

## ABSTRACT:

### Ni-doped CeO<sub>2</sub> with square-planar NiO as highly active catalyst for CCU process

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The Sabatier reaction ( $\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$ ) is attracting growing interest in the context of limiting anthropogenic CO<sub>2</sub> emissions. Despite its low reaction temperature (200-400 °C), CO<sub>2</sub> activation remains difficult to achieve and requires the formulation of highly active catalysts. In that context, Ni-doped CeO<sub>2</sub> nanoparticles synthesized by a method relying on Schiff base pyrolysis were tested for CO<sub>2</sub> hydrogenation to CH<sub>4</sub> under neutral atmosphere [1]. The performance of Ni-doped ceria reported in Figure 1a was found comparable with that of supported Ni/CeO<sub>2</sub> catalysts containing 5 times higher Ni loading. Indeed, the nickel mass-specific CO<sub>2</sub> conversion (right-axis, Fig. 1a) and CH<sub>4</sub> yield are among the highest reported for Ni/CeO<sub>2</sub> catalysts [2].

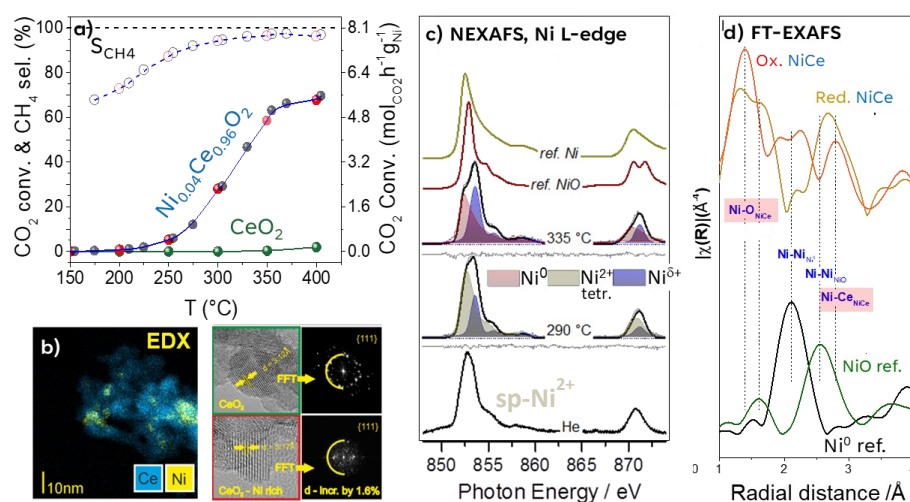


Figure 1. a) Catalytic evaluation of  $\text{Ni}_{0.04}\text{CeO}_2$  and  $\text{CeO}_2$  (GHSV = 12000  $\text{h}^{-1}$ ,  $\text{CO}_2:\text{H}_2$  ratio of 1:4, activated in  $\text{H}_2$  at 400 °C); b) EDX mapping and HR-TEM images, c) Ni L-edge evolution during reduction and d)  $k^3$ -FT-EXAFS spectra (calcined/reduced) of  $\text{Ni}_{0.04}\text{CeO}_2$  NPs.

HR-TEM/EDX analysis (Fig. 1b) showed that Ni is atomically dispersed and probably occupies interstitial sites within  $\text{CeO}_2$  lattice (no pure NiO). Insights on the specific Ni configuration were obtained from *in situ* NEXAFS (Fig. 1c, APE-HE beamline, Elettra, Italy) and EXAFS (Fig. 1d, BM23 beamline, ESRF, France) studies, revealing the presence of square-planar  $\text{Ni}^{2+}$  sites ( $\text{sp-Ni}^{2+}$ ) resulting from integration into ceria lattice (and supported by theoretical simulation of Ni L-edge spectra). The reduction of  $\text{Ni}^{2+}$  ions in 1 bar  $\text{H}_2$  (Fig. 1c) was found hindered while reduction of  $\text{Ce}^{4+}$  was promoted on  $\text{Ni}_{0.04}\text{CeO}_2$  NPs, as compared to pure NiO with standard octahedral  $\text{Ni}^{2+}$  and  $\text{CeO}_2$  reference samples. More interestingly, reduction of  $\text{Ce}^{4+}$  is accompanied by further oxidation of  $\text{Ni}^{2+}$  into  $\text{Ni}^{\delta+}$  ( $2 < \delta < 3$ ). This is quite unexpected observation, for nickel oxide treated in 1 bar  $\text{H}_2$ , and indicates an electronic interaction between Ni and Ce ions ( $\text{Ni}^{\delta+}\text{-Ce}^{3+}$  pair) which was also observed under reaction conditions. Further mechanistic details, corroborated by NAP-XPS, were obtained from DFT calculations including the impact of interstitial ionic Ni on the charge modification for adsorbed carbonate therefore on  $\text{CO}_2$  activation over ceria surface.

Overall, stable ionic Ni species, associated with interstitial Ni atoms in contact with  $\text{Ce}^{3+}$  lattice were identified as very active sites for  $\text{CO}_2$  conversion, indicating that metallic nickel is not indispensable for  $\text{CO}_2$  hydrogenation. This finding may provide the design principles that could lead to more effective catalysts towards the targeted reaction.

[1] M. Barreau *et al.*, *Mat. Tod. Chem.* 26, 101011 (2022)

[2] M. Barreau *et al.*, *Angew. Chem. Int. Ed.* 62, e202302087 (2023)