Supported Metal Nanoclusters as Heterogeneous Catalysts in Flow

Toby Maccormack[1*], Emerson C. Kohlrausch[2], Yifan Chen[2], Jesum Alves Fernandes[2], Anabel E. Lanterna[2], Andrei N. Khlobystov[2], Karen Robertson[1]

[1]Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD

[2]School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD

*pcytm3@nottingham.ac.uk

Introduction

- Heterogeneous metal catalysis plays an integral role in chemical manufacture
- Metal nanocluster catalysts could enable metal loadings to be drastically reduced without compromising activity
- The use of flow chemistry to maximise the potential of these catalysts remains underexplored
- This work investigates how these catalysts perform in a packed bed flow reactor, with a focus on their catalytic activity and stability

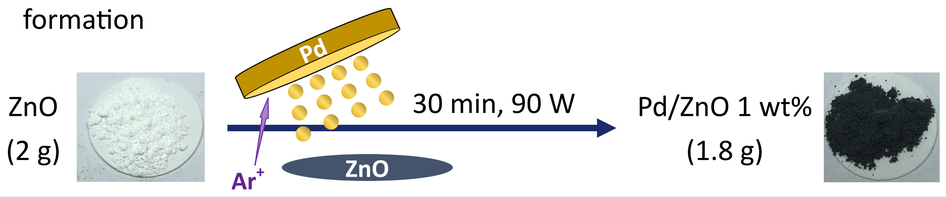
Catalyst synthesis *via* magnetron sputtering

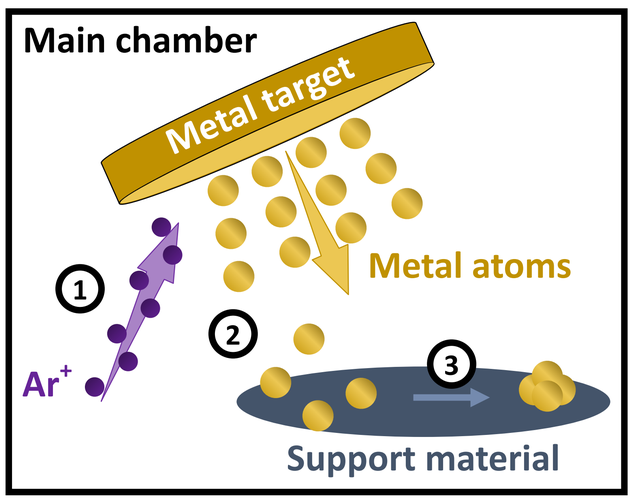
1. Argon ions fired at metal target
2. Metal atoms ejected from target and fall onto support
3. Metal atoms diffuse over support to form clusters[1]

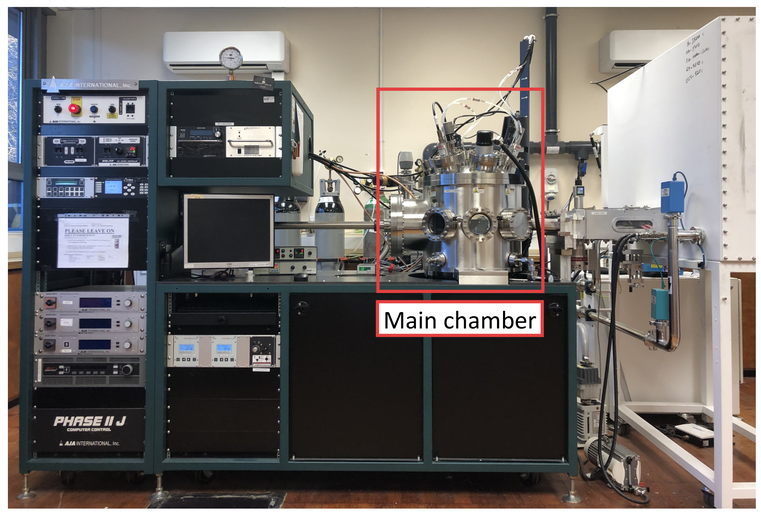
✓ Controlled and reproducible cluster formation

✓ Physical process (no solvent waste)

✓ High throughput



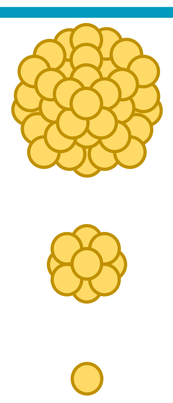




Advantages of metal nanoclusters

✓ **High proportion of atoms on surface enables high activity**[2]

✓ **Multiple atoms in cluster provides stability**



Nanoparticle

diameter 10 - 100 nm

lower percentage of surface atoms

Nanocluster

diameter < 10 nm

higher percentage of surface atoms

Single atom

Advantages of heterogeneous catalysis in flow

- Flow chemistry can improve the efficiency and safety of heterogeneous catalysis over batch

✓ Improved heat transfer

✓ Improved mixing

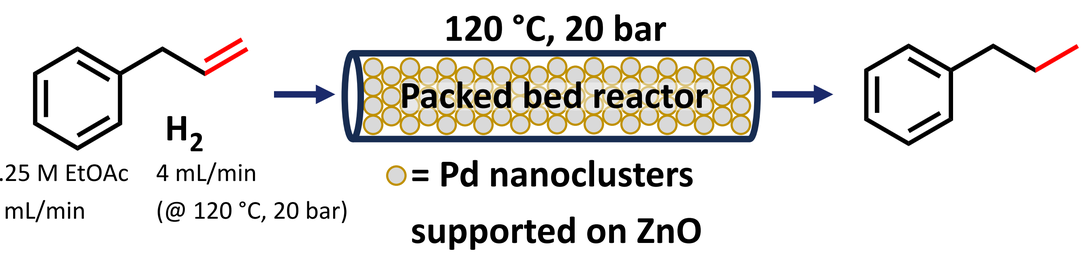
✓ Safer at elevated temperatures and pressures

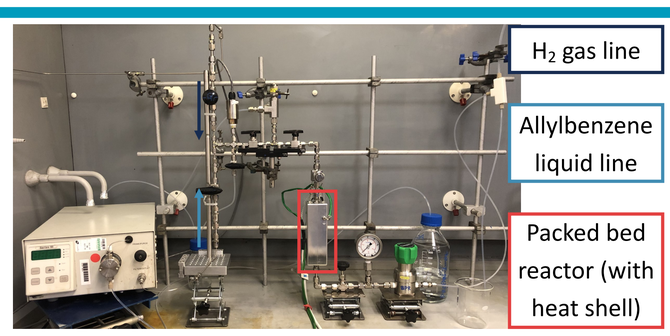
✓ Scale-up by running reaction for longer

- Packed bed reactors are often used to investigate heterogeneous catalysts in flow due to their simple set-up:

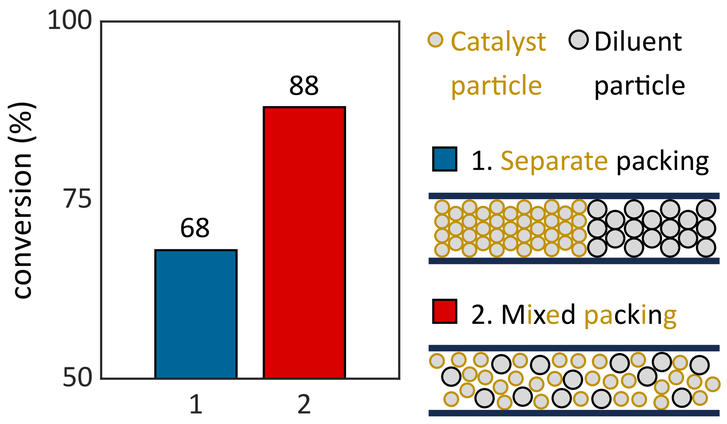
Catalyst testing and characterisation

Hydrogenation of allylbenzene used as a model reaction:

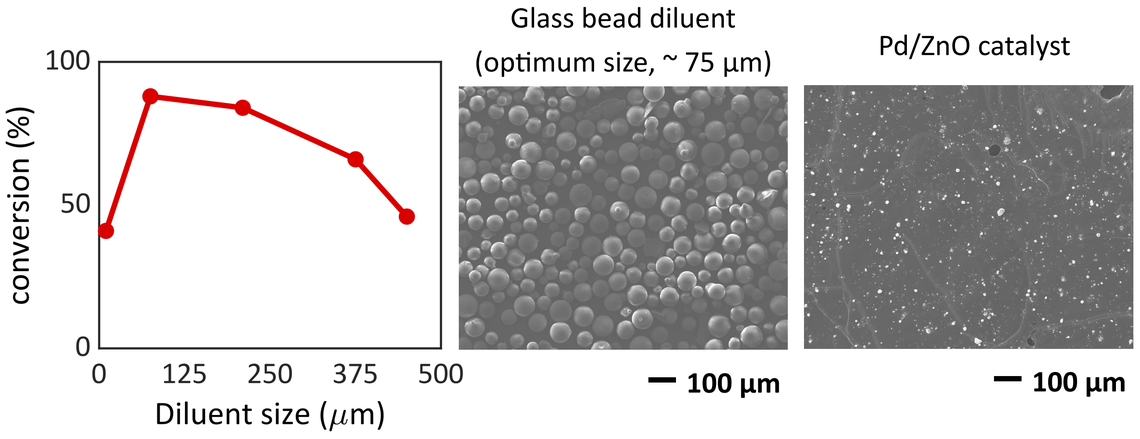




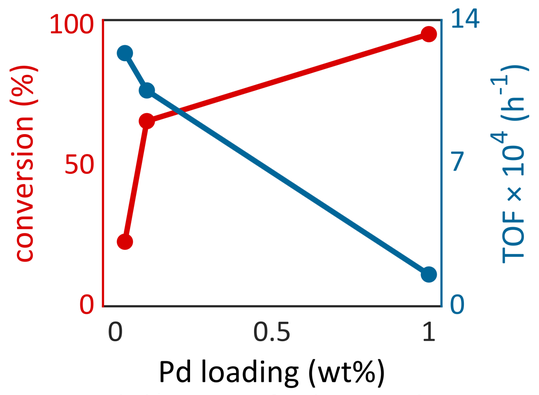
1 Catalyst/diluent packing regime impacts activity



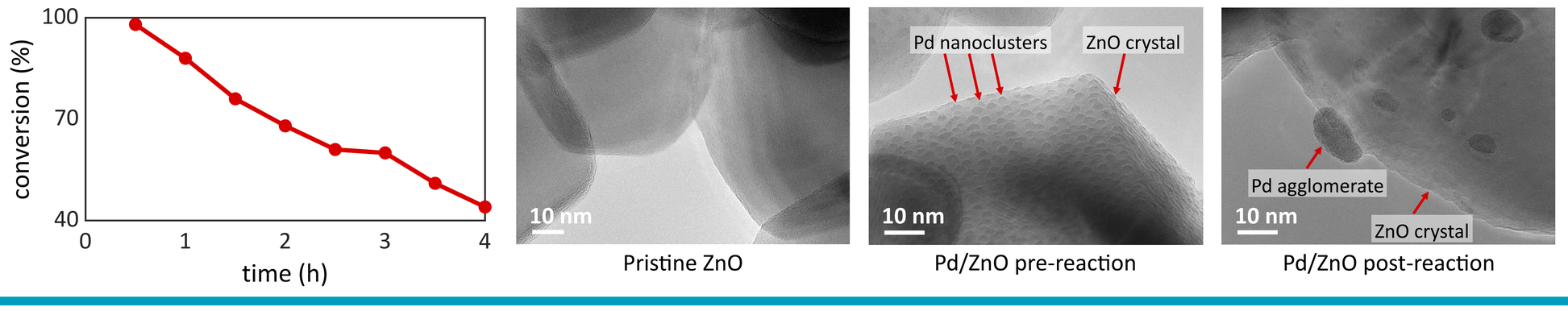
2 Particle size of the diluent mixed with Pd/ZnO can impact catalyst performance



3 Under an optimised mixed packing regime, Pd/ZnO displays high activity



4 Catalyst deactivation remains a challenge, and is attributed to cluster agglomeration



Conclusions

- Pd nanoclusters supported on ZnO have been synthesised by magnetron sputtering, and demonstrated high activity for allylbenzene hydrogenation in a packed bed reactor
- Packing regime of the catalyst within the reactor, as well as particle size of the diluent used, can impact catalyst performance

Future work

- Catalyst support modification to reduce Pd nanocluster agglomeration during reaction
- Test alternative support types to further understand nanocluster performance, e.g. static mixer[3]:

✓ Improved mixing

✓ Reduced pressure

References

1. I. Popov, *et al.*, *Nano Lett.*, 2023, 23 (17), 8006-8012

2. E. Tyo, S. Vajda, *Nat. Nanotechnol.,* 2015, 10, 577–588

3. C. Hornung, *et al.*, *J. Flow Chem.,* 2021, 11, 515-523

University of Nottingham
UK | CHINA | MALAYSIA

Programme Grant MASI Making every atom matter

EPSRC CDT in Sustainable Chemistry

UKRI Engineering and Physical Sciences Research Council