

Supported Pt-colloid catalysts for the selective hydrogenation of 3,4-dichloronitrobenzene

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Pre-prepared Pt hydrosols stabilized by surfactants may be used as precursors for heterogeneous hydrogenation catalysts active in the selective high-pressure transformation of 3,4-dichloronitrobenzene to the corresponding aniline. The catalytic performance of the new systems was evaluated in batchwise and continuous tests and the results are compared to conventional Pt/C systems.

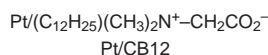
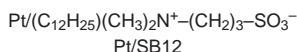
Heterogeneous Pt catalysts—apart from those used in petrochemical processes—have found a number of industrial applications in the hydrogenation/dehydrogenation or the oxidation of organic substrates. The selective reduction of 3,4-dichloronitrobenzene, giving the corresponding aniline (Scheme 1),¹ is a major challenge for the appropriate design and optimization of the catalyst.² The resulting dichloroaniline is an important intermediate for the production of crop-protecting chemicals.

Supported Pt is preferred as an industrial catalyst because this noble metal combines a good activity in nitro group reduction with a low degree of dehydrohalogenation.^{3,4} By using basic additives such as ammonia or morpholine⁵ and partial poisoning of the catalyst, for example *via* sulfidation,⁶ the unwanted dechlorination reaction path (Scheme 1) may be suppressed. A further problem associated with the catalytic reduction of halonitroarenes lies in the unwanted formation of small amounts of toxic azo compounds, such as 3,3',4,4'-tetrachloroazobenzene (TCAB) and 3,3',4,4'-tetrachloroazoxybenzene (TCAOB). This, however, can be minimized by doping the catalyst with certain non-noble metals such as Ni and Co.^{2,7} The object of the present work was to test the applicability of nanostructured Pt colloids as precursors⁸ for heterogeneous Pt catalysts effective in the selective reduction of 3,4-dichloronitrobenzene.

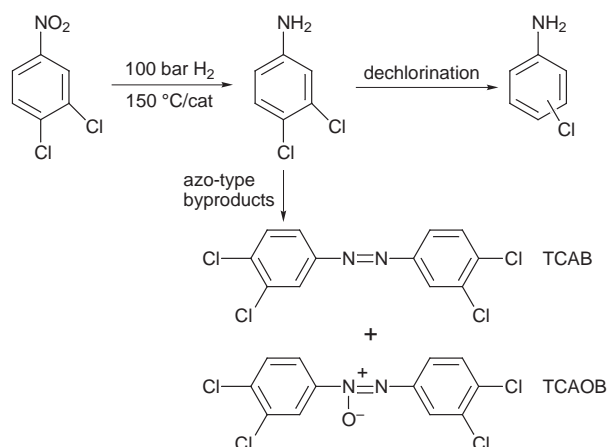
Results and Discussion

Preparation of the Pt colloid precursors

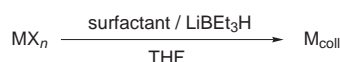
The colloidal metal precursors used in this work were exclusively Pt hydrosols (size 2.8–3.7 nm), highly soluble in water and stabilized by strongly hydrophilic zwitterionic surfactants (shown below), namely sulfobetaine SB12 [3-(*N,N*-dimethyldodecylammonio)propanesulfonate] and carboxybetaine CB12 [2-(*N,N*-dimethyldodecylammonio)acetate].



The preparation of the colloids Pt/SB12 and Pt/CB12 followed the general pathway given in Scheme 2 and the experimental procedures described earlier.^{9,10} The resulting Pt hydrosols were isolated in dry form and redispersed in water



Scheme 1 Reaction scheme for the hydrogenation of 3,4-dichloronitrobenzene



Scheme 2 General scheme for colloid synthesis

with high Pt concentrations.

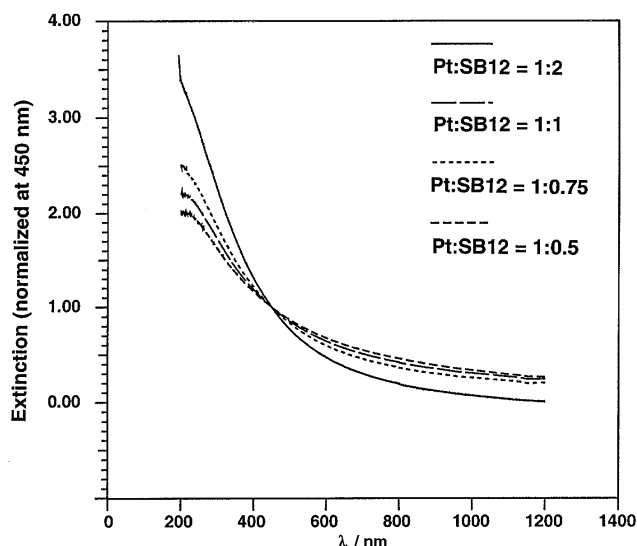
In the case of the Pt/SB12 hydrosols TEM studies have revealed a certain influence of the SB12 concentration applied during the reduction step (Table 1). Whereas ratios of SB12 : Pt between 2 : 1 and 0.75 : 1 in colloids 1–3 gave virtually no changes in the particle size, the lower ratio of 0.5 mol SB12 per mol Pt salt gave significantly larger particles (3.7 nm, hydrosol 4) on reduction. Pt colloids produced with SB12 : metal ratios < 0.5 : 1 were no longer fully redispersible.

The difference in particle size is reflected also in the UV/VIS spectra (See Fig. 1, extinction *E* normalized to 1 at 450 nm). The strong decay of the unstructured absorptions is typical for metal colloids. The dispersive power of the smaller Pt colloids 1–3 (2.8 nm) at shorter wavelengths was found to be stronger than in the case of colloid 4 in which the particle diameter is 3.7 nm. Inspection of Table 1 shows that at a molar ratio SB12 : Pt = 2 : 1 (colloid 1) the so-called *S* value (derived from a double logarithmic plot of the UV/VIS spectral data) reaches 3.1. According to Duff *et al.*¹¹ such a high *S* value is a good proof for the presence of uniform, spherical particles

Table 1 Preparation conditions and physical data of Pt/SB12 hydrosols, showing the effect of stabilizer concentration on particle size

Colloid	SB12 : Pt ratio	PtCl ₂ /g (mmol)	SB12/g (mmol)	LiBEt ₃ H/ml (mmol)	TEM particle size/nm	S ^a	EA ^b /wt% Pt
1	2 : 1	1.8 (6.77)	4.53 (13.5)	8.2 (13.53)	2.8	3.1	16
2	1 : 1	1.8 (6.77)	2.27 (6.77)	8.2 (13.53)	2.8	1.4	33
3	0.75 : 1	1.8 (6.77)	1.7 (5.08)	8.2 (13.53)	2.7	1.6	30
4	0.5 : 1	1.8 (6.77)	1.14 (3.38)	8.2 (13.53)	3.7	1.3	5.2

^a Derived from the UV/VIS spectra (double logarithmic plot of log *E* vs. log λ). ^b EA = elemental analyses.

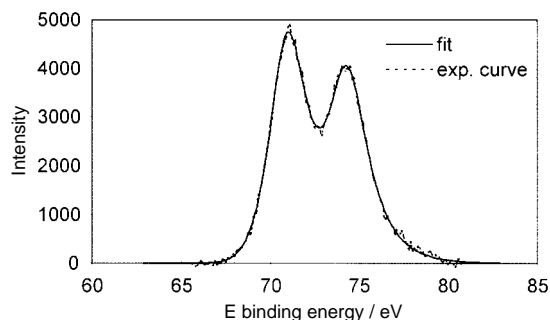
**Fig. 1** UV/VIS spectra of the Pt/SB12 colloids 1–4

present in solution without agglomeration. However, if the stabilizer is applied in low concentrations during the salt reduction, the resulting Pt particles tend to coagulate, which is shown in the TEM micrographs of colloids 2–4; this is reflected by the low *S* values of these materials. For this study the Pt hydrosol 1 containing 16 wt% Pt was chosen as the colloidal precursor for the preparation of the heterogeneous catalyst. An XPS investigation carried out with the Pt/SB12 colloid 4 gave a bond energy value of 71.0 eV, corresponding to metallic Pt (see Fig. 2). After redispersion of the dry material in water and subsequent redrying, the XPS spectrum showed an electron bond energy of 71.2 eV; obviously the oxidation state of the Pt particles remained unchanged when the Pt hydrosol was dissolved in water. Even after exposure of the dry sample to air (4 h), the particles still consisted of metallic Pt, according to the XPS data (71.3 eV). So SB12 acts as an efficient agent to protect the nanostructured Pt particles from oxidation.

For comparison, the sulfur-free Pt/CB12 hydrosol 10 was prepared according to the general reaction in Scheme 2 using LiBEt₃H in THF as the reducing agent at a molar ratio CB12 : PtCl₂ of 2 : 1. The dried material (particle size of 2.3 nm) contained 22 wt% Pt and was very soluble in water. The UV/VIS and XPS spectra confirmed the colloidal nature and the zero-valent state of the Pt particles.

Preparation of the catalysts

Preparation of heterogeneous Pt catalysts from the surfactant-stabilized metal hydrosols 1 and 10 may be performed by simple adsorption of the metal colloids on standard charcoal in concentrated aqueous solution. Unwanted agglomeration of Pt particles on the support and the distribution of the particles on the surface after adsorption can be controlled by TEM.¹² Since the metal is already stabilized in the zero-valent



Sample	Energy of Pt(4f _{7/2}) peak/eV
Pt metal powder	71.1
Pt/SB12 (1 : 0.5) 4	71.0
Pt/SB12 (1 : 0.5) 4/Air	71.3
Pt/SB12 (1 : 0.5) 4/H ₂ O	71.2
PtO ₂	75.9
PtCl ₂	73.1

Fig. 2 XPS spectrum of the Pt/SB12 colloid 4. Electron binding energies and reference data.

state by the precursor, no subsequent reduction step is necessary. The catalysts tested at Bayer AG for this study were prepared at Degussa AG on a laboratory scale, following these basic lines, *via* the adsorption of the Pt precursors on charcoal at *ca.* 80°C (eventually in the presence of small amounts of auxiliary ions).¹³ Examination of the metal concentration profiles of the catalyst particles by TEM of thin cuts of the new Pt-colloid catalysts showed a *shell* structure, rather than a thoroughly impregnated charcoal. The size distribution of the Pt particles proved to be virtually the same in the conventional and the metal-colloid catalysts. From CO chemisorption the accessibility of the platinum surface, however, was significantly higher in the case of Pt/SB12 than in the Pt/CB12/charcoal catalyst. The physical data for the different catalysts are summarized in Table 2.

Hydrogenation of 3,4-dichloronitrobenzene: batchwise test of the Pt-colloid/charcoal catalysts

A batchwise test provides good basic information about the activity, selectivity, filterability, dosage and lifetime of a given catalyst. The performance of the colloidal Pt/SB12/C and Pt/CB12/C catalysts in nitro group hydrogenation (Scheme 1) was first compared batchwise under high pressure/liquid phase conditions with an industrial standard Pt/C catalyst and an optimized Pt/C system from Degussa (**R7S**). The test conditions were 100–170 °C and 100 bar H₂. All catalysts used Pt supported on the same type of charcoal (high surface area) with a loading of *ca.* 1% of the noble metal. The optimized system (**R7S**) was poisoned with 0.1–0.5% sulfur. The sulfonic acid group present in the colloidal Pt/SB12/C catalyst was converted under the test conditions into sulfidic components.

Table 2 Physical data of the Pt catalysts

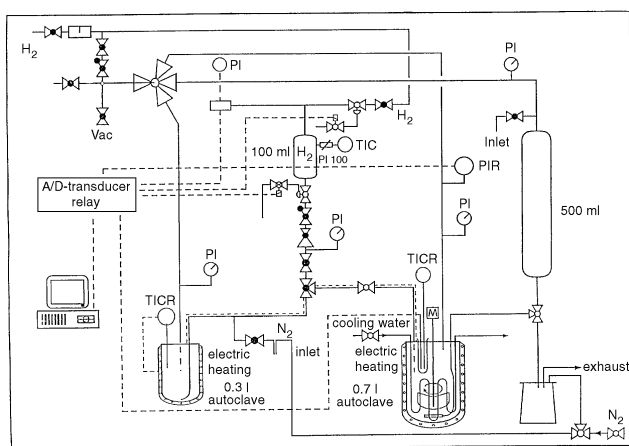
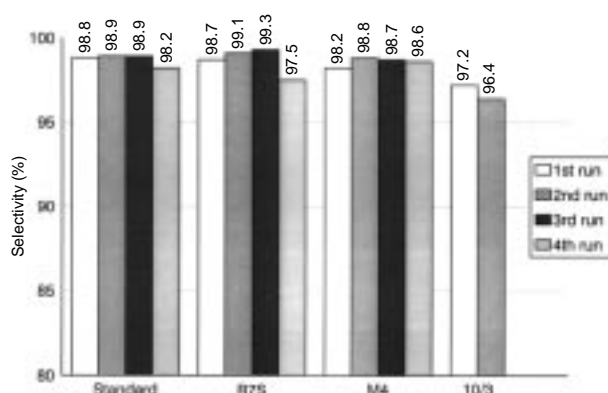
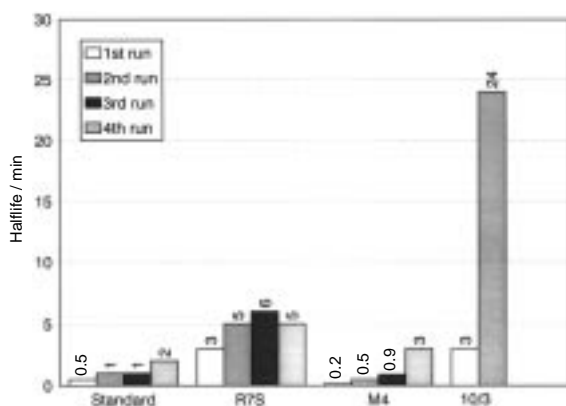
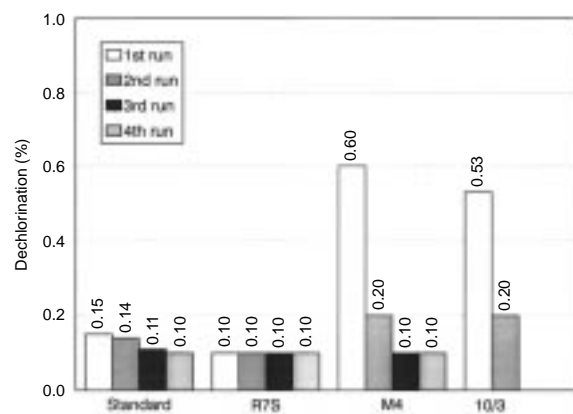
Catalyst	Origin	Pt content/wt%	CO chemisorption/ml g ⁻¹	Particle size/nm	Penetration depth/nm
R7S	Degussa	1 (sulfidized)	ND	2–3	thoroughly impregnated
M4	Pt/SB12 (1 : 0.75)	0.81	0.23	2–3	≤ 50
10/3	Pt/CB12 (1 : 2)	0.78	0.14	2–5	50–100

In contrast, the tested Pt/CB12/C catalyst was sulfur-free. Since the catalytic reduction of nitro compounds in the liquid phase is strongly exothermic (553.5 kJ mol⁻¹), the reaction parameters (concentration of the nitro compound, hydrogen pressure, temperature) have to be carefully controlled in order to determine the true catalytic activity. The experimental set-up for the batchwise test apparatus is shown in Fig. 3.

The 3,4-dichloronitrobenzene is molten at 80°C and poured into the 0.3 l dispensing autoclave, where the H₂ pressure is adjusted to 200 bar. The catalyst sample is suspended in the 0.7 l test autoclave, which is kept at 40 bar H₂ and 150°C. The reaction starts when the balanced valve between the two autoclaves is opened and the substrate is passed over to the 0.7 l test autoclave. The hydrogenation is performed under strictly controlled isobaric (100 bar H₂) and isothermal (150°C) conditions. Finally, the product solution is filtered and the isolated catalyst may be reused in further test runs. The catalyst selectivity is controlled *via* GC/HPLC analysis of the product. The time needed for 50% substrate conversion (called the half-life) is reciprocal to the catalyst activity and serves as a good criterion for it. Fig. 4 compares the half-lives of the two conventional and the two Pt-colloid-based catalysts in the batchwise test.

It seems that the colloidal Pt⁰ eggshell-type catalysts (**M4** and **10/3**), in which the total metal loading (1 wt%) only penetrates an outer 100 nm layer of the support, are less stable compared to the homogeneously impregnated Pt/C catalyst (**R7S**). An inspection of Fig. 4 reveals, however, that with respect to activity and stability the eggshell **M4** catalyst based on the sulfur-containing Pt/SB12 colloid competes well with the standard system and surpasses the homogeneously impregnated **R7S** system. In contrast, the sulfur-free catalyst **10/3**, based on the colloid Pt/CB12, is less active. This result correlates with the low CO adsorption and Pt dispersity values found for this catalyst.

In the batch test the colloidal Pt catalyst **M4** based on Pt/SB12 exhibits a significantly better overall selectivity (Fig. 5) than the sulfur-free Pt-colloid **10/3** system. The selectivity of **M4** is at the same level as the standard catalyst and the optimized conventional Pt/C **R7S** system, which was modified

**Fig. 3** Apparatus used for the batchwise catalyst test**Fig. 5** Comparison of the overall selectivity of the conventional and colloidal Pt/C catalysts**Fig. 4** Comparison of catalyst half-lives from the batchwise test**Fig. 6** Comparison of the dechlorination rates of the conventional and colloidal Pt/C catalysts

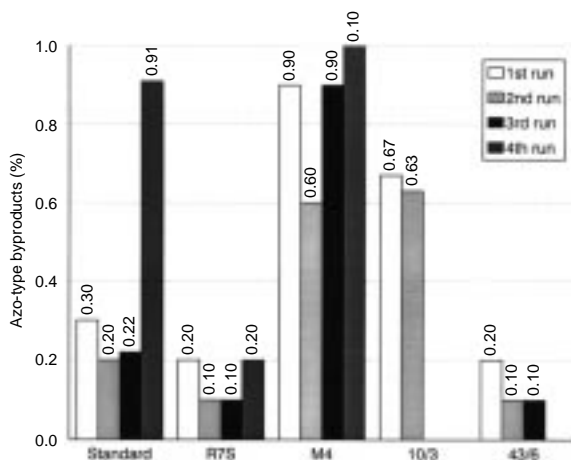


Fig. 7 Formation of azo compounds using the conventional and colloidal Pt/C catalysts

with a sulfur-containing compound.

The amount of unwanted dechlorination found in the batch test of the catalysts is compared in Fig. 6. With respect to the dechlorination rates the optimum performance is delivered by the modified standard catalyst **R7S** right from the first run. The dechlorination reaction is known to be suppressed through poisoning at the Pt surface by sulfidic additives. The strong decay of the dechlorination rate that is seen with the Pt/SB12/C catalyst **M4** between the first and fourth runs may be rationalized by assuming a partial reduction of SO_3^- in the sulfobetain to S^{2-} under the reaction. Additionally, the dechlorination seems to decrease with decreasing activity of the catalysts.

Fig. 7 shows the formation of azo-type byproducts in the batchwise test of the different Pt/C catalysts. Using the sulfidized conventional Pt/C catalysts **R7S**, the amounts of unwanted azo byproducts are found to be the lowest. The residual surfactant of the colloid catalysts does not seem to suppress the formation of the azo-type compounds, as in the case of the sulfur-modified catalyst **R7S**. Following reports that the formation of azo byproducts could be suppressed by doping the Pt/C catalyst with non-noble metals,^{2,7} we have tried to optimize the colloidal Pt/C catalyst further using bimetallic Pt/Cu colloids (in the molar ratio Pt : Cu = 4 : 1) as the precursor. These materials are available by simple coreduction of PtCl_2 and CuCl_2 , analogous to the procedures described in ref. 10. The resulting bimetallic Pt/Cu/C catalyst **43/6** led to a considerable suppression of the unwanted azo byproducts in the first attempt (see Fig. 7). This finding indicates that the concept of selectivity control *via* the addition of non-noble metals, as applied to conventional Pt catalysts,^{2,7} may be successfully transferred to bimetallic colloidal precursors.

Continuous 3,4-dichloronitrobenzene hydrogenation with the Pt/SB12 colloid catalyst **M4**

On the basis of the results achieved in the batchwise hydrogenation test, the Pt/SB12 colloid catalyst **M4** was selected for further examination under continuous conditions, in comparison to the standard catalyst. During 100 h of continuous operation almost complete conversion of the nitro groups was observed with both catalyst systems. Consequently, there is no relevant difference in activity between the standard system and the colloid catalyst **M4**. An inspection of the dechlorination rate, however, reveals that compared to the standard catalyst the amount of unwanted HCl cleavage in the products was four times higher in the case of the colloidal Pt/SB12/C catalyst **M4**. The amount of azo byproducts was $\leq 0.3\%$ in both cases. In this respect, however, on the basis of

the continuous test a certain advantage may be stated for the Pt/SB12/C catalyst **M4**.

Conclusion

Heterogeneous metal colloid catalysts based on pre-prepared nanometal precursors stabilized by surfactants may be used for the selective high-pressure hydrogenation of nitrobenzene derivatives into the corresponding anilines in the liquid phase. Compared to the optimized Pt/C catalyst used in the industrial process the catalytic performance of the new catalysts reached all standards. The potential of this new type of heterogeneous catalyst lies in the possibility of optimizing the properties of the catalyst precursor for special applications by the addition of doping agents or poisons (such as sulfur) to the colloidal nanometal. Further fine-tuning may be achieved by using the synergistic effect of bimetallic precursors (*e.g.*, Pt/Cu). Finally, the surfactant used for the stabilization of the colloidal metal precursors acts as an effective modifier of the colloidal metal surface.

Experimental

Preparation of the Pt hydrosols

The alkaline triethylhydroborates are accessible in various solvents.¹⁴ For the reduction of the platinum salts a suspension of the surfactant in *ca.* 50 ml THF is first treated with ultrasound (55 kHz, 200 W) for 30 min. Then a THF solution of the alkaline triethylhydroborate is added dropwise. The suspension clarifies to give a solution (*e.g.*, SB12/LiEt₃H/THF). This solution is added to the metal salt suspension in *ca.* 50 ml THF at ambient temperature over 16 h and the mixture is stirred for several hours. Any excess of the reducing agent may be removed by addition of 2 ml dry acetone; the mixture is again stirred for 1 h. The clear solution of the raw colloid is filtered off from possible precipitates and the solvent removed *in vacuo*. The raw colloid is dried for 16 h at 10^{-3} mbar and collected as a bright brown powder that is very soluble in water. For purification the SB12-stabilized Pt colloids are first dissolved in *ca.* 5 ml distilled water and re-precipitated by the addition of 50 ml acetonitrile. The purified colloid is allowed to deposit for 16 h and the supernatant is removed. The dark grey powder for the purified Pt colloid is then dried at 10^{-3} mbar for 16 h. As an example, using this procedure, hydrosol **1** (prepared with a Pt : SB12 ratio of 1 : 2) was concentrated to give a water soluble powder containing 45 wt% Pt.

Sulfobetain-12-stabilized Pt hydrosols [Pt/SB12], 1–4. Reducing agent used: LiEt₃H in THF. Preparation conditions of the different hydrosols and their characteristics are given in Table 1.

Bimetallic Pt/SB12 hydrosol [Pt₈₀Cu₂₀/SB12]. Reducing agent used: LiBH₄ in H₂O. H₂PtCl₆ (1.35 g, 2.65 mmol) and CuCl₂ · 2H₂O (0.11 g, 0.66 mmol) were suspended with SB12 (4.3 g, 12.7 mmol) in 100 ml H₂O under argon and subsequently stirred for 1 h. A fresh solution of LiBH₄ (0.36 g, 17 mmol) in 50 ml H₂O was added dropwise over 1 h. The resulting hydrosol (7.05 g) is very soluble in H₂O. Elemental analysis: 7.57 wt% Pt; 0.73 wt% Cu (corresponding to Pt₇₉Cu₂₁). The UV/VIS spectrum showed an unstructured, decreasing absorption typical for colloidal metals. Mean particle size from TEM was 4.5 nm.

Carboxybetain-stabilized Pt hydrosol [Pt/CB12], 10. Reducing agent: LiEt₃H in THF. The preparation followed the general procedure given above using PtCl₂ (5.5 g, 20.67 mmol), CB12 (11.3 g, 41.7 mmol) and LiEt₃H (32 ml, 41.7

mmol). The resulting very water-soluble powder gave an elemental analysis of 22 wt% Pt and a UV/VIS spectrum typical of a metal colloid. The TEM result gave a particle size of 2.3 nm.

Preparation of colloidal Pt/activated carbon catalysts

The adsorption of the Pt hydrosols (1 wt% Pt) on activated carbon (Degussa No. 101, Charge 514) in aqueous solution followed the procedures described previously.^{9,13,15}

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