



	<b>Experiment title:</b> Understanding the effect of ZrO <sub>2</sub> phase on the structure and catalytic activity of ZrO <sub>2</sub> supported In <sub>2</sub> O <sub>3</sub> nanoparticles for CO <sub>2</sub> hydrogenation	<b>Experiment number:</b> 31-01-75
<b>Beamline:</b> BM31	<b>Date of experiment:</b> from: 29.05.2018 to: 05.06.2018	<b>Date of report:</b> 25-07-2019  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Wouter van Beek	
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## Report:

### Abstract 1

We report an operando examination of a model nanocrystalline In<sub>2</sub>O<sub>3</sub> catalyst for methanol synthesis via CO<sub>2</sub> hydrogenation (300 oC, 20 bar) by combining X-ray absorption spectroscopy (XAS), X-ray powder diffraction (XRD) and in situ TEM. Three distinct catalytic regimes are identified during CO<sub>2</sub> hydrogenation: activation, stable performance, and deactivation. The structural evolution of In<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) with time on stream (TOS) followed by XANES-EXAFS-XRD associates the activation stage with a minor decrease of the In-O coordination number and a partial reduction of In<sub>2</sub>O<sub>3</sub> due to the formation of oxygen vacancy sites (i.e. In<sub>2</sub>O<sub>3-x</sub>). As the reaction proceeds, a reductive amorphization of In<sub>2</sub>O<sub>3</sub> NPs takes place, characterized by decreasing In-O and In-In coordination numbers and intensities of the In<sub>2</sub>O<sub>3</sub> Bragg peaks. A multivariate analysis of the XANES data confirms the formation of In<sub>2</sub>O<sub>3-x</sub> and, with TOS, metallic In. Notably, the appearance of molten In<sub>0</sub> coincides with the onset of catalyst deactivation. This phase transition is also visualized by in situ TEM, acquired under reactive conditions at 800 mbar pressure. In situ TEM revealed an electron beam assisted transformation of In<sub>2</sub>O<sub>3</sub> nanoparticles into a dynamic structure in which crystalline and amorphous phases co-exist and continuously interconvert. The regeneration of the deactivated In<sub>0</sub>/In<sub>2</sub>O<sub>3-x</sub> catalyst by re-oxidation was critically assessed revealing that the spent catalyst can be re-oxidized only

partially in a CO<sub>2</sub> atmosphere or air yielding an average crystallite size of the resultant In<sub>2</sub>O<sub>3</sub> that is approximately an order of magnitude larger than the initial one.<sup>1</sup>

## Abstract 2

*Operando* X-ray absorption spectroscopy (XAS) associates the superior activity and stability of the In<sub>2</sub>O<sub>3</sub>/m-ZrO<sub>2</sub> catalyst for the direct hydrogenation of CO<sub>2</sub> to methanol (300 °C, 20 bar) to indium sites with an average oxidation state of +2.3 atomically dispersed in the lattice of monoclinic ZrO<sub>2</sub>. The active sites in this solid solution m-ZrO<sub>2</sub>:In catalyst are In–V<sub>o</sub>–Zr sites (V<sub>o</sub> is an oxygen vacancy) that are stabilized in the lattice of poorly reducible m-ZrO<sub>2</sub> against deactivation by over-reduction to In<sup>0</sup>. In contrast, the amorphous ZrO<sub>2</sub> support does not form a (crystalline) solid solution with In<sub>2</sub>O<sub>3</sub> and, as a result, In<sub>2</sub>O<sub>3</sub>/am-ZrO<sub>2</sub> reduces to metallic In within minutes under the reaction conditions. Furthermore, a tetragonal ZrO<sub>2</sub> support stabilizes dispersed indium nanocrystals (In<sub>2</sub>O<sub>3</sub>/t-ZrO<sub>2</sub>) against over-reduction only partially, yielding a catalyst with an average oxidation state of the In sites below +2: i.e., In<sub>2</sub>O<sub>3</sub>/t-ZrO<sub>2</sub> also suffers deactivation by over-reduction. Our results demonstrate that the phase of the ZrO<sub>2</sub> support determines whether an active solid solution with indium forms, which has major implications for the reducibility of In<sup>3+</sup> sites and their local structure. Comparing the stability and activity of indium-based catalysts, we identified the monoclinic solid solution m-ZrO<sub>2</sub>:In as a superior catalyst for the direct conversion of CO<sub>2</sub> to methanol, which contains active In–V<sub>o</sub>–Zr surface species that are significantly more stable toward reduction than In–V<sub>o</sub>–In sites in bixbyite-type In<sub>2</sub>O<sub>3</sub>.

## Publications:

1. Tsoukalou, A.; Abdala, P. M.; Stoian, D.; Huang, X.; Willinger, M.-G.; Fedorov, A.; Müller, C. R., Structural Evolution and Dynamics of an In<sub>2</sub>O<sub>3</sub> Catalyst for CO<sub>2</sub> Hydrogenation to Methanol: An *Operando* XAS-XRD and In Situ TEM Study. *J. Am. Chem. Soc.* **2019**, *141* (34), 13497-13505.
2. Tsoukalou, A.; Abdala, P. M.; Armutlulu, A.; Willinger, E.; Fedorov, A.; Müller, C. R., *Operando* X-ray Absorption Spectroscopy Identifies a Monoclinic ZrO<sub>2</sub>:In Solid Solution as the Active Phase for the Hydrogenation of CO<sub>2</sub> to Methanol. *ACS Catal.* **2020**, *10* (17), 10060-10067.
3. *Operando* study relates the structural dynamics of an In<sub>2</sub>O<sub>3</sub> catalyst with its activity for CO<sub>2</sub> hydrogenation to methanol. *ESRF Highlights* **2019**, 154-156.