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QEXAFS Investigation of the Particle Growth of PtRh Clusters Supported on NaY

F. Cimini and R. Prins

ETH-Zentrum, Universitätstr. 6, 8092 Zürich, Switzerland

Abstract. The Quick EXAFS technique was used to study the formation and growth of bimetallic PtRh particles in zeolite NaY during reduction. Before reduction, only metal-oxygen signals were detectable. While increasing the temperature at a rate of 5°C/min and flowing H₂ through the in-situ cell, 1 minute EXAFS scans were recorded at the Rh and Pt edges. At 40°C, an intense Rh-Rh signal appeared within few degrees, indicating the formation of monometallic Rh clusters (20-25 atoms). The Rh-O signal slowly decreased between 100 and 200°C, simultaneous with the appearance and slow growth of a small Rh-Pt signal. The Pt edge EXAFS changed less abruptly than the Rh edge EXAFS. Above 80°C, the Pt-O signal started to decrease, and at 100°C the Pt-Pt and Pt-Rh signals appeared simultaneously, pointing to the formation of small bimetallic particles. These signals grew slowly until 300°C, even after the Pt-O signal had already disappeared. This indicates that small bimetallic particles move through the channels of the zeolite and merge to larger particles. This merging should also involve the big monometallic Rh clusters formed at 40°C, probably situated in the supercages of the zeolite. At the end of the reduction, two kinds of clusters are present: one having a big Rh core (maybe also completely monometallic), the other consisting of Pt-rich bimetallic PtRh clusters. It is concluded that the different reduction behaviour of Rh and Pt drastically influences the final structure of the metal particles.

1. INTRODUCTION

The structure of small metallic clusters supported on porous oxides has been of great interest in catalysis for many years. EXAFS (extended X-ray absorption fine structure) demonstrated to be a very efficient tool for studying such materials, giving information on the environment about a particular atom in the metal clusters, i.e. the number and kind of neighbouring atoms and their interatomic distances. The quick EXAFS (QEXAFS) technique provides an alternative way of recording X-ray absorption fine structure data, allowing a much quicker scan of a single spectrum [1]. It is therefore possible to make use of such technique to investigate processes that change with time. Our work was aimed at understanding and following the fate of the Rh and Pt atoms supported on zeolite NaY during the genesis of the metal atoms and their growth to metal clusters.

2. EXPERIMENTAL

A bimetallic sample was prepared by the ion-exchange method, adding zeolite to an aqueous solution of Pt(NH₃)₄(NO₃)₂ and Rh(NO₃)₃·2H₂O. The mixture was filtered, washed, and the recovered solid was dried (100°C) and calcined (300°C). The reduction was then started by increasing the temperature of the *in-situ* cell [2] with the heater, and by flowing simultaneously H₂ through the cell. The cell temperature was raised up to 300°C with a heating rate of 5°C/min and kept for 2 h at 300°C. A series of QEXAFS spectra was recorded at each absorption edge (Pt L_{III} and Rh K) during reduction and every single spectrum was subsequently analysed. The QEXAFS spectra were measured at the Synchrotron Radiation Source (SRS) in Daresbury (UK). The following operating conditions were chosen: 1 minute scan from -30 to 570 eV with respect to the energy threshold at the Pt edge and a 1 minute scan from -30 to 750 eV at the Rh edge. Standard data reduction procedure has been employed to isolate the EXAFS oscillation from the raw spectra [3]. To reliably determine the parameter values, multiple-shell fitting in *k*-space and in *R*-space was done, using *k*¹ as well as *k*³ weighting. The backscattering amplitudes and phase shifts of the Rh-Rh and Pt-Pt contributions were obtained from the EXAFS signals of the pure metal foils, measured at the same temperature as the spectrum under analysis, to limit the anharmonicity problems caused by the high temperature. In order to do that, it was necessary to measure the EXAFS signals of the Rh and Pt foils at many different temperatures between room temperature and 300°C. As for the Pt-Rh (Pt is the absorber) and Rh-Pt contributions we used phase shift functions obtained from FEFF codes [4], and experimental backscattering amplitude functions extracted from Pt foil when Pt was the backscatterer atom (Rh-Pt), and from Rh foil when Rh was the backscatterer (Pt-Rh).

3. RESULTS AND DISCUSSION

Two kinds of information were extracted from the data. Qualitative information was provided by the Fourier Transform profiles of the EXAFS data, which visualise the evolution of the metal environment during reaction. Quantitative results were obtained by the full EXAFS analysis, performed on the most significant spectra recorded.

The evolution of the FT of the k^3 weighted EXAFS at the Rh-edge is represented in Fig. 1a. Before reduction (RT), two peaks are visible. The first peak at 1.5 Å represents a Rh-O signal, probably due to Rh oxides formed in the zeolite after the calcination at 300°C. The second peak at 2.7 Å can be attributed to a Rh-Rh signal belonging to Rh₂O₃. Between RT and 35°C only small differences around 2.5 Å can be noticed. At 39°C a big peak at 2.3 Å suddenly appeared, simultaneous with the disappearance of the Rh-Rh signal from the oxide and with a decrease of the Rh-O signal. The peak at 2.3 Å, corresponding to a real distance of about 2.7 Å from the absorber (Rh), demonstrates that Rh metal particles have been formed. After a further increase of the metal-metal peak at 46°C, the FT profile did not change significantly until 104°C. From 104 to 188°C the Rh-O signal slowly decreased while the metal-metal peak underwent no remarkable change. After the disappearance of the Rh-O signal at about 180°C, the FT profile remained almost unchanged until the end of the reduction.

Some of the recorded EXAFS spectra were then analysed quantitatively to obtain detailed information about the coordination numbers (CN) and interatomic distances. After isolation of the first shell region (1-3 Å) by an inverse Fourier transformation, a typical k -space range for the fitting procedure was 3-12.5 Å⁻¹. The progress of the coordination numbers during reduction is depicted in Fig. 2a. The results basically confirm what was obtained in the qualitative analysis, and enabled us to accurately determine the dimensions of the particles involved in the reduction. At the beginning we are dealing with small Rh₂O₃ particles as pointed out by the interatomic distances and coordination numbers. At 46°C a big Rh-Rh contribution was detected. The Rh-Rh interatomic distance (2.69 Å) is very similar to that of pure metal (2.68 Å), pointing to the presence of Rh metal clusters. The Rh-Rh coordination number of 4.7 indicates a quite considerable size of the clusters. At the same time the Rh-O CN decreased remarkably. The situation did not change significantly until 104°C, when a small Rh-Pt (CN = 0.5) signal appeared. The following spectra pointed out a gradual growth of the Rh-Pt signal, simultaneous with a decrease of the Rh-O signal. In conclusion, the reduction of the Rh atoms consists of two steps. First, three quarters of the atoms are quickly reduced at 40°C and give rise to large monometallic clusters. Second, from 90°C to the end of the reduction, a gradual reduction of the remaining Rh atoms is accompanied by the formation of bimetallic clusters.

The FT of some k^3 weighted EXAFS spectra measured at the Pt-edge during reduction are represented in Fig. 1b. Before the reduction we can observe a large peak at 1.6 Å, due to a Pt-O signal from Pt oxides or/and Pt²⁺ bonded to the oxygen atoms of the zeolite framework. From RT to 99°C a decrease of the Pt-O signal took place with no evidence of new peaks. At 118°C a shoulder to the right of the Pt-O signal around 2.2 Å appeared, and at 137°C this shoulder had grown in size and an additional small peak at 2.8 Å appeared. From 118°C to 253°C a very gradual decrease of the Pt-O signal simultaneous with the gradual increase of the signals at 2.2 and 2.8 Å was observed. These latter signals could be attributed to the overlap between two metal-metal coordination shells (Pt-Pt and Pt-Rh). After the disappearance of the Pt-O signals the two metal-metal signals continued to undergo small change.

Also in this case the quantitative analysis confirmed the qualitative conclusions, and brought new information. The progress of the coordination numbers during reduction is reported in Fig. 2b. At the beginning the interatomic distance and coordination number point to the presence of very small Pt oxides particles (PtO, PtO₂) and isolated Pt ions. At 95°C two metal-metal signals, Pt-Pt and Pt-Rh, appeared simultaneously. From 100 to 200°C we measured a constant increase of the metal-metal coordination numbers and a decrease of the Pt-O contribution. Also after the O signal had disappeared (~220°C), the metal-metal contributions still increased. This slight growth continued during the temperature plateau at 300°C. In conclusion, at the Pt-edge there is no definite step. From 90°C to the final reduction temperature one observes a gradual reduction leading to the formation and gradual growth of bimetallic particles.

Considering the results obtained at both edges, we can infer that some particles of Rh₂O₃, presumably contained in the supercages of the NaY zeolite are immediately reduced at 40°C, probably in an autocatalytic way (the first atoms which are reduced catalyse the further reduction of the oxide particles). The quick reduction at 40°C of a considerable amount of Rh ions is also proved by the TPR spectrum of our sample, which presents a sharp peak at 40°C, overlapping on the high temperature side with a broader peak. The latter has its maximum at 150°C and continues above 200°C. The form of this TPR-spectrum is very consistent with our EXAFS results.

Once formed, the metal clusters (20-25 atoms) cannot escape from the supercages. Some Rh atoms are still in oxidic form, i.e. situated in other cages of the zeolite or mixed with Pt oxides. The decrease of the Pt-O signals is, until 90°C, not accompanied by the formation of Pt-Pt(Rh) bonds. Two reactions, not mutually exclusive, could account for that: on the one hand the reduction PtO₂ → PtO, and on the other hand the reduction of Pt²⁺ to isolated Pt⁰ atoms.

Around 100°C, small bimetallic particles were formed, as proved by the Pt-Rh contributions detected at both edges. The disappearance of the Rh-O signal simultaneous with the formation of the bimetallic particles (from ~ 100°C to the end) suggests that the Rh atoms which are still in the oxidic form are slowly reduced contemporary to or together with the Pt atoms, giving rise to the bimetallic clusters. These small clusters are Pt-rich. The slow increase of the coordination numbers at the Pt-edge points to a gradual reduction of the oxidic particles and to their successive merging. The absence of any step seems to indicate a similar behaviour of all (different) oxidic Pt species with respect to the clusters formation. The growth

of the particles continues even after the Pt-O contribution has disappeared, indicating that the growth of the bimetallic clusters continues, probably by diffusion through the channels of the zeolites. At the Rh edge, the presence of the large Rh-Rh contribution makes the spectra less sensitive to the small variation caused by the enlargement of the bimetallic particles (i.e. the Rh-Pt signal is detected 10°C later). The bimetallic clusters which move through the channels probably also meet the large Rh monometallic clusters situated in the supercages, covering part of them with a bimetallic Pt-rich layer. The movement (and the successive merging) of each particle through the channels should stop when the particle size exceeds the size of the entrance of the supercage (7.4 Å). From that point on, only a further merging with other small particles that can still enter the supercage is possible. At the end one expects to have clusters just fitting the supercages. Different cluster structures are, however, possible. Some of them could have a Rh core, or even could be completely monometallic Rh particles, formed at the beginning of the reduction (40°C); others could be Pt-rich bimetallic particles, slowly formed and grown during the whole reduction step.

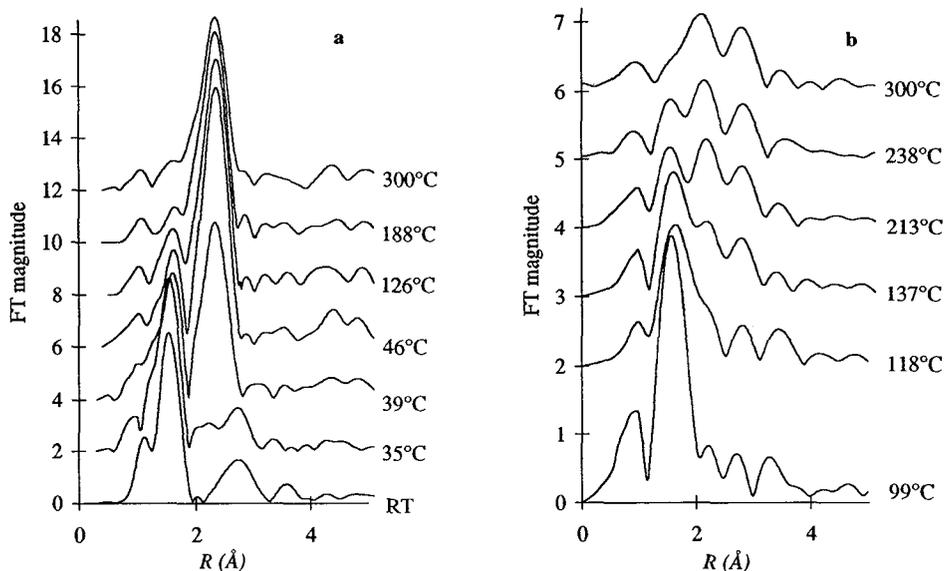


Fig. 1: Bimetallic sample during reduction: evolution of the FT of $\chi(k)k^3$ measured at the Rh (a) and Pt-edge (b).

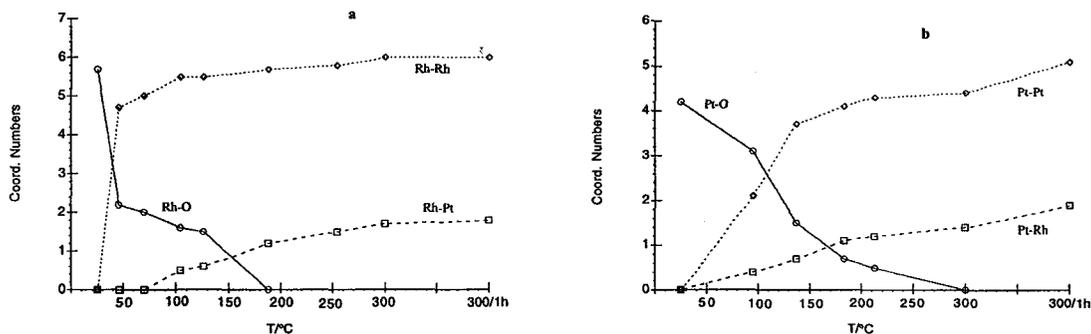


Fig. 2: Coordination numbers during reduction (as obtained by the fitting procedure) vs. temperature, at the Rh (a) and Pt-edge (b).

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