ESRF	**Experiment title: Surface x-ray absorption fine structure study of Rh deposits on Al_2O_3 / NiAl(110)**	**Experiment number**: SI404
Beamline: ID32	**Date of experiment**: from: 23.8.98 to: 1.9.98	**Date of report**: 18.2.99
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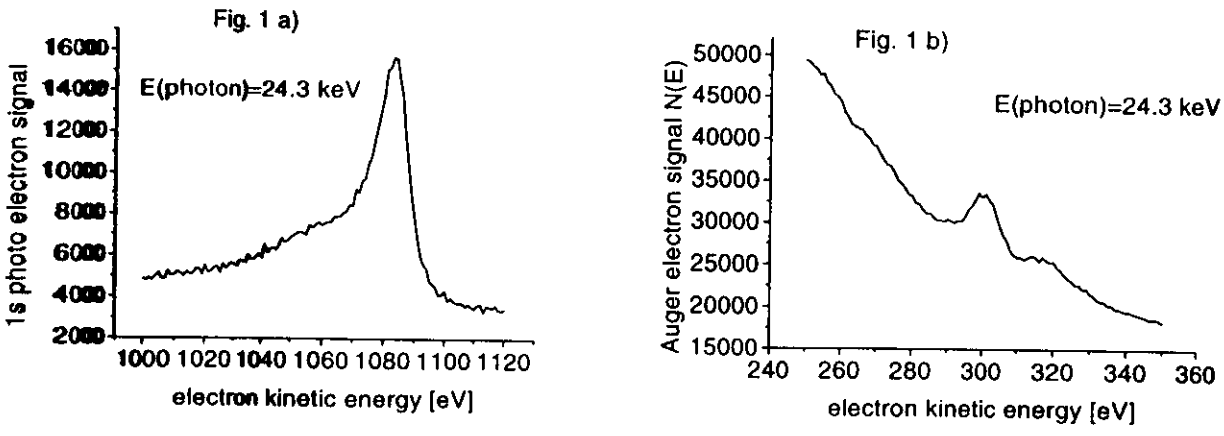
Report: The aim of our experiment was to study the local structure of small Rh clusters on a thin ordered Al_2O_3 film on NiAl(110) using extended x-ray absorption fine structure spectroscopy (EXAFS). The identification of structure - reactivity correlations is of extreme importance to understand and control the first steps of heterogeneous catalytic reactions.

The experiment was performed in the ID32 SEXAFS and XSW UHV chamber (old version) equipped with a PHI hemispherical electron energy analyzer. After sputter-cleaning the sample the ordered Al_2O_3 layer was prepared according to a well established procedure. Unfortunately no LEED system was available to check the surface structure. A nominally 0.4 nm thick Rh layer was deposited by e-beam evaporation at a substrate temperature of 300 K. This corresponds to an average Rh cluster size of 4 nm. First we studied the x-ray photoemission and Auger electron spectrum at a photon energy of 24.3 keV, above the Rh K-edge at 23.22 keV. Fig. 1 a) shows the Rh 1s photoelectron peak and Fig. 1 b) the Rh MVV Auger lines exited by secondary processes. The Auger lines are more suited to be traced during the EXAFS scan, because they do not change in energy position. To do an energy scan combined with electron analyzer data acquisition a remote control process has to be started from SPEC on the analyzer controlling PC and several acquisitions are done



by the PC. A major problem in this type of acquisition is the missing correlation between the monitor reading by SPEC and the data taken by the PC. This led to crucial normalization problems resulting in a noisy EXAFS signal. Apart from that the re-alignment of the electron energy analyzer was barely impossible, which was necessary because the analyzer had to be retracted for each new Rh deposition (about 4 shifts lost).

To finally observe the EXAFS signal we used the Rh Kα fluorescence signal. Fig. 2 a) shows a typical fluorescence spectrum taken with a Ge solid state detector at an incident photon energy above the Rh K-edge. In the high energy part of the spectrum (not shown) a strong λ/3 contamination due to the missing mirror is present, which contributes significantly to detector saturation. The detector was placed outside the chamber at a distance of ca. 300 mm at 90° to the direct beam and a 15μm thick inox filter was used to reduce the Ni Kα+β signal coming from the bulk. The Mo Kα+β peak arises from the Mo plate behind the sample and the PBN sample heater. The Rh Kα peak at 20.22 keV can be clearly identified and Fig. 2 b) shows the Rh Kα signal as a function of energy for Rh coverages of 0.4 nm and 0.2 nm nominal thickness corresponding to cluster sizes of 4 nm and 1 nm respectively. In both cases the step jump at the Rh K edge is clearly visible and also some of the first EXAFS oscillations. In the case of 1 nm cluster size the amplitude of the oscillations starts to be strongly damped, indicative for the reduced number of nearest neighbors. During the EXAFS scans the SILENA MCA of the Ge detector lost six times the connection to the device server during 24 h (3 shifts lost, all scans had to be repeated).They have been collected in the last 12 hours of the experiment and their quality could be significantly improved by an optimized sample - detector geometry which is available in the new version of the SEXAFS and XSW chamber of ID32. Including the 3 shifts lost because the beamline was not ready after the summer shutdown (leaking monochromator, mono cooling not working, new operation system and spec version not tested etc...) we lost 10 shifts from 18. Our conclusion is that the experiment is feasible using Rh Kα fluorescence also for small cluster sizes. Therefore the proposal will be resubmitted.