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In situ EXAFS studies of modifications to supported metallic catalysts under reactive atmospheres

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Extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to study the structural evolution of monometallic (Pt/Al_2O_3) and bimetallic ($Pt–Re/Al_2O_3$) catalysts with metal loadings representative of those used industrially under conditions close to those seen during preparation (calcination and reduction), during catalysis (under a hydrogen–hydrocarbon mixture), and during regeneration (simulated by cycles of reduction and oxidation). During the catalytic reforming of *n*-heptane, the formation of bonds to carbon species is observed directly by EXAFS. Despite the fact that only platinum–carbon bonds are observed, bimetallic systems show significant differences compared with monometallic systems with, in the case of Pt–Re, a reduction in the temperature range over which carbon bonding is observed, and structural modifications of the metallic particles. Under the same conditions, no carbon bonding is observed for the Pt–Sn system. In the case of $Pt–Sn/Al_2O_3$, the EXAFS results, confirmed by transmission electron microscopy, demonstrate the high resistance to sintering of this bimetallic system compared to the monometallic system.

Keywords: EXAFS; Pt; Pt–Re; Pt–Sn; in situ; deactivation; coking; sintering

1. Introduction

Bimetallic platinum based catalysts are of increasing importance in the petroleum industry, the addition of a second metal conferring useful improvements in the stability of the catalysts against deactivation by coke deposition or by sintering. The mechanisms by which these improvements are achieved are not yet fully understood, partly because of a lack of information on the structural modifications induced. Indeed, very few structural characterisation techniques can be applied to these systems due to the low loadings and the high dispersions (small particle sizes) of the metals. Synchrotron based extended X-ray absorption fine structure (EXAFS) spectroscopy allows an in situ characterisation of the local structure of highly disordered solids and is thus able to provide useful clues as to the nature of these systems and their response to reactive environments.

Deactivation of reforming catalysts is caused principally by the build-up of coke deposits. Recently [1] the use of an X-ray transparent reaction cell has allowed the detection of platinum to carbon bonds in monometallic Pt/Al_2O_3 catalysts during a test reaction, thus suggesting that EXAFS may be used to investigate the details of the chemical bonding occurring during this type of deactivation.

Poisoned catalysts are regenerated by burning off the deposited coke using high temperature oxidation followed by reactivation of the catalyst under hydrogen. Industrial catalysts are regenerated several times during their life cycle. Sintering may take place during this treatment, reducing the activity of the catalyst and thus necessitating expensive redispersion of the metals.

The aim of the present study is to extend the study of metal–carbon bonding to bimetallic Pt–Re and Pt–Sn systems used in the reforming industry. As in the previous study on monometallic catalysts, *n*-heptane reforming has been taken as a test reaction. In addition, the stability against sintering of a Pt–Sn system has been compared to that of similar monometallic platinum catalysts by simulating the regeneration process. The catalysts were subjected to successive cycles of oxidation and reduction and characterised by EXAFS and conventional transmission electron microscopy (CTEM) at various stages in order to observe the effects of regeneration.

2. Experimental

Chlorinated mono- and bimetallic catalysts (Pt/Al_2O_3-Cl, Pt–Re/Al_2O_3-Cl and Pt–Sn/Al_2O_3-Cl) were prepared by impregnation of a high surface γ-alumina (200 m^2/g) from the following precursors: hexachloroplatinic acid (H_2PtCl_6) for platinum, ammonium perrhenate (NH_4ReO_4) for rhenium and tin dichloride ($SnCl_2$) for tin. After drying at 393 K, the catalysts were calcinated in air at 773 K. The metal loadings were 1 wt% Pt for the monometallic catalyst, 1 wt% Pt, 1 wt% Re and 1 wt% Pt, 1 wt% Sn for the bimetallics. Chlorine content was 1.2 wt% for all chlorinated catalysts.

Chloride free catalysts (Pt/Al_2O_3-K and Pt–Sn/Al_2O_3-K) were prepared by methods known in the literature [2,3] using organometallic complexes as metallic precursors. The alumina support was a high-area (200 m^2/g) γ-alumina. This support was previously neutralised with potassium carbonate and calcined at 803 K before use. The metal loading of this catalyst was: 0.79 wt% Pt, 0.5 wt% Sn and 0.94 wt% K.

EXAFS spectra were collected at the LURE synchrotron facility in Orsay, using synchrotron radiation from the DCI storage ring running at 1.85 GeV with an average current of 250 mA. Experiments were carried out at the Pt L_{III} edge using a double crystal monochromator (Si 111), in the transmission mode, with two ion chambers as detector. Spectra were collected in situ during the reduction of catalysts in H_2 at 773 K and under *n*-heptane reforming conditions ($H_2/n\text{-}C_7 = 0.9$) at high temperature (733 or 573 K) and pressure (0.3 MPa) for the chlorinated catalysts or, for the chloride free catalysts, at room temperature after several oxidation (under air flow) and reduction (hydrogen flow) cycles performed at 773 K.

Fourier transforms of the k^3 weighted EXAFS functions were obtained using a Hanning type window, and the first shell peak was backtransformed and fitted using the classical relationship described elsewhere [4]. The EXAFS phase shifts and amplitude functions were extracted from the appropriate experimental references. Since platinum and rhenium are very close in the periodic table, their backscattering amplitude and phase shift functions are similar, and it is not possible to distinguish between them. For this reason, we will allude to the metallic nearest neighbours of platinum in the Pt–Re/Al_2O_3-Cl catalysts as Pt–Me (Me = Pt and/or Re).

CTEM was performed using a Jeol 120 CX microscope operating at 100 kV. The catalyst samples were previously reduced at 773 K and passivated in flowing air at room temperature before analysis. Only particles with diameter greater than 7 Å are detected by this technique.

3. Results and discussion

3.1. CHARACTERISATION BY IN SITU EXAFS SPECTROSCOPY OF MONO- AND BIMETALLIC CATALYSTS UNDER REFORMING REACTION CONDITIONS

In all cases, the EXAFS spectra for the reduced sample and the "working" catalysts have been measured at high temperature (573 and 733 K). Fig. 1 shows a typi-

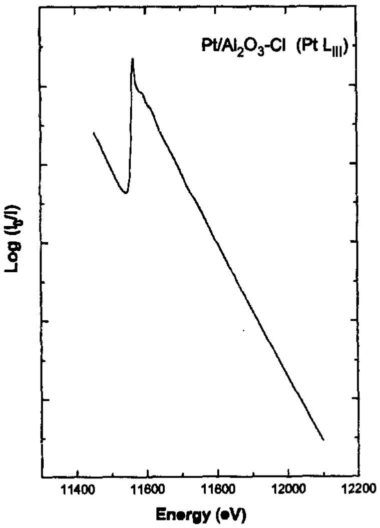

Fig. 1. X-ray adsorption spectrum at 773 K in the region of the L_{III} edge of platinum for a reduced Pt/Al_2O_3-Cl sample.

cal X-ray adsorption spectrum obtained at 733 K in the L_{III} edge region of platinum, showing the feasibility of the experimental set-up used in this work.

The normalised EXAFS functions obtained from the reduced Pt/Al_2O_3-Cl or Pt–Re/Al_2O_3-Cl at the L_{III} edge of platinum are presented in fig. 2. These plots show an acceptable signal to noise ratio over the range of energies 50–500 eV, used to study the first coordination shell of platinum. The Fourier transforms of the EXAFS functions over the above-mentioned range of energies are represented in fig. 3. The functions obtained by inverting the transforms over the range of 1–3 Å were submitted to mathematical fitting and the results are presented in table 1.

The calcined samples present environments of oxygen and chlorine around the platinum as described before by Bazin et al. [4] for this kind of system.

After reduction of the Pt/Al_2O_3-Cl at 733 K in flowing hydrogen, the platinum is practically fully reduced, the oxygen coordination being at trace level. Similarly, for the reduced bimetallic catalyst Pt–Re/Al_2O_3-Cl, EXAFS shows only metal neighbours (Pt or Re) around the platinum atoms, with a coordination number (CN) slightly lower than the CN found for the monometallic catalyst. For both catalysts, the CN determined by EXAFS is consistent with a particle size lower than 10 Å, in accordance with CTEM analyses of these samples.

The normalised EXAFS functions obtained at the Pt L_{III} edge for the Pt/Al_2O_3-Cl or Pt–Re/Al_2O_3-Cl catalysts under reactive atmosphere (H_2, n-C_7) at high temperature (733 or 573 K) and under 0.3 MPa of pressure are presented in fig. 4 and the Fourier transforms over the energy range 50–400 eV are shown in fig. 5.

As can be observed from fig. 5, the treatment of the Pt/Al_2O_3-Cl catalyst with H_2/n-heptane at 733 K produces the formation of a new peak, which can be ascribed, in agreement with previous results [1], to Pt–C bonds (CN = 1.2 at 1.94

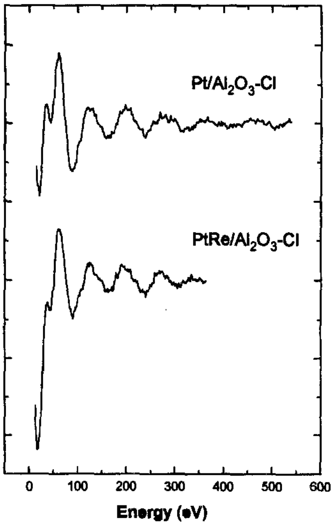

Fig. 2. Normalised EXAFS data (Pt L_{III} edge) for the Pt/Al_2O_3-Cl and Pt– Re/Al_2O_3-Cl catalysts collected during reduction in flowing hydrogen at 773 K.

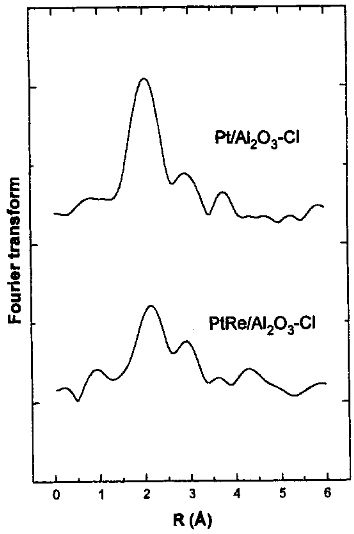

Fig. 3. Fourier tranforms of the data shown in fig. 2.

Å). This result shows that hydrocarbon species are linked to the metallic phase of the monometallic catalyst. The fact that the formation of this Pt–C bond occurs without remarkable changes of the structural parameters for the Pt/Al$_2$O$_3$-Cl catalyst may be accounted for by the fixation of these hydrocarbon species at the surface of the metallic particles.

Table 1
Structural parameters for Pt/Al$_2$O$_3$-Cl and Pt–Re/Al$_2$O$_3$-Cl at the Pt L_{III} edge [a]

Treatment	Nearest neighbours	Pt/Al$_2$O$_3$-Cl			Pt–Re/Al$_2$O$_3$-Cl		
		CN	*R*	DW	CN	*R*	DW
original	O	6.1	2.01	0.01	5.7	2.01	0.01
	Cl	0.8	2.32	0.01	0.4	2.32	0.01
H_2 733 K	O	0.5	2.00	0.09	0.2	1.98	0.09
	Me	5.0	2.65	0.02	3.6	2.66	0.04
H_2/*n*-C_7 773 K	C	1.2	1.94	0.08	0.0	–	–
	Me	4.4	2.67	0.04	3.6	2.68	0.03
H_2-C_7 533 K	C	ud	ud	ud	2.0	2.09	0.01
	Me	ud	ud	ud	5.5	2.72	0.02

[a] Me = Pt or Re; CN = coordination number ± 15%, DW = Debye–Waller factors (Å) ± 20%, *R* = interatomic distance (Å) ± 0.02; ud = undetermined.

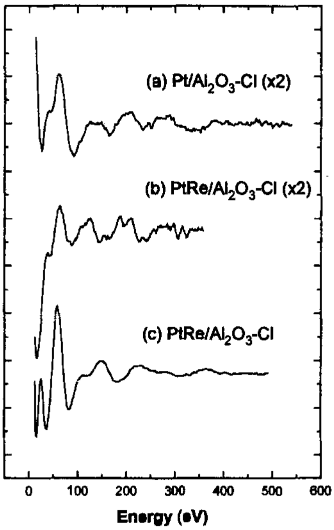

Fig. 4. Normalised EXAFS data (Pt L_{III} edge) for the Pt/Al_2O_3-Cl and Pt– Re/Al_2O_3-Cl catalysts. Data were collected during *n*-heptane reforming, at 773 K for Pt/Al_2O_3-Cl (a) and at 773 K (b) or 573 K (c) for the Pt–Re/Al_2O_3-Cl.

During *n*-heptane reforming at 773 K over Pt–Re/Al_2O_3-Cl, no modification of structural parameters of platinum can be detected by EXAFS. Indeed, as shown in fig. 5, the Fourier transform obtained after this treatment does not display the peak at low distance assigned previously to platinum carbon bonds (table 1). If one assumes that the carbonaceous species corresponding to this particular Pt–C bond are responsible for the coke deposition on the metallic surface, these results

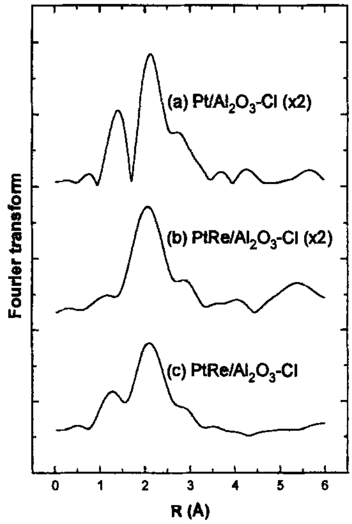

Fig. 5. Fourier transforms of the data shown in fig. 4.

may explain why the bimetallic catalyst is more resistant to the coke deposition than the monometallic sample. Note that the results obtained by mathematical fitting presented in table 1, show that platinum does not change its atomic environment during this treatment.

In contrast to the results obtained at 733 K, the state of the metallic particles is strongly modified during the *n*-heptane reforming at 573 K. As it can be seen in fig. 5, the Fourier transform corresponding to this treatment gives clear evidence for the formation of the peak at low distance, previously detected in the monometallic catalyst. Both the Pt–C distance and coordination number are different from those obtained for monometallic catalysts (Pt–C interatomic distances of 2.09 Å instead of 1.94 Å). The natures of the carbonaceous species deposited over both catalysts are probably different. Contact of the bimetallic catalyst with the reactive atmosphere at 573 K is also accompanied by an increase in the Pt–Me coordination number, reaching a value similar to that obtained previously for the monometallic catalyst.

For Pt–Sn/Al_2O_3-Cl catalysts we have detected no metal to carbon bonds for the working catalysts even when the reforming reaction is performed at low temperature (573 K).

3.2. STUDY BY EXAFS AND CTEM OF THE EFFECT OF REDUCTION–OXIDATION CYCLES OVER Pt/Al_2O_3-K AND PtSn/Al_2O_3-K CATALYSTS

The normalised EXAFS function obtained at the Pt L_{III} edge for Pt/Al_2O_3-K catalyst after calcination (0 cycle) and after two and four reduction–oxidation cycles are presented fig. 6. The Fourier transforms are presented fig. 7. For the Pt–

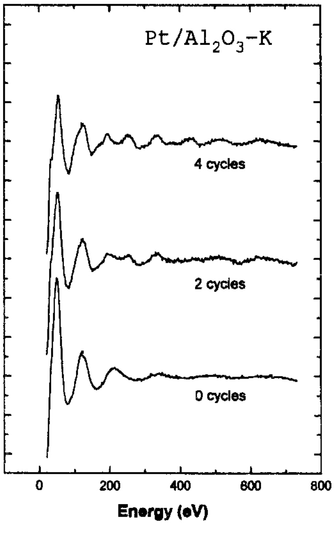

Fig. 6. Normalised EXAFS data (Pt L_{III}) of Pt/Al_2O_3-K after different oxidation–reduction cycles.

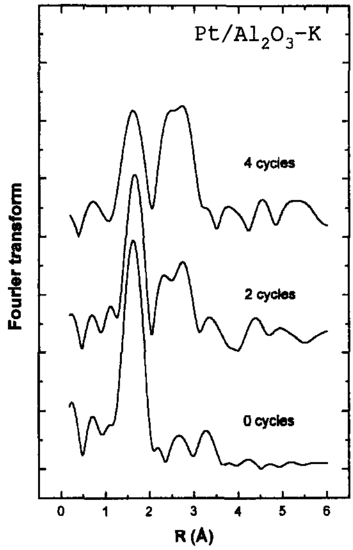

Fig. 7. Fourier transforms corresponding to the data shown in fig. 6.

Sn/Al$_2$O$_3$-K, the normalised EXAFS function at the Pt L$_{III}$ edge and the corresponding Fourier transforms after calcination and after two and four reduction–oxidation cycles are given in figs. 8 and 9.

Representative micrographs of mono- and bimetallic catalysts after calcination and after six reduction–oxidation cycles are shown in figs. 10 and 11. The average

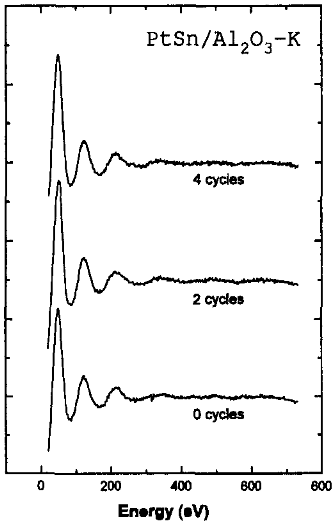

Fig. 8. Normalised EXAFS data (Pt L$_{III}$) of Pt–Sn/Al$_2$O$_3$-K after different oxidation–reduction cycles.

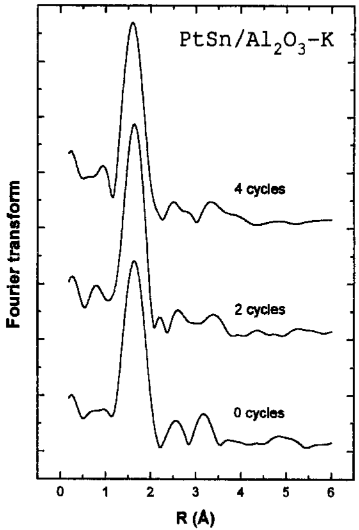

Fig. 9. Fourier transforms corresponding to the data shown in fig. 8.

particle sizes of the different catalysts after different treatments are reported in table 2.

After calcination (0 cycle), both catalysts present an oxidised phase of platinum, with a Pt–O coordination number of 6 at an interatomic distance of 2.01 Å (table 3). The Fourier transforms do not present the peaks corresponding to the higher coordination shells of platinum oxide. This shows that this phase is very well dispersed on the alumina support. This point is confirmed by the CTEM analyses of these samples which reveal only few metallic particles with an average diameter close to 10 Å. The fact that very few metallic particles are observed on these samples indicates that a part of the metal is highly dispersed on the support ($d < 7$ Å).

In contrast to the results obtained after the initial calcination step, the behaviours of the two catalysts after the successive reduction–oxidation cycles are very different. Thus, as can be seen from fig. 7, the Fourier transforms obtained for the Pt/Al$_2$O$_3$-K monometallic catalyst show a progressive decrease of the peak situated at 1.6 Å accompanied by an increase in the intensity of several overlapping peaks located between 2 and 3 Å. As shown in table 3, these changes are produced by, firstly, the gradual increase in the coordination number of the second shell of platinum oxide (Pt neighbours at 3.10 Å) and, secondly by the successively higher quantity of metallic platinum (Pt neighbours at 2.77 Å) detected after two or four reduction–oxidation cycles (see table 3). The fact that a proportion of reduced platinum is found after treatment under oxidising conditions is not surprising because it is known that supported platinum oxide particles decompose to platinum metal and oxygen in flowing air at 873 K [5] and that, for large supported particles, it is difficult to reoxidises all the platinum after reduction.

These results show very clearly that platinum in the Pt/Al$_2$O$_3$-K catalyst is pro-

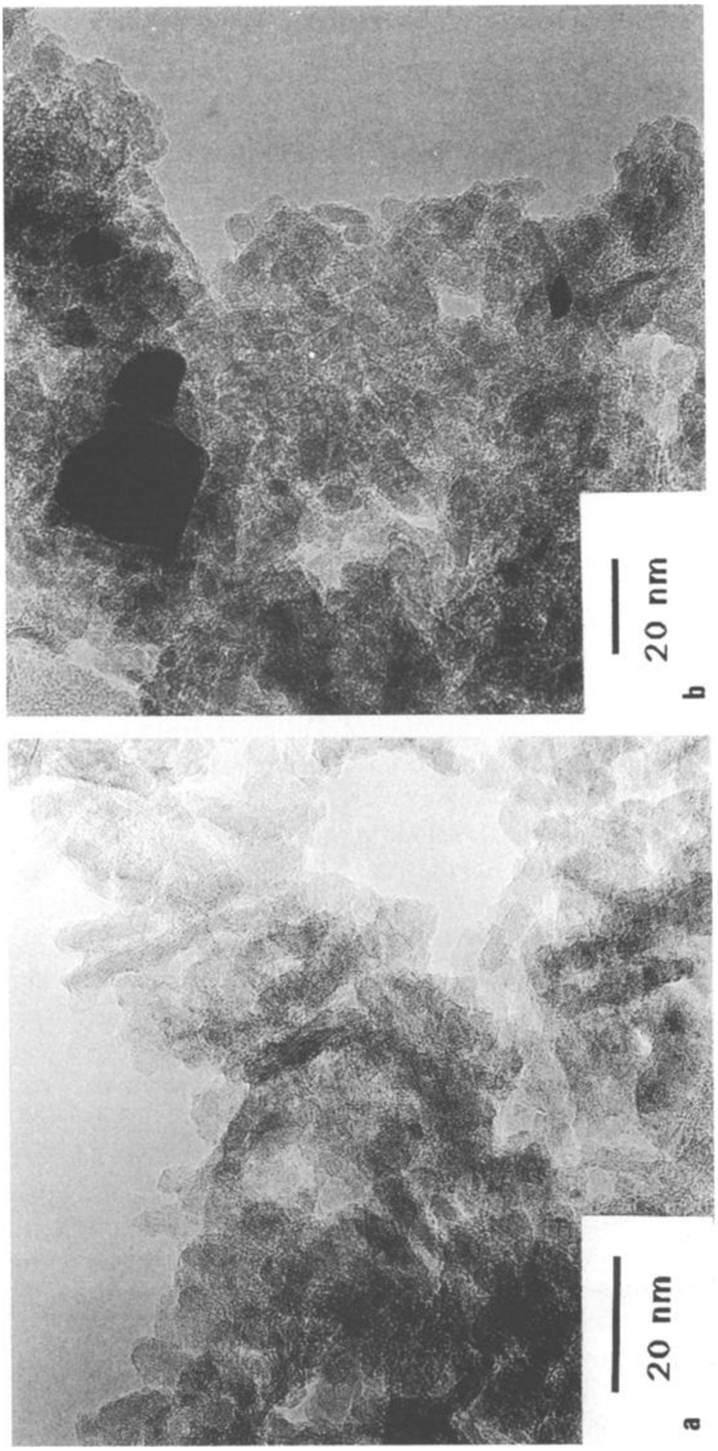

Fig. 10. Micrographs of monometallic Pt/Al_2O_3-K catalyst after 0 (a) and 6 (b) reduction–oxidation cycles.

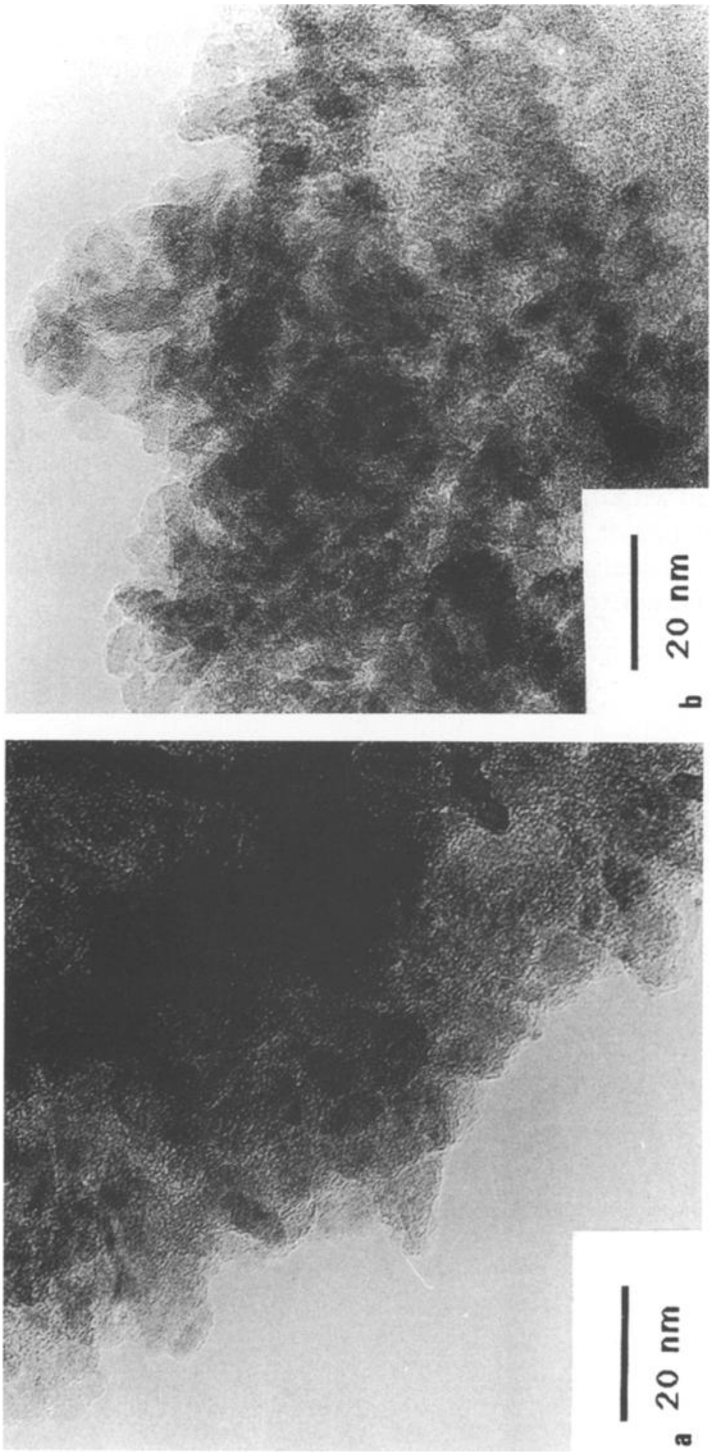

Fig. 11. Micrographs of bimetallic Pt–Sn/Al_2O_3-K catalyst after 0 (a) and 6 (b) reduction–oxidation cycles.

Table 2
Particle diameters (Å) of the Pt/Al_2O_3-K and Pt–Sn/Al_2O_3-K catalysts after different oxidation–reduction cycles

Treatment	Pt/Al_2O_3-K			Pt–Sn/Al_2O_3-K		
	min.	max.	aver.	min.	max.	aver.
original	7	16	10	7	23	15
3 cycles	40	220	110	7	23	15
6 cycles	40	470	140	7	23	12

gressively sintered after successive reduction–oxidation cycles. This is also confirmed by CTEM analyses (figs. 10 and 11 and table 2), which show a wide particle size distribution between 40–470 Å after six reduction–oxidation cycles.

In contrast to results obtained with the monometallic catalyst, the platinum environment in the Pt–Sn/Al_2O_3-K bimetallic catalyst does not change during the different reduction–oxidation cycles. As can be seen in fig. 9 the Fourier transforms obtained with this catalyst show that platinum keeps the same atomic environment after two or four cycles, with six oxygen atoms at 2.01 Å (table 3). In addition, CTEM analyses show that the particles have the same size throughout the reduction–oxidation treatment.

4. Conclusions

EXAFS spectroscopy as a means of providing detailed information on the local structure of catalysts has enabled us to follow modifications to the environment of platinum in bimetallic systems subjected to treatments under reactive atmospheres. The in situ capability of EXAFS allows detection of metal to carbon bond-

Table 3
Structural parameters at Pt L_{III} edge of Pt/Al_2O_3-K and Pt–Sn/Al_2O_3-K catalysts after different oxidation–reduction cycles

Treatment	Nearest neighbours	Pt/Al_2O_3-K		Pt–Sn/Al_2O_3-K	
		CN	*R*	CN	*R*
original	O	6.0	2.01	6.0	2.01
2 cycles	O	4.0	2.00	6.0	2.01
	Pt	3.0	2.77	–	–
	Pt	1.0	3.10	–	–
4 cycles	O	3.00	2.00	6.0	2.01
	Pt	4.8	2.77	–	–
	Pt	0.5	3.10	–	–

ing during the catalytic reaction itself. Of particular significance is that, for the systems and conditions studied here, only platinum seems to bond directly to carbon.

The results demonstrate clearly that the presence of rhenium and tin on the catalysts inhibit the formation of a particular adsorbed carbonaceous species. If we assume that these particular species are responsible for the coke deposition on the metallic phase, these results illustrate the well known higher stability of bimetallic compared with monometallic catalysts. Differences in the temperature range over which platinum to carbon bonds are detected, as well as quantitative differences in bond numbers and lengths, may provide clues to explain this improvement, although further work is necessary to clarify this point.

In the case of the Pt–Sn/Al_2O_3-K catalysts the presence of tin favours the resistance of platinum to sintering during the reduction–oxidation cycles. It is known that a similar effect of increasing the resistance of platinum to sintering is induced by the presence of chlorine in Pt/Al_2O_3-Cl catalysts [5]. This particular property of chlorine could be due to the formation of oxychloride species of platinum, which are better anchored to the alumina surface than the platinum particles. Thus, although tin is not incorporated in the platinum environment at the oxidised state, we can suggest that there is a particular interaction between tin and platinum in the Pt–Sn/Al_2O_3-K catalysts which improves the interaction of platinum with the support. Here again, the compatibility of EXAFS with in situ studies suggests a wide range of possibilities for future investigations of these solids under reactive atmospheres.

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