Nanosized platinum particles by sol-gel processing of tethered metal complexes: influence of the precursors and the organic group removal method on the particle size

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Highly dispersed platinum on silica pellets was prepared by sol-gel processing. A solution of a platinum compound, a silane of the type $(RO)_3Si(CH_2)_nA$ (A = coordinating organic group) and $Si(OR)_4$ as the network former was reacted with water and then sprayed on silica pellets. The organic groups were then removed by oxidation and/or pyrolysis. Elemental Pt was formed at temperatures above 500 °C. Lower temperatures require subsequent reduction by hydrogen. The average Pt particle size was determined by XRD and the percentage of accessible Pt atoms by CO titration. Both strongly depend on the chemical composition of both the platinum precursor and the organo(alkoxy)silane. Particularly small particles were obtained if removal of the organic groups was carried out by a combination of pyrolysis and oxidation or by treatment with an oxygen plasma, instead of removing the organic groups by air oxidation at high temperatures.

The sol-gel process allows the preparation of metal nanoparticles in oxide matrices with narrow particle size distributions and adjustable metal loadings. One of the prerequisites to control the metal dispersion in the nano-composites is the maximum dispersion of the metal precursor during the sol-gel step. This is achieved by tethering the metal precursor to the gel matrix. In our approach, the compounds $(RO)_3Si(CH_2)_nA$ are employed for silica-based materials, in which the group A is an organic group capable of coordinating to metal ions.

The dispersed metals are prepared by a three-step procedure, as previously reported.[1–3] A solution of a metal salt (MX_m), the silane $(RO)_3Si(CH_2)_nA$ and $Si(OR)_4$ is processed by the sol-gel method in the first step. Complexes of the type $[(RO)_3Si(CH_2)_nA]_nMX_m$ are formed *in situ*. The metal coordination is retained during sol-gel processing. The metal complexes are tethered to the silicate matrix *via* the $(CH_2)_nSiO_{3/2}$ groups and aggregation of the metal ions is thus prevented. The resulting gels have the idealized composition $[O_{3/2}Si(CH_2)_nA]_nMX_m \cdot xSiO_2$. The composition of the final composite is determined by the M : Si ratio of the starting compounds. The metal complex-containing gels are then dried and heated in air to oxidize all organic moieties. Due to the high dispersion of the metal ions in the first step, nano-sized metal oxide particles [*i.e.*, the nano-composites $MO_y \cdot (x + n)SiO_2$] are formed, which are then reduced to metal particles [composites $M \cdot (x + n)SiO_2$]. If one wants to get carbon-free composites, the oxidation temperature has to be high enough to ensure complete oxidation of all organic components, but should not be higher than necessary to avoid excessive sintering of the metal particles. The particle size does not change very much during reduction, because in most cases $T_{red} < T_{ox}$. Some noble metals already give metal particles in the oxidation step due to the thermal instability of the oxides.

The metal particles obtained by this approach are highly dispersed, not agglomerated, and homogeneously distributed throughout the SiO_2 matrix, even in the materials with high metal loadings. The particle size distributions are very narrow. The metal dispersion obtained by this method depends on the kind of metal, the reaction conditions, and for some metals, also on the metal loading.[2–4] For example, the nano-composite $Pt \cdot 62SiO_2$ was prepared starting from a mixture of $Pt(acac)_2$, two equivalents of $H_2NCH_2CH_2NH(CH_2)_3Si(OEt)_3$ (AEAPTS) and 60 equivalents of $Si(OEt)_4$ (TEOS). When the oxidation temperature did not exceed 550 °C, the size and size distribution of the Pt particles (3–5 nm) was not affected by the period of heating. However, the average particle size increased considerably and the size distribution became very broad at oxidation temperatures between 750 and 950 °C, particularly for extended periods of heating.[2] Particle size and size distribution are also affected by the $(RO)_3Si(CH_2)_nA$: metal ratio. This was studied for nano-composites of the composition $Cu_{0.6}Ni_{0.4} \cdot 5SiO_2$ prepared from nickel and copper acetate, AEAPTS and TEOS. The AEAPTS : metal ratio in the precursor mixture was varied, while the molar amount of (AEAPTS + TEOS) was kept constant. An increasing portion of AEAPTS resulted in larger alloy particles. This is probably due to the higher local temperatures caused by the exothermic oxidation/ pyrolysis of a greater amount of organic groups. However, complexation of the metal ions had a beneficial effect on the particle size *distribution*. It was narrowest if only the amount needed for complexation of all metal ions was added to the starting solution.[3]

The latter results suggest that the precursor composition also has a significant influence on the metal dispersion. Highly dispersed platinum on various supports has many applications in catalysis. Some of the reactions are structure sensitive, that is the rate and selectivity depend on the size and facet distribution of the metal clusters. Therefore, preparation methods that allow for a variation of the metal particle size are necessary.

In the present paper we report on how the *average* Pt particle size is influenced when the complexing silane and the metal precursor are varied. The *size distribution* was not investigated at this point. Furthermore, we looked for methods to remove the organic moieties from the initially formed gels under conditions that disfavor particle growth.

Results and Discussion

The composites were prepared by the method previously reported by us.[1] One of the advantages of the sol-gel method

for preparing highly dispersed metal particles is that solid supports can be coated with the sols containing the tethered metal complexes. Formation of the metal oxide or metal particles in the subsequent steps (oxidation/reduction) then occurs on the support.[5] The preparation of the metal-loaded pellets includes of the following steps: (*i*) *In situ* preparation of the metal complex $[(RO)_3Si(CH_2)_nA]_nPtX_m$ by reaction of a platinum salt PtX_m with an organo(alkoxy)silane $(RO)_3Si(CH_2)_nA$. (*ii*) Addition of $Si(OR)_4$ as the network former and 0.2 N aqueous ammonia to start the sol-gel reactions. (*iii*) Spraying of the sol onto pellets (Kieselgel 60, Riedel de Haen. The silica pellets had a diameter of 0.2–0.5 mm, a specific surface area of 400 m² g⁻¹ and 6 nm pores). (*iv*) Drying of the coated pellets. (*v*) Oxidation. (*vi*) Reduction.

Only the metal salt and the organo(alkoxy)silane were varied and the other reaction parameters were kept constant, if possible. We want to emphasize that to get the optimum particle size and size distribution, the whole set of parameters has to be optimized. However, in this work we wanted to concentrate just on the influence of a subset of parameters.

In the remainder, the following set of parameters is labeled as '*standard*':

(*i*) 5–6 molar equivalents $(RO)_3Si(CH_2)_nA$ per platinum atom; (*ii*) TEOS (as the network former) and $(RO)_3Si(CH_2)_nA$ in a 1:1 ratio; (*iii*) 7.5 mol water per mol hydrolyzable OR groups; (*iv*) oxidation conditions: heating in air to 550 °C at 10° min⁻¹ and holding at 550 °C for 30 min; (*v*) reduction conditions: 1 h at 100 °C in a stream of H_2 (when the oxidation is carried out at temperatures >450 °C the samples already contain elemental Pt. Reduction was nevertheless routinely carried out to ensure complete formation of the metallic phase and to make all samples comparable.) and (*vi*) metal loading: 1.5 wt% of the whole mass of the coated pellet (*i.e.*, including the mass of the pellet).

Influence of the precursors on the metal particle size

The following metal compounds and silanes were used: $Pt(acac)_2$, $PtCl_2$, H_2PtCl_6, Na_2PtCl_6, $Pt(CN)_2$, $Pt(NH_3)_4(NO_3)_2$, 3-(2-aminoethylamino)propyltriethoxysilane (AEAPTS), aminopropyltriethoxysilane (APS), *N*-methylaminopropyltrimethoxysilane (NMS), 2-(trimethoxysilylethyl)pyridine (PyS) and (3-trimethoxysilylpropyl)diethylenetriamine (TAS). Only silanes with nitrogen donor groups were employed because they coordinate Pt^{2+} very effectively and can be completely removed in the oxidation step. The average metal particle size was determined from the

half widths of the [111] reflection of metallic Pt in the XRD spectra. The average metal particle size obtained for some metal precursor–silane combinations is shown in Table 1.

It is evident that the combination of the precursors has a significant influence on the final metal particle size, although there are no clear trends with regard to a particular metal compound or silane. We have previously shown that the thermochemistry of the oxidation or pyrolysis of the organic groups has a decisive influence. If oxidation or pyrolysis are strongly exothermic, the locally generated heat will promote the particle growth. Since both the counter ion of the metal and the organic parts of the silane contribute to this process, the combination of both is decisive for getting a certain particle size and has to be optimized. This is illustrated, for example, for AEAPTS. This silane, with a high proportion of organic groups, appears to result in relatively large metal particles in combination with most metal precursors. However, if combined with $PtCl_2$, the obtained metal particles are small.

The percentage of accessible Pt atoms was determined by CO titration for some samples prepared from $Pt(acac)_2$ (Table 1). This does not necessarily correlate with the average metal particle size obtained by XRD, because a different portion of Pt atoms may be blocked by the matrix and the particle size *distributions* may be different.

We checked for the combination $Pt(acac)_2$–APS whether the amount of TEOS influences the average particle size. In the standard set of conditions, a TEOS:$(RO)_3Si(CH_2)_nA$ ratio of 1 was used. Even with a 15- or 30-fold excess of TEOS, no significant change of the average Pt particle diameter was found (the mass of the pellets was correspondingly reduced in these experiments to keep the metal loading constant). Increasing the metal loading by a factor of three also did not significantly influence the metal particle size in the case of Pt (it does influence the size for some other metals[3]).

The kind of hydrolyzable group of the organo(alkoxy)silane also has no significant influence (although the hydrolysis and condensation rates are different). The use of 3-(2-aminoethylamino)propyltri*methoxy*silane instead of AEAPTS for the complexation of H_2PtCl_6 did not change the particle size.

The time required for complexation of $Pt(acac)_2$ with five equivalents of nitrogen donor ligands is several days. The reaction rates are enhanced by using an excess of the donor ligand.[6] However, we have previously shown for the Cu,Ni–AEAPTS combination that increasing the complexing silane:metal ratio results in larger metal particles and broader size distributions (if more silane is employed than necessary for coordination of the metal ions).[3] This trend was confirmed in the present study. Table 2 shows the average metal particle

Table 1 Average metal particle diameters (from XRD) for some metal precursor–silane combinations and percentage of accessible metal atoms (by CO titration)

Metal precursor	Silane	Average particle diameter/nm	Percentage of accessible metal atoms
$Pt(acac)_2$	AEAPTS	7.1	17.0
$Pt(acac)_2$	APS	3.5	24.8
$Pt(acac)_2$	NMS	4.0	
$Pt(acac)_2$	TAS	4.0	24.3
$Pt(acac)_2$	PyS	5.0	21.5
$PtCl_2$	AEAPTS	5.7	
$PtCl_2$	APS	5.6	
$PtCl_2$	TAS	10.2	
H_2PtCl_6	AEAPTS	22.2	
Na_2PtCl_6	AEAPTS	16.6	
Na_2PtCl_6	APS*ᵃ*	4.2	
$Pt(CN)_2$	AEAPTS	13.8	
$Pt(NH_3)_4(NO_3)_2$	AEAPTS	6.4	

ᵃ Only 1.2-fold molar excess.

Table 2 Average Pt particle sizes starting from Pt(acac)$_2$, 12 equivalents of TEOS and 5 or 60 equivalents of APS, AEAPTS or TAS

Silane	Molar equivalents of silane	Average particle size/nm	Oxidation temperature/°C and period/min	Percentage of accessible metal atoms
APS	5	3.8	550/30	24.8
APS	60	13.4	550/65	2.5
AEAPTS	5	7.1	550/30	
AEAPTS	60	11.0	600/65	
TAS	5	4.0	550/30	24.3
TAS	60	8.1	600/95	2.7

sizes when Pt(acac)$_2$ was reacted with 5 or 60 equivalents of APS, AEAPTS or TAS. Because the proportion of organic groups is considerably increased, the oxidation temperature and period had to be adjusted when a large excess of the amino-substituted silane was used.

Influence of the organic group removal method on the metal particle size

The oxidation step is most critical with regard to the particle size and size distribution. A certain temperature is required to remove the organic groups. On the other hand, the temperature should be kept as low as possible to restrict particle growth. Heating in pure oxygen is not advisable, because burning of the organic groups is strongly exothermic (this may even result in explosions) and large particles are obtained due to the local heating. When the standard conditions are employed, the samples are heated in air. We looked for modifications of the process to reduce the locally generated heat.

A significant improvement was achieved when removal of the organic groups was performed by a two-step process. In the first step, the sample was heated to 550 °C within 55 min in a stream of Ar and kept at 550 °C for 30 min. After this pyrolysis step, the remaining organic groups were removed by

heating the cooled sample to 400 °C within 40 min in a stream of air and kept at 400 °C for 30 min. The maximum temperatures and the ramping time were optimized by TGA. Table 3 shows that this procedure resulted in a dramatic improvement of the metal dispersion. In most cases the metal particle sizes were so small (<3 nm) that the XRD reflections were too broad for the particle size determination (assuming that all metallic particles are crystalline). Fig. 1 shows the percentage of accessible metal atoms for the different methods of removing the organic groups. Although it depends on the metal precursor–silane combination, it was increased by approximately a factor of two by the two-step process.

Another method is the use of a cold oxygen plasma. Table 3 and Fig. 1 show that this method also results in very small metal particles and further increases the percentage of accessible metal atoms. However, the residual C,H,N contents after plasma treatment is somewhat higher than after the two-step (pyrolysis/oxidation) or the oxidation-only procedure.

Experimental

All chemicals were used as received. All operations were carried out under ambient conditions, if not otherwise stated. The set of standard conditions is given in the Results section.

Complexation of the metals

Pt(acac)$_2$ is dissolved in 10 ml ethanol per 0.1 mmol Pt(acac)$_2$ at 55 °C. Then the calculated amount of the organo(alkoxy)silane is added. The solution is stirred at 55 °C until UV spectra indicate the complete complexation of the metal. This takes 5–7 days with 5–10 molar equivalents and 1 day with a higher excess of silane.

PtCl$_2$, Pt(CN)$_2$ and Pt(NH$_3$)$_4$(NO$_3$)$_2$ are suspended in 10 ml ethanol per 0.5 mmol metal compound. After addition of the organo(alkoxy)silane, only PtCl$_2$ dissolves completely upon stirring at room temperature. For the other two compounds, the suspensions were stirred for several days and then processed.

Reaction of H$_2$PtCl$_6$ or Na$_2$PtCl$_6$ with AEAPTS is performed according to the procedure given in ref. 6 for the reaction with ethylenediamine. For the reaction of Na$_2$PtCl$_6$ with APS the silane is added at room temperature and the solution is stirred overnight.
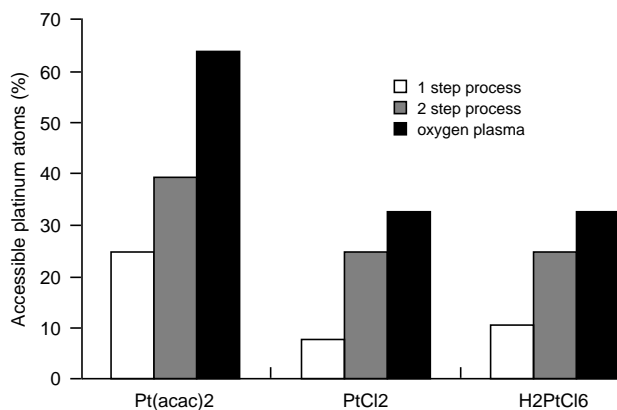
Fig. 1 Percentage of accessible metal atoms depending on the conditions for the removal of the organic groups (see text)

Table 3 Average Pt particle diameters (from line broadening in XRD) depending on the conditions for the removal of the organic groups (see text)

Metal compound	Silane	Average particle size/nm		
		1-Step procedure	2-Step procedure	Plasma oxidation
H$_2$PtCl$_6$	AEAPTS	21.6	[a]	4.4
Pt(acac)$_2$	PyS	5.0	[a]	
Pt(acac)$_2$	AEAPTS	7.1	[a]	
Pt(acac)$_2$	TAS	4.0	[a]	[a]
PtCl$_2$	APS	5.6	4.1	4.8

[a] Signal at the detection limit (corresponds to particle sizes <3 nm).

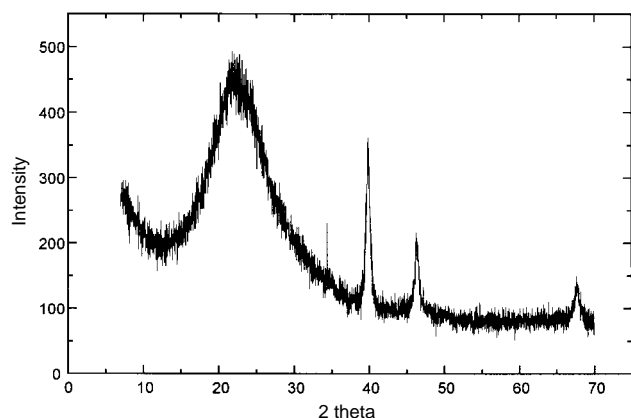**Fig. 2** XRD pattern of the sample prepared from $Pt(acac)_2$ and 60 equivalents of APS (ave. particle size 13.4 nm, see Table 2). The broad peak around 22.2° ($d = 4.003$) is assigned to amorphous silica. The three peaks at 39.85° ($d = 2.262$), 46.27° ($d = 1.962$) and 67.57° ($d = 1.386$) are attributed to reflections for elemental platinum (JCPDS entry number 04-0802: $d = 2.26500$, 100% [111]; 1.9616, 53% [200]; 1.3873, 31% [220])

Loading of the pellets and sol-gel processing

The pellets are placed in a beaker that is tilted by about 40° and continuously rotated. The solution obtained after the complexing step is diluted to about 0.1 mmol metal per 10 ml and divided in four parts. Then the calculated amount of TEOS and 0.2 M aqueous ammonia is added to the first part of the solution. This solution is immediately added dropwise to the pellets in a way that the pellets are moist, but there is no liquid in the vessel. For this reason, the pellets are occasionally dried with a heat gun. After loading the pellets with the first quarter of the sol, the pellets are dried at 150 °C for 10 min. Then the loading is repeated three times with the other quarters of the solution. The completely loaded pellets are dried at 70 °C at ambient pressure and at 10^{-3} torr for 3 h. When the sol is not used immediately after addition of the water, it becomes more viscous and is therefore more difficult to spray. Furthermore, the average particle size in the final material gets larger for extended pre-hydrolysis periods.

Oxidation and reduction

The dried pellets are placed in a horizontal quartz tube heated by a tube furnace. The furnace temperature is then ramped at $10°$ min^{-1} to the required oxidation temperature and held at this temperature for 30 min while a slight stream of air (200 ml min^{-1}) passes over the sample. The two-step procedure (see Results section) is performed analogously.

For oxidation in an oxygen plasma, the sample is placed in the RF chamber, which is evacuated to 0.14 torr, and treated with the oxygen plasma (150 W, 13.56 MHz) for 2 × 30 h. A dynamic O_2 pressure of 1.15–1.2 torr is maintained during the treatment.

Reduction is carried out in a horizontal tube as described above, with a stream of H_2. The reduction temperature is 100 °C, except for the plasma-treated samples, where 400 °C is used.

Chemisorption experiments

Each sample is heated in a stream of N_2 (50 ml min^{-1}) for 2 h at 250 °C and then cooled to room temperature. Helium is passed over the sample and 0.1–0.2 ml portions of CO are injected into the He stream. The amount of CO not chemisorbed is detected by a thermal conductivity detector. From the amount of chemisorbed CO the percentage of the accessible Pt atoms can be calculated, assuming the adsorption of one CO molecule per metal atom.[4]

Particle size determination

The XRD spectra were measured with Cu Kα radiation. Only the peaks of metallic Pt were detected. A representative diffractogram is shown in Fig. 2. The average metal particle size is calculated from the width of the [111] reflection by the Debye–Scherrer equation. The peaks were approximated by a Gaussian function without correction, assuming a symmetric peak.

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