

**Experiment title:**Unraveling the unprecedented activity and stability of Co-In catalysts for the direct hydrogenation of CO<sub>2</sub> to methanol**Experiment number:**

CH 5572

<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 14 Nov 2018 to: 20 Nov 2018	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Antonio Aguilar	<i>Received at ESRF:</i>
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**Report:**

A novel In-Co based catalyst shows twice higher yield of methanol than state-of-the art reported In<sub>2</sub>O<sub>3</sub>@ZrO<sub>2</sub> in carbon dioxide hydrogenation reaction under industrially relevant conditions (5.0 MPa, 573 K, CO<sub>2</sub>:H<sub>2</sub> = 1:4) without producing any significant amount of methane.<sup>1</sup> Catalyst exhibits high stability, however requires a long activation period prior to reaching its maximum and stable activity. To reveal the active phase formed during the induction period, XANES and EXAFS spectroscopy are measured successively at the In K-edge (27.9 keV) and Co K-edge (7.7 keV) to assess the In and Co local environment at different moment of the reactions: initial state at room temperature and atmospheric conditions, heated to 300 °C for 1 h in He flow, with a CO<sub>2</sub>/H<sub>2</sub> mixture (4:1) at 300 °C at 50 bars for about 50 hours with a GHSV = 16000 h<sup>-1</sup>. The figure 1 and 2 below shows the various XAS spectra taken with a fresh catalyst and selected reaction times (1h, 9h, 15h, and 50h).

After the catalyst preparation cobalt and indium are respectively in a mixed divalent/trivalent state and trivalent state. Consideration of the FT-EXAFS spectra suggests the Co<sub>3</sub>O<sub>4</sub> and In(OH)<sub>3</sub> phases, in accordance with the PXRD results. After one hour of reaction in CO<sub>2</sub>/H<sub>2</sub> mixture (T = 300 °C, P = 50 bars), both indium and cobalt atoms appears mostly in a reduced state especially cobalt. As the time on stream, is extended up to 50 h of reaction, the FT-EXAFS spectra of cobalt shows the clear fingerprint of metallic fcc structure. Since the amplitude is increasing overtime, it suggests that metallic Co nanoparticles are progressively

enlarging their size. For indium, the type of reduced state after 1h of reaction is not clear. There is no direct correspondence with the EXAFS spectra of the metallic indium or the mixed carbide phase ( $\text{Co}_3\text{InC}_{0.75}$ ). A Co-In metallic alloy may be a possibility. However, what is interesting with the indium counterpart, is the presence of isobestic points with the XANES spectra. This is a good indication that only two structures are present and evolving from one to another. The final FT-EXAFS spectra after 50 h of reaction show that small  $\text{In}_2\text{O}_3$  nanoparticles are progressively formed during the reaction. Consequently, the initial phase obtained after 1h of reaction including indium in its reduced state is the starting precursor for the formation  $\text{In}_2\text{O}_3$  phase. Since, pure Co metallic is known to produce methane in the same operating conditions, and STEM-EELS imaging have shown indium atoms redistribute on the surface of cobalt after catalytic testing, XAS spectroscopy results suggest that  $\text{In}_2\text{O}_3$  supported on metallic cobalt may be the active phase for the formation of methanol during  $\text{CO}_2$  hydrogenation.

The qualitative assessments provided in this report will be completed by a thorough analysis of the ensemble of XAS spectra and by a publication.

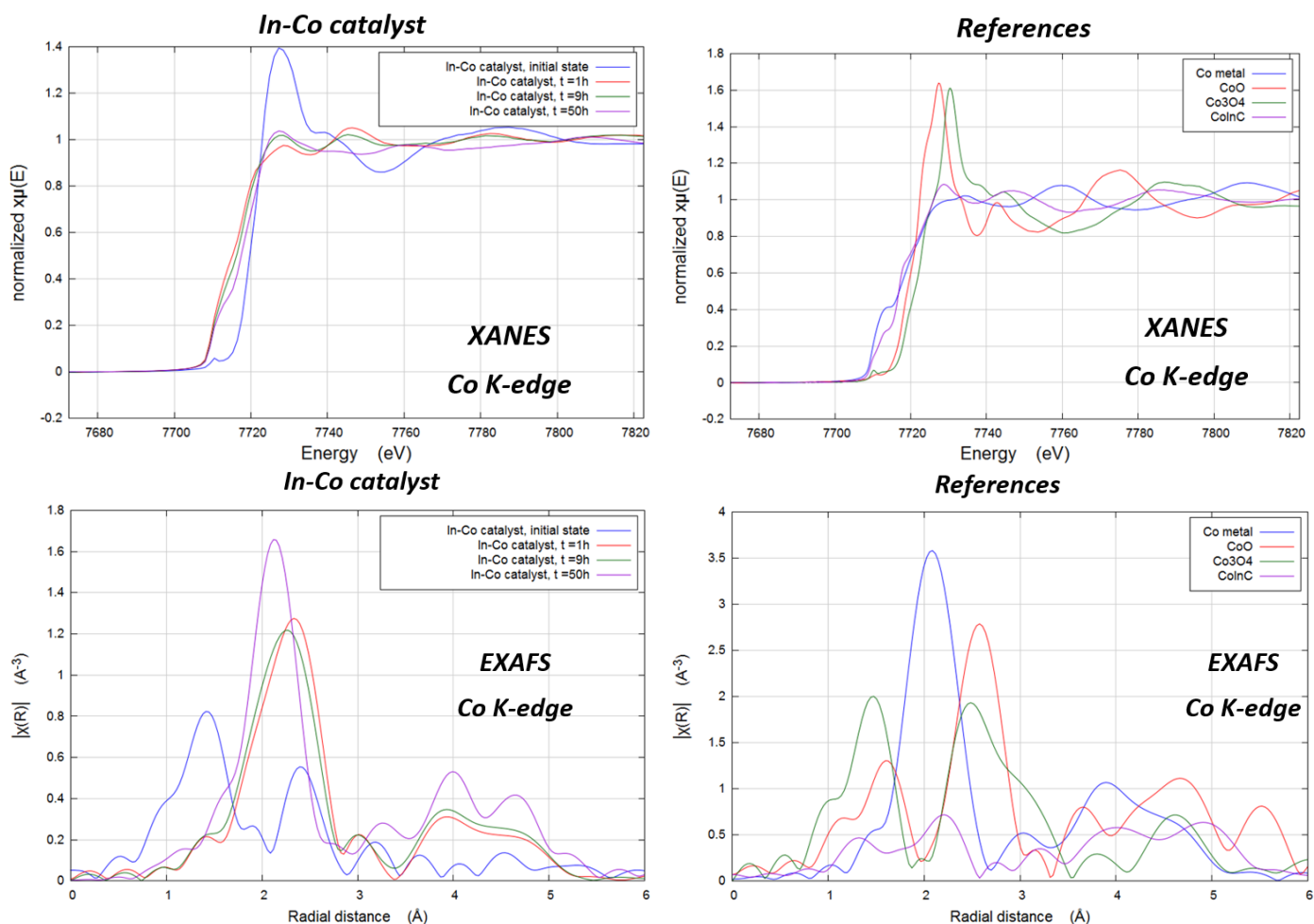


Figure 1: XANES and FT-EXAFS spectra acquired at Co K-edge of the In-Co catalyst measured at various time of  $\text{CO}_2$  hydrogenation and references

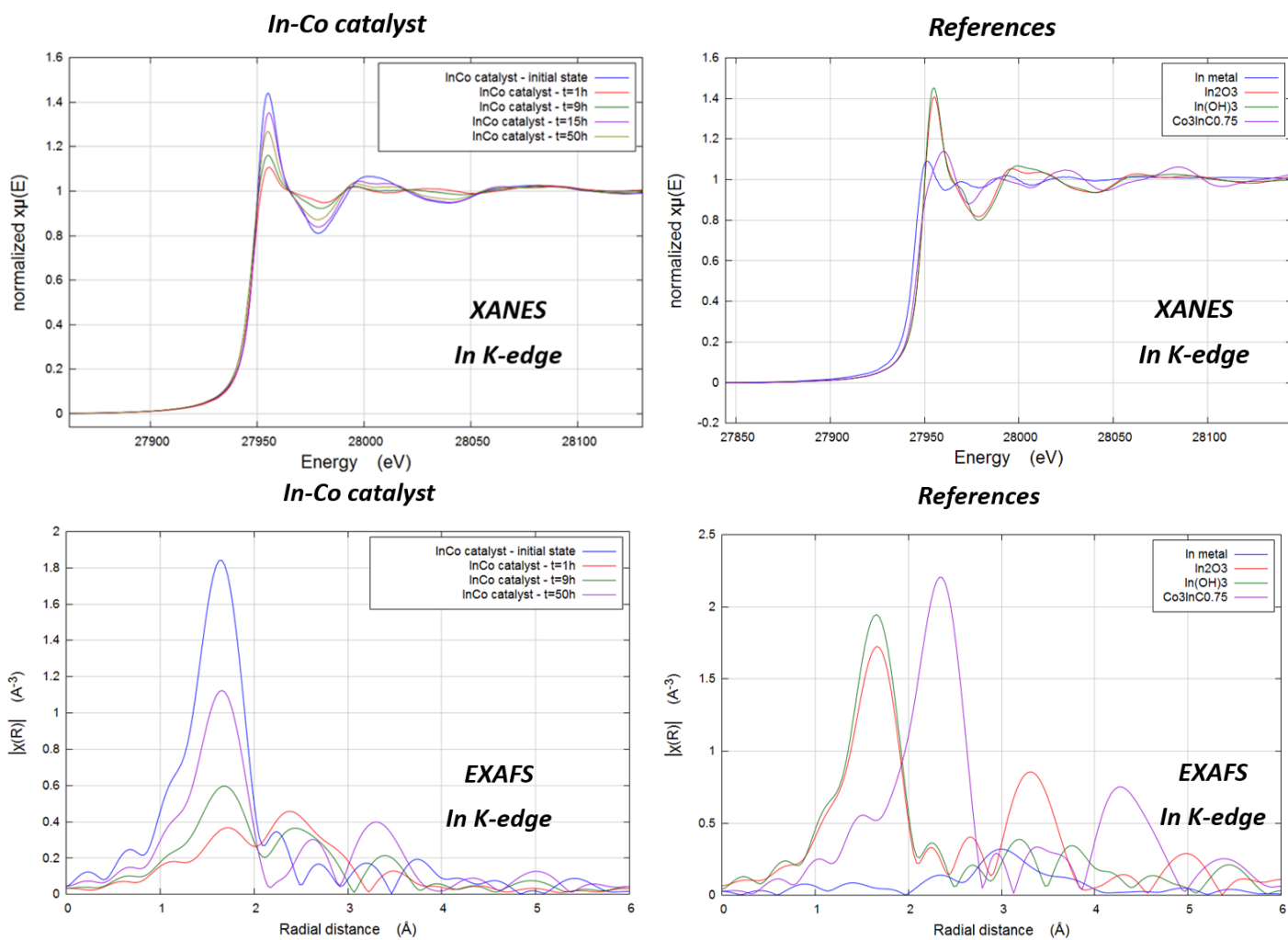


Figure 2: XANES and FT-EXAFS spectra acquired at In K-edge of the In-Co catalyst measured at various time of CO<sub>2</sub> hydrogenation and references