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Sintering of Pt/Al_2O_3 reforming catalysts: EXAFS study of the behavior of metal particles under oxidizing atmosphere

A. Borgna [1], F. Le Normand [2], T. Garetto [1], C.R. Apesteguia [1]
and B. Moraweck [3],*

[1] *INCAPE, CONICET, Santiago del Estero 2654, (3000) Sante Fe, Argentina*
[2] *IPCMS, Institut Le Bel, Université Louis Pasteur, 4 Rue Blaise Pascal, F-67070 Strasbourg Cedex, France*
[3] *CNRS, Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, F-69626 Villeurbanne Cedex, France*

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The effect of an oxidative atmosphere (300°C) is studied on fresh and sintered unchlorinated naphtha reforming catalysts containing 0.6–1% Pt. The TPR profiles show that only one species is formed using our experimental conditions, regardless of the mean crystallite size of the metal particles. The structural information supplied by EXAFS compared with cuboctahedral particle modeling, implies that such species is a surface platinum oxide, the structure of which is close to that of PtO_2, but largely distorted. This is true whether the catalyst is sintered or not.

Keywords: EXAFS; Pt/Al_2O_3; reforming catalyst; sintering; platinum oxide; TPR; chemisorption measurements

1. Introduction

Sintering is one of the main causes of deactivation of naphtha reforming catalysts. It mainly occurs during catalyst regeneration performed under oxidizing mixtures after each operative cycle [1,2]. In spite of the extensive literature regarding sintering of Pt supported catalysts, few investigations were carried out under industrial conditions. Several physical models were developed in the past in order to correlate the operational parameters with the sintering of metal catalysts [3–7]. Additional studies indicated that sintering depends on the

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* To whom correspondence should be addressed.

chemical nature of surface intermediate species, which in fact determines the mechanism and the kinetics of sintering [8,9].

In a previous paper [10], we studied the sintering of Pt/Al_2O_3 catalysts under different atmospheres. In an inert or reductive atmosphere, sintering occurs by migration of atoms and crystallites of platinum in metallic state, whereas under oxidizing mixtures a decomposition-nucleation-migration mechanism would take place. The aim of this work is to identify by X-ray absorption spectroscopy (EXAFS) the chemical nature of the species which are formed during the sintering of unchlorinated Pt/Al_2O_3 catalysts under oxidative conditions.

2. Experimental procedures

CATALYST PREPARATION

Two catalysts of 0.58% Pt (catalyst A) and 0.98% Pt (catalyst B) were prepared as described previously [10]. A high purity γ-Al_2O_3 powder (Cyanamid Ketjen CK-300) was impregnated with an aqueous solution containing H_2PtCl_6 and HCl. After impregnation, the samples were dried 12 h at 120°C and then calcined under air at 500°C. Chlorine was eliminated by using a solution of NH_4OH (1N) at 50°C. Finally, the catalysts were washed with distilled water and dried at 120°C. The main characteristics of the catalysts employed in this work are given in table 1. Catalyst B_s was catalyst B sintered at 600°C in air for 2 hours.

CHEMISORPTION MEASUREMENTS

The accessible metal fractions were determined from hydrogen chemisorption by using the strongly chemisorbed hydrogen $(HC)_i$ calculated from the double isotherm method [12]. A stoichiometric ratio of $(HC)_i/Pt_s = 1$, where Pt_s implies surface Pt atoms, was used. The volumetric adsorption experiments were performed in a conventional glass vacuum apparatus in which a final dynamic vacuum of 10^{-5} Torr was attainable. The pressure range of isotherms was 0–50 Torr and the extrapolation to zero pressure was used as a measurement of the gas uptake by the metal.

Table 1
Main characteristics of the catalysts used in this work

Catalyst	% Pt	% Cl	D_0 (%)	S_g (m^2/g)
A	0.58	0	65	175
B	0.98	0	62	170
B_s	0.98	0	32	170

D: metal dispersion; S_g: BET surface area.

TPR MEASUREMENTS

The thermoprogrammed reduction (TPR) experiments were performed as described in [11] by using 5% hydrogen in argon. Samples were heated with a linear temperature-programmer at 6°C min^{-1} within the temperature range of 25–600°C. Gases were carefully purified to remove water and oxygen traces. The water formed during reduction of the samples was eliminated by passing the gases through a cold trap before entering the thermal conductivity cell.

EXAFS SPECTROSCOPY

EXAFS experiments were carried out by using the synchrotron radiation emitted by the DCl storage ring at LURE. All the measurements were performed on the D42 station in transmission mode by using a Si(111) channel-cut monochromator and two ion chambers filled with pure argon at atmospheric pressure. Raw data were recorded by using a special "in-situ" cell equipped with beryllium windows, which allows working from liquid nitrogen temperature to 600°C in either flowing gas (H_2, O_2 or air) or vacuum. The energy range was about 1000 eV above the Pt-L_{III} edge (11564 eV) and the counting time was 1 to 3s in step-by-step mode (2 eV) depending upon the sample. Several spectra (3 to 6) were recorded for summation before the complete analysis. The EXAFS signal was extracted from raw data by a conventional procedure [13]. A linear background was determined from the lower energy part of the spectrum below the edge and then extrapolated to higher energies. The atomic-like absorption coefficient calculated by a polynomial fit was used as spectrum normalization. The k^3 weighted EXAFS function was Fourier transformed over a 3–15 Å^{-1} Hanning window. Then, a Fourier filtering was done to produce the Pt EXAFS functions which were modeled by using an optimization program which computes coordination numbers (n), bond lengths (R) and variations of the Debye-Waller like factors ($\Delta\sigma^2$). In this process we used experimental backscattering amplitudes and phase-shifts obtained from reference materials. Standard functions were obtained from the spectrum of a 4 μm platinum foil for the Pt-Pt bond (12 nearest neighbors at 2.772 Å) and from that of platinum dioxide purchased from Johnson Matthey for the Pt-O bond (6 neighbors at a mean value of 1.998 Å [14]). Finally, a reliability factor, Q, is obtained which allows the comparison of various fits [15,16].

3. Results and discussion

TPR MEASUREMENTS

Prior to TPR measurements, all the samples were reduced in hydrogen at 300°C during 1 h and then oxidized with oxygen for 1 h at the same temperature. Fig. 1 shows the TPR profiles obtained after sintering of sample A in flowing O_2/N_2 (2% O_2) at increasing temperatures. It is clear that reduction occurs in a

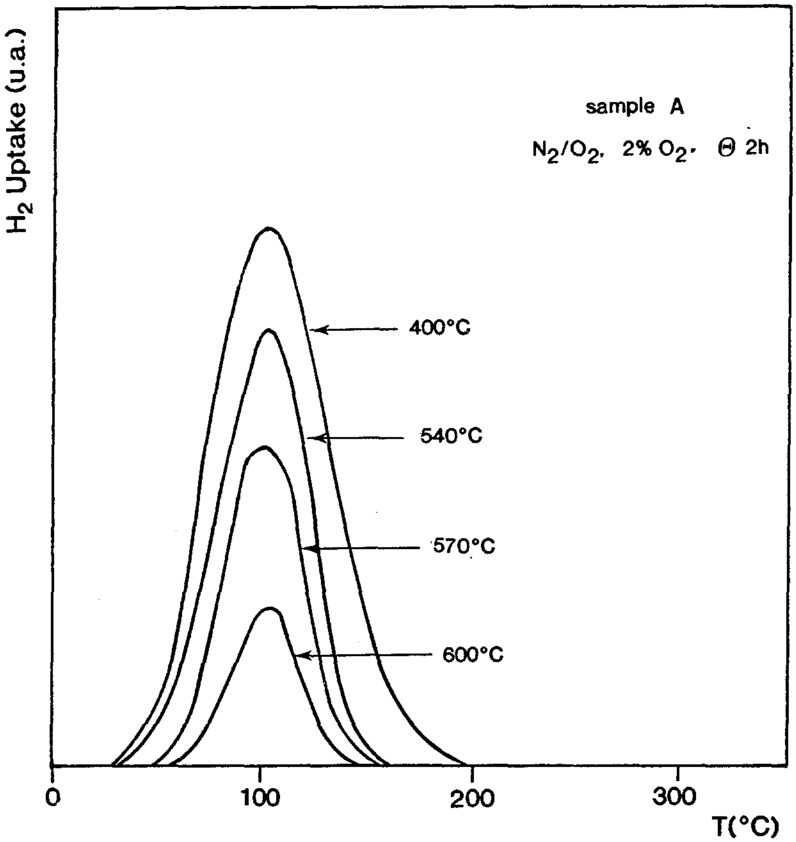


Fig. 1. TPR profiles for sample A at increasing temperatures.

single step, suggesting that only one species is involved. The maxima in the TPR profiles are centered at 95–105°C. This range of temperatures corresponds to the maximum in the TPR trace of amorphous PtO_2 taken as a reference [21]. Fig. 1 also shows that the hydrogen uptake decreased when the catalyst was sintered at higher temperatures increasing the mean particle size. This fact suggests that the formation of oxidized species involves only the surface layers of the metal particles. A quantitative analysis of TPR profiles is presented in table

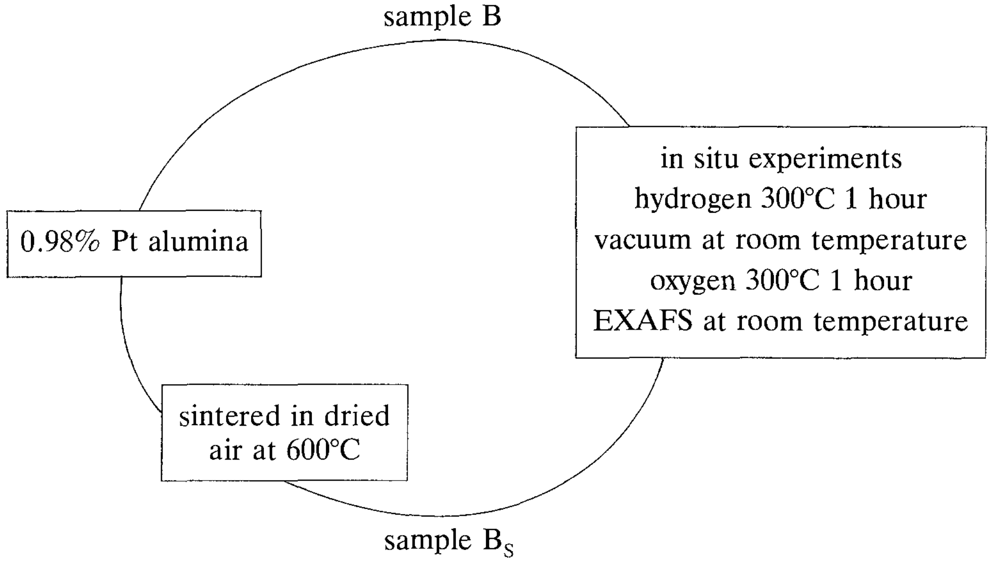
Table 2
Quantitative TPR analysis for sample A: sintering temperature (T_s), relative dispersion (D_r) after sintering, hydrogen uptake (H μmol/g), hydrogen uptake per surface atom (H/Pt_s)

T_s (°C)	D_r	H	H/Pt_s
400	1.00	35	3.6
540	0.85	32	3.9
570	0.65	26	4.1
600	0.33	12	3.8

2. Approximately four hydrogen atoms were consumed per surface platinum atom regardless of the mean particle size. This value corresponds to the reduction of two oxygen atoms per surface Pt atom. We checked that increasing the metal loading up to 1% does not affect the main feature of TPR profiles for a non sintered catalyst.

EXAFS SHORT-RANGE ORDER

In order to obtain more insight on the chemical nature of the surface species formed under oxidizing atmosphere, EXAFS in situ experiments were performed on the catalyst containing 0.98% Pt (samples B and B_s). The samples were submitted to the following treatment:



The particle diameters of catalysts B and B_s were estimated from chemisorption data by assuming that particles are spheres with an average distribution of metal low index planes at the surface [17]. The mean particle diameters were approximately 15 Å and 35 Å for samples B and B_s, respectively. EXAFS spectra were collected at room temperature. Figs. 2a-2b show the raw EXAFS data for the Pt foil and PtO_2 used as references. For samples B and B_s, the raw EXAFS data are shown in figs. 2c-2d.

The Fourier transform modules (*FT*) calculated from the complete EXAFS spectra are presented in figs. 3a-3d. From the inspection of the *FT*'s, it is clear that two kinds of coordinated atoms exist around platinum. The peak at 1.62 Å can be attributed to a Pt-O coordination, whereas the 2.30 Å peak corresponds to a Pt-Pt metal coordination. It is significant to note that for the unsintered sample a small Pt-Pt metal coordination was detected. An inverse *FT* was then applied to obtain the EXAFS contribution due to both Pt-O and Pt-Pt coordination.

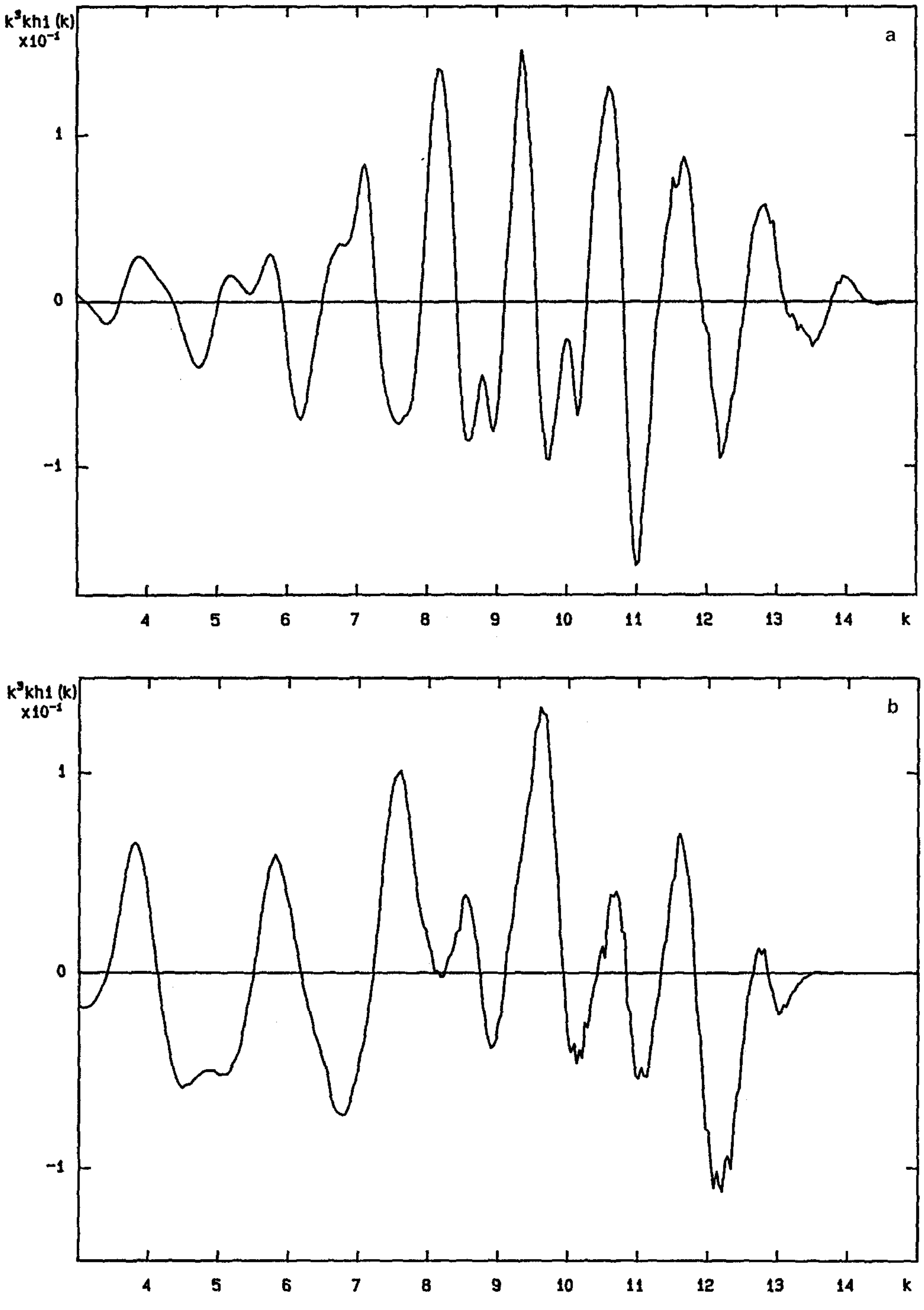


Fig. 2. EXAFS raw data after background substraction and normalisation to the atom like absorption coefficient: a-platinum 4μ foil; b-platinum oxide; c-sample B; d-sample B_s.

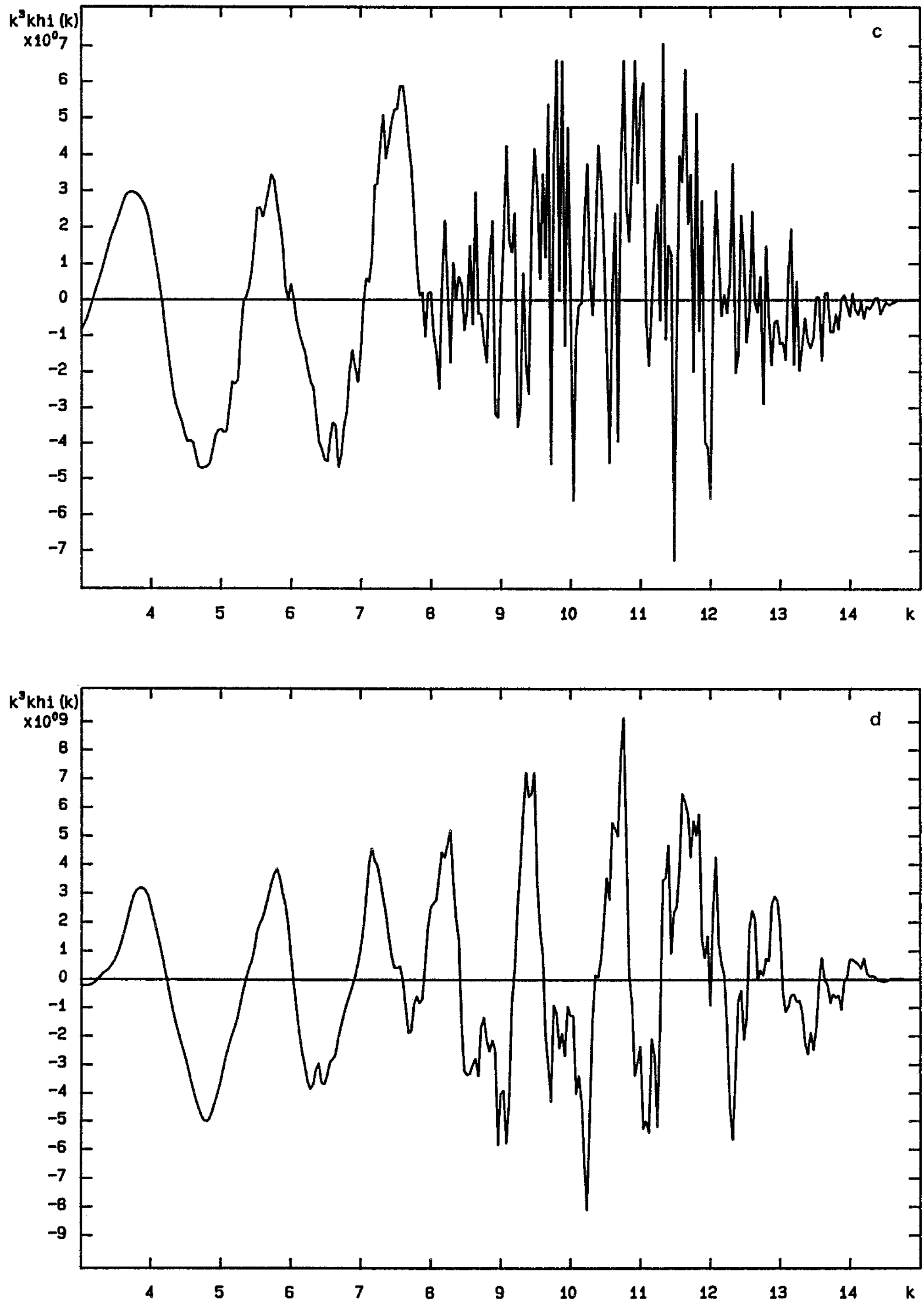


Fig. 2. (continued).

For sample B, a good fit between experimental and calculated EXAFS curves was observed (fig. 4). The EXAFS parameters are summarized in table 3. The average metal coordination is very low, thereby indicating that small metal particles exist in the oxidized catalyst. Besides, the mean interatomic distance (2.64 Å) is significantly lower than in bulk metal (2.772 Å). Such a distance contraction has been recently reported by Guyot-Sionnest et al. [18] for similar Pt/Al_2O_3 catalysts and has been already discussed by several authors [13,19,20].

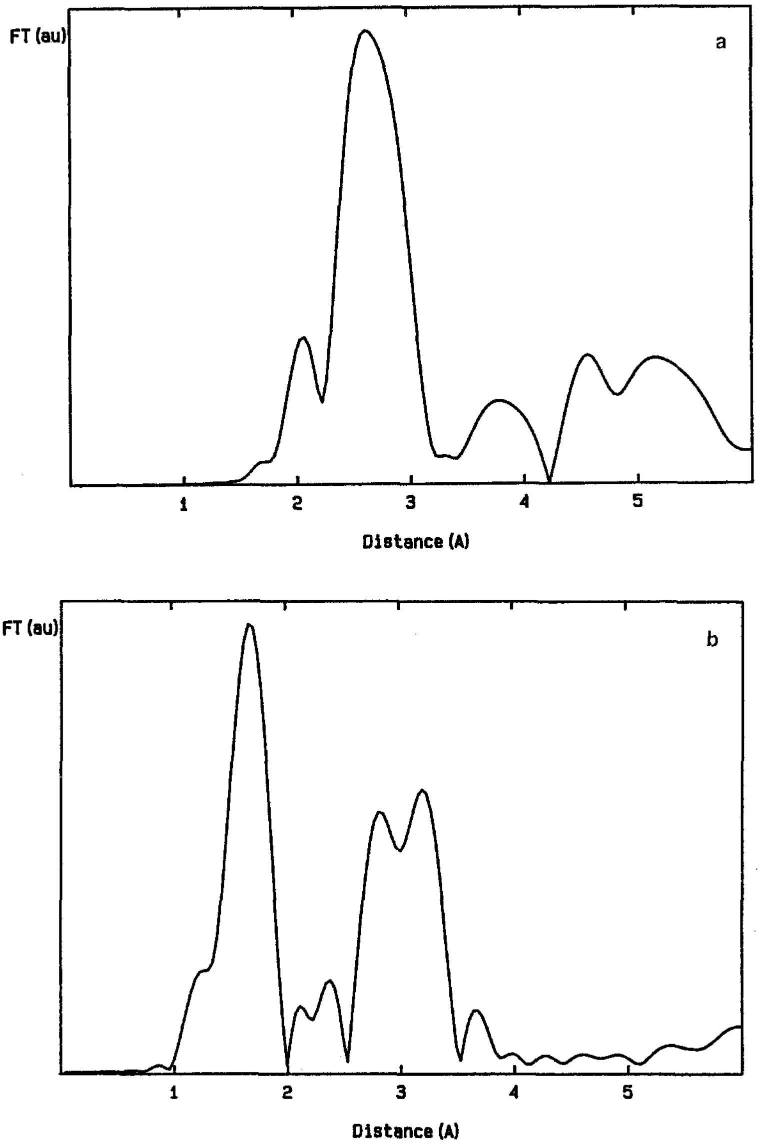


Fig. 3. Radial distribution functions obtained by Fourier transforming the data shown in fig. 2. The vertical bars mark the selected range in R to compute the inverse Fourier transform.

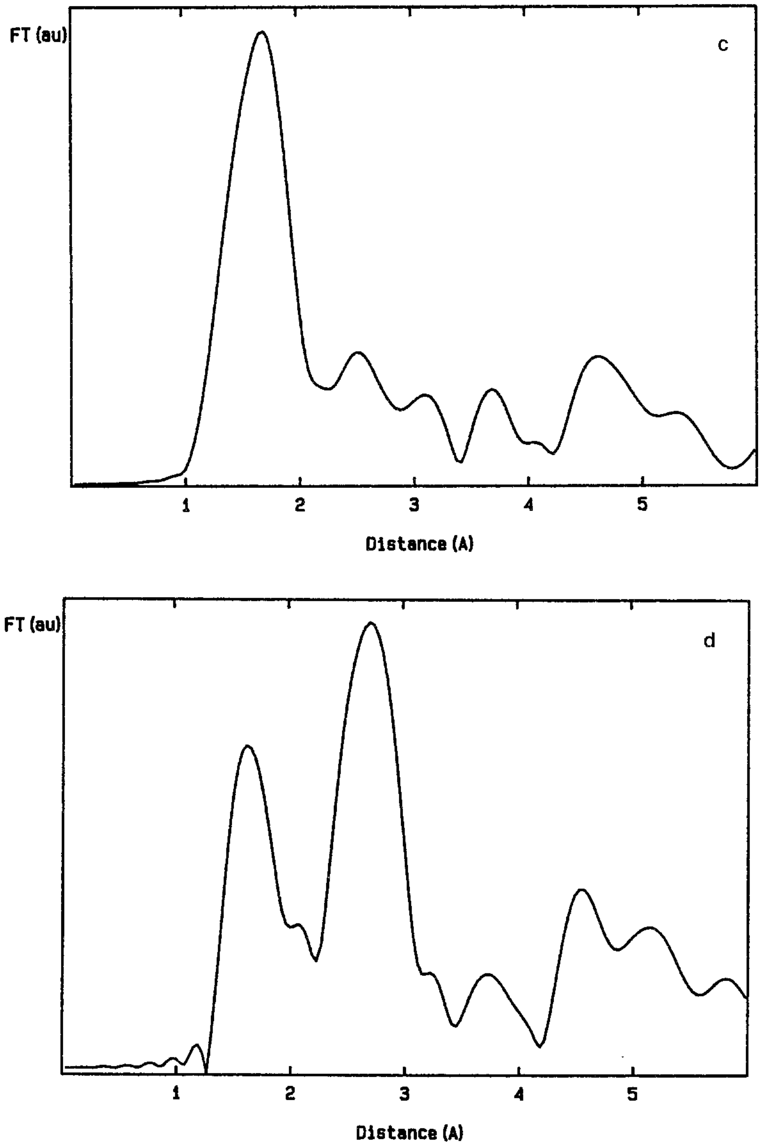


Fig. 3. (continued).

The relatively important Pt-O coordination suggests that a large amount of platinum is in oxidized form.

The results concerning the sintered catalyst B_s are summarized in fig. 4b and table 3. Compared to catalyst B, the Pt-Pt coordination is increased while the Pt-O coordination is lowered. The Pt-Pt interatomic distance is very close to that of bulk metal, as it can be expected for large metal particles. As far as the Pt-O distance is concerned no important difference with respect to sample B was found.

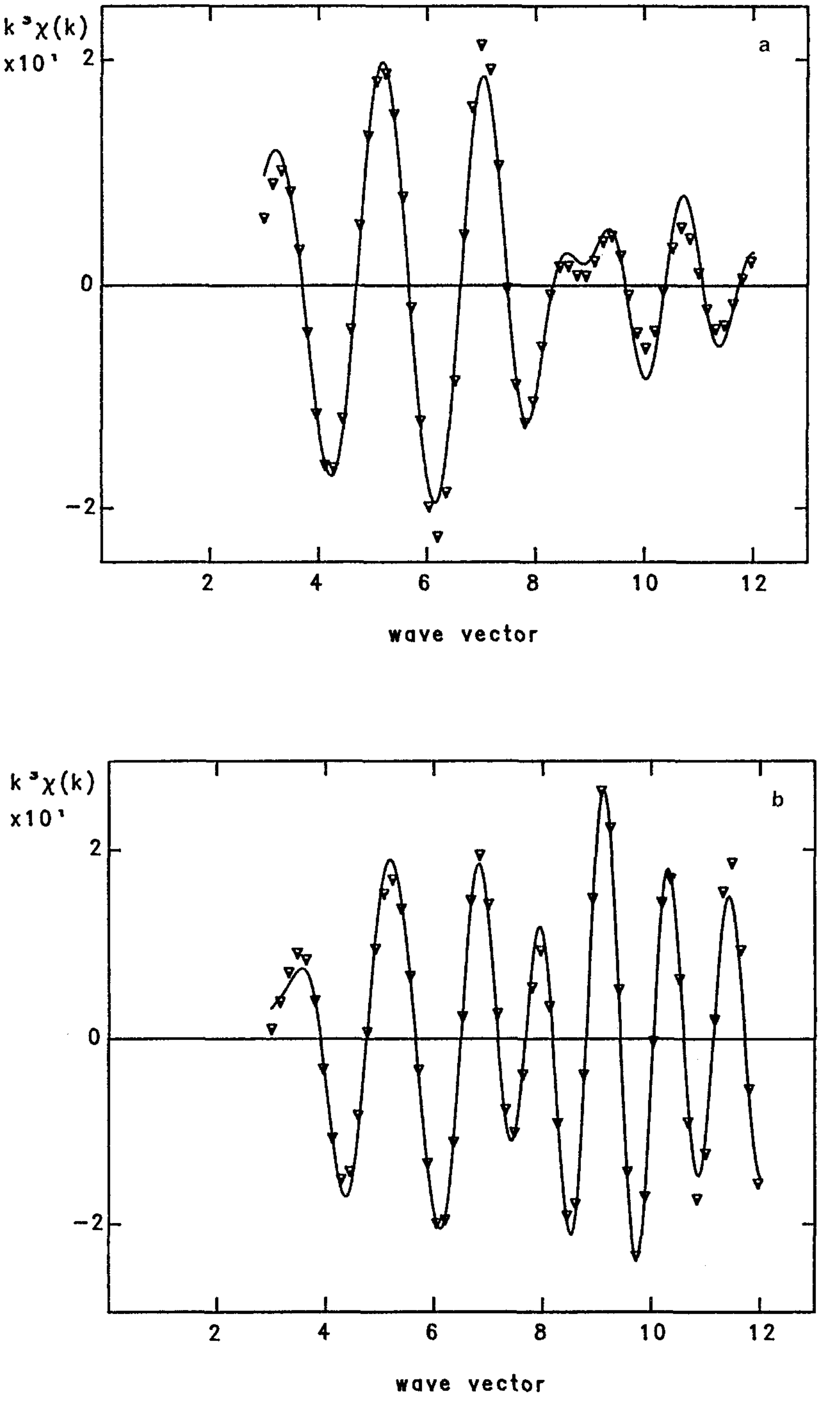


Fig. 4. Experimental (triangles) and modeled (full line) EXAFS contributions around a platinum atom: a-sample B; b-sample B_S.

Table 3
EXAFS parameters for Pt-O and Pt-Pt bonds (B and B_s samples)

Catalyst	Pt-O bond			Pt-Pt bond			Q
	n	R	$\Delta\sigma^2$	n	R	$\Delta\sigma^2$	
B	6.00	2.04	0.0076	1.90	2.64	0.0035	13.83
B_s	3.57	2.04	0.0042	6.18	2.76	0.0016	10.96

The Pt-O and Pt-Pt coordination numbers deduced from EXAFS experiment suggest that a passivation coating was formed at 300°C. Such an assumption has been already proposed by McCabe et al. [21]. In table 4 we reported some results concerning coordination numbers for cuboctahedral particles made of 13 to 5083 atoms. These figures have been obtained from the relationships cited by Gordon [22]. In order to obtain the mean coordination numbers in oxygen (n_s, n_s, n_0) given in table 4, we assumed that the passivation shell is formed of a surface layer of $[PtO_6]$ octahedra which corresponds to the crystallographic arrangement in bulk PtO_2 [14]. Consequently, each Pt surface atom is coordinated to 6 oxygen atoms whereas each Pt atom of the subshell is coordinated to 3 oxygen atoms of the surface layer. Since the EXAFS technique leads to the mean coordination number per atom present in the sample, it follows that the contribution of a Pt surface atom to the overall coordination number is given by:

$$n_s = 6N_s/N_t$$

Table 4
Data for cuboctahedral particles involving m atoms per edge (see text)

m	N_t	N_s	N_x	$D(\%)$	D_m	D_s	n_m	n_s	n_x	n_0	n_p
2	13	12	1	92.3	5.54	4.58	5.54	5.54	0.46	6.00	0.00
3	55	42	12	76.4	11.09	9.15	7.96	4.58	0.65	5.23	1.31
4	147	92	42	62.6	16.63	13.73	9.09	3.76	0.86	4.62	2.98
5	309	162	92	52.4	22.18	18.31	9.73	3.15	0.89	4.04	4.32
6	561	252	162	44.9	27.72	22.89	10.14	2.70	0.87	3.57	5.36
7	923	362	252	39.2	33.26	27.46	10.43	2.35	0.82	3.17	6.16
8	1415	492	362	34.8	38.81	32.04	10.64	2.09	0.77	2.86	6.80
9	2057	642	492	31.2	44.35	36.62	10.80	1.87	0.72	2.59	7.32
10	2869	812	642	28.3	49.90	41.19	10.92	1.70	0.67	2.37	7.74
11	3871	1002	812	25.9	55.44	45.77	11.03	1.55	0.63	2.18	8.09
12	5083	1212	1002	23.8	60.98	50.35	11.11	1.43	0.59	2.02	8.40

N_t: total number of atoms per particle; N_s: number of surface atoms; N_x: number of atoms in the subsurface shell; $D(\%)$: dispersion as it would be obtained from hydrogen chemisorption measurements; D_m: maximum diameter of a cuboctahedral metal particle; D_s: mean diameter of a same volume spherical particle; n_m: mean coordination number in Pt for a metal particle; n_s: mean coordination number in oxygen for a surface atom; n_x: mean coordination number in oxygen for a subsurface atom; n_0: total mean coordination number in oxygen for an oxidized particle ($= n_s + n_x$); n_p: mean coordination number in platinum for an oxidized particle.

where N_s is the number of surface atoms in the metal particle and N_t the total number of atoms in the particle. Similarly, N_x being the number of atoms of the subsurface shell, n_x is obtained by the relationship:

$$n_x = 3N_x/N_t.$$

For a comparison with the dispersion measured by hydrogen chemisorption we calculated the metallic dispersion $D(\%)$ by:

$$D(\%) = 100N_s/N_t.$$

In table 4, D_m represents the diameter of the cuboctahedron and D_s is the diameter of the equivalent sphere. Moreover, n_0 represents the total mean coordination in oxygen ($n_0 = n_s + n_x$), m is the number of metal atoms per edge of the cuboctahedron and n_p is the resulting mean coordination in metal atom after forming the passivation shell. The n_p values are obtained by the formula:

$$n_p = n_{t-1}N_{t-1}/N_t$$

in which the index t – 1 corresponds to the cubooctahedron having t – 1 atoms per edge. From the inspection of tables 1 and 4, we can assume that catalyst B (dispersion = 62%, mean particle diameter = 15 Å) is formed of cuboctahedral particles having about 147 atoms. After oxygen treatment, the mean coordination number of a Pt atom is 6 in oxygen and 1.9 in platinum (table 3). These values are close to those reported in table 4 for a 55 atoms cuboctahedron. However, the coordination number in oxygen appears overestimated compared to the 5.23 value obtained for n_0. This fact may be explained by considering that the reference compound could be defective in oxygen relative to the stoichiometric formula PtO_2. Therefore, an underestimation of the backscattering amplitude results in increasing the oxygen coordination number in our catalysts. On the other hand, since the precision of the coordination number determined by EXAFS is about 10%, it seems quite justified to assume that the passivation coating proposed by McCabe et al. [21] is made of an overlayer of oxidized platinum in the PtO_2 arrangement.

In a similar way, we can assume that sintered catalyst B_s is formed of cuboctahedral particles involving between 1500 and 2000 atoms ($m = 8$). In this case, the final Pt-Pt coordination number is about 7, and the oxygen coordination is 2.7. These values are also in good agreement with the corresponding values obtained from the EXAFS analysis. Moreover, it must also be considered that electron microscopy showed that catalyst B_s presents a bimodal distribution of the metal particles [10], small particles of 15 Å coexisting together with sintered particles. Such a particle distribution would decrease the Pt-Pt mean coordination and increase the Pt-O one. Therefore we can reasonably conclude that oxidized catalyst B_s also presents a surface passivating species having the PtO_2 structure.

We generally obtain from EXAFS analysis large $\Delta\sigma^2$ values compared to the reference values ($\sigma = 0$) taken for the standard samples. If the oxidized particles are formed by a bulk Pt core surrounded by a PtO_2 layer, then the inner oxygen atoms are in interaction with the Pt atoms of the metal core and with those belonging to the surface PtO_2 like phase. Therefore, an adjustment of Pt-Pt bond lengths in the platinum subshell and of the inner Pt-O ones must take place. The large difference between the normal Pt-O bond length in platinum oxide (2.0 Å) and Pt-Pt bond length in bulk metal (2.77 Å) strongly suggests that a large static disorder may exist. This is supported by the large $\Delta\sigma^2$ values computed for both Pt-Pt and Pt-O bonds in the passivated particles, whether the catalyst is sintered or not. This effect is, of course, more pronounced for oxidized catalyst B for which the Pt-Pt distance is shortened (2.64 Å).

4. Conclusion

The sintering of unchlorinated Pt/Al_2O_3 catalysts has been investigated using temperature programmed reduction (TPR) and X-ray absorption spectroscopy (EXAFS). The existence of Pt-Pt metal distances after oxidizing treatment at 300°C is clearly demonstrated. Moreover, a comparison of EXAFS parameters with those calculated from a cuboctahedral model gives strong support to the fact that the oxidation of platinum particles only involves the outermost metal shell in a PtO_2 arrangement. Although temperature programmed reduction profiles qualitatively suggest that oxidation only concerns the accessible metal fraction, a complete analysis of EXAFS oscillations indicates a “cherry” model using our experimental conditions and gives a supplementary proof that EXAFS is a powerful tool to determine the chemical nature of intermediate species which are involved in catalyst deactivation.

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