

**Experiment title:**

XAS/MS Study of Ni-based Ce-promoted Bialcohol Reforming Catalysts

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Report:

The evolution of a catalyst having a ternary Ni-Mn-Ce composition and (initial) fluorite-type structure was studied with in-situ XAS in the biobutanol (butanol:ethanol:acetone 6:3:1) reforming reaction. This system displays a significant activity in terms of hydrogen yield with respect to the appropriate reference compounds consisting in similar binary, fluorite-type Ni-Ce or Ni supported on fluorite-type Mn-Ce binary oxides. To analyze the catalyst performance, at BM23 we carried out isothermal experiments using a reactive mixture consisting in biobutanol:H₂O = 9:1 at increasing temperatures from 300 to 500 C.

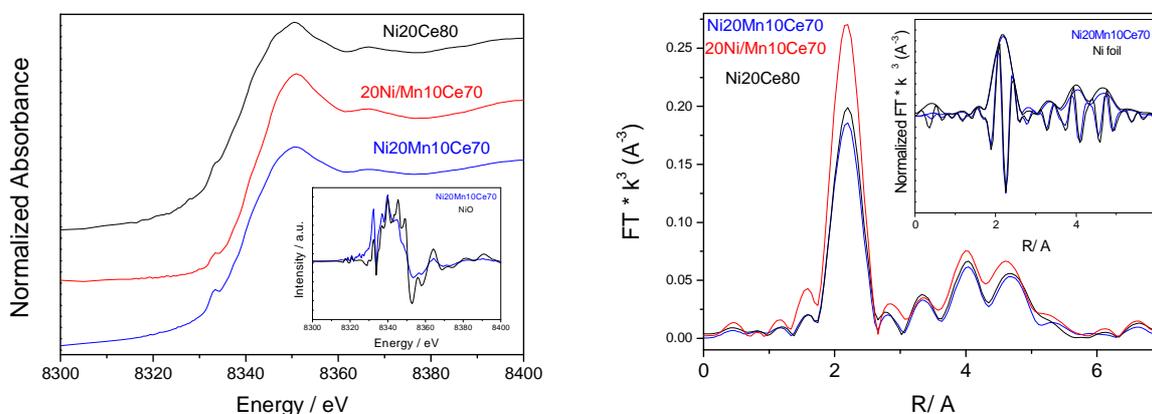


Fig.1. Ni K-edge data for the Ni₂₀Mn₁₀Ce₇₀ sample and reference samples: (A) XANES spectra of the initial catalyst and references with inset presenting derivative signals of Ni₂₀Mn₁₀Ce₇₀ and NiO reference; (B) EXAFS spectra (k range ca. 2.45-12.05 Å⁻¹ for all samples) at RT after reaction at 500 °C with inset showing a (normalized) comparison with the Ni foil.

Fig. 1 provides information of the Ni component. As mentioned, in the catalyst the Ni ion is present at the fluorite structure (the only phase detected by laboratory XRD) with a local structure with strong similarities with the NiO reference. Under reaction conditions the base metal becomes reduced producing nanoparticles with the characteristic metallic fcc structure. The comparison with the Ni foil (see inset in Fig. 1) provides strong evidence that such particles have spherical-type shape. These Ni nanoparticles present similar particle size irrespective of the presence or absence of Mn at the initial fluorite phase. However, the production of such nanoparticles from a single fluorite structure appears to provide lower particle size (Ni-Ni 1st shell C.N. 6.1; ca. 50 atoms) than a reference catalyst having similar weight percentage of Ni but produced by impregnation onto a Mn-Ce fluorite-type mixed oxide.

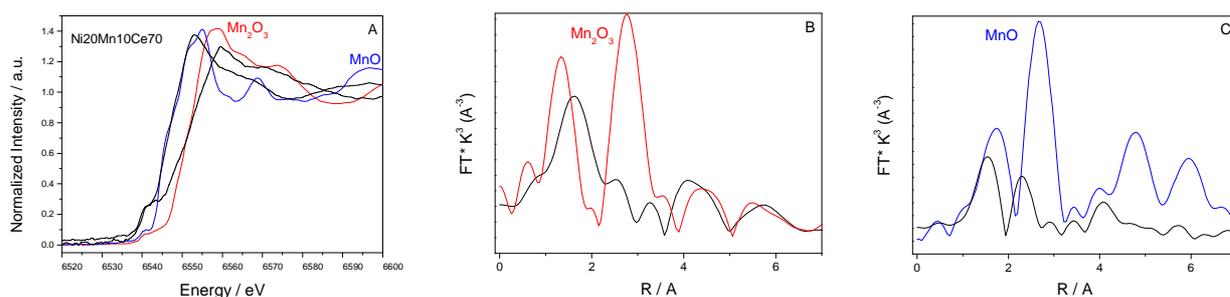


Fig.2. Mn K-edge data for the Ni20Mn10Ce70 sample and reference compounds. (A) XANES spectra of the initial and final catalyst states and MnO and Mn₂O₃ references; (B and C) EXAFS spectra (k range ca. 2.6-9.05 Å⁻¹ for all samples) at RT of the initial and final (after reaction at 500 °C) states of the catalyst.

Figure 2 gives information about the Mn component. The normalized XANES spectra of the initial and final (post-reaction) states of the ternary catalyst indicate that Mn evolves from a Mn(III) to a Mn(II) like oxidation state during reaction. Pre-edge features however point out near tetrahedral symmetries in both cases, with significant differences with the Mn single oxide references. Differences presented at EXAFS signals between the sample signals and the corresponding references are again significant, confirming the above mentioned differences detected by XANES and concerning the local structure. The Mn behavior in our ternary Ni-Mn-Ce catalyst with respect to the reference consisting in a Ni-supported phase onto the Mn-Ce mixed oxide (Fig. 3) was used to further analyze the structural details of the ternary materials.

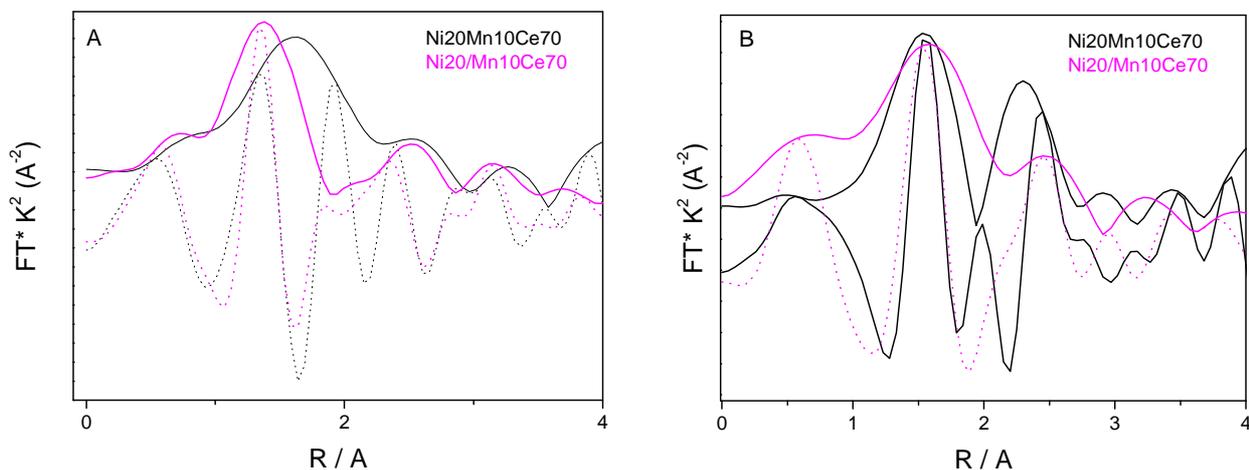


Fig.3. Mn K-edge data EXAFS for Ni₂₀Mn₁₀Ce₇₀ sample and Ni₂₀ supported on Mn₁₀Ce₉₀ reference compound. (A and B) EXAFS spectra (k range ca. 2.6-9.05 Å⁻¹ for all samples) at RT of the initial and final (after reaction at 500 °C) states of the catalyst.

While the XANES spectra (data not shown) of samples presented in Fig. 3 do not display marked differences in behaviour under reaction, EXAFS uncovered some differences. Importantly, the initial state (Mn-O shell C.N. 6.9; r 2.08) evidences the strong variation (in terms of coordination distance and disorder) occurring at the Mn local environment and triggered by its inclusion in the ceria lattice in presence of Ni. Also, under reaction a structure at ca. 2.5-3.0 Å appeared and the fitting provide evidence of a Mn-O-Ni bond at ca. 2.6 Å, indicative of the presence of Mn at the interface between the metallic Ni fcc and oxide fluorite-type phases.

In summary, the changes observed at the Ni and Mn K-edges indicates the complex evolution of the system under reaction conditions. While Ni is extracted from the fluorite structure and generates metallic fcc nanoparticles in close contact with the oxide component(s), the fluorite-type phase evolves in such a way that (in addition to throw out Ni) Mn is reduced and appears to be preferentially in contact with Ni and thus at the metal-support interface. The detailed analysis of the EXAFS signals (particularly Ce L₃/K edges) as well as the future XRD (and PDF) study will provide further information about the exact location of each cation as well as the behaviour of the metallic (and particularly) the oxide, fluorite-type phase. After combining XAS-XRD information, we will try to correlate the results of the structural and electronic characterization of the catalytic solid with its chemical performance in the reforming of biobutanol. The key role of the metallic Ni as well as the structural information about the metal-support interface are obviously key pieces to understand the reforming performance of these Ni-based, ceria-promoted reforming catalysts.

Finally, we would like to acknowledge Dr G. Agostinni for supporting the experiments carried out at BM23.