Master of Science HES-SO in Life Sciences

Opportunities and challenges of applying single-atom heterogeneous catalysts in the formation of Si-O bonds

Camille Blanchy

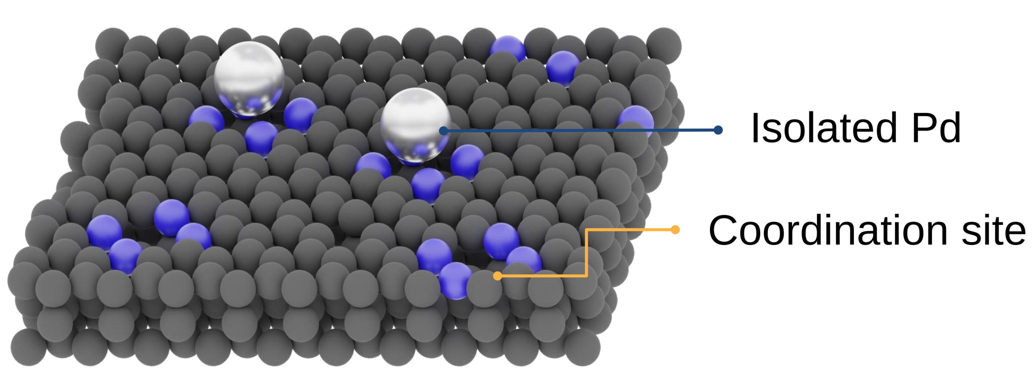
CHEMICAL DEVELOPMENT & PRODUCTION

HEIA-FR

Advisor: Dr. Roger Marti. Expert: Dr. Sharon Mitchell and Dario Poier // In collaboration with **ETHZ**

DESCRIPTION

- Transition-metal homogeneous catalysts are widely used in fine chemistry due to their high activity and selectivity. However, their single-use and non-recyclability are major limitations for sustainable processes.
- Replacing the conventional catalysts with heterogeneous catalysts containing nanoparticles improved recyclability. However, the active sites of the catalysts exhibited low selectivity and suffered from leaching which affected their activity.[1]
- Single-atom catalysts (SACs) have the potential to overcome the limitations of both homogeneous and heterogeneous catalysts with a view to sustainability.[2] They have isolated monoatomic active sites that enable maximum atom utilization.[3] In addition, they can increase atom efficiency, reduce metal use, and improve catalytic selectivity during transformations.



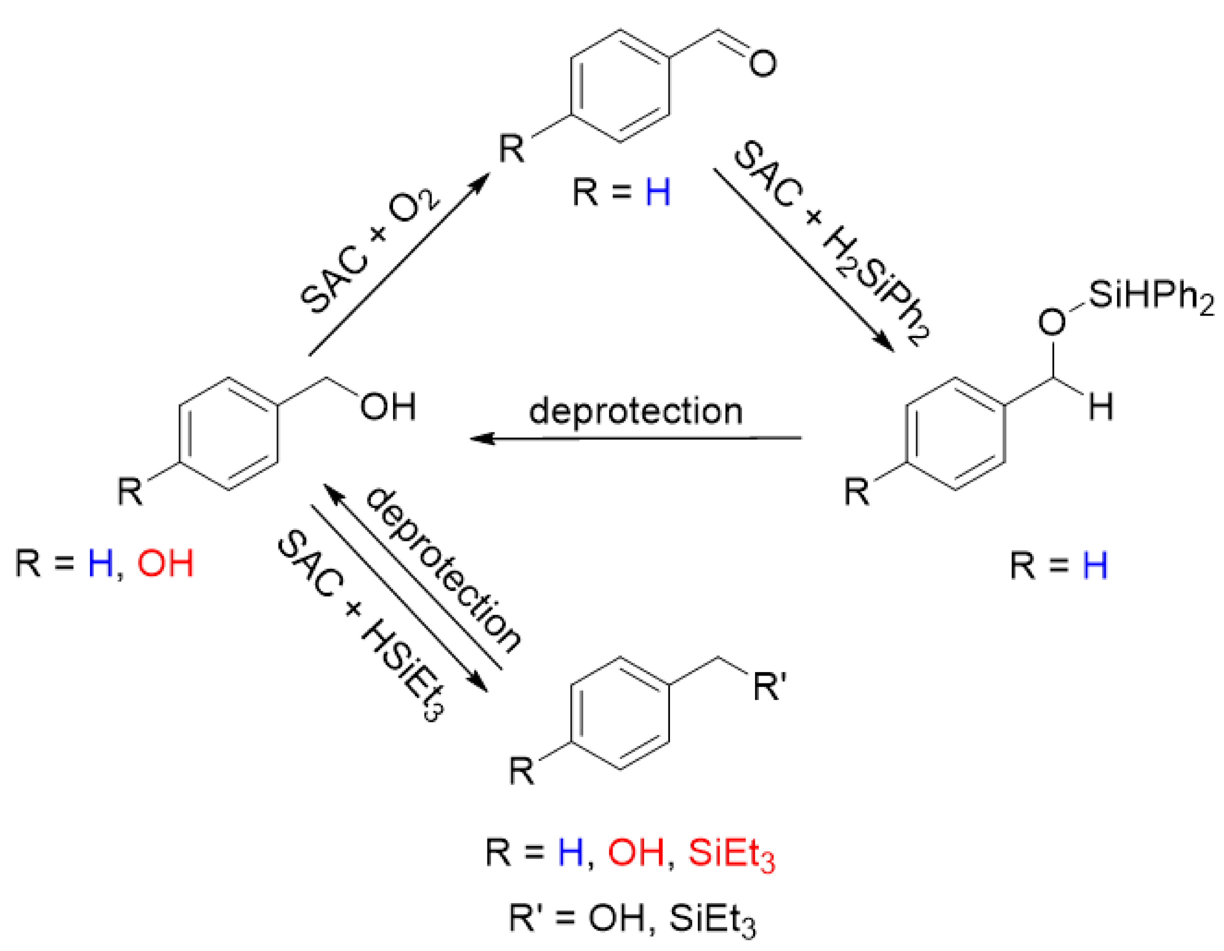
OBJECTIFS

- Explore the synthetic potential of SACs through various reactions to understand their advantages and limitations in catalyst-based synthesis.

→ Alcohol Oxidation

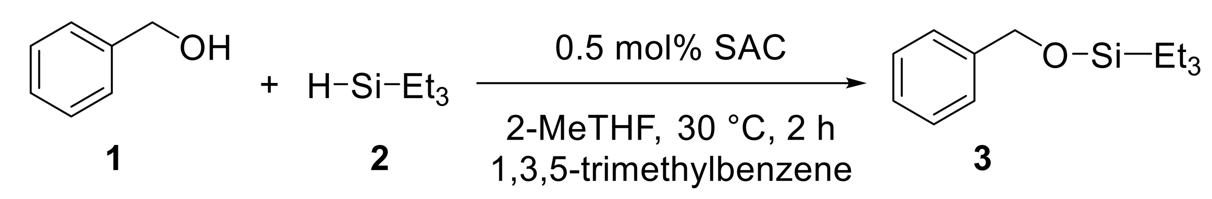
→ Alcohol Protection

→ Aldehyde Reduction



RESULTS

- Protection of the alcohol group with SACs has been carried out to investigate the influence of the single-atom catalyst (SAC) support material.

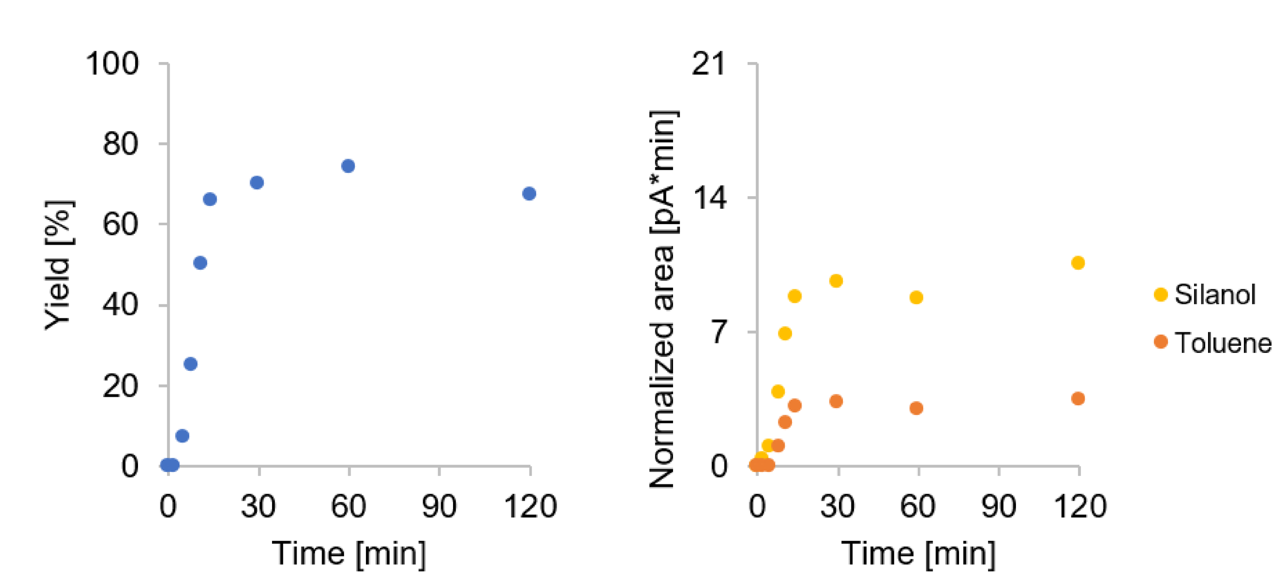


SACs Screening

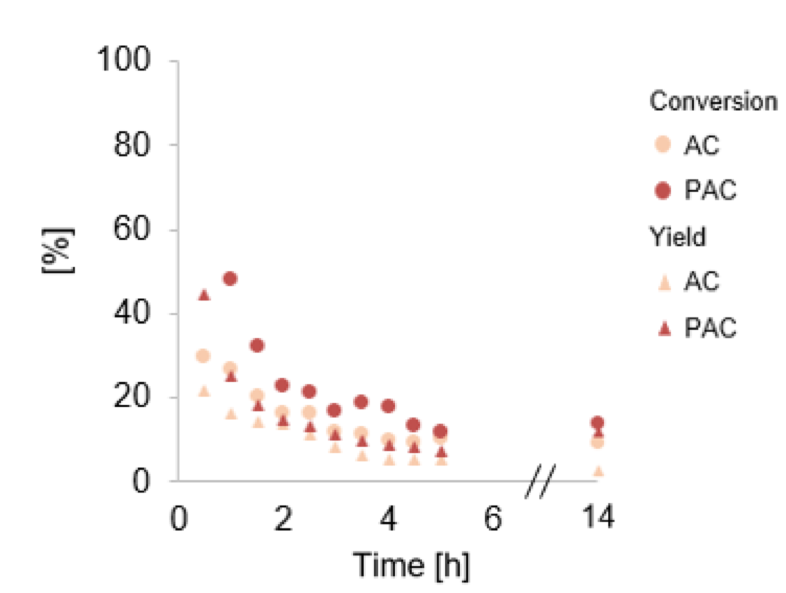
Catalyst	Conversion[a] [%]	Yield[b] [%]	TON[c] [%]	TOF[d] [h^{-1}]
Pd_1@AC	91	60	289	144.5
Pd_1@NC	23	13	73	36.5
Pd_1@ECN	13	14	41	20.5
Pd_1@PAC	77	63	245	122.5
Pt_1@AC	50	39	159	79.5
Au_1@AC	15	4	48	24
no SAC	0	0	0	0

[a]Conversion of benzylic alcohol **1**. [b]Yield of phenoxytriethylsilane **3**.[c]TON: mol of substrate converted/mol of active sites.[d]TOF= TON/time.

Reaction Tracking



SACs stability - Flow



- Still active centers on the catalyst after 14 hours use.

CONCLUSION

- Alcohol oxidation difficult to achieve with our current catalysts.
- Benzyl alcohol protection very promising with more than 60% yield in batch.
- Flow test demonstrated their future use on a large scale, with still catalyst activity after 14 hours.
- 4-hydroxybenzyl alcohol have selectivity challenges.
- Aldehyde reduction shows activity of SACs.

Try new silanes.

Test other SACs in flow.

Try new alcohol substrates.

[1] Y. Chen, S. Ji, C. Chen, Q. Peng, D. Wang, Y. Li, *Joule* **2018**, *2*, 1242–1264. [2] Z. Chen, J. Liu, M. J. Koh, K. P. Loh, *Adv. Mater.* **2022**, *34*, 1–16. [3] D. Faust Akl, D. Poier, S. C. D'Angelo, T. P. Araújo, V. Tulus, O. V. Safonova, S. Mitchell, R. Marti, G. Guillén-Gosálbez, J. Pérez-Ramírez, *Green Chem.* **2022**, *24*, 6879–6888.