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IN SITU HIGH TEMPERATURE AND HIGH PRESSURE EXAFS STUDIES OF Pt/Al_2O_3 CATALYSTS. PART I: REDUCTION AND DEACTIVATION

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EXAFS has been used to follow in situ the structural evolution of a chlorinated and non-chlorinated Pt/Al_2O_3 catalyst during reduction in the temperature range of 300–500°C. Smaller metal clusters are formed from the hydrogen reduction of the chlorinated catalyst, in contrast to the larger cluster formed from the non-chlorinated one. At 460°C, the total hydrogen pressure was raised to 5 atm. and n-heptane was injected over the samples. EXAFS measurements at the Pt edge were carried out while hydrocarbon conversion was monitored with a gas chromatograph. We observe the rapid formation of a carbon-platinum bond. This is unmodified while turnover rates and selectivities indicate evidence for deactivation. From this structural information supplied by EXAFS, correlated with the data obtained from gas chromatography, we find that our results are consistent with a model proposed by others where deactivation is due to the build-up of a multilayer of carbon.

Keywords: EXAFS, Pt/Al_2O_3 catalysts, chlorine, temperature, pressure, reduction, deactivation

1. Introduction

Monometallic Pt/Al_2O_3 and bimetallic derivatives are catalysts typically used in petroleum reforming. The aim of reforming is to produce molecules capable of increasing the octane number of gasoline. These molecules are commonly high carbon number branched alkanes or aromatics. As these catalysts are exposed, with time, to harsh operating conditions ($P = 10$–25 atm., $T = 480$–535°C), they become poisoned by carbon, deposited from the hydrocarbon feed, and have to be regenerated. It is important to understand the mechanism by which deactivation and regeneration occurs in order to eventually control it and extend the catalyst's life. Since the metal particles deposited on the alumina support are small (typically less than 20 Å in size), the metal loading is low (< 1 wt.%), and the hydrocarbon reaction conditions severe, it is difficult to find a technique

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capable of yielding information on the local (nearest neighbor) atomic structure and environment of the Pt atoms under these conditions. The EXAFS (Extended X-Ray Absorption Fine Structure) technique is element specific and can be utilized even when the material is subjected to various conditions of pressure and temperature. It is a useful method to examine the structural changes of reforming catalysts. It has previously been successfully applied in this field as shown by numerous publications [1–4]. A number of studies have previously been done using EXAFS to examine the structure of reduced Pt/Al_2O_3 catalysts. Some authors first reduced the sample and then collected EXAFS spectra at room temperature [5] or at liquid nitrogen temperature [6,7]. Others collected EXAFS data as a function of reduction temperature at atmospheric pressure [8] and different chlorine contents [9].

In order to monitor the catalyst's structure during reforming reactions, a system was designed that permits in situ EXAFS studies at high temperatures and pressures. A gas chromatograph allowed on-line simultaneous studies of hydrocarbon conversion at the same time that EXAFS data was collected.

In this paper, we report on our in situ EXAFS and gas chromatograph results of a 1.0 wt.% Pt/Al_2O_3 catalyst, calcined, reduced in H_2 and then coked with n-heptane. The reaction investigated is the conversion of n-heptane to branched isomers or dehydrocyclization products. In order to determine the effect of chlorine on the structure of the sample, two different Pt catalyst samples are studied, one chlorinated, the other not chlorinated. From the EXAFS at the Pt edge, we monitor the platinum coordination number and particle structure throughout the various heat treatments and attempt to relate the structure of our samples with their catalytic activity in the presence of deposited carbon.

2. Experimental

The samples were prepared using a wet impregnation of gamma alumina by a hexachloroplatinic acid solution for the chlorinated sample and a platinum acetylacetonate in toluene solution for the non-chlorinated sample. Both samples were then dried at 120°C for 12 hours and calcined for 2 hours. Chlorinated Pt/Al_2O_3 was calcined in air at 500°C, while non-chlorinated Pt/Al_2O_3 was calcined at 300°C to follow the preparation conditions used in industrial practice. We used 1.0 wt.% Pt supported on gamma alumina having a specific surface area of 240 m^2/g. The chlorinated catalyst had 1.57 wt.% Cl deposited. Metal and chlorine contents were measured by X-ray fluorescence. Oxygen chemisorption showed ~ 100% dispersion for the metal particles after reduction. The maximum size of these particles, as shown by transmission electron microscopy was ~ 7 Å.

EXAFS spectra were collected at the LURE synchrotron facility in Orsay using synchrotron radiation from the DCI storage ring (1.85 GeV, 300 mA). The spectra were measured at the L_3 edge of Pt (11560 eV) using a Si(111) double crystal monochrometer. The X-ray absorption measurements were carried out in the transmission mode using two argon filled ionization chambers. The catalysts were in powder form screened to 100–200 μm. They were placed in a furnace, capable of withstanding hydrogen pressures up to 20 atm. and temperatures up to 500°C. The furnace had transparent entrance and exit beryllium windows for the X-ray beam, allowing for maximum transmission through the sample.

EXAFS was used to follow changes in Pt-O, Pt-Pt and Pt-C coordination for the catalysts: after calcination, during reduction, during carbon deposition and deactivation.

The catalysts were reduced under flowing hydrogen at a total hydrogen pressure of 1 atm. The temperature was raised to 460°C with plateaus at 150°C for 1 hour and at 450°C for 2 hours to minimize sintering of the metal particles and to ensure complete reduction of the metal phase.

Deactivation was then studied after reduction, at a temperature of 460°C, after the total hydrogen pressure was raised to 5 atm. and n-heptane was injected over the samples for 4 hours; $H_2 : HC = 2:1$.

3. Conditions of EXAFS analysis

EXAFS spectra were measured for the catalysts and reference compounds at the temperatures of interest. An extended description of EXAFS analysis can be found elsewhere [10].

In this work, Pt metal foil, PtO_2, H_2PtCl_6, and $K_2Pt(CN)_4$ were chosen as references for the Pt-Pt, Pt-O, Pt-Cl and Pt-C absorber-scatterer pairs. The EXAFS spectra were Fourier transformed (k^3 weighing) over a 10 $Å^{-1}$ Hanning window. An inverse Fourier transform was then applied over the range 1.0–3.15 Å to give the Pt EXAFS function which was then fitted using either Pt-O, Pt-Cl, Pt-Pt or Pt-C reference backscattering amplitudes and phase shifts depending on the chemical step where the EXAFS spectra were collected. We used a two-shell least squares fitting procedure to extract the coordination numbers (N) and the interatomic distances (R): Pt-O and Pt-Cl (after calcination), Pt-O and Pt-Pt (reduction) or Pt-C and Pt-Pt (hydrocarbon reaction) are the combinations of atomic parameters we considered for these successive steps. For Pt-Pt and Pt-C pairs, since the metal foil and $K_2Pt(CN)_4$ are stable at high temperatures, these references were measured at the same temperature as those applied to the catalysts. For Pt-O or Pt-Cl contributions, an extrapolation was made from data collected at $T < 200°C$. All fittings were performed in E space and R space. For the reference compounds, we found that variations of the Debye-Waller factor were limited to ±0.02 Å. Due to the large oxide environment of the platinum after calcination, we did not consider any signal coming from coordination of platinum with Al atoms of the support. The error limits presented here for coordination number and interatomic distance are based upon calculating their average values and variances for the best fits of the spectra.

4. Results and discussion

STRUCTURAL EVOLUTION AFTER THE CALCINATION AND DURING THE H_2 REDUCTION OF THE Pt/Al_2O_3 CATALYSTS IN THE TEMPERATURE RANGE OF 25–460°C

a) Calcination

Before the experiment, each sample was recalcined to ensure elimination of any adsorbed water, the chlorinated catalyst at 500°C, the non-chlorinated at 300°C, both for two hours. The samples were then cooled to room temperature under inert gas and placed in the furnace for EXAFS measurements. EXAFS spectra were then taken at 25 °C before raising the temperature. Chlorinated samples have been previously studied after the drying step in the catalyst preparation, before calcination [11]. An average Pt-O coordination number of 2.9 and an average Pt-Cl coordination of 4.4 were found after drying. In another work [5], an average Pt-Cl coordination of 5.5 and no Pt-O coordination was detected under different experimental conditions. The apparent discrepancy in these results has been linked to the different amounts of chlorine used in preparing the samples and to the difference in the nature of the alumina supports. Following the experimental procedure reported in this paper, significant Pt-O coordination was observed for calcined catalysts, agreeing with results of others [12]. After calcination, the Pt-O coordination number on average was 5.9 for the chlorinated sample and 6.2 for the non-chlorinated one. The various atomic distances and coordination numbers that were determined along with their experimental uncertainties

Table 1
EXAFS parameters for Pt/Al_2O_3 catalysts with variable treatment
Conditions for the hydrocarbon reaction were the following: $T = 460°C$, $P(H_2 \text{ total}) = 5$ atm., $H_2 : n\text{-}C_7H_{16} = 2:1$.

Catalyst	Pretreat-T (°C)	EXAFS parameters					
		N(Pt-O)	R(Pt-O,Å)	N(Pt-Pt)	R(Pt-Pt,Å)	N(Pt-C)	R(Pt-C)
Pt/Al_2O_3-Cl	Air-500	5.9(±0.5)	2.03(±0.03)	–	–	–	–
	H_2-150	5.3	2.04	–	–	–	–
	H_2-460	0.3(±0.3)	2.04(±0.10)	4.1(±0.5)	2.67(±0.03)	–	–
	C_7/H_2	–	–	3.5(±0.8)	2.69(±0.04)	1.1(±0.3)	1.98(±0.04)
Pt/Al_2O_3	Air-500	6.2(±0.5)	2.01(±0.03)	–	–	–	–
	H_2-150	3.7	2.01	–	–	–	–
	H_2-460	0.3(±0.3)	2.05(±0.10)	5.4(±0.6)	2.68(±0.03)	–	–
	C_7/H_2	–	–	5.7(±0.5)	2.66(±0.03)	0.6(±0.2)	2.02(±0.04)

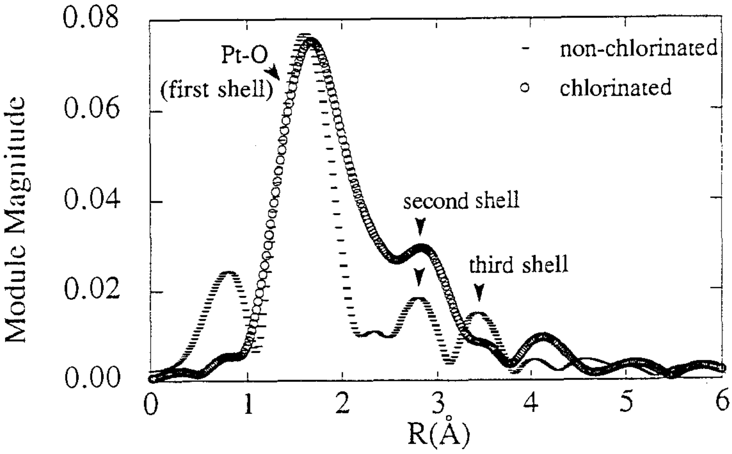

Fig. 1. Module of the Fourier transform of the EXAFS oscillations for chlorinated and non-chlorinated 1.0 wt.% Pt/Al_2O_3 after calcination in air, before reduction in H_2 ($T = 25°C$). The module magnitude is plotted as a function of interatomic distance (Å).

are listed in table 1. The non-chlorinated sample yielded a well formed oxide species after calcination, since three coordination shells of this oxide are clearly visible on the Fourier transform module as shown in fig. 1. A third coordination shell was not detected for the oxide of the chlorinated sample. Quantitative analysis of the second and third coordination shells for the oxide of the samples will not be presented in this paper. The chlorinated sample shows a wider principal peak indicating the possible presence of some chlorine in the first neighboring shell of platinum. Upon analyzing the data however, no significant Pt-Cl was found to be present in the nearest neighboring environment of platinum: if we introduce an average Pt-Cl coordination of 0.5 to 1 in the fitting procedure, the gain in the quality of the simulations is not clear enough to prove the existence of chlorine around platinum. Since chemical analysis after calcination shows a chlorine content of 1.57%, we thus propose that during the calcination process, most of the chlorine atoms migrated to the alumina.

b) H_2 reduction

Reduction results are shown in table 1. As the temperature was raised to 460°C, in the presence of flowing hydrogen, reduction was evident by the decreasing Pt-O coordination number. For the chlorinated sample, N(Pt-O) decreased from 5.9 at 25°C to 0.3 at 460°C; for the non-chlorinated sample, N(Pt-O) decreased from 6.2 to 0.3 as well. The average Pt-O distances remained constant at around 2.04 Å, as in the reference compound. It is important to note that at high temperatures, the error we get on these values becomes quite important (±0.1 Å), due to the weak number of oxygen atoms detected in the platinum neighboring environment.

At 150°C, N(Pt-O) is significantly reduced to $N = 3.7$ at 2.01 Å for the non-chlorinated sample, while there is basically no modification within our accuracy of Pt-O coordination in the chlorinated one. These analysis results at 150°C have shown that the samples still maintain an oxide nearest neighbor environment. This is expected as temperature programmed reduction measurements taken after sample preparation showed reduction occurring at ~ 235°C.

At 25°C, no metallic Pt-Pt coordination was detected. However, by 460°C, the existence of these bonds, having an average interatomic distance of 2.67 Å and 2.68 Å, became evident. Compared to 2.75 Å in bulk platinum, the metal particles seemed to have undergone inward displacement and thus the platinum cluster became more dense. An explanation for this bond contraction at high temperature could be due to the small Pt-Pt coordination numbers obtained (4–5). The less coordinated the Pt atom is to surrounding Pt atoms, could mean that each Pt atom tends to share more electrons with each of its nearest neighbors and therefore, the bond between them will be shorter. The average Pt-Pt coordination numbers for the chlorinated sample by 460°C are N(Pt-Pt) = 4.1. For the non-chlorinated sample, the average Pt-Pt coordination number has increased to 5.4 by 460°C, indicating increased mobility of the Pt atoms on the non-chlorinated sample as the temperature was raised. The growth of the Pt clusters is more striking in the absence of chlorine, a phenomenon observed previously [14]. These results give structural evidence to support the works of others who found that chlorine maintains Pt particle dispersion [15]. By 460°C, we assume that the Pt particles are fully reduced since only trace Pt-O coordination values were detected.

Fig. 2 qualitatively illustrates the evolution of the Fourier transform modules of the chlorinated sample before (25°C) and after (460°C) reduction, where, as reduction is completed, no obvious Pt-O coordination exists. Fig. 3 is an example

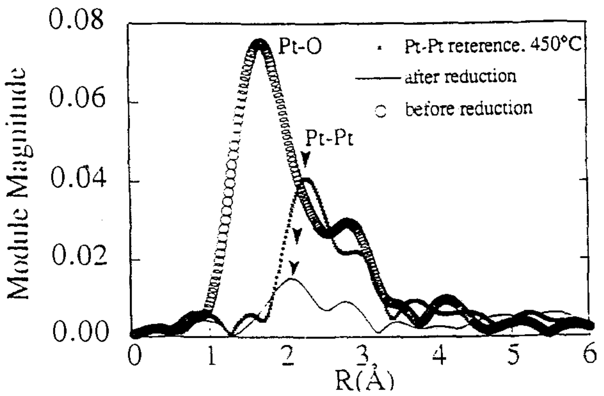

Fig. 2. Evolution of the Fourier transform modules for chlorinated 1.0 wt.% Pt/Al_2O_3 before reduction under flowing H_2 ($T = 25$°C), and after reduction ($T = 460$°C), $P(H_2$ total$) = 1$ atm. Disappearance of Pt-O coordination and formation of Pt-Pt coordination is shown as temperature is raised.

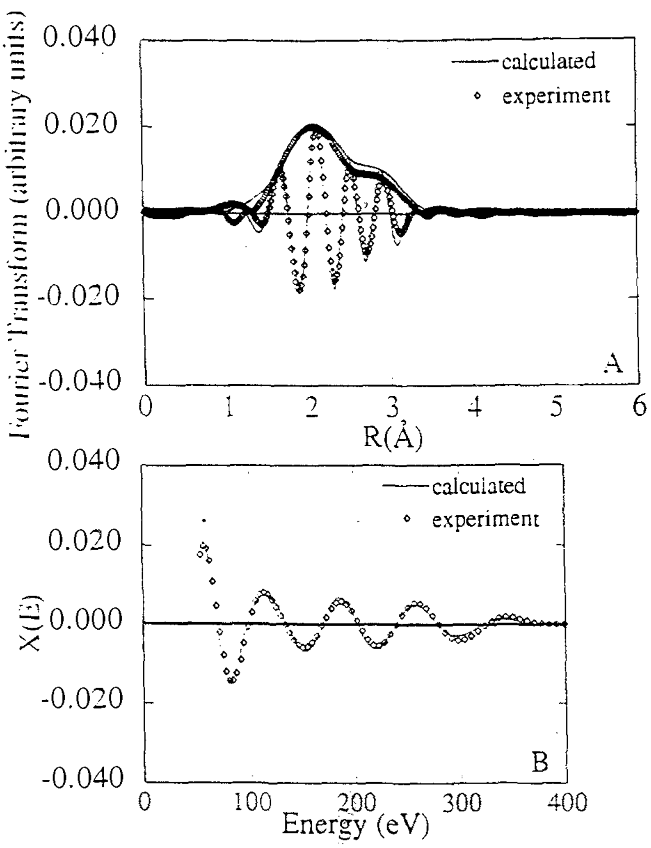

Fig. 3. Comparison of the imaginary and absolute k^3 weighted Fourier transforms with the Hanning window ranging from 40–400 eV, for the experimental spectrum (◇◇◇) and the theoretical spectrum (solid lines) after reduction ($T = 460°C$), $P(H_2$ total$) = 1$ atm. Lack of Pt-O coordination is shown.

of the high quality simulation between the experimental spectrum (◇◇◇) and the theoretical (solid lines) spectrum in our experiments and shows the lack of Pt-O coordination after reduction at 460°C.

STRUCTURAL CHANGES DURING HYDROCARBON CONVERSION

After reducing the samples, the temperature was maintained at 460°C and the total hydrogen pressure was raised to 5 atm. Normal heptane was injected over the catalysts for 4 hours during simultaneous collection of EXAFS data where $H_2 : n\text{-}C_7H_{16} = 2 : 1$. These particular conditions were determined as necessary for detecting Pt-C coordination with EXAFS. Many tests were done, using the synchrotron beam, to best determine the experimental parameters required for detection of the Pt-C distances with EXAFS, yet close enough to conditions actually used in industry.

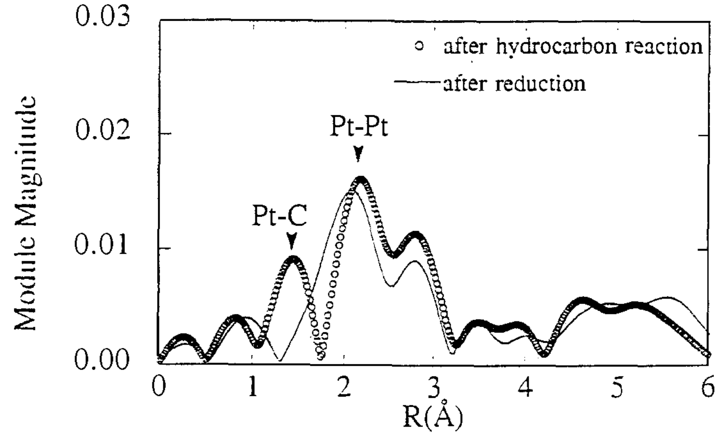

Fig. 4. Evolution of the Fourier transform modules for chlorinated 1.0 wt.% Pt/Al_2O_3 after reduction under flowing H_2 ($T = 460°C$) and after hydrocarbon reaction ($P(H_2$ total$) = 5$ atm., $T = 460°C$, $H_2 : n\text{-}C_7H_{16} = 2:1$). Existence of Pt-C coordination is very clearly shown.

The interatomic distances between Pt-C and Pt-O, are very close to each other; the Pt-O distance in platinum oxide is 2.04 Å and the distance of Pt-C is 1.99 Å and the separation of these peaks is quite difficult from EXAFS alone. The experimental conditions will therefore play a key role in determining the existence of either oxygen or carbon in the vicinity of platinum. Indeed, it is highly unlikely for oxygen to remain in the immediate vicinity of platinum at 460°C, under reducing conditions of hydrogen and hydrocarbon flow. If there are any Pt-O bonds signifying bonding of platinum with oxygen of the support, we did not detect it. We can thus propose that the peak appearing at 1.98 Å in the Fourier transform module in fig. 4 is that due to Pt-C coordination, and not that of Pt-O. Up to 10 spectra were collected at each step of interest during the EXAFS experiments. We can thus rule out the possibility that this distinct peak at 1.98 Å is due to random noise caused by fluctuations in the stability of the beam or movement of the particles, since this same peak was found to be present even upon analyzing the sum of the absorption spectra.

Although the Pt-C and Pt-O interatomic distances are similar, the difference in the backscattering amplitudes between these two pairs of neighbors should indeed make it possible to separate the two contributions as shown in fig. 5. This is the basis for the following EXAFS analysis. Figs. 6a and 6b illustrate the imaginary and absolute k^3 weighted Fourier transforms of the sum of the EXAFS spectra with a Hanning window ranging from 40–400 eV for the experimental spectrum (◇◇◇) during reduction (fig. 6a) and after hydrocarbon reaction (fig. 6b). The theoretical fit (solid lines) are obtained with the parameters extracted from the Pt-O and Pt-C references. The good quality of the EXAFS fit supports our earlier assignment (from the experimental conditions) that we detect Pt-C coordination in the sample after carbon deposition.

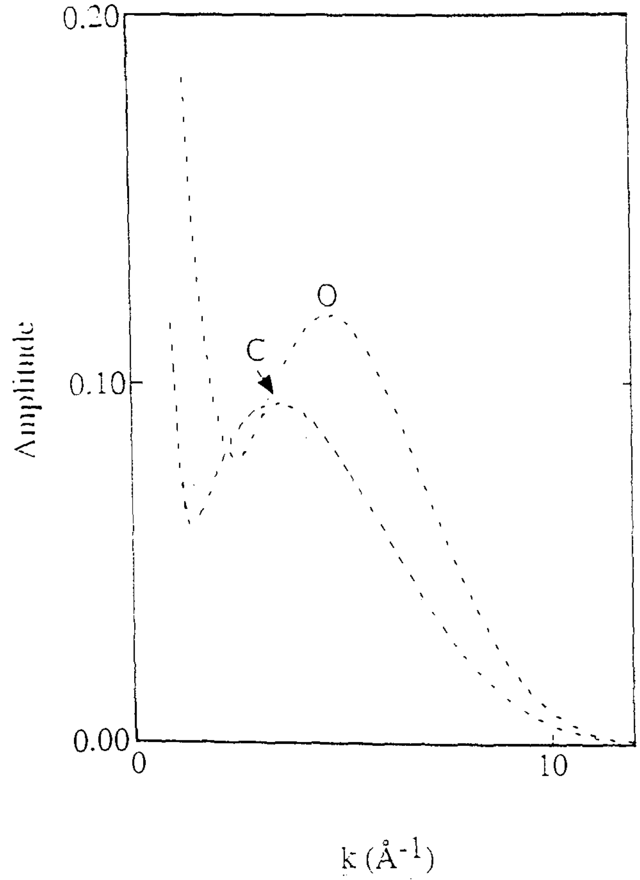

Fig. 5. Backscattering amplitude functions derived from our Pt-O and Pt-C references where Pt is the absorber atom and oxygen and carbon are the scatterer atoms. Amplitude is plotted as a function of k (Å^{-1}).

The EXAFS results before and after hydrocarbon injection are summarized in table 1. After injection of n-heptane, for the chlorinated sample, on the average, one carbon atom per Pt atom (1.1) was detected at 1.98 Å, while a slightly lower average coordination number (0.6) at 2.02 Å was found for the non-chlorinated sample. The Pt-C bond distances detected by EXAFS seem to agree with Pt-C bond distances found for ethylidyne, propylidyne and butylidyne (2.0 Å) using LEED intensity analysis [15,16]. The Pt-C distances are also similar, within error limits, to the 2.1–2.3 ± 0.1 Å distances found for adsorbed benzene on platinum [17]. Thus, the EXAFS data could support the use of aromatics as models for graphitic layers that are known to be bonded parallel to the surface in non-epitaxial, rotationally disordered domains. Meanwhile, Pt-Pt nearest neighbors have increased from 3.5 in the chlorinated sample to 5.7 in the non-chlorinated one. A possible explanation for the detection of less carbon on the non-chlorinated sample could be due to the formation of a larger Pt cluster. However, it is

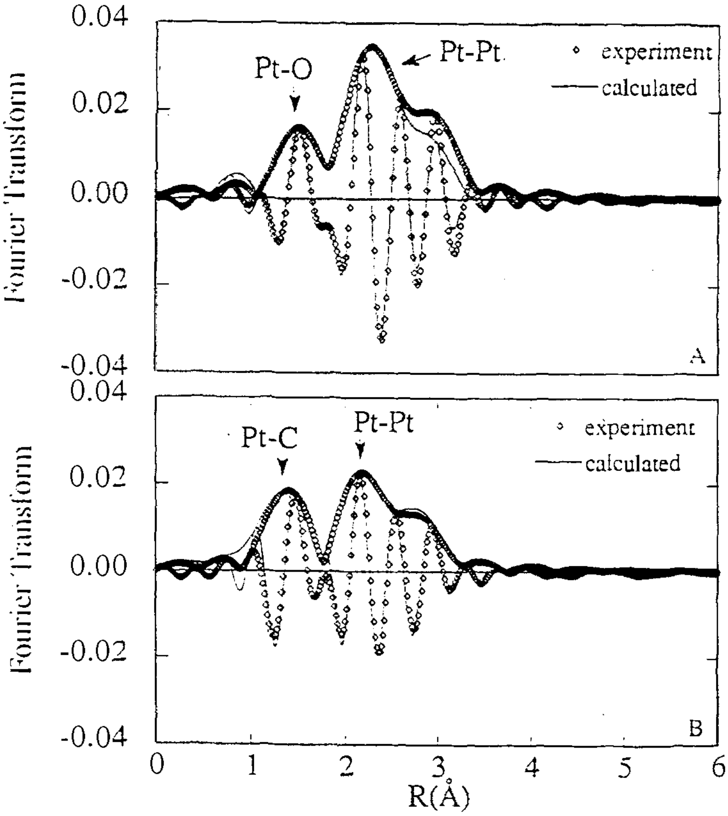

Fig. 6. Comparison of the imaginary and absolute k^3 weighted Fourier transforms with the Hanning window ranging from 40–400 eV for the experimental spectrum (◇◇◇) and the theoretical spectrum (solid lines). A. During reduction under flowing H_2 ($T = 300°C$). B. After hydrocarbon reaction ($P(H_2 \text{ total}) = 5$ atm., $T = 460°C$, $H_2 : n\text{-}C_7H_{16} = 2:1$).

difficult to say for certain within the error limits, that there is a significant difference in the quantity of carbon detected by EXAFS on the two samples. The average Pt-Pt interatomic distances, within our error, do not give evidence for relaxation in the presence of deposited carbon. There also seemed to be no evident change in Pt-Pt coordination numbers before or after hydrocarbon injection. Importantly, from within the first 10 minutes of the reaction to the end, Pt-C coordination remained constant. This indicates that the Pt/gamma-Al$_2$O$_3$ catalyst remains stable under conditions of hydrocarbon conversion and carbon deposition, at least for the 4 hours during which we follow the sample evolution. This observation is confirmed by industrial experience.

Upon completion of our experiments, temperature programmed combustion was used to measure the total amount of carbon deposited on the sample. The chlorinated sample had ~ 1.8 wt.% carbon deposited, and the chlorinated sample had ~ 2.0 wt.% deposited. Conventional transmission electron microscopy showed for both samples a metallic particle size between 7 and 15 Å. These ex situ

Table 2
Turnover rates and selectivities for Pt/Al_2O_3 catalysts over 4 hours of hydrocarbon injection. Conditions were the following: $T = 460°C$, $P(H_2 \text{ total}) = 5$ atm., $H_2 : n\text{-}C_7H_{16} = 2 : 1$.

Catalyst	Turnover rate (molec/site sec)	Selectivities (mol/mol C_7)
	Cracking	*Cracking*
	Isomerization	*Isomerization*
	Cyclization	*Cyclization*
	Dehydrocyclization	*Dehydrocyclization*
Pt/Al_2O_3-Cl	0.093	0.362
	0.089	0.343
	0.009	0.034
	0.048	0.185
Pt/Al_2O_3	0.062	0.533
	0.025	0.211
	0.007	0.063
	0.027	0.233

analysis results show that about the same amount of carbon was deposited on the catalysts, chlorinated or not, and both showed similar particle sizes. However, EXAFS shows clearly a difference between the two samples as evidenced by the larger Pt-Pt coordination number for the non-chlorinated sample.

REACTION RATE STUDIES

The gas chromatograph data for the chlorinated and non-chlorinated catalysts are compared in table 2. The turnover rates (number of molecules produced/exposed catalyst sites × seconds) and selectivities (number of mols of product/number of mols of n-heptane consumed) over 4 hours of n-heptane conversion, for cracking, isomerization, cyclization and dehydrocyclization (or aromatization) product formation are shown, where $H_2 : HC = 2 : 1$. The major reaction products obtained with either catalyst are: 1) cracking (hydrogenolysis and hydrocracking products)-n-butane, n-pentane, isopentane, 2-methyl pentane and 3-methyl pentane; 2) isomerization-2-methyl-hexane and 3-methyl-hexane; 3) cyclization-2,5 dimethyl hexane; 4) dehydrocyclization-benzene and toluene. The reactions desired are isomerization, cyclization and dehydrocyclization. The sample with the chlorinated gamma-alumina support has significantly higher isomerization and dehydrocyclization turnover rates than the sample with the non-chlorinated support. This indicates the importance of the acidic support, along with the metal function, in catalyzing these reactions and supports industrial experience [18]. Under our operating conditions, chlorinated catalysts in the presence of chemisorbed carbon, favor cracking and isomerization, over cyclization and dehydrocyclization. Non-chlorinated catalysts favor cracking product formation over formation of isomerization, cyclization and dehydrocyclization products, again showing the necessity of an acidic support to catalyze desired reactions and supporting industrial results.

During the four hours of reaction studies, the total amount of carbon deposited has changed from 0 to 2 wt.%. Since the Pt-C coordination numbers detected by EXAFS stayed constant throughout the 4 hours for both samples, (after at most 10 minutes of reaction time) while the total amount of carbon deposited increased, we propose that the Pt atoms were covered rapidly with a chemisorbed layer of carbon, after which carbon continued to accumulate. This argument is supported by the total number of carbon deposited (~ 40C/Pt) compared with ~ 1C/Pt detected with EXAFS. Our results agree with the original research detailling the presence of carbonaceous multilayers using Auger Electron Spectroscopy [19]. It was found that during steady state hydrocarbon conversion, platinum surfaces always become covered with about one or more layers of carbonaceous deposits. It was shown that the carbon deposits not only block platinum surface sites from incident reactant molecules, but these deposits also readily exchange hydrogen with reactant molecules and provide desorption sites for product molecules [20]. Thus carbon was found to act not only as a poison and but to also make a catalyst out of platinum.

Industrial experience has shown that the initial carbon deposit on the catalyst does not inhibit desired reactions [21]. As the amount of deposited carbon accumulates and the catalysts deactivate, their selectivities change to yield isomerization (chlorinated) and cracking products (non-chlorinated and chlorinated). The number of Pt-C bonds detected by EXAFS, however, remains unchanged. Thus deactivation of the Pt/Al_2O_3 catalyst is not caused by changes in the number of Pt-C bonds. It has been proposed in the literature that the long term deactivation of the catalyst could be due to the accumulation of a graphite layer or a carbon multilayer on top of a chemisorbed C-Pt layer [22]. Our results are consistent with this mechanism although we cannot confirm that beyond the chemisorbed Pt-C layer, the accumulation of carbon occurs on the clusters or on the support nor determine the stucture of this carbon deposit. Data obtained from EXAFS measurements at the carbon edge might confirm this explanation.

5. Conclusion

In the present study, we have:

- obtained good quality EXAFS results at high temperature and pressure on a catalyst under reforming conditions.
- provided the first EXAFS evidence at high temperature and pressure for chemisorbed carbon on Pt, the quantity detected perhaps being limited by Pt cluster size.

– shown that the initial chemisorbed Pt-C layer is not affected while carbon continues to accumulate and the turnover rate and selectivity are modified.

Thus this study provides the first direct evidence that the local structure of the metal cluster in reforming conditions is not modified significantly during the initial process of deactivation apart from a stable chemisorbed carbon layer. This provides indirect support for models in which the long term deactivation of these catalysts is due to a carbon or graphite multilayer on top of the chemisorbed C-Pt layer. This phenomenon would block active catalytic sites crucial in maintaining the selectivity of the catalyst toward desired hydrocarbon reactions. Finally, the results of this work open the way for other detailed studies of various catalytic processes using EXAFS under reaction conditions of high temperature and high pressure.

References

[1] F.W. Lytle, D.E. Sayers and E.B. Moore, J. Appl. Phys. Lett. 24 (1974) 45.
[2] P. Lagarde and H. Dexpert, Adv. Phys. 33 (1984) 567.
[3] J.C. Bart and G. Vlaic, in: Adv. in Catalysis 35 (Academic Press, New York, 1987) 1–138.
[4] R. Prins and D.C. Koningsberger, in: *X-ray Absorption: Principles, Applications, Techniques of EXAFS, Sexafs and XANES* (John Wiley & Sons, New York, 1987).
[5] P. Lagarde, T. Murata, G. Vlaic, E. Freund, H. Dexpert and J.P. Bournonville, J. Catal. 84 (1983) 333.
[6] D.C. Koningsberger and D.E. Sayers, Solid State Ionics 16 (1985) 23.
[7] F.W. Lytle, R.B. Greegor, E.C. Marques, V. A. Biebesheimer, D.R. Sandstrom, J.A. Horsley, G.H. Via and J.H. Sinfelt, ACS Symposium Series, Vol. 288 (1985) p. 280–293.
[8] A.N. Mansour, J.W. Cook, D.E. Sayers, R.J. Emrich and J.R. Katzer, J. Catal. 89 (1984) 462.
[9] J. Berdala, E. Freund and J.P. Lynch, Journal de Physique 47 (1986) C8269.
[10] Boon K. Teo, in: *EXAFS: Basic Principles and Data Analysis* (Springer-Verlag, Berlin, 1986).
[11] F. Le Normand, D. Bazin, H. Dexpert, P. Lagarde and J.P. Bournonville, in: *Proc. 9th Int. Congress on Catalysis*, Calgary, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) 1401.
[12] J.R. Katzer, G.C.A. Schuit and J.H.C. Van Hoff, J. Catal. 50 (1979) 278.
[13] D.W. Blakely, Ph.D. Thesis, U.C. Berkeley, 1976.
[14] J.P. Bournonville and G. Martino, in: *Catalyst Deactivation*, eds. Delmon and Froment (Elsevier, Amsterdam, 1980) 159.
[15] G.A. Somorjai and B.E. Bent, *Proc. 8th Scand. Symp. Surf. Chem.*, Lund, 1984.
[16] L.L. Kesmodel, L.H. Dubois and G.A. Somorjai, J. Chem. Phys. 70 (1979) 2180.
[17] D.F. Ogletree, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 183 (1987) 1.
[18] R. Maurel and M. Graulier, Act. Chimique 1 (1973) 8.
[19] S.M. Davis, F. Zaera and G.A. Somorjai, J. Catal. 77 (1982) 439.
[20] S.M. Davis, Thesis, University of California, Berkeley, 1981.
[21] C.H. Alvarez, Thesis, Poitiers, 1977.
[22] Hu Zi-Pu, D.F. Ogletree, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 180 (1987) 433.