Modelling Solid Micellar Catalysts: a platform for the development of active catalysts.

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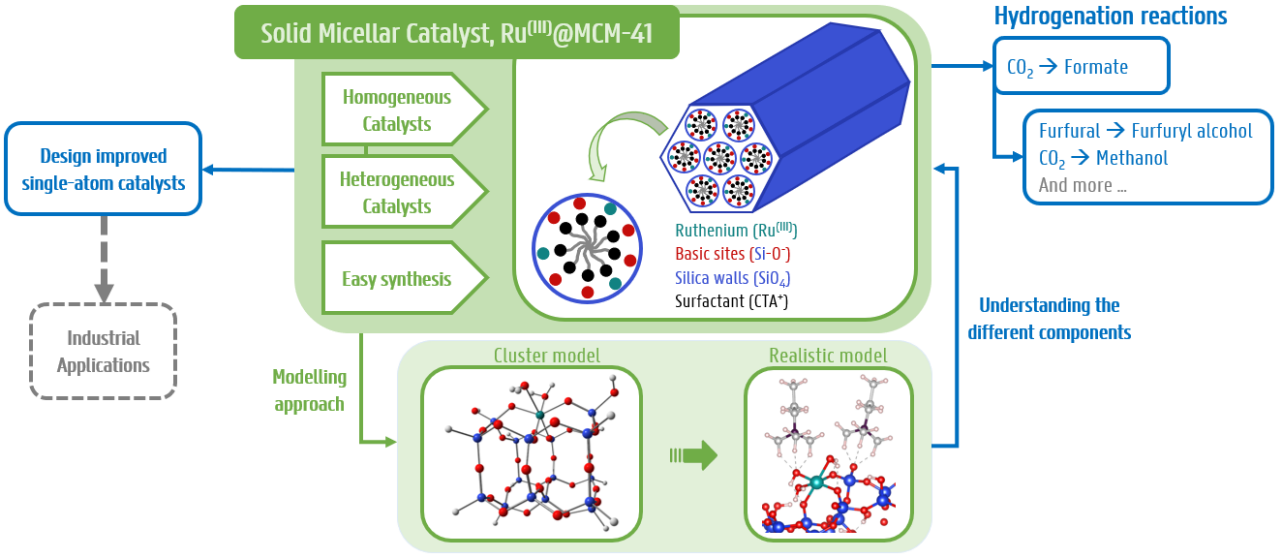
Solid micellar catalysts (SOMIC) are a new class of complex heterogeneous catalytic materials consisting of isolated active sites incorporated in the walls of an amorphous silica matrix stabilized by surfactant molecules. $Ru^{(III)}$@MCM-41 is the first of this family to be synthesized and characterized. It consists of $Ru^{(III)}$ sites and silanoxo basic sites incorporated into the walls of MCM-41 and stabilized by a quaternary ammonium surfactant. It is highly active on CO_2 hydrogenation to formate, reaching high concentrations of formate in a water-free environment, under mild reaction conditions.[1]

The computational models we developed, allowed us to understand the structure of $Ru^{(III)}$@MCM-41, an homogeneous-like ruthenium active center incorporated in the silica framework. Insight into the nature of the active sites suggested expanding the scope to the selective hydrogenation of polar bonds such as carbonyl groups and, to low-temperature CO_2 hydrogenation to methanol.[2] $Ru^{(III)}$@MCM-41 demonstrated selective and high catalytic performance for these different reactions, similar to state-of-the-art homogeneous Ru catalysts, however with superior stability and recyclability.[3-5] SOMIC catalysts are a dynamic and multicomponent system, and the presence of the surfactant in the pores plays a crucial role. When the surfactant is removed, the activity and stability are significantly affected.

To elucidate the nature of the active sites, their coordination environment and the effect of the stabilizing surfactant, first-principles models were developed. Initial cluster models focused on the $Ru^{(III)}$ active site and its direct environment. More recent periodic models of the silica matrix capture the variety of $Ru^{(III)}$ sites, the effect of the surfactant, and the role of water molecules near the silica walls.

In this presentation, we will discuss how modelling provides insight into the role of the various components of the SOMIC materials, their stability, and activity for polar bond hydrogenation reactions. We will also discuss the design space offered by SOMIC materials, by varying the metal centre, the surfactant and the matrix composition.



Representation of the molecular modelling approach leading to the development of active solid micellar catalysts.

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