



	<b>Experiment title:</b> Novel Ni-containing La-promoted hydrotalcite-derived catalysts for CO <sub>2</sub> methanation. Investigation of the local environment of La atoms	<b>Experiment number:</b> MA-3563
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## Report:

The rising levels of CO<sub>2</sub> in the atmosphere created concerns and increased social awareness about the climate change caused by the emission of greenhouse gases through combustion of fossil fuels by power generators and other industrial activities. New carbon dioxide emissions regulations, implemented by European Union, demand energy production from renewable sources or CO<sub>2</sub> utilization, which is an important issue for the countries (i.e. East Europe), where energy production sector is based on fossil fuels. A promising method of reduction of carbon dioxide emissions is catalytic hydrogenation of CO<sub>2</sub> into valuable chemicals such as e.g. methane, higher hydrocarbons or methanol. This process offers the possibility of storing off-peak renewable energy, i.e. in the form of hydrogen via water electrolysis, and, at the same time, treating CO<sub>2</sub> as raw material, to produce storable and transportable fuels (methane), or other commodities.

During this beamtime we investigated the structure and electronic properties of lanthanum in Ni,La-hydrotalcite materials by X-ray adsorption and emission spectroscopy. We carried out high resolution XANES and EXAFS as well as valance-to-core measurements under operando conditions. The self-supported samples of hydrotalcite catalysts were placed in the Maxthal cell, provided by Sample Environment Pool. The cell was coupled with the mass flow controllers and  $\mu$ GC-MS analyser in order to follow evolution of CO<sub>2</sub> conversion and methane formation under realistic conditions. For our investigation we selected following catalysts: NiLa1\_CP, NiLa4\_CP, NiLa1\_EDTA and NiLa4\_EDTA which were prepared by co-precipitated method (CP) or by post-synthesis treatment (ion-exchange) with La-EDTA complexes (EDTA). These preparation methods allow to obtain materials with various concentration of lanthanum and its introduction into framework or extra-framework positions, respectively. All catalyst after calcination were in-situ reduced under fa flow of H<sub>2</sub> at 800 °C. The results of HERFD-XANES measurements are depicted in Figure 1 that

composes of 4 graphs representing different model conditions. At the first glance the spectra of the catalysts after calcination (Fig. 1A) look very similar, however some important differences might be notice after more careful analysis. Especially, significant variations between the samples appear in the white line intensity and post-edge features sharpening. The higher white line intensity of NiLa\_EDTA that their NiLa\_CP analogues suggests greater La coordination number and presence in the form of very small oxide clusters.

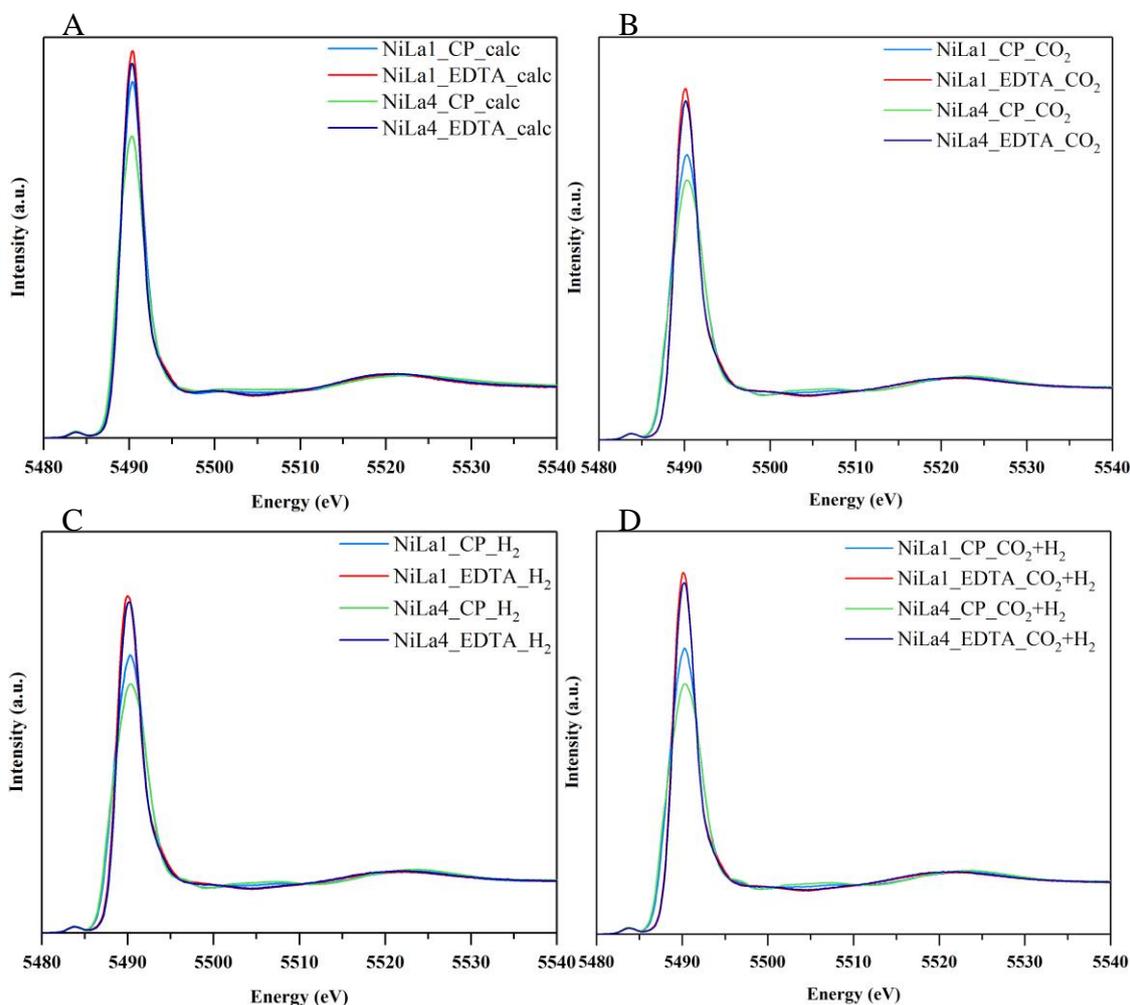


Figure 1. Evolution of the La  $L_3$  edge HERFD-XANES spectra of hydrotalcite-derived catalysts under various treatment: after calcination (A), after exposure to  $H_2$  (B), after exposure to  $CO_2$  (C), after exposure to  $H_2 + CO_2$  (D).

To elucidate the influence of reaction reagents on the Ni state, the catalysts were exposed separately to the streams of  $H_2$  and  $CO_2$ , as well as to their mixture at 300 °C. The HERFD-XANES spectra of NiLa1\_EDTA and NiLa4\_EDTA underwent only slight changes under reduction step and exposure to methanation process conditions suggesting that La species interact strongly with catalyst supports and remain well dispersed on the surface. On the other hand, the spectra of NiLa1\_CP and NiLa4\_CP were severely changed after treatment with  $H_2$  at high temperature. Clearly, significant decrease of white line peak intensity along with its broadening occurred indicating strong modification in the local environment of La species. These modifications might be assigned to La species sintering and dehydration. Moreover, the EXAFS data (results not shown) confirmed different coordination number of lanthanum's ligands in the first coordination shell and differences in La – O bond distance. The significant differences in the behaviour shows that application of the proper preparation method is crucial for obtaining stable and efficient catalyst for the reaction of  $CO_2$  conversion into value added products. With those findings and results of catalytic tests we will be able to explain different activity and selectivity among discussed catalysts and propose the correct approach in synthesis of La-promoted hydrotalcite derived catalyst for direct  $CO_2$  conversion into methane.