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N,N-Dialkylcarbamato complexes as precursors for the chemical implantation of metal cations on a silica support. Part 3† Palladium

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Chemical implantation of palladium(II) has been carried out under mild conditions by reacting *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ with the silanol groups of amorphous silica, carbon dioxide and secondary amine being released in the process. The palladium-containing silica has been characterized and the coordination environment of the implanted cation has been defined by ^{13}C CP MAS NMR, DRIFT and XPS spectra, and by WAXS measurements. Silica-bonded palladium(II) was reduced thermally *in vacuo* or with dihydrogen at room temperature. Catalytic activity in the hydrogenation of cyclohexene was found for all samples containing the silica-supported reduced palladium; the best results, with rates independent of olefin concentration, were found for the samples treated thermally (200 °C) under reduced pressure.

Earlier papers from these laboratories have pointed out that cationic implantation on silica can be carried out with tin(IV)[1a] and platinum(II),[1b] by using the corresponding N,N-dialkylcarbamato complexes, of general formula $M(O_2CNR_2)_n$, as precursors. As the silanol groups are the reactive sites, it was anticipated that cations would be homogeneously distributed on the surface. This method therefore appears to be an useful alternative to more traditional ones,[2] and to the methodology based on organometallics.[3] The use of N,N-dialkylcarbamates presents several advantages, which have been pointed out earlier;[1] implanted species and their reduction products can be investigated by conventional surface methods.

The availability of the N,N-diethylcarbamato derivative of palladium(II)[4] has urged us to use this compound as starting material for the implantation of palladium(II) on silica; its further reduction was predicted to occur easily ($E^0 = 0.951$ V[5]), both thermally and chemically. The use of reduced palladium in the hydrogenation of cyclohexene is also reported. Supported palladium represents an important technical problem;[6a] this metal has been implanted on inorganic supports by ion exchange,[6b] by metal evaporation,[6c] by solvent extraction followed by reduction,[6d] by organometallic chemical vapor deposition (OMCVD) using allyl derivatives,[6e] and by cluster generation in the presence of an inorganic support.[6f] In spite of this intense activity in the field, we are not aware of any prior use of a non-organometallic compound of palladium for a chemoselective reaction with an oxide support under mild conditions. On the other hand, palladium on copper has been obtained by chemical vapour deposition of volatile palladium(II) coordination compounds.[6g] Also, the chemical interaction of π-allyl derivatives of palladium(II) with partially dehydrated silica has been reported in the literature, with release of propylene upon reaction with the silanol groups.[6h]

Experimental

Materials and reagents

All operations were carried out in conventional Schlenk tubes under a dry dinitrogen or argon atmosphere, unless otherwise specified. Solvents were dried according to conventional methods. Carbon dioxide was dried over calcium chloride. The secondary amine was distilled from sodium prior to use. The compound *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ was prepared according to a method reported earlier.[4] Commercial silica (Grace SD 3217/50; surface area, 318 $m^2 g^{-1}$; pore volume, 2.22 $cm^3 g^{-1}$) was heated at 160 °C at *ca.* 10^{-2} mmHg for 16 h to eliminate most of the physisorbed and chemisorbed water, cooled down to room temperature, and flame-sealed in vials under carbon dioxide (label: $SiO_{2\text{-}160}$). The silanol content was assumed to correspond to the weight loss after calcination at 850 °C. The silanol content (expressed as mmol of OH per gram of silica) was thus estimated to be 2.8.

Gas-volumetric and elemental analyses

The carbon dioxide content of the silica-supported palladium species and the carbon dioxide evolved in the course of the implantation reaction were determined in a thermostatted gas burette,[7] using liquid media previously saturated with carbon dioxide at the temperature of the experiment.

Elemental (C, H, N) analyses were carried out with a C. Erba mod. 1106 elemental analyzer at the Microanalytical Laboratory of the University of Pisa (Faculty of Pharmacy) or in the house. Other elemental analyses were carried out by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a Perkin-Elmer Plasma II instrument (Pd).

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Instrumental analysis

^1H and ^{13}C NMR solution spectra were measured with a Varian Gemini 200 BB instrument, and chemical shifts are expressed in ppm with respect to $SiMe_4$. IR spectra were measured with a FTIR Perkin-Elmer mod. 1725X instrument equipped with a KBr beam splitter and a TGS detector, in the 4000–400 cm^{-1} range, using CaF_2 windows for liquid samples and KBr or CaF_2 plates for Nujol mulls. Diffusion reflectance infrared Fourier transform (DRIFT) spectra were measured with the same spectrophotometer by mixing the sample with dry KBr under an inert atmosphere and by rapid transfer to the cell (Spectra Tech).

The cross polarization magic angle spinning (CP MAS) ^{13}C NMR spectra were measured at room temperature with a MSL 200 Brucker instrument operating at 50.321 MHz, chemical shifts being referred to external TMS.

XPS spectra were measured with a Perkin-Elmer PHI 5500 ESCA spectrometer equipped with a monochromatic X-ray source and an aluminium anode (Al-Kα radiation, $h\nu =$ 1483.6 eV), the source being maintained at 14 kV, with a power of 200 W. Powdered samples pressed on clean indium foils were used and the diameter of the analyzed sample area was *ca.* 400 μm while the background pressure in the analysis chamber was 10^{-8} Pa. For each sample, a preliminary general analysis was performed, in order to detect the presence of possible contaminants; the relevant photoemission peaks (Pd 3d , O 1s, C 1s, Si 2p) were recorded under high resolution conditions. From the photoemission peak intensity, the surface atomic concentrations were estimated, using the elemental sensitivity factors method.[8] Electrostatic charge was attenuated by using a low-energy flow electron gun: generally, peaks free from the typical deformations due to this phenomenon were obtained.

Transmission electron microscopy (TEM) images were obtained with a JEOL TEM 2010 instrument operating at 200 kV. The material was ground in a mortar until a very fine powder was obtained, which was deposited on a lacy carbon film supported on a standard copper grid. To avoid deterioration or contamination, the time required for sample preparation, carried out under dinitrogen, was reduced to a minimum (*ca.* 10 min). Bright field images were used in order to obtain the size distribution of the palladium particles.

Wide-angle X-ray spectroscopy (WAXS) and small angle X-ray spectroscopy (SAXS) data were collected with a non-commercial energy scanning diffractometer[9a] equipped with an X-ray generator (water-cooled, tungsten target, 3.0 kW maximum power), a germanium solid-state detector (SSD) connected to a multichannel analyzer by means of an electronic chain, a collimator system, step motors and sample holder. The X-ray tube and the detector can rotate in the vertical plane around a common centre in order to reach the appropriate 2θ scattering angle. A schematic drawing of the diffactometer has been published earlier.[9b]

WAXS, as applied to liquid[10] and amorphous[11] systems, allows the static structure function $i(q)$ to be derived, the scattering parameter being $q = (4\pi/\lambda)\sin\theta$; 2θ is the scattering angle, and λ is the radiation wavelength. Since q depends on both E and θ, an angular scanning with a monochromatic X-ray radiation (ADXD technique) or an energetic scanning with a white X-ray beam at a fixed value of θ (EDXD technique) can be performed. In the present case, the latter procedure was used. The EDXD technique presents several advantages, namely: (a) the time of measurement is strongly reduced at approximately constant statistical accuracy; (b) measurements are independent of the intensity fluctuation of the primary beam; (c) the instrument is static during the measurement, which simplifies the instrumental geometry and reduces the errors due to misalignment. On the other hand, energy-dependent phenomena have to be considered, such as absorption, polarization and inelastic scattering of the incident X-ray radiation; thus, the total intensity, observed by an energy dispersive detector, was corrected accordingly and for the escape peak suppression as well. Experimental conditions were: voltage, 45 kV; current, 35 mA; total power, 1.575 kW; energy interval, 16.0–38.0 keV; θ values, 26.0, 21.0, 15.5, 10.5, 8.0, 5.0, 3.5, 3.0, 2.0, 1.5, 1.0, 0.5 and 0.4°; scattering parameter range (q), 0.16–15.64 $Å^{-1}$. Normalization to a stoichiometric unit volume containing one palladium atom was performed. The static structure function $i(q)$ was obtained from the observed intensity $I(E, \theta)$, and expressed as $qi(q)M(q)$, where $M(q)$ is a sharpening factor for a given atom (silicon in this case), defined ($c = 0.01$) as for eqn. (1).

$$M(q) = f_{\mathrm{Si}}^{2}(0)/f_{\mathrm{Si}}^{2}(q)\exp(-cq^{2}) \qquad (1)$$

The Fourier transformation of the experimental static structure functions gives the radial distribution function $D(r)$:

$$D(r) = 4\pi r^{2}\rho_{0} + \frac{2r}{\pi}\int_{q_{\min}}^{q_{\max}} qi(q)M(q)\sin(qr)\,\mathrm{d}q \qquad (2)$$

In this equation, ρ_0 is the average electronic density of the sample $[\rho_0 = \sum_i n_i f_i(0))^2 V^{-1}]$, V is the stoichiometric unit volume, n_i is the number of atoms i per unit volume and f_i is the scattering factor for atom i.

The EDXD measurements were carried out on both the parent silica and the palladium-containing silica. The static structure functions are similar, see Fig. 1, thus showing that the presence of palladium(II) does not appreciably modify the structure of the matrix.

This experimental observation made the application of the difference or isomorphous substitution method possible.[12] In the difference curve of the radial distribution functions ($SiO_2/Pd^{II}-SiO_2$), which contains the contributions due to the implanted atoms only, the area of each peak is proportional to the number of scattering atoms and to their scattering factors.

The coordination environment of palladium was established by a curve fitting procedure of the experimental difference radial distribution function. The experimental static structure function $i(q)$ can be interpreted as a weighted sum of partial structure functions due to pairs of interacting atoms, by using the Debye function $i(q)$[13] [eqn. (3)] and by adjusting the σ_{ij} and the r_{ij} parameters, σ_{ij} being the rms variation of the interatomic distance r_{ij} [starting parameters are those obtained in the parent compound[4] *trans*-$Pd(O_2CNEt_2)_2(Et_2NH)_2$, namely Pd–O 2.022(3), Pd–N 2.058(3) Å. For the non-bonding Pd···Si distance, reference has been made to several molecular complexes of transition metal cations with alkyl- and aryl-silanolato ligands which have recently appeared in the literature,[14] in addition to the structural data of an iron(III)

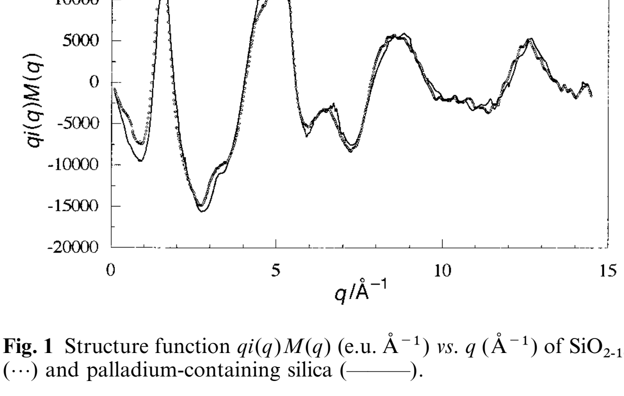

Fig. 1 Structure function $qi(q)M(q)$ (e.u. $Å^{-1}$) *vs.* q ($Å^{-1}$) of $SiO_{2\text{-}160}$ (···) and palladium-containing silica (———).

silicate[14a]].

$$i(q)=\sum f_i(q)f_j(q)\frac{\sin(qr_{ij})}{qr_{ij}}\exp(-1/2\sigma_{ij}{}^2q^2) \qquad (3)$$

The palladium containing silica samples were reduced both thermally and chemically (with dihydrogen), *vide infra*, and were subjected to both WAXS and SAXS measurements. In the latter case, the intensity of the scattered X-ray radiation $I(E,\ \theta)$, with $\theta<1°$, is related to the size and shape of the scattering centres, as for the Guinier law expressed by eqn. (4),[15] where R_g is the gyration radius of the scattering particle, which depends on both its shape and size. The gyration radius can be determined from the slope of the plot of $\ln I(q)$ *vs.* q^2.

$$I(q)=I(0)\ \exp(-1/3R_g{}^2q^2) \qquad (4)$$

For a given shape of the particle, the gyration radius is related to the particle size by simple equations [for a cube, $R_g{}^2=l^2/4$; for a sphere, $R_g{}^2=(3/5)\ R^2$].

For the small-angle X-ray scattering (SAXS) measurements, the scattering angle θ was 0.3, 0.4, and 0.5°, with a slit width of about 60 µm in order to reduce the X-ray angular divergence. A blank measurement showed that no intensity was monitored by the detector.

Chemical implantation

Palladium implantation on silica was carried out by the following procedure. Silica $SiO_{2\text{-}160}$ (DB-14–214, 5.6 g, corresponding to 15.7 mmol of silanol groups) was added to a toluene (100 cm^3) solution of *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ (1.01 g, 2.08 mmol; OH/Pd molar ratio, 7.5) in a 500 cm^3 flask and the mixture was stirred at room temperature for 2 h, occasionally reducing the partial pressure of carbon dioxide released in the process. After being recovered by filtration, the yellow palladium-containing silica was dried *in vacuo* for 20 h (5.75 g) and the following analytical results were obtained: AT-19, C, 5.5; H, 1.3; N, 1.5; Pd, 4.0; CO, 1.5%, corresponding to a substantially quantitative yield (see Table 1) of the implantation reaction and to the following molar ratios: CO_2/Pd, 0.9; N/Pd, 2.8. The ^{13}C CP MAS NMR spectrum showed resonances (δ, ppm from $SiMe_4$) at 12.0 (CH_3), 41.1 (CH_2), and 164.0 (O_2C), see Fig. 2. The ^{13}C NMR spectrum of the parent compound *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ has bands ([$^2H_8$]toluene, δ, ppm from $SiMe_4$) at 14.1 [$NH(CH_2\mathit{C}H_3)_2$], 14.5 [$O_2CN(CH_2\mathit{C}H_3)_2$], 41.6 [$NH(\mathit{C}H_2CH_3)_2$], 46.0 [$O_2CN(\mathit{C}H_2CH_3)_2$], 164.9 ($O_2C$). The DRIFT spectrum showed bands at 3259, 2978, 2939, 2882, 1598, 1549, 1483, 1463, 1426, 1382 and 1303 cm^{-1}. The parent compound has IR bands (PCTFE mull) at 3060, 2985, 2935, 2870, 1590, 1555, 1475, 1455, 1440, 1410, 1375 and 1325 cm^{-1}. For the XPS data and other details on the implantation reactions, see Table 1.

The implantation reaction was monitored gas volumetrically, using a large excess of silica. A toluene (25 cm^3) suspension of $SiO_{2\text{-}160}$ (5.4 g, 15.1 mmol of silanol groups), presaturated with carbon dioxide, was treated with the palladium(II) complex (0.20 g, 0.41 mmol, for a OH/Pd molar ratio of 37) at 20 ± 0.1 °C: the evolved carbon dioxide corresponded to a CO_2/Pd molar ratio of 0.8. Addition of excess acetic acid caused the evolution of 1.2 mol of carbon dioxide per palladium. In another experiment (AT-203), the suspension after the reaction with the silica was filtered under carbon dioxide and the filtrate was treated with excess acetic acid: no carbon dioxide was evolved.

Table 1 Implantation of palladium(II) on silica

Sample	Molar ratio OH/Pd	Yield (%)	Pd (%)	XPS[a] E_b/eV
AT-19	7.5	quant.	4.0	336.3
AT-323[b]	6.9	83	3.4	336.3
AT-355	20.5	88	1.8	336.1

[a]Pd $3d_{5/2}$ binding energy. Reference data (eV) (±0.2 eV): $Pd_{(s)}$, 335.1; PdO, 336.1.[8] [b]Sample used for WAXS experiments.

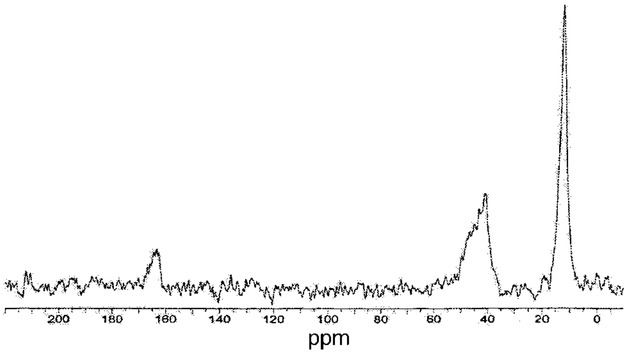

Fig. 2 ^{13}C CP MAS NMR spectrum of palladium(II) supported on SiO_2 resulting from the reaction of *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ with the silanol groups (sample AT-323). Irradiating field, 50 kHz; spinning rate, 5 kHz; contact time, 5 ms; sequence recycle time, 4 s; number of transients, 16 640; spectral width, 20 kHz; time domain points, 2048; chemical shifts are referred to $SiMe_4$.

Reduction of palladium

With dihydrogen. In a preparative experiment, the palladium-containing silica was reduced at room temperature under dihydrogen at atmospheric pressure in benzene (AT-166, Found: C, 4.2; H, 1.0; N, 0.6; Pd, 2.2%), see Table 2. WAXS and SAXS measurements were carried out on this sample. Reduction was also achieved by treating silica-supported palladium(II) with dihydrogen at room temperature for 6 d, in the absence of any solvent.

In a gas volumetric experiment, the palladium-containing silica (AT-323; 0.92 g; Pd, 3.4%; 0.29 mmol of palladium) was added to cyclohexane (25 cm^3) presaturated with dihydrogen and the volume of dihydrogen was measured at constant temperature (24.0 ± 0.1 °C) and pressure (1 atm). The originally yellow silica became brown and finally black after the completion of the gas absorption (0.43 mmol, corresponding to a H_2/Pd molar ratio of 1.5). In a blank experiment (AT-395) carried out with $SiO_{2\text{-}160}$, no H_2 was found to be absorbed under the same experimental conditions.

Thermal reduction. A sample of the palladium-containing silica (AT-323; 2.1 g; Pd, 3.4%; 0.67 mmol of palladium) was heated at 100 °C *in vacuo* (3 mmHg) for *ca.* 7 h; the brown product was stored under dinitrogen (AT-381, Found: C, 3.6; H, 0.9; N, 0.7%).

Another sample (AT-323; 1.7 g; Pd, 3.4%, corresponding to 0.54 mmol of palladium) was heated at 200 °C *in vacuo* (5×10^{-2} mmHg) for 6 h; at the end of the treatment the

Table 2 Reduction of palladium

Sample	Precursor	Reduction method[a,b]	XPS[c] E_b/eV	TEM[d] *d*/nm
AT-166[e]	AT-90	*a′*	335.3	n.d.
DB-16–9	AT-323	*a″*	n.d.	6–8
AT-381[e]	AT-323	*b′*	335.7	3–6
AT-408[e]	AT-323	*b″*	335.5	2–5

[a]Reduction with H_2 at room temperature: *a′*, in benzene; *a″*, without solvent. [b]Thermal reduction: *b′*, $T=100$ °C; *b″*, $T=200$ °C. [c]Pd $3d_{5/2}$ binding energy (eV) (±0.2 eV); for reference E_b values see Table 1, footnote *a*. [d]Palladium particle, mean diameter. [e]Samples used for WAXS experiments.

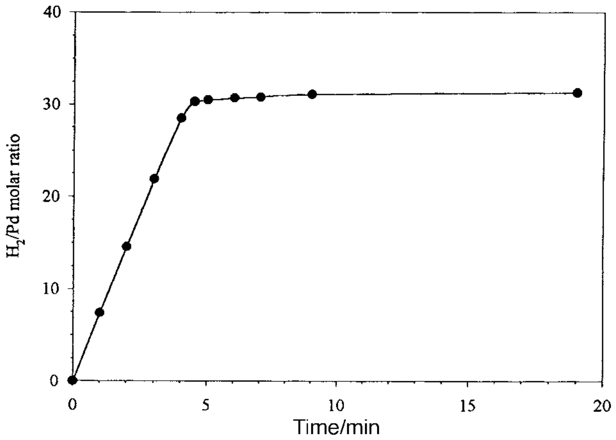

Fig. 3 Catalytic hydrogenation of cyclohexene. Moles of dihydrogen absorbed as a function of time (●). Solvent, cyclohexane; temperature, 24.1 ± 0.1 °C; cyclohexene, 2.3 mmol.

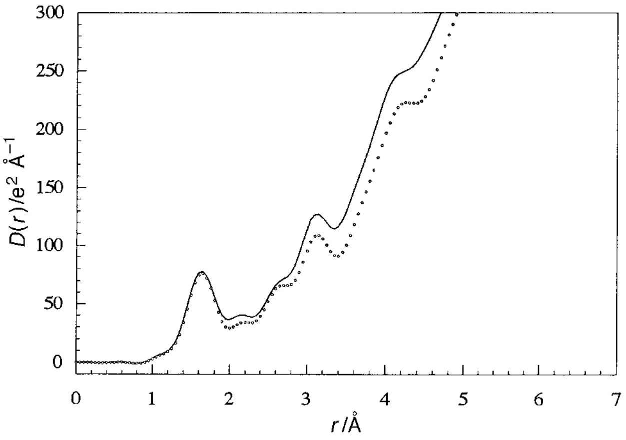

Fig. 4 WAXS data: radial distribution function $D(r)$ ($\times 10^{-3}$ e^2 Å^{-1}) *vs.* r for $SiO_{2\text{-}160}$ (···) and palladium-containing silica (———), AT-323.

sample became brown (AT-408, Found: C, 0.6; H, 0.0; N, 0.0%). For further data concerning the reduced samples, see Table 2.

Catalysis

Palladium-containing silica (AT-408, 0.23 g; Pd, 3.4%; 0.073 mmol of palladium), thermally pre-treated at 200 °C was suspended in cyclohexane (25 cm^3); the suspension was saturated with dihydrogen at 24.1 ± 0.1 °C for 3 h and then added of cyclohexene (0.25 cm^3, 2.4 mmol) under vigorous magnetic stirring. The olefin hydrogenation was independent of the cyclohexene concentration and substantially complete in *ca.* 5 min, corresponding to a H_2/Pd molar ratio of 33. The plot of dihydrogen absorption as a function of time is shown in Fig. 3. A catalytic activity of 70 mmol of H_2 min^{-1} $g_{Pd}{}^{-1}$ was estimated from the plot of Fig. 3; this corresponds to an apparent turnover frequency of 0.12, expressed as mols of dihydrogen absorbed per mol of palladium per second.

A commercially available sample of palladium supported on a silico-aluminate matrix (AT-416, 0.11 g; Pd, 2%; 0.021 mmol of palladium) suspended in cyclohexane (25 cm^3) and cyclohexene added (0.3 cm^3, 2.9 mmol) absorbed the expected amount of dihydrogen for complete hydrogenation in about 6 min at 24.2 ± 0.1 °C (for a H_2/Pd molar ratio of 138). The rate of cyclohexene hydrogenation was substantially independent of olefin concentration: a catalytic activity of 250 mmol of H_2 min^{-1} $g_{Pd}{}^{-1}$ was estimated, corresponding to an apparent turnover frequency (as defined above) of 0.44 s^{-1}.

Samples of silica-supported palladium, prereduced with dihydrogen at room temperature or thermally at 100 °C were found to catalyze cyclohexene hydrogenation, the gas absorption being dependent on olefin concentration (initial rates, respectively: 2.9 and 22 mmol of H_2 min^{-1} $g_{Pd}{}^{-1}$).

Results and discussion

Implantation

The *N,N*-diethylcarbamato complex of palladium(II), *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$, reacts with the silanol groups of partially dehydroxylated silica in toluene at room temperature. On the basis of the experimentally determined volume of carbon dioxide evolved in the reaction, see eqn. (5), the implantation was found to involve the evolution of about one mol of carbon dioxide per palladium.

$$\textit{trans}\text{-}Pd(O_2CNEt_2)_2(NHEt_2)_2 + n\ \#Si\text{–}OH \rightarrow$$

$$\rightarrow (\#Si\text{–}O)_nPd(O_2CNEt_2)_{2-n}(NHEt_2)_2 + n\ CO_2 + n\ NHEt_2 \quad (n \leqslant 1) \qquad (5)$$

The gas volumetric data, see Experimental section, show that at least 80% of palladium is chemically bonded to the silica surface. The XPS binding energies (336.1–336.3 eV) are to be compared with the value of 336.1 for PdO.[8a,b] Moreover, the ^{13}C CP MAS NMR data, see Fig. 2, show the presence of residual carbamato groups (resonances around 160 ppm), thus confirming that the silica-bonded palladium still maintains part of the original coordination environment. As far as other resonances are concerned (amine or carbamato ethyl groups), the intrinsic low resolution of the solid-state NMR spectrum does not allow any specific assignment to be made. The IR reflectance spectra show bands in the 1600–1300 cm^{-1} region, which closely resemble those of the parent palladium(II) compound.

WAXS measurements allowed the radial distribution function, see Fig. 4, to be calculated, in comparison with the data for the parent silica.

The difference radial distribution function was calculated (see Experimental section) and a curve fitting procedure of this function was carried out by Fourier transformation of the intensities obtained by the Debye formula of eqn. (3), using the same $M(q)$ and q_{max} as for the experimental data. Starting bonding and non-bonding parameters are from the literature:[4,14] particularly relevant in this connection are the results of a crystallographic study[14f] on a silanolato complex of palladium(I) showing Pd···Si non bonding distances of 2.981 and 3.520 Å. The Debye–Waller factors (σ_{ij}, Å) are considered as parameters in the curve fitting procedure ($\sigma_{ij}=0.04$ Å for $r_{ij} \leqslant 1.50$ Å; $\sigma_{ij}=0.08$ Å for $1.50 < r_{ij} \leqslant 2.20$ Å; $\sigma_{ij}=0.13$ Å for $2.20 < r_{ij} \leqslant 3.50$ Å; $\sigma_{ij}=0.20$ Å for $r_{ij} > 3.50$ Å). The experimental and calculated difference radial distribution functions are shown in Fig. 5; in the model, see Fig. 6, which gave the best fit of the experimental curve, each palladium atom is coordinated to one silanolato and two diethylamine ligands, and to a residual carbamato group as well.

Reduction

The reduction of the silica-supported palladium was carried out both with dihydrogen at room temperature or thermally (at 100 or 200 °C) under reduced pressure.

Reduction with dihydrogen. The reduction process was followed gas volumetrically and found to require 1.4 mol of H_2 per palladium. Eqn. (6) represents the idealized reduction process for a palladium(II) centre containing both carbamato and silanolato groups. The most efficient reduction method, as judged from the XPS binding energies approaching that of palladium bulk, is the treatment with dihydrogen, see Table 2.

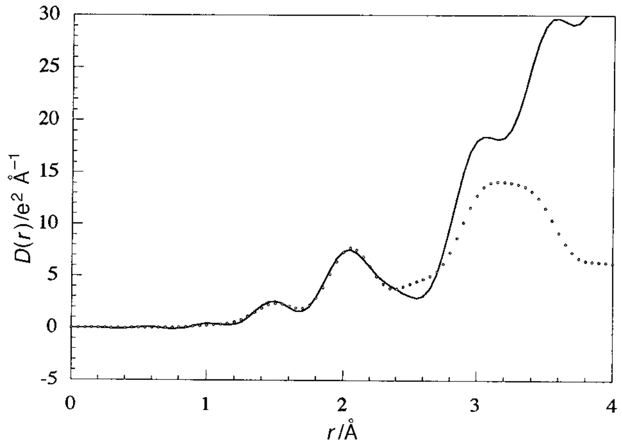

Fig. 5 WAXS data. Experimental (——) and calculated (···) difference radial distributions of silica-coordinated palladium (sample AT-323). $D(r)$ values ($\times 10^{-3}$) were calculated by using the Debye formula and the interatomic parameters specified in text.

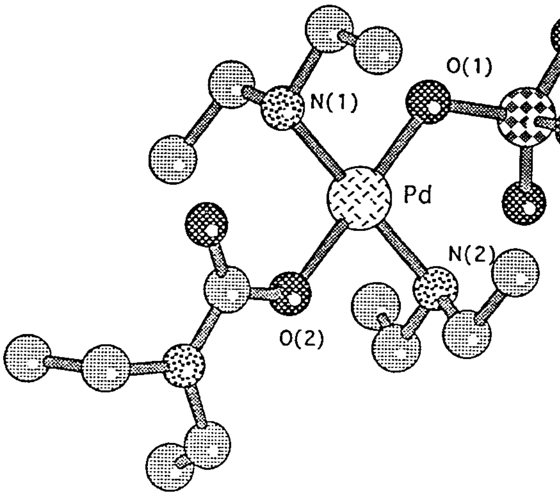

Fig. 6 Suggested model of the coordination shell of silica-bonded palladium(II), see text; bond distances (Å): Pd–N(1) 2.06(8), Pd–N(2) 2.06(8), Pd–O(1) 2.02(8), Pd–O(2) 2.02(8), the Pd···Si non-bonding distance is 3.08(0.13) Å.

$$\begin{aligned}&\#\text{Si–O–Pd}(\text{O}_2\text{CNEt}_2)(\text{NHEt}_2)_2+\text{H}_2\rightarrow\\&\text{CO}_2+3\ \text{NHEt}_2+\#\text{Si–OH}+\text{Pd}\end{aligned}\qquad(6)$$

The excess of dihydrogen absorbed with respect to the stoichiometry of reaction (6) is presumably used to form Pd–H bonds (palladium is reported [16] to react with dihydrogen forming a so-called β phase characterized by a H/Pd molar ratio of 0.6 at room temperature, with a dihydrogen equilibrium pressure of *ca.* 10 mmHg; other palladium hydride phases are known[16c–g]) or to reduce part of carbon dioxide formed in the process.

The palladium-containing silica was also treated thermally under reduced pressure; the sample showed only partial reduction to palladium(0), as suggested by the XPS data, with an E_b (335.7 eV for the sample thermally treated at 100 °C and 335.5 eV for that treated at 200 °C), slightly but significantly higher than those pertaining to bulk palladium (335.1 eV) and to the sample reduced with dihydrogen at room temperature (335.3 eV). The WAXS and SAXS data of the samples reduced with dihydrogen will be discussed first and then compared with those obtained by thermal reduction.

The radial distribution functions for the reduced palladium-containing silica and for the parent silica are shown in Fig. 7.

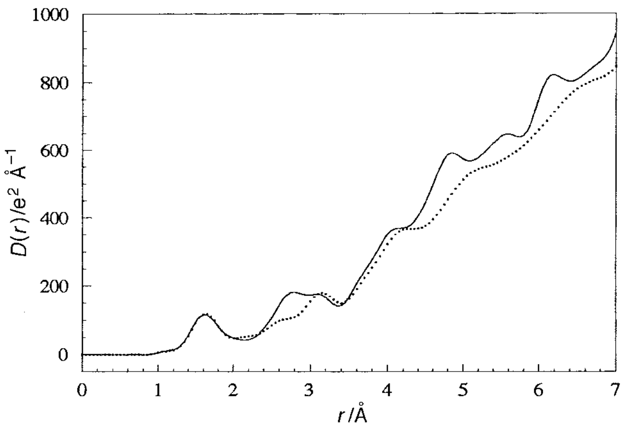

Fig. 7 WAXS data. Radial distribution functions $D(r)$ ($\times 10^{-3}$) for palladium containing silica after reduction with dihydrogen at room temperature (———), sample AT-166 and for $SiO_{2\text{-}160}$ (···).

After correction for the contribution by the average bulk electron density ($4\pi r^2\rho_0$), the Diff(r) functions of sample AT-166 and the silica support were obtained, see Fig. 8. These data show that reduced palladium gives metallic crystallites, with some long-range ordered structure. Fig. 8 shows peaks at *ca.* 2.7, 3.9 and 4.8 Å, corresponding, respectively, to the palladium–palladium distances of the twelve nearest- (2.751 Å), the six second-nearest- (3.891 Å), and the twenty-four third-nearest (4.765 Å) neighbours of the fcc crystal lattice of bulk palladium[17] [$a=3.8900(7)$ Å], the twelve fourth-nearest neighbours being at 5.502 Å.

An approximate evaluation of the mean dimension of the metal particles was carried out by SAXS measurements: a value of 19 ± 1 Å was obtained for the gyration radius, corresponding to a radius of 24 ± 2 Å for a spherical shape and to an edge of 38 ± 2 Å for cubic shape.

The theoretical structure function $qi(q)M(q)$ was calculated for metal particles containing 2457 palladium atoms ($d=2.750$ Å), corresponding to cubic particles with $l=31$ Å, the Debye–Waller factors being $\sigma=0.15$ Å for $0\leqslant d\leqslant5.60$ Å and $\sigma=0.20$ Å for $d>5.60$ Å. The curve of the structure function superimposed on the experimental one is shown in Fig. 9.

For the palladium-containing samples subjected to thermal treatment under reduced pressure (at 100 or 200 °C), reduction to palladium(0) was anticipated by the darkening of the substance and by the slight decrease of the XPS binding energy values with respect to PdO (336.1 eV). On the other hand, the WAXS structure functions for both samples, see Fig. 10, are similar to that of the unreduced substance, thus showing that only partial reduction had occurred (the analytical nitrogen content decreasing with increasing temperature is suggestive

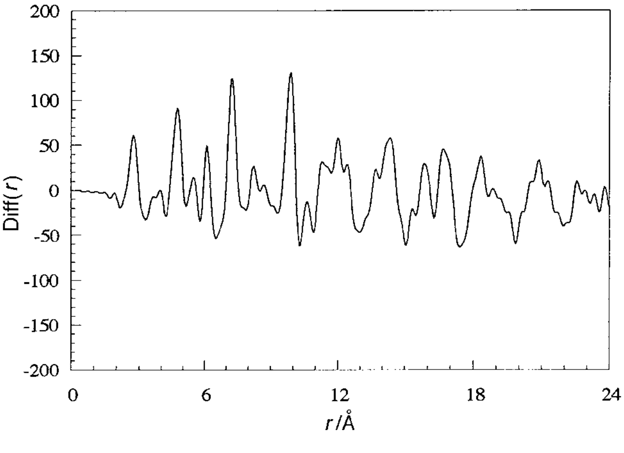

Fig. 8 WAXS data. Experimental Diff(r) ($\times 10^{-3}$) of AT-166 after reduction with dihydrogen at room temperature. The silica contribution was subtracted.

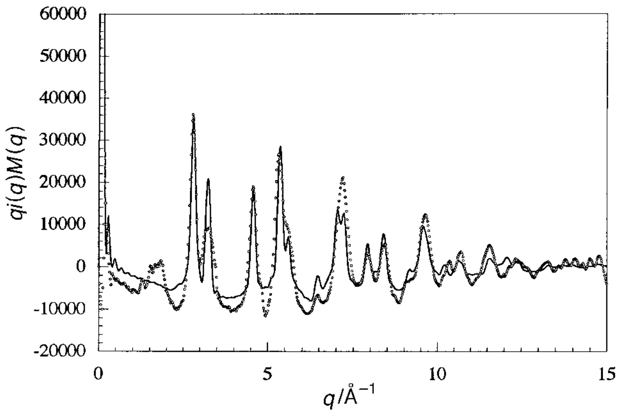

Fig. 9 Calculated structure function $qi(q)M(q)$ *vs.* q for palladium metal particles (clusters of 2457 atoms, $l=31$ Å) with face-centred cubic unit cell (———) compared with the experimental curve (···), AT-166.

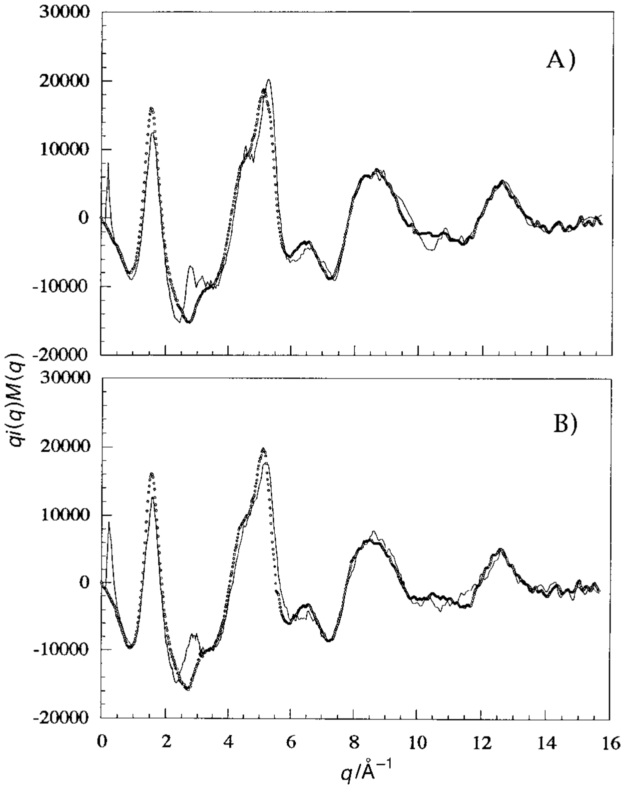

Fig. 10 Structure functions $qi(q)M(q)$ (e.u. Å^{-1}) *vs.* q (Å^{-1}) of $SiO_{2\text{-}160}$ (···) and palladium-containing silica (———): (A) after thermal treatment at 100 °C (AT-381); (B) after thermal treatment at 200 °C (AT-408). These curves should be compared with those shown in Fig. 1.

of palladium(II) persisting in the thermally treated samples at lower temperature).

Reduction to palladium(0) in all three cases (room temperature with dihydrogen, 100 or 200 °C) has been confirmed by transmission electron microscopy (TEM) measurements which have evidenced the formation of metallic particles. The particle size appears to increase as the temperature of the reduction decreases, the larger distribution being comprised between 6 and 8 nm for the sample reduced with dihydrogen at room temperature. The apparent disagreement between the SAXS and TEM measurements concerning the particle size may be reconciled by considering that TEM measurements may overestimate the particle size due to the fact that the contribution by the smaller sizes may become almost negligible. An enlargement of one of the palladium particles is shown in the TEM image of the thermally (200 °C) treated sample, see Fig. 11; the picture shows two different orientations of the atomic planes within the same particle.

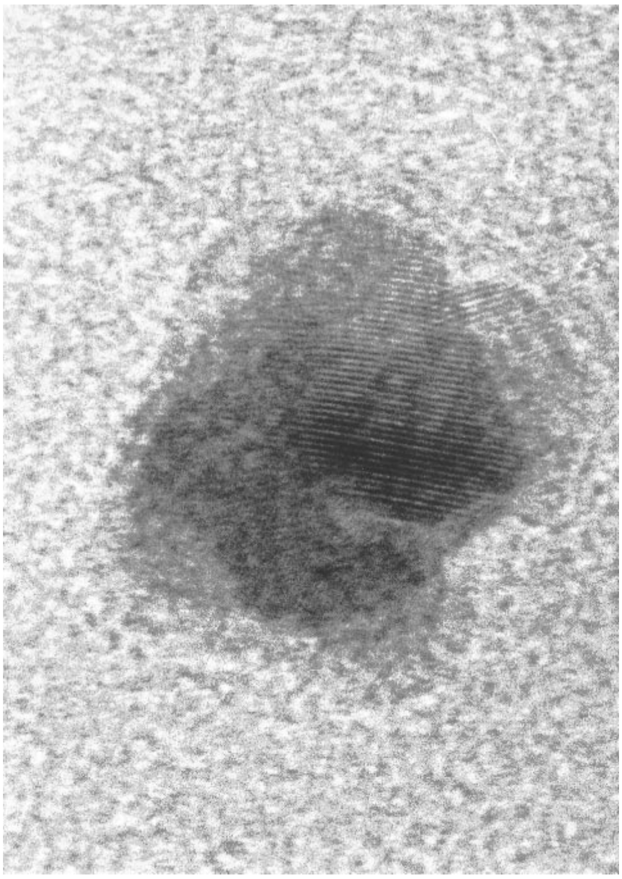

Fig. 11 TEM image (1.7 nm cm^{-1}; ×6 000 000) of one of the palladium particles; sample DB-16.1, obtained by thermal reduction at 200 °C under reduced pressure.

Catalytic hydrogenations

The highest catalytic activity was observed with the palladium catalyst thermally pretreated under reduced pressure at 200 °C, see Experimental section and Fig. 3. In this case, the plot of the dihydrogen absorbed *vs.* time shows a zero-order dependence with respect to olefin concentration (under the conditions of the experiment, the dihydrogen concentration is constant). Heterogeneous catalytic hydrogenations of unsaturated substrates have been extensively studied.[18] Rates have frequently been found to be zero-order with respect to olefin concentration, and this has been attributed to the dissociative adsorption of dihydrogen being rate determining.[19] On the other hand, poisoning may lead to a decreased adsorption rate of the olefin by the catalyst, thus possibly leading the overall rate to become dependent on substrate concentration. Some of the catalysts prepared in the course of this study retain secondary amine, after thermal (100 °C under reduced pressure) or chemical (by dihydrogen at room temperature) activation. The thermal treatment at 200 °C under reduced pressure shows no residual amine and the rate of hydrogenation is independent of substrate concentration, in agreement with similar findings for other supported palladium catalysts in hydrogenation reactions.[19b,20] Although the time required for completing the reaction is *ca.* 5 min, a diffusion-controlled process is unlikely because of the very efficient stirring. Similar observations were made for the silica-supported catalysts based on platinum.[1b]

Conclusions

This paper has shown that a palladium silicate can be prepared on a partially hydroxylated amorphous silica by protonation (the silanol groups are the reactive sites on the surface) of a hydrocarbon-soluble *N*,*N*-dialkylcarbamato derivative of palladium(II). The implantation reaction depends on the OH/Pd molar ratio used; in the present case, when such a ratio is $\gtrsim 7$, the implantation reaction is substantially quantitative.This third paper of the series shows that a readily available molecular compound of palladium(II) can be used to carry out the chemical implantation on the silica surface, with a presumably uniform distribution of the palladium(II) centres. As the palladium(II) precursor is easily prepared from the cationic acetonitrile complex of palladium(II) $[Pd(MeCN)_4]^{2+}$ through the oxidation of palladium metal by NO^+, this paper discloses a facile method of ultimately obtaining palladium particles on silica based on a simple and selective chemical methodology in the preliminary step. It is easy to predict that this methodology can be extended to implant palladium(II) and thus to produce palladium particles on other inorganic, partially hydroxylated, matrices, such as alumina and titania and work is now in progress aimed at verifying this prediction.

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Paper 8/04456B