Operando gas TEM for the study of Ni nano-catalysts during the Sabatier reaction

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In the last past years, the use of transmission electron microscopy (TEM)-based techniques for the in-situ analysis of catalytic materials has received an increasing interest due to the possibility to generate, inside the microscope, various gas environments at atmospheric pressures and high temperatures. The sealed environmental gas cell within specially designed TEM holders, as for example the Atmosphere™ gas cell from Protochips [1], became thus a very suitable tool for mimicking conditions of full-scale reactors for some specific catalytic reactions, and therefore to develop "operando" methodologies. In addition, connecting a residual gas analyzer (RGA) directly to the gas exhaust line of the environmental TEM cell allows establishing a direct correlation between the dynamics of the structural modifications of the nano-catalyst and the evolution of its catalytic performances.

In this study, we present in the context of the operando experiments, such a combined "environmental TEM-RGA" approach. By considering the CO_2 methanation as the reaction of interest (Sabatier reaction), one of the most active catalysts is made out of Ni based nanoparticles supported on alumina support. The Ni particles were initially in the oxide state and were thus firstly activated under H_2 at atmospheric pressure. By directly following individual NiO particles from 200 to 400°C, we have observed that the oxide to metallic nickel transformation starts at 270°C and that the reduction is accompanied by the Kirkendall effect. The metallic Ni particles as obtained were then used in the methanation reaction under a mixture of H_2/CO_2 (ratio=4) at atmospheric pressure with the temperature ranging from 300 to 900°C. In this case, we clearly demonstrated that by combining the TEM in-situ approach with the gas analysis through a mass spectrometer, we are able to measure the reaction products generated by the small amount of catalyst deposited within the cell, to monitor their evolution as a function of the temperature and to correlate them with the microstructural modifications of the catalyst. A striking relative change in the CO_2 / CO / H_2O ratios has been evidenced and assigned to a progressive defragmentation of the particles when increasing the temperature under CO_2/H_2 at atmospheric pressure.

[1] L. F. Allard, S. H. Overbury, W. C. Bigelow, M. B. Katz, D. P. Nackashi, J. Damiano, *Microsc. Microanal.* **2012**, *18*, 656 - 666.

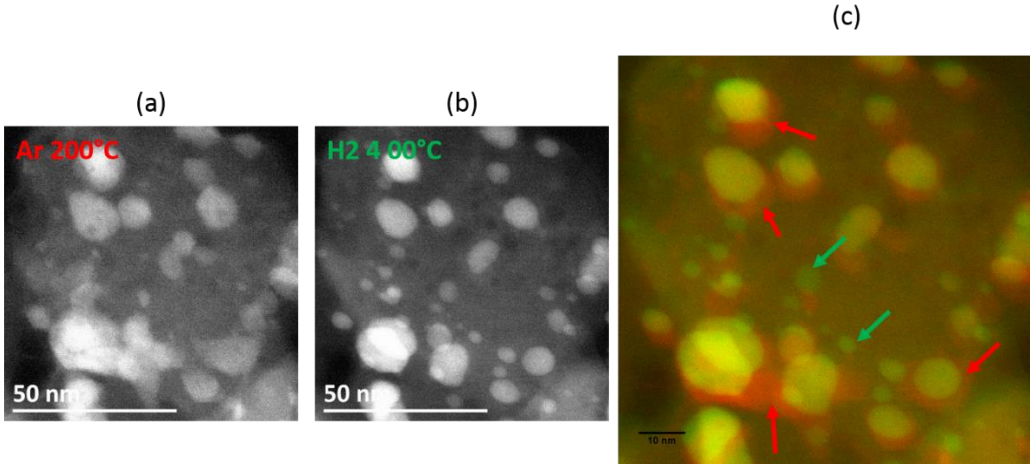

Figure1: STEM-HAADF analysis of the reduction process of the Ni/Al_2O_3 catalysts: (a) initial state under Ar at 200°C: NiO particles (b) after reduction under H_2 at 400°C: Ni metal particles and (c) the superposition of the two images (a) in red and (b) in green. Red arrows show the oxide phase before reduction and green arrows the particles formed after the reduction step.

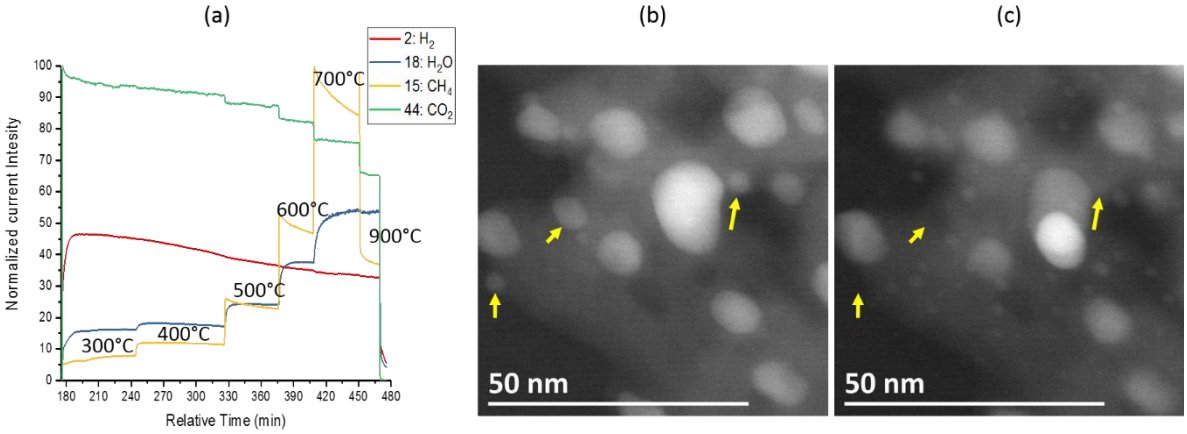

Figure 2: In-situ TEM operando study of Ni catalysts for the CO_2 methanation reaction under a mixture of H_2/CO_2=4 at temperature between 300°C and 900°C: (a) Monitoring of the main gas compound using RGA, (b) STEM-HAADF image of one of the typical Ni/Al_2O_3 areas at 400°C, (c) STEM-HAADF image of the same Ni/Al_2O_3 area at 600°C. Yellow arrows point out the particles fragmentation process from 400°C to 600°C.