Mechanistic insight of CO_2 methanation on hydrotalcite-derived catalysts by operando XAS and XES spectroscopy

<u>R. Baran</u>[a,*], D. Wierzbicki[b,c,*], R. Debek[b], M.E. Galvez[c], P. Da Costa[c], M. Motak[b]

[a] *ESRF – The European Synchrotron, 71 Avenue des Martyrs, Grenoble, France*

[b]*AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, 30-059 Krakow, Poland*

[c] *Sorbonne Universités, UPMC, Univ. Paris 6, CNRS, UMR 7190, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210, Saint-Cyr-L'Ecole, France*

**Corresponding author: rafal.baran@esrf,fr. dwierzb@agh.edu.pl*

Abstract: Hydrotalcite-derived Ni-containing and Ni-La promoted catalysts showed very high activity in CO_2 methanation, which is an efficient way of carbon dioxide conversion into methane – a valuable product. The catalysts were obtained by co-precipitation method followed by thermal decomposition. The physico-chemical characterization of prepared samples confirmed the formation of periclase-like structure materials, with nickel present as Ni nanoparticles and suggested successful incorporation of lanthanum into the catalytic system. The catalysts were characterized by complementary HERFD-XANES and XES spectroscopy under model operando conditions. The results uncovered that the presence of lanthanum strongly influenced the chemical nature and oxidation state of nickel species and its crucial role in catalyst activity enhancement in CO_2 methanation.

Keywords: CO_2, methanation, XANES.

1. Introduction

The problem of global warming is mostly related to strong increase of CO_2 concentration in the atmosphere. New carbon dioxide emissions regulations, implemented by The Paris Agreement, demand energy production from renewable sources or CO_2 utilization, which is an important issue for many countries, where the energy sector is still based on natural resources (such as lignite and coal). A promising method is catalytic hydrogenation of CO_2 into valuable chemicals such as e.g. methane, higher hydrocarbons and methanol. This process offers the possibility of storing off-peak renewable energy, i.e. in the form of hydrogen (water electrolysis), and, at the same time, treating CO_2 as raw material, to produce storable and transportable fuels resulting in stabilization of CO_2 emissions, in a global zero-emission closed cycle [1].

Our study revealed that the application of La-promoted Ni-hydrotalcite in CO_2 methanation led to considerable increase in the conversion of carbon dioxide and high yield of methane in comparison to non-promoted Ni-hydrotalcite catalyst at low temperature. From our previous study we found out that introduction of La affects the CO_2 adsorption capacity by formation of new medium strength basic sites [3]. Nevertheless, despite much research on CO_2 methanation, the mechanism of this reaction and role of promoters is still unclear and remain an open question.

2. Experimental

Ni40 and Ni40La2 hydrotalcites were prepared through a co-precipitation method at constant pH (from 9.5 to 10) as was described elsewhere [2].

The XAS and XES experiments were carried out at beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The incident energy was tuned through the Ni K edge by pair of cryogenically-cooled Si(111) monochromator crystals. The XES spectra were collected at incident energy of 8400 eV with a X-ray emission spectrometer equipped with a set of five spherically bent Si(551) crystals for Ni Kβ line, and detected with an avalanche photodiode. The analyzers crystals were arranged in vertical Rowland geometry. The HERFD-XANES spectra were detected at the maximum of the Ni $K\beta_{1,3}$ emission line. In-situ measurements of self-supported samples were performed with use of the Maxthal cell, provided by Sample Environment Pool of ESRF. The spectra were recorded under individual He, H_2 and CO_2, and under gas mixture with H_2/CO_2 ratio of 4:1 and argon as balance gas at 300 ^{o}C. The composition of exhaust gases was monitored by μGC-MS analyser.

3. Results and discussion

We started our experiment by collecting the XANES spectra for each sample at ambient atmosphere. After that sample was reduced in the flow of 12%H_2/He mixture. The temperature was gradually increased with the rate of 10^{o}C/min and again the spectra were registered at 400, 500, 600 and 700 ^{o}C in order to follow the evolution of spectral changes. As an example, the results obtained for two samples Ni40 (without La) (Fig. 1A) and Ni40La2 (Fig. 1B) containing 2 wt. % of La are presented. A transition from oxide to metallic phase was observed with increasing reduction temperature. After reaching 700 ^{o}C the samples were slowly cooled down to 300 ^{o}C in the He flow and stream of CO_2 was switched on. The concentration of carbon dioxide was 30% in He and samples were kept in continuous flow for 30 min. Then, the XANES spectra were recorded. The same procedure was repeated for CO_2/H_2 mixture. The data analysis revealed significant changes in the behavior between both samples. In the case of CO_2 adsorption at 300 ^{o}C the state of nickel in Ni40 sample remained almost the same as after reduction. However, for the Ni40La2, a partial oxidation was observed confirmed by an increase of white line intensity and appearance of the features related to oxide phase. Similar behavior was notice when H_2 and CO_2 reacted on catalytic surface to form CH_4. The obtained results suggest that in the case of Ni40 catalyst the active centers are metallic species whereas for Ni40La2 the composite of oxide/metal phases play major role resulting in different reaction mechanism and catalysts durability.

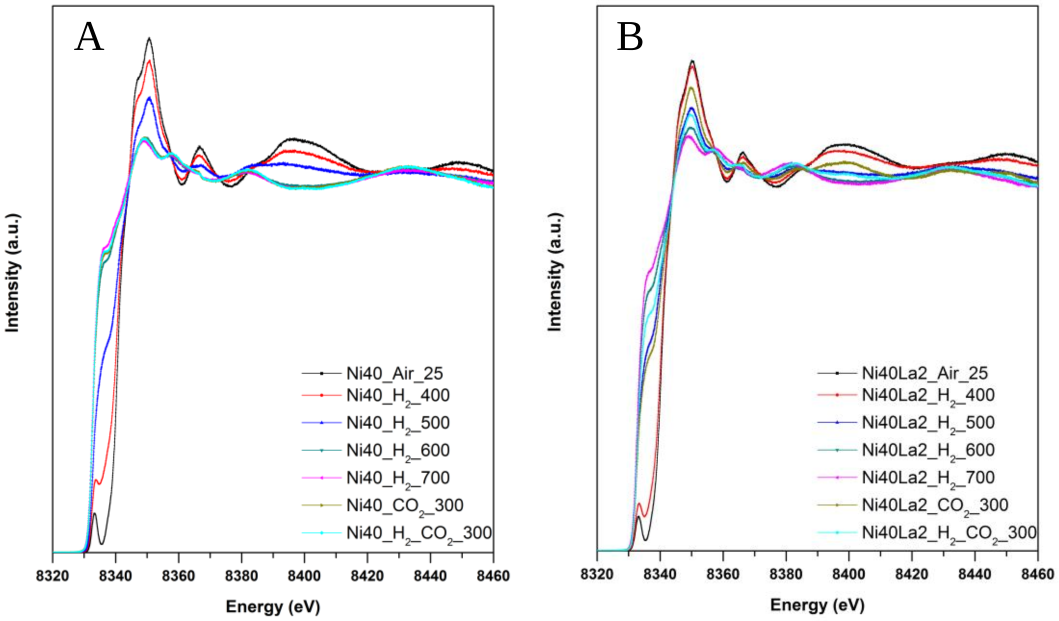

Figure 1. HERFD-XANES spectra recorded at Ni K edge and under operando conditions for Ni40 (A) and Ni40La2 (B) hydrotalcites.

4. Conclusions

La-promoted Ni-Mg-Al hydrotalcite-derived catalysts were prepared through co-precipitation. The role of nickel species in CO_2 hydrogenation reaction was studied by operando XAS measurements. We observed that the introduction of La affected the CO_2 adsorption capacity of the catalyst. The presence of La led to modification of nickel chemical state and possible different mechanism of CH_4 formation.

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