Journal of Catalysis **209,** 135–144 (2002)
doi:10.1006/jcat.2002.3616

Preparation of a Pt/SiO_2 Catalyst

I. Interaction between Platinum Tetrammine Hydroxide and the Silica Surface

A. Goguet,* M. Aouine,† F. J. Cadete Santos Aires,† A. De Mallmann,‡ D. Schweich,* and J. P. Candy‡,[1]

**Laboratoire de Génie des Procédés Catalytiques (UMR CNRS-CPE), ESCPE Lyon, 69616 Villeurbanne, France; †Institut de Recherche sur la Catalyse (UPR 5401-CNRS), 2 Av. Albert Einstein, 69626 Villeurbanne, France; and ‡Laboratoire de Chimie Organométallique de Surface (UMR CNRS-CPE), ESCPE Lyon, 69616 Villeurbanne, France*

Received November 21, 2001; revised February 15, 2002; accepted March 22, 2002

This paper describes a detailed study of exchange, drying, and thermal decomposition processes utilized to prepare Pt/SiO_2 catalysts from Aerosil silica (Degussa) and platinum tetrammine hydroxide. It is shown that exchange is complete 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 ligands upon drying at 25°C under vacuum. At 100°C and under vacuum the exchanged complex forms clusters of $[Pt(NH_3)_4(OH)_2]_n$ deposited on the surface. Upon increasing the temperature under reduced pressure, the adsorbed complex looses the NH_3 ligands progressively. At 200°C, about half the ammonia ligands are lost, and at 300°C the complex is fully decomposed, mainly into PtO particles of 1–2 nm. About 10% of PtO is reduced to $Pt^{(0)}$ by NH_3 decomposition. 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 suggest that drying is the crucial step in the preparation of a Pt/SiO_2 catalyst. This result was unexpected, because none of the earlier studies found this step to be crucial. The proposed procedure leads to a metal dispersion of $65 \pm 5\%$, which is close to the maximum value reported in the literature. The second part of this article presents time-resolved mass spectrometric analyses of the species released during thermal treatment in various atmospheres. They support the conclusions given here. © 2002 Elsevier Science (USA)

Key Words: **Pt/SiO_2; platinum particles preparation; platinum tetrammine hydroxide.**

1. INTRODUCTION

The exact preparation method of many catalysts is still a matter of know-how, even in the simple case of a monometallic catalyst supported on alumina or silica. For this type of simple catalyst, activity and selectivity are mainly governed by the size of the metal particles. It is still unknown which step(s) in the preparation method is (are) predominantly responsible for the size of the particles. For a given carrier and metal precursor, the following procedure can be followed: pretreatment of the carrier, "adsorption" of the precursor onto the surface, drying, thermal decomposition (in various atmospheres or under vacuum), and eventually reduction. A Pt/SiO_2 catalyst such as EUROPT-1 is probably the simplest catalyst, which illustrates this problem (1). Table 1 lists the wide range of operating conditions reported in the literature for preparing this catalyst using $Pt(NH_3)_4^{2+}$ as the precursor. As a result, metal dispersion varies from 5 to no more than 80%. Finally, this dispersion is often found to depend on the amount of catalyst prepared. Thus, it seems obvious that the variability in these conditions and results reveals a lack of a clear understanding of the mechanisms involved in the successive preparation steps.

Although Pt/SiO_2 is not a typical industrial catalyst, it is widely used as a model catalyst in basic research. Thus, understanding and controlling the preparation of this catalyst is a relevant problem. This paper describes a detailed study of the exchange, drying, and thermal decomposition processes utilized to prepare a Pt/SiO_2 catalyst from aerosil silica (Degussa) and platinum tetrammine hydroxide. This first paper (part I) is devoted to the analysis of (i) the kinetics of the exchange reaction between the silanol groups of the silica surface and the platinum tetrammine hydroxide in the aqueous solution, (ii) the consequences of the drying process, and (iii) the various species formed during the decomposition of the exchanged species at increasing temperature under reduced pressure. The second paper (part II) will describe more realistic preparation conditions using time-resolved mass spectrometric analysis of the gaseous products that evolve during the drying and thermal decomposition steps in various atmospheres.

2. BRIEF LITERATURE REVIEW

It is widely recognized that dissolved $Pt(NH_3)_4^{2+}$ cations interact with the silica surface via ion exchange provided that the pH of the solution is high enough. According to

---

[1] To whom correspondence should be addressed. E-mail: candy@mulliken.cpe.fr.

TABLE 1

Typical Experimental Conditions Reported in the Literature for the Preparation of Pt/SiO_2 Catalysts

Step	Conditions	References
Impregnation	From 3 min to 17 days	8, 9, 11, 15, 17–19
Drying	From 2 to 20 h; from 25 to 120°C	7–9, 11, 15, 17–19, 23
Thermal decomposition	O_2/inert or inert gas; from 0.5 to 12 h; from 50 to 700°C (various temperature programs)	7, 8, 15, 17–21, 23
Reduction	H_2/inert; from 0.5 to 5 h; from 300 to 800°C (various temperature programs)	7–9, 15, 17–20, 22, 23

Brunelle (2), the charge in a silica surface is close to 0 from pH 1–7, and surface ionization becomes significant above pH 7 according to

$$\equiv\text{Si–OH} + \text{OH}^- \leftrightarrows \equiv\text{Si–O}^- + \text{H}_2\text{O}.$$

However, at pH greater than 10 a significant amount of silica dissolves (2). It is, thus, obvious that a cationic platinum precursor may interact with the silica surface within a rather narrow range of basic pH. Platinum tetrammine hydroxide, referred to as Reiset base (3), is a white powder at room temperature, and it melts at 110°C (4). In water solution, it is a strong base and appears to be a good precursor for Pt/SiO_2 catalyst (2).

Most authors (2, 5–8) suggest that adsorption of dissolved $Pt(NH_3)_4(OH)_2$ is described by the cationic exchange reaction

$$2(\equiv\text{Si–O}^-, \text{H}^+) + (\text{OH}^-)_2, \text{Pt}(\text{NH}_3)_4^{2+} \overset{\text{H}_2\text{O}}{\leftrightarrows} (\equiv\text{Si–O}^-)_2, \text{Pt}(\text{NH}_3)_4^{2+} + 2(\text{OH}^-, \text{H}^+).$$

This reaction can be very fast and numerous authors suggest that a reaction time as short as 3 min may be enough to reach equilibrium. However, although no detailed study was undertaken, other authors (2, 9) observed that after 2 days of solid–liquid contact, the homogeneity of the platinum distribution over the silica surface clearly improves. It was also proposed (5, 10) that the addition of NH_4^+ ions to the solution slows down the reaction as a result of the following exchange reaction:

$$2(\equiv\text{Si–O}^-, \text{NH}_4^+) + (\text{OH}^-)_2, \text{Pt}(\text{NH}_3)_4^{2+} \overset{\text{H}_2\text{O}}{\leftrightarrows} (\equiv\text{Si–O}^-)_2, \text{Pt}(\text{NH}_3)_4^{2+} + 2(\text{OH}^-, \text{NH}_4^+).$$

Some authors (11, 12) suggested that the exchange of the platinum complex on the silica surface may occur with the loss of two NH_3 ligands and the formation of the $(\equiv Si–O)_2Pt(NH_3)_2$ surface complex.

After exchange, the solid is recovered, generally by filtration, and dried, commonly at about 100°C in an oven. This preparation step is usually considered to be unimportant (13, 14) and, to the best of our knowledge, a fundamental study of the processes that take place during drying has not been made.

Following the drying step, the supported precursor is thermally decomposed in order to obtain platinum or platinum oxide particles on the surface. Previous studies report decomposition performed in flowing oxidizing (7, 8, 15–21), neutral (15, 16), reducing atmospheres (7–9, 15, 17–20, 22, 23) or under vacuum (9). Even if the conditions under which those thermal treatments are performed are usually specified (gas flow rate, temperature program...), no unambiguous fundamental studies of the behavior of the precursor during those treatments have been carried out.

3. EXPERIMENTAL

3.1. Materials

The silica Aerosil 200 support was purchased from Degussa. Its surface area, measured by nitrogen adsorption (77 K, N_2, B.E.T., Micromeretics ASAP 2010) is 194.2 $m^2 \cdot g^{-1}$. The adsorption–desorption isotherms showed that this silica is nonporous (Type II isotherms with no hysteresis loop). Although the individual nonporous silica particles are about 20 nm in diameter, the bulk powder is made up of aggregates of about 200 elementary particles with diameters of about 100 nm.

Platinum tetrammine hydroxide ($Pt(NH_3)_4(OH)_2$) was obtained from platinum tetrammine chloride (Strem Chemicals; purity, 99%), by exchange of the Cl^- ions with OH^- using an ion-exchange resin (Aldrich, IRA 400), according to the procedure described by Benesis *et al.* (22).

3.2. Analysis

3.2.1. Platinum concentration and pH of the aqueous solution. The concentration of Pt in the suspension was determined using ICP (Jobin Yvon) analysis after filtering through a Millipore SLSR025NB.

The pH of the suspension was measured using a SCHOTT CG 840 pH meter.

Elemental analysis of dried samples was performed in the C.N.R.S. laboratory SCA (Service Central d'Analyses).

3.2.2. Hydrogen and oxygen chemisorption studies. H_2 or O_2 chemisorption experiments were carried out at 25°C using conventional Pyrex volumetric adsorption equipment (24). The vacuum (10^{-6} mbar) was achieved with a liquid-nitrogen-trapped mercury diffusion pump. The equilibrium pressure was measured with a Texas Instrument gauge (pressure range, 0–1000 mbar with an accuracy of 0.1 mbar). The catalyst sample was placed in a Pyrex cell and outgassed at 25 and then at 300°C for 2 h under vacuum before the chemisorption measurements. The oxidation state of platinum was deduced from the amounts of H_2 and O_2 adsorbed.

3.2.3. Electron microscopy studies. The dry catalysts were suspended in ethanol. A drop of the suspension was deposited onto a carbon film supported on a copper grid, and the ethanol evaporated quickly at room temperature. The samples were observed using a JEOL 2010 electron microscope with energy-dispersive X-ray (EDX) analysis.

For EDX analysis, the electronic beam was focused on a single silica particle, and the Pt/Si ratio was determined after calibration. About 100 silica particles of each sample were observed to obtain the Pt/Si frequency distribution.

The unsupported precursor was also examined. It was prepared using a drop of platinum tetrammine hydroxide previously dissolved in ethanol.

The mean metallic particle size was determined from the examination of at least 500 particles.

3.2.4. EXAFS studies. All the samples were taken under dry nitrogen atmosphere and placed into air-proof cells equipped with kapton windows. Spectra of PtO_2 and an aqueous solution of $Pt(NH_3)_4(OH)_2$ ($0.17\ \mathrm{mol \cdot L^{-1}}$) were also recorded as a reference. Moreover, the spectrum of a EUROPT-1 reference catalyst was recorded after reduction for 1 h at 400°C under hydrogen.

The X-ray absorption spectra were recorded at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (L.U.R.E.) at Orsay, France, on the DCI ring using 1.85-GeV positrons with an average current intensity of 250 mA. The acquisitions were carried out on the D44 beam line at the L_{III} platinum transition edge using a transmission mode between 11,400 and 12,600 eV and an increment step of 2 eV. The counting time was 2 s. A Si(111) double crystal was used as a monochromator, and the γ photons flux was measured at the entrance and the exit of the cell using ionization chambers.

The EXAFS analyses were performed according to the single scattering theory using Michalowicz's software (25). The support absorption (μ_0) was computed using the theoretical expression developed by Lengeler and Eisenberger (26), and the platinum atomic absorption (μ_1) was modeled by a fifth- or sixth-order polynomial between 11,600 and 12,400 eV. Each EXAFS contribution was carefully extracted in order to minimize the low-frequency noise. The edge energy E_0 (around 11,565 eV) was measured at half height of the absorption threshold. The pseudo radial distribution function around the platinum $|F(R)|$ was obtained by a Fourier transform of the weighted spectrum $\omega(k) \cdot k^3 \cdot \chi(k)$, where $\omega(k)$ is a Kaiser-type function ($\tau = 2.5$) defined between 3 and 13.5 $Å^{-1}$.

The spectra simulations were performed using theoretical files from FEFF software for phases and amplitudes and the results obtained from the reference compound simulations were taken into account. The following structural parameters were adjusted using the simplex and least-squares methods: the number, N, of atomic neighbors of definite type (O, Pt...), the distance R between the Pt atom and its neighbor, and the Debye–Waller factor, σ, characterizing the thermal and structural disorder. The adjustment residue ρ was computed using the following formula:

$$\rho = \frac{\sum_k [k^3\chi_{\exp}(k) - k^3\chi_{calc}(k)]^2}{\sum_k [k^3\chi_{\exp}(k)]^2}.$$

3.3. Adsorption of the Pt Precursor

Prior to the studies, 3 ± 0.02 g of silica were treated under flowing dry air at 520°C for 5 h in order to remove any pollutants that may have adsorbed. Moreover, treatment at temperatures above 500°C leads to an almost fully dehydroxylated silica surface. Rehydroxylation of the treated sample leads to ≡Si–OH silanol groups only. There is no formation of the =Si(–OH)$_2$ or –Si(–OH)$_3$ silanol groups initially present (27). After cooling to room temperature, the treated silica was introduced into a "Pyrex" reactor filled with a known volume of water and stirred well with a magnetic agitator to generate a suspension. The pH of the silica suspension was then increased to pH 9 using an aqueous solution of NH_3. In some experiments, NH_3 was not added.

For kinetic studies, a known volume of solution containing the desired amount $Pt(NH_3)_4(OH)_2$ was added to the silica suspension. Analyzing samples of the suspension taken at regular time intervals enabled the study of exchange kinetics. The concentration of $Pt(NH_3)_4^{2+}$ fixed on the silica surface was deduced from the difference between the amount of $Pt(NH_3)_4^{2+}$ introduced and the amount of $Pt(NH_3)_4^{2+}$ remaining in the solution.

For studies of platinum distribution over the silica surface, samples were prepared using the method described for kinetic studies (see above) and contact times of 5 min, 1 h, and 24 h. Then, the samples were filtered and washed with 50 ml of distilled water. The subsequent heat treatment included the following steps: (i) drying under vacuum at $T = 25$°C for 24 h, and (ii) temperature increase from $T = 25$ to 300°C (2°C/min), 1 h at 300°C under vacuum, and cooling to 25°C. Finally, some of the samples were reduced at 400°C for 2 h under hydrogen. The samples were observed by electron microscopy with energy-dispersive X-ray (E.D.X.) analysis (JEOL 2010).

3.4. Drying and Decomposition of $Pt(NH_3)_4^{2+}$ Adsorbed on the Silica Surface

3.4.1. In situ measurement of ammonia released during the drying and thermal decomposition steps. The experimental setup for exchange, drying, and thermal decomposition consisted of two flasks connected from above. They could be evacuated singly or simultaneously or fed with an inert gas. The "main" flask (200 ml) was used to prepare the catalyst. The "trap" flask (50 ml) was used to recover the gaseous products released during the successive steps described below. Silica (3 ± 0.02 g) was treated under flowing dry air at 520°C for 5 h. After cooling to room temperature, the solid sample was introduced into the main flask together with 30 ml of water and 2.3×10^{-4} mol of $Pt(NH_3)_4(OH)_2$ or 6.4×10^{-4} mol of NH_3. The suspension was stirred for 1 h (magnetic stirrer), the main flask was cooled to liquid nitrogen temperature, and both flasks were evacuated to about 10^{-4} mbar (mercury diffusion pump).

The flasks were then isolated from the vacuum line, and the main flask was heated to 25°C for 24 h while the trap flask was cooled to liquid nitrogen temperature to condense the vapor of the bulk liquid phase in the main flask into the trap flask. After this step the pressure in the flasks was lower than 0.01 mbar. Then both flasks were filled with argon up to atmospheric pressure, and the main flask was isolated. The trap flask was heated to room temperature, and a known amount of HCl in aqueous solution was introduced to neutralize the ammonia that evolved during the heat treatment. The trap flask was then disconnected, and the remaining amount of hydrochloric acid was determined using a titrated NaOH aqueous solution. The difference between the initial and final amounts of HCl gave the amount of NH_3 evolved from the main flask.

The trap flask was then washed, dried, and reconnected (under argon). The same sequence of operations (evacuation under vacuum at 25°C, heating of the main flask, NH_3 analysis) was repeated successively at 100, 200, and 300°C for 30 min using the same sample of solid. The temperature was increased by $2^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$ from 25°C to the desired temperature. During the steps at 25, 100, 200, and 300°C the residual pressure remained constant and lower than 10^{-2} mbar while the flasks were isolated from the vacuum line.

3.4.2. Other catalyst samples. The catalyst samples required for EXAFS studies (see below) were prepared as follows: the exchange reaction was performed according to the procedure described in Section 3.3 with no addition of NH_3 and with a contact time of 1 h. The wet solid was placed in the chemisorption apparatus (see Section 3.2.2) and dried at 25°C for 24 h under vacuum ($P < 10^{-5}$ mbar along the vacuum line). It was then heated ($2^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$) and maintained for 30 min at a desired temperature (100, 200, or 300°C) still under vacuum. When necessary, it was reduced under hydrogen at 400°C for 1 h. With the exception of reduction, these steps were as similar as possible to those described in Section 3.4.1.

4. RESULTS

4.1. Kinetics of the Exchange Reaction

Figures 1 and 2 show the variation in the Pt concentration and pH of the liquid phase with time when 3 ± 0.02 g of silica in suspension in 30 ml of water (pH 9) come into contact with 30 ml of $Pt(NH_3)_4(OH)_2$ aqueous solution (see Section 3.3).

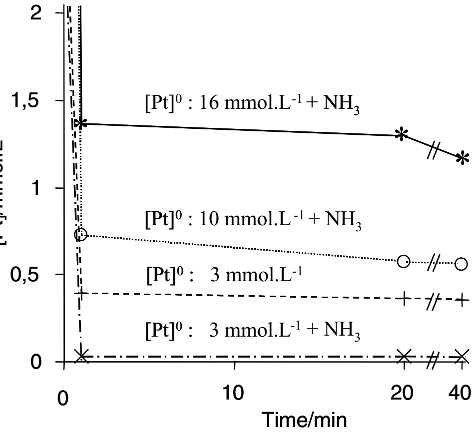

FIG. 1. Evolution of Pt concentration during $Pt(NH_3)_4^{2+}$ exchange on silica for various initial Pt concentrations ($[Pt]^0$), corresponding to various Pt loadings. (∗) 5.9%; (○) 3.7%; (×) 1.0% Pt with addition of NH_3 (pH 9); and (+) 1.0% Pt without addition of NH_3.

The interaction between the platinum complex and the silica surface is clearly very fast: in all cases, the platinum concentration and pH reach almost constant values after less than 1 min. Following the addition of NH_3 to the suspension, before the interaction (see Section 3.3), the exchange process does not slow down significantly but affects the final equilibrium concentration. The platinum residual concentration decreases upon addition of NH_3 (Fig. 1) and, conversely, the final pH increases (Fig. 2). The initial pH is only an indication, since pH varies quickly upon addition of the complex into the suspension. The exchange rate does not depend significantly on the initial concentration of the platinum precursor C_0, which varied from 3 to 16 $\mathrm{mmol} \cdot \mathrm{L}^{-1}$, as can be seen from Figs. 1 and 2.

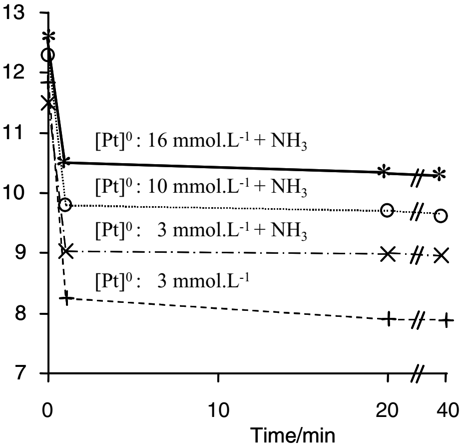

FIG. 2. Evolution pH corresponding to the conditions given in Fig. 1.

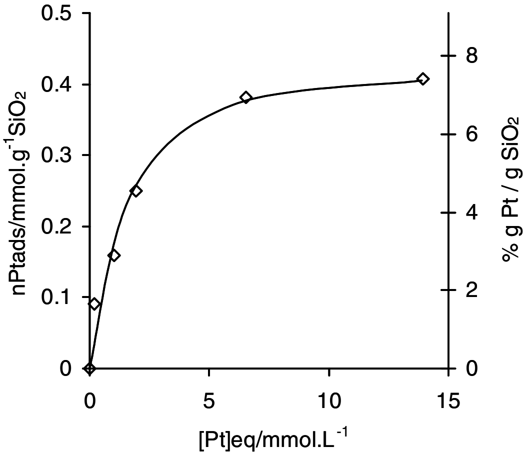

FIG. 3. $Pt(NH_3)_4^{2+}$ exchange isotherm on silica.

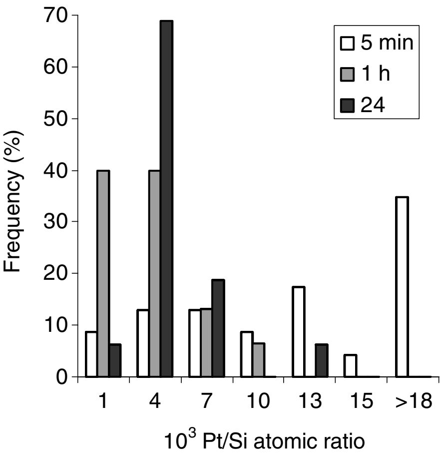

FIG. 4. Pt distribution over the silica support after 5 min, 1 h and 24 h of contact time.

4.2. Exchange Isotherm of $Pt(NH_3)_4(OH)_2$ on the Silica Surface

From the above observation, it can be assumed that the exchange equilibrium is reached within 5 min. This leads to the "exchange isotherm" shown in Fig. 3. For a residual platinum concentration close to 7 $mmol \cdot L^{-1}$, the amount of the exchanged platinum complex corresponds to a metal loading of 7.5% (w/w) and does not significantly increase with the concentration of the residual platinum.

All these observations are in agreement with the exchange process described in Section 2, although a quantitative estimation of the equilibrium constants was not attempted. It is, however, certain that the exchange equilibrium is very favorable for the Pt complex.

4.3. Distribution of the Exchanged Platinum Complex on the Silica Surface

An aqueous solution (30 ml) of $Pt(NH_3)_4(OH)_2$ (1.71 $mmol \cdot L^{-1}$) came into contact with 1 g of silica. The average Pt/Si value was then 0.003. After 5 min, 1 h, and 24 h of contact, electron microscopy with X-ray emission analysis (EDX) of the samples gave the results shown in Fig. 4. After 5 min, Pt/Si values as high as 0.018 were obtained for about 40% of the individual silica particles. After 1 h, the average Pt/Si value shifts to lower values, and after 24 h, there is a rather narrow distribution close to the expected Pt/Si ratio of 0.003.

4.4. Stoichiometry of the Exchanged Platinum Complex on the Silica Surface

4.4.1. Blank experiment. Silica was put into contact with 30 ml of an aqueous solution of NH_3 (21.33 $mmol \cdot L^{-1}$) as described in Section 3.4.1. After drying and heating, the amount of ammonia evolved was measured. The results are reported in Table 2.

It is clear that more than 90% of the exchanged NH_4^+ can be recovered from the sample after 30 min at 100°C.

4.4.2. Decomposition of platinum tetrammine exchanged on silica. The experiment described in Section 4.4.1 was performed using 30 ml of aqueous $Pt(NH_3)(OH)_2$ (7.67 $mmol \cdot L^{-1}$) instead of NH_3. The results are also listed in Table 2. Note that silica was in contact with the solution for 1 h to obtain a rather uniform distribution of the platinum complex over the surface, as suggested by the results in Fig. 4.

At all temperatures from 25 to 300°C, the residual pressure in the isolated flasks was close to 10^{-2} mbar at each step. This very low pressure corresponds to 0.04 mmol of permanent gas in the flasks, which is much less than the amount of NH_3 recovered above 100°C (see Table 2). This proves that most of the released gaseous products are condensed in the trap flask, i.e., hardly any NH_3 decomposes to N_2 and H_2. These results show that Pt–NH_3 bonds do not break during the exchange and drying processes at 25°C under reduced pressure. Up to 100°C, the complex does not decompose significantly, whereas more than 90% of the

TABLE 2

Ammonia Evolved after Drying and Heat Treatment of NH_4^+ (Blank Experiment) and $Pt(NH_3)_4^{2+}$ Exchanged on Silica

Temperature	25°C	100°C	200°C	300°C
Time (h)	24	0.5	0.5	0.5
NH_4^+/SiO_2	0.27 mmol (42%)	0.59 mmol (92%)	0.63 mmol (98%)	0.63 mmol (99%)
$Pt(NH_3)_4^{2+}/SiO_2$	0.01mmol (1%)	0.025 mmol (3%)	0.345 mmol (38%)	0.835 mmol (91%)

Note. Cumulative amount of ammonia evolved in millimoles and corresponding percentage of introduced ammonia recovered (in parentheses). Time: Duration of the temperature step in hours.

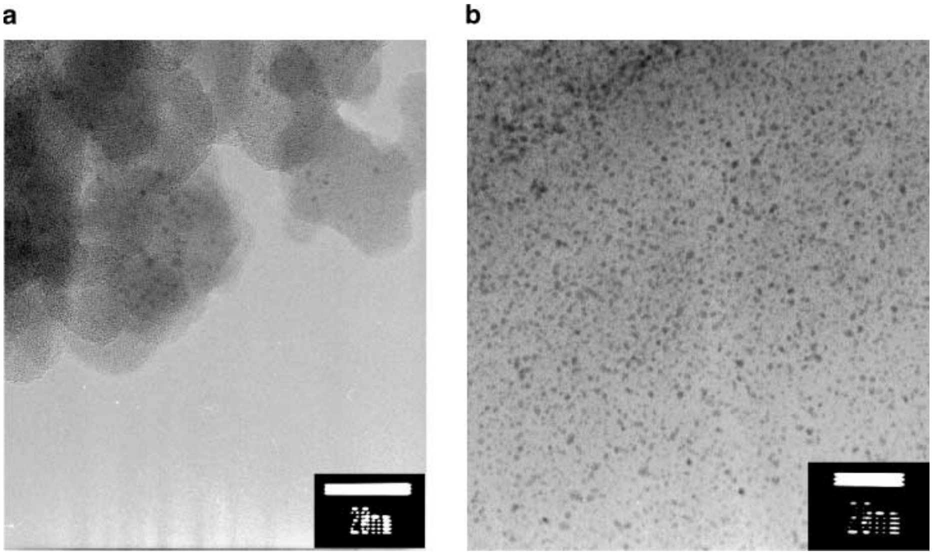

FIG. 5. TEM pictures of samples after 25°C vacuum drying. (a) $Pt(NH_3)_4(OH)_2/SiO_2$ (4.5% Pt); (b) unsupported $Pt(NH_3)_4(OH)_2$.

ammonia was recovered at that temperature in the blank experiment (Table 2).

Treatment under reduced pressure at 200 and 300°C causes the exchanged complex to progressively lose the NH_3 ligands. At 300°C, 91% of the ammonia ligands are recovered; the remaining 9% are decomposed into N_2 and H_2 (see Discussion).

4.5. Transmission Electron Microscopy Study of the Adsorbed $Pt(NH_3)_4^{2+}$ Complex

Figure 5 shows typical TEM pictures obtained with vacuum-dried supported (Fig. 5a) and unsupported (Fig. 5b) silica samples at 25°C.

Both samples exhibit similar small particles (1.5- to 2-nm diameter) with low contrast. It must be emphasized that additional microanalysis, carried out on supported and unsupported samples of $Pt(NH_3)_4(OH)_2$, revealed a ratio of 4 nitrogen atoms per platinum atom.

After treatment under vacuum at 300°C, the samples display similarly low-contrast particles with roughly the same diameter (i.e., 1.5–2 nm).

For the sample treated under vacuum at 300°C and then reduced at 400°C, well-contrasted particles with an average diameter of 1.5 nm were distributed homogeneously on the silica surface (Fig. 6).

4.6. EXAFS Studies

A 4.5% (w/w) silica catalyst was prepared as explained in Section 3.4.2. The spectra of the solid were recorded after each step of catalyst preparation:

- after drying 24 h under vacuum at 25°C only (sample Pt025),
- after drying and 30 min at 100°C under vacuum (sample Pt100),
- after drying and 30 min at 200°C under vacuum (sample Pt200),
- after drying and 30 min at 300°C under vacuum (sample Pt300),
- after drying, 30 min at 300°C under vacuum, and reduction at 400°C under hydrogen (sample PtR400).

The corresponding EXAFS spectra and Fourier transform curves are reported in Fig. 7. The structural parameters obtained for the samples from the simulations (N, R, σ) are reported in Table 3 together with the known structural parameters of bulk platinum oxide (PtO_2), 8-μm- thick platinum foil, and $Pt(NH_3)_4(OH)_2$ in aqueous solution.

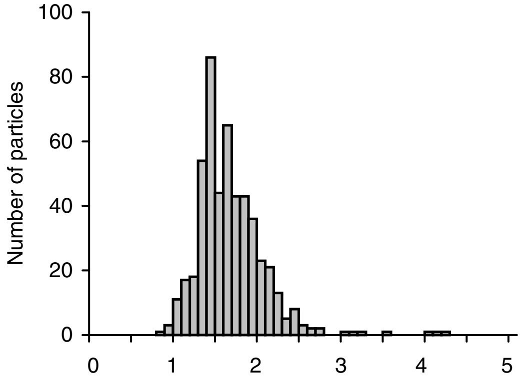

FIG. 6. Particle size distribution of a 4.5% Pt catalyst after drying at 25°C, vacuum heat treatment at 300°C, and reduction under hydrogen at 400°C.

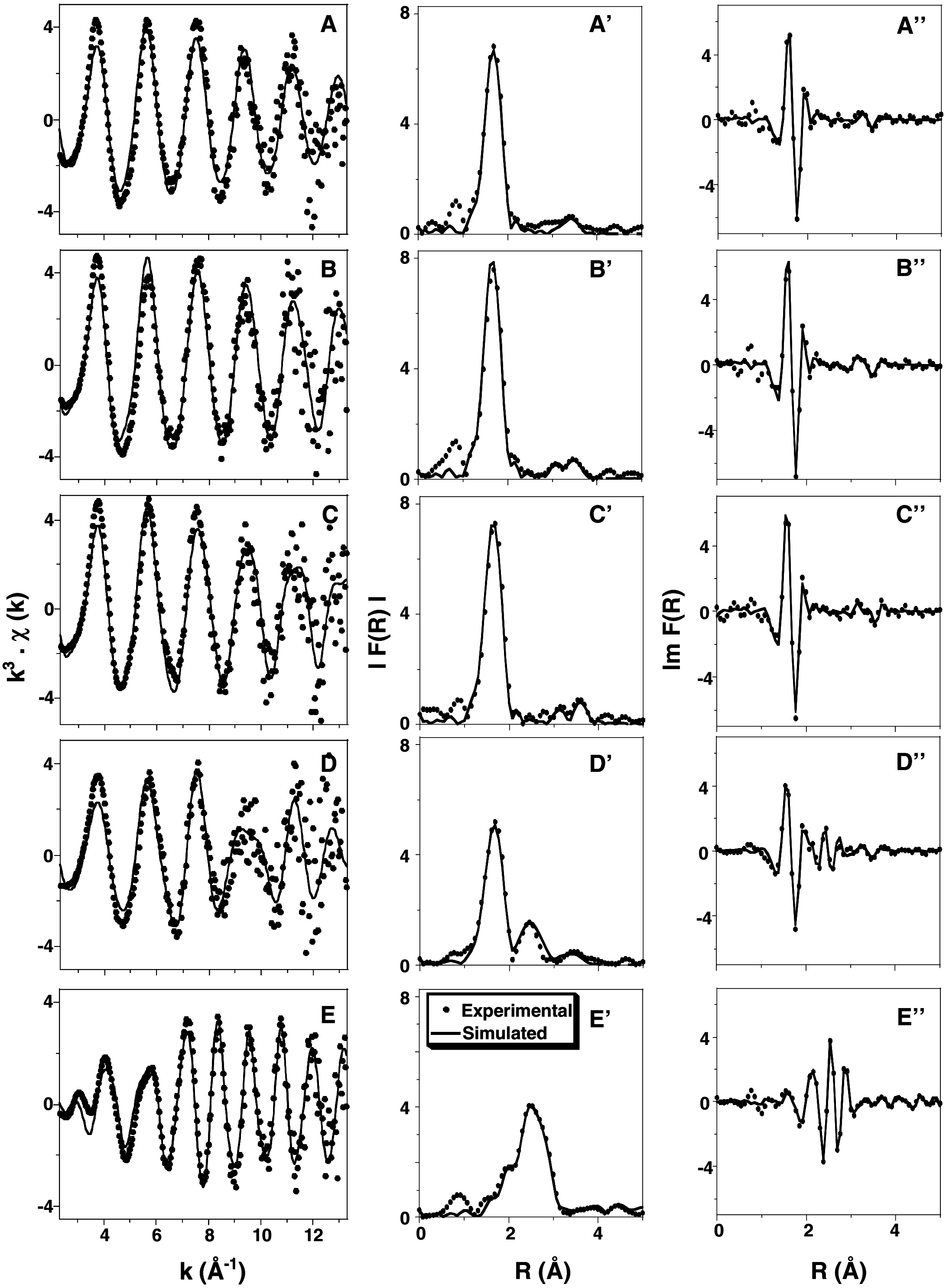

FIG. 7. EXAFS spectra of the various samples. (A) Pt025; (B) Pt100; (C) Pt200; (D) Pt300; and (E) PtR400 and corresponding Fourier transform.

It is not possible to distinguish O from N as Pt neighbors by EXAFS. Thus, based on the results of Section 4.4.2, we assume that there were about two nitrogen neighbors per Pt atom at 200°C and none at 300°C. The other atoms required by the coordination sphere of Pt were assumed to be oxygen.

From these results, it appears that the EXAFS spectra of Pt(NH$_3$)$_4$(OH)$_2$ in aqueous solution and of Pt025 (vacuum

TABLE 3

Structural Parameters Obtained for the Studied Samples

Sample	Scattering atom	N	R (Å)	$2\sigma^2$ (Å^2)	ρ
Pt025	N	4.0	2.04	0.0060	14%
	O	2.2	3.71	0.012	
Pt100	N	4.1	2.02	0.0048	19%
	O	2.5–3.5	3.56–3.74	0.0098–0.0104	
Pt200	N + O	2.0 + 2.0	2.03 + 1.99	0.0051 + 0.0075	16%
	O	2.3–3.2	3.60–3.80	0.0056	
Pt300	O	2.93	2.00	0.0095	35%
	Pt	~1.2	~2.57 ± 0.1	0.013	
PtR400	Pt	5.8	2.69	0.0172	15%
EUROPT-1	Pt	5.6	2.68	0.0169	14%
EUROPT-1 (29, 30)	Pt	5.5	2.76		
PtO_2(39)	Pt	8	3.350		
	O	2	1.984		
	O	4	2.004		
Pt (foil)(40, 41)	Pt	12	2.772		
	Pt	6	3.920		
$Pt(NH_3)_4(OH)_2$(40)	N	4	2.040		

Note. σ: Debye–Waller factor. First six rows, our results; next four rows, literature data (reference in parantheses).

dried at 25°C only) are very similar. The platinum environment (four light atoms in the first shell) is only slightly modified by heat treatment at 100°C. The distances obtained from simulations are fully compatible with Pt–N bonds in $Pt(NH_3)_4^{2+}$ (40). At 200°C, about half the NH_3 ligands are lost, and there are still four light atoms (O or N) as neighbors. The distances obtained from simulations are in the domain of the Pt–O bonds in PtO_2 (39). This would imply stronger bonding of the complex to the ≡SiO surface. For the sample heated to 300°C, the spectrum was more difficult to simulate. The results obtained for this sample did not show clearly that platinum was a second neighbor (like the Pt–O–Pt structure observed in bulk PtO_2). This may be compatible with partially reduced platinum mixed with oxide within the same particle. Joyner (28) did not observe Pt second neighbors when studying the EUROPT-1 catalyst previously reduced at 300°C under hydrogen and then exposed to air. Finally, as expected, the spectra of the reduced sample (PtR400) and the EUROPT-1 reference catalyst are similar. Note that the structural parameters obtained (5.8 Pt at 2.69 Å for PtR400 and 5.6 Pt at 2.68 Å for EURPOT-1) are in good agreement with the results obtained by Wells and co-workers (29, 30) (5.5 Pt at 2.76 Å for EUROPT-1).

5. DISCUSSION

In aqueous solution and at pH above the point of zero charge, the silica surface ionizes according to

$$\equiv SiOH \leftrightarrows \equiv SiO^- + H^+. \qquad [1]$$

The platinum tetrammine hydroxide in aqueous solution is completely dissociated into platinum tetrammine cations and hydroxyl anions according to

$$Pt(NH_3)_4(OH)_2 \leftrightarrows Pt(NH_3)_4^{2+} + 2OH^-. \qquad [2]$$

When the platinum tetrammine solution is added to the silica suspension, there is a strong increase in pH that is responsible for silica ionization according to Eq. [1]. Then platinum tetrammine cations are exchanged for the surface H^+ cations. When an aqueous solution of NH_3 is used to create NH_4^+ as competing cations, the residual platinum concentration is lower (Fig. 1). This is explained easily by the higher pH, which promotes ionization of the silica surface. Although NH_4^+ competes with platinum there are many more sites available for exchange. Thus, it is not recommended that an aqueous solution of NH_3 be used as a competing agent.

Depending on the mixing intensity, the surface ionization process and, thus, the distribution of the adsorbed complex may be more or less heterogeneous. The driving force for redistribution is mixing in the bulk solution and diffusion across the external boundary layer or inside the silica aggregates (31). The diffusional flux is proportional to the difference between the concentrations of the actual and the equilibrium platinum in the liquid phase. Although this difference is not known, the concentration is almost certainly lower than the residual concentration. Consequently, the lower the residual platinum concentration, the smaller the diffusional flux and the slower the redistribution process. This explains why about 24 h are required to obtain a homogeneous distribution for the lower Pt loading (Section 4.3, Fig. 4). According to this explanation, with a higher residual concentration or in the presence of a pH-neutral competing cation, redistribution is probably faster.

From our kinetic measurements (Fig. 1), it is clear that ammonium ions do not significantly lower the rate of the exchange processes, as was proposed by Ribeiro and Marcilly (10). This suggests that the exchange rates and selectivity factors of the platinum complex cation compared to NH_4^+ or H^+ are similar.

We did not perform further measurements of the Pt/Si distribution. Consequently, the tentative explanation of ion exchange given above should be checked by a detailed and specific analysis of the exchange process together with the surface ionization process.

Our results definitely show that the adsorbed complex does not lose NH_3 ligands up to 100°C, and that the formation of the $(\equiv SiO)_2Pt(NH_3)_2$ species, proposed by Sermon and Silvaningam (11) and by Mang *et al.* (12), must be excluded. It is thus proposed that, at 25°C, the platinum tetrammine cations in a water solution are simply trapped in the electrical double layer at the silica interface.

After drying at 25°C under vacuum, the sizes of the particles of the complex measured by TEM are similar regardless of whether or not they are supported by silica. It is surprising to observe small particles of the precursor on the silica surface; instead atomic dispersion of platinum owing to the exchange mechanism may have been expected. However, it can be argued that when the solid comes into contact with ethanol during the preparation of the samples for TEM, the analysis may yield biased results if the previously exchanged precursor "dissolves." Several observations, however, have shown that this is not so. (i) When a freshly prepared sample is washed with a small amount of water, desorption is not observed, in agreement with the strong affinity of the Pt cations for the silanol groups. (ii) Even if a small amount dissolves in ethanol, the subsequent drying of the sample reproduces the previous drying step of the catalyst. (iii) EXAFS spectra show similar results, both for $Pt(NH_3)_4(OH)_2$ in aqueous solution and for a supported sample dried at 25°C. (iv) The supported sample treated at 300°C consists mainly of PtO particles, which cannot dissolve; nevertheless, the same particle size is observed. This suggests that the exchanged platinum complex hardly continues to interact electrostaticly with the surface. The system behaves as if the following "transformation" had taken place upon drying:

$$n(\equiv \text{Si–O}^-)_2\left(\text{Pt(NH}_3)_4^{2+}\right) + (x+2)\text{H}_2\text{O}_{\text{adsorbed}}$$
$$\rightarrow 2n(\equiv \text{Si–OH}) + (\text{Pt(NH}_3)_4(\text{OH})_2, x\text{H}_2\text{O})_n.$$

The resulting "free" hydroxide forms $[Pt(NH_3)_4(OH)_2, xH_2O]_n$ clusters (or colloids), regardless of whether they are supported on silica or unsupported. This explains why the dry silica-complex system exhibits TEM patterns similar to the unsupported dry complex (Fig. 5). The size of the resulting clusters (or colloids) determine the size of Pt particles after thermal decomposition and reduction. The process that governs the cluster size is still unknown.

Heat treatment at 100°C does not lead to NH_3 release (EXAFS and NH_3 release measurements). This result is in agreement with the work of Kinoshita *et al.* (32), who found that thermal decomposition of $Pt(NH_3)_4(OH)_2$ does not occur below 150°C.

After heating under vacuum at 200°C, the surface complex loses 38% of the NH_3 ligands (Table 2) and it must be concluded from the EXAFS analysis that there are still four light atoms (either O or N) about 2 Å away from Pt. It seems that the surface complex is usually bonded to the silica surface by two Pt–O bonds to form the surface species $(\equiv SiO)_2Pt(NH_3)_2$. It is noteworthy that the melting point of bulk platinum tetrammine hydroxide is close to 110°C (4). It may be that the complex clusters melt on the surface above 100°C and then become "rafts," where Pt atoms are close to the oxygen atoms of the silanol groups. A raftlike structure was proposed by Jackson *et al.* (29, 30) for crystallites of Pt on silica obtained after reduction under moderate conditions. Our results present evidence that the precursor can adopt a raftlike structure prior to reduction. Since the amount of NH_3 released at 200°C differs significantly from 50%, the possible explanation above is tentative at best. It will be considered again in the second part of this series, when time-resolved mass spectrometric analyses during T.P.D. experiments will be dealt with.

Heating to 300°C leads to the release of the remaining NH_3 ligands and to the formation of poorly contrasted particles with diameters of 1–2 nm. These particles chemisorbed either 0.1 oxygen atom or 3.1 hydrogen atoms per platinum atom. This shows that the platinum tetrammine complex decomposes mainly into PtO (90%) and a small amount of $Pt^{(0)}$ (10%). The reactions with hydrogen or oxygen may be

$$0.1\text{Pt} + 0.9\text{PtO} + 0.05\text{O}_2 \rightarrow \text{Pt–O} \quad (\text{O/Pt} = 0.1),$$
$$0.1\text{Pt} + 0.9\text{PtO} + 1.55\text{H}_2$$
$$\rightarrow \text{Pt–H}_{1.3} + 0.9\text{H}_2\text{O} \quad (\text{H/Pt} = 3.1).$$

The self-reduction of $Pt(NH_3)_4(OH)_2$ adsorbed on zeolite (33) or alumina (34) during treatment under He at a temperature higher than 300°C was proposed elsewhere, although these authors did not give the extent of self-reduction.

According to our interpretation, the size of these PtO and $Pt^{(0)}$ particles reflects the size of the dry complex clusters due to the drying step.

Reduction at 400°C weakly modifies the size of the particles obtained after thermal decomposition under vacuum. The resulting solid is very similar to EUROPT-1 (1, 35–37). This step of the preparation does not appear to be critical with respect to the size of the particles.

6. CONCLUSION

Preparation of Pt/SiO_2 catalyst is still based on recipes. Although many of them lead to well-dispersed platinum, some of them differ considerably from each other, and the chemical and engineering processes are not well understood or controlled. Our study shows the following:

- As already shown, the interaction between the dissolved complex and the silica surface is governed by ion exchange. However, this exchange process is extremely fast and can be affected by the mixing process. A uniform distribution of platinum over the silica surface may require about 24 h at low Pt loading ($<1\%$ (w/w)Pt/SiO_2). Adding NH_3 to create NH_4^+ counterions within the usual concentration range does not slow the exchange process. The possible competition between NH_4^+ and $Pt(NH_3)_4^{2+}$ for the exchange reaction with SiO^-H^+ is masked by the increase in the ionization of the silica surface owing to the pH increase. Further studies of silica ionization versus pH, of the exchange equilibrium between Pt-containing cations and H^+ or NH_4^+, and of diffusion-limited redistribution are necessary to better define the solid–liquid contact conditions. Nevertheless, this exchange step does not seem to be crucial provided that platinum redistribution is achieved.
- The platinum tetrammine complex does not decompose from the exchange step to the heat treatment at 100°C under vacuum. However, between 25 and 100°C the complex consists of clusters of platinum tetrammine hydroxide deposited on the silica surface. These clusters define the final particle size of Pt. At about 100°C, these clusters may melt, which would enable spreading of the platinum complex over the silica surface in the immediate vicinity of the original cluster. This would mean that drying is the crucial step. This is an unexpected result since no previous studies reported this step to be crucial.
- At 200°C, about half the NH_3 ligands are lost. This would imply a stronger bond to the $\equiv$SiO surface groups, which would prevent the melted complex from spreading over the surface. This could explain why the size of the crystal, which was frozen at drying, is reflected in the size of the metal particle.
- At 300°C under vacuum the complex essentially fully decomposes to PtO. Although PtO is known to be a mobile species, the temperature treatment was probably too short to promote particle sintering (38). A further reduction under hydrogen at 400°C does not alter the particle size.

All the samples treated as described above (see Section 3) lead to a metal dispersion of $65 \pm 5\%$, which is close to the maximum value reported in the literature. Although this result is encouraging, drying and heating under vacuum is costly from an industrial point of view. Using time-resolved mass spectrometry, the next paper will describe what happens when the exchanged catalyst decomposes in various atmospheres and is eventually reduced under hydrogen.

REFERENCES

1. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18**, 225 (1985).
2. Brunelle, J. P., *Pure Appl. Chem.* **50**, 1211 (1978).
3. Reizet, J., *Ann. Chem. Phys.* **XI**, 417 (1844).
4. Duval, C., *in* "Nouveau Traité de Chimie Minérale" (Masson et Cie, Ed.), Vol. XIX, p. 860. Libraries de l'Académie de Médecine, Paris, 1958.
5. Brunelle, J. P., and Sugier, A., *C. R. Acad. Sci. Paris* **276**, 1545 (1973).
6. Morrow, B. A., and McFarlan, A. J., *Langmuir* **7**, 1695 (1991).
7. Gonzalez, R. D., and Miura, H., *Rev. Sci. Eng.* **36**, 145 (1994).
8. Zou, W., and Gonzalez, R. D., *J. Catal.* **133**, 202 (1992).
9. Boronin, V. S., Nikulina, V. S., and Poltorak, O. M., *Russ. J. Phys. Chem.* **37**, 626 (1963).
10. Ribeiro, F., and Marcilly, C., *Rev. IFP* **34**, 405 (1979).
11. Sermon, P. A., and Silvaningam, J., *Colloids Surf.* **63**, 59 (1992).
12. Mang, T., Breitscheidel, B., Polanek, P., and Knozinger, H., *Appl. Catal.* **106**, 239 (1993).
13. Marcilly, C., and Le Peltier, F., *Rev. IFP* **39**, 337 (1984).
14. Foger, K., *in* "Catalysis: Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 6, p. 247. Springer-Verlag, Berlin/New York, 1984.
15. Brunelle, J. P., Sugier, A., and Lepage, J. F., *J. Catal.* **43**, 273 (1976).
16. Zou, W., and Gonzalez, R. D., *Catal. Today* **15**, 443 (1992).
17. Dorling, T. A., Eastlake, M. J., and Moss, R. L., *J. Catal.* **14**, 23 (1969).
18. Dorling, T. A., Lynch, B. W., and Moss, R. L., *J. Catal.* **20**, 190 (1971).
19. Alerasool, S., and Gonzalez, R. D., *J. Catal.* **124**, 204 (1990).
20. Tsurimi, K., and Inoue, K., *Kagaku Kogaku Ronbunshu* **22**, 542 (1986).
21. Tsurimi, K., and Inoue, K., *Kagaku Kogaku Ronbunshu* **22**, 1294 (1986).
22. Benesis, A. H., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).
23. Wilson, G. R., and Hall, W. K., *J. Catal.* **24**, 306 (1972).
24. Candy, J. P., El Mansour, A., Ferretti, O. A., Mabilon, G., Bournonville, J. P., Basset, J. M., and Martino, G., *J. Catal.* **112**, 201 (1988).
25. Michalowicz, A., "Logiciel pour la Chimie." Société Française de Chimie, Paris, 1991.
26. Lengeler, B., and Eisenberger, P., *Phys. Rev. B* **21**, 4507 (1980).
27. Iller, R. K., "The Chemistry of Silica." Willey, New York, 1979.
28. Joyner, R. W., *J. Chem. Soc. Faraday Trans.* **76**, 357 (1980).
29. Jackson, S. D., Keegan, M. B. T., McLellan, G. D., Meheux, P. A., Moyes, R. B., Webb, G., Wells, P. B., Whyman, R., and Willis, J., *Stud. Surf. Sci. Catal.* **63**, 135 (1991).
30. Jackson, S. D., Willis, J., McLellan, G. D., Webb, G., Keegan, M. B. T., Moyes, R. B., Simpson, S., Wells, P. B., and Whyman, R., *J. Catal.* **139**, 191 (1993).
31. Goguet, A., Aouine, M., Cadete Santos Aires, F. J., Schweich, D., and Candy, J. P., *Chem. Commun.* 1417 (2000).
32. Kinoshita, K., Routsis, K., and Bett, J. A. S., *Thermochim. Acta* **10**, 109 (1974).
33. Van den Broek, A. C. M., van Grondelle, J., and van Santen, R. A., *J. Catal.* **167**, 417 (1997).
34. Munoz-Paez, A., and Koningsberger, D. C., *J. Phys. Chem.* **99**, 4193 (1995).
35. Frennet, A., and Wells, P. B., *Appl. Catal.* **18**, 243 (1985).
36. Geus, J. W., and Wells, P. B., *Appl. Catal.* **18**, 231 (1985).
37. Wells, P. B., *Appl. Catal.* **18**, 259 (1985).
38. Chen, M., and Schmidt, L. D., *J. Catal.* **55**, 348 (1978).
39. Range, R. J., Rau, F., Klement, U., and Heynes, A. M., *Mater. Res. Bull.* **22**, 1541 (1972).
40. Wyckoff, R. W. G., "Crystal Structures." Interscience, New York, 1974.
41. Schroder, R. H., Schmitz-Pranghe, N., and Kohlaas, R., *Z. Metallkd.* **63**, 12 (1972).