

J. Synchrotron Rad. (1999). **6**, 465–467

XAS of electronic state correlations during the reduction of the bimetallic PtRe/Al₂O₃ system

Dominique Bazin^a, Hervé Dexpert^a, John Lynch^b and Jean Paul Bournonville^b

^aLURE, Bat 209D, Université Paris-Sud, 91405 Orsay, France, ^bInstitut Français du Pétrole, B. P. 311, 92506 Rueil Malmaison, France

We have developed an approach able to follow the formation of heterometallic bonds for nanometer scale metallic clusters in the case where the two metals are close in the periodic table. In order to illustrate our purpose, experiments have been performed on bimetallic PtRe/Al₂O₃ catalysts.

Keywords : electronic state; Pt; Re; Catalysts.

1. Introduction

Many bimetallic systems are easy to study due to differences in the backscattering function of the two elements but this is not the case for a system like the PtRe bimetallic system (D. BAZIN et al. 1997). For this catalyst, the proximity of the L edges of the metals as well as their similar backscattering amplitude and phase constitutes a major limitation.

Here, we describe a new approach using the proximity of the L edges of the metals in order to follow "simultaneously" the evolution of their electronic states during reduction.

2. Experimental conditions

Highly dispersed Pt-Re systems deposited on γ alumina extrudates (B. E. T. surface area, 240 m²/g) were prepared by successive impregnation from the same precursors (H₂PtCl₆ for Pt and NH₄ReO₄ for Re) starting with the Pt impregnation.

We distinguish :

- hydrated calcined samples (samples A, A') which were reduced after a three month exposure to air, implying that they have been largely rehydrated,
- dehydrated calcined sample (sample B) which was reduced after a new *in situ* drying operation of 2 hours at 150°C.

Measurements were performed at the EXAFS IV station of the LURE-DCI storage ring (E=1.85 GeV, I=300mA, lifetime = 300 h). A double (Si 111) crystal monochromator with two ion chambers as detectors in transmission geometry from below the Pt L_{III} edge (11560. eV) to above the Re L_{II} edge (11957. eV) was used, the counting time per point being one second. Due to the closeness of the Pt and Re in the periodic table, we are unable to distinguish their contributions to the EXAFS spectra. For *in situ* experiments, samples were mounted in a cell made of boron nitride holders set in a furnace.

3. Reduction process

3.1. Rehydrated samples A, 1.0%wt Pt - 1.0%wt Re/Al₂O₃.

For the first spectra (Fig. 1), the two edges are intense, as expected since the initial coordination sphere of Pt is composed by oxygen atoms. As the reduction proceeds, these electronic states evolve towards metallic ones (the population of the 5d band increases). The point which must be emphasised here is that the reduction of the two elements starts and finishes simultaneously.

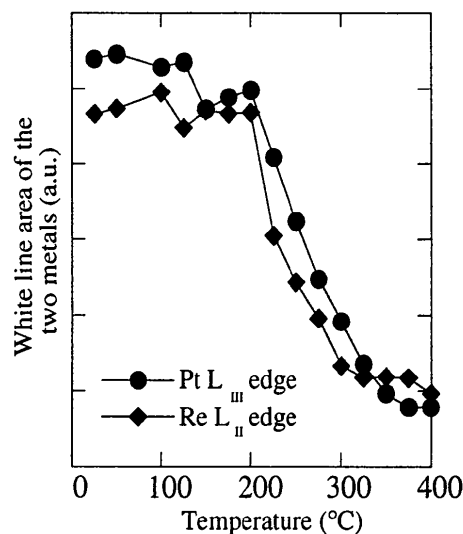


Figure 1
Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the hydrated sample A.

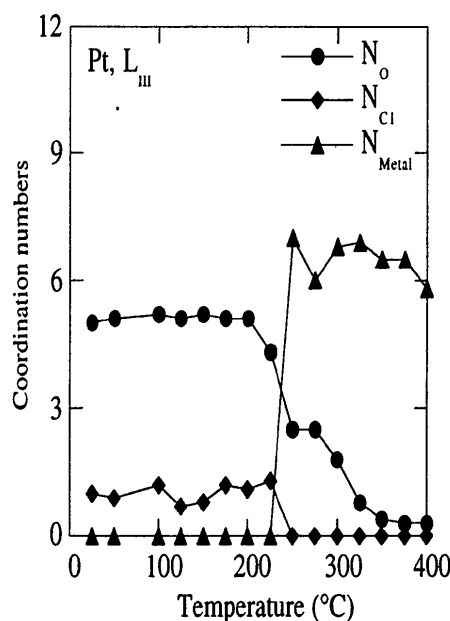


Figure 2
Variation of the different numbers of oxygen, chlorine and metal atoms around platinum atoms versus the temperature during the *in-situ* reduction of the hydrated sample A.

Regarding the Exafs at the Pt L_{III} edge, we found a constant oxygen environment until the appearance of the first Pt-metal bonds where we measured quite long Pt-metal bonds (Fig. 2). Finally, the analysis of the last spectrum gives a Pt environment composed of 6 metal atoms.

Assuming a cuboctahedral morphology for the metal particle, the average diameter of the aggregates generated is approximately 10 Å.

3.2. Rehydrated samples A', 1.0%wt Pt - 0.5%wt Re/ Al_2O_3 .

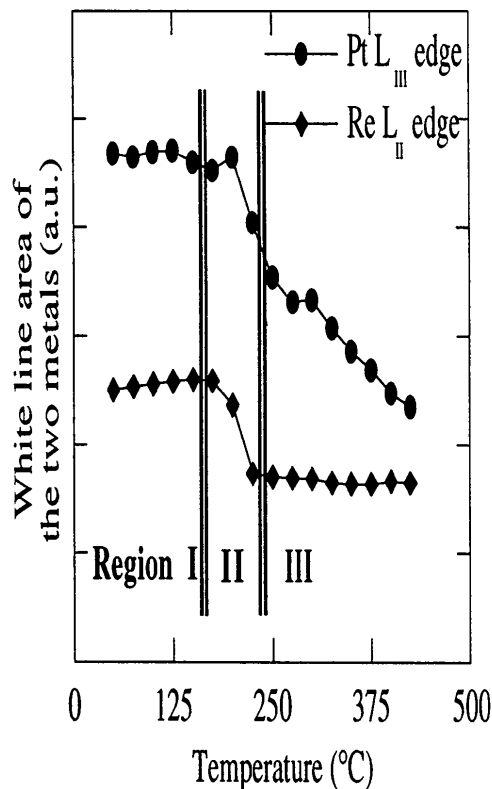


Figure 3
Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the hydrated sample A'.

Three steps can be distinguished (Fig. 3).

- A first regime where the two elements keep unchanged their electronic configuration (region I),
- a second regime, when the reduction of Pt and Re atoms begin at the same time, the white line intensity of both species decreasing rapidly (region II), the end of the process is then different depending on the element ,
- a stabilisation of the Re electronic state and by a change in the rate of the Pt reduction which goes on but at a slower speed (region III).

Some remarks derived from the simple observation of the numerical results relative to sample A (Fig. 4) can be repeated here i.e. the Pt environment is stable until the beginning of the reduction process, the white line intensity of the Pt is closely correlated to the oxygen coordination, the final number of metallic neighbours is approximately 4.

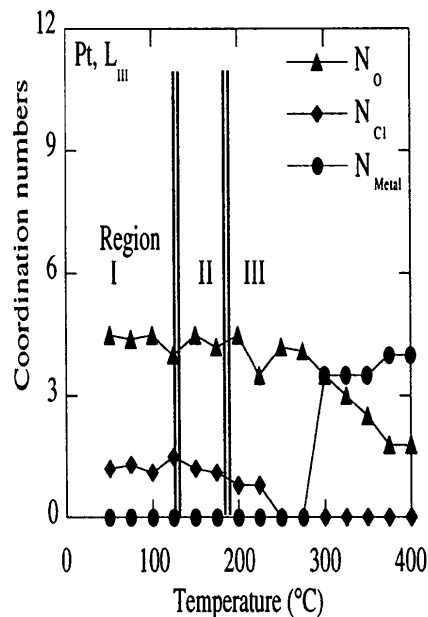


Figure 4
Variation of the different numbers of oxygen, chlorine and metal atoms around platinum atoms versus the temperature during the in-situ reduction of the hydrated sample A'.

3.3. Dehydrated sample B : 1.0%wt Pt- 1.0%wt Re/ Al_2O_3 .

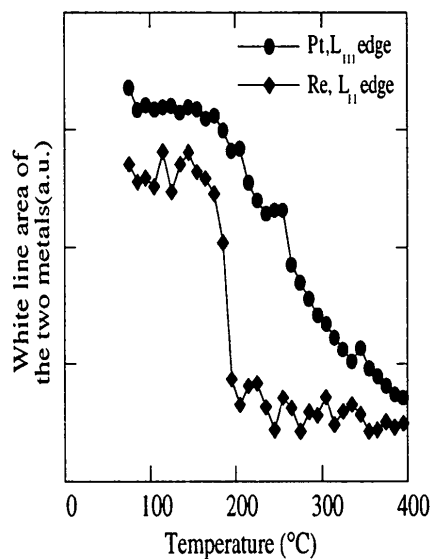


Figure 5
Evolution of the white line intensities of the two metals (platinum and rhenium) during the reduction of the dehydrated sample B.

The situation is drastically different (Fig. 5). The Re reduction is very sudden, the Pt one being relatively smooth. Starting at the same time as Re, Pt evolves slowly towards the electronic configuration of the metal reaching that state one hour later than Re.

The former strong correlation observed between the two metals no longer exists and thus seems linked to the hydrated character of the sample.

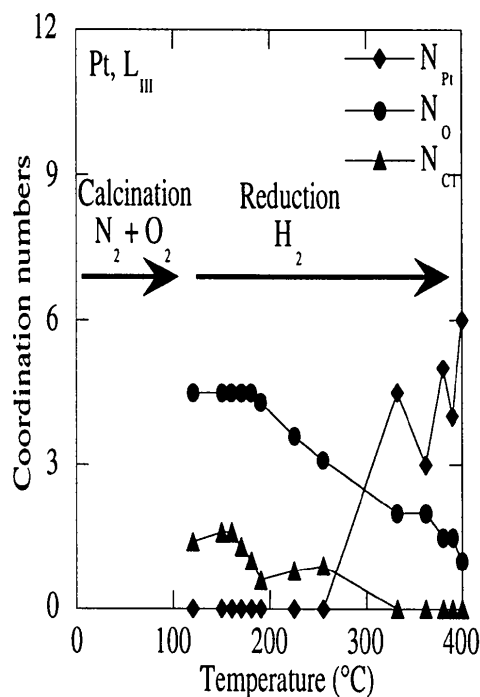


Figure 6
Variation of the different numbers of oxygen, chlorine and metal atoms around platinum atoms versus the temperature during the in-situ reduction of the dehydrated sample B.

For the Pt Exafs oscillations (Fig. 6), once again, the formation of Pt-metal bonds detected by Exafs occurs in a region where the Re electronic state is stable.

4. Discussion

The reduction by H_2 occurred at a rather low temperature in the bimetallic solid (C. BOLIVAR et al. 1987). Pt and Re atoms were reduced to the metallic state, the reduction of the Re compound being strongly catalysed by Pt. This greater reducibility is very sensitive to the presence of water which controls the migration of the Re oxide phase (B. D. McNICOL et al. 1977). For low drying temperatures, below 200°C, the water is not removed and the Re oxide is still hydrated.

Thus, hydrated Re_2O_7 phases are mobile and able to migrate to the Pt reduction centres (N. WAGSTAFF et al. 1979). The reduction of the two oxides is essentially simultaneous and an alloy is formed. In contrast, at the high drying temperature, the Re oxide is no longer able to migrate. In this case, two distinct phases are therefore generated, Pt particles on one side, Re on the other. In fact, the higher the drying temperature, the lower the mobility of Re_2O_7 .

We have found similar results but the fact that we can follow the reduction of the two metals separately allows us to describe the nature of the metallic phase finally generated. In the case of the reduction of the hydrated sample A, the fact that the reduction of the two metals begins and ends simultaneously suggests strongly that the Pt and Re species exchange bonds during the growth of the metal particle.

Thus, we can say that a Pt-Re alloy with an atomic ratio equal to 1 is formed during the chemical treatment. In the reduction of sample A', a correlation and a decorrelation regime are measured.

Considering the results obtained on the sample A, we can assume that the first regime is linked to the building of the Pt/Re alloy, the atomic ratio being equal to the value obtained for the sample A. In region III, the electronic state of Re is not modified while the electronic state of Pt atom changes continuously.

The fact that the electronic state of Pt and Re atoms are decorrelated indicates that the Pt atoms for which the electronic state varies, are not involved in a phase containing Re atoms. It emerges thus from all these considerations that the Re/Pt ratio of the alloy phase is close to one, the decorrelation regime corresponds in fact to an excess of Pt atoms on the support.

From the results obtained on the sample A and A', the reduction (as measured by white line intensity) starts at 200°C with removal of Pt-O bonds as measured by Exafs, not by the formation of Pt-M bonds. Particle formation is abrupt at about 250°C with particle size (coordination number) being immediately established. At this stage Pt-M bond distance is high ($>2.75\text{\AA}$). Reduction continues with a shortening of Pt-M bonds to 2.70\AA at 350°C. This seems to suggest that particle size is determined before the formation of metal-metal bonds and that reduction essentially involves separation of the particles from the support interaction. On the contrary, for the dehydrated samples, the reduction process is controlled by different kinetics depending on the respective nature and composition of the phases present.

5. Conclusion

Electronic state studies of the two metals correlated to a detailed analysis of the Exafs oscillations beyond the Pt edge constitute a powerful tool for the description of the PtRe bimetallic system. The complete set of the results we show in this paper leads to a coherent structural model. Moreover, this approach seems to give the Pt/Re ratio for the metallic atoms which are engaged in the alloy phase.

References

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(Received 10 August 1998; accepted 17 December 1998)