Engineering metal nanoclusters with atomic precision

The design and development of materials for cost-effective and sustainable chemical production

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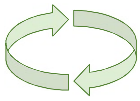
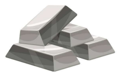
The importance of nanoclusters

Catalysts lower energy requirements of reactions to make them more efficient. Their surfaces provide active sites where molecules can adsorb to allow for lower energy reaction pathways.

Nanoclusters, particles ≤1 nm in diameter, have a much higher percentage of their atoms on the surface to provide active sites for catalysis[1].


More cost-effective


More sustainable

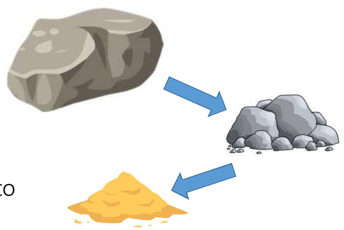

Resources used in smaller amounts

The issue of stability

Despite the benefits of such catalysts, their implementation can prove challenging.

Nanoclusters are highly unstable, due to the high ratio of surface atoms compared to those in their bulk[2].

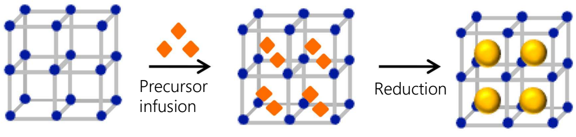
Supporting materials are used to stabilise them, holding them in place[3].



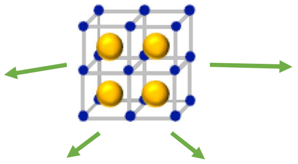
Breaking the same volume of a substance into smaller pieces dramatically increases the surface area. However, this greatly reduces the stability of the material.

Our solution: metal-organic frameworks (MOFs)

MOFs make for ideal 3-dimensional supports due to their well-defined pore geometries, able to anchor nanoclusters from every side[4].

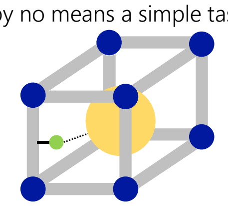


Synthesis of nanoclusters in the pores of MOFs[5].



Key findings in developing MOF-supported nanoclusters

Despite the benefits of using MOFs as supports for nanoclusters, it is by no means a simple task.



The linkers in MOFs can be modified to interact with nanoclusters in the pores.

My work involves modifying MOFs to determine factors that can; a) increase the chance of successfully embedding nanoclusters in their pores and b) enhance their catalytic activity.

The samples can be imaged to probe the size and location of the nanoclusters that form.

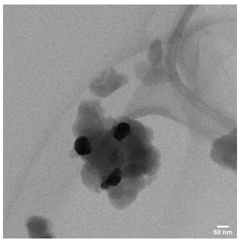
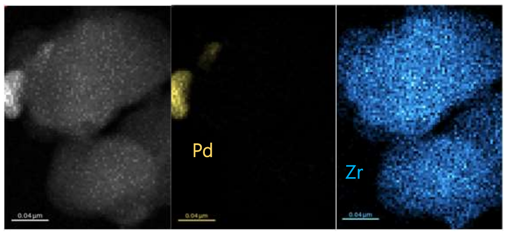


Image (left) of a sample with large nanoclusters on the MOF surface, with elemental mapping (right). ✗



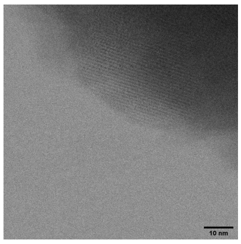
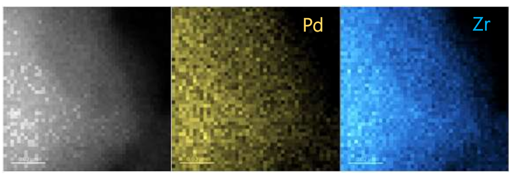


Image (left) of a sample with no obvious nanoclusters, with elemental mapping (right) revealing even Pd distribution. ✓

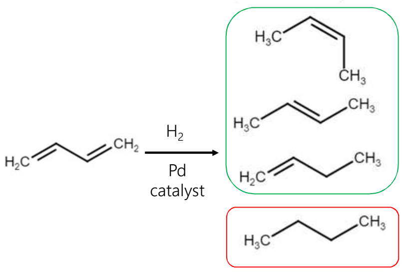


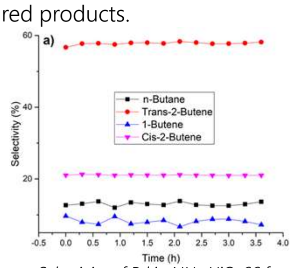
Applications

Samples shown to successfully embed nanoclusters in their pores have been tested as catalysts for a few industrially important reactions.

Butadiene hydrogenation: chemical feedstocks with enhanced selectivity

Pd in NH_2-UiO-66 was found to be highly active for butadiene hydrogenation, used to produce the building blocks of polymers such as polyethylene, with a high selectivity for the desired products.



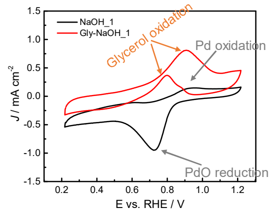


Selectivity of Pd in NH_2-UiO-66 for butadiene hydrogenation.

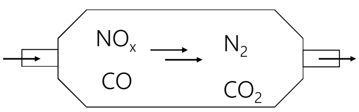
Glycerol oxidation: value-added products from waste

Glycerol is a chemical that can be converted into useful chemicals for the food and pharmaceutical industries. It can be derived from sustainable biomass sources or even as a waste product during biodiesel production.

Pd in NH_2-UiO-66 has been found to be an active catalyst for the electrochemical conversion of glycerol into value-added products useful in the food and pharmaceutical industries.



$DeNO_x$ reaction for cleaner exhausts



The same catalyst has also been found to be active for $DeNO_x$ reactions, vital for reducing toxic emissions while we continue to phase out the use of liquid fossil fuels.

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References

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