MODELLING OF SOLID MICELLAR CATALYSTS

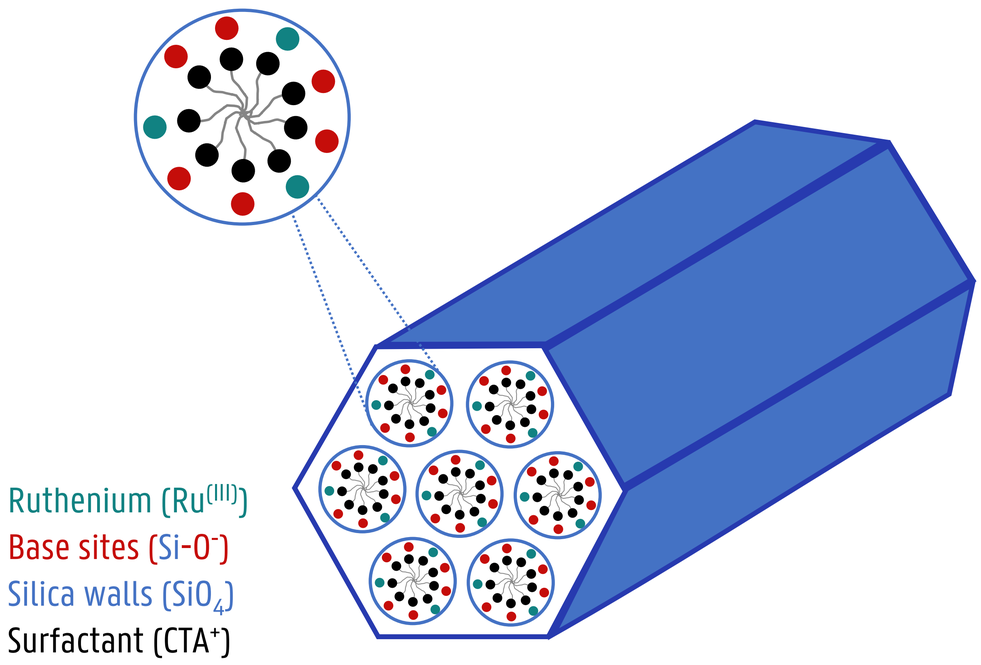
Sara Santos,[1] Catarina Mendes,[1] Maria Vieira,[1,2] Ines Marques,[1,2] Cesar A. Urbina-Blanco,[1] Mark Saeys,[1]

[1]Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 125, 9052 Ghent, Belgium
[2]Department of Chemical Engineering, Instituto Superior Tecnico de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal

Solid Micellar Catalysts

$Ru^{(III)}$@MCM

- Homogeneous-like Ru active centre
- Heterogeneous Silica framework



Hydrogenation reactions:

- CO_2 → Formate (water-free conditions)[1]
- Furfural → Furfuryl alcohol (selective on polar carbonyl bonds)[2]
- CO_2 → Methanol (low-T conditions)
- Many more…

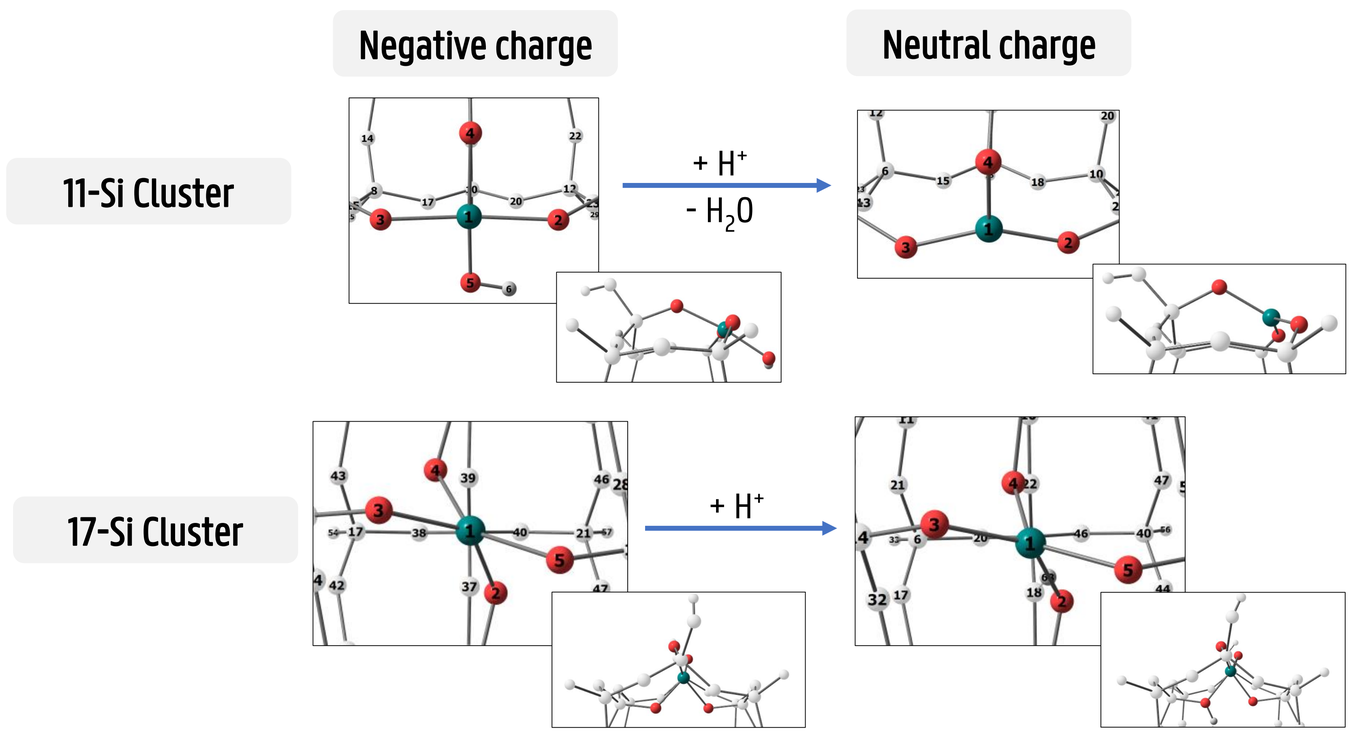
Modelling-guided approach: Cluster Model (based on silsesquioxane cages.[3, 4])

Cluster Model

Exploring the effects

Size	Charge	Relaxation of atoms
11 Si atoms (11-Si)	Neutral	Total (Unfrozen)
17 Si atoms (17-Si)	Negative	Partial (Frozen Bottom)

3- and 4-coordinated $Ru^{(III)}$



H_2 Activation

Cluster Size	Cluster Charge	Relaxation of atoms	$\Delta G_{Activation}$ (kJ/mol)	$\Delta G_{Reaction}$ (kJ/mol)
11-Si	Neutral	Unfrozen	13	-61
17-Si			52	-35
11-Si	Negative		79 [1]	-49
17-Si			69	**-73** [2]
11-Si	Neutral	Frozen Bottom	21	-30
17-Si			47	-24
11-Si	Negative		29	-82 [3]
17-Si			**63**	**-66** [2]

[1] $Ru\text{-}H_2$ structure very stable.
[2] H^+ moved to 02/04.
[3] H_2O was formed.

$Ru^{(III)}\text{-}(H_2O)_2$@MCM (17-Si negative cluster)

DFT calculations performed with Gaussian16, PBE0-D3(BJ)/Def2SVP, 298 K.

Conclusions

- Cluster models varying in size, charge and degree of optimization were used to model $Ru^{(III)}$ active centre.
- H_2 dissociation more favorable over a neutral cluster (no counterion).
- The 17-Si model structurally more stable than the 11-Si model.

References

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3. F. J. Feher *et al.*, *Journal of the American Chemical Society*, 1989, 111, 1741-1748.
4. C. Liu *et al.*, *Polyhedron*, 2018, 152, 73-83

Chemical Technology Symposium, LCT - Ghent University, 21/12/2021

Contact

Sara.Santos@UGent.be, Mark.Sayes@UGent.be

www.lct.ugent.be / Universiteit Gent