

**CO<sub>2</sub> Hydrogenation of Copper Nanoparticles Supported on Zirconium Modified Silica**E. Lam<sup>1</sup>, K. Larmier<sup>1</sup>, P. Wolf<sup>1</sup>, C. Copéret<sup>1\*</sup><sup>1</sup>ETH Zurich

To date, there is no efficient way to employ and transform the ever-increasing amount of carbon dioxide (CO<sub>2</sub>) into more valuable resources. One approach to use CO<sub>2</sub> could be its transformation into more valuable compounds such as methanol (MeOH). [1] Copper based catalysts have shown promising efficiency in terms of activity and selectivity for transforming CO<sub>2</sub> to MeOH when supported on specific metal oxides. Of them zirconia (ZrO<sub>2</sub>) is known to promote MeOH synthesis. [2] Recently we proposed a reaction mechanism leading to MeOH occurring on the interface between copper and zirconia going via formate as an intermediate.[3]

Herein we use a surface organometallic chemistry (SOMC) combined with a thermolytic precursor (TMP) approach as well as incipient wetness impregnation (IWI) to maximize the ratio between Zr at the interface vs. the bulk on silica (SiO<sub>2</sub>). Cu nanoparticles on such supports show greatly enhanced activity and selectivity towards MeOH under CO<sub>2</sub> hydrogenation conditions compared to Cu nanoparticles on SiO<sub>2</sub>.

Solid state nuclear magnetic resonance spectroscopy and X-ray absorption spectroscopy was further used to investigate the catalyst and reaction intermediates.

[1] Goeppert, A.; Czaun, M.; Jones, J.-P.; Prakash, G.K.S.; Olah, G. A., *Chem. Soc. Rev.*, **2014**, *43*, 7995

[2] Fisher, I.A.; Bell, A.T.; *J. Catal*, **1997**, *172*, 222

[3] Larmier, K, Liao, W.-C.; Tada, S.; Lam, E; Vérel, R.; Bansode, A.; Urakawa, A.; Comas-Vives, A.; Copéret, C., *Angew. Chem. Int. Ed.*, **2017**, *56*, 2318