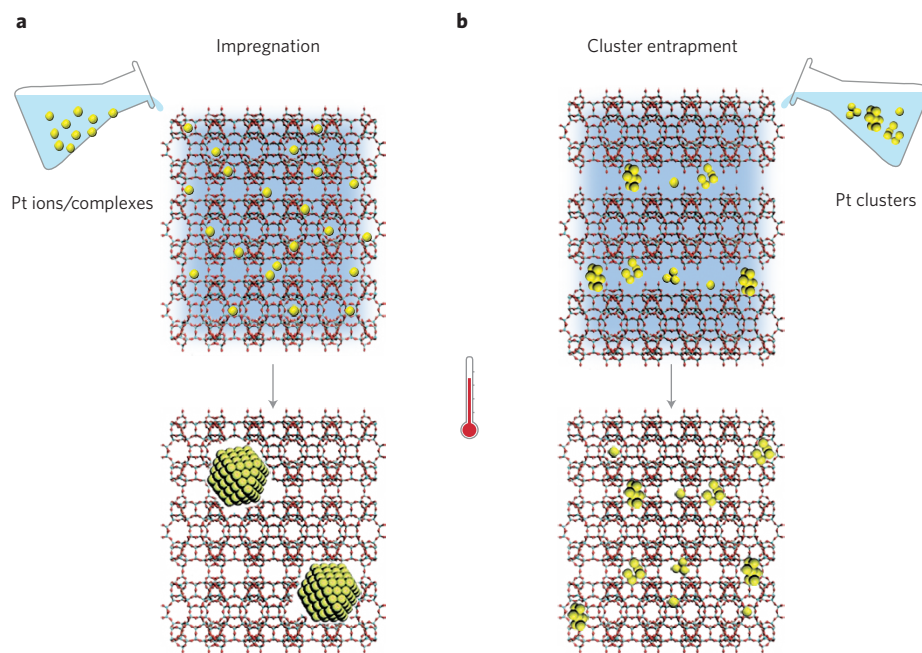


Figure 1 | Schematic comparison of Pt impregnation and entrapment, and the structural effects of heat treatment. **a**, A dissolved molecular Pt precursor (complexes, ions) is added to a zeolite framework or a precursor thereof, which often leads to Pt nanoparticles upon subsequent heat treatment, especially when a siliceous zeolite is used. **b**, The new method involves adding previously synthesized Pt clusters to swelled 2D sheets of siliceous zeolite, which become entrapped upon condensing the sheets into the 3D siliceous zeolite, thus rendering them stable against growth during high-temperature operation. This overcomes the drawbacks of weak Pt interactions and particle growth. Adapted from ref. 8, Nature Publishing Group.

The authors compared the properties of their new Pt@MCM-22 with a reference catalyst Pt/MCM-22-imp, which they obtained by impregnating pre-synthesized Pt clusters into a ready-made MCM-22 framework. The Pt clusters in the reference catalyst were present probably at the outer surface of the MCM-22 crystals, and the size of the Pt particles after reduction was mainly in the range 2–4 nm. To probe catalytic functionality, the authors carried out alkene hydrogenation using differently sized molecular substrates (Fig. 2). Hydrogenation of propene by Pt@MCM-22 was approximately five times higher than that for Pt/MCM-22-imp, which indicates higher Pt dispersion in the former. Molecular sieving effects

were then apparent when testing the alternative substrate isobutene, with both catalysts exhibiting comparable rates of hydrogenation. The authors concluded therefore that Pt clusters were located within the micropores of the MCM-22 in Pt@MCM-22, and that their new catalysts can be used for size-selective conversions — a feature that will be further explored with these systems. Most importantly, the authors also studied the stability of their Pt clusters by exposing the catalysts to harsh conditions of reduction and oxidation at 650 °C. In such conditions, the Pt species within the reference Pt/MCM-22-imp catalyst underwent significant aggregation, with some nanoparticles observed as large as

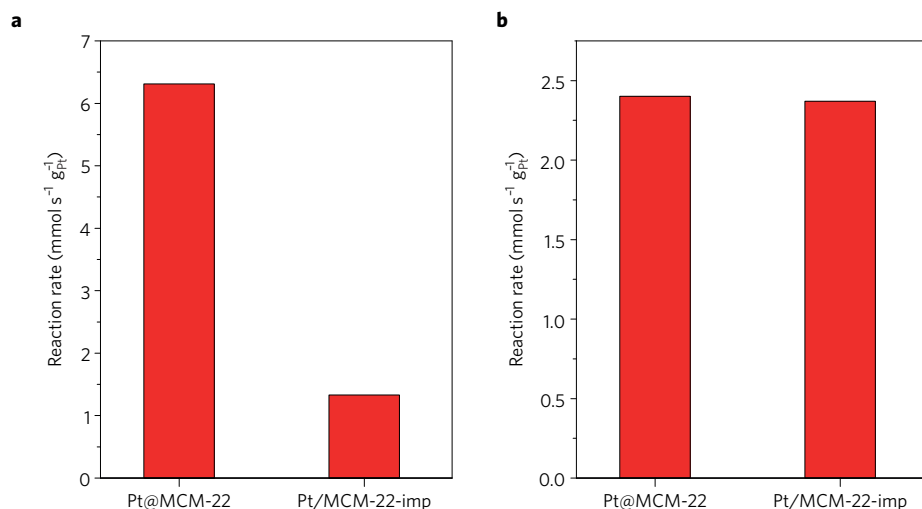


Figure 2 | Size-selective catalysis. **a,b**, Comparing hydrogenation rates of propylene (**a**) and isobutene (**b**) catalysed by Pt@MCM-22 and Pt/MCM-22-imp, respectively, provides evidence of molecular sieving. Reproduced from ref. 8, Nature Publishing Group.

30–50 nm. On the other hand, Pt particle growth within Pt@MCM-22 was restricted to 1–2 nm, probably due to their capture by the cups and supercages that comprise the micropores of MCM-22. By combining these compelling catalytic and stability features, the authors report the use of these catalysts for dehydrogenation reactions at 550 °C with cyclic catalyst regeneration. Although Pt/MCM-22-imp lost a significant portion of its catalytic capability over five reaction cycles, Pt@MCM-22

retained near-maximal activity (~90%) with limited Pt aggregation.

Future work on these catalysts might shed further light on the genesis of Pt@MCM-22, and specifically on the occurrence of Pt atoms. In particular, further evidence to explain how the synthesis of Pt clusters using this modified method leads to formation of Pt atoms would be welcome. A possible explanation for this is the re-dispersion of PtO_x during the oxidation step at 540 °C,

possibly involving defects in MCM-22, similar to previous studies of Pt on ceria⁹. Furthermore, the transmission electron microscopy imaging performed by Liu and colleagues, as has been observed elsewhere in the literature, reveals that the distribution of metal in Pt@zeolite systems is far from uniform. Non-uniform distributions of metal particles or clusters may affect stability, activity and selectivity in catalysis¹⁰. We foresee a great future for this synthesis method and its potential materials, particularly if expanded to other metals and zeolites, or related microporous materials. □

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ELASTIC SHEETS

Cracks by design

Stretching elastic membranes over curved substrates can be used to guide and control crack paths.

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Different methods exist to control fracture in thin media in order to produce some desired shape or curved edge. Commonly, inhomogeneities are placed along a specific path to guide a fracture, such as scoring a material's surface or introducing a sequence of perforations. In some circumstances, the ability to guide fractures without altering the material is advantageous or even necessary, and could provide a key design tool in areas such as flexible electronics, thin films and monolayer materials. Writing in *Nature Materials*, Mitchell, Irvine and colleagues explore the possibility of guiding crack paths in thin, elastic sheets by draping

them on surfaces with non-zero Gaussian curvature¹. The out-of-plane elastic deformation imposed by the surface curvature causes an inhomogeneous stress distribution within the sheet. If a small crack is introduced, the pre-load in the membrane can cause the fracture to grow spontaneously. Depending on how the substrate geometry is chosen, the crack growth can be made to conform to a curved path and possibly arrest after a desired crack length has been reached. This opens up the possibility of a new methodology for incising two-dimensional shapes from sheets by fracturing them over a tailored bumpy substrate surface.

The true challenge of this idea lies in the complexity of fracture mechanics. Predicting the curved path a crack will take in an inhomogeneously loaded brittle media is a difficult problem, and few closed-form solutions have been found through analytical means^{2–4}. Fracture growth and crack turning are phenomena driven by elastically singular stress fields in the vicinity of a crack tip. These fields develop as part of a global stress field, which must be modified continuously as a fracture grows. To consider guiding a crack by the curvature of a substrate surface, one must determine how draping a cracked membrane over such a surface impacts the stress intensity at the