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Advancing the Sabatier Reaction Through the use of Small Metal Clusters Supported on TiO_2 Nanoparticles

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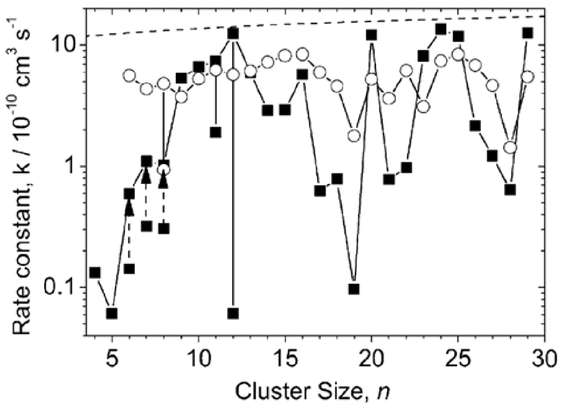
ASTRI AUSTRALIAN SOLAR THERMAL RESEARCH INITIATIVE

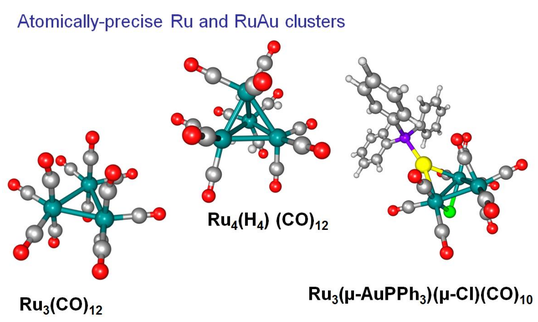
The catalytic reduction of CO_2 to clean, versatile fuels under moderate conditions not only provides an energy efficient and renewable energy source but when coupled with other fuel production processes, is able to effectively reduce the CO_2 footprint of the whole system and turn a waste product into profit.

Why use Clusters?

- Clusters have very strong size and shape dependencies in addition to the electronic effects of their composition
- Majority of atoms can be exposed, creating the largest possible surface area/volume ratio
- Atomically precise clusters allow us to target specific size regimes and fine tune their properties

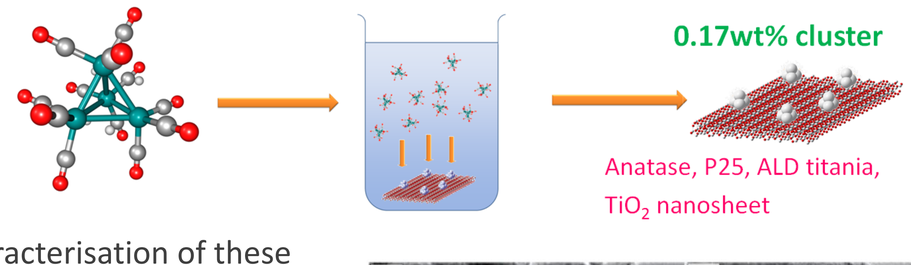


Above: Rh_n cluster anions (circles) and cations (squares) selectively reacting with N_2O[1]



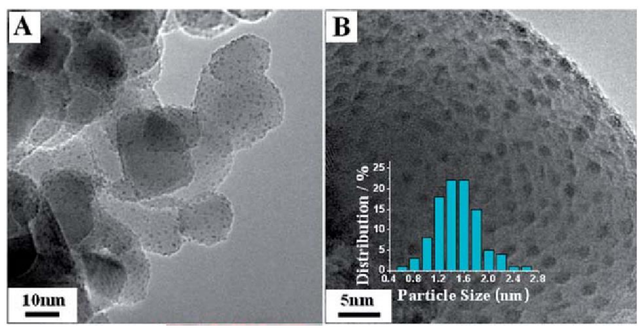
- Clusters can be anchored to TiO_2 by photohole assisted oxidation of the metal to yield metal oxide clusters on a surface, which can then be reduced to their metallic form[2]

Ligand stabilised cluster → Cluster deposition in sol^n → Ligand removal



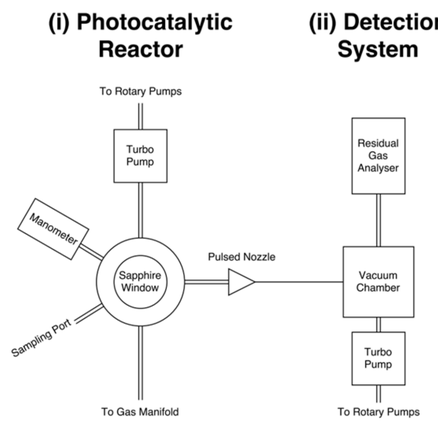
- Characterisation of these changes (morphology, agglomeration, charge transfer) after deposition is important for understanding their catalytic performance

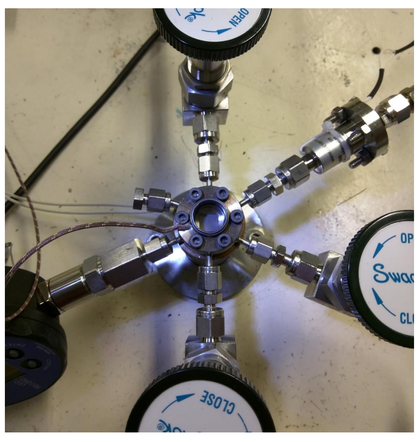
Right: Electron microscopy images of Ru/TiO_2 prepared by photohole oxidation[2]



Experimental Apparatus

- Our specially designed reactor has a volume of only 5.5 mL allowing for the investigation of very small quantities of catalytic materials, down to 1 mg.
- Stainless steel construction allows the cell to be heated to 350 °C and can withstand pressures up to 27 bar



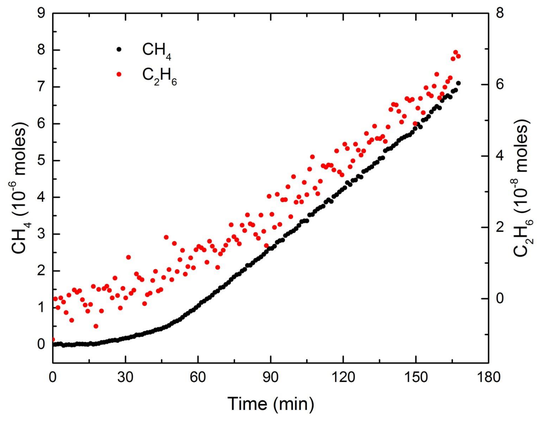


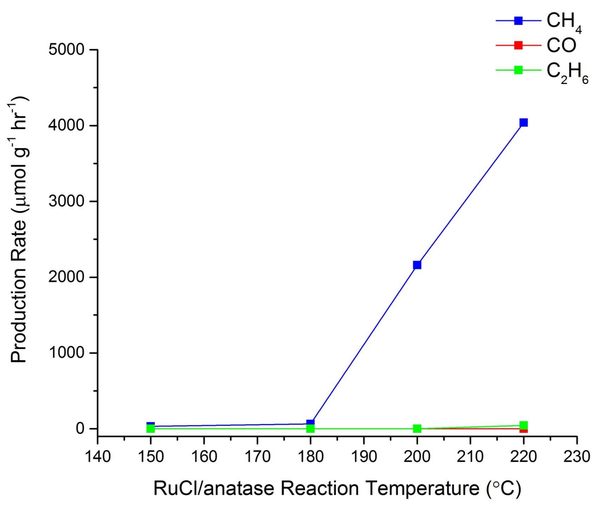
- Computer controlled pulsed valve delivers precise gas flow, enabling catalytic reactions to be monitored across a wide range of pressures
- Residual gas analyser (mass spectrometer) provides rapid, real-time analysis of the gas composition within the reaction chamber.
- The sampling port can also be used to extract gas for analysis with a gas chromatograph system

Catalytic Results

Right: 5 bar 4:1 mix of H_2:CO_2 over 1.5 mg 3% w/w RuCl/anatase NPs prepared by photohole oxidation, drop-casted onto a 1 cm^2 silicon wafer.

- This experiment was left at ambient temperature for 15 minutes then ramped at 9.8°C per minute to 220 °C .





Left: 2 bar 4:1 mix of H_2:CO_2 summarised over a range of reaction temperatures

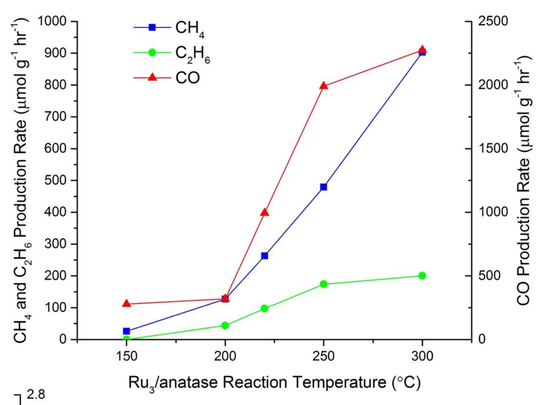
- Samples prepared by photohole oxidation show almost no ethane or CO production as opposed to Ru_3 (shown below), Ru_4, or $AuRu_3$ clusters
- Ru NPs show capability for Sabatier lower than traditional temperatures and pressures

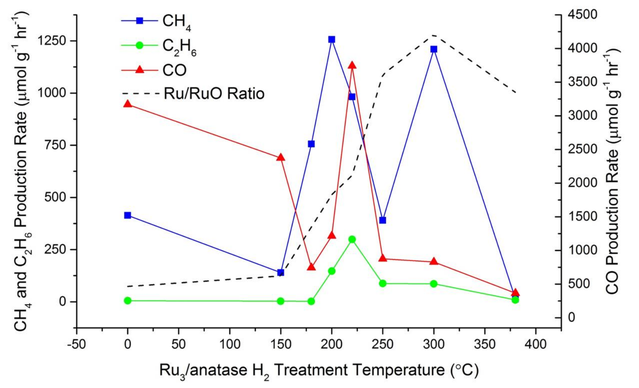
Extended Sabatier Results

Right: 0.17% Ru_3/anatase, reduced at 250 °C in H_2

- These clusters show activity at much lower temperatures and near ambient (2 bar) pressure

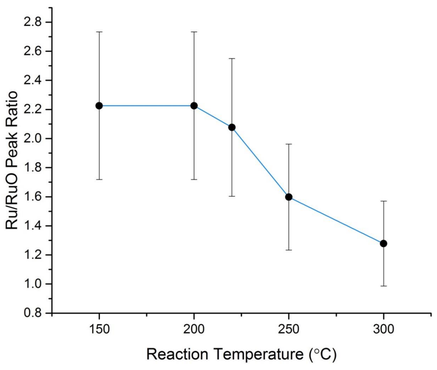
Below: The effect of H_2 treatment temperatures on the catalytic efficiency of 0.17% Ru_3/anatase.





- Because samples are prepared on Si wafers they can also be measured using surface science techniques such as XPS and MIES

Right: Change in metallic Ru content after catalytic reaction at various temperatures. Metallic Ru decreases with increased catalysis reaction temperature



Conclusions

We have shown increased catalytic activity for a given amount of precious metal by using well-defined clusters at low temperatures and pressures, in addition to extending the selectivity for other products. Furthermore, we have demonstrated the capability to correlate our surface science techniques with catalytic results to understand and optimise these materials in the future.

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ARENA Australian Government Australian Renewable Energy Agency