NiAl-LDH as catalyst precursors for ethanol reforming: An *in situ* and *operando* XAS/MS/Raman study from activation to regeneration

Aline R. Passos (1,2), Sandra H. Pulcinelli (2), Celso V. Santilli (2), <u>Valérie Briois (1)</u>
(1) Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, Gif-sur Yvette 91192, France
(2) UNESP - Univ Estadual Paulista, Rua Prof. F. Degni, 55, Araraquara, SP 14800900, Brazil
valérie.briois@synchrotron-soleil.fr

The environmental pollution problems associated with the use of fossil fuels have generated interest in processes based on the use of clean energy. Hydrogen is considered as a promising source of clean energy, especially when it is produced from renewable sources such as ethanol.[1] Ni catalyst is very active on H_2 production from ethanol steam reforming (ESR). However, Ni catalysts suffer deactivation due to coke deposition. As coking is often inevitable, significant efforts have been directed towards regeneration of the deactivated catalysts. In this work an in-depth time-resolved study is reported to investigate the activation and catalytic performance of Ni/Al_2O_3 catalysts derived from Layered Double Hydroxides (LDHs) precursors. For this purpose *in situ* and *operando* combined measurements have been carried out with information gained on the nickel speciation using X-ray absorption spectroscopy (XAS), reaction products by mass spectrometry (MS) and coke formation by Raman spectroscopy during ESR.

The Ni/Al-LDH were produced by one-pot sol-gel method, the loading amount of Ni was 33 wt% in the calcined catalyst. The calcined catalyst was reduced in H_2 atmosphere at 500°C for 3h. The activity to ESR were monitored on the same sample at 500°C using a dedicated cell connected to the gas feeding system installed on the quick-XAFS ROCK beamline (SOLEIL).[2]

The intensity of the contribution of the Ni-Ni second shell on the Fourier transform of the Ni K-edge EXAFS spectrum for the calcined catalyst is much lower than the one measured on a NiO polycrystalline reference. This is compatible with the formation of isolated and/or small nickel oxide nanoparticles. *In situ* XAS shows that the reduction under H_2 leads to 93% of Ni^0 at 500 °C. The catalyst is active for ESR leading to a gaseous mixture of products containing H_2 at higher proportion and small amounts of CO_2, CH_4, C_2H_4 and CH_3CHO. The deactivation of the catalysts is mainly due to carbon deposition as observed by *in situ* Raman spectroscopy. After the first 180 minutes under ESR conditions, the coke deposits were removed by the introduction of 5% O_2/He to the reactive feed, the metallic particles becoming partially oxidized. The duration of the regeneration treatment was chosen on the basis of the evolution of the *operando* Raman results. As soon as the intensity of the Raman D and G lines characteristic of coke decreases, the introduction of O_2 was stopped, limiting the further oxidation of the catalyst observed by Quick-XAS. Subsequently to regeneration, the catalyst activity was restored leading to an increase of H_2 production measured by MS. The H_2 so-produced promotes the self-reactivation of the catalyst with the further reduction of NiO particles as shown by Quick-XAS.

In conclusion, the thermal decomposition of LDHs is a powerful strategy for the preparation of ESR catalyst. The combination of XAS/Raman/MS evidenced that the coke deposition is the main cause of the catalyst deactivation. After removal of coke by O_2 introduction in the ESR feeding, regeneration of active species can be done by self-reduction using ESR products. The process described herein is an economic way to regenerate ESR catalysts and could be extended for other catalytic reactions.

(1)   Mattos, L. V; Jacobs, G.; Davis, B. H.; Noronha, F. B. *Chem. Rev.* **2012**, *112*, 4094..
(2)   Briois, V.; La Fontaine, C.; Belin, S.; Barthe, L.; Moreno, T.; Pinty, V.; Carcy, A.; Girardot, R.; Fonda, E.; Journal of Physics Conference Series; 2016; Vol. 712.