



	<b>Experiment title:</b> Siting of small Pt clusters in zeolites; influence of zeolite on cluster size and character of metal-support interaction	<b>Experiment number:</b> 1-01-173
<b>Beamline:</b> BM1B	<b>Date of experiment:</b> from: 25 April, 1999 to: 29 April, 1999	<b>Date of report:</b> 17 February, 2000
<b>Shifts:</b> 9	<b>Local contact(s):</b> Hermann Emerich	<i>Received at UNIL:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

L. Drozdová\*, R. Cattaneo\* and R. Prins

Laboratory for Technical Chemistry, ETH Zürich, 8092 Zürich, Switzerland

**Report:**

*Introduction*

Interesting physical and chemical properties of nano-meter-sized metal clusters such as particle - size effects in catalysis, enhanced the interest in the synthesis and characterization of well - dispersed metal particles. Channels and cages of zeolites have proved to be a valuable matrices for the stabilization of supported metal clusters of sizes up to a few nano-meters and with narrow size distributions. NaX zeolites were used as matrices for the synthesis of Pt carbonyl complexes  $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ , which in turn served as precursors for the synthesis of small Pt clusters. The carbonyl complexes were decomposed in vacuum at 150 and 400 °C, or in oxygen at 150 °C.

*Experimental*

Pt-L<sub>III</sub> edge EXAFS spectra were recorded in transmission mode at liquid nitrogen temperature. The data were analyzed by standard procedures using the XAFS Data-Analysis

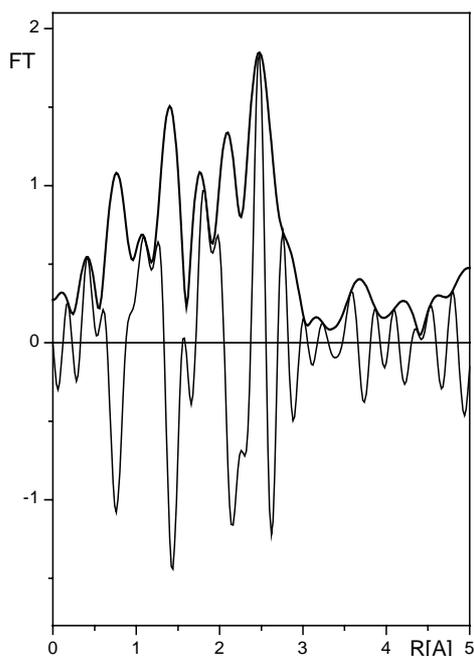


Fig.1  $[\text{Pt}_3(\text{CO})_6]_n^{2-}/\text{NaX}$

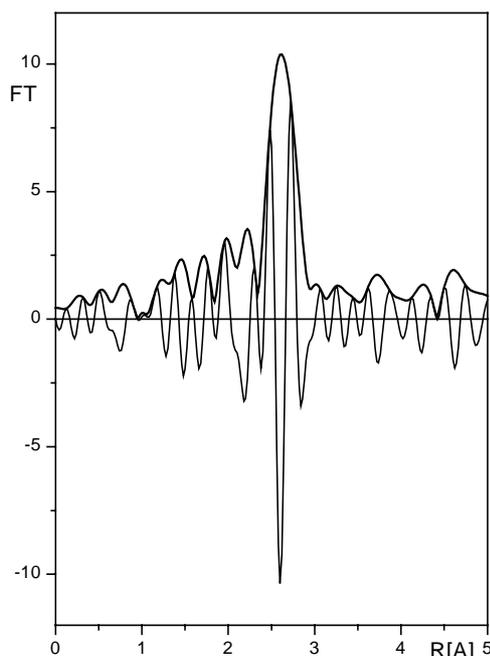


Fig.2  $[\text{Pt}_3(\text{CO})_6]_n^{2-}/\text{NaX}$  decomposed  
in vacuum at 400 °C

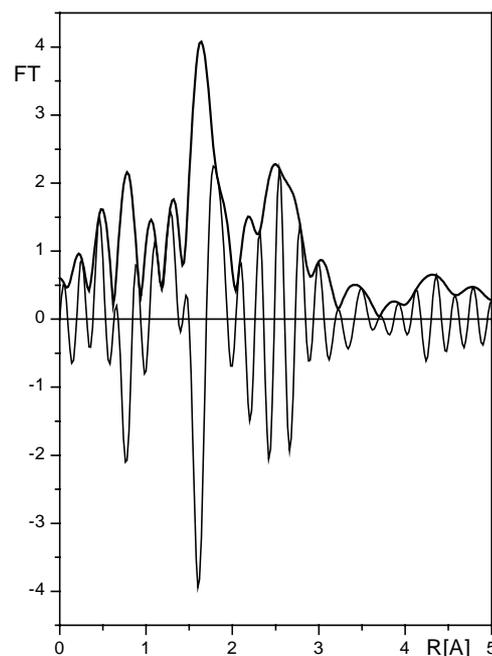


Fig.3  $[\text{Pt}_3(\text{CO})_6]_n^{2-}/\text{NaX}$  decomposed  
in  $\text{O}_2$  at 150 °C

Program XDAP – Version 2.2.2.

### Results

Fourier transformation (FT) of the  $k^3$  weighted experimental  $\chi$  data of the  $[\text{Pt}_3(\text{CO})_6]_n^{2-}/\text{NaX}$  carbonyl complexes is shown in Fig. 1. The most intense peak at 2.48 Å in the uncorrected FT corresponds to the intra-triangular Pt-Pt shell which overlaps with the Pt-Pt inter-triangular and Pt-(C)O shells. The bands in the region between 1 and 2 Å (uncorrected FT) can be assigned to Pt-C bridging and terminal shells. Higher Pt-Pt shells, visible in FTs of Pt foil or large Pt clusters, are absent in the FTs of the carbonyl complexes decomposed in vacuum at 150 °C (not shown) and 400 °C (Fig. 2). This is evidence of the formation of relatively small Pt clusters, which seem to be stable even at 400 °C.

The carbonyl complexes decomposed in oxygen at 150 °C provided a qualitatively different spectrum (Fig. 3). A new very intense peak at 1.64 Å appeared in the uncorrected FT besides the band typical for Pt-Pt shells in the range between 2-3 Å. This peak can be assigned to a Pt-O shell and suggests that small platinum oxide clusters are formed after the decomposition of the carbonyl precursors.