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Combining in-situ synchrotron and electron microscopy techniques to study NiFe catalysts for CO2 methanation

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Background

Nickel-based catalysts on various supports have been widely studied for CO2 methanation due to higher activity, nickel's natural abundance, and relative low cost. However, most Ni-based catalysts suffer from deactivation due to carbon deposition, oxidation, sintering, and chemical poisoning. Recently, significant progress has been made in the exploitation of novel/modified Ni-based catalysts for CO2 methanation. As far as the support is concerned, the effect of various supports (CeO2, ZrO2, TiO2, MgO and mixed oxides) on Ni-based catalysts was studied with the goal to increase metal dispersion as well as induce an electronic effect for improving the selectivity towards methane over CO. In our collaborative study we investigated the effect of promoters of both support and active metal on hydrotalcite derived Ni/Al2O3 catalysts. From our catalyst screening experiments, we were able to select TiO2 as best support modifier and Fe as an active metal promoter. Amongst the prepared novel catalysts for CO2 methanation Ni-Fe/Al2O3 and Ni/CeO2-TiO2-ZrO2-Al2O3 were found to be exceptionally active and relatively more stable than commercially available catalysts (Ni/Al2O3). We apply multi-length-scale structural characterization in operando to these systems to gain mechanistic insights of general validity.

Methods

In this contribution we will combine in-situ TEM gas phase experiments with in-situ hard X-ray experiments to reveal the changes of the electronic structure the catalysts undergo under reduction and methanation conditions. We will present a comparative analysis of the following systems: Ni/Al2O3, Ni-Fe/Al2O3, Ni/CeO2-Al2O3 and Ni/CeO2-TiO2-ZrO2-Al2O3. In-situ TEM experiments will be complimented by in-situ gas phase experiments carried out on the i14 nanoprobe beamline utilizing an adapter which allows us to study the sample under the same experimental conditions [1]. This capability allows us to carry out multilength scale in-situ experiments by combined TEM and nanoprobe XANES, thereby linking dynamics observed on a nm- scale with those at the um scale. Mass spectrometer data acquired during the experiments will be used to correlate structural changes with catalytic activity.

Results

Figure 1 shows, as an example, the changes Ni-Fe/Al2O3 undergoes from its fresh form, during reduction at 500°C in H2/He and during reaction conditions at 300°C in a mixture of CO2, H2 and He. The distribution of Ni metal and oxide species as well as the changes in Fe oxidation state as function of the experimental conditions are obtained by in situ EELS mapping. Two regions can be identified: Metallic Ni nanoparticles are exsolved during the hydrogenation step (blue square in Figure 1 a, c), which contain a small amount of Fe; Highly dispersed NiO species are collocated with Fe(II)/Fe(III) species (black and red squares in Figure 1a, c and corresponding EELS spectra in Figure 1 e)). In addition, operando XANES unveil the presence of metallic Ni and Fe species, more so in the core of the particle (Figure 1 f, g).

Conclusion

The comparative analysis of these systems allows to clarify the role of the heteroatoms on the electronic structure of Ni. We will show that similarly to Fe, Ce acts as a sacrificial Oscavenger, maintaining Ni in a metallic state during the methanation thereby favouring methane formation over CO. We will also clarify the role of TiO2 in preserving a high dispersion of Ni.

Graphic:

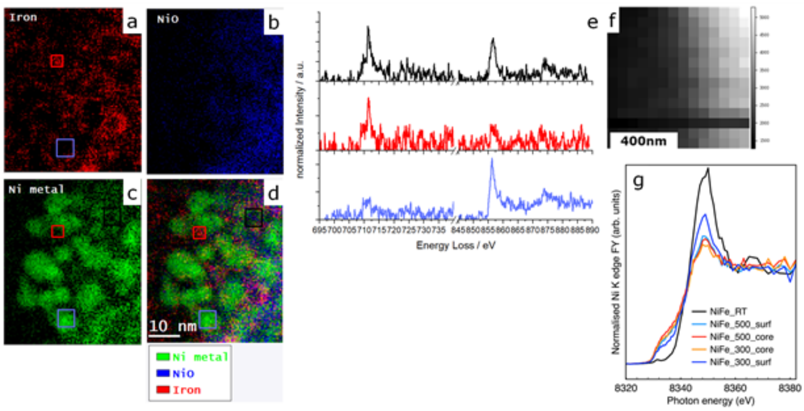

Figure 1: in-situ TEM EELS a) Iron L edge, b) NiO, c) Ni metal L edge EELS map, d) RGB EELS map of Iron, NiO and Ni metal species; e) extracted EELS spectra from ROIs within d) acquired at 300°C in reaction conditions; in-situ hard X-ray 8.5 keV XRF map f) and extracted Ni XANES spectra g) acquired at 300°C in reaction conditions

Keywords:

in-situ, TEM-synchrotron, multilengthscale, CO2-methanation, catalysis

Reference:

[1] J. Synchrotron Rad. 2022, 29, 431-438.