

**Experiment title:**

Novel Ni-containing La-promoted hydrotalcite-derived catalysts for CO₂ methanation. Investigation of the local environment of Ni and La atoms

Experiment number:

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Report:

Carbon dioxide methanation is an extremely interesting reaction from the industry point of view, because of the possibility of off-peak energy storing in the form of hydrogen obtained via water electrolysis powered by renewables. It allows transforming CO₂ into valuable compound – CH₄ – which is an excellent energy carrier chemical.

During this beamtime we investigated the structure and electronic properties of nickel and lanthanum in Ni- and Ni₂La-hydrotalcite materials by X-ray adsorption and emission spectroscopy. In the case of Ni we carried out HERFD-XANES at maximum energy of K β line, K β core-to-core and valance-to-core measurements. For La HERFD-XANES spectra were collected at maximum energy of La α_1 line. Our experiments were divided into two parts. In the first part we studied environment of nickel and lanthanum centres by ex-situ measurements of hydrotalcite and reference sample pellets. The pellets were prepared by mixing 5 mg of material with 95 mg of cellulose in the agate mortar and

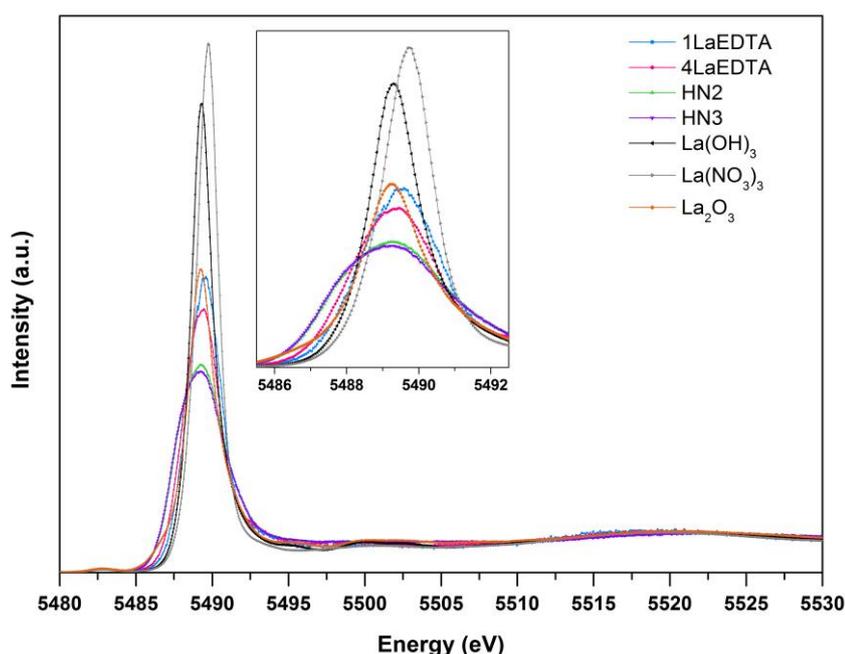


Figure 1. HERFD-XANES spectra recorded at La L α_1 line for 1LaEDTA, 4LaEDTA, HN2, HN3, La(OH)₃, La(NO₃)₃ and La₂O₃

pressed into wavers. We measured the hydrotalcite samples containing 5 – 50 wt. % of nickel before and after calcination as well as standard samples (Ni foil, NiO, Ni(OH)₂ and Ni(NO₃)₂). Similarly, we measured the hydrotalcites containing both nickel and 1 – 4 wt. % of La and prepared with various method such as co-precipitaion (HN2 and HN3), ion-exchange (1LaEDTA, 4LaEDTA). The selected HERFD-XANES spectra of La-containing samples are shown in Fig. 1.

The second part consisted of in-situ measurements of self-supported samples in the Maxthal cell, provided by Sample Environment Pool, in the continuous flow of gas mixture at various temperatures. The composition of exhaust gases was monitored by μ GC-MS analyser in order to follow evolution of CO₂ conversion and methane formation. Thanks to use of combined techniques of XAS/XES and gas analysis we performed operando experiments under realistic conditions. Unfortunately, due to insufficient time we were able to investigate only the changes in the nickel environment for several samples but not lanthanum.

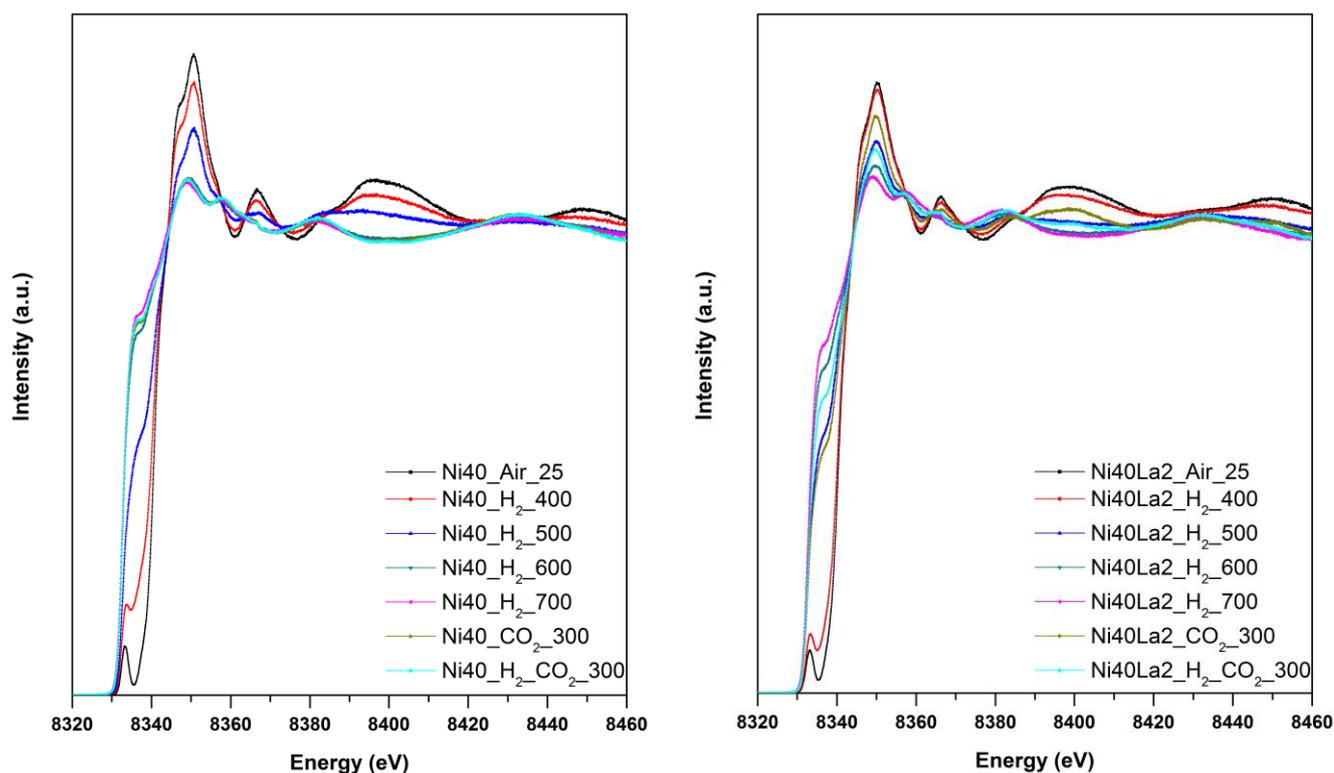


Figure 2. HERFD-XANES spectra recorded at Ni K β line and under operando conditions for Ni40 (left) and Ni40La2 hydrotalcites

Before experiments we registered the XAS/XES spectra for each sample at ambient atmosphere. After that sample was reduced in the flow of 12% H₂/He mixture. The temperature was gradually increased with the rate of 10°C/min and again the XAS/XES spectra were registered at 400, 500, 600 and 700 °C in order to follow the evolution of spectral changes. As an example in the Fig. 2 we showed obtained results for two samples: Ni40 (without La) and Ni40La2 containing 2 wt % of La. For both of them it was seen gradual transition from oxide to metallic face with increasing reduction temperature. After reaching 700 °C the samples were slowly cooled down to 300 °C in the He flow and stream of CO₂ was switched on. The concentration of carbon dioxide was 30% in He and samples were kept in continuous flow for 30 min. Then, the XAS/XES measurement was done. The same procedure was repeated for CO₂/H₂ mixture. The data analysis revealed significant changes in the behaviour between both samples. In the case of CO₂ adsorption at 300 °C the state of nickel in Ni40 samples remained almost the same as after reduction. However, for the Ni40La2, containing 2 % of La, the partial oxidation was observed confirmed by an increase of white line intensity and appearance of the features related to oxide phase. Similar behaviour was notice when H₂ and CO₂ reacted on catalytic surface to form CH₄.

It might be concluded that in the case of Ni40 catalyst the active centres are metallic species whereas for Ni40La2 the composite of oxide/metal phases plays major role resulting in different reaction mechanism and catalysts durability. The more deeply analysis of obtained data is in progress.