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NAP-XPS and NEXAFS investigations of Ni@CeO₂-doped catalysts for the catalytic conversion of CO₂

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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 of growing interest in the context of limiting anthropogenic CO₂ emissions. Despite its low reaction temperature (200-400°C), the activation of CO₂ remains difficult to achieve and requires the formulation of highly active catalysts. Among them, Ni, Co or Ru based catalysts supported on CeO₂ are often considered for the reaction but still suffer from low activity at low temperature and/or rapid deactivation [1]. An amelioration of the catalyst formulation is therefore needed to envisage industrialization of the CO₂ methanation process.

We have recently developed a synthesis method to produce Ni-doped CeO₂ nanoparticles (NPs) based on Schiff base metal complexes [2,3]. This method produces nanoparticles with well-defined composition of Ni_{0.04}Ce_{0.96}O₂, a particle size distribution ranging between 5–7 nm and a considerably higher methanation activity in comparison to classical Ni/CeO₂ prepared with same nominal Ni loading. A first NAP-XPS study conducted at the TEMPO beamline of SOLEIL synchrotron (France) showed a better reducibility of cerium (Ce⁴⁺ → Ce³⁺) between 200 and 700 °C under different gases encountered in methanation conditions (H₂, H₂O, CO₂) for the doped sample in comparison to pure CeO₂ prepared via the same synthesis method. Ce³⁺ species is accompanied by the formation of oxygen vacancies in ceria lattice and better ability to activate CO₂ for its gradual hydrogenation [4].

To gain insight on the Ni oxidation state evolution, the surface state of the NPs was studied under reducing conditions (1 bar of H₂) by NEXAFS at the APE-HE beamline of ELETTRA synchrotron (Italy). It was found that the reduction of Ni²⁺ ions in 1 bar H₂ is hindered while reduction of Ce⁴⁺ is promoted on Ni_{0.04}Ce_{0.96}O₂ NPs, as compared to pure NiO and CeO₂ reference samples. Interestingly, reduction of Ce⁴⁺ is accompanied by further oxidation of Ni²⁺ into Ni^{δ+} (2-δ<3). This is quite unexpected observation, for nickel oxide treated in 1 bar H₂, and indicates an electronic interaction between Ni and Ce ions which was also observed under reaction conditions (CO₂/H₂ = 1:4). Theoretical simulation of Ni L-edge spectra suggested that Ni atoms are tetrahedrally coordinated into ceria lattice, in contrast to the familiar octahedral symmetry of bulk NiO.

References

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if "Other", please specify:

I apply for a travel grant

Yes

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