	Experiment title: The state of catalytic metal nanoparticles under non-steady state conditions: modulation excitation spectroscopy applied to ED-EXAFS	**Experiment number**: CH-2850
Beamline: ID24	**Date of experiment**: from: 8.7.2009 to: 14.7.2009	**Date of report**: 18 February 2010
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Report:

We provide here a description of a typical experiment performed within the allocated beam time. The data refer to a concentration modulation experiment consisting in the periodic switch between two gas flows, i.e. CO and NO pulses (both gases 5 vol.% in He) at 300°C over a 2 wt.% Rh/Al_2O_3 catalyst, reduced in situ at the same temperature in 5 vol% H_2/He. The two gases are admitted to the cell for an equal time (66 sec. each pulse). During pulsing, time-resolved DRIFT and ED-EXAFS spectra have been continuously and synchronously collected. A full modulation period (T) is defined as the time required to conclude a full NO vs. CO sequence. A modified DRIFT cell for a combined use with X-rays has been used as the reactor.[1] Online MS analysis of the exhaust gas of the reactor cell has been performed as well simultaneously. Only the issues related to the evaluation of the ED-EXAFS data are demonstrated here. Crucial to the experiment is the synchronization of the acquisition of ED-EXAFS and DRIFTS spectra, which was achieved by using the FReLoN camera to initiate the sequence of valve switching events controlled from the IR software. From then on the modulation experiment was determined by the infrared spectrometer. Typically, the subsequent trigger signal for EXAFS data collection was provided at each CO pulse of the modulation experiment. The full sets of time-resolved spectra (504 spectra/period, 0.26 sec time res.) can be independently processed into sets of phase-resolved spectra by the phase sensitive detection procedure (or demodulation).[2] Demodulation allows generating spectra with enhanced signal-to-noise ratio and free from spectral contributions responding with a frequency different from that of the stimulation. Therefore, only the changes biased by the external stimulus, for example the concentration variation, are emphasized by this technique; all static signals including noise are filtered out and do not appear in the phase-resolved spectra.

The time-resolved ED-EXAFS spectra collected during a modulation experiment (504 spectra x 7 periods, 3528 total spectra, Fig, 1(a)) display only subtle changes in the absorption spectra. Importantly, Rh remains in the reduced state throughout the experiment. Difference spectra within a single modulation period obtained by subtracting from the nth spectrum (n= 504) the very first one of that period are shown in Fig. 1(b). The whole absorption jump is then removed by subtraction and the difference spectra exhibit second derivative-like profiles with positive and negative signals. The noise level of these spectra is still significant

and does not allow a clear resolution of features at high energy (> 23.5 keV). On the contrary, the demodulation algorithm[2] uses the set of 504 averaged time-resolved spectra to produce a set of phase-resolved spectra (Fig. 2). Thus, the absorption jump is again filtered out as well as all other features not responding to the external stimulation (the NO vs. CO switches). It is clear that the processing considerably reduces the noise in the spectra. Features in the EXAFS region are clearly resolved whereas they were not in the simple difference spectra obtained within a single period (Fig. 1(b)). An estimation of the S/N ratio indicates a factor 40 improvement for the spectra shown in Fig. 2 compared to those in Fig. 1(b). It is clear that the demodulation approach provides surface sensitivity to the EXAFS method, since the small changes enhanced by the demodulation algorithm occur on a basically reduced Rh catalyst, as observed above.

The detailed structural-dynamic behavior of the system can be clearly uncovered. From the demodulation envelopes one can precisely assess the temporal behavior of the structural changes using the 504 averaged time-resolved spectra (Fig. 3). It can be seen that at the CO→NO and NO→CO switches all signal experience intensification or attenuation. Signals exhibiting similar behaviour can be associated with specific states of Rh. When the signals at 23.22 and 23.256 keV are at maximum intensity, the signal at 23.344 keV is at its minimum. The signal at 23.22 keV coincides with the edge threshold energy and its intensity variation needs to be associated with reduction-oxidation phenomena. Therefore, the data reveal that during the CO-NO pulses the Rh phase continuously changes from reduced to partially oxidized and back. Examination of the temporal response of the signals also reveals that the observed subtle changes occur at different rates depending on the switch direction. When the atmosphere is changed from NO to CO, the edge threshold intensifies linearly. On the contrary, at the CO→NO switch no change occurs before oxidation lights off. Oxidation is accomplished at the NO pulse conclusion but is slow compared to reduction and not linear. The oxidation rate is consistent with the rapid formation of a thin oxidic layer followed by its slower growth.

All this information needs to be coupled to the DRIFT and MS data. A number of samples treated under various conditions have been analysed in this way and the evaluation is ongoing. Part of these data are already being reported in a manuscript.[3]

Fig. 1 (a) Time-resolved ED-EXAFS of reduced 2 wt.% Rh/Al_2O_3 collected at the Rh K-edge at 300°C and averaged over 7 modulation (CO/NO) periods. (b) Difference spectra within a single modulation period.

Fig. 2 Phase-resolved spectra obtained by phase sensitive detection from the set of time-resolved spectra shown in Fig. 1(a) together with the scaled spectra of bulk Rh_2O_3 and the Rh foil for comparison.

Fig. 3 Temporal response of signals from the time-resolved spectra of Fig. 1(a) and selected according to the spectra of Fig. 2.
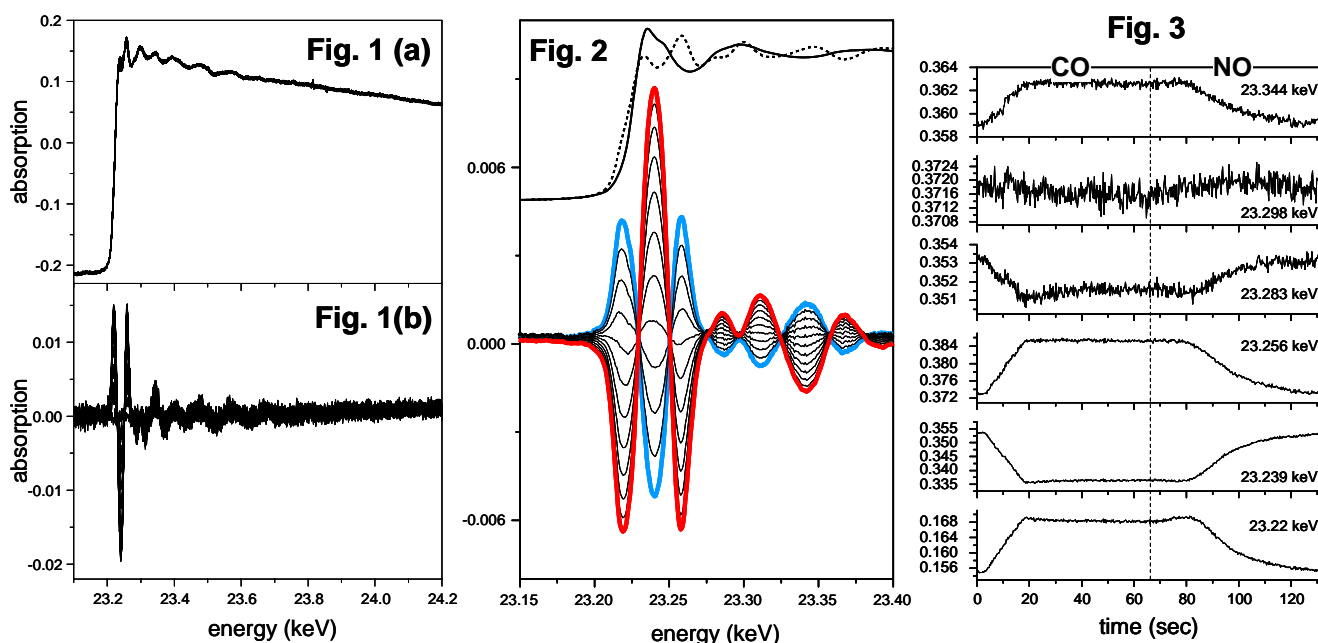
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