



**Experiment title:**  
EXAFS of alloy particles in zeolites

**Experiment number:**  
**CH-98**

**Beamline:**  
D8-GILDA

**Date of experiment:**  
from: 06.12.95 to: 17.12.95

**Date of report:**  
**04.03.96**

**Shifts:**  
**24**

**Local contact(s):**  
S. Pascarelli

*Received at ESRF:*  
**18 MAR 1996**

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

R. Prins,  
*Eidgenössische Technische Hochschule, Laboratory for Technical Chemistry, 8092 Zurich, Switzerland*

F. Cimini\*,  
*Eidgenössische Technische Hochschule, Laboratory for Technical Chemistry, 8092 Zurich, Switzerland*

---

**Report:**

**EXAFS** measurements were performed in order to characterize mono (Pt, Rh) and bimetallic (Rh-Pt) clusters supported on zeolite NaY. The data were collected at the GILDA beamline, working at liquid nitrogen temperature and using the Si 311 double crystal monochromator. Many different samples (including the metal foils used as references) were studied; the absolute amount of the metal atoms per gram of support as well as the molar Pt/Rh ratio were varied. Some spectra were also measured after adsorption of Xenon on the metal particles. From the quantitative analysis of the EXAFS spectra by means of the fitting procedure (see fig. 1) it was possible to determine the first coordination numbers of the absorbing atom (Rh, Pt or both in the bimetallic case) and the interatomic distances, thus obtaining information about the size and structure of the metal clusters. In the samples containing both metals, the shape of the EXAFS spectra and their Fourier transformations clearly showed the overlap between two different metal-metal shells (see *fig. 2*). Comparing the coordination numbers obtained by varying the metal/metal molar ratio and the total metal amount, it was possible to draw the following conclusions.

First, the particle size proved to be independent of metal loading (within our loading limits), thus suggesting that the support is the limiting factor for growth of the metal particles.

Second, substantial surface enrichment was not present, as concluded by comparing the coordination numbers at the Rh and Pt-edges, as well as by considering the variation in the spectra caused by Xc-absorption.

Third, every metal atom tends to bind preferentially to its own kind, and this tendency depends on the Rh/Pt ratio. This is probably due to a difference in the kinetics of reduction of Pt and Rh. In particular, the analysis of two complete series (differing in the total amount of metal) of samples having different Rh/Pt molar ratios (1/0, 7/1, 4/1, 2/1, 1/1, 1/2, 1/4, 1/7, 0/1), enabled us to determine the influence of the molar ratio on the final structure of the clusters. It was concluded that, when Rh predominates, the randomness of the structure is quite small, and monometallic bonds are favoured. On the contrary, when Pt predominates, the coordination numbers resemble those corresponding to a completely random structure.

These results are very important to correctly interpret and then modify the catalytic activity of zeolite-supported metal clusters.

Because of some problems encountered in determining the right amount of Xe for the adsorption on the metal clusters (at the same time avoiding an excessive absorption of the radiation from the gas itself) additional time was required. We decided to complete the Rh-Pt project and to postpone our second project (*EXAFS of selenophene adsorbed on Ni-MoS<sub>2</sub> catalysts*).

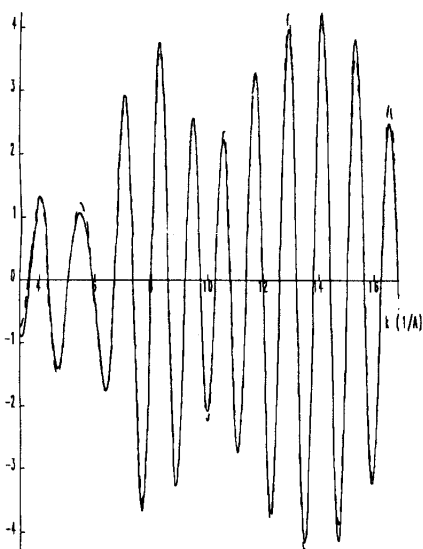


Fig.1 EXAFS signal and fitted signal of a Pt/Rh=1/2 sample

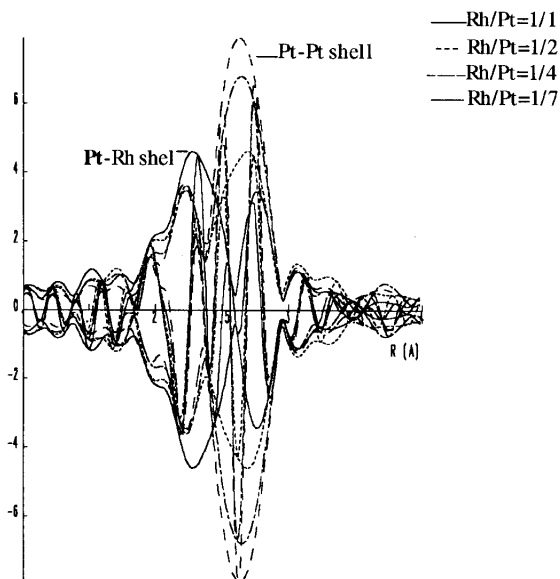


Fig.2 Fourier transforms of the EXAFS signals of samples with various Rh/Pt ratios