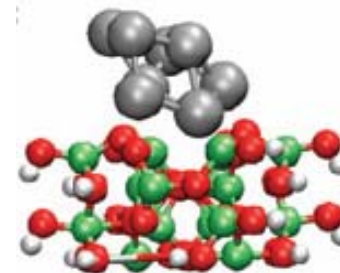


Subnanometre platinum clusters as highly active and selective catalysts for the oxidative dehydrogenation of propane

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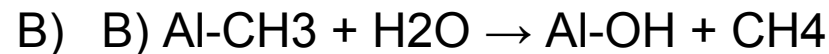
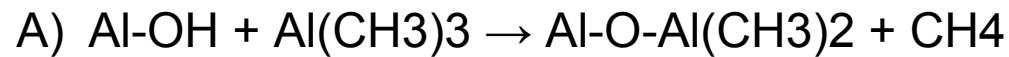
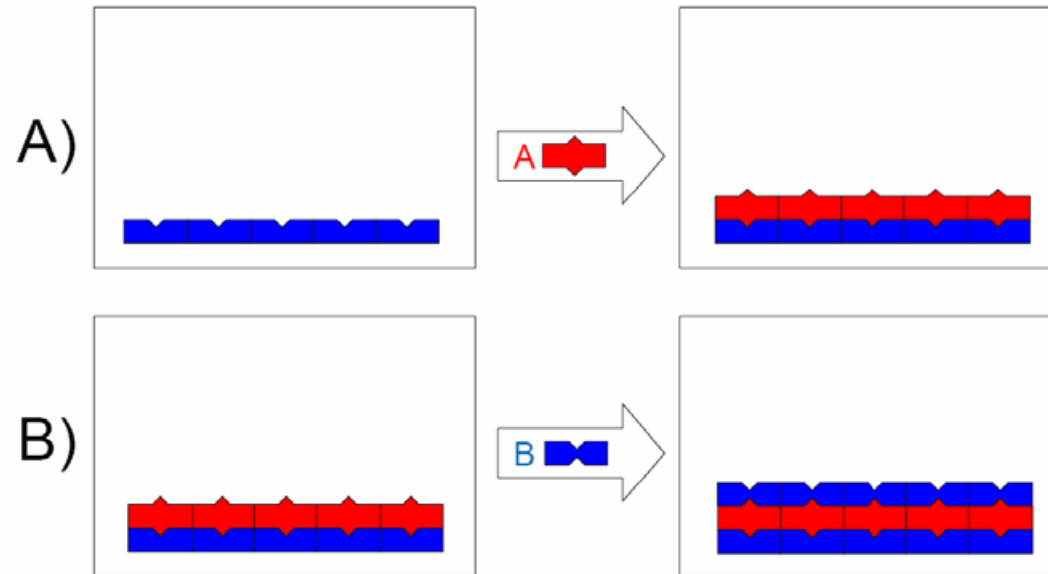
Yale University, USA



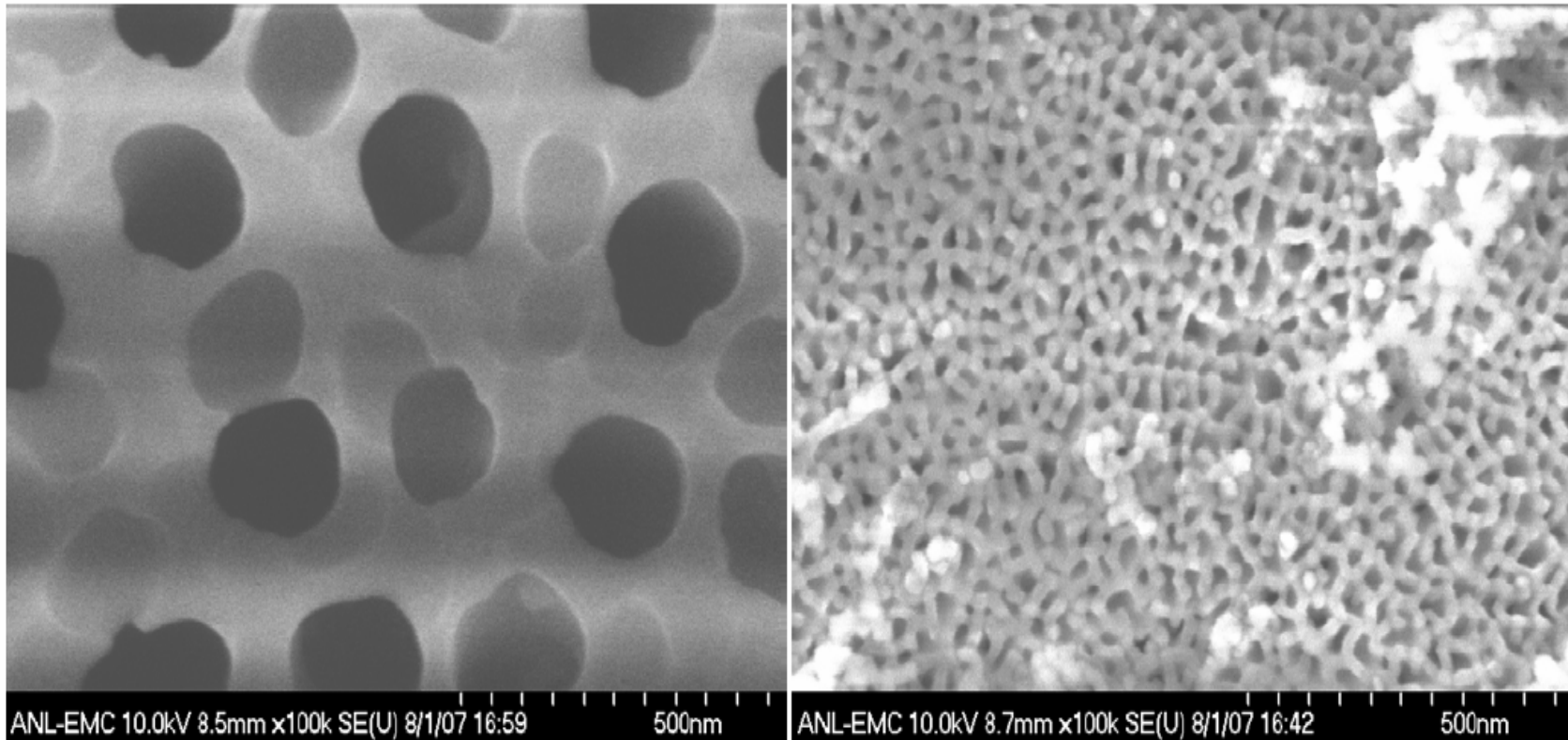
Pt₈ on Al₂O₃

- Size preselected (through mass filter) Pt₈₋₁₀ clusters stabilized on high surface area supports are 40-100 times more active than Platinum and vanadia (VO_x) catalysts
- Oxidative dehydrogenation (ODH) is exothermic but not dehydrogenation
- 3-D structure clusters, no agglomeration over a temperature range of 20-400 °C
- No change in cluster size as there was no change in activity and selectivity after 30 h of testing
- Density functional theory calculations used to investigate the structure of Pt₈ cluster
- Catalyst tests were carried out under atmospheric pressure in a flow reactor at 400-550 °C
- The temperature range was chosen to give a direct comparison with Pt-and VO_x based ODH catalysts
- Comparison based on TOF : Turnover frequencies (No. of propylene molecules produced per Pt atom per second)
- At 400 °C , the observed TOFs are 40-100 times higher than the previously reported Pt- and VO_x based ODH catalysts
- In overall reaction scheme, oxygen serves for removal of hydrogen as water
- The energy barrier is 0.2 e V (propane C-H bond cleavage)

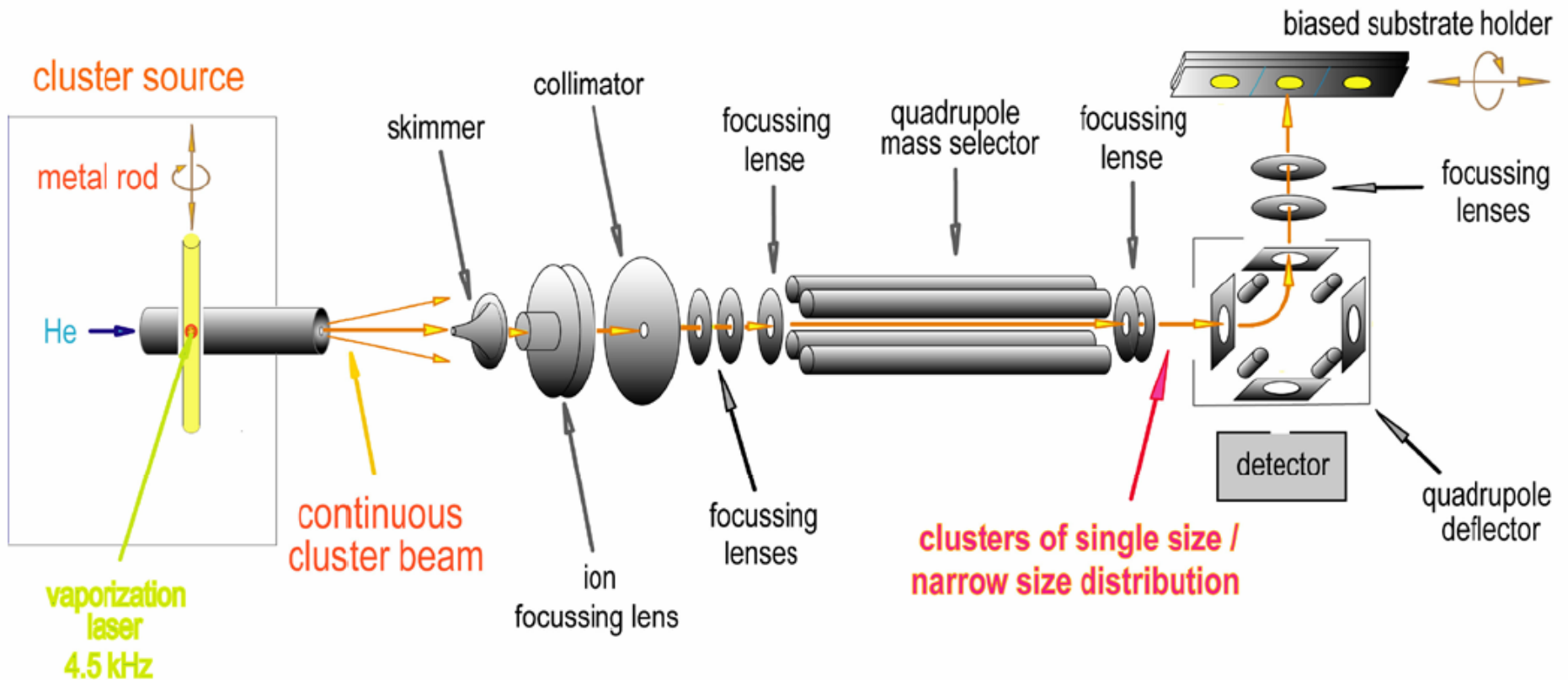
Atomic Layer Deposition process



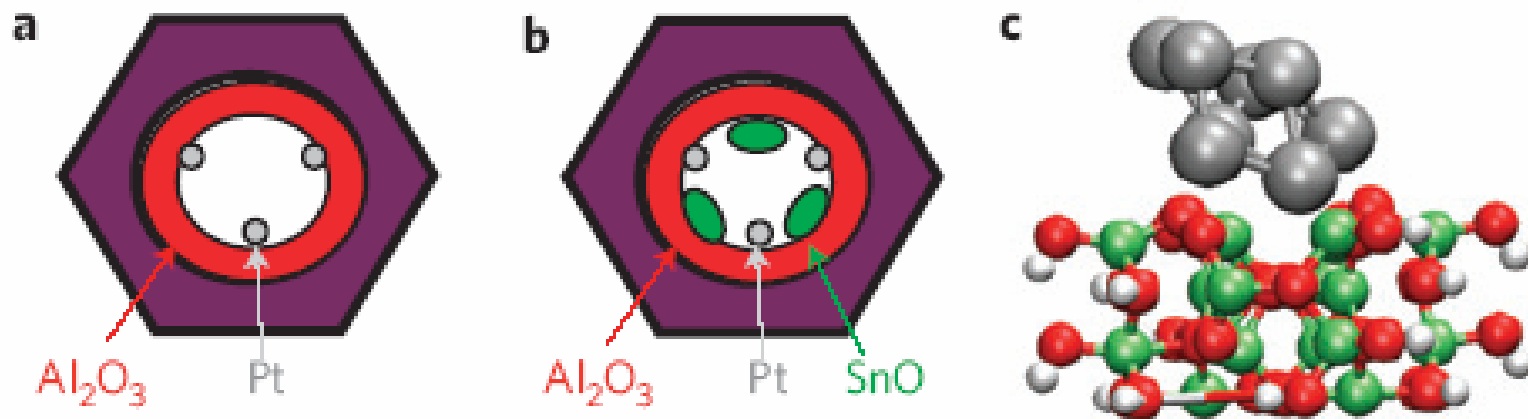
Schematic illustration of ALD process. The notches in the starting substrate for reaction A represent discrete reactive sites. Exposing this surface to reactant A results in the self-limiting chemisorption of a monolayer of A species. The resulting surface becomes the starting substrate for reaction B. Subsequent exposure to molecule B covers the surface with a monolayer of B species. Consequently, one AB cycle deposits one monolayer of the compound AB and regenerates the initial substrate. By repeating the binary reaction sequence in an ABAB... fashion, films can be deposited with atomic layer precision.



SEM of the AAO membranes used: Large pore side (left) and small pore side (right). Clusters were deposited on the large pore side of the membrane.

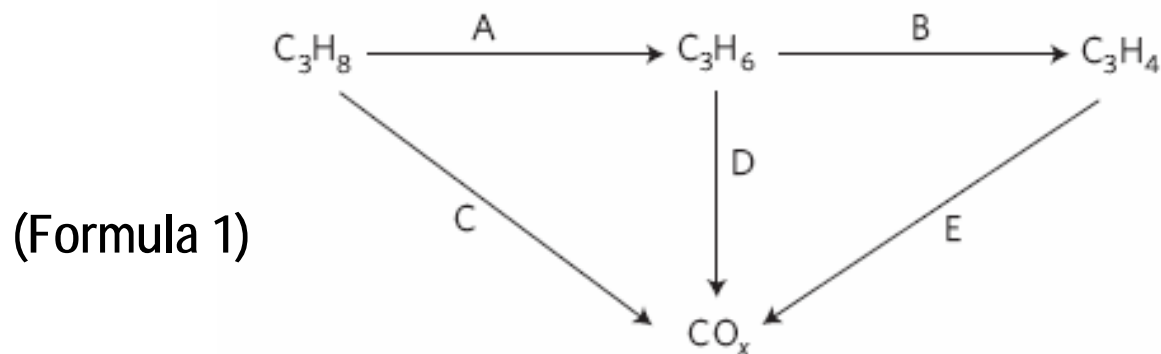


Schematic of the size-selected cluster deposition setup allowing for soft-landing and controlled surface coverage. The continuous beam of metal clusters is generated in a laser vaporization cluster source which utilizes a Nd:YAG laser operating at 4.5 kHz. The beam of neutral and charged platinum clusters passes through a biased skimmer into the ion guide of the second differentially pumped vacuum stage and then into the third vacuum stage. The positively charged clusters are then guided and focused into the quadrupole mass spectrometer for analysis.



Depiction of the catalytic system. **a,b**, Illustration of Pt clusters deposited in AAO membrane with ALD coating of Al_2O_3 (**a**), and with added SnO (**b**). **c**, Structure of Pt₈ cluster on an Al_2O_3 surface from density functional calculations.

The reaction scheme for propane ODH



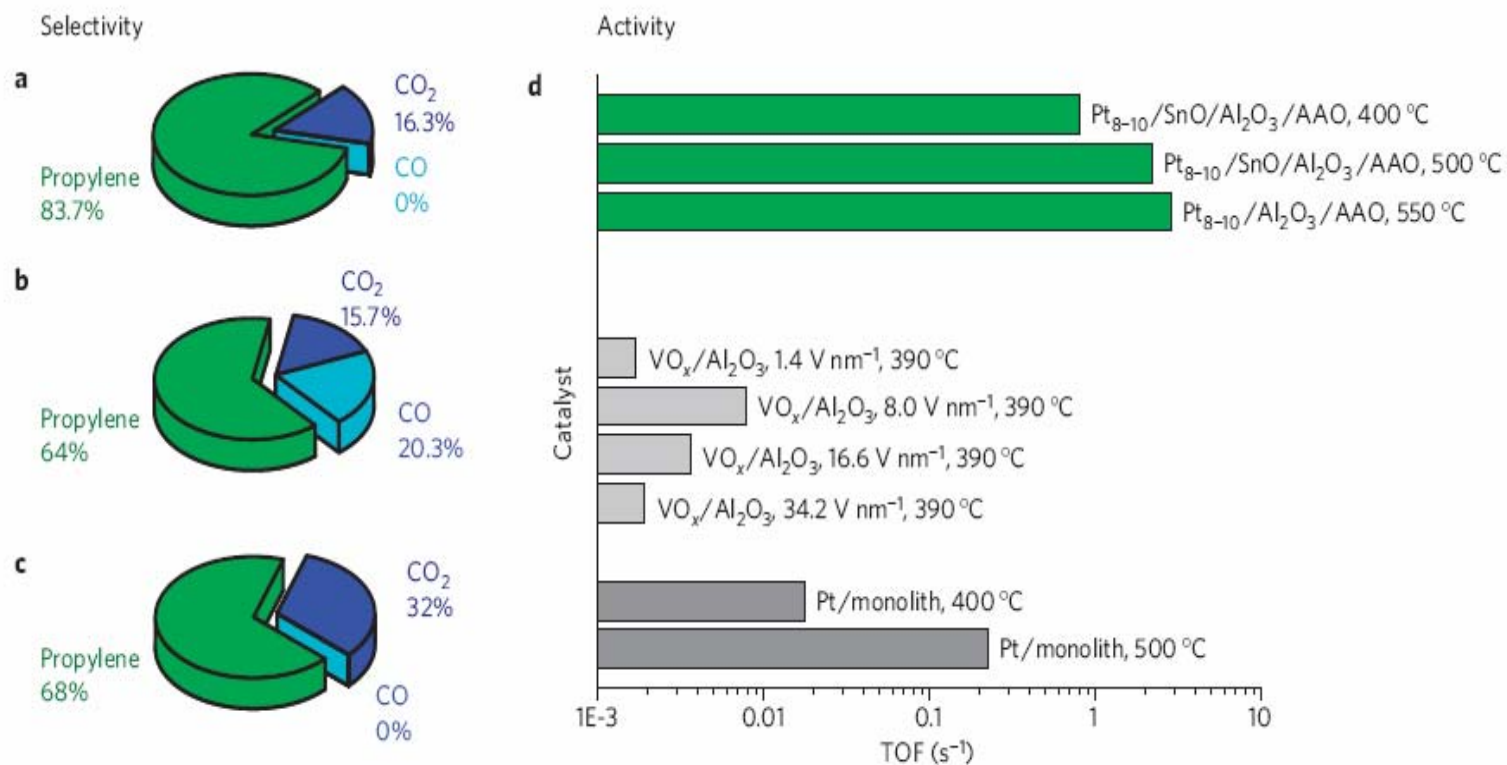


Figure 2 | Catalyst activity and selectivity. a-c, Selectivity of the Pt₈₋₁₀-based catalysts at various temperatures and support compositions: SnO/Al₂O₃ at 400 °C (a), SnO/Al₂O₃ at 500 °C (b) and Al₂O₃ at 550 °C (c). **d,** TOFs of propylene produced on the Pt₈₋₁₀ catalysts (green) and reference ODH catalysts (grey) expressed as number of propylene molecules formed per metal atom. Pt monolith and vanadia data from refs 29 and 22, respectively. See Supplementary Information for more details.

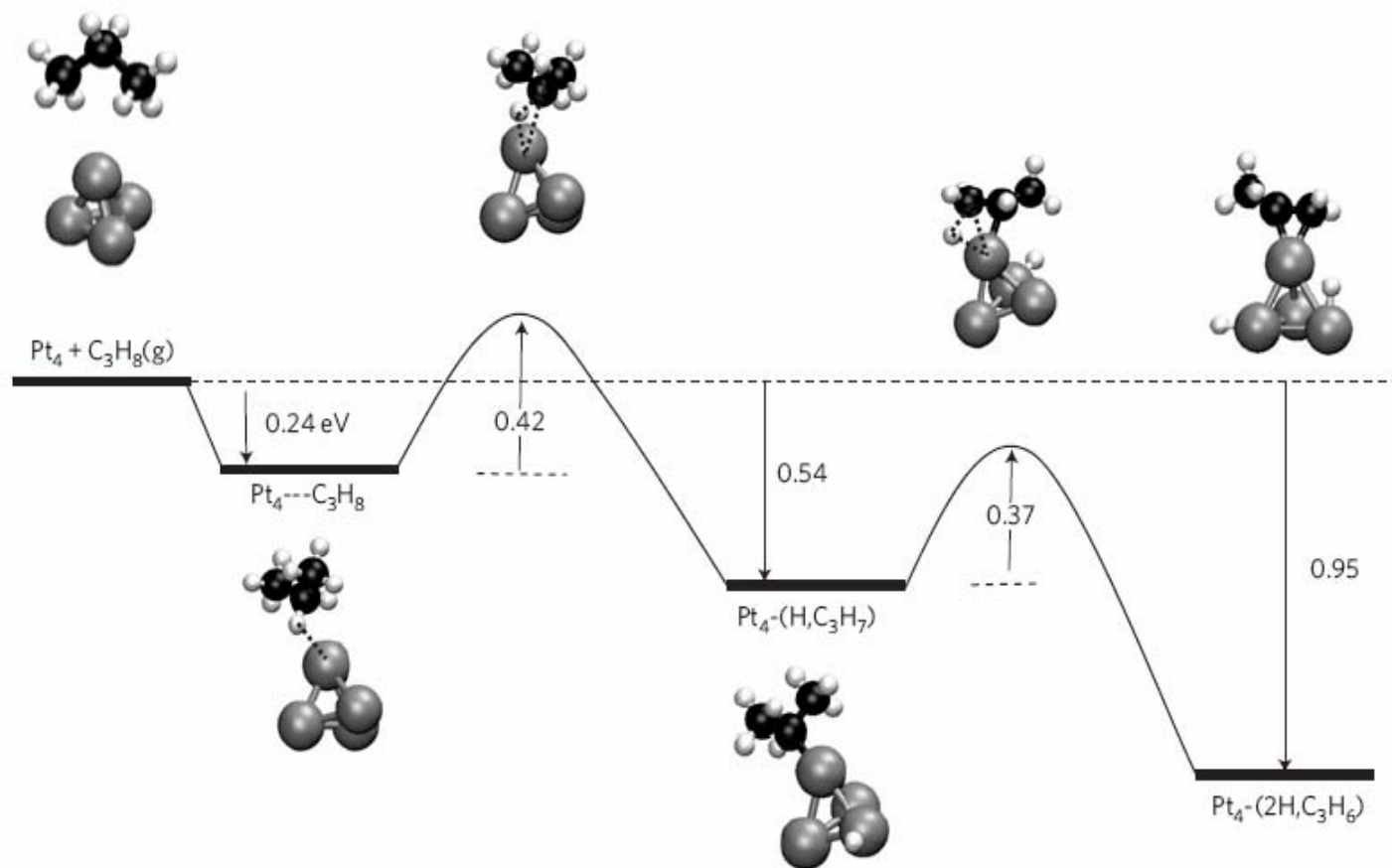


Figure 3 | Reaction path. Diagram of primary reaction steps in channel A (see formula (1)) from DFT calculations for the dehydrogenation of propane on a Pt₄ cluster leading to formation of propylene adsorbed on the cluster. Energies (in eV) of the equilibrium structures are relative to the reactants. Energy barriers for the transition state structures are relative to the preceding equilibrium structure ('true' barriers). The first barrier corresponds to breaking of the first C-H bond (on the CH₂ group) and the second barrier corresponds to breaking of the second C-H bond (on a CH₃ group). A number of other reaction steps involving hydrogen migration are not included in this diagram. The dotted lines in the structures indicate partial bonds. See Supplementary Information for more details of structures and energies and other reaction pathways.

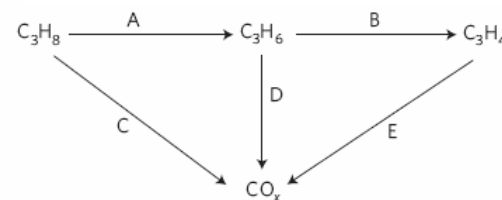
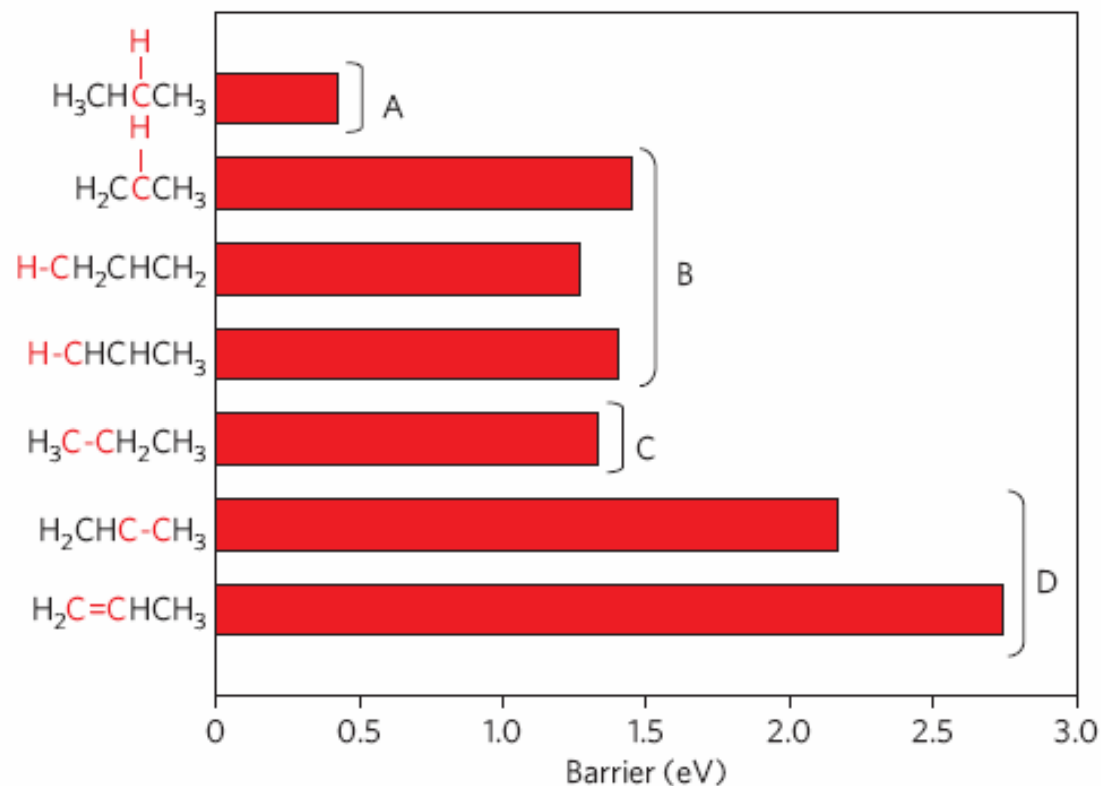
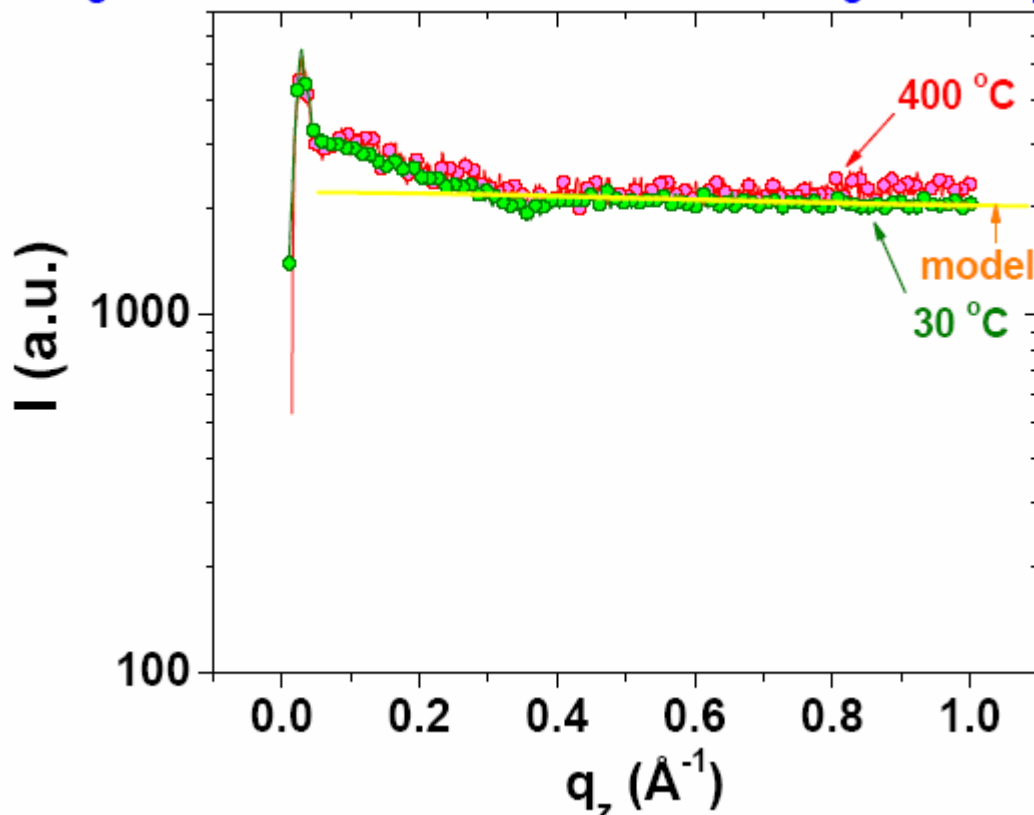
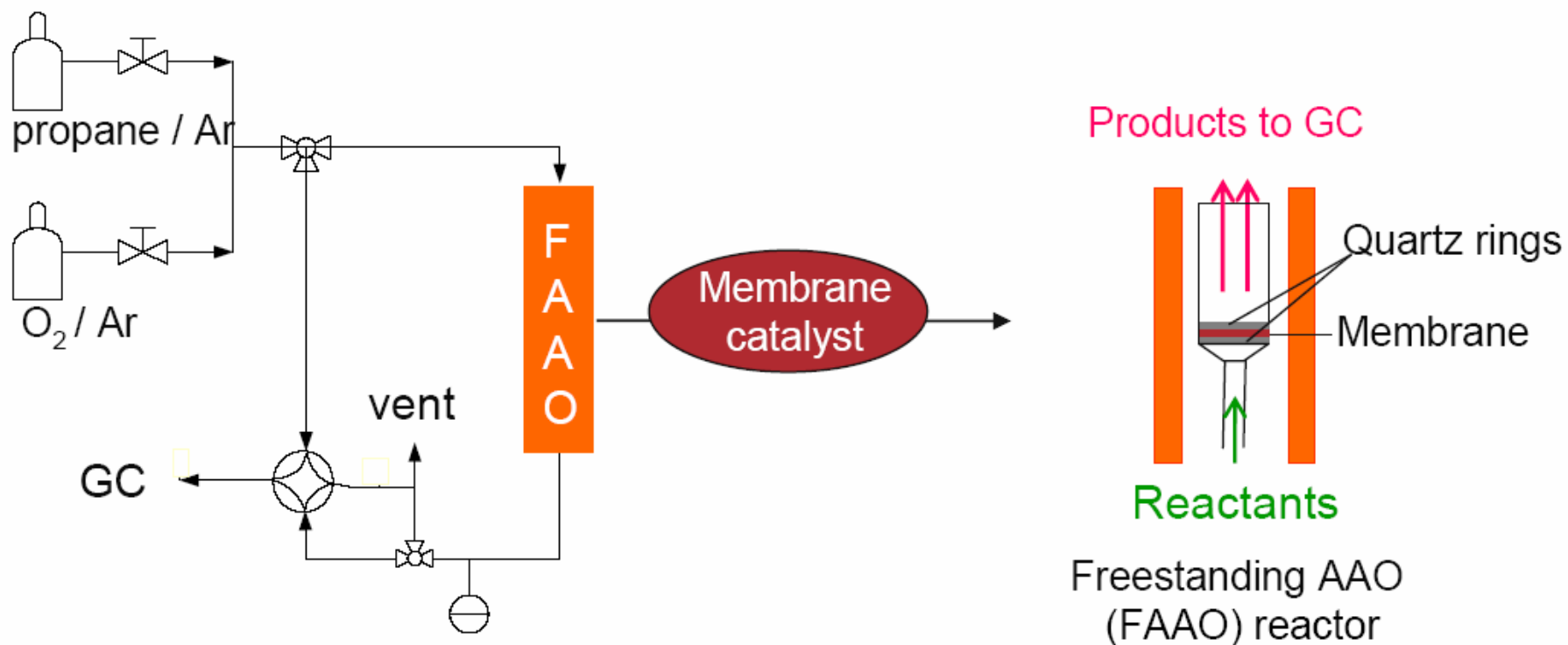


Figure 4 | Energy barriers of bond breaking. ‘True’ barriers for breaking C-C and C-H bonds in propane and propylene reactions on a Pt₄ cluster. Bonds that are broken are shown in red. Letters correspond to channels in formula (1). All of the barriers plotted here correspond to energies relative to the reactants (propane or propylene). In propane, the C-H bond breaking on the centre carbon (A) is favoured over a terminal carbon. In propylene C-H bond breaking all three sites (B) have similar barriers. See Supplementary Information for more details of structures and energies.



Stability of Pt7-10 clusters on with alumina film coated flat Si-wafer at elevated temperatures. The plot shows grazing incidence small angle X-ray scattering (GISAXS) data at room temperature and after keeping the temperature at 400 °C for several hours (scattered X-ray intensity I as a function of the scattering vector q). The two X-ray scattering signals are practically identical, thus providing a proof of absence of sintering of the Pt clusters at elevated temperatures. The straight line in the plot is the calculated scattering pattern obtained using the coordinates of a spherical Pt10 cluster, showing an excellent match with the experimental data.



Schematic of the freestanding AAO (FAAO) flow reactor setup for catalyst tests. By reversing the AAO membrane, the catalytically active particles will be at the entrance or at exit of the pores. The catalysts' tests were performed at temperatures up to 550 °C and the products formed were analyzed by on-line gas chromatography (GC).

SUMMARY

- High activity is due to the under-coordination of the Pt in the clusters
- Theoretical studies are like B3LYP, DFT, RPBE etc.
- Significant charge transfer occurs from propane C-H bonding orbital to the cluster

