	Experiment title: *In situ* XAS study of Al_2O_3 overcoated Pt-Ga/$MgAl_2O_4$ catalysts for Alkane dehydrogenation	**Experiment number**: **26-01-1169**
Beamline**:** BM26A	Date(s) of experiment : 05/12/2018 – 10/12/2018	**Date of report**: 24-1-2019
Shifts: 15	**Local contact(s)**: Alessandro Longo	

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Summary

Pt dehydrogenation catalysts are typically promoted with a second metal such as Ga, to form a bimetallic nanoparticles by alloying, which show improved catalytic performance. Still, this bimetallic catalyst suffers from coke formation, sintering and side reactions. In order to minimize these effects several strategies are applied: 1. Adding some CO_2 in the feed, 2. Incorporating Ga in the support, 3. Overcoating the PtGa bimetallic nanoparticles with Al_2O_3. This proposal is meant to explore the effect of these strategies. Catalysts were prepared by wet-incipient impregnation (WI) of Pt & Ga on $MgAl_2O_4$ support (HSA – $100 m^2/g$) and WI of Pt on a $Mg(Ga)(Al)O_x$ hydrotalcite-like support. After reduction to induce alloy formation, these were overcoated with Al_2O_3 by atomic layer deposition (ALD).

Experimental conditions

The samples for all in-situ experiments was loaded in a quartz capillary allowing to record all combined measurements. The catalysts were subjected to separate H_2-TPR and CO_2-TPO treatments with a temperature program from room temperature till 873K. Subsequently, isothermal cycling treatments (873 K) were performed, with periodic CO_2 & H_2 gas switching, each cycle lasting 40 min (H_2 for 20 min and CO_2 for 20 min). Structural changes occurring during separate treatments were monitored by XAS and SAXS. While in-situ XAS gives information about the chemical state and short range order, the SAXS probes the particle size and inter-particle distance. For all samples, the experiments as in **Error! Reference source not found.** have been conducted at the Pt L_{III}-edge and for samples $PtGa/MgAl_2O_4$ and $Al_2O_3/PtGa/MgAl_2O_4$ equally at the Ga K-edge:

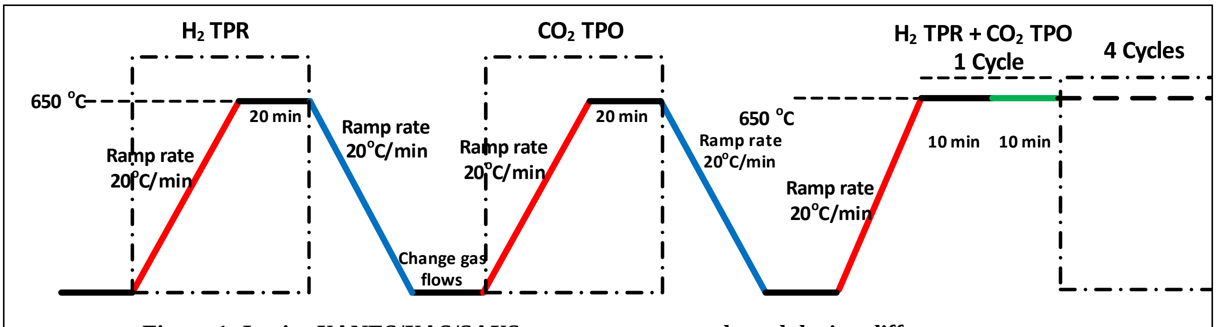

Figure 1: In-situ XANES/XAS/SAXS measurements conducted during different treatments

XANES was measured during all temperature program treatments and during the cycling measurements, while EXAFS was recorded close to room temperature after cool down. SAXS was measured in parallel with both XANES and EXAFS. The XAS was recorded using a photodiode, while a Pilatus detector measured the scattered X-ray intensity. The SAXS and XAS measurements were synchronized such that SAXS was triggered to measure every time the energy was at 11.4keV while measuring at the Pt-edge.

Experiments performed and preliminary results

H_2-TPR, CO_2-TPO, H_2-CO_2 cycling: PtGa/$MgAl_2O_4$ at the Pt L_{III} edge, XANES

Figure 2 shows the XANES spectra at the Pt edge. All the spectra are the final ones obtained at the end of each treatment. There is a clear reduction during TPR and a small hint of increase in white line intensity after CO_2-TPO, which is an occurrence not expected for Pt catalysts when present without any promoters. This indicates that Ga plays a role for this CO_2-oxidation to take place. Maybe it is present on the surface of the Pt as an oxide and thus contributes to this signal.

H_2-TPR, CO_2-TPO, H_2-CO_2 cycling: PtGa/$MgAl_2O_4$ at the Pt L_{III} edge, EXAFS

Figure 3 shows the R-space signal of the sample measured at room temperature subsequent to every treatment. The reduction of the oxide is evident. Upon CO_2-oxidation there are small changes in the first neighbour peaks and there is a slight change in the sample upon CO_2/H_2 cycling.

SAXS measurements during the treatments for PtGa/$MgAl_2O_4$

SAXS was measured in transmission for all the experiments that were performed in order to track the evolution of the particle size. Figure 4 shows the SAXS results after the respective treatments for the PtGa sample. The support contribution has been subtracted to obtain the contributions from the metals present. There are some changes evident, different intensity level and crossing of scattering curves, which will be modelled to get detailed results in terms of particle size and inter-particle distance.

SAXS was measured for $MgAl_2O_4$, Pt/$MgAl_2O_4$, Pt/Mg(Ga)(Al)O_4 and PtGa/$MgAl_2O_4$, as well as Al_2O_3/Pt/$MgAl_2O_4$, Al_2O_3/PtGa/$MgAl_2O_4$ and Al_2O_3/PtGa/Mg(Ga)(Al)O_4. This was done so that the contribution from each component can be quantified by subtracting each of the other components as a background.

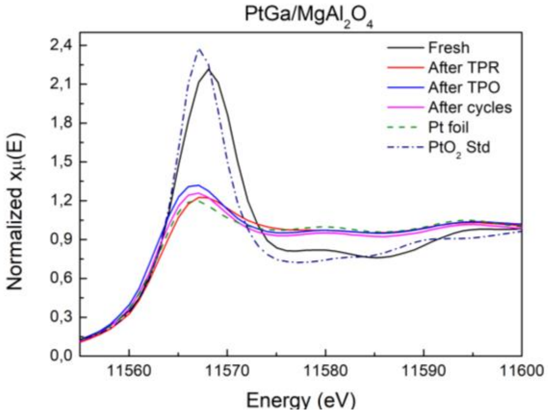

Figure 2: Pt edge for the PtGa/$MgAl_2O_4$ sample: XANES spectra after every treatment.

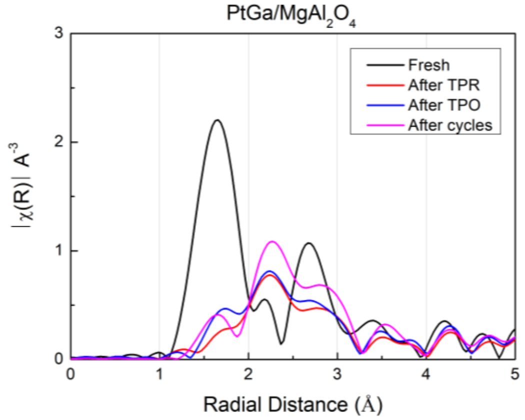

Figure 3: Pt edge for the PtGa/$MgAl_2O_4$ sample: R-space spectra after every treatment.

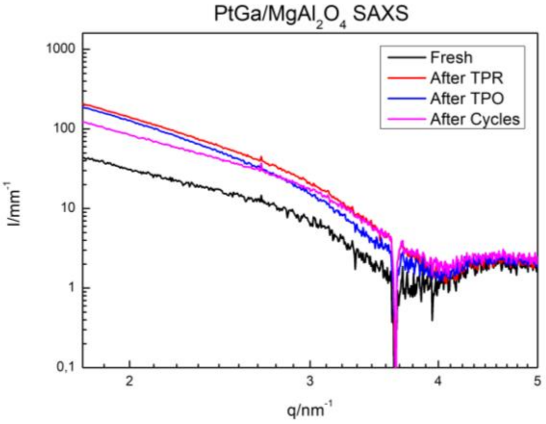

Figure 4: SAXS data for the PtGa/$MgAl_2O_4$ sample. Clear variations are observed upon each treatment.

Concluding

A nice set of XAS data has been collected on several PtGa/$MgAl_2O_4$ [Mg(Ga)(Al)O] samples both at the Pt and Ga edge under different conditions (reduction, CO_2-oxidation and CO_2/H_2 cycling). This will allow for several comparisons to be made, e.g. evolution of particle size, effect of Al_2O_3 overcoat on particle size, etc. Some differences already appear from a first comparison of XANES and R-space spectra. This will be further examined by modelling of these data. In addition, a first use of combined in situ XAS-SAXS was made and evaluated in collaboration with beam line scientist A. Longo.