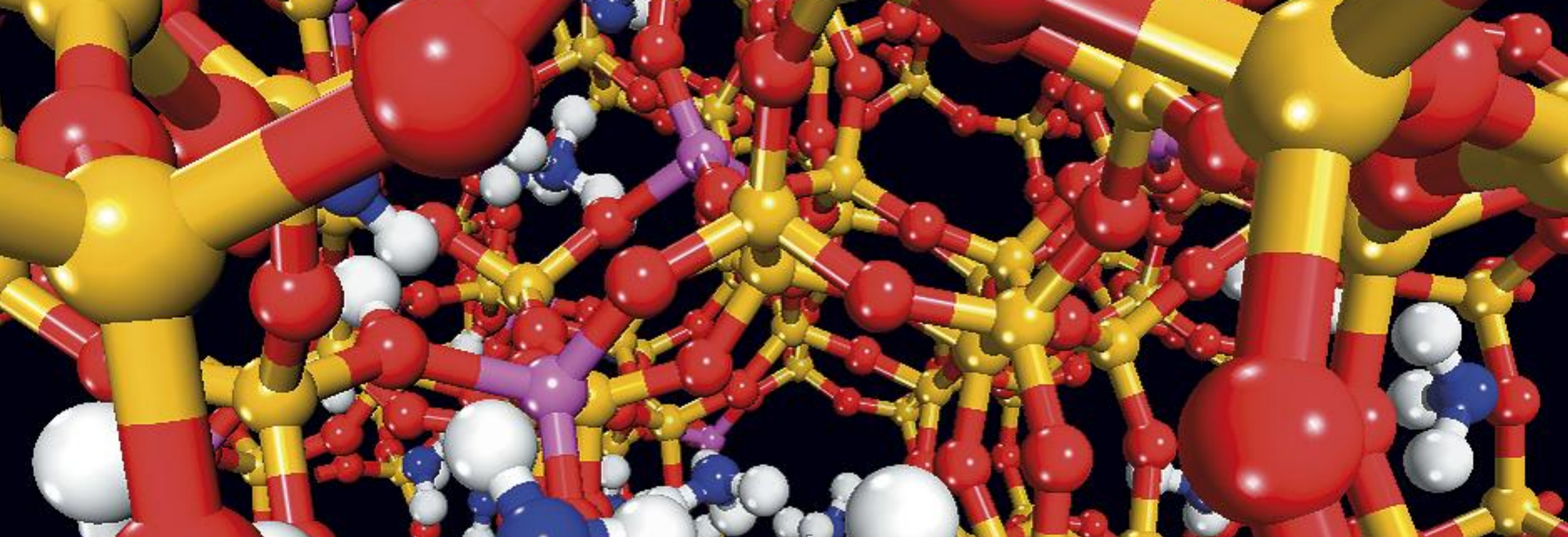


Application Challenges for Nanostructured Porous Materials

Dr Liz Rowsell

Director, Johnson Matthey Technology Centre

Johnson Matthey

Paradigm Shift in Automotive NOx Control Catalysts

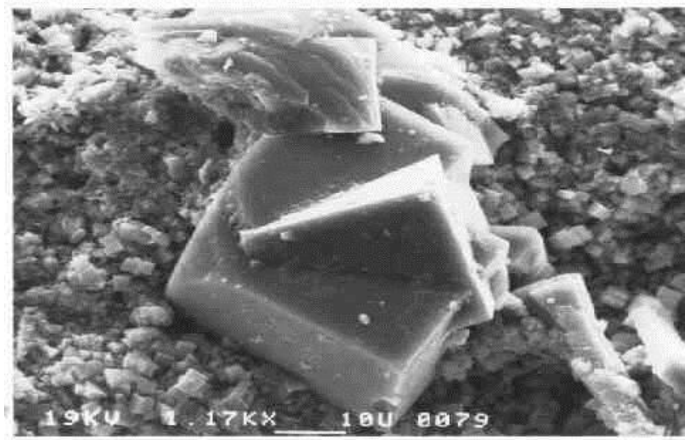
- A paradigm shift describes a fundamental change in approach or assumptions - such a shift has occurred in automotive NOx emission control catalysis.
- The ever present demand to develop highly fuel and energy efficient engines which produce minimal air pollution provides a rich opportunity for functional new materials.
- Selective catalytic reduction (SCR) of NO_x by NH_3 over Cu and Fe promoted zeolites has been known and studied for over 30 years. Major advances were made in material characterisation and mechanism, but the major problem preventing real life automotive use was the poor thermal durability of the systems.
- The advent of small pore Cu zeolites is the paradigm shift that met this challenge.

Porous Materials

- Porous materials such as zeolites have been of interest to industry for many years as catalysts (e.g. cracking), adsorbers/separators and as ion exchange systems (e.g. in water purification).

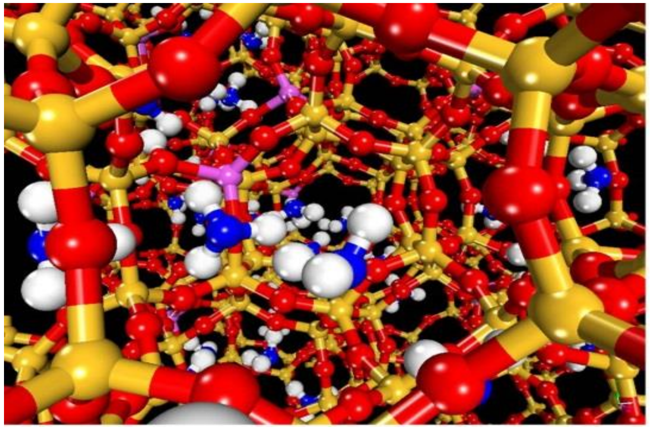
- Zeolites are natural and synthetic hydrated aluminium silicates with high surface area. The materials can be tailored to a particular application by controlling pore size, channel structure, active sites and durability. There are over 200 topologies.

- In recent years zeolites are undergoing something of a renaissance in industry with applications in electronics, medicine and consumer goods.

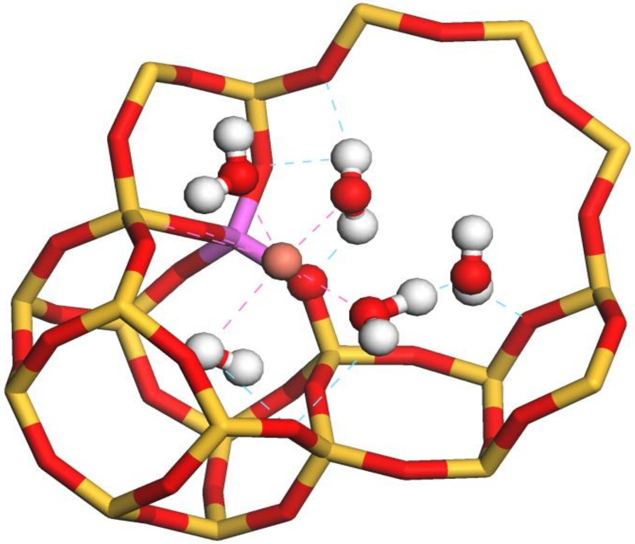


- Manufacture of designer zeolites at scale is the industrialists challenge.

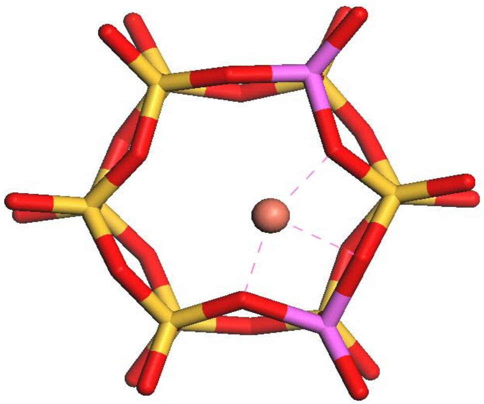
Zeolite Modelling



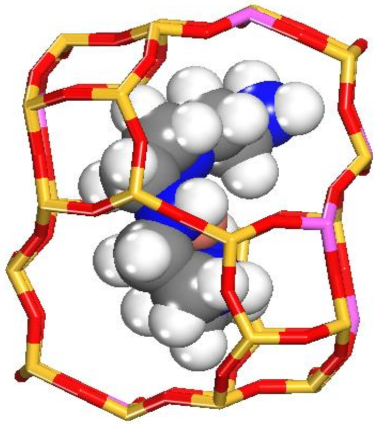
Diffusion of reactants/products to and from active sites (Molecular Dynamics)



Interaction with adsorbates



Location of active sites
Use simulation to aid characterisation :
PDF fitting and computing NMR shifts



Design of new zeolite systems via new templates for zeolite synthesis

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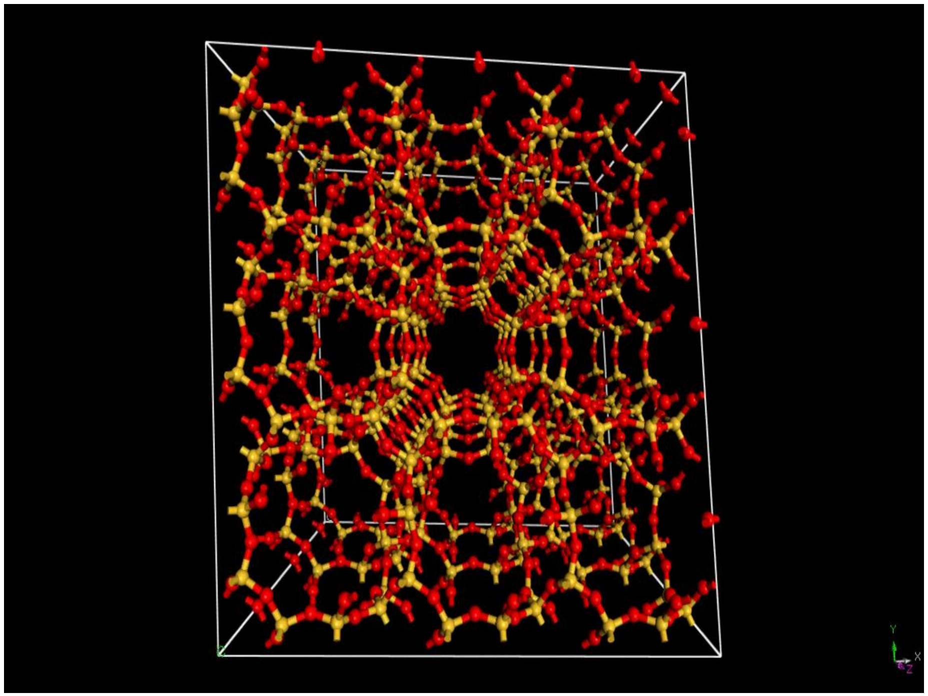
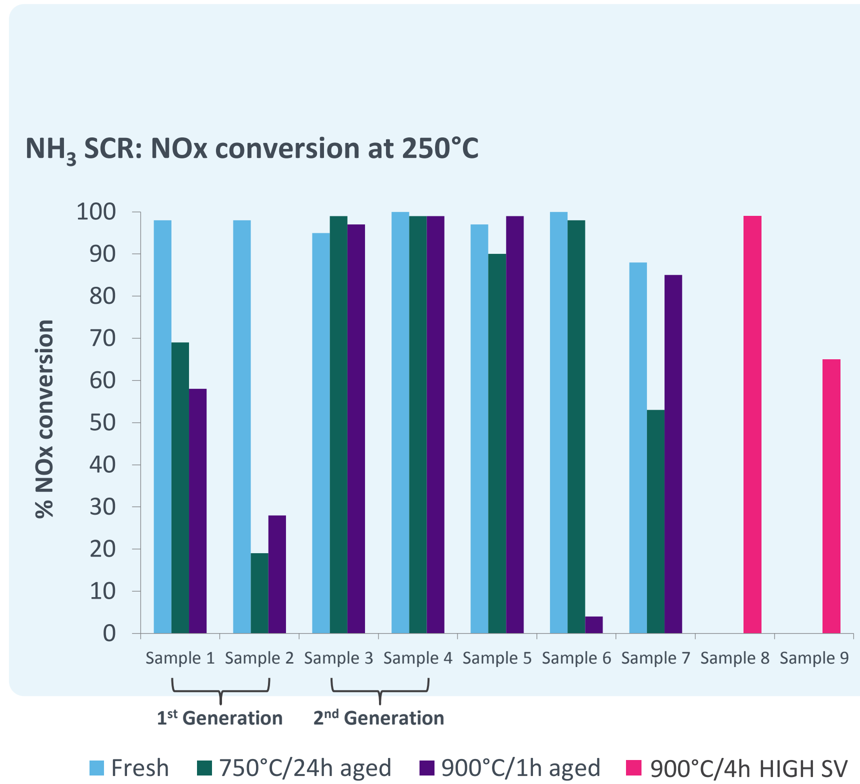
Small Pore Zeolites for Selective Catalytic Reduction (SCR)

Selective catalytic reduction (SCR) systems work by chemically reducing NO_x (NO and NO_2) to nitrogen (N_2).



Copper promoted zeolite materials become active for NOx reduction using ammonia (NH_3) as a reductant



Small pore copper zeolites

- More thermally durable and selective for NOx reduction

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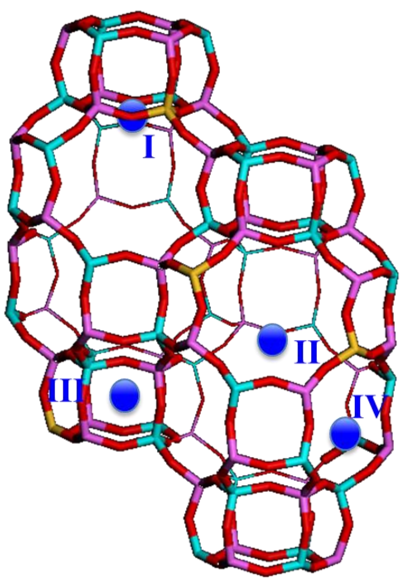
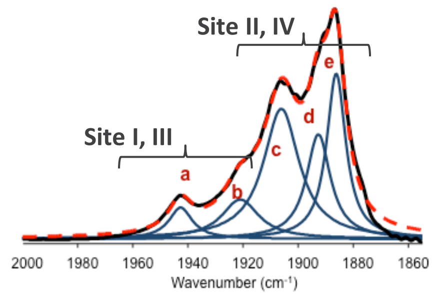
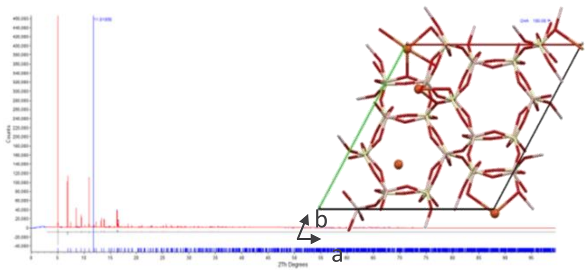
Where is the Cu?

- Cu zeolites are examples of single site catalyst materials
  - Isolated Cu atoms represent the reaction site for the reaction of NOx and NH_3
  - Locating the Cu within the structure is key to understanding the superiority of the latest generation of catalysts





Use of probe molecules to bind to Cu and analyse using *in-situ* infra-red spectroscopy



Use of high resolution X-ray diffraction to identify Cu locations (at Diamond Light Source)

Possible Cu sites from modelling

Cu in Site II and IV

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Material Challenges for Future NOx Control

- Reducing hydrocarbons and nitric oxides reduces the amount of ground level ozone. Improves air quality.

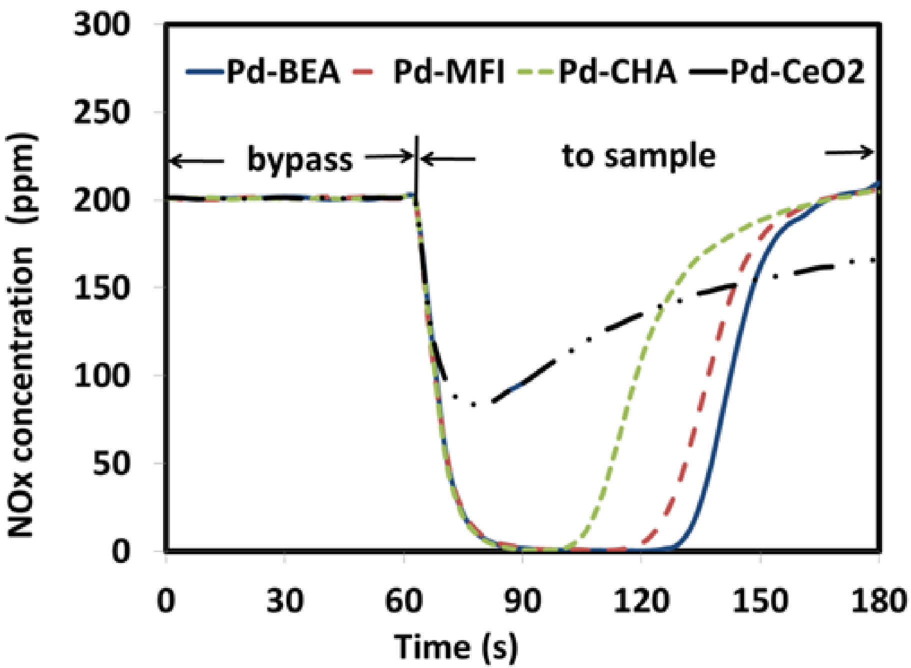
- Fuel economy and GHG legislation lead to lower exhaust temperatures overall. New materials are required to operate at low temperature but maintain activity.

- Emissions from cars are greatest when an engine is cold. We need to design materials that are able to trap NOx that is emitted when the after-treatment systems are cold and which can release the NOx to be treated by the deNOx system once it has reached the appropriate temperature.

- **Diesel Cold Start Concept (dCSC™)** catalysts integrate NOx/HC storage/conversion and CO/NOx conversion functions and are based on Pd promoted zeolites.

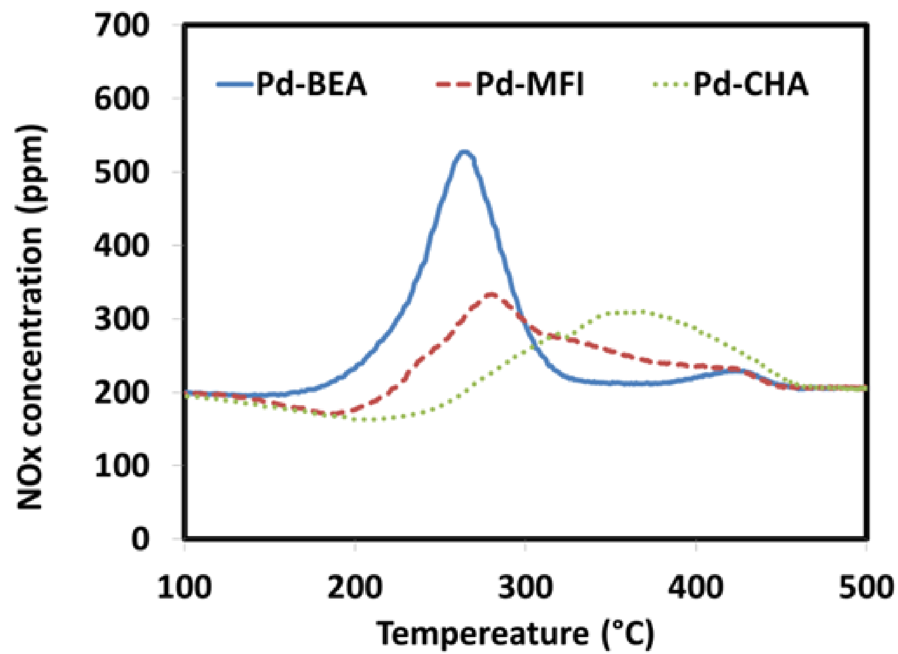
Pd doped zeolites exhibit high NO storage capacity and efficient thermal release

NO storage at 100ºC on Pd-zeolites



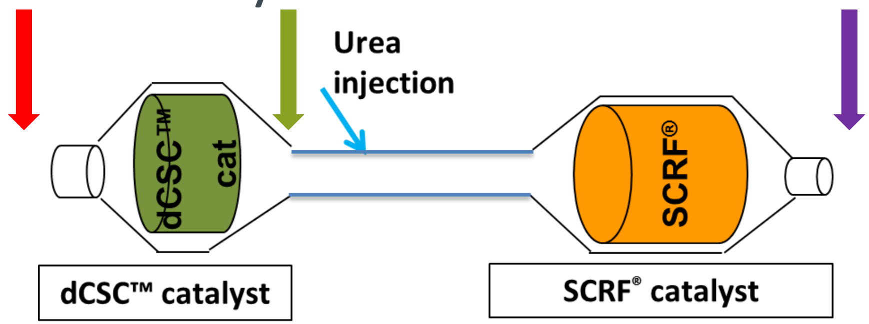
Zeolite framework structure affects NO storage capacity

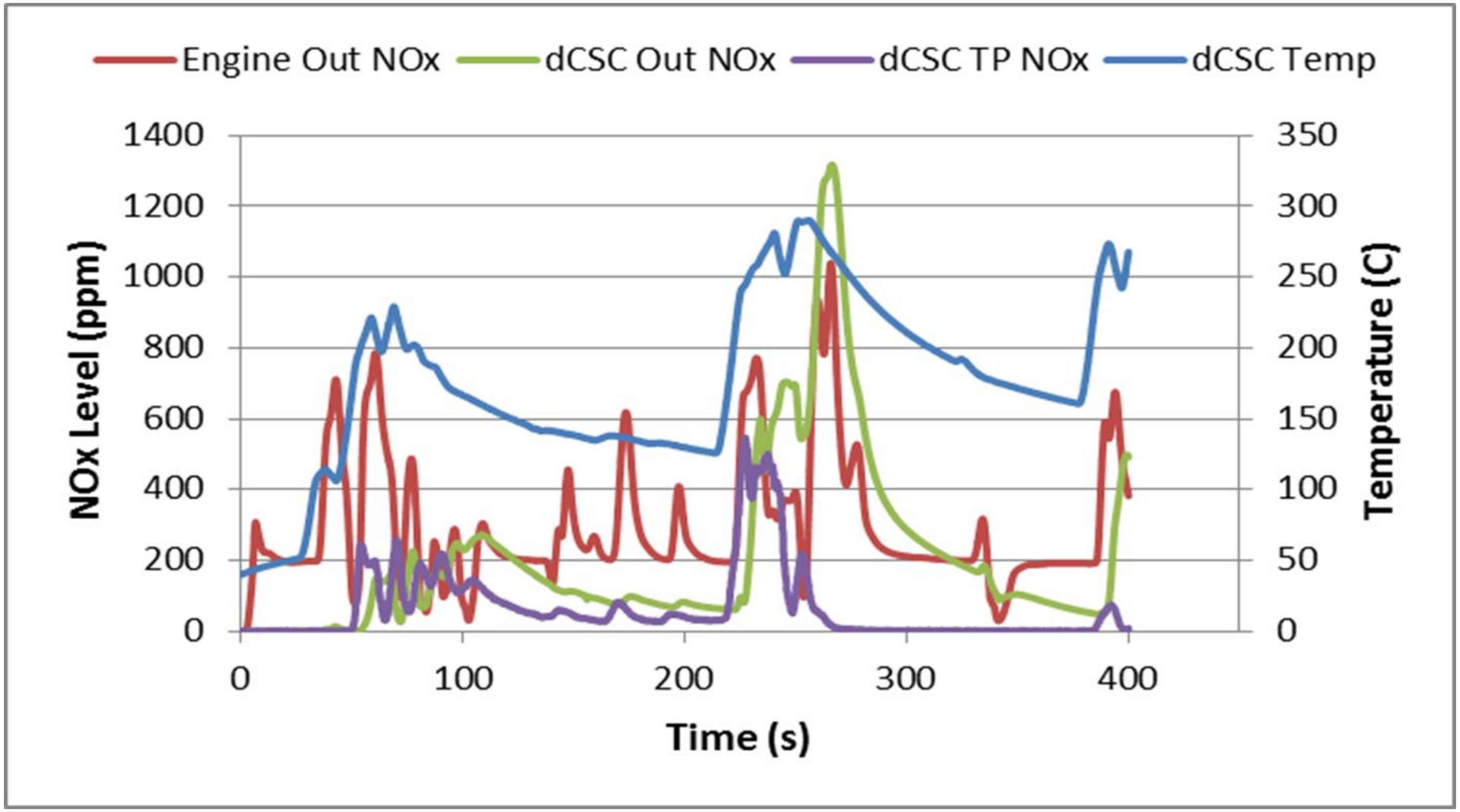
NO release at below 400ºC



Zeolite framework structure affects NO release temperature

Pd-zeolites in automotive catalysts enables cold-start NOx emission control





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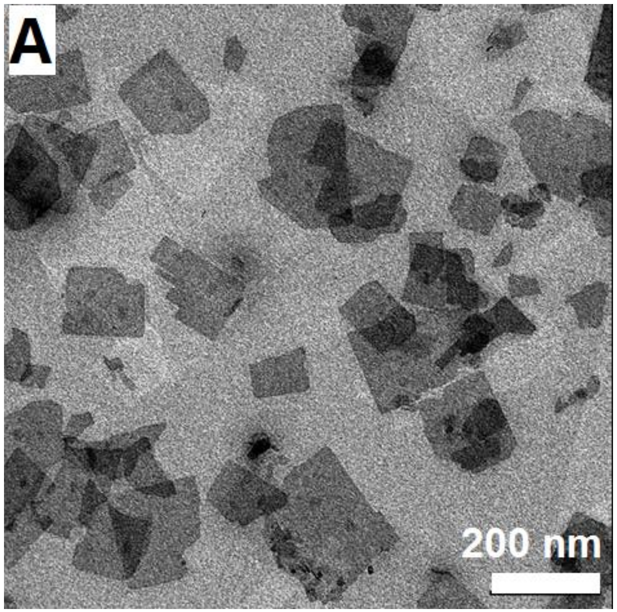
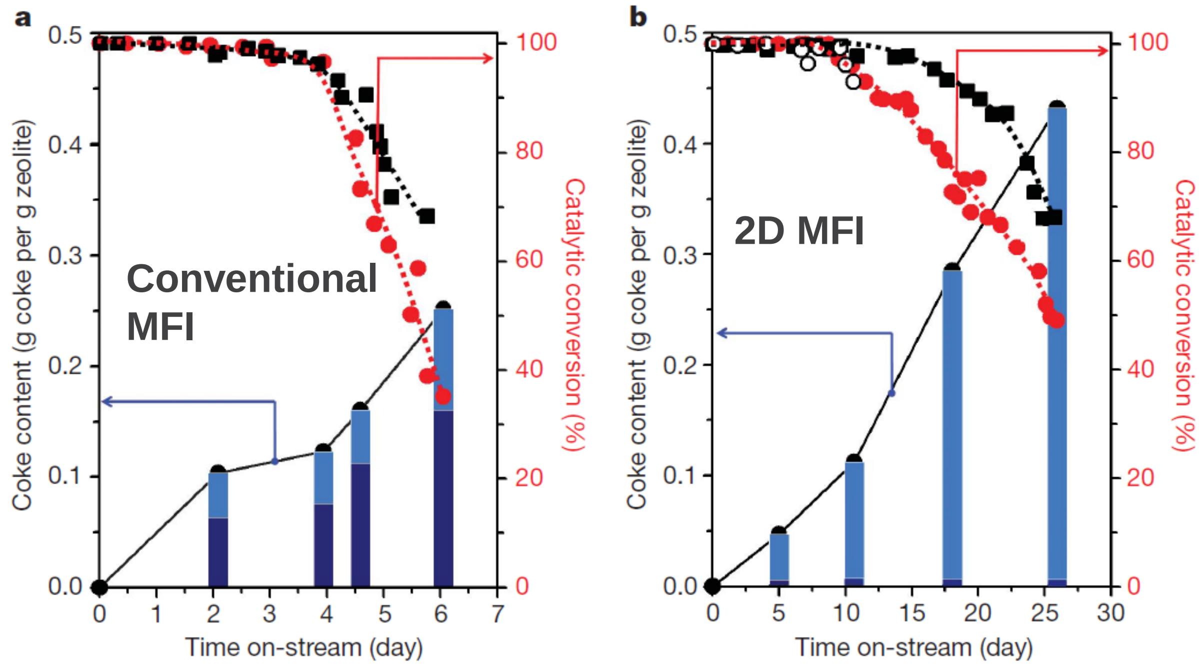
Other Applications for Nanostructured Porous Materials

2D Zeolites for Efficient Methanol to Gasoline Conversion



Exfoliated 2D MFI zeolite

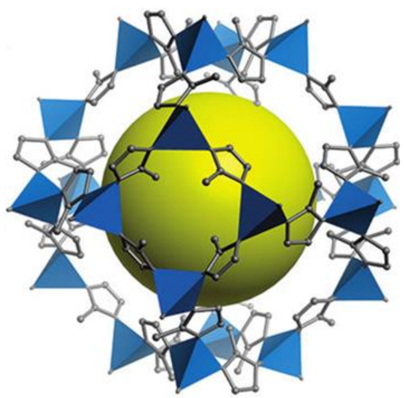


Higher conversion and reduced coke deposition during MTG conversion by using 2D MFI zeolites.

Choi, M.; et al., *Nature* **2009**, *461*, 246.

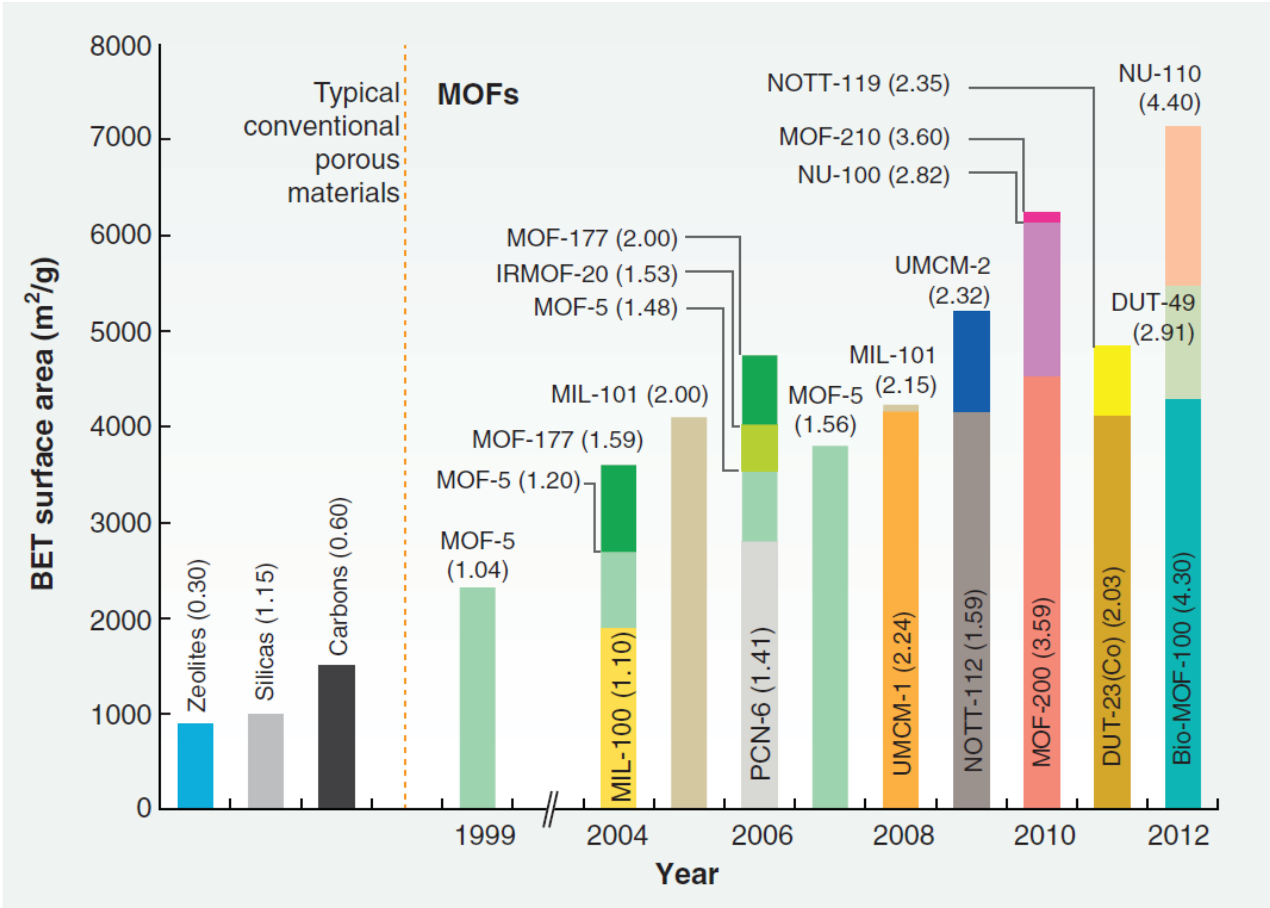
Varoon, K.; et al., *Science* **2011**, *334*, 72.

Beyond Zeolites – Metal Organic Frameworks (MOFs)
Ultrahigh-porosity materials



ZIF-8

A MOF is a crystalline 3D inorganic-organic hybrid compound and consists of rigid organic moieties and inflexible inorganic clusters



Progress in the synthesis of ultrahigh porosity MOFs

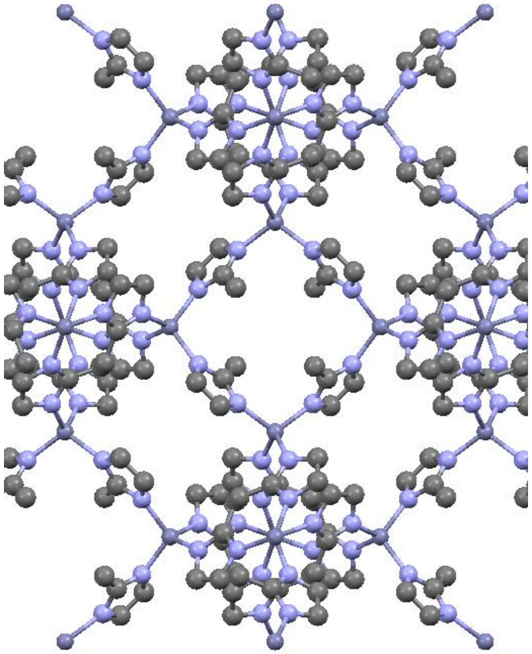
Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*.
Cravillon, J.; et al., *Chem. Mater.* 2011, 23, 2130

MOFs as Templates – Fuel Cells and Battery Materials

Recent developments have led to the use of MOFs as templating agents

- Pyrolysed to produce microporous carbon materials or metal / metal oxide nanoparticles

These materials have been shown to have potential application in gas storage, catalysis, Li-ion batteries



ZIF-8 (right) has been used to produce a Pt-free oxygen reduction reaction catalyst[1]

- Material is approaching the DOE performance target for a non-PGM electrode catalysts
- Potentially the future of non-PGM based ORR catalysts

ATAPULT

SEVENTH FRAMEWORK PROGRAMME

New Energy World JU fuel cells & hydrogen for sustainability

1; Proietti *et al*, Nature Comms, **2011**, 2, 416

MOFs Pros and Cons

- ✓High SSA
- ✓High porosity
- ✓Shaped pores
- ✓Crystalline
- ✓Open metal sites
- ✓Possible to functionalise
- ✓Chirality
- ✓Modification with insertion of guest molecules – e.g. conduction

- ✘ Stability after solvent/guest removal
- ✘ Limitation in thermal stability (350-400 °C)
- ✘ Cost effective manufacture at scale

Opportunity