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Preparation of a Pt/SiO$_2$ catalyst
II. Temperature-programmed decomposition of the adsorbed platinum tetrammine hydroxide complex under flowing hydrogen, oxygen, and argon

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Abstract

The temperature-programmed decomposition of platinum tetrammine hydroxide mixed with or exchanged on silica in a flow of neutral, oxidizing, or reducing gas is studied using mass-spectrometric analysis of the effluent. A unified interpretation mechanism is proposed whatever the nature of the gas. It involves $(\equiv\text{SiO})_2\text{Pt}(\text{NH}_3)_y$ with $y \approx 2$ as the intermediate species. This species anchors the particles defined at the drying step. Anchoring takes place at 100–150 °C whatever the gas. The subsequent decomposition of this species leads either to Pt$^{(0)}$ (reducing gas), mobile PtO (oxidizing gas), or a mixture of both (neutral gas). The dispersion of the platinum particles ranges between 70 and 80% for metal loading up to 5% when the decomposition is performed under the reducing gas up to 500 °C. In the neutral gas, the dispersion ranges from 42 to 72% and depends on the final temperature and on metal loading. In an oxidizing gas, the dispersion can be about 65% provided that the final temperature does not exceed 250 °C. Subsequent reduction at a higher temperature reproduces the decomposition under the reducing gas. When the final temperature is raised above 250 °C in the oxidizing gas, the dispersion decreases and falls to 20% at 500 °C. It is proved that PtO is responsible for low dispersions. Conversely, under reducing conditions, the size of the particles obtained upon drying is kept unchanged. The proposed mechanism explains why a neutral gas gives intermediate results that depend on pressure and metal loading. In the case of high metal loading, decomposition under the reducing gas leads too small particles grouped together, although dispersion remains within 70–80%.

Keywords: Pt/SiO$_2$ catalyst; Platinum particles; Platinum tetrammine hydroxide

1. Introduction

In the first part of this paper [1], a detailed study of the exchange, drying, and thermal decomposition processes under vacuum when preparing Pt/SiO$_2$ catalysts from Aerosil silica (Degussa) and platinum tetrammine hydroxide was described. It was demonstrated that exchange reaches completion after about 1 min. However, more than 1 h is required to achieve a uniform distribution of the platinum complex over the silica surface. The exchanged complex does not lose any NH$_3$ ligand upon drying at 25 °C under vacuum. At 100 °C still under vacuum the exchanged complex forms clusters of $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]_n$ deposited on the surface. Increasing the temperature under vacuum progressively removes the NH$_3$ ligands from the exchanged complex. At 200 °C, about half of the ammonia ligands are lost and at 300 °C the complex is fully decomposed mainly into PtO particles of 1–2 nm in size. About 10% of PtO is reduced to Pt$^{(0)}$ due to reduction of Pt by NH$_3$. A further reduction under hydrogen at 400 °C does not alter the particle size. Chemisorption of H$_2$ and O$_2$, electron microscopy, and EXAFS analyses were used to characterize the various species formed. The results obtained suggest that drying could be the crucial step of the Pt/SiO$_2$ catalyst preparation.

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This second part of the paper describes the thermal decomposition of the exchanged complex under oxidizing, neutral (or inert), and reducing atmospheres, using time-resolved mass spectrometric analyses of the gaseous products evolved.

Literature data exhibit large discrepancies concerning the influence of the nature of the flowing gas on the size of the platinum particles. Some authors [2–5] claimed that the smallest particles were obtained under an oxidizing atmosphere (calcination), whereas other authors [6–12] observed that they were obtained under a reducing atmosphere. Recently, Oudenhuijzen et al. [13] observed that starting with $Pt(NH_3)_4(NO_3)_2$, the smallest particles were obtained after heating at 400 °C under a flowing mixture of argon and helium. Finally, the nature of the flowing gas could have an influence on the shape of the particles. According to Schmidt and co-workers [12,14] the platinum particles are perfect cubes after heating in hydrogen, whereas they are spherical after heating in oxygen.

In order to understand the decomposition mechanism of the $[Pt(NH_3)_4(OH)_2]_n$ clusters deposited on the silica surface, the nature and the amount of the gases evolved during the temperature-programmed decomposition under various flowing gases were studied. The influence of the nature of the feed gas and the metal loading was investigated as well as the influence of the final temperature. The various catalysts thus obtained were characterized by chemisorption of probe molecules (H_2 and O_2) and electron microscopy and the relation between decomposition conditions and platinum particle size was clarified.

2. Experimental

2.1. Thermodesorption

2.1.1. Apparatus

A home-made temperature-programmed decomposition (TPD) apparatus was built according to the previous work of Falconer and Schwarz [15]. Analysis of the exhaust gas was performed using a mass spectrometer. The quadrupole mass spectrometer from Vacuum Generator was calibrated with respect to the following species: H_2O, NH_3, N_2, N_2O, and NO. Eleven m/e were recorded during the TPD experiments. The five molecular concentrations were then calculated solving the over determined linear system by singular value decomposition [16]. The various gases (N_2, O_2, Ar, He) were fed to the TPD apparatus through Brooks mass flow controllers. A constant flow rate of helium was superimposed to the main gas stream and was used as an internal calibration standard.

The decomposition reactor was made of a Pyrex tube 35 mm i.d. and 270 mm long located in an oven. The catalyst was deposited on a sintered glass support. Then SiC was used to fill the remaining dead space volume (200 cm^3) of the reactor. The gas flowed downward and was preheated in the SiC bed before entering the catalyst bed. The temperature of the catalyst was measured at the catalyst bed inlet by a thermocouple. Residence time distribution experiments showed that plug flow was achieved.

2.1.2. Procedure

Two grams (6 mm layer) of catalyst was introduced into the reactor.

The TPD experiments were performed under neutral (10% He, 90% Ar) reducing (10% He, 10% H_2, 80% Ar), or oxidizing (10% He, 10% O_2, 80% Ar) atmospheres, with a constant flow rate of 150 $mL\,min^{-1}$ STP.

The temperature program was as follows: dwell 30 min at room temperature, ramp at 2 °C min^{-1} up to 500 °C, and then dwell at 500 °C for 30 min. For some experiments the final dwell temperature was 200, 300, or 400 °C.

At the end of a TPD experiment, the catalyst was treated at 500 °C under the reducing atmosphere.

2.1.3. Preparation of the samples

2.1.3.1. Support. Two grams of silica (Aerosil from Degussa, 200 $m^2\,g^{-1}$) was treated under flowing dry air at 500 °C for 5 h and then introduced into a vessel filled with 60 mL of water. After 1 h of stirring (500 rpm), the solid was filtered and dried under vacuum at room temperature.

2.1.3.2. Mechanical mixture. Two grams of silica was treated under flowing dry air at 500 °C for 5 h and then mixed at room temperature in a grinder with 160 mg of $Pt(NH_3)_4(OH)_2$ (0.5 mmol, metal loading: 5% w/w). The hydroxide solution was prepared as described elsewhere [1] and the solid $Pt(NH_3)_4(OH)_2$ was obtained by drying the solution at room temperature under vacuum.

2.1.3.3. Ion-exchanged silica. Fifteen grams of silica was treated under flowing dry air at 500 °C for 5 h and then introduced into a vessel filled with 450 mL of a $Pt(NH_3)_4(OH)_2$ solution (0.25 or 2.0 $g\,L^{-1}$, metal loading: 0.5 or 4% w/w). After 1 h of stirring (500 rpm), the solid was filtered, washed with 50 mL of water, and dried under vacuum at room temperature (see [1]). TEM picture of the 4% w/w sample shows small particles (1.5 to 2 nm diameter) with low contrast, similar to that previously reported for 4.5% w/w Pt samples after 25 °C vacuum drying $Pt(NH_3)_4(OH)_2/SiO_2$ in part I (Fig. 5a).

2.2. Characterization of the samples

The various samples were characterized by elemental analysis, H_2 or O_2 chemisorption, and electron microscopy, according to the procedure already described elsewhere [1].

Metal dispersion ($D = Pt_s/Pt$) was deduced from H_2 or O_2 chemisorption, assuming 1.8 H and 1.0 O per Pt_s [17,18]. The samples were reduced under flowing hydrogen at 500 °C and then out gassed under vacuum at 300 °C before H_2 chemisorption at 25 °C. They were then out gassed under vacuum at 300 °C and O_2 chemisorption was performed at 25 °C. We checked that the difference between dispersions measured with either H_2 or O_2 was never greater than 10% and the dispersion reported in this article is the average value.

Assuming that the metallic particles are of spherical shape [19], the platinum particle diameter (d) was deduced from electron microscopy observation. In the case of platinum, the dispersion is given by $D = 1.017/d$ if d is expressed in nanometers (nm).

3. Results

3.1. Thermodecomposition

3.1.1. Silica

A blank experiment with 2 g of pure silica was first performed under neutral, reducing, and oxidizing atmospheres. Only water was detected all along the spectrum and its concentration never exceeded 10^{-4} mol L^{-1} (STP). This means that the water signal shown in subsequent thermodecomposition spectra is only significant if it is higher than 10^{-4} mol L^{-1}.

3.1.2. Thermodecomposition of $Pt(NH_3)_4(OH)_2 \cdot xH_2O$–$SiO_2$ under neutral atmosphere

The thermodecomposition at increasing temperature under flowing Ar of a mechanical mixture of $Pt(NH_3)_4(OH)_2 \cdot xH_2O$ and SiO_2, and $Pt(NH_3)_4(OH)_2 \cdot xH_2O$ exchanged on silica are reported in Fig. 1.

After thermal decomposition, the elemental analysis of samples gave the Pt loading indicated in Table 1. The curves for the exchange samples were similar whatever the metal loading; however, they are very noisy at 0.5% w/w and only the curves corresponding to the greater Pt loading were reported in Fig. 1. For any sample, water was mostly evolved as a broad peak from 25 to 180 °C. NH_3 appeared at 90 °C

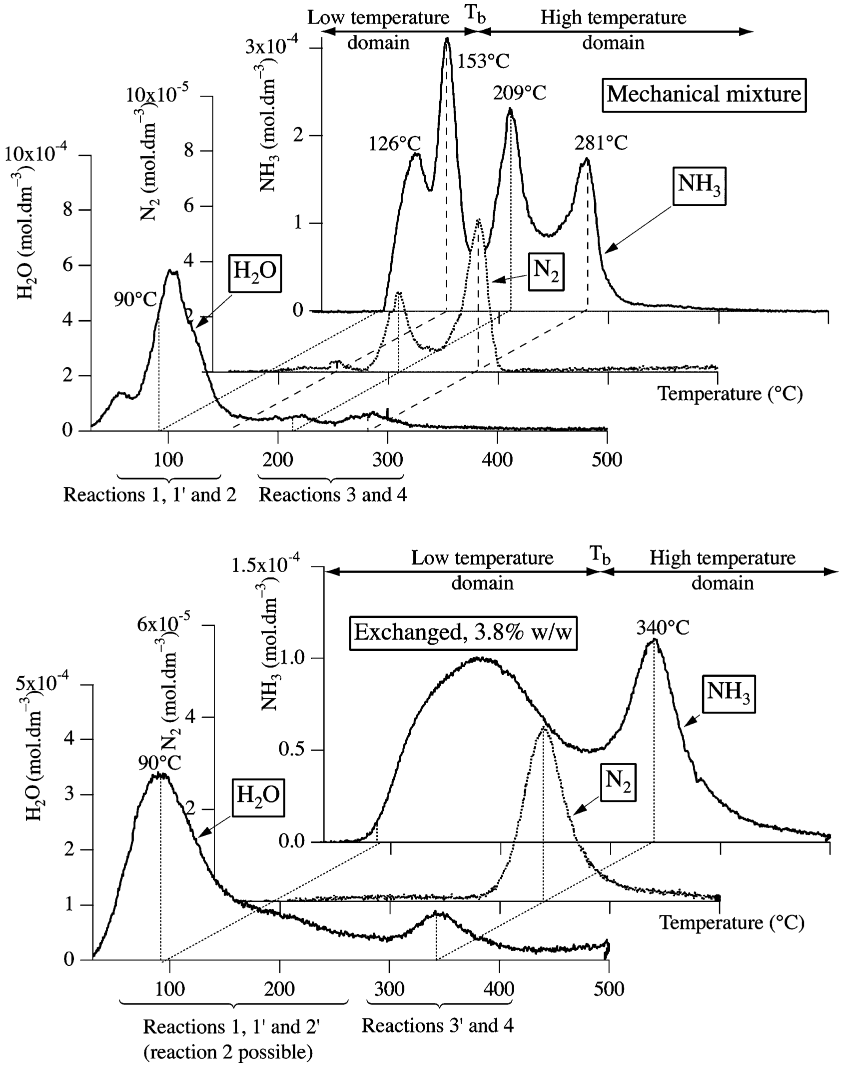


Fig. 1. Thermodecomposition of a thin layer (2 g) of a mechanical mixture of $Pt(NH_3)_4(OH)_2 \cdot xH_2O$ and SiO_2, and of an exchanged sample. Neutral gas flow (10% He, 90% Ar), 150 mL min^{-1}, 2 °C min^{-1}, from 25 to 500 °C.

Table 1
Amounts of gas species evolved per Pt atom under neutral atmosphere

	Species (x)			
	H_2O	NH_3	NH_3	N_2
Mechanical mixture, 5% w/w Pt				
T range (°C)	25–150	90–180	180–320	180–320
T_{max} (°C)	100	126 and 153	209 and 281	209 and 281
X/Pt	3.4	1.5	2.0	0.3
Exchanged samples: 3.8 and 0.5% w/w Pt				
T range (°C)	25–150	90–280	280–500	280–500
T_{max} (°C)	100	180	340	340
X/Pt (3.8% Pt)	4.5	2.3	1.4	0.4
X/Pt (0.5% Pt)	–	2.0	1.2	0.2

for both systems. The spectra can be divided into two main temperature domains depending on whether N_2 was evolved or not. The low temperature domain is made of the first two NH_3 peaks between 90 and 180 °C for the mechanical mixture and of a single broad peak between 90 and 280 °C for the exchanged catalyst. The second temperature domain is made of two peaks of NH_3 and N_2 between 180 and 320 °C for the mechanical mixture, and of one peak between 280 and 450–500 °C for the exchanged catalyst. Later on, T_b will represent the temperature at the boundary between the two domains. These domains have two important features: (a) the second domain is shifted by more than 100 °C toward higher temperatures for the exchanged catalyst; (b) the amount of nitrogen atoms recovered (as NH_3 and N_2) in each domains is approximately 50 ± 10% of the amount introduced (as N in $Pt(NH_3)_4(OH)_2 \cdot xH_2O$) for both systems.

The quantities of gases evolved in the various domains are reported in Table 1. They are calculated by integration of the curves versus time within the specified temperature range.

For both solids, the amount of water evolved between 25 and 150 °C is equivalent and the whole quantity of NH_3 initially present on the samples was evolved as NH_3 mainly and a small amount of N_2. The number of nitrogen atoms per Pt atom was found to be 4.1 for the mechanical mixture and 4.5 and 3.6 for the exchanged catalysts (3.8%) and (0.5%). The deviation from 4 will be discussed later.

3.1.3. Thermodecomposition of $Pt(NH_3)_4(OH)_2 \cdot xH_2O$–$SiO_2$ under reducing atmosphere

Fig. 2 illustrates the same experiment as Fig. 1 except that the gas contained 10% of hydrogen. After thermal decomposition, the elemental analysis of the samples gave the Pt loading indicated in Table 2. As in Fig. 1, peak locations are independent of Pt loading of the exchanged samples. Conversely, the lower the Pt loading, the more noisy the curves, and the less accurate the mass balances.

Here again, water was mostly evolved as a broad peak from 25 to 180 °C, and NH_3 appeared at 90 °C for both systems. Clearly, the presence of H_2 in the flowing gas promoted complex decomposition in a narrower and lower range of temperatures. Two temperature domains can again be guessed (T_b about 120–130 or 170–180 °C), although they are less well defined than under the neutral atmosphere. Here again, the exchanged catalyst is more reluctant to decomposition than the mechanical mixture. Conversely, no N_2 was detected.

The quantities of gases evolved in the various domains are reported in Table 2.

For both the mechanical mixture and the exchange catalyst, the amount of water evolved between 25 and 180 °C is equivalent and slightly above the amount observed under the neutral atmosphere. The number of nitrogen atoms per Pt atom was found to be 4.6 for the mechanical mixture and 5.1 and 3.7 for the exchanged catalyst (3.8%) and (0.5%). The deviation from 4 will be discussed later.

3.1.4. Thermodecomposition of $Pt(NH_3)_4(OH)_2 \cdot xH_2O$–$SiO_2$ under oxidizing atmosphere

Fig. 3 illustrates the same experiment as Fig. 1 using an oxidizing atmosphere (10% O_2, 10% He, 80% Ar). After thermal decomposition, the elemental analysis of the samples gave the Pt loading indicated in Table 3. As in Figs. 1 and 2, the effect of the Pt loading is essentially reflected in the signal/noise ratio.

For both cases, water evolved first as a broad peak from 25 to 150 °C and then as a peak with a maximum at 166 or 267 °C for the mechanical mixture and the exchanged catalyst, respectively. As usual, NH_3 appeared at 90 °C as a wide peak with a maximum around 116 or 180 °C. The most striking features are: (a) the synchronous narrow peaks of water, N_2, and N_2O at either 166 or 267 °C; (b) the trace level of free ammonia after these temperatures.

The quantities of gases evolved in the various domains are reported in Table 3.

The agreement between the amount of nitrogen atoms recovered as NH_3, N_2, or N_2O and the amount of platinum is excellent (4.0 N per Pt). The production of N_2 and N_2O coincides with the production of about 3.9 H_2O molecules per Pt atom. This means that there are from 5.5 to 5.9 other water molecules per Pt. This is in agreement with the 5 H_2O/Pt found under the reducing atmosphere.

3.2. Metal dispersion

3.2.1. Influence of metal loading and of the atmosphere

The dispersion of the metallic Pt particles obtained after reduction at 500 °C at two metal loading was measured by H_2 and O_2 chemisorption and electron microscopy. The results are reported in Table 4 and illustrated in Fig. 4.

In both cases, the dispersion of the metallic particles depends drastically on the nature of the gas. It is obvious that decomposition under oxidizing conditions gives very low dispersions whereas decomposition under reducing conditions gives high dispersions. Curiously, under neutral atmosphere, the dispersion of the metallic particles depends on metal loading. However, for high metal loading (3.8% Pt), the particles are grouped together as islands or strings. This

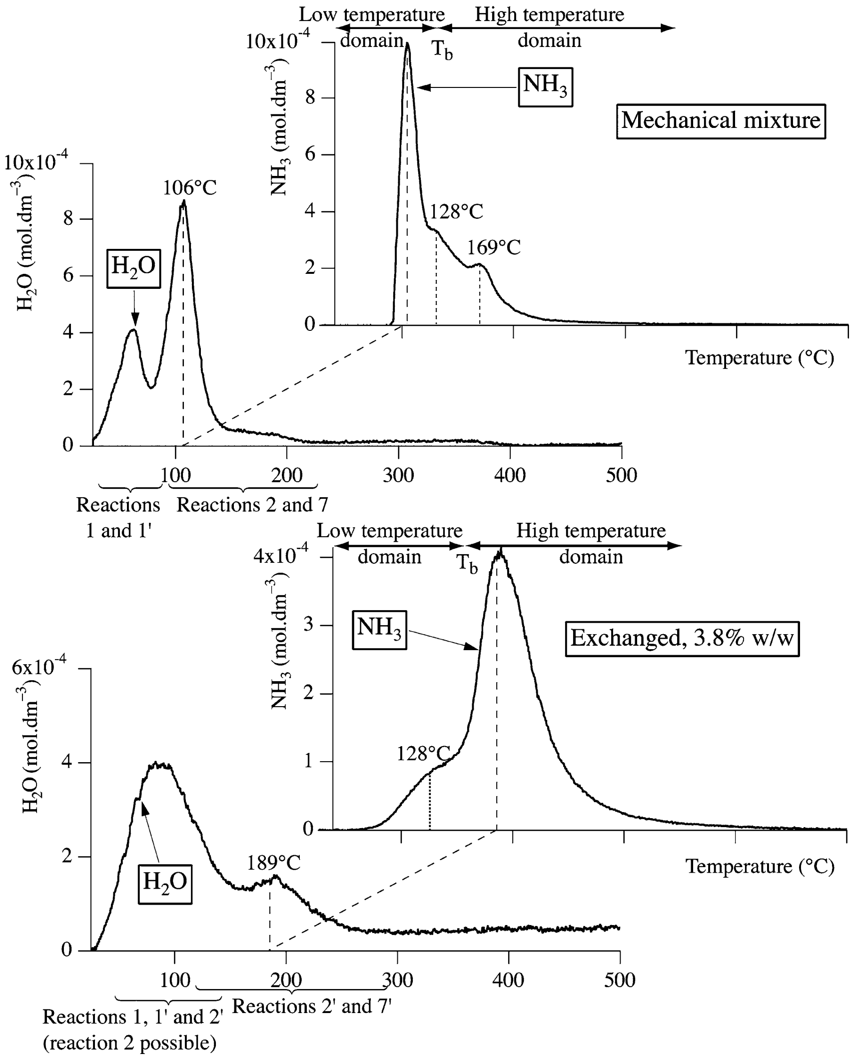


Fig. 2. Same as Fig. 1, reducing gas flow (10% He, 10% H_2, 80% Ar).

Table 2
Amounts of gas species evolved per Pt atom, under reducing atmosphere

	Species (x)	
	H_2O	NH_3
Mechanical mixture, 5% w/w Pt		
T range (°C)	25–150	90–250
T_{max} (°C)	106	106
X/Pt	5.0	4.6
Exchanged samples: 3.8 and 0.5% w/w Pt		
T range (°C)	25–150	90–350
T_{max} (°C)	90	189
X/Pt (3.8% Pt)	5.3	5.1
X/Pt (0.5% Pt)	–	3.7

structure was not observed when the catalyst (4.5% Pt) was decomposed under vacuum (see part I) [1].

3.2.2. *Influence of the final decomposition temperature*

Fig. 5 shows the drastic decrease of the dispersion with increasing final decomposition temperature under the oxidizing atmosphere. Conversely, the dispersion was found to be nearly independent of the final temperature under the reducing atmosphere. As expected, an intermediate behavior was observed with the neutral atmosphere.

Mass-spectrometric analyses of the effluent were performed during the reduction step. It was found that: (a) no nitrogen-containing species were detected when the sample was previously decomposed up to 500 °C under a neutral, reducing, or oxidizing atmosphere; (b) a broad NH_3 peak extending from 150 to 300 °C (maximum about 190–200 °C) was detected for samples previously decomposed under the neutral atmosphere up to 300 °C or under the oxidizing atmosphere up to 250 °C. This peak was similar to the NH_3 peak obtained above T_b under the reducing atmosphere.

4. Discussion

The mass spectrograms shown in Figs. 1 to 3 clearly illustrate the differences in behavior of the samples according

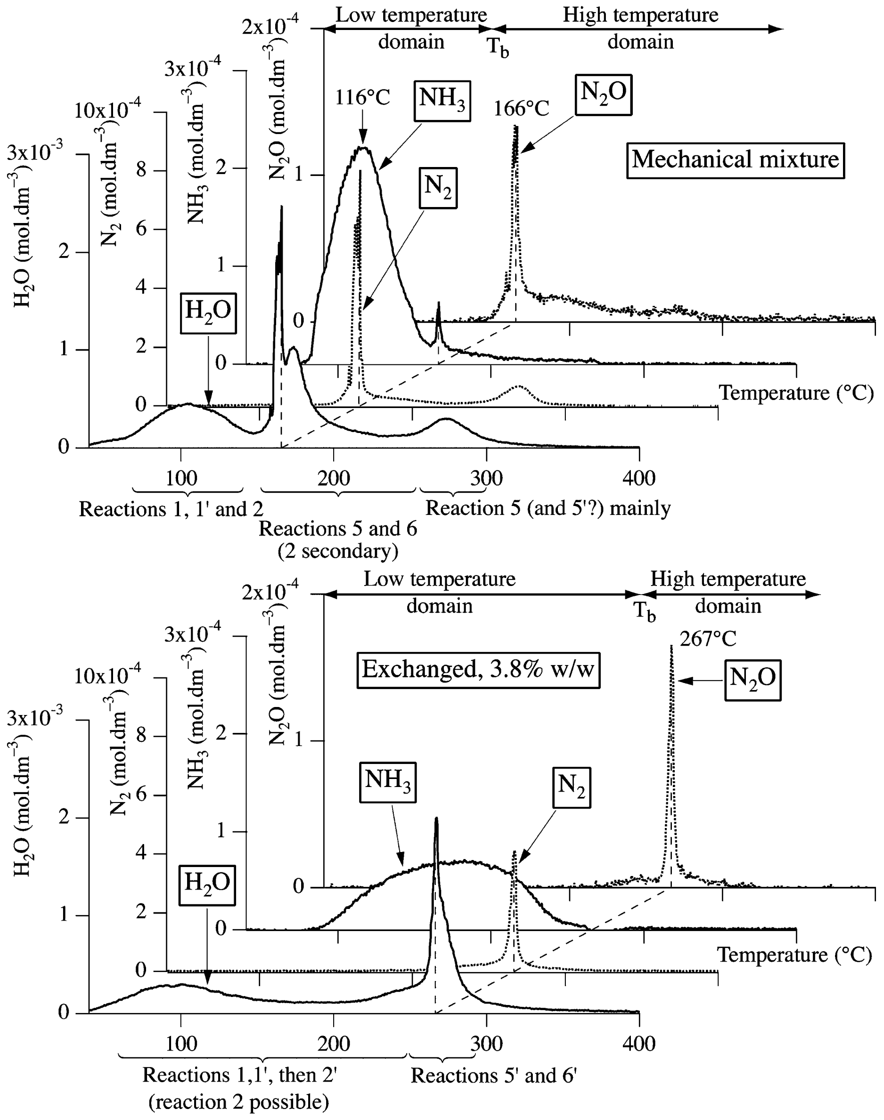


Fig. 3. Same as Fig. 1, oxidizing gas flow (10% He, 10% O_2, 80% Ar).

Table 3
Amounts of gas species evolved per Pt atom, under oxidizing atmosphere

	Species (x)				
	H_2O	H_2O	NH_3	N_2	N_2O
(a) Mechanical mixture, 5% w/w Pt					
T range (°C)	25–150	150–350	80–150	150–300	150–300
T_{max} (°C)	100	166	116	166	166
X/Pt	3.6	6.2	1.4	0.9	0.4
Exchanged samples: (b) 3.8 and (c) 0.5% w/w Pt					
T range (°C)	25–150	150–500	80–260	180–500	180–500
T_{max} (°C)	100	267	180	267	267
X/Pt (3.8% Pt)	4.1	5.3	1.4	0.9	0.4
X/Pt (0.5% Pt)	–	–	1.6	0.8	0.4

Table 4
Pt dispersions according to metal loading and gas nature

Metal loading	Atmosphere		
(w/w)	Neutral	Reducing	Oxidizing
0.5%	42%	80%	26%
3.8%	72%	70%	26%

to the method of preparation (exchanged complex or mechanical mixture) and/or the atmosphere under which they were treated. The quantitative analyses of the spectra are more difficult. One may observe that the uncertainty in the mass balances reported in Tables 1 to 3 is about 20% (from the amount of total nitrogen recovered per platinum atom). This can be attributed to baseline drift, calibration uncertainty, interference between the various m/e of the products, and determination of metal loading by elemental analysis. As a consequence, the mass balances can only be used for comparing orders of magnitude. Nevertheless, we can observe that the amounts of NH_3, N_2, and N_2O evolved are proportional to the Pt loading.

After drying at room temperature under vacuum, the platinum tetrammine hydroxide complex forms $[Pt(NH_3)_4(OH)_2$

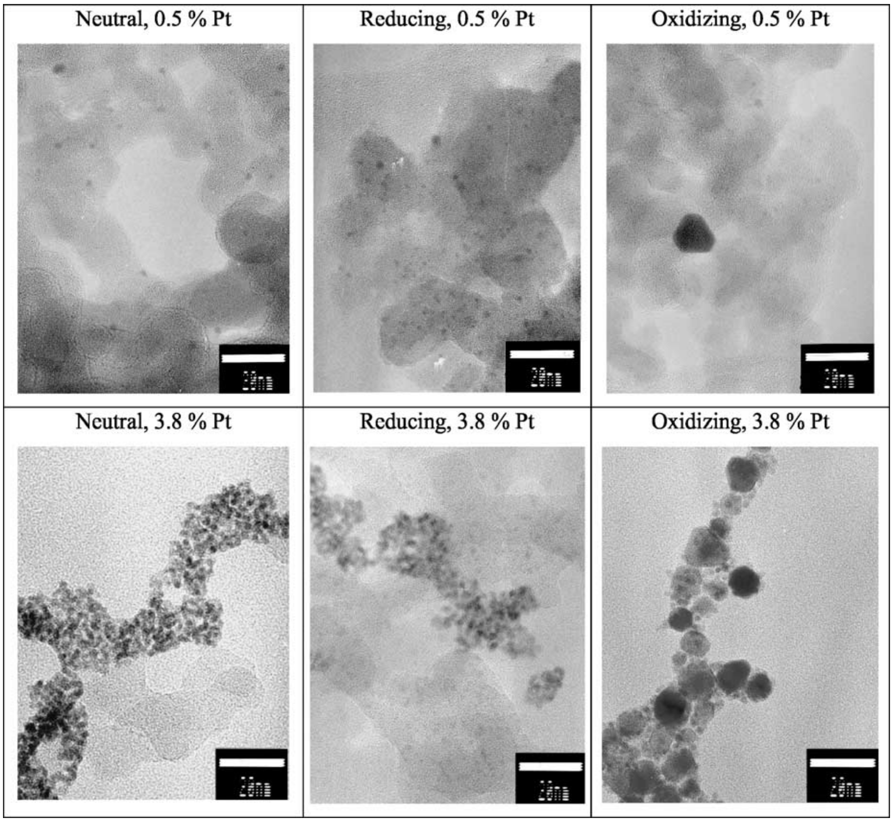


Fig. 4. TEM pictures of samples after treatment under neutral, reducing, or oxidizing atmosphere.

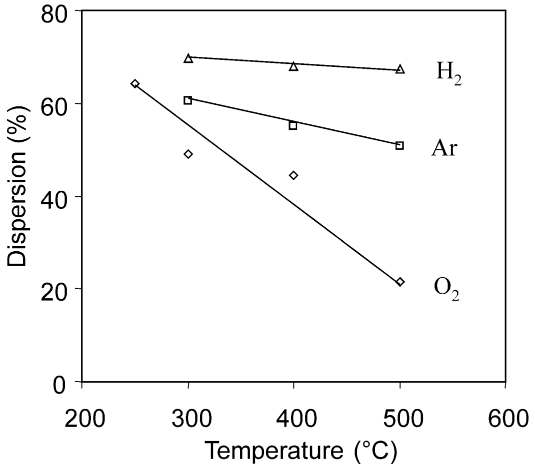


Fig. 5. Dispersion of the samples obtained after decomposition under neutral (Ar), oxidizing (O_2), and reducing (H_2) atmospheres at increasing temperature, followed by reduction under flowing hydrogen at 500 °C. Metal loading: 1.5%.

$\cdot\, xH_2O]_n$ clusters, regardless of whether they are supported on silica or unsupported (see part I) [1].

Figs. 1 to 3 show that the decomposition profiles of the $[Pt(NH_3)_4(OH)_2 \cdot xH_2O]_n$ clusters are similar to those observed with the mechanical mixture, but a clear shift of the peaks toward high temperature is observed for the exchanged samples. It is obvious that above ca. 150 °C, the exchanged complex is stabilized by the support which means that it exhibits chemical interaction with the surface $\equiv$SiOH groups, as it will be explained below [Eq. (2′)].

In the range 25–180 °C, dehydration of the silica surface occurs together with dehydration of the platinum complex to give $[Pt(NH_3)_4(OH)_2]_n$ clusters for both the mechanical mixture and the exchanged complex. Referring to a single Pt atom or $\equiv$SiOH group, this dehydration process obeys Eqs. (1) and (1′) which explain the broad water peak in the low-temperature domain whatever the sample and feed gas:

$$Pt(NH_3)_4(OH)_2 \cdot xH_2O \rightarrow Pt(NH_3)_4(OH)_2 + xH_2O, \qquad (1)$$

$$\equiv SiOH \cdot x'H_2O \rightarrow \equiv SiOH + x'H_2O. \qquad (1')$$

Under both neutral or oxidizing atmospheres, about half of the NH_3 ligands are lost in the low-temperature domain whereas the remaining ligands are lost at a much higher temperature together with N_2 (and N_2O). The temperature boundary, T_b, between these domains depends on the solid and on the feed gas composition. Comparing the mechanical mixtures and the exchanged samples shows that the low-temperature domains are more similar than the second domains. We may thus interpret the results as follows: Between 90 and T_b, under argon or oxygen (Figs. 1 and 3), the $[Pt(NH_3)_4(OH)_2]_n$ clusters of the mechanical mixture lose about half of the NH_3 ligands and the remaining water to form $[OPt(NH_3)_y]_n$ species, following Eq. (2):

$$Pt(NH_3)_4(OH)_2 \rightarrow OPt(NH_3)_y + (4-y)NH_3 + H_2O, \quad y \approx 2. \tag{2}$$

In this low temperature domain, the $[Pt(NH_3)_4(OH)_2]_n$ clusters resulting from the exchange process could melt on the surface above 100 °C and then could become “rafts” (See [1]), where Pt atoms are close to the oxygen atoms of the silanol groups, and form $(\equiv SiO)_2Pt(NH_3)_y$ species, following Eq. (2′):

$$Pt(NH_3)_4(OH)_2 + 2\equiv SiOH \rightarrow (\equiv SiO)_2Pt(NH_3)_y + (4-y)NH_3 + 2H_2O, \quad y \approx 2. \tag{2′}$$

This was already observed when the tetrammine complex decomposes under vacuum (see part I, EXAFS studies) [1]. Later on, we will speak of “reactions” like (2) and (2′). However, one must keep in mind that these “reactions” are no more than atom balances with no mechanistic meaning. In other words, the chemical formulas cited in the reactions do not reflect necessarily the structure of the species.

It would be hazardous to claim that reactions (2) and (2′) occur alone in the mechanical mixture and on the exchanged catalyst, respectively. The mechanical mixture was obtained in a grinder under ambient conditions and traces of exchanged complex cannot be excluded owing to ambient humidity; furthermore a fraction of the complex in mechanical contact with silica may react according to (2′). It is evident that reactions (2) and (2′) could also compete on the exchanged catalyst. For reactions (2) and (2′), one or two water molecule(s) per Pt atom should be evolved in the first domain, respectively. Tables 1 and 3 shows that more water is released from the exchanged catalyst than from the mechanical mixture in the range 25–150 °C. Unfortunately, the difference falls within the uncertainty of the water mass balances.

Above T_b, under argon (Fig. 1), the remaining NH_3 ligands are progressively removed from the complex, leading to $Pt^{(0)}$ and PtO particles or particles made of a mixture of metal and oxide (part I) [1]. PtO is produced either by reaction (3) (mechanical mixture) or reaction (3′) (exchanged catalyst):

$$OPt(NH_3)_y \rightarrow PtO + yNH_3, \tag{3}$$

$$(\equiv SiO)_2Pt(NH_3)_y \rightarrow PtO + yNH_3 + \equiv Si\text{–}O\text{–}Si\equiv. \tag{3′}$$

The presence of small amounts of dinitrogen and water indicates that a part of PtO is reduced by NH_3, to form $Pt^{(0)}$, H_2O, and N_2 [Eq. (4)] as was previously proposed (part I) [1,13,20].

$$3PtO + 2NH_3 \rightarrow 3Pt + 3H_2O + N_2. \tag{4}$$

Comparing the heights of the H_2O and N_2 peaks at 340 °C (Fig. 1) gives a ratio H_2O/N_2 of 2.4 which agrees with reaction (4) within 20%.

Combining (3) and [4] and assuming complete reduction of PtO and $y = 2$, one obtains the following balance:

$$(\equiv SiO)_2Pt(NH_3)_2 \rightarrow Pt + \frac{4}{3}NH_3 + \frac{1}{3}N_2 + H_2O + \equiv Si\text{–}O\text{–}Si\equiv. \tag{4′}$$

From Table 1 we observe 1.4 NH_3 and 0.4 N_2 per Pt instead of 4/3 and 1/3, respectively following (4′). It is thus concluded that most of PtO is reduced to $Pt^{(0)}$ in the experiment of Fig. 1. As a consequence the dispersion is almost as high as under a reducing atmosphere as shown by Table 4 (metal loading 3.8%). The effect of NH_3 partial pressure on the extent of partial reduction is further demonstrated by the decomposition under vacuum. In the latter case, the partial pressure was very low and only about 10% of the platinum was reduced (Part I) [1]. Similarly, at low metal loading, the partial pressure of NH_3 is low when the sample is reduced under an inert atmosphere, then, the extent of partial reduction and thus the dispersion are low (Table 4, metal loading 0.5%). All these quantitative observations give support to the proposed description.

Under oxygen (Fig. 3), at 166 °C (mechanical mixture) or at 267 °C (exchanged sample), there is a sudden oxidation of the remaining NH_3 ligands with formation of H_2O, N_2, and N_2O. These reactions are strongly exothermic and the decomposition is very fast; the thermocouple at the bed inlet recorded an overshoot of several degrees centigrade at the same time. The overall mechanism can be described mainly by Eqs. (5) and (6) for the mechanical mixture and by Eqs. (5′) and (6′) for the exchanged sample:

$$OPt(NH_3)_y + \frac{3y}{4}O_2 \rightarrow PtO + \frac{3y}{2}H_2O + \frac{y}{2}N_2, \tag{5}$$

$$(\equiv SiO)_2Pt(NH_3)_y + \frac{3y}{4}O_2 \rightarrow PtO + \equiv Si\text{–}O\text{–}Si\equiv + \frac{3y}{2}H_2O + \frac{y}{2}N_2, \tag{5′}$$

$$OPt(NH_3)_y + yO_2 \rightarrow PtO + \frac{3y}{2}H_2O + \frac{y}{2}N_2O, \tag{6}$$

$$(\equiv SiO)_2Pt(NH_3)_y + yO_2 \rightarrow PtO + \equiv Si\text{–}O\text{–}Si\equiv + \frac{3y}{2}H_2O + \frac{y}{2}N_2O. \tag{6′}$$

These reactions are only indicative of the mechanism. Nothing excludes that the complex does release gas-phase NH_3 which is then rapidly oxidized to N_2 and N_2O. The last water and nitrogen peaks of the mechanical mixture are observed at $T \approx 270$ °C, i.e., close to the sharp peak of the exchanged catalyst at $T = 267$ °C (see Fig. 3). This can be explained by exchange during grinding or reaction (2′) at the mechanical contact between the complex and silica.

Under hydrogen (Fig. 2), the complex fully decomposes at temperatures lower than under neutral or oxidizing atmospheres. The two temperature domains still exist, although they are overlapping. The interpretation used for neutral and oxidizing atmospheres can thus be extended. At about 100–120 °C reactions (2) and (2′) take place leading to

$OPt(NH_3)_y$ and $(\equiv SiO)_2Pt(NH_3)_y$. At higher temperatures (T_b about 120 °C, mechanical mixture; T_b about 180 °C, exchanged sample) these species decomposes according to Eqs. (7) and (7′) where adsorption of H on Pt is ignored.

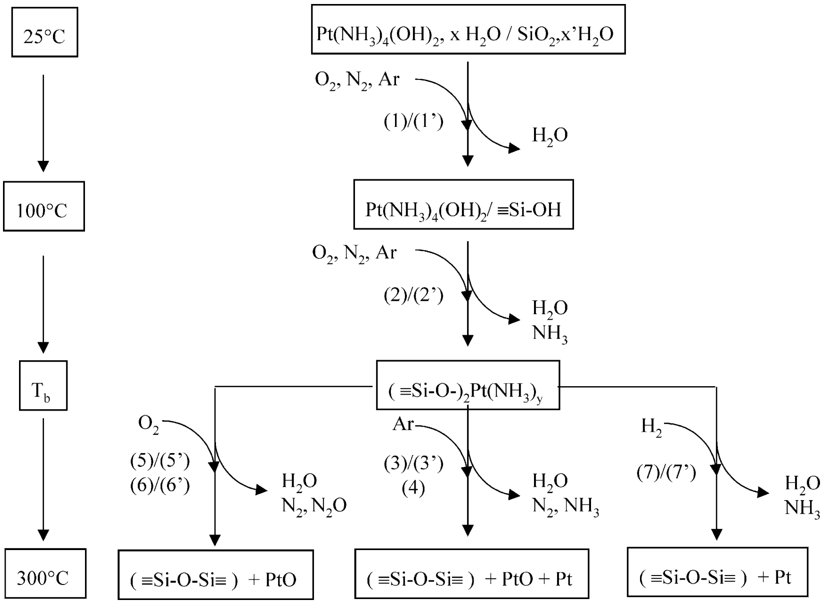
$$OPt(NH_3)_y + H_2 \rightarrow Pt + H_2O + yNH_3, \tag{7}$$

$$(\equiv SiO)_2Pt(NH_3)_y + 2H_2 \\ \rightarrow Pt + \equiv Si\text{–}O\text{–}Si\equiv + yNH_3 + H_2O. \tag{7′}$$

The overlap between the temperature domains may be explained by a decomposition catalyzed by reduced platinum or activation energies of reactions (7) and (7′) smaller than those of (3), (3′), (5), (5′), (6) and (6′). The heights of the water and ammonia peaks give support to this interpretation. For the mechanical mixture, the heights of the peaks at 106 °C give a ratio H_2O/NH_3 of 0.9. According to Eq. (2) this would imply $y = 2.9$. Conversely, the heights of the peaks at 189 °C for the exchanged catalyst give a ratio of 0.4 which leads to $y = 2.5$ according to (7′). It must be noted that because of peak overlap there may be some error in the interpretation of peak heights. However, considering reactions (2) and (2′) (any atmosphere), (3), (3′), and (4) (neutral atmosphere), (5), (5′), (6), and (6′) (oxidizing atmosphere), (7) and (7′) (reducing atmosphere) and inserting y is close to 2 lead to a unified and coherent interpretation summarized by Scheme 1.

According to our preparation method, two key steps govern the size of the resulting metallic particles. The first one takes place between 100 and 150–200 °C (i.e., T_b) and it involves reactions (1), (1′), (2′), and to a lesser extent reaction (2). Reaction (2′) is responsible for anchoring of the complex and thus determines the starting particle size. Since y is found close to 2, one may assume that the anchoring species is $(\equiv SiO)_2Pt(NH_3)_2$. The second key step is the decomposition of this species above 150–200 °C which leads to either metallic or oxide particles. Dispersion as high as 80% can be obtained under a reducing atmosphere at a temperature as high as 500 °C while, under the same conditions, an oxidizing atmosphere leads to a low dispersion. These results are in agreement with the works of Benesis et al. [10], Brunelle et al. [7], or Dorling et al. [6] who found that smaller particles were obtained by decomposing the exchanged tetrammine complex under reducing conditions. Conversely, they contradict the observations of Gonzalez and co-workers [2–5], and they partially agree with those of Oudenhuijzen et al. [13].

Gonzalez and co-workers [2–5] showed that small particles can be obtained under oxidizing conditions whereas a reducing atmosphere leads to larger particles. These authors suggested that under an oxidizing atmosphere, there was formation of Pt^{2+} species in strong interaction with the support and that under a reducing atmosphere, the platinum hydride diammine formed was very mobile on the surface, leading to large metallic particles. Oudenhuijzen et al. [13] used the same explanation for comparing decomposition under Ar/He and H_2. The work presented here does not allow proposing the formation of platinum hydride diammine since no water would be released when it decomposes (see water peak at 189 °C, Fig. 2). Conversely, formation of mobile PtO under an oxidizing atmosphere is known [21,22]. Bulk PtO does not melt but decomposes at 550 °C and it is difficult to propose that large PtO particles can migrate quickly on the silica surface. If we consider that the heat of combustion of NH_3 is about 293 kJ mol^{-1} (for comparison, $H_2 + \frac{1}{2}O_2 = H_2O$ is 286 kJ mol^{-1}), the exothermicity of the ligand combustion could trigger the sintering of the newly formed oxide. Fig. 6 shows the dispersion of the metallic particles reported in the literature for oxidizing atmospheres, as a function of the final decomposition temperature. All the



Scheme 1. Simplified overview of the changes on the surface during treatments of the exchanged sample with the three gasses.

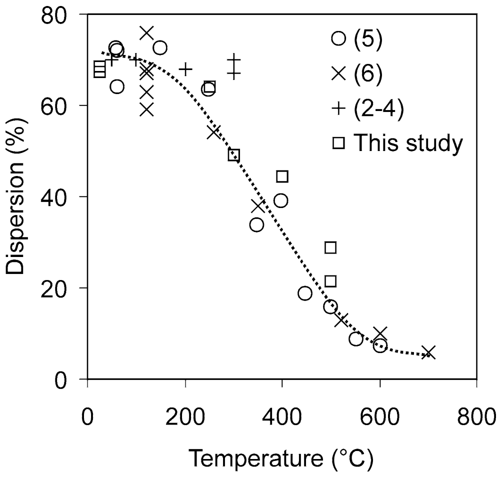


Fig. 6. Dispersion of the metallic particles as a function of the final decomposition temperature under flowing oxidizing atmosphere, from literature data and from this work.

results point toward the negative effect of too a high final temperature.

It is worth noting that dispersions as high as 70% were obtained under oxidizing atmospheres provided that the final temperature does not exceed 200–250 °C, i.e., just below the temperature at which NH_3 oxidation is “fired” (see Fig. 3). This means that samples decomposed under oxidizing atmospheres up to 200–250 °C are only partially decomposed into anchored $(\equiv SiO)_2Pt(NH_3)_y$. Further reduction above 250 °C then reproduces the decomposition under a reducing atmosphere and leads to stable and small Pt particles. This is supported by the effluent analysis during reduction (see Section 2.1.3). It is then clear that the increase in particle size which occurs above 350 °C, under oxidizing atmospheres, is due to mobile PtO species as proposed above. If this interpretation reconciles the results of Gonzalez and co-workers [2–5] with those of other authors, it does not explain why Gonzalez and co-workers obtained low dispersions under a reducing atmosphere. Under a neutral atmosphere, the exchanged complex decomposes above 300 °C and particles of both PtO and $Pt^{(0)}$ are formed, depending on metal loading. It is then logical that the dispersion measured after treatment above 300 °C under a neutral atmosphere lies between that measured under reducing and oxidizing atmospheres (Fig. 5).

Oudenhuijzen et al. [13] used mass spectrometry and Quick EXAFS spectroscopy to study the decomposition of $Pt(NH_3)_4(NO_3)_2$. These authors observed that complete decomposition of the $Pt(NH_3)_4^{2+}$ complex under hydrogen occurs at a much lower temperature (150–200 °C) than under argon/helium (200–250 °C). They also observed, as we did, that decomposition under oxygen gives a low dispersion. These observations partially agree with our results. Conversely, the thermo decomposition profiles measured by Oudenhuijzen et al. under argon/helium and oxygen did not show the peaks that we observed in the range 250–350 °C (see Figs. 1 and 3). If we compare the temperature ranges, Oudenhuijzen’s spectrograms under O_2 and Ar/He are more reminiscent of our results obtained with the mechanical mixtures than those obtained with the exchanged samples. The authors explained their results by the formation of HNO_3 and $Pt(NH_3)_4(OH)_2$ during impregnation and drying, and then of NH_4NO_3 and $Pt^{(0)}$ (under H_2 and Ar/He) during the early stage of the decomposition process. The subsequent decomposition of NH_4NO_3 is then responsible for various gaseous species according to the atmosphere. If they are true, the decomposition of their $Pt(NH_3)_4(OH)_2$ intermediate should be similar to that observed in our experiments although they are not. We have no explanation for these differences; we can only invoke the nature of the counteranion (NO_3^- versus OH^-), the impregnation method (incipient wetness versus solid-liquid suspension), and the nature of the support (porous silica versus nonporous aerosil).

Let us now compare the results obtained by decomposing the complex either under a reducing atmosphere or under vacuum (see Part I) [1]. We can observe that the size of the metallic particles measured by electron microscopy and the dispersion of the samples measured by chemisorption of H_2 and O_2 are the same in both cases, respectively, about 1.5 nm and 70%. However, as demonstrated by electron microscopy, the metallic particles are isolated from each other and regularly distributed on the support when decomposition is done under vacuum (see Part I) [1] and they are, in some cases, agglomerated when decomposition is performed under flowing gas (Fig. 4). There is no clear explanation for this observation. It is only suggested that some gaseous species (e.g., water) could be responsible for the metallic particle mobility under nonvacuum conditions. Conversely, under vacuum, the partial pressure (of water?) would be to small to promote mobility.

5. Conclusion

From the results of the two parts of this study, the decomposition of exchanged platinum tetrammine complex under flowing neutral, reducing, or oxidizing atmosphere can be interpreted by a stepwise process.

- First, upon drying up to about 100 °C, the exchanged complex loses the electrostatic interaction with the $\equiv SiO^-$ groups and then loses water to give $[Pt(NH_3)_4(OH)_2]_n$ clusters.
- At about 100 °C, these clusters melt on the surface to form “rafts,” where Pt atoms are close to the oxygen atoms of the silanol. The surface complex loses some NH_3 ligands and forms $(\equiv SiO)_2Pt(NH_3)_y$ species anchored to the surface with y of the order of 2. This step is independent of the nature of the flowing gas. The melting/anchoring process freezes the particle size. Since the size is independent of whether the complex is supported or not, this is the size of the clusters obtained upon drying up to about 100 °C.

- The final step takes place at a higher temperature and involves the loss of the remaining NH_3 ligands. It depends on the nature of the flowing gas:
  - Above 250 °C under oxygen, there is a sudden oxidation of the NH_3 ligands with formation of PtO particles. When the temperature further increases, the small and mobile PtO particles merge which leads to a low metal dispersion. Alternatively, the sudden and exothermic NH_3 oxidation may promote particle sintering. The higher the final temperature, the higher the mobility of PtO and the lower the dispersion. Below 250 °C, the complex is not fully decomposed.
  - Between 150 and 250 °C under a hydrogen flow, NH_3 and H_2O are released while $Pt^{(0)}$ is formed. The particle size remains that defined at the previous step. H_2O release in the high temperature domain proves that platinum hydride diammine cannot be a significant intermediate species.
  - Above 300 °C under argon, NH_3 is released while PtO is formed. However, a fraction of NH_3 reduces PtO to $Pt^{(0)}$. Since both $Pt^{(0)}$ and PtO are coexisting, the particle size is intermediate between those obtained under reducing and oxidizing atmospheres. For a given gas flow rate, the higher the metal loading, the higher the partial pressure of released NH_3. It is thus logical that the extent of self-reduction, and thus the dispersion increase with metal loading.

According to this interpretation, decomposition of $Pt(NH_3)_4(OH)_2$ under a reducing atmosphere is the best preparation method which leads to dispersions of 70–80% for metal loadings up to 5% w/w. Decomposition under a neutral atmosphere is efficient only when significant self-reduction takes place. In that case, decomposition under reduced pressure is not recommended. Decomposition under an oxidizing atmosphere above 250 °C gives the least dispersed catalysts. Oudenhuijzen et al. [13] who studied the decomposition of $Pt(NH_3)_4(NO_3)_2$ found that the best dispersion was obtained under Ar/He and suggested that $Pt(NH_3)_4(OH)_2$ be used to avoid the "multistep reduction" during autoreduction. Our results show that autoreduction is not sufficient especially at low metal loading.

Under reducing conditions, the final dispersion is independent of the metal loading of the catalyst. However, for high loading, Pt particles may agglomerate whereas agglomeration is not observed if decomposition is performed under vacuum (see Part I). Under pressure, the higher the metal loading, the higher the partial pressure of the released species in the catalyst bed. This means that agglomeration is due to one of the released species. Since water is a candidate, further experiments with controlled water vapor pressure would be necessary. If water is responsible for agglomeration, higher gas flow rates should be used when decomposing the catalyst under hydrogen. All the observations point toward a particle size defined at drying by the size of $[Pt(NH_3)_4(OH)_2]_n$ clusters deposited on the silica surface. It is not clear which process is responsible for the size of these clusters.

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