	Experiment title: *In situ* XAS study of Pt-Ga bimetallic formation in Pt/Mg(Ga)(Al)O_x	**Experiment number**: **26-01-979**
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Shifts: 18	**Local contact(s)**: Alessandro Longo, Dipanjan Banerjee	

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Report: (max. 2 pages)

Summary

During this DUBBLE campaign, deeper insights were acquired into the mechanisms occurring during Pt-X/Mg(X)(Al)O_x (X = Ga, Sn, In) bimetallic catalyst formation by *in situ* XAS measurements. In addition, the reversible Pt-X segregation/alloying of the final Pt-X catalyst was studied during O_2/H_2 redox cycling. The analysis will combine conventional methods for XANES and EXAFS as well as wavelet transformed XAS.

Experiments performed

The experimental strategy was optimized compared to the first campaign (26-01-940). Short XANES measurements (5 min) were recorded during TPO/TPR to track the catalyst state. In addition, EXAFS measurements (45 min) were performed at certain stages of catalyst formation after quenching to room temperature to improve the data quality and to connect to the XANES evolutions observed. Five major branches were investigated:

1. An EXAFS spectrum was recorded of the alloyed Pt-Ga/Mg(Ga)(Al)O_x final catalyst state to complete a manuscript in preparation on the formation process of Pt-Ga bimetallic catalysts, studied during the first DUBBLE campaign.

2. Experiments were performed at the Pt L_{III} edge during bimetallic Pt-X (X = Ga, In, Sn) formation and redox cycling (O_2/H_2) for different systems: Pt/Mg(Ga)(Al)O_x, Pt/Mg(In)(Al)O_x, Pt/Mg(Sn)(Al)O_x. A comparative study of the obtained data should allow for novel insights into the redox behaviour of the different promoting elements (X).
3. Extensive experiments were performed to elucidate the mechanisms of Pt-Ga alloying within Pt/Mg(Ga)(Al)O_x. It is found that H_2 dissociation is promoted by Pt: Ga_2O_3 is reduced in (Pt+Ga_2O_3)/HT but not in Ga_2O_3/HT (HT = Mg(Al)O_x). The dissociated hydrogen atoms spill-over to the support and possess a high mobility on the substrate surface (reduction of Ga_2O_3 observed in mechanical mixture of Pt/HT + Ga_2O_3/HT). Only part of the reduced Ga_2O_3, i.e. Ga in the neighbourhood of Pt clusters, migrates towards these Pt clusters to form a Pt-Ga alloy (alloying for (Pt+Ga_2O_3)/HT and Pt/Mg(Ga)(Al)O_x but not for mechanical mixture Pt/HT + Ga_2O_3/HT).
4. Calcined Pt and In incorporated hydrotalcites, i.e. Mg(Pt)(In)(Al)O_x, form very dispersed Pt-In alloyed nanoparticles after H_2 TPR.
5. Two formation routines to prepare bimetallic Pt-In/Mg(In)(Al)O_x catalysts were compared by *in situ* XAS, starting from Pt(acac)$_2$/Mg(In)(Al)O_x. These routines consist of O_2 calcination followed by H_2 TPR on the one side and only H_2 TPR on the other side. It is possible that during the latter single H_2 TPR, the precursor ligands are (partially) oxidized by the In_2O_3 residing in the support, making a calcination prior to H_2 TPR unnecessary. This could be an efficient way of catalyst synthesis since (1) ligand fragments are removed through In_2O_3 in the support and (2) the ligand combustion enhances In_2O_3 reduction and thereby Pt-In alloy formation. These mechanisms will be further investigated.

<u>Example</u>

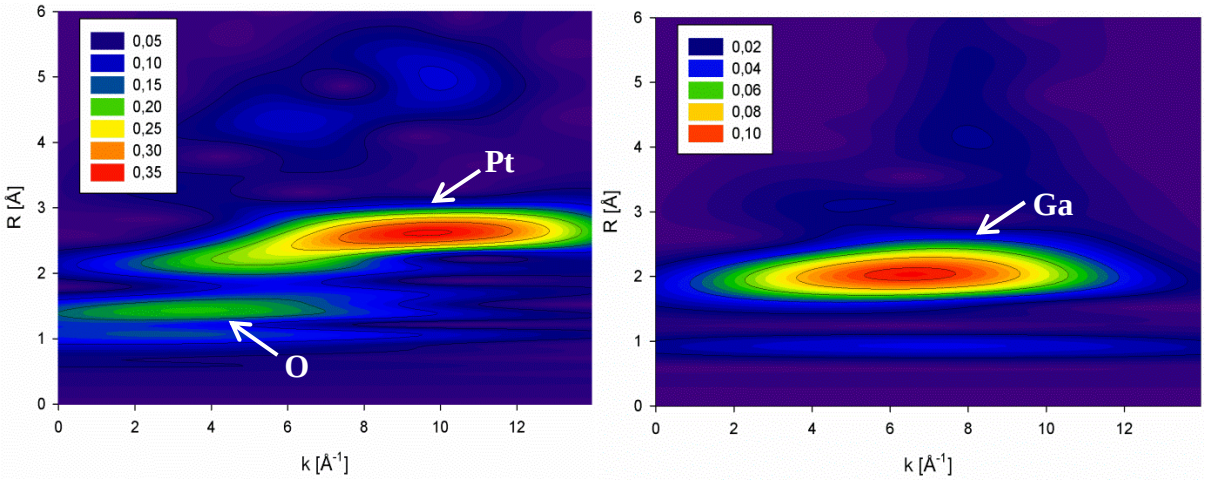

Figure 1: Wavelet transformed XAS provides simultaneous k- and R-space resolution. This opens up the opportunity to assign precise atomic species to each R-space peak since the k-region of backscattering is proportional to the atomic mass. (left) wavelet transformed XAS modulus of a room temperature measurement after a 450°C reduction in H_2/He. Around R = 1.5 Å, an O peak is present at 3 – 4 Å^{-1} (atomic mass O = 16). Around R = 2.7, Pt is dominantly present at a higher k-range from 8 – 12 Å^{-1} (atomic mass Pt = 195); (right) wavelet transformed XAS modulus of a room temperature measurement after a 650°C reduction in H_2/He. Only a single Ga peak can be detected at intermediate k- and R-values compared to the O and Pt peaks, i.e. R = 2 and k = 6 – 8 Å^{-1} (atomic mass Ga = 70). Therefore, Pt-Ga alloying occurs during reductive heating from 450°C - 650°C.