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## Monitoring active sites for CO<sub>2</sub> methanation on Ni/CeO<sub>2</sub> catalysts by NAP-XPS

### Content

CO<sub>2</sub> hydrogenation is a hot topic in heterogeneous catalysis and a key step to satisfy future energy demand and to supply building blocks for the petrochemical industry while mitigating CO<sub>2</sub> emissions. Ni/CeO<sub>2</sub> catalysts are very active and selective for total hydrogenation of CO<sub>2</sub> to methane and, however, the nature of the active sites is still unclear. On the basis of ex-situ techniques, it has been suggested that Ni/CeO<sub>2</sub> catalysts combine two types of active sites, surface oxygen vacancies located at the Ni<sub>2</sub>-CeO<sub>2</sub> interface, where chemisorption and dissociation of CO<sub>2</sub> take place, and reduced Ni<sup>0</sup> sites for H<sub>2</sub> dissociation. The best Ni/CeO<sub>2</sub> catalysts are those that combine both types of active sites and distribute the nickel available on the catalyst in an optimum proportion. If this balance is not appropriate, in the case of Ni<sup>2+</sup>-CeO<sub>2</sub> interface sites excess, the surface of the catalyst suffers strong accumulation of carbon species (formates, bicarbonates carbonates, etc.) waiting for further hydrogenation or remaining as reaction spectators that cover the surface. This occurs if Ni<sup>2+</sup>-CeO<sub>2</sub> interface sites prevail at expenses of Ni<sup>0</sup> sites. On the contrary, in case of Ni<sup>0</sup> sites excess, there is a lack of Ni<sup>2+</sup>-CeO<sub>2</sub> sites, where CO<sub>2</sub> is efficiently chemisorbed and dissociated, what results in poor CO<sub>2</sub> chemisorption and dissociation. The aim of the current study is to monitor the behavior of the different nickel and cerium species on a Ni/CeO<sub>2</sub> catalyst, prepared according to a previously optimized protocol, under CO<sub>2</sub> methanation conditions using Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS).

The surface of a model 12 wt.% Ni/CeO<sub>2</sub> catalyst has been investigated under CO<sub>2</sub> methanation conditions (20% CO<sub>2</sub> + 80% H<sub>2</sub>) at the CIRCE beamline of ALBA synchrotron. The Ce3d and Ni2p core levels were monitored with hv=1090 eV.

It was concluded that the species involved in the redox processes taking place during CO<sub>2</sub> methanation are the Ni<sup>2+</sup>-CeO<sub>2</sub>/Ni<sup>0</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> pairs. In addition, a small fraction of nickel is present on the catalyst surface forming Ni<sup>0</sup> and Ni<sup>2+</sup>-carbonates/hydroxyls (around 20% of the total surface nickel), but these species do not participate in the redox processes of the methanation mechanism.

Under CO<sub>2</sub> methanation conditions the H<sub>2</sub> reduction rate of the Ni<sup>2+</sup>-CeO<sub>2</sub>/Ni<sup>0</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> couples is much faster than their CO<sub>2</sub> reoxidation rate (at least 2 times faster, at 300C), but a certain proportion of nickel always remains oxidized under reaction conditions. The high activity of Ni/CeO<sub>2</sub> catalysts for CO<sub>2</sub> methanation is tentatively attributed to the simultaneous presence of Ni<sup>2+</sup>-CeO<sub>2</sub> and Ni<sup>0</sup> active sites where CO<sub>2</sub> and H<sub>2</sub> are respectively expected to be efficiently dissociated [1].

[1] S. López-Rodríguez et al., J. of CO<sub>2</sub> Utiliz. 2022, 60: 101980.

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