Evolution of Pd/SiO$_2$ catalysts prepared from chlorine-free precursors

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The effect of pretreatment conditions on the final metal dispersion and chemistry of precalcination of Pd/SiO$_2$ catalysts prepared from Pd(NH$_3$)$_4$(NO$_3$)$_2$ and palladium acetylacetonate [Pd(acac)$_2$] have been studied. The fate of the Pd(NH$_3$)$_4$$^{2+}$/SiO$_2$ precursor strongly depends on precalcination conditions. In helium, a vast majority of the ammine ligands desorb in a stepwise fashion, whereas considerable amounts of N$_2$, N$_2$O and NO are also liberated at various stages of precalcination in O$_2$–He. The latter finding, not observed by others, is explicable by the known propensity of palladium to catalyse NH$_3$ oxidation. Pretreatment of the Pd(NH$_3$)$_4$$^{2+}$/SiO$_2$ in He leads to well dispersed reduced Pd species, but an analogous pretreatment in O$_2$–He results in the formation of an even more dispersed PdO species. In precalcination of the Pd(acac)$_2$/SiO$_2$ precursor, an oxidizing atmosphere and temperatures $\geqslant 250\,^\circ$C are essential for complete removal of carbonaceous species. After decomposition in He, the catalytic role of a carbonaceous material, retained by Pd/SiO$_2$, depends on the temperature of the pretreatment. The low-temperature treatment (at 250 °C), followed by reduction in H$_2$, supposedly leads to a loosely packed carbonaceous residue, leaving a considerable part of the palladium surface still capable of 2,2-dimethylpropane conversion. On the other hand, a high-temperature decomposition of the Pd(acac)$_2$ precursor (at 500 °C) in He greatly suppresses the activity. It is speculated that the decomposition in He at 500 °C leads to a carbide-like surface material, which is not eliminated by reduction in H$_2$.

It is known that the catalytic behaviour of supported metals strongly depends on a great number of variables involved in preparation and pretreatment procedures.[1–11] Although in recent years there has been a substantial understanding of the problem of preparation of palladium catalysts using tetraamminepalladium(II) complexes[2–8] or palladium acetylacetonate [Pd(acac)$_2$],[9–11] several details concerning the chemistry of the precalcination–reduction step are still missing or are controversial. For example, according to Gubitosa *et al.*,[8] direct reduction of a mildly dried (partly decomposed) ammine precursor leads to a higher palladium dispersion on silica than the reduction of a dispersed PdO precursor. This was rationalized by the fact that PdO, easily reducible at lower temperatures, transforms into β-palladium hydride species (responsible for an increased mobility of Pd). On the other hand, Pd ammine complexes are reducible at > 100 °C, when the formation of Pd hydride is minimized or avoided. Other workers[3,12] found, however, that direct reduction of Pd(NH$_3$)$_4$$^{2+}$/silica leads to lower metal dispersions than pretreating the precursor in an oxidizing or inert atmosphere prior to reduction. Very high mobility of a surface precursor containing Pd, ammine ligands and hydrogen formed during direct reduction of a Pd(NH$_3$)$_4$$^{2+}$/SiO$_2$ was invoked to explain the tendency of palladium surface-species to agglomerate.[3]

Bonivardi and Baltanás[7] found that elevated precalcination temperatures (> 150 °C) are beneficial for obtaining higher Pd dispersions. This finding was rationalized by assuming a significant surface mobility of Pd aquoammine complexes existing after precalcination at lower temperatures. The presence of water during reduction of Pd ammine complexes supported on SiO$_2$ leads to lower metal dispersion.[4]

The chemistry of precalcination of the Pd(NH$_3$)$_4$$^{2+}$/SiO$_2$ precursor is also not fully understood. It is recognized that the decomposition of silica-supported Pd(NH$_3$)$_4$$^{2+}$ ions proceeds in a stepwise fashion and complete removal of NH$_3$ ligands occurs at temperatures above 250–350 °C.[5] Other details are

not so certain. For instance, the UV–VIS and thermochemical studies of Bonivardi and Baltanás[5,6] showed that the calcination at 150 °C leads to Pd(NH$_3$)$_2$$^{2+}$/SiO$_2$ whereas a similar investigation of Bouchemoua *et al.*[2] indicates the presence of monoammine species after an analogous pretreatment. It has not been decided if an oxidizing atmosphere (compared with an inert gas) during calcination is beneficial,[13] harmful[3] or indifferent[7] for obtaining significant Pd dispersions. Although all of these points would be rationalized by using different silicas (*e.g.*, of different porosities) and pretreatment conditions, clarification is required. In this work we decided to look more closely at the chemistry of the precalcination step of Pd(NH$_3$)$_4$$^{2+}$/SiO$_2$ precursor by using mass spectrometric analysis of a liberated gas and by the UV–VIS study of the palladium ammine precursor subjected to various pretreatments.

Similar questions can be raised in the preparation of supported Pd catalysts by grafting Pd(acac)$_2$. It seems reasonable that pretreatment in an oxidizing atmosphere is needed to remove (burn) all coke obtained from the decomposed precursor. However, it is not clear how critical are the conditions of the precalcination step. If some carbonaceous material remains after decomposition in an inert or even reducing atmosphere, it is not known how such 'coke' influences the catalytic behaviour of the Pd/support. Also, it is not known if excessively severe oxidizing conditions (supposedly needed for a careful removal of carbon) have a detrimental effect on metal dispersion.

Most of these questions are addressed in this work.

Experimental

The support was Davison 62 silica gel, 75–120 mesh, washed with dilute HCl, redistilled water, dried in the oven at 110 °C for 12 h and, finally, calcined in air in an oven at 450 °C for 4 h. Two Pd/SiO$_2$ catalysts were prepared from chlorine-free precursors: tetraamminepalladium(II)

nitrate, $[Pd(NH_3)_4(NO_3)_2]$ and palladium acetylacetonate $[Pd(acac)_2]$.

Ion exchange using $Pd(NH_3)_4(NO_3)_2$ (Alfa Produkte, Karlsruhe, Germany, lot no. 031482109), between pH 9.6 and 10, and room temperature was undertaken according to the description given elsewhere.[6] The suspension obtained was filtered and carefully washed with aqueous NH_3. The solid, referred to later as 'ex-$Pd(NH_3)_4^{2+}$', was dried in air in an oven at 60 °C for 8 h.

The slurry of SiO_2 in a benzene (analytical grade, POCh, Gliwice, Poland) solution of $Pd(acac)_2$ (99.8%, Alfa Produkte, Karlsruhe, Germany, lot no. 314882112) was maintained at 80 °C for 2 h.[11] After cooling and filtration, the resulting solid was dried in an oven at 80 °C for 2 h. After drying, the catalysts were closed in glass-stoppered bottles and kept in a desiccator. The palladium content in the prepared solids was determined as described previously.[1] The catalyst prepared from $Pd(NH_3)_4(NO_3)_2$ had 1.1 wt.% palladium loading, whereas the ex-$Pd(acac)_2$ was 1.6 wt.%.

Sample precalcination was carried out in a flow system, either in a 1% O_2–He stream or in pure He (both 25 cm³ min⁻¹) as described elsewhere.[1] The outlet of a tubular reactor with the Pd ammine/SiO_2 or $Pd(acac)_2$/SiO_2 precursor (≈ 0.5 g) was connected via a T-union to the sampling valve of a Dycor M200 quadrupole mass spectrometer and a vent. The temperature of the reactor was programmed using an Omega CN2011 temperature controller at a 4 °C min⁻¹ ramp. The evolutions of the most relevant m/z were monitored: (a) for Pd ammine precursor: 2 (H_2), 12 (C), 14 (N), 15 (NH), 16 (NH_2, O), 17 (NH_3, OH), 18 (H_2O), 28 (CO, N_2), 30 (NO), 44 (N_2O, CO_2), 46 (NO_2), and (b) for precalcination of $Pd(acac)_2$/SiO_2: 15 (CH_3^+), 18 (H_2O), 28 (CO), 43 (CH_3CO^+ and ex-hydrocarbons), 44 (CO_2) and 57, 85 and 100 (ex-acetone and acetyloacetone). In order to determine changes in relative amounts of various species it was necessary to acknowledge that one mass in a spectrum may result from contributions of different species, i.e., m/z 17 results from H_2O and NH_3. In order to separate such contributions, the obtained mass spectra were elaborated in terms of standard mass spectra of respective compounds.

Temperature-programmed reduction (TPR) experiments (at 8 °C min⁻¹ ramp) were carried out in a flow of 8% H_2–Ar, using a Gow–Mac thermal conductivity detector.

Diffuse reflectance spectra were recorded on a Beckman 5270 spectrophotometer (spectral range 230–2500 nm) equipped with an integrating sphere coated with $BaSO_4$.

Two samples of differently pretreated 1.6 wt.% Pd/SiO_2[ex-$Pd(acac)_2$] were investigated by transmission electron microscopy (TEM) (JEM-100α11). 1.1 wt.% and 1.6 wt.% Pd/SiO_2 were screened as catalysts in the reactions of the conversion of 2,2-dimethylpropane and n-hexane with dihydrogen. The reactions were conducted in flow systems under atmospheric pressure as described previously.[1,14] Reaction products were analysed by an on-line gas chromatograph (HP 5890 Series II) with an FID detector. For 2,2-dimethylpropane conversion a 6 m column packed with squalane–chromosorb P was used, whereas for the n-hexane reaction, a 50 m PONA (type 19091S-001-HP) capillary column was employed. The partial pressures of reactants were: 2,2-dimethylpropane, 6 Torr and H_2, 60 Torr in the 2,2-dimethylpropane conversion reaction; and n-hexane, 45 Torr and H_2, 720 Torr, in the n-hexane reaction. Turnover frequencies (TOFs) were calculated on the basis of the dispersion measured by H_2 chemisorption. Selectivities were calculated as the carbon percentage of 2,2-dimethylpropane (or n-hexane) consumed in the formation of a designated product.

Results

Temperature-programmed decompositions (TPDs) in He

[TPD(He)–MS] and 1% O_2–He [TPD(Ox)–MS] of the precursor of 1.1 wt.% Pd/SiO_2 prepared by ion exchange of silica with $Pd(NH_3)_4(NO_3)_2$ are shown in Fig. 1. Evolutions of the most important masses are shown: 2, 16, 28, 30 and 44. TPD–MS runs were repeated at least three times, giving excellent agreement for all respective mass profiles. Direct comparison of evolutions of m/z 16 (Fig. 1) with m/z 17 and 18 (not shown in Fig. 1) indicates that, apart from a massive release of water in both cases, more NH_3 is liberated during the pretreatment in He than in 1% O_2–He. The presence of non-negligible amounts of m/z 30 and 44 in Fig. 1B suggests liberation of nitrogen oxides during TPD(Ox). On the other hand, the profile of the TPD(He) is characterized by a considerable evolution of m/z 2 (H_2) at higher temperatures (Fig. 1A).

The results of TPD of the precursor of 1.6 wt.% Pd/SiO_2 prepared from $Pd(acac)_2$ are shown in Fig. 2 (A, for He pretreatment; B, for precalcination in 1% O_2–He). The most important profiles concern the following: m/z 28, 43, 44 and 85. It is seen that oxidative pretreatment produces an abrupt termination of all investigated m/z values at ca. 250 °C (Fig. 2B).

The UV–VIS diffuse reflectance spectra of the precalcined precursors are shown in Fig. 3. Fig. 4 presents TPR data of differently calcined supported palladium precursors. Metal dispersion data, based on H_2 chemisorption, indicated that
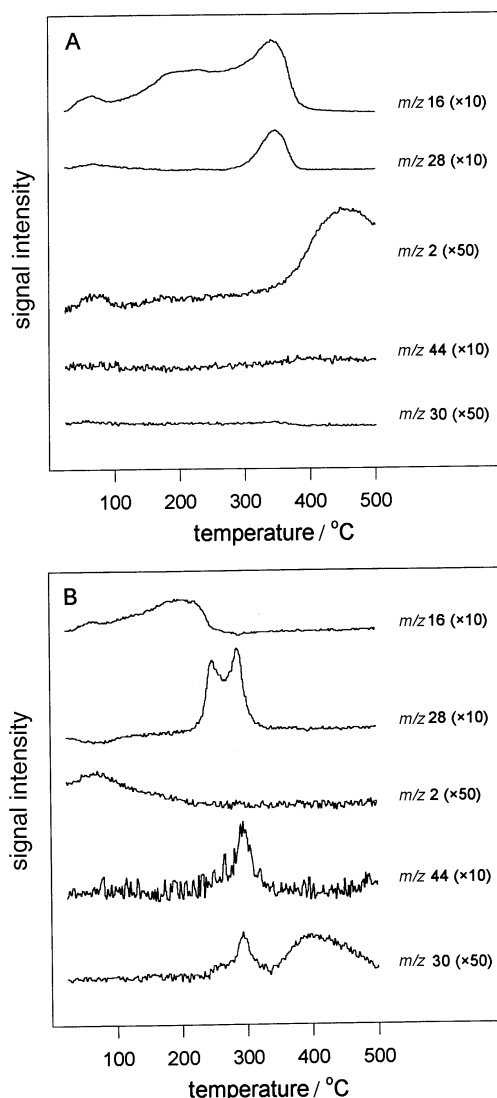

Fig. 1 Temperature-programmed decomposition spectra of 1.1 wt.% $Pd(NH_3)_4^{2+}$/SiO_2. A, calcination in helium; B, calcination in 1% O_2–He.

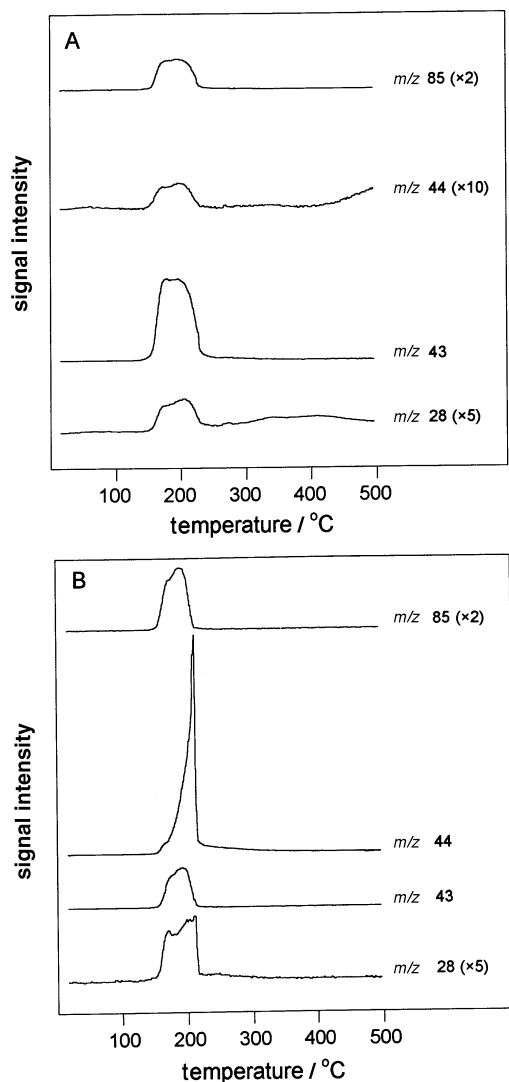**Fig. 2** Temperature-programmed decomposition spectra of 1.6 wt.% $Pd(acac)_2/SiO_2$. A, calcination in helium; B, calcination in 1% O_2–He.
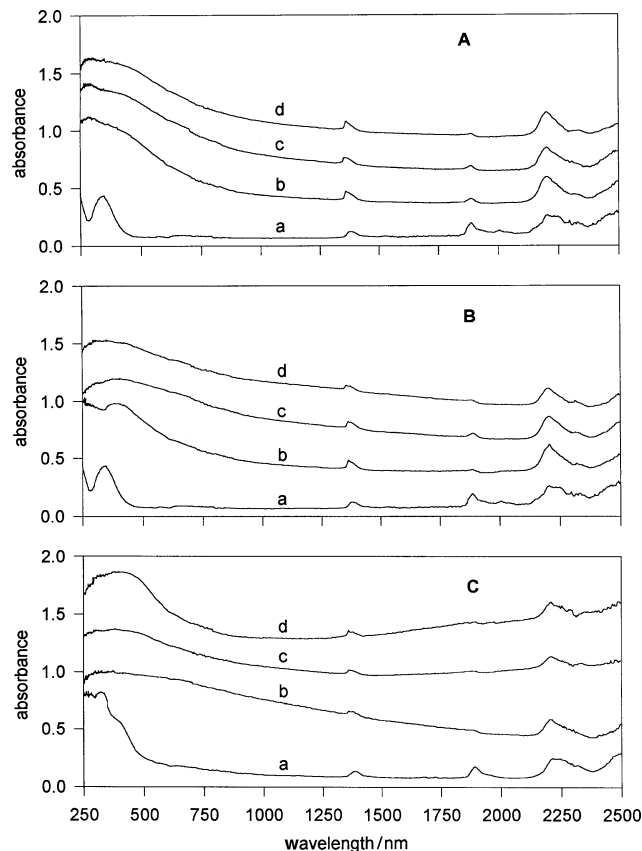

Fig. 3 UV–VIS diffuse reflectance spectra of differently precalcined $Pd(NH_3)_4^{2+}/SiO_2$ (in 1% O_2–He, A; in He, B) and $Pd(acac)_2$ (in 1% O_2–He, C). a, Fresh catalyst; b, after pretreatment to 250 °C; c, after pretreatment to 400 °C; d, after pretreatment to 500 °C.

the 1.1 wt.% Pd/SiO_2 catalyst is well dispersed. H_{ad}/Pd, as a measure of metal dispersion, is somewhat higher for samples pretreated in 1% O_2–He (≈ 0.75) than after helium pretreatment ($H_{ad}/Pd \approx 0.64$). For 1.6 wt.% Pd/SiO_2, which was less dispersed than the ex-$Pd(NH_3)_4^{2+}$ catalysts, the samples precalcined in 1% O_2–He chemisorbed roughly double the

Table 1 2,2-Dimethylpropane conversion on 1.6 wt.% Pd/SiO_2 [ex-$Pd(acac)_2$]: turnover frequencies (TOF), product distributions and apparent activation energies ($E_{A, app}$)

| reaction temperature/°C | conversion (%) | product distribution (%)[a] | | | | | | | TOF[b] s^{-1} | $E_{A, app}$/ kcal mol^{-1} |
		Me	Et	Pr	iBu	nBu	iP	nP		
O_2–He, 250 °C; H_2, 500 °C[c]										
270	1.534	16.8	0.4	1.1	61.6	3.4	16.3	0.3	2.12×10^{-3}	73.1 ± 2.6
261	0.447	16.1	–	–	61.3	1.5	21.1	–	6.19×10^{-4}	
251	0.132	15.3	–	–	61.1	2.4	21.1	–	1.83×10^{-4}	
He, 250 °C; H_2, 500 °C[c]										
280	1.065	18.5	0.2	1.2	66.7	2.0	11.1	0.3	9.67×10^{-4}	67.4 ± 1.2
270	0.368	17.8	–	–	67.8	0.7	13.6	–	3.35×10^{-4}	
261	0.122	17.1	–	–	68.7	–	14.3	–	1.11×10^{-4}	
251	0.035	13.9	–	–	66.1	5.7	14.3	–	3.21×10^{-5}	
O_2–He, 500 °C; H_2, 500 °C[c]										
270	0.996	15.2	0.5	1.0	54.3	3.3	24.9	0.8	1.36×10^{-3}	68.6 ± 1.8
261	0.333	14.2	–	–	54.3	2.0	29.5	–	4.55×10^{-4}	
251	0.088	12.6	–	–	52.3	5.2	29.9	–	1.21×10^{-4}	
He, 500 °C; H_2, 500 °C[c]										
280	0.384	18.0	–	0.9	67.0	1.0	13.1	–	2.78×10^{-4}	63.5 ± 1.5
270	0.134	17.0	–	–	66.6	3.0	13.3	–	9.72×10^{-5}	
261	0.045	15.8	–	–	65.0	5.4	13.8	–	3.29×10^{-5}	

[a] Product distribution based on carbon balance: methane (Me), ethane (Et), propane (Pr), isobutane (iBu), n-butane (nBu), isopentane (iP) and n-pentane (nP). [b] TOF, assuming Pd dispersion = 0.25. [c] Catalyst pretreatment, for further details see text.
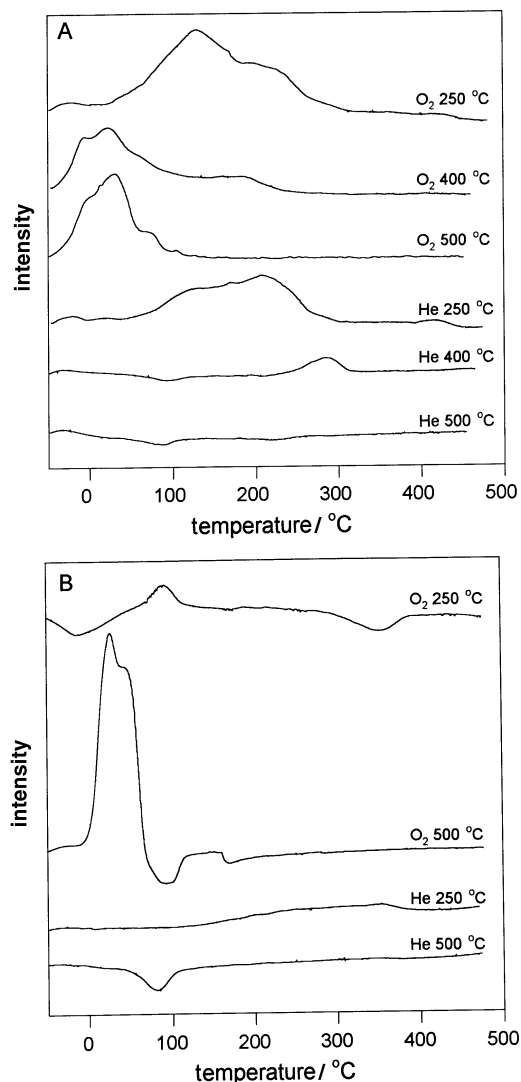
Fig. 4 TPR profiles of differently precalcined $Pd(NH_3)_4^{2+}/SiO_2$ (A) and $Pd(acac)_2/SiO_2$ precursors (B). Precalcination in He (marked as 'He') or 1% O_2–He (marked as 'O_2') up to indicated temperatures.

amount of hydrogen compared with the samples pretreated in helium ($H_{ad}/Pd \approx 0.25$ *vs.* 0.13). TEM studies showed that all samples, irrespective of their pretreatment, exhibit similar mean metal particle sizes, *ca.* 3 nm, upon reduction.

Results of kinetic studies using 1.6 wt.% Pd/SiO_2 after various pretreatments are shown in Table 1 (2,2-dimethylpropane conversion) and Table 2 (*n*-hexane conversion). It must be stressed that in order to limit secondary reactions and self-poisoning, the level of the overall conversion was kept very low, usually <1%. With such a precaution, self-poisoning was negligible for 2,2-dimethylpropane conversion. However, for *n*-hexane conversion, self-poisoning was significant, exemplified by a marked decrease of TOF at highest reaction temperatures. Therefore, in order to calculate the activation energies, it was checked that, after reaching the highest reaction temperature in a run, all experimental points collected on cooling the reactor were reasonably stable. Calculation of activation energies was performed by considering these stable ('downwards') points.
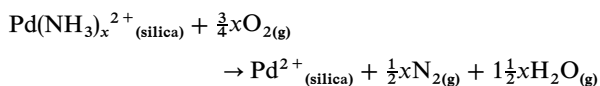
Discussion

Evolution of Pd/SiO_2 prepared from $Pd(NH_3)_4(NO_3)_2$

The UV–VIS diffuse reflectance spectra (Fig. 3) of variously precalcined $Pd(NH_3)_4^{2+}/SiO_2$ precursors show a gradual removal of NH_3 ligands from palladium ammine. First, the sample dried in air at 60 °C for 8 h and stored in air exhibited a band at 341 nm, characteristic of a $Pd(NH_3)_2(H_2O)_2$ complex.[15] Heating in He to 250 °C clearly removes an additional NH_3 ligand; this is evidenced by the band shift up to 391 nm (Fig. 3B, profile b). The presence of NH_3 in this sample is also manifested because the band at *ca.* 2000 nm characteristic of ammonia,[16] clearly seen in the overtone region of profile a (combination band, $v + \delta$), is still detectable in profile b (250 °C), but is invisible in profiles c (400 °C) and d (500 °C). Obviously, more serious heating leads to a complete removal of ammine ligands. The TPD(He)–MS spectrum (Fig. 1A) shows that the evolution of ammonia, indicated by changes in *m/z* 16 (the parent peak, *m/z* 17, is heavily influ-

Table 2 *n*-Hexane reaction on 1.6 wt.% Pd/SiO_2 [ex-$Pd(acac)_2$]: turnover frequencies (TOF), product distributions and apparent activation energies ($E_{A, app}$)

$T/°C$	α^a (%)	product distribution[b]						$\dfrac{2MP}{3MP}$	ζ^c	$M_f{}^d$	$TOF^e/$ s^{-1}	$E_{A, app}/$ kcal mol^{-1}
		$C_{<6}$	$C_{6,is}$	MCP	Bz + cH	Ol	$C_{>6}$					
O_2–He, 250 °C; H_2, 500 °C[f]												
340	0.942	26.9	14.5	44.3	13.8	–	0.5	2.39	2.29	1.07	1.09×10^{-3}	71.4 ± 0.9
330	0.345	28.0	12.2	47.3	12.5	–	–	2.73	2.28	1.17	3.98×10^{-4}	
320	0.126	32.6	12.3	43.4	9.0	–	–	3.21	2.46	0.95	1.45×10^{-4}	
310	0.047	38.0	12.7	35.3	14.1	–	–	3.05	2.62	0.86	5.42×10^{-5}	
He, 250 °C; H_2, 500 °C[f]												
350	0.696	35.4	10.2	35.4	10.9	8.2	0.2	2.03	2.31	1.04	4.94×10^{-4}	
340	0.269	36.3	8.7	33.7	9.4	12.0	–	2.15	2.38	1.02	1.91×10^{-4}	64.1 ± 3.1
331	0.111	35.5	7.9	26.7	6.5	23.5	–	2.19	2.58	0.83	7.88×10^{-5}	
320	0.052	38.3	7.0	16.7	5.4	32.6	–	2.23	2.97	0.68	3.70×10^{-5}	
O_2–He, 500 °C; H_2, 500 °C[f]												
341	0.729	21.4	16.5	47.8	13.9	–	0.4	2.15	2.31	1.26	8.32×10^{-4}	
330	0.266	23.9	14.3	49.7	12.1	–	–	2.19	2.34	1.31	3.04×10^{-4}	59.8 ± 3.4
320	0.094	28.0	14.0	47.0	11.0	–	–	2.04	2.51	0.92	1.08×10^{-4}	
300	0.022	45.4	13.2	38.7	2.7	–	–	2.04	3.01	0.60	2.49×10^{-5}	
He, 500 °C; H_2, 500 °C[f]												
361	0.661	35.5	8.7	33.0	11.0	11.7	–	2.17	2.26	1.11	7.72×10^{-4}	
350	0.256	33.8	7.2	28.7	8.6	21.8	–	2.28	2.30	1.05	3.00×10^{-4}	59.5 ± 3.4
340	0.117	31.3	6.2	22.6	6.9	33.1	–	2.80	2.45	0.95	1.37×10^{-4}	
330	0.059	32.3	5.2	13.5	5.5	43.5	–	2.40	2.53	0.99	6.92×10^{-5}	

[a] Extent of conversion (%). [b] Product distribution based on carbon balance; hydrogenolysis products ($C_{<6}$), hexane isomers ($C_{6, is}$), methylcyclopentane (MCP), benzene + cyclohexane (Bz + cH), C_6 alkenes (Ol), higher alkanes ($C_{>6}$). [c] Fragmentation factor, for definition see ref. 30. [d] Multiplicity factor, for definition see ref. 31. [e] TOF, assuming Pd dispersion 0.25. [f] Catalyst pretreatment, for further details, see text.

enced by water evolution), commences above 100 °C and terminates at *ca.* 350 °C. The last portion of liberated NH_3, between 300 and 360 °C is accompanied by a massive evolution of nitrogen. Evidently, a part of NH_3 is decomposed at *ca.* 350 °C, because hydrogen (*m/z* 2) begins to release at this temperature, showing a maximum rate of its evolution at *ca.* 450 °C. It appears that hydrogen is more strongly held than nitrogen by the catalyst, and also some of the generated H_2 is used for palladium reduction. There is no indication of the formation of nitrogen oxides, in agreement with others.[5] Precalcination of the $Pd(NH_3)_4^{2+}/SiO_2$ precursor in 1% O_2–He leads to different results. First, after the pretreatment to 250 °C, a featureless profile of the respective UV–VIS spectrum (Fig. 3A, profile b) indicates that at this stage palladium does not coordinate NH_3 ligands. The mass spectrum (Fig. 1B) is compatible with such a statement. The evolution of *m/z* 16 strictly corresponds to the profiles of *m/z* 17 and 18 (not shown); thus, *m/z* 16 reflects the evolution of water. The tail of *m/z* 16, *i.e.*, at *ca.* 250 °C, is somewhat distorted by oxygen consumption, as evidenced by a simultaneous 'negative' peak of *m/z* 32, not shown in Fig. 1B. At the same time, *i.e.*, at 250 °C and above, N_2 (*m/z* 28) is seen in the gas phase. It should be mentioned that the rate of production of N_2 mirrors the rate of O_2 consumption. Since at the same time we observe the appearance of water, the oxidation of ammine ligands may be visualized similarly, as suggested by Homeyer and Sachtler[17] for precalcination of $Pd(NH_3)_4(NO_3)_2/NaY$:

$$Pd(NH_3)_x^{2+}{}_{(silica)} + \tfrac{3}{4}xO_{2(g)}$$
$$\rightarrow Pd^{2+}{}_{(silica)} + \tfrac{1}{2}xN_{2(g)} + 1\tfrac{1}{2}xH_2O_{(g)}$$

Interestingly, for precalcination in 1% O_2–He, we observed some, non-negligible production of N_2O and NO, not seen by others.[5,17,18] This is evidenced by evolution of *m/z* 30 (NO) and 44 (N_2O, after careful subtraction of the contribution from CO_2). *m/z* 46 (NO_2) was not seen in the mass spectrum in both cases. The mass balance of nitrogen present in various species released during calcination of the $Pd(NH_3)_4^{2+}/SiO_2$ precursor in 1% O_2–He yields the percentage ratio of NH_3, N_2, N_2O and NO equal to $58:22:14:5$. The presence of nitrogen oxides found here was not seen during calcination in air of zeolite-supported Pd ammine complexes (zeolite Y[17] and X[18]). The reason for this difference would be that very small Pd ammine aggregates in zeolite cages are unable to coordinate molecular oxygen and activate it for the reaction with ammonia. Instead, a final removal of NH_3 ligands triggers a swift transfer of bare Pd^{2+} (or $PdNH_3^{2+}$) ions to sodalite cages.[17] For Pd/SiO_2, precursor aggregates may possess some Pd atoms which have already lost ammonia and may serve as sites for activation of oxygen, which, upon activation, may enter the reaction with ammonia still attached to vicinal Pd atoms. It is known that ammonia oxidation proceeds on palladium at relatively low temperatures (<300 °C) giving N_2 and N_2O.[19] The presence of NO in the mass spectrum, above 400 °C, is not unexpected, either. Recently, Hoost *et al.*[20] investigated adsorption of NO on Pd/Al_2O_3 by FTIR. They found a pronounced adsorption of bridge-bonded NO at 300 °C. The presence of Pd in an oxidized state seems to intensify the adsorption of NO.[20] Therefore, it seems conceivable that NO may be formed by oxidation of an ammine precursor at a temperature as low as 300 °C but it is released to the gas phase at a higher temperature. It should be mentioned that, in contrast with the present results, previous thermochemical studies of calcination of a $Pd(NH_3)_4^{2+}/SiO_2$ precursor excluded the possibility of nitrogen oxides formation.[5]

TPR profiles of differently precalcined $Pd(NH_3)_4^{2+}/SiO_2$ precursors indicate that precalcination in He at 500 °C leads to the formation of reduced Pd species (Fig. 4A). This is in agreement with others[5] and compatible with the results of temperature-programmed decomposition [evolution of hydro-

gen at >400 °C during TPD(He), Fig. 1A]. Moreover, the amount of hydrogen consumed in TPR runs, gradually decreases with increase of the temperature of He pretreatment (250, 400 and 500 °C, Fig. 4A). Small negative peaks at *ca.* 90 °C in TPR profiles after heating in He up to 400 and 500 °C indicate a release of hydrogen during β-PdH decomposition.[21] The amount of the β-PdH phase must be rather small, typical for highly dispersed Pd catalysts[12] (metal dispersion, $H_{ad}/Pd \approx 0.75$ indicates that mean Pd particle size in 1.1 wt.% Pd/SiO_2 is $1.12/0.75 \approx 1.5$ nm[13]).

In the case of samples precalcined in 1% O_2–He, the amounts of hydrogen consumed during TPR are similar; however, the respective TPR profiles exhibit some differences (Fig. 4A). The increase of calcination temperature causes a systematic decrease of the fraction of a 'hardly reducible' material, which is not seen in the TPR spectrum after calcination to 500 °C, where the reduction is completed at *ca.* 100 °C. We think that after calcination at 500 °C we are dealing with reduction of small PdO particles, which are more easily reduced than the material after decomposition of Pd ammine ligands but still containing nitrogen oxide species (after calcinations at 400 °C). Metal dispersions of Pd/SiO_2 after reduction of differently precalcined $Pd(NH_3)_4^{2+}/SiO_2$ precursors do not exhibit major variations. The only difference is that the samples precalcined in O_2–He are slightly more dispersed ($H_{ad}/Pd \approx 0.75$) than those pretreated in He ($H_{ad}/Pd \approx 0.64$). It appears that oxygen involved in the pretreatment preserves somewhat higher Pd dispersions which cannot be maintained during extensive heating in He. On the other hand, the presence of different species left after different precalcinations does not seem to be very important for the final palladium dispersion.

Evolution of Pd/SiO_2 prepared from $Pd(acac)_2/SiO_2$

According to the UV–VIS diffuse reflectance spectra of the precursor precalcined in O_2–He, palladium oxide begins to form at >250 °C, giving a gradually developing band at 440–450 nm (Fig. 3C), previously ascribed to small PdO clusters for precalcined $Pd(acac)_2/Al_2O_3$.[10] In agreement with such an assignment, TPD on O_2–He monitored by MS shows that evolutions of several masses, which could originate from carbon-containing species, terminate at 250 °C (Fig. 2B). Therefore, it is assumed that after oxidation of $Pd(acac)_2/SiO_2$ at 250 °C, the sample should not contain any carbonaceous residues. On the contrary, during decomposition of $Pd(acac)_2/SiO_2$ in helium, although *m/z* 43, 57 and 100 do not appear in the spectrum above 250 °C, the evolution of *m/z* 28 and 44 does not terminate even at 500 °C (Fig. 2A). It is evident that an oxidizing atmosphere is needed for complete carbon removal from this catalyst.

TPR runs of a differently precalcined $Pd(acac)_2/SiO_2$ precursor show that, in line with TPO and UV–VIS data, after precalcinations in O_2–He at >250 °C, *e.g.* at 500 °C (Fig. 4B), H_2 consumption is typical for reduction of PdO (sharp, low-temperature peaks), indicating that we are dealing with oxidized palladium particles. On the other hand, the TPR profile of the sample precalcined at 250 °C has a very peculiar character, which may suggest some presence of carbonaceous residues after precalcination. The negative peak at *ca.* 90 °C represents hydrogen evolution during the β-PdH decomposition.[21]

It is more difficult to interpret the TPR spectra of the samples pretreated in He (Fig. 4B). As was mentioned earlier, these samples contain massive amounts of carbonaceous residues. The catalyst pretreated to 500 °C shows, in principle, only the presence of a sharp negative 'PdH' peak, and no H_2 consumption during the whole TPR run. This may suggest that heating in He up to 500 °C results in a significant reduction of palladium (by carbon or hydrogen). For the

samples pretreated at lower temperature (250 °C), TPR profiles are also rather flat but the absence of a negative peak at *ca.* 90 °C indicates that the β-PdH cannot be formed during the TPR run. It is possible that the surface of palladium is more effectively blocked by a carbonaceous deposit, which prohibits PdH formation. We also speculate that in the sample precalcined in He at 500 °C we deal with another type of carbonic material containing, most probably, much less hydrogen than the coke left after calcination at lower temperatures, *i.e.*, it is more 'carbide-like'. The presence of the 'PdH' peak in the TPR spectrum is not unlikely because it has been found that a partially carbided Pd phase (PdC$_{x'}$ where $x < 0.13$) is still able to absorb hydrogen.[22] Because differently pretreated ex-Pd(acac)$_2$ samples were subsequently investigated as catalysts, one would ask if they still contain carbonaceous species after reduction in hydrogen. Additional TPR–MS and TPD(Ox)–MS experiments displayed that, in spite of the known hydrogenation activity of palladium, hydrogen reduction up to 500 °C does not remove all the carbon. First, TPR–MS runs showed that hydrogen removes only a part of the carbon as methane, because the appearance of m/z 15 does not terminate at 500 °C (Fig. 5A). Secondly, the same samples reduced to 500 °C were subjected to TPD(Ox)–MS and revealed the presence of coke left after the reduction (evolution of CO$_2$, Fig. 5B).

In general, metal dispersions, based on H$_2$ chemisorption, of the 1.6 wt.% Pd/SiO$_2$ catalysts pretreated in He are roughly two times lower than those after an analogous precalcination in O$_2$–He. TEM data, based on metal particle size distributions, do not confirm such a difference: for both samples, mean particle size was *ca.* 3 nm. In effect, one may

conclude that some part of superficial palladium of the precursor precalcined in He up to 500 °C, prior to reduction, is not 'detected' by H$_2$ chemisorption, most probably because it is blocked by some carbonaceous species. Palladium deposited on silica *via* ion exchange of Pd(NH$_3$)$_4^{2+}$ is better dispersed than the ex-Pd(acac)$_2$ (H$_{ad}$/Pd ≈ 0.75 *vs.* 0.25). This confirms a poorer interaction of Pd(acac)$_2$ with silica resulting in a considerable agglomeration of this precursor during sample pretreatment.

Catalytic probing of Pd/SiO$_2$ catalysts by the reactions of 2,2-dimethylpropane and *n*-hexane with hydrogen

As shown above, for partly decomposed Pd(acac)$_2$/SiO$_2$, *ca.* 50% of superficial palladium does not chemisorb hydrogen. The results of 2,2-dimethylpropane conversion for 1.6 wt.% Pd/SiO$_2$ ex-Pd(acac)$_2$ after different pretreatments (Table 1) show that the catalytic behaviour in this reaction suffers even larger changes (*i.e.*, more than twofold). In basic agreement with the conclusions resulting from TPO and TPR studies, precalcinations in O$_2$–He at 250 and 500 °C give similar TOFs, selectivities and activation energies, *i.e.*, it may be accepted that the reaction proceeds on fully reduced Pd catalysts characterized by a similar metal dispersion. On the contrary, the catalyst pretreatment in He, prior to reduction, results in a much lower catalytic activity, differing from the previously mentioned results by more than one order of magnitude. It is interesting to note that the sample pretreated in He up to 500 °C is less active than that pretreated at 250 °C, in spite of the expectation that more carbon should be removed by more intense heating. It seems that although helium pretreatment at 250 °C supposedly leaves more carbonaceous material on palladium than pretreatment at 500 °C, the nature of the deposit seems to play an important role in catalysis. Pretreatment at 250 °C may decompose the Pd(acac)$_2$ precursor, but still leaves a carbonaceous material in a state that covers the surface of palladium more loosely, *i.e.*, the structure of the 'coke' is more 'open'. Although the overall activity of such a carbonized Pd surface is lower than that of 'clean' Pd/SiO$_2$, the similar activation energies (67.4 kcal mol^{-1}) may indicate that the reaction proceeds on exposed surface palladium atoms. In the case of the acac precursor heated to 500 °C, the surface layer seems to be more 'carbidic', and bare surface Pd atoms are even less accessible. This results in lower values of TOF and activation energy (63.5 kcal mol^{-1}). Carbiding of palladium during reactions of alkynes at relatively low temperatures is a well known phenomenon.[22–24] The coke originating from decomposition of Pd(acac)$_2$ may also give rise to Pd carbide species. However, such a transformation supposedly requires temperatures well in excess of 250 °C.

TPO of reduced, differently pretreated Pd acac precursors indicates that the 'coke' after He pretreatment to 500 °C is more resistant to oxidation than that after He pretreatment to 250 °C (Fig. 5B). The course of *n*-hexane conversion on the same series of 1.6 wt.% Pd/SiO$_2$ catalysts differs in many respects from that displayed in 2,2-dimethylpropane conversion (Table 2). First, severe self-poisoning occurred for all samples. This effect is likely to be associated with coke accumulation with time-on-stream. As mentioned earlier, the catalysts precalcined in He, prior to reduction, already retain some carbonaceous material originated from an incompletely decomposed Pd(acac)$_2$ precursor. Second, it is interesting that in *n*-hexane conversion, the precursors pretreated in helium, at both 250 °C and 500 °C, exhibit, upon 'stabilization', a similar level of activity, somewhat lower than that of the samples precalcined in 1% O$_2$–He, prior to reduction. However, this activity difference is not as high as for 2,2-dimethylpropane conversion. This may suggest that, in *n*-hexane conversion, 'working' surfaces are not very different for all the catalyst
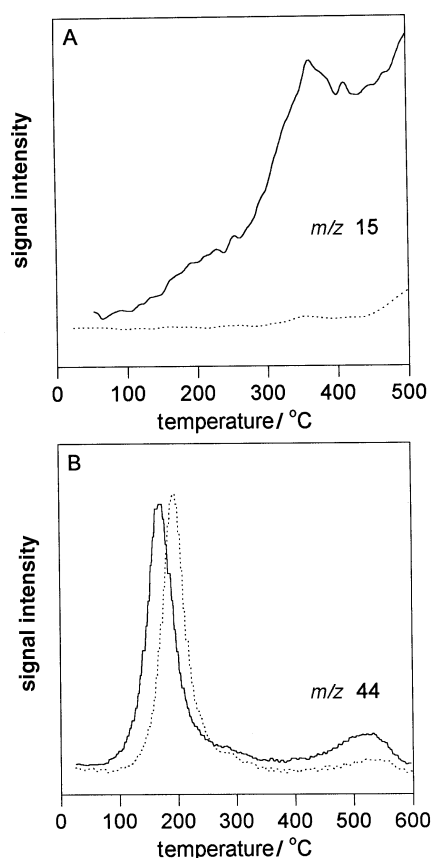

Fig. 5 Temperature-programmed study of 1.6 wt.% Pd/SiO$_2$ catalyst prepared by helium pretreatment of the Pd(acac)$_2$/SiO$_2$ precursor. A, Evolution of m/z 15 (CH$_3^+$) during TPR–MS to 500 °C; B, evolution of m/z 44 (CO$_2^+$) during TPO of the samples prereduced in A. (——) Sample pretreated in He to 250 °C; (·····), sample pretreated in He to 500 °C.

samples, which, in turn, implies that this reaction proceeds on a carbonaceous overlayer that does not depend on whether it was deposited on a clean or carbonized Pd surface.

C_6-Alkenic products were only seen in the case of the precursor decomposed in He (both at 250 and 500 °C, Table 2). The presence of alkenes was always more marked at the end of catalytic runs (even after decreasing the temperature of reaction). This may suggest that the carbonized Pd surface is less efficient in providing the hydrogen needed for hydrogenating all unsaturated intermediates of n-hexane conversion.

Activation energies, multiplicity (M_f) and fragmentation (ζ) factors, and selectivities presented in Table 2 do not change much with the catalyst pretreatment. This implies that the reaction mechanism is similar for all the samples. Fragmentation factors of ca. 2.5 suggest that single splitting of n-hexane predominates. In addition, multiplicity factors of ca. 1 imply that single splitting must be mainly terminal demethylation. This is in agreement with others.[25–28] Similarly, an isomer ratio of 2-methylpentane to 3-methylpentane (2MP/3MP) which is generally slightly higher than two may indicate that the C_5-cyclic mechanism of isomerization operates. It should be mentioned here that the reaction temperatures employed here were > 300 °C. In our previous work,[29] n-hexane conversion on Pd/SiO$_2$, carried out at lower temperatures (250–290 °C), showed somewhat different characteristics: more internal splitting in the hydrogenolysis pattern (much higher M_f values) and much higher 2MP/3MP ratios ($\gg$2), indicating an important contribution of a bond-shift isomerization route.

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