

## Heterogeneous Ru(III) oxidation catalysts via 'click' bidentate ligands on a Periodic Mesoporous Organosilica support

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The use of selective catalysts and easy recycling thereof, preferably with full recovery, is a major trend in green chemistry. Heterogenization of the active site on a porous solid support is an elegant method, often explored nowadays, to obtain a catalyst that can be easily separated from the medium by filtration. Another important trend is the use of water as a solvent which, restricts the use of non-hydrolytically stable supports.

In 2015, we developed an allyl-functionalized interconnected  $[\text{CH}_2\text{Si}]_3$  ring-type Periodic Mesoporous Organosilica (PMO) and applied it as a HPLC packing.<sup>1</sup> We also showed its exceptional hydrolytic stability ( $>\text{pH } 12$  and  $>150^\circ\text{C}$ ). In order to develop this ultra-stable material into a catalytic support a different synthesis approach is required, e.g. to improve the pore morphology.

Now, we developed a 100% monoallyl ring-type (mAR) PMO as a novel, versatile and exceptionally stable catalytic support with a high internal surface area and 5.0 nm pores.<sup>2</sup> Thiol-ene 'click' chemistry allows straightforward attachment of bifunctional thiols ( $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{SH}$ ) which, exploiting the thioether functionality formed, give rise to 'solid' bidentate ligands.  $[\text{Ru}(\text{acac})_2(\text{CH}_3\text{CN})_2]\text{PF}_6$  is attached and complex formation on the solid is studied via Density Functional Theory. All resulting solid catalysts show high activity and selectivity in alcohol oxidation reactions performed in green conditions ( $25^\circ\text{C}$ /water). The PMO catalysts do not leach Ru during reaction and are thus easily recuperated and re-used for several runs. Moreover, the hydrophobic/hydrophilic reaction environment and ordered pores of the mAR-support enable high catalytic activity for a poorly water-soluble substrates.

1 M. Ide, E. De Canck, I. Van Driessche, F. Lynen and P. Van der Voort, RSC Adv., 2015, 5, 5546-5552.

2 S. Clerick, E. De Canck, K. Hendrickx, V. Van Speybroeck, P. Van Der Voort, Green Chem., 2016, DOI: 10.1039/C6GC01494A