An EXAFS study of the interaction of different reactant gases over nanometer scale Pt clusters deposited on γ-Al_2O_3

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Face to the difficulty to find an efficient catalyst in the reduction of NO by hydrocarbon in diesel exhaust gases, we have examined the interaction of some concerned reactant gases, NO, C_3H_6 and O_2, with a catalyst constituted of nanometer scale platinum particles deposited on alumina. Indeed, in order to understand the catalytic process, it seems essential to have information on the adsorption process and on the evolution of the structural parameters of the particles when submitted to such gases. This work has been performed on a 1% Pt/Al_2O_3 catalyst by using *in situ* EXAFS measurements. We have concentrated our study, on the one hand, on the influence of NO, C_3H_6 in the presence or not of an excess of oxygen and, on the other hand, on the influence of the total mixture. The most striking result is the growth of the platinum particles under NO. Moreover, when the catalyst is submitted either to a mixture of $NO + O_2$ or $C_3H_6 + O_2$, the particles are not fully oxidised. With the total mixture, the particles both grow and are oxidised.

KEY WORDS: platinum-based catalysts; *in situ* EXAFS; NO; reduction

1. Introduction

Due to their particular properties respective to bulk material, nanometer scale materials are more and more at the core of various problems linked to major economic and environmental challenge of our society. Our study focuses on the reduction of nitrogen oxides emissions from diesel car exhaust gases. Numerous studies have been made in order to find a solution to remove these unwanted pollutants [1,2]. Among them, the catalytic reduction by hydrocarbons leads to probing results. An impressive number of catalytic systems have been tested, such as Cu/ZSM-5 which has been considered for a long time as a reference material to reach the goal [3]. But this catalyst is not stable under real conditions [4]. Pt-based catalysts supported on oxides or zeolites represent now one of the most promising materials [5–7]. That is why we have engaged an *in situ* EXAFS study on a 1% Pt/Al_2O_3 catalyst in order to determine the structural modifications of platinum particles associated to particular gas phase conditions [8–12]. Regarding academic studies [13–15], despite the fact that a size dependence of physical properties of nanometer scale particles has been studied in many metallic systems, less is known on the chemisorption process of small molecules at their surface. Because catalytic reaction includes an adsorption process of the reactants, we have decided to examine carefully the influence of different reactant gases involved in the SCR of NO by propene, namely NO, C_3H_6 and O_2 on the structural characteristics of supported nanometer scale Pt clusters. We have concentrated our attention on the influence of the presence or not of oxygen, as diesel exhaust gases contain oxygen in excess.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared as described earlier [16] by wet impregnation of γ-alumina with a hexachloroplatinic acid solution. After calcination and reduction, high-resolution transmission electronic microscopy (HRTEM) investigations were done on the sample. The mean particle diameter is found around 15 Å, which shows how important the dispersion is.

2.2. Experimental analysis

X-ray absorption spectra were measured at the LURE laboratory in Orsay, France, Exafs IV station using a Si(111) double crystal monochromator. The storage ring was operated with an electron energy of 1.85 GeV and a current between 260 and 360 mA. At the Pt L_{III} edge (11564 eV), the estimated resolution was 3 eV. The measurements were performed in the transmission mode, using ion chambers filled with air to absorb 20% of the X-ray beam in the first ion chamber and 80% of the X-ray beam in the second ion chamber. To increase the signal to noise ratio, each data point was counted for 1 s and 10 scans were averaged. An example of the X-ray absorption spectrum near the Pt L_{III} edge is shown

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(figure 1). The energies of the X-ray absorption spectra were calibrated at the Pt L_{III} edge using a Pt foil (7.5 μm thickness).

The EXAFS spectra were analysed in the same manner, as described earlier in a previous paper [14] where Pt metal foil ($N = 12$, $R = 2.765$ Å), PtO_2 ($N = 6$, $R = 2.04$ Å) and $K_2Pt(CN)_4$ ($N = 4$, $R = 2.02$ Å) were chosen as references for the Pt–Pt, Pt–O and Pt–C absorber–scatterer pairs. The Fourier transform (FT) was performed over 6 $Å^{-1}$ and two coordination shells were used in the fitting procedure. The shells were determined by the chemical step where the EXAFS spectra were collected. Figure 2 is an example of the high quality of agreement between the experimental and calculated spectra.

First, the sample is placed in the furnace for EXAFS measurements. EXAFS spectra were then taken at room temperature before raising the temperature. As in our previous study, we observed an average Pt–O coordination number of 1.8 and an average Pt–Cl coordination number of 1.1. That is why before each study dedicated to reactant gases, the sample was reduced at 450 °C under pure H_2 in order to build nanometer scale platinum clusters. The sample was then cooled to 25 °C under H_2 before introducing the reactant gases at different temperatures.

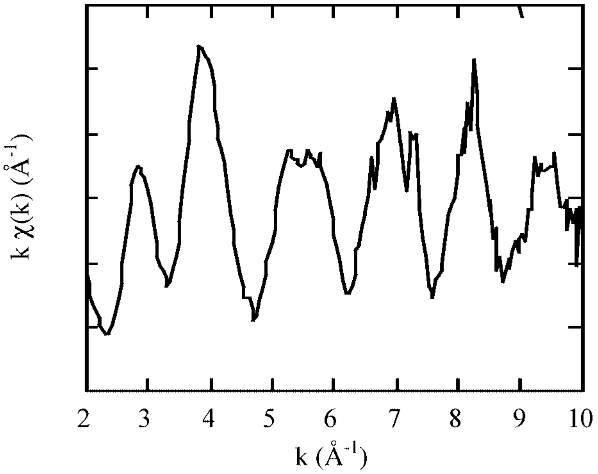

Figure 1. EXAFS modulations of 1% Pt/Al_2O_3 at 25 °C, after reduction, at the L_{III} Pt edge.

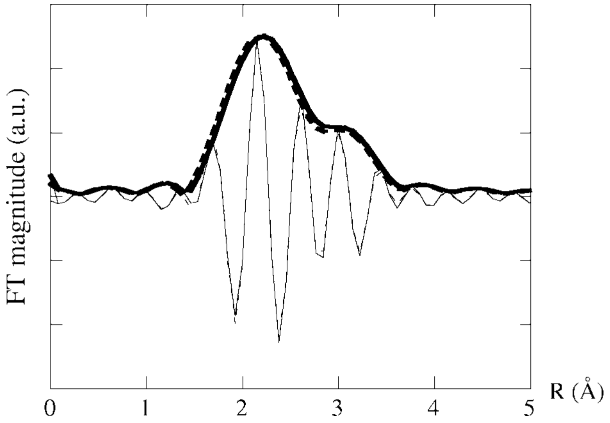

Figure 2. Refinement result of the 1% Pt/Al_2O_3 at 25 °C, after reduction at the Pt L_{III} edge, experimental (solid line) and calculated (dashed line).

3. Results

3.1. Influence of one reactant gas

3.1.1. Influence of NO (1%) + N_2

After the *in situ* reduction of the catalyst, a flow of NO (1%) in N_2 was introduced on the sample. The temperature was raised from 25 to 300 °C. Five steps were made (25, 100, 200, 300 and back to 25 °C) where EXAFS spectra were collected.

The evolution of the FT magnitude versus temperature is represented in figure 3. The position of the FT magnitude compared to the reference Pt foil one indicates that platinum atoms in the catalyst are mainly surrounded by Pt atoms. This is confirmed by quantitative analysis, as shown in table 1. At room temperature, when H_2 is replaced by NO, we observed a contraction of the distances which could be explained by the reaction of chemisorbed H_2 at the surface of the aggregates with NO. Two important facts are to be put in a prominent position:

- Firstly, no light backscatterers are present around Pt atoms during this experiment.
- Secondly, the coordination number increases remarkably after 100 °C, which signifies the growth of the Pt particle sizes under NO. This phenomenon has already been

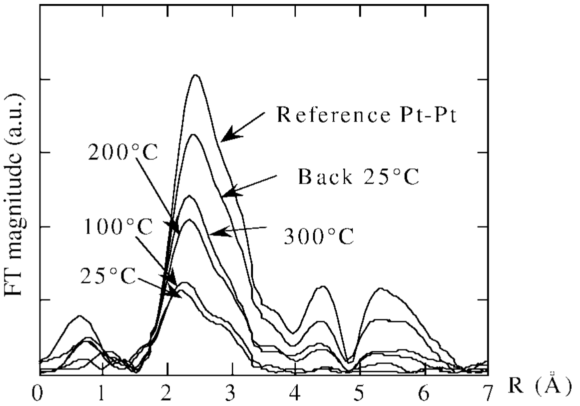

Figure 3. Comparison of the FT magnitude of the reduced catalyst measured under hydrogen at 25 °C, under NO at 100, 200, 300 and back to 25 °C with the Pt foil reference.

Table 1
Numerical simulations associated with the evolution of the Pt environment for the reduced catalyst under a NO flow versus temperature.

T (°C)/gas	N_{PtPt}	$\Delta\sigma^2$ ($Å^2$) × 10^3	$R_{Pt\text{–}Pt}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.0
25/NO	6.4	6.4	2.69	−6.6
100/NO	7.4	4.9	2.72	−5.5
200/NO	8.6	0.4	2.75	−3.6
300/NO	10.8	0.2	2.76	−4.1
25/NO	10.0	1.0	2.765	−3.3

observed by HRTEM on the same kind of catalyst [19]. At 300 °C, the mean particle size is estimated to be at least equal to 55 Å. This indicates how important the sintering is. As the particle size increases, the aggregates draw nearer to the bulk Pt properties. The statistic disorder becomes weaker, which explains the decrease of the Debye–Waller factor when the temperature rises. This striking result has already been mentioned in our previous paper [18].

3.1.2. *Influence of 20% O_2 + 80% N_2*

The FT was performed in the 3–9.2 Å interval. The evolution of the FT magnitude versus temperature is represented in figure 4. By comparison with Pt–O and Pt–Pt reference magnitude a significant shift toward lower distance of the maximum of the FT magnitude is measured. The quantitative analysis of the EXAFS modulations after the Pt L_{III} edge indicates that this shift corresponds to the loss of Pt–Pt bonds which are replaced by Pt–O ones. From 300 °C, the Pt particles are totally oxidised.

This substitution of Pt atoms by oxygen atoms in the local order around Pt atoms is linked to the disappearance of the nanometer scale Pt clusters on the alumina. This first experiment is in line with previous work already published regarding the high sensitivity of nanometer scale particles versus the presence of air, even at room temperature [20].

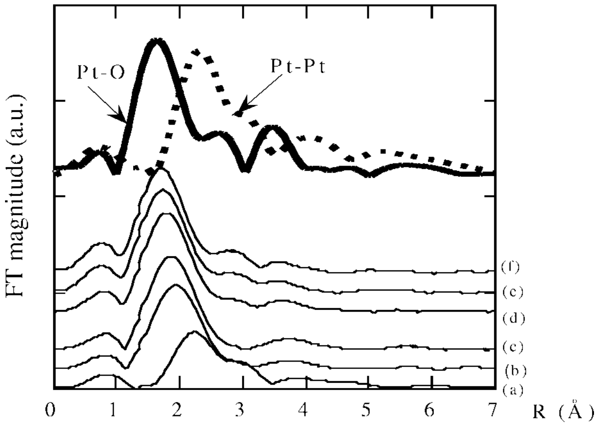

Figure 4. FT magnitude of the reduced catalyst at 25 °C (a), under O_2 at 100 (b), 200 (c), 300 (d), 400 (e) and 500 °C (f).

At 400 °C, the Pt–O interatomic distance gets closer to the one characteristic of PtO_2. As proposed by Hwang et al. [21], we can suppose that the platinum is at the 4th oxidation state. Under this temperature, the Pt–O interatomic distance is slightly higher than the crystallographic value found in PtO_2. This could be explained with either a metal–support interaction as suggested by Koningsberger et al. [22] or the presence of chemisorbed oxygen at the surface of the platinum particles, since the particles are small. This last explanation is more realistic, especially as we cannot distinguish between chemisorbed oxygen atoms and oxygen atoms issued from an oxide [23]. Moreover, the large distance between platinum and oxygen in the 100–300 °C range implicates that the bond between these two kinds of atoms is weakened.

3.1.3. *Influence of C_3H_6 (3000 ppm in N_2)*

The gas mixture was injected on the reduced catalyst at 100 °C. Three temperature steps were done at 100, 200 and 300 °C where EXAFS spectra were collected. The evolution of the FT magnitude versus temperature is represented in figure 5. The FT was calculated in the 3.5–10.2 Å interval. Since the experiment is realised with propene, we have envisaged the presence of carbon atoms around platinum. But we could not exclude the presence of oxygen atoms in the first coordination shell of platinum, coming from some impurities in the gas phase. That is why the FT magnitude of the sample is compared with Pt–Pt, Pt–O and Pt–C reference

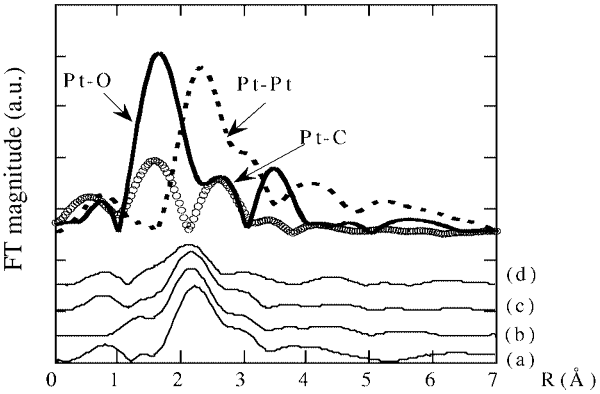

Figure 5. FT magnitude of the reduced catalyst at 25 °C (a), under propene at 100 (b), 200 (c) and 300 °C (d).

Table 2

Numerical simulations associated with the environment of Pt for the catalyst submitted to an air flow in function of temperature.

T (°C)/gas	Pt L_{III}, platinum neighbour				Pt L_{III}, oxygen neighbour			
	N_{Pt-Pt}	$\Delta\sigma^2$ (Å^2) × 10^3	R_{Pt-Pt} (Å)	ΔE (eV)	N_{Pt-O}	$\Delta\sigma^2$ (Å^2) × 10^3	R_{Pt-O} (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.0	–	–	–	–
100/O_2	3.0	0.0	2.74	−1.0	3.5	0.0	2.16	5.4
200/O_2	2.4	0.0	2.74	−0.3	4.5	0.0	2.15	4.8
300/O_2	–	–	–	–	5.8	0.0	2.12	4.7
400/O_2	–	–	–	–	6.0	0.0	2.09	3.2
500/O_2	–	–	–	–	6.0	0.0	2.08	2.7

Table 3
Numerical simulations associated with the evolution of the Pt environment with carbon neighbours.

T (°C)/gas	Pt L_{III}, platinum neighbour				Pt L_{III}, carbon neighbour			
	$N_{Pt–Pt}$	$\Delta\sigma^2$ (Å^2) $\times 10^3$	$R_{Pt–Pt}$ (Å)	ΔE (eV)	$N_{Pt–C}$	$\Delta\sigma^2$ (Å^2) $\times 10^3$	$R_{Pt–C}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.3	–	–	–	–
100/HC	5.3	1.5	2.75	−5.1	1.3	0.4	2.11	3.6
200/HC	5.2	2.0	2.74	−5.1	1.1	0.6	2.08	1.6
300/HC	5.3	0.3	2.75	−5.3	0.9	1.2	2.10	4.0

Table 4
Numerical simulations associated with the evolution of the Pt environment with oxygen neighbours.

T (°C)/gas	Pt L_{III}, platinum neighbour				Pt L_{III}, oxygen neighbour			
	$N_{Pt–Pt}$	$\Delta\sigma^2$ (Å^2) $\times 10^3$	$R_{Pt–Pt}$ (Å)	ΔE (eV)	$N_{Pt–O}$	$\Delta\sigma^2$ (Å^2) $\times 10^3$	$R_{Pt–O}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.3	–	–	–	–
100/HC	5.0	0.1	2.76	−5.3	1.0	0.0	2.11	3.9
200/HC	4.9	2.0	2.75	−5.5	1.0	0.0	2.09	2.5
300/HC	3.1	0.4	2.75	−6.0	0.8	1.0	2.10	5.8

magnitude. We can notice that the magnitude of the first coordination shell around platinum from Pt–C and Pt–O are quite similar. The analysis of this figure leads to the following information:

– Carbon and/or oxygen neighbours appear around platinum.

– Platinum atoms still exist around the central platinum atoms.

Numerical simulations were more difficult to realise. The presence of both oxygen and/or carbon in the first coordination shell of platinum is delicate to interpret. Taking into account the experimental conditions, it is more realistic to find some carbon atoms around Pt atoms, especially as Guyot-Sionnest et al. [13,14] have detected some in their experiments with hydrocarbon. But we cannot exclude the presence of oxygen coming either from impurities in the gas bottle or from an interaction between small platinum particles and the support.

In fact, we have compared both kinds of numerical simulations. It appears that the fitting procedure gave best results when carbon atoms are present in the first coordination shell of platinum. The two solutions are however given in tables 3 and 4.

From the results presented in the tables 3 and 4, we can say that:

– The numerical simulations were done with a Pt–C reference taken at room temperature. This explains why the Debye–Waller factor increases when the temperature is higher.

– The Pt–C interatomic distance is a bit larger than that of the reference. But, another study has already mentioned such high distances [24].

– The Pt–O interatomic distance is greater than the crystallographic value of PtO_2. It could result either from an interaction with the oxygen from the support or from chemisorbed oxygen atoms, as mentioned previously.

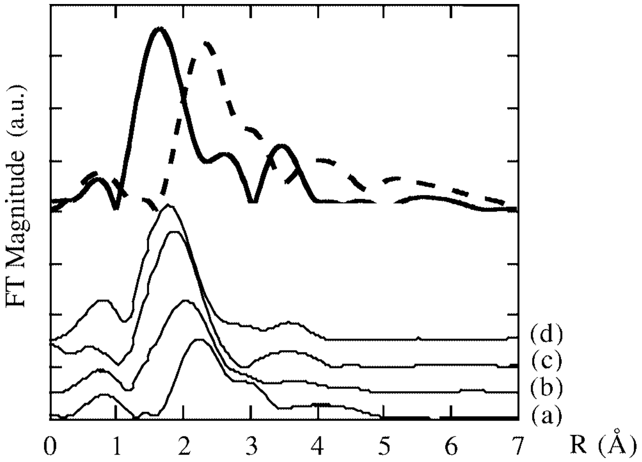

Figure 6. FT magnitude of the reduced catalyst at 25 °C (a), under NO + O_2 at 100 (b), 200 (c) and 300 °C (d).

In fact, it is difficult to choose between these two possibilities. The most important to say is that platinum particles maintain in majority Pt–Pt bondings.

3.2. Gas mixture: the influence of oxygen

After having studied the influence of each gas separately, we decided to analyse first the effect of gas mixtures (NO + O_2 and HC + O_2) with oxygen in excess and then the total gas mixture containing all three gases.

3.2.1. Influence of NO (500 ppm) + O_2 (14%) (balance N_2)

The FT has been done in the 3–9.2 Å^{-1} window. Figure 6 shows the evolution of the radial distribution function around platinum measured with this reactant mixture. When the reduced platinum catalyst is under a flow of NO + O_2 in excess, there is a progressive disappearance of the Pt–Pt

Table 5
Numerical simulations associated with the Pt environment when the reduced catalyst is under a ($NO + O_2$) flow.

T (°C)/gas	Pt L_{III}, platinum neighbour				Pt L_{III}, oxygen neighbour			
	$N_{Pt–Pt}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–Pt}$ (Å)	ΔE (eV)	$N_{Pt–O}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–O}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.3	–	–	–	–
100/$NO + O_2$	6.3	0.7	2.73	−6.3	1.7	0.0	2.11	3.6
200/$NO + O_2$	4.9	1.4	2.71	−6.0	4.1	0.0	2.13	1.6
300/$NO + O_2$	2.7	1.2	2.75	−7.3	4.6	1.0	2.11	4.0

characteristic peak in the aid of a light backscatterer. This is confirmed by the numerical simulations exposed in table 5 for each temperature. It appears that oxygen atoms are present at 100 °C and above around platinum. However, even if this gas is present in excess, some Pt–Pt bondings persist up to 300 °C, which was not the case when oxygen was present alone. The presence of NO allowed the Pt particles to conserve a metallic character. These results could be explained by two models:

- first, Pt particles surrounded by a shell of oxide;
- secondly, coexistence of Pt particles of a large diameter with smaller oxidised Pt particles.

However, as the Pt–O interatomic distance does not match with the crystallographic value found in PtO_2 (2.04 Å), it is more realistic to suppose the presence of oxidised Pt particles in the surface.

3.2.2. *Influence of C_3H_6 (500 ppm) + O_2 (14%) (balance N_2)*

We have studied the influence of the $C_3H_6 + O_2$ mixture directly after the hydrocarbon only experiment. After collecting spectra at 300 °C under propene, the catalyst was cooled down under a flow of nitrogen before introducing the ($C_3H_6 + O_2$) gas mixture at 100 °C. At this stage the Pt particles are surrounded by a few carbon or oxygen neighbours. We have then collected spectra at 100, 200 and 300 °C. The FT were realised in a 3–9.2 Å^{-1} window. The evolution of the FT magnitude in function of the temperature is represented in figure 7. We can already notice that some oxygen neighbours (or carbon) appear in the first co-ordination shell of platinum, which can be seen by the displacement of the FT maxima to smallest interatomic distance.

Contrary to the other fit, the numerical simulations were difficult to achieve. Indeed, we have supposed the presence of both carbon and oxygen in the first coordination shell of platinum (table 6). The result obtained for 200 °C has no real physical sense but it corresponds to the best refinement. Indeed, the Pt–O interatomic distance is abnormally high as compared to the crystallographic value of 2.04 Å.

What is important to say is that, even if the gaseous atmosphere is strongly oxidative, there is persistence of Pt–Pt bonding. The presence of propene in the mixture seems to be responsible of this passivation to oxidation.

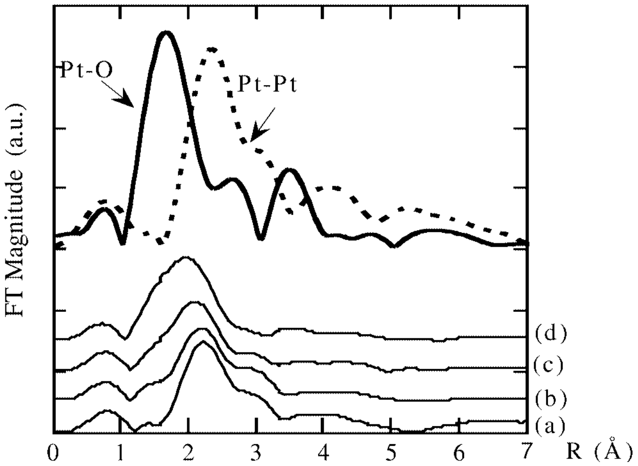

Figure 7. FT magnitude of the reduced catalyst at 25 °C (a), under $C_3H_6 + O_2$ at 100 (b), 200 (c) and 300 °C (d).

3.3. *Influence of the total gas mixture: NO (500 ppm) + C_3H_6 (500 ppm) + O_2 (14%) – balance N_2*

The FT has been performed in a range comprised between 3.5 and 8.6 Å^{-1}. The qualitative analysis of the evolution of the FT magnitude (figure 8) shows the disappearance of the initial structure and the appearance of a light backscatterer in the first co-ordination shell of platinum. This is confirmed by the numerical simulations (table 7).

First, it is important to note that no carbon or oxygen atoms are present in the first coordination shell of platinum. Moreover, at 300 °C, the catalyst is not fully oxidised. The presence either of NO and/or propene prevents the total oxidation. The passivation phenomenon is not so striking as with the $NO + O_2$ mixture, which could result from a reaction between the propene and the NO. We could propose two models of particles:

- mean size platinum particles coexisted with fully oxidised ones;
- Pt particles oxidised in surface.

4. Discussion

This study dedicated to the influence of gas and gas mixtures in a simplified DeNOx reaction mixture becomes essential to understand the catalytic process. First, we will discuss the effect of each gas alone.

Table 6
Numerical simulations associated with the evolution of the Pt environment under flowing ($C_3H_6 + O_2$) gas mixture.

T (°C)/gas	Pt L$_{III}$, platinum neighbour				Pt L$_{III}$, oxygen neighbour			
	$N_{Pt–Pt}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–Pt}$ (Å)	ΔE (eV)	$N_{Pt–O}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–O}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.3	–	–	–	–
100/HC + O_2	4.8	0.0	2.74	−5.0	0.4	0.0	2.06	0.7
200/HC + O_2	3.5	0.0	2.74	−5.0	1.6	0.0	2.14	5.0
300/HC + O_2	3.6	0.0	2.73	−4.5	2.6	0.0	2.12	2.9

Table 7
Numerical simulations associated with the evolution of Pt under ($C_3H_6 + NO + O_2$) gas mixture in function of temperature.

T (°C)/gas	Pt L$_{III}$, platinum neighbour				Pt L$_{III}$, oxygen neighbour			
	$N_{Pt–Pt}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–Pt}$ (Å)	ΔE (eV)	$N_{Pt–O}$	$\Delta\sigma^2$ (Å^2) × 10^3	$R_{Pt–O}$ (Å)	ΔE (eV)
25/H_2	7.0	2.5	2.75	−5.3	–	–	–	–
25/MIX	5.3	1.1	2.74	−2.8	0.9	0.2	2.05	0.3
100/MIX	5.7	0.3	2.75	−3.1	1.5	0.2	2.09	1.8
200/MIX	5.6	0.3	2.74	−3.2	3.3	0.1	2.10	2.3
300/MIX	6.5	0.6	2.73	−1.7	4.6	0.1	2.07	0.3

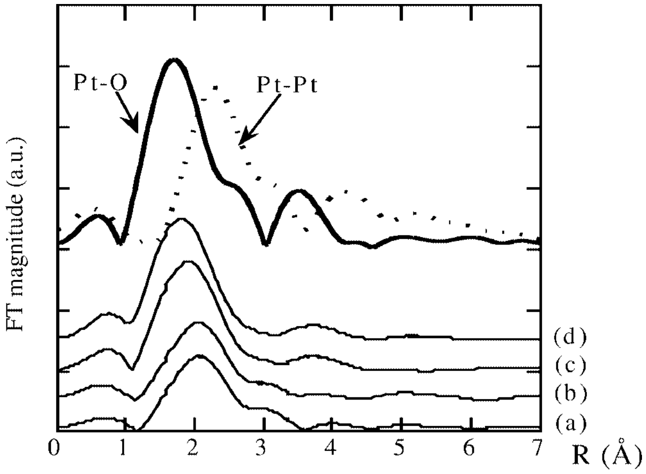

Figure 8. FT magnitude for the reduced catalyst at 25 °C (a), under NO + $C_3H_6 + O_2$ at 100 (b), 200 (c) and 300 °C (d).

4.1. Influence of one reactant gas

4.1.1. NO

As noted previously [18], the effect of NO is the rapid sintering of Pt particles with no appearance of light element (oxygen or nitrogen) in the first coordination shell of platinum. This could be explained by the formation of (Pt–NO) complexes which could be more mobile at the platinum surface.

4.1.2. O_2

When the reduced catalyst is under a flow of oxygen, the platinum is entirely surrounded with oxygen atoms at 300 °C. Under this temperature, we observe a large Pt–O interatomic distance. As suggested by Hwang et al. [21], we may be not in presence of species like PtO_2. Indeed, they have evaluated the different oxide phases in function of the temperature for a Pt/Al_2O_3 catalyst which was reduced during 2 h at 400 °C under hydrogen before being oxidised. These oxygen atoms could be less in interaction with platinum, which could result in an increase of the Pt–O interatomic distance. When the temperature increases, as we get closer to an oxidation in the bulk, the interatomic distance value should approach the crystallographic data.

4.1.3. C_3H_6

We have examined the influence of propene diluted in N_2 on the reduced Pt particles. As we mentioned previously, the numerical simulations were rather difficult to achieve since we were not sure to detect some carbon atoms around the platinum. Guyot-Sionnest et al. [13,14] have already detected, by *in situ* EXAFS measurements, the presence of carbon in the isomerisation reaction of n-heptane on a platinum-based catalyst. In this case, the Pt–C distance was around 1.99 Å which differs significantly from the Pt–C distance we have found. However, benzene adsorption on platinum gave Pt–C interatomic distance between 2.1 and 2.3 Å [24]. Moreover, an *in situ* infrared study on the adsorption of a mixture of $C_3H_6 + O_2 + NO$ on a Pt-based catalyst has shown that propene adsorbs as a π-allylic complex [25]. This species comes near a benzenic nucleus where the electrons are delocalised. The formation of such a complex in our experiment is rather realistic, especially as its quantity diminishes with the growth of temperature with no alteration of the platinum particles which remain metallic. However, we could not exclude also the presence of oxygen.

Table 8
Species adsorbed (*) and desorbed when NO and O_2 are admitted on a polycrystalline surface of Pt in function of temperature, detected by TAP experiments.

<table>
<tr><th></th><th colspan="5">T (°C)</th></tr>
<tr><th></th><th>−173</th><th>57</th><th>147</th><th colspan="2">177</th></tr>
<tr><td>O_2</td><td>O–O**</td><td colspan="3">O*</td><td>O*, O_2</td></tr>
<tr><td>NO</td><td colspan="2">N–O*</td><td>N–O*, NO</td><td colspan="2">N–O*, N*, O*, N_2, NO, O_2</td></tr>
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4.2. *Influence of gas mixture*

4.2.1. *NO + O_2*

When NO and oxygen are admitted simultaneously on the reduced catalyst, the platinum particles are not fully oxidised up to 300 °C, contrary to what is observed when there is only oxygen. Moreover, no particles sintering occurs, as under NO only. The two gases act in fact together, that is to say NO adsorbs on particles even in presence of an excess of oxygen, which allows particles to preserve a metallic character.

Lacombe et al. [26], in their study on the reduction of NO by n-butane on polycrystalline Pt sponge, have reported the different adsorbed and desorbed species in function of the temperature on a Pt polycrystalline surface, knowing that the desorption temperature depends on the coverage ratio. The results are summarised in table 8.

NO adsorbs molecularly up to about 150 °C. Above this temperature, it begins to dissociate in oxygen and nitrogen atoms. The oxygen atoms remain at the surface up to 180 °C where it is supposed to recombine to desorb as oxygen. The inhibitor effect of this gas is then not total [27,28].

In our case, NO and O_2 should compete in the adsorption process. Under 200 °C, the coverage ratio of NO seems to be the greatest, so that the platinum particles could not be oxidised. Moreover, the sticking coefficient of this gas decreases with temperature and is at its maximum in this temperature range [29]. Below 200 °C, NO adsorbs preferentially. Moreover, NO and O_2 react together to form NO_2 at temperature $\geqslant$150 °C. The NO_2 species could adsorb on platinum particles and move to the support by a spill-over effect where they are stabilised. This step could delay the oxygen action on platinum particles.

4.2.2. *$C_3H_6 + O_2$*

When C_3H_6 and O_2 are sent simultaneously on the catalyst, the effect is the same as for a NO + O_2 mixture, that is to say, no oxidation in the bulk of the Pt particles is observed. The catalytic combustion of hydrocarbon goes through a Langmuir–Hinshelwood mechanism where oxygen and hydrocarbons adsorb on the same site [30]. In the presence of an excess of oxygen, we have verified in a flow reactor system that propene is totally burnt around 150 °C. Moreover, no carbon deposit could occur, or with difficulty since we have an excess of oxygen. Propene delays oxygen influence, first because, they react together, second because they may adsorb competitively on the same sites.

4.3. *Effect of the total gas mixture: $C_3H_6 + NO + O_2$*

When all three gases are admitted together on the reduced catalyst, the effect is surprising: we notice both the growth of the particles size and their oxidation. This implies that the NO-only effect is maintained. This sintering was still observed in the work of Ringler [31] after DeNOx catalytic experiments on a Pt/alumina catalyst.

To explain this result, we can suppose several possibilities:

- Propene reacts with oxygen issued from the dissociation of adsorbed oxygen. This implies that a patch of platinum is maintained at a metallic state, allowing the NO adsorption. NO could in that case act as it is alone. In fact, we did not detect any carbon atoms in this experiment. Since the platinum particle size is low, we should detect some of them. The propene or a hydrocarbon derivative do not stay at the surface: either it reacts between 100 and 200 °C, or it is adsorbed on the support.
- A part of NO is oxidised into NO_2 in these conditions. A reaction between a hydrocarbon intermediate and NO_2 could occur. NO and propene could adsorb on different sites. Oxygen could react preferentially with the hydrocarbon, which will allow NO to act as if it was alone.

To clarify these hypotheses, we have done on a catalytic flow reactor the experiments with 500 ppm NO, 375 ppm C_3H_6 and 10% O_2. We have noticed that propene has entirely disappeared above 200 °C at the temperature where the oxidation of NO begins. The NO reduction occurs at 180 °C to finish at 250 °C. In the same temperature range begins the NO oxidation.

We can conclude that a patch of platinum particles is maintained near a metallic state to allow sintering under NO below 200 °C. Oxygen seems to react rather with propene until the latter has totally disappeared.

5. Conclusion

In this study, we have examined the effect of several gases, components of a simplified DeNOx reactional mixture, on the structural modifications of Pt particles pretreated under hydrogen. The most striking results are as follows:

- In presence of NO, Pt particles sinter remarkably at temperature $\geqslant$200 °C.
- In presence of either NO or propene simultaneously with oxygen, platinum particles are not fully oxidised even if oxygen is present in excess. NO or propene should adsorb on the sites responsible for oxidation. Adsorption competition is in favour of these two gases up to 200 °C.
- In a total mixture, the observed phenomenon, that is to say, the growth of the platinum particles and their oxidation, expresses both the effect of NO alone and simplified gas mixture.

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