



	<b>Experiment title:</b> Investigation of CO <sub>2</sub> methanation over highly active Ni-doped CeO <sub>2</sub> catalysts: insights into the active nickel sites	<b>Experiment number:</b> CH-6666
<b>Beamline:</b> BM-23	<b>Date of experiment:</b> from: 5/04/2023 to: 11/04/2023	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Davide Salusso	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Spyros Zafeiratos <sup>1*</sup> , Mathias Barreau <sup>1*</sup> , Davide Salusso <sup>2*</sup> , Elisa Borfecchia <sup>3*</sup> , Leonardo Spuri <sup>*3</sup> 1 : Laboratory ICPEES Catalysis and Materials 25, rue Becquerel FR - 67087 STRASBOURG 2 2 : European Synchrotron Radiation Facility 3 : University of Turin, Chemistry Department, Turin, Italy		

## Report:

Cost efficient and long-term stable catalysts are in great demand for the CO<sub>2</sub> hydrogenation to methane (Sabatier reaction), a key process involved in conversion of CO<sub>2</sub> into useful chemicals and fuels. Recently we prepared Ni-doped ceria nanoparticles 3.5 times more active than conventional Ni-supported on ceria. We then proposed to investigate by combined DRIFT/XAFS two Ni/CeO<sub>2</sub> samples under reaction conditions.

The experiment started with the challenging alignment of the DRIFT and XAFS set-up which we successfully reached in 1 shift. Due to the low Ni content Ni K-edge XAFS spectra were collected in fluorescence mode. Hence a fluorescence detector was installed within the DRIFT set-up, demonstrating the high potentiality of the employed set-up. Ni K-edge XAFS and DRIFT spectra were collected during the following protocol : I) RT, He, II) heat (5C/min) to 400C under O<sub>2</sub> (20%)/He mixture and steady state at 400C for 30'. III) Cooling to 100C followed by heating to 400C under H<sub>2</sub> (20%)/He mixture and steady state at 400C for 30'. IV) Cooling to 230C where the reaction section begun. First we sent stoichiometric CO<sub>2</sub>:H<sub>2</sub> (1:4) mixture at 230C for 1h and then we heated to 350C to monitor catalytic variations.

The experiment was successful for both samples and the collected data for one of them, reported in the figure 1, can be summarized as following.

Ni K-edge XANES clearly showed as Ni is present as NiO nanoparticle in the as prepared material. During H<sub>2</sub> activation we observed as Ni is reduced to metallic Ni (active state for Sabatier reaction) without a clear variation of Ni particle size confirmed from EXAFS and FT-EXAFS spectra. It is worth to note as high quality EXAFS spectra ( $k > 10 \text{ \AA}^{-1}$ ) were successfully collected in 10 minutes in fluorescence mode. At the same time DRIFT spectra clearly presented the presence of Ce<sup>3+</sup> band which can be used to qualitatively monitor the

presence of  $\text{Ce}^{3+}$ . High quality XAFS and DRIFT spectra were collected under reaction conditions as well however, their analysis is still in progress.

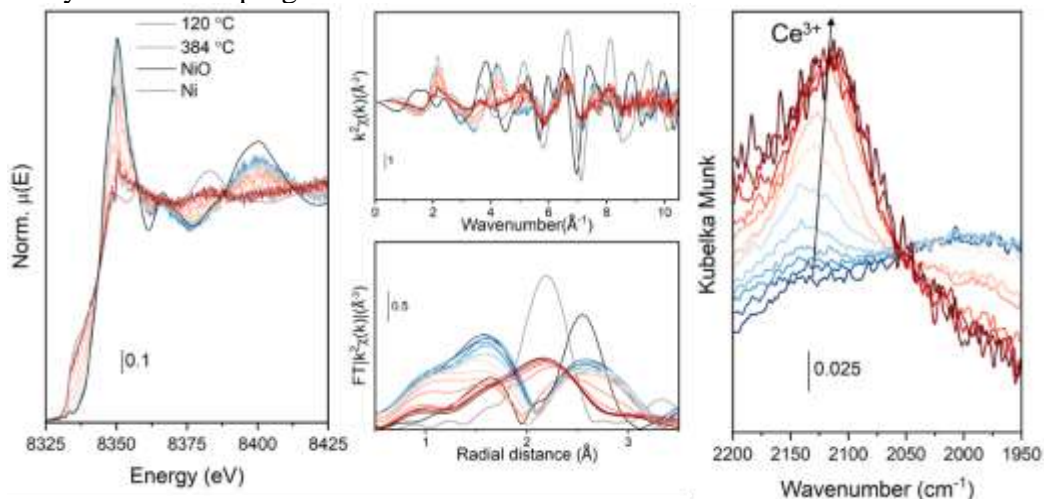


Figure 1 Ni K-edge left) XANES and center)  $k^2$ -weighted EXAFS and (magnitude) FT-EXAFS spectra collected during  $\text{H}_2$ -activation. Right) detail of DRIFT spectra collected parallelly with XAFS. Temperature increases from blue to red line.

Finally, Mass Spectroscopy data indicated  $\text{CH}_4$  productivity in line with catalytic tests conducted in our laboratories. Overall the beamtime CH6666 : I) demonstrated as the DRIFT/XAFS set-up not only provides unvaluable complementary spectroscopic results but allows to approach closer to reaction conditions and II) it allowed to test and implement the fluorescence detector to the DRIFT set-up, allowing to widen the number measurable systems.