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IN SITU HIGH TEMPERATURE AND HIGH PRESSURE EXAFS STUDIES OF Pt/Al_2O_3 CATALYSTS. PART II: CARBON REMOVAL

N.S. GUYOT-SIONNEST, F. VILLAIN, D. BAZIN, H. DEXPERT

Laboratoire pour l 'Utilisation du Rayonnement Electromagnétique, Centre Universitaire Paris-Sud, F 91405 Orsay, France

F. Le PELTIER and J. LYNCH

Institut Français du Pétrole, F 92506 Rueil Malmaison, France

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EXAFS has been used to follow in situ the structural evolution of a Pt/Al_2O_3 catalyst during removal of carbon by hydrogenation, after reduction and carbon deposition. After reduction at 350°C, the total hydrogen pressure was raised to 3 atm. and n-heptane was injected over the sample. EXAFS measurements at the Pt edge were carried out with simultaneous on-line EXAFS analysis of the spectra. After observing the rapid formation of a carbon-platinum bond which is unmodified with time, we stopped the heptane flow, raised the temperature to 450°C, and maintained hydrogen flow at 3 atm. The disappearance of the platinum-carbon bond during heat treatment in hydrogen was monitored via on-line analysis. No sintering of the metal particles was observed. EXAFS is thus proven to be an efficient tool to study not just structural changes of a catalyst during a hydrocarbon reaction [1], but also to use it as a technique to study other catalytic phenomena as well.

Keywords: EXAFS, Pt/Al_2O_3 catalyst, temperature, pressure, carbon deposition, carbon removal

1. Introduction

Monometallic Pt/Al_2O_3 and bimetallic derivatives are catalysts typically used in petroleum reforming to convert crude oil into high octane gasoline. The metal particles deposited on the alumina support are typically less than 20 Å in size and the metal loading is < 1 wt.%. Due to the severe operating conditions of reforming ($P = 10–25$ atm., $T = 480–535$°C), the catalysts become poisoned by carbon deposited from the hydrocarbon feed, and have to be regenerated. In order to extend the life of reforming catalysts, the process of their deactivation and regeneration needs to be studied and understood.

In a previous paper [1], we have shown how EXAFS can be used to study changes in Pt-O and Pt-Pt coordination during reduction in H_2 of a 1.0 wt.%

Pt/Al_2O_3 catalyst. Running a hydrocarbon reaction under conditions of high temperature and pressure, we also studied Pt-C formation during catalyst deactivation by deposited carbon.

In this paper, we use EXAFS to follow first, the deposition of carbon on platinum and then the removal of deposited carbon by hydrogenation from the metal particles. This study is of fundamental interest since it directly addresses the question of the interaction between hydrogen and the carbon on the metal particle. Indeed, it has been found that noble metals are good catalysts for the hydrogenation of carbon [2]. It has been suggested that as hydrogen dissociates on the metal surface, followed by surface diffusion across the metal/carbon interface, it interacts with carbon to produce methane [3]. It has also been proposed that in the hydrogenation of carbon by platinum, the rupture of carbon-carbon bonds was followed by the formation of a carbon-platinum bond, while the final removal of carbon from the metal was achieved by interaction with hydrogen to form methane [4].

The work presented here was undertaken to specifically follow the local environment of a carbon covered platinum particle in the presence of hydrogen. From the EXAFS at the Pt edge we find that carbon forms a chemical bond with Pt during hydrocarbon reaction. We also find that this bond can be broken under hydrogen treatment. However, no changes are detected in the metal particle size or structure.

2. Experimental and data analysis

The catalyst was prepared as described earlier [1] by a wet impregnation of gamma alumina using a hexachloroplatinic acid solution. 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 DCI storage ring (1.85 GeV, 300 mA) in Orsay at the LURE synchrotron facility. Measurements were made at the L_3 edge of Pt(11560 eV) using a Si(111) double crystal monochrometer, in the transmission mode using two argon filled ionization chambers as described earlier [1].

Four types of EXAFS studies of changes in Pt-O, Pt-Pt and Pt-C coordination are reported in this paper: after calcination, reduction, carbon deposition and carbon removal by hydrogenation. The goal of these studies is to show the feasibility of using EXAFS to follow the structural evolution of catalysts during reactions and chemical treatments under working conditions of high temperature and pressure.

The catalysts were reduced under flowing hydrogen at a total hydrogen pressure of 1 atm. The temperature was raised to 350°C with plateaus at 150°C for 1 hour and at 350°C for 2 hours to minimize sintering of the metal particles and to ensure complete reduction of the metal phase.

At 350°C, the total hydrogen pressure was raised to 3 atm. N-heptane was injected over the samples for 2.5 hours where $H_2 : HC = 0.7 : 1$. Injection was then stopped and the temperature was raised to 450°C, keeping total hydrogen pressure constant at 3 atm.

The EXAFS spectra were analyzed in the same manner as described in our preceding paper [1] where Pt metal foil, PtO_2, H_2PtCl_6, and $K_2Pt(CN)_4$ were again chosen as references for the Pt-Pt, Pt-O, Pt-Cl and Pt-C absorber-scatterer pairs. The Fourier transform was performed over 10 $Å^{-1}$ and a maximum of two shells were used in the fitting procedure, the shells being determined by the chemical step where the EXAFS spectra were collected.

The error limits presented in the text and tables for coordination number and interatomic distance are based upon calculating their average values and variances for the best fits of the spectra.

3. 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 25–350 °C

a) Calcination

Before the experiment, the sample was recalcined at 500°C for two hours to ensure elimination of any adsorbed water. The sample was 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. As in our previous study [1], we observed an average Pt-O coordination number of 5.9, no Pt-Cl coordination, and no detectable metallic Pt-Pt.

b) H_2 reduction

Table 1 provides a summary of the observed coordination numbers and bond distances during reduction at various temperatures. Here again, the sample must

Table 1
EXAFS parameters for Pt/Al_2O_3 catalysts with variable treatment. Conditions for the hydrocarbon reaction were the following: $T = 350°C$, $P(H_2\text{total}) = 3$ atm., $H_2 : \text{n-}C_7H_{16} = 0.7 : 1$. Conditions for carbon removal were: $T = 450°C$, $P(H_2\text{total}) = 3$ atm

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)
$PtAl_2O_3$-Cl	Air-500	5.9(±0.5)	2.03(±0.03	–	–	–	–
	H_2-150	6.3	2.02	–	–	–	–
	H_2-350	0.5(±0.3)	2.07(±0.10)	4.2(±0.5)	2.67(±0.03)	–	–
	C_7/H_2	–	–	4.6(±0.8)	2.67(±0.04)	1.4(±0.3)	1.96(±0.04)
	H_2(450)	–	–	4.7	2.65	0.4	2.05

be heated to temperatures higher than 235°C to see the beginning of the reduction of the platinum oxide. As the temperature was raised to 350°C, in the presence of flowing hydrogen, reduction became evident by the decreasing Pt-O coordination number. N(Pt-O) decreased from 6.3 at 150°C to 0.5 at 350°C. Therefore by 350°C, we see that the Pt particles have been mostly reduced. At 25° or 150°C, no Pt-Pt coordination was detected. However, by 350°C, the existence of Pt-Pt bonds was evident, having an average interatomic distance of 2.67 Å, compared to 2.75 Å in bulk platinum. Thus, the platinum clusters have become more dense perhaps due to inward relaxation of the metal atoms. The average Pt-Pt coordination number by 350°C was N(Pt-Pt) = 4.2.

STRUCTURAL CHANGES DURING HYDROCARBON CONVERSION

Our objective is to demonstrate how EXAFS can follow changes in structure of Pt clusters not only in the presence of deposited carbon, but also in the desorption of this carbon once it has been put on the metal.

In our previous paper [1], we have already described how the EXAFS determination of Pt-C coordination is non-trivial, especially in the analysis of the data, and that as a result, the experimental conditions play a key role in determining the existence of either oxygen or carbon in the vicinity of platinum. Up to 10 spectra were collected at each step of interest. We showed that the peak appearing at 1.96 Å in the Fourier transform module in fig. 1 is that due to Pt-C coordination, and not that of Pt-O.

One of the main conclusions was that from within the first 10 minutes of the reaction to the end, Pt-C coordination remained constant. We proposed that the Pt atoms were covered rapidly with a chemisorbed layer of carbon, after which carbon continued to accumulate. This agreed with previous existing models [5].

Our objective in this study was to deposit just enough carbon on the sample to detect it with EXAFS, and then not to get too much so that we could not remove it under hydrogen flow and heat treatment. Therefore, after reducing the samples, the temperature was maintained at 350°C and the total hydrogen pressure was raised to 3 atm. Normal heptane was injected over the catalysts for 2.5 hours during simultaneous collection of EXAFS data where $H_2 : n\text{-}C_7H_{16} = 0.7 : 1$. As n-heptane was injected over the sample, the subsequent bonding of carbon to platinum was carefully monitored by performing on-line data analysis while EXAFS spectra were being collected. After 2.5 hours, we had collected and analyzed a sufficient number of spectra for us to confirm the presence of Pt-C coordination. The EXAFS results before and after hydrocarbon injection are summarized in table 1. After injection of n-heptane, on the average, ~ 1.4 carbon atoms per Pt atom were detected. 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 change in Pt-Pt coordination numbers before or after hydrocarbon injection.

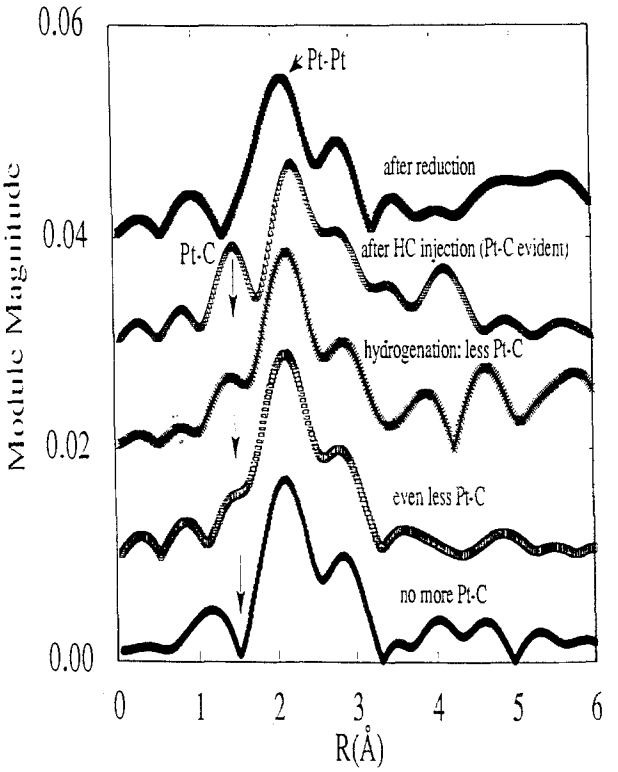

Fig. 1. Modules of the Fourier transform of the EXAFS oscillations for 1.0 wt.% Pt/Al_2O_3 after reduction in H_2 ($T = 350°C$, $P(H_2\text{total}) = 1$ atm.), after hydrocarbon reaction for 2.5 hours ($T = 350°C$, $P(H_2\text{total}) = 3$ atm., $H_2 : n\text{-}C_7H_{16} = 0.7 : 1$), and during carbon removal by hydrogen ($T = 450°C$, $P(H_2\text{total}) = 3$ atm.). The lack of Pt-O coordination (after reduction), the presence of Pt-C coordination (after hydrocarbon reaction), and its disappearance during carbon hydrogenation are shown. The module magnitude is plotted as a function of interatomic distance (Å).

The sample was then removed and analyzed ex situ by transmission electron microscopy (TEM) and Temperature Programmed Combustion (TPC). TEM showed metallic particles having sizes between 7 and 15 Å. TPC measurements taken at 950°C showed that ~ 0.4 wt.% carbon was deposited on both the metal and the support, corresponding to ~ 7C/Pt compared with ~ 1.4C/Pt detected with EXAFS.

REMOVAL OF DEPOSITED CARBON FROM PLATINUM PARTICLES AT 450°C

In a different series of measurements, the samples were treated using the same procedure described above. After on-line analysis unequivocally confirmed the presence of Pt-C coordination, hydrocarbon injection was stopped and the temperature was raised to 450°C, with total hydrogen pressure maintained at 3 atm.

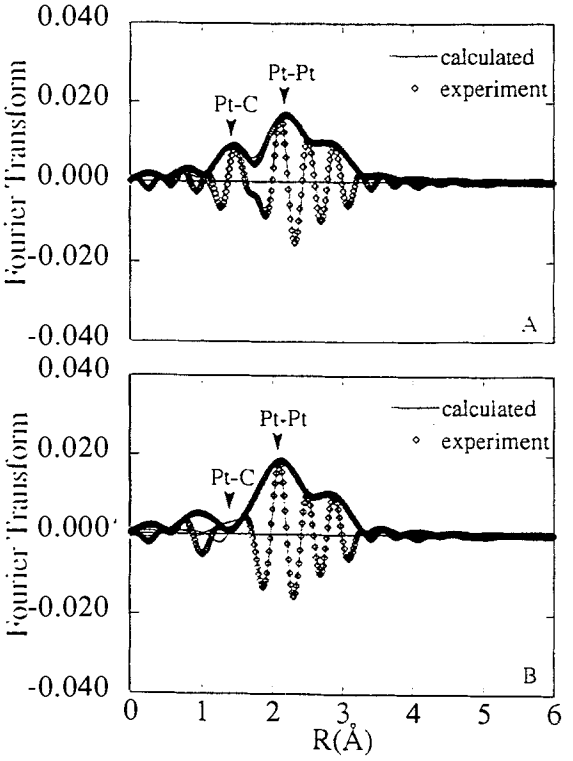

Fig. 2. The imaginary and absolute k^3 weighted Fourier transforms of the sum of the EXAFS spectra are shown with a Hanning window ranging from 40–400 eV for the experimental spectrum (◇◇◇) for the sample with carbon deposited (fig. 2a) and the sample with carbon removed from the platinum (fig. 2b). Parameters extracted from the Pt-C and Pt-Pt references are used to obtain the theoretical fit (solid lines). A. Carbon deposited ($T = 350°C$, $P(H_2\text{total}) = 3$ atm., $H_2 : n\text{-}C_7H_{16} = 0.7 : 1$). B. Carbon removed ($T = 450°C$, $P(H_2\text{total}) = 3$ atm.).

Since carbon deposition is favored by high temperatures and low pressures, its removal depends on the control of these two parameters [6]. It has been shown that the amount of carbon deposited decreases with increasing pressure [7]. Since we wanted to obtain rapid deposition of carbon, but not too much to prevent desorption, suitable pressure (3 atm.) and temperature (450°C) were chosen.

Table 1 presents the EXAFS results during carbon hydrogenation. It is possible to follow with EXAFS the disappearance of Pt-C coordination. Fig. 1 compares the Fourier Transform modules of the catalysts after reduction, after hydrocarbon reaction and during heat treatment in hydrogen. The evolution of Pt-C coordination is illustrated qualitatively by the diminishing Pt-C peak. Figs. 2a and 2b show 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 (◇◇◇) for the sample after hydrocarbon reaction with carbon deposited (fig. 2a) and the sample during heat treatment in hydrogen (fig. 2b). Parameters extracted from the Pt-C reference were used to obtain the

theoretical fit (solid lines). After hydrocarbon injection, the Pt-C coordination number on average was 1.4 at an average interatomic distance of 1.96 Å. Upon stopping hydrocarbon flow, raising the temperature to 450°C and maintaining the total hydrogen pressure at 3 atm., the average Pt-C coordination number decreased to 0.4, being barely detectable after 4 hours. Therefore after 4 hours under hydrogen we can assume that no remaining Pt-C coordination exists.

Pt-Pt coordination stays constant within the experimental error where Pt-Pt coordination after hydrocarbon injection on average is 4.6 at an average interatomic distance of 2.67 Å. After carbon removal at 450°C for 4 hours, the Pt-Pt average coordination number is 4.7 at 2.65 Å. Therefore, EXAFS did not detect any change in the Pt-Pt coordination numbers during the removal of deposited carbon by hydrogenation. Therefore significant modification of the Pt cluster can be ruled out. This will restrict the models for platinum cluster restructuring during carbon removal.

Ex situ analysis of the total amount of carbon deposited on the sample after 2.5 hours of hydrocarbon reaction, followed by 4 hours of heat treatment in hydrogen using TPC showed that ~0.5 wt.% carbon was deposited on the catalyst. Within the accuracy of the ex situ TPC measurements, we can consider that the total amount of carbon deposited on the catalyst was not modified by the heat treatment. Conventional transmission electron microscopy showed a metallic particle size between 7 and 15 Å.

Our EXAFS results show that the carbon deposited on the metal under our experimental conditions, could be removed by hydrogen. This is consistent with a model proposed by others where the regeneration of the metal component in a hydrogen environment could occur through the breaking of C-Pt bonds [4]. In addition, EXAFS has shown that as carbon is eliminated from Pt, the metal cluster structure remains unchanged. Finally, since ex situ analysis by TPC showed that the amount of carbon deposited on the catalyst was virtually not affected by hydrogen treatment, we propose that the remaining carbon could be located on the alumina.

4. Conclusion

In the present study, we have:

– detected with EXAFS at high temperature and pressure, chemisorbed carbon on Pt.

– shown with EXAFS that the desorption of the carbon deposited on the metal could be monitored and that during carbon removal, metal cluster size was unmodified.

– proposed that the carbon remaining on the catalyst after heat treatment in hydrogen could be located on the alumina

We proposed in a previous paper [1] that our EXAFS results provided indirect support for models in which the long term deactivation of these catalysts could be due to a carbon 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. In the present paper we have followed with EXAFS the elimination of carbon from the metal during heat treatment in hydrogen, a process during which the size of the metal clusters is unmodified. Based on our TPC and EXAFS results, we suggest that the carbon deposit continues to exist on the alumina after it had been removed from the platinum particles by hydrogen.

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