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	Experiment title: Fundamental study of the formation of bimetallic PtGa catalysts: in situ XAS study of Pt/Mg(Ga)(Al)Ox	**Experiment number**: 26-01-940
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Report: (max. 2 pages)

Introduction

This research looks into the interaction of Pt with Ga in Pt-based catalysts supported on a novel type of hydrotalcite material, Mg(Ga)(Al)O_x, containing Ga as extra-framework metal cations. Such Ga-promoted Pt particles are expected to yield improved performance in the dehydrogenation of light alkanes to alkenes. Starting from the Pt precursor impregnated upon hydrotalcite, a calcination treatment leads first to Pt nanoparticle formation, followed by alloying with the framework Ga upon additional treatment in H_2.

Experiments performed

With the 1wt% Pt fluorescence measurements were tried at first. However, the nearby Ga fluorescence (9250 eV) dominated the Pt signal at 9442 eV, and the Pt EXAFS quality was on the poor side. In transmission at the Pt L_{III} edge (11564 eV), the absorption jump was small, but the signal quality reasonably good. New samples with larger amount of Pt were prepared on site and it was decided to proceed in transmission mode (see fig. 1). After measuring Pt, experiments were repeated at Ga K (10367 eV) on similar samples.

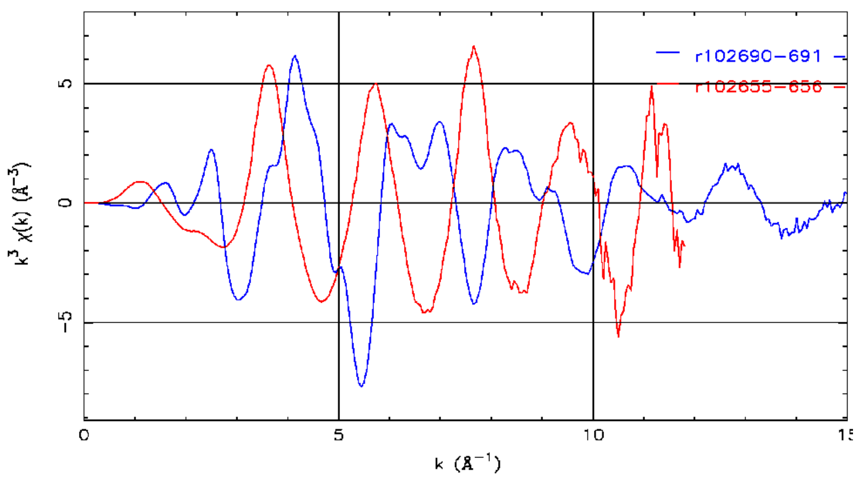

***Fig. 1**: Pt L_{III}-edge (red) and Ga K-edge (blue) $k^3\chi(k)$ EXAFS signal in transmission for 5wt% Pt(acac)$_2$/Mg(3.75wt%Ga)(Al)O_x as prepared; 45 min. data collection at 25°C*

The initial state of a series of samples with different loadings of Ga was measured in as prepared and calcined state. The Pt L_{III}-edge EXAFS signal, measured at ambient conditions, showed only a difference between as prepared and calcined samples and seems independent of Ga/Pt loadings. In Figure 2, the standard $k^2\chi(k)$ profile of the as prepared and calcined sample are compared. The difference between these signals yields 2 Fourier transformed functions $|\chi(R)|$, which are fingerprints in further analysis (see Figure 3). At the Ga-edge, no difference could be noted between as prepared and calcined samples.

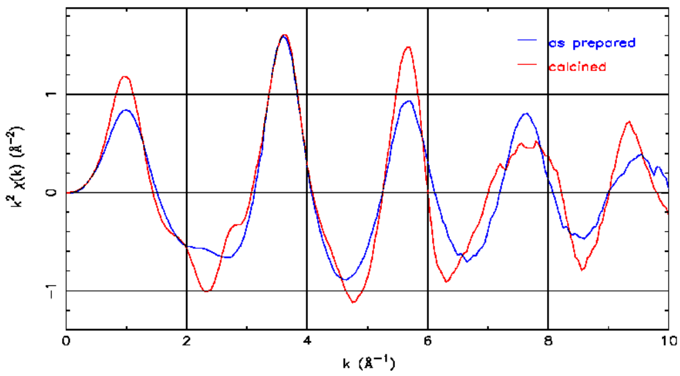

***Fig. 2**: Pt-edge EXAFS signal $k^2 \cdot \chi(k)$ of as prepared vs. calcined sample*

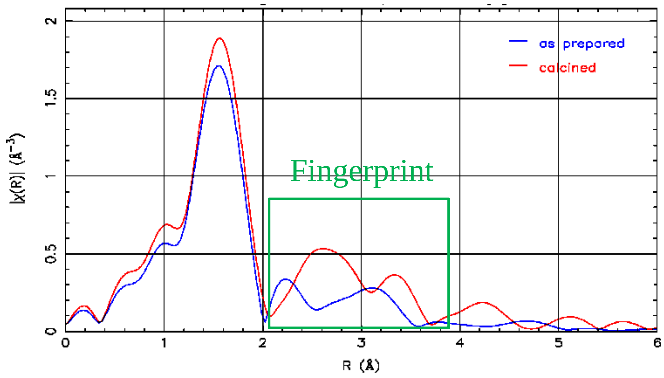

***Fig. 3**: Pt-edge $|\chi(R)|=|FT\{k^2 \cdot \chi(k)\}|$ radial distribution function of as prepared vs. calcined sample*

For the calcination – alloying experiment, an as prepared sample with good quality EXAFS was selected (i.e. as prepared 5wt% $Pt(acac)_2/Mg(3.75wt\%\ Ga)(Al)O_x$). After measuring at room temperature, it was heated in O_2 to 150°C, 350°C and 650°C. At each temperature EXAFS was measured. Then, the sample was cooled to 250°C in O_2 and another EXAFS scan was taken subsequently. After this scan, a reducing treatment in H_2 was started to induce reduction of the support causing the alloying of Pt and Ga. EXAFS was measured at 350°C, 450°C and 650°C. The same experiment was repeated at the Ga K edge with a similar sample, but starting from the reduction treatment.

For the same sample, a shift from an as prepared state to a calcined state is noted during the O_2 treatment between 150°C and 350°C (Figure 4), which is clearly in correspondence with the fingerprint in Figure 3. Figure 5 shows several $k^2\chi(k)$ spectra which seem to have a similar shape and, as such, a similar structure at increasing temperatures. Different Pt-edge $|\chi(R)|$ radial distribution functions are plotted in Figure 6, i.e. during the reduction treatment at 3 fixed temperatures. Differences in these Fourier transformed spectra could occur due to temperature effects, particle growth and alloying, most probable at 650°C. Clear discrepancies can be noticed when one compares the spectra in Figure 4 and Figure 6, suggesting a very different structure in the Pt environment. The analogous Ga K-edge spectra to those shown in Figure 6 can be seen in Figure 7 and seem to be influenced only by temperature.

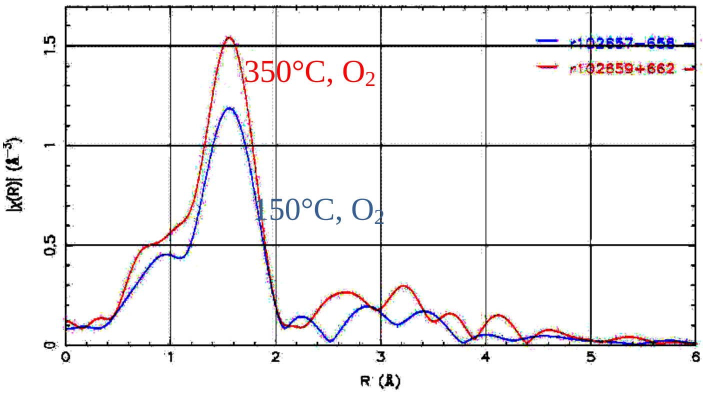

***Fig. 4**: Pt-edge $|\chi(R)|$ signal during O_2 calcination at 150 and 350°C*

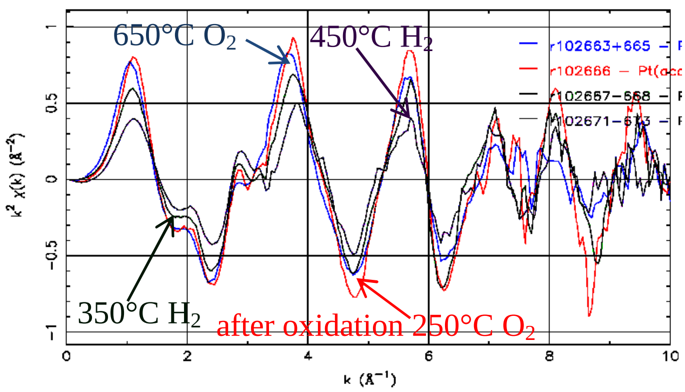

***Fig. 5**: Similar Pt-edge EXAFS signals $k^2 \cdot \chi(k)$ during O_2 and H_2 treatments.*

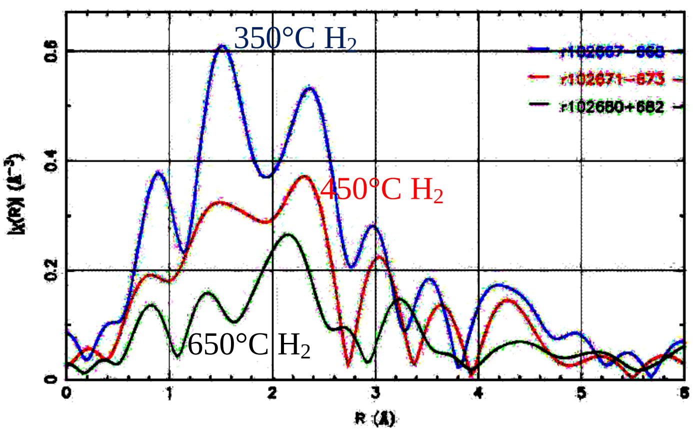

***Fig. 6**: Pt-edge $|\chi(R)|=|FT\{k^2 \cdot \chi(k)\}|$ signal during H_2 reduction of the 5wt% $Pt(acac)_2/Mg(3.75wt\%Ga)(Al)O_x$ sample at rising temperatures*

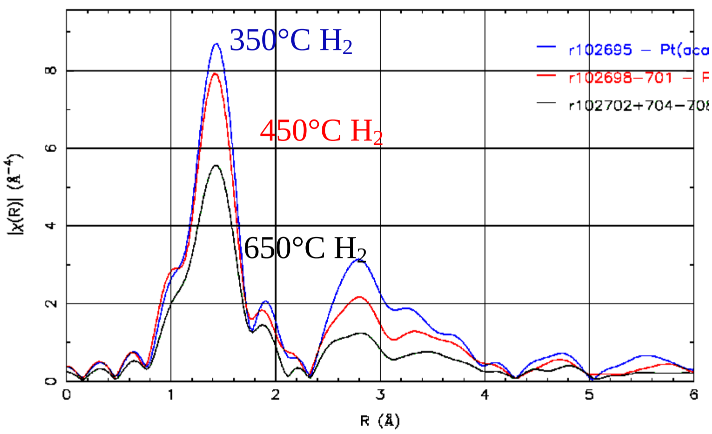

***Fig. 7**: Ga-edge $|\chi(R)|=|FT\{k^2 \cdot \chi(k)\}|$ signal during H_2 reduction of the 5wt% $Pt(acac)_2/Mg(3.75wt\%Ga)(Al)O_x$ sample at rising temperature.*