Research highlight

Jens Baumgard, Marga-Martina Pohl, Udo Kragl and Norbert Steinfeldt*

Preparation of tailor-made supported catalysts using asymmetric flow field flow fractionation and their application in hydrogenation

Abstract: The optical, chemical, and catalytic properties of metallic nanoparticles (NPs) depend strongly on their particle size and shape. Therefore, the preparation of monodisperse metallic NPs is very important for fundamental studies and practical applications. However, the isolation of the different structures by separation from a polydisperse sample, especially in the size range below 10 nm, is not well applied so far. Here, the asymmetric flow field flow fractionation (AF4) is adapted for the preparative separation of the Pd NPs regarding their size and shape in the sub-10-nm size range. To prove the efficiency of the applied method, small-angle X-ray scattering (SAXS) and high-resolution transmission electron microscopy (TEM) were utilized to determine the particle size distribution at different stages of the separation process. A major benefit of this method compared to most of the other separation techniques, the removal of impurities during the separation process, was proven by proton nuclear magnetic resonance (NMR). The obtained results demonstrate that the AF4 is well suited for the rapid preparation of the purified uniform precious metal NPs at the applied size range. Single fractions of the different-sized and -shaped Pd NPs were deposited on titania (TiO₂) and tested in the catalytic hydrogenation of 2,5-hydroxymethylfurfural (HMF) in aqueous solution under mild conditions. While the spherical-shaped particles show a high activity, the separated agglomerated particles show a higher selectivity to the desired products.

Keywords: asymmetric flow field flow fractionation; hydrogenation; nanoparticles; preparative size separation; supported catalyst.

1 Introduction

Metallic nanoparticles (NPs) are integral parts of many areas of daily life [1, 2]. They are used in the fields of research (coatings, catalysis) [3], consumers (toiletries) [4, 5], and industrial applications (varnishes, fuel cells) [6]. As their physical properties strongly depend on the size and shape [7, 8], it is important to develop efficient preparation methods. Especially, the sub-10-nm sized NPs are very interesting for current research. A popular method for the preparation of metallic NPs in the sub-10-nm size range is the polyol process. With this method, catalytically active precious metal particles can be synthesized using batch [9], semi-batch [10], or continuous operation mode [11, 12]. Depending on the applied synthesis conditions, the presence of the polymeric stabilizers like poly(vinylpyrrolidone) (PVP) is necessary to protect the formed NPs from aggregation and coalescence. For certain applications, the presence of the polymeric stabilizer can be detrimental and, therefore, it has to be removed. Such processes mostly include a thermal treatment [13], which often enlarges the size distribution.

Another approach to remove the polymeric stabilizer is a phase transfer process [14, 15], which can also lead to a broadening of the size distribution. But here, the particles stay in solution, and a following size separation is still possible. A number of techniques is described in the literature to separate the NPs regarding their size, such as sedimentation [16, 17], electrophoresis, [18–21] nano and ultra-filtration [22, 23], chromatography [24–27], and the different kinds of field flow fractionation [20, 28–35]. Sedimentation separates the NPs according to their differences in density and hydrodynamic radius. In electrophoresis, the separation is determined by the differences in
the electrophoretic mobility, which depends, e.g., on the hydrodynamic radius, zeta potential, etc. The chromatographic methods separate the NPs due to their interaction with the stationary phase of the column. Nano and ultrafiltration are based on the theory of the solubility in the membrane and the sieving effect, respectively.

For the size separations of NP fractions with particle sizes below 10 nm, the above methods are not suitable because of different limitations. However, such small structures are of great interest for medicine because they can overcome biological barriers, and so, they can be used as a marker [36], contrast agents [37, 38], and for cancer therapy [39]. In physics, there are various applications due to their Plasmon resonance, which offers advantages in photovoltaics [40] and optics [41]. In chemistry, they offer, due to their unique properties, the possibility to develop new processes [42] or ways to design better catalysts [43, 44].

A promising separation technique for NPs in the sub-10-nm range is the asymmetric flow field flow fractionation (AF4). Field flow fractionation was developed by Giddings in 1966 [45]. The AF4 technique was already successfully applied in (bio-) polymer analytics and pharmacology [46, 47], e.g., for the separation of the protein monomers from dimers and trimers. Also, applications to analyze the NPs online are already known; particularly, great potential offers the coupling with dynamic light scattering, small-angle X-ray scattering (SAXS), and mass spectrometry.

Here, it will be demonstrated that the AF4 is a suitable technique for the size separation of the real NP mixtures with particle sizes below 10 nm. Furthermore, it will be shown that this technique delivers reproducible results and that a method once developed can be used for similar sized particles from various elements. Furthermore, it will be shown that the NPs collected from various fractions of the separation process can be used for the preparation of heterogeneous catalysts, which differ in their catalytic performance.

2 Experimental

2.1 Materials

The metal precursor sodium tetrachloropalladate (98%), the stabilizer poly(vinylpyrrolidone) K-30 (≥99.95%), the support TiO₂ (P25, ≥99.5%), and toluene (≥99.7%) were purchased from Sigma-Aldrich (Deisenhofen, Germany), ethylene glycol (≥99.5%) was from Carl Roth (Karlsruhe, Germany); dodecyl amine (≥99%), sodium hydroxide (≥99%), and acetone (≥99.5%) were obtained from Fluka (Deisenhofen, Germany). All the chemicals were used without any further purification. For the use as eluent in the AF4, the toluene was recycled by distillation (GC purity ≥98%).

2.2 Preparation of Pd/PVP nanoparticles

117.7 mg of the Na₂PdCl₄ (0.4 mmol) and 133.4 mg PVP K-30 (1.2 mmol of the repeating unit) were dissolved in 18 ml ethylene glycol. This solution is preheated to 373 K while stirring under argon atmosphere. Then, 2 mL of a 0.5-M sodium hydroxide solution in ethylene glycol is added quickly. The color changes within seconds from orange over yellow to dark brown. After 3 h, the solution is cooled to room temperature.

2.3 Ligand exchange from Pd/PVP nanoparticles to Pd/C₁₂-amine nanoparticles

To separate the NPs from the synthesis solution, 10 ml of the NP solution was transferred in a centrifugal glass. After the addition of acetone (100 ml), the Pd/PVP NPs precipitated. Then, the suspension was centrifuged at 1000 g for 15 min. The ethylene glycol acetone mixture was decanted, and the NPs were dried with compressed air. Afterwards, the Pd/PVP NPs were dissolved in 10 ml of deionized water. The NP solution was added to a 10 ml solution of C₁₂-amine dissolved in toluene (0.1 M), and under vigorous stirring and argon atmosphere, the mixture was heated to 373 K for 2 h and then cooled to room temperature.

2.4 Preparation of Pd@TiO₂

Owing to the different Pd concentrations of the collected fractions, the amount of TiO₂ must be adjusted for every fraction. The aim was a Pd content of 0.5 wt.% on the support. The NP-containing solution is diluted with the same volume of acetone; then, the TiO₂ is added. The suspension is stirred for 24 h at room temperature. Then the solution and catalyst are separated by centrifugation at 13,000 g for 15 min.

2.5 Hydrogenation of 2,5 Hydroxymethylfurfural (HMF)

In a 100 ml Büchi – glass (Büchi Glas Uster, Uster, Switzerland) autoclave, 80 mg of the prepared catalyst and 20 ml of a 0.1-M HMF solution are given. The hydrogenation is
carried out at a 5 bar excess pressure of hydrogen, under vigorous stirring at 298 K. The samples are collected once an hour. The reactions are driven to about 40% conversion.

### 2.6 UV/Vis spectra

The UV/Vis spectra were recorded at 298 K with a Jasco (Gross-Umstadt, Germany) MD-2010 plus multi wavelength detector in the 240–600 nm range with 1 cm length of beam path. The time interval between recording two UV/Vis spectra was 2 s.

### 2.7 Small-angle X-ray scattering (SAXS)

The SAXS measurements were carried out with a Kratky-type instrument (SAXSess, Anton Paar, Graz, Austria) operated at 40 kV and 50 mA in slit collimation using a two-dimensional (2D) CCD detector (T=233 K). The 2D scattering pattern was converted into a 1D scattering curve as a function of the magnitude of the scattering vector \( q \) with SAXSQuant Software (Anton Paar).

\[
q = \frac{4\pi}{\lambda} \sin(\theta/2)
\]

where \( \lambda \) is the wavelength and \( \theta \) is the scattering angle.

A G"obel mirror was used to convert the divergent polychromatic X-ray beam into a collimated line-shaped beam of Cu K\( \alpha \) radiation (\( \lambda=0.154 \) nm). The slit collimation of the primary beam was applied in order to increase the flux and to improve the signal quality. The liquid sample cell consisted of a quartz capillary (internal diameter: 1 mm) stacked in a metal body with two windows for the X-ray beam. Using this sample cell, an identical volume of the solution was always irradiated. The scattering profiles of the Pd NPs were obtained by the subtraction of the detector current and the scattering profile of the solvent from the scattering profiles of the Pd NP-containing solution. From the scattering curves then, both the Guinier radius and the volume-weighted size distribution by indirect Fourier transformation (IFT) were obtained [48–51]. The scattering curves were obtained as the average of 100 measurements of 20 s.

### 2.8 Transmission electron microscopy (TEM)

The TEM measurements were made at 200 kV by using a JEM-ARM200F (JEOL, Tokyo, Japan) instrument, aberration-corrected by a CESCOR (CEOS) for the scanning transmission electron microscopy (STEM) applications below the condenser. The microscope was equipped with a JED-2300 (JEOL) energy-dispersive X-ray spectrometry (EDXS) instrument for chemical analysis. For the preparation of the samples, the initial sample was diluted by a factor of 20 with toluene. The AF4-separated samples were used without any further dilution. One droplet of the NP samples was applied onto carbon-coated 400-mesh copper TEM grids and dried at 323 K in high vacuum prior to the inspection via TEM.

### 2.9 ImageJ

The particle size distribution was determined from TEM images with the open source software ImageJ, (NIH, USA) [52] using the PSA (Particle Size Analyzer)-macro. The macro can be downloaded from http://code.google.com/p/psa-macro. It is able to detect and count particles that match user-given parameters like minimum and maximum values for the particle size and circularity.

The following parameters were used for the macro routine: background removal (Inverted Gaussian 10%), smoothing filter (Gaussian r=1), manual global threshold, and no separation of the touching particles. The particle size was calculated as a circle equivalent diameter from the area of each individual particle (equation 2). The circularity describes how well the 2D image of the particle matches a circle (equation 3). For a perfect circle the value is 1.

\[
d = \frac{2(A/\pi)^{1/2}}{d...diameter}
\]

\[
A...particle~area
\]

\[
c = 4\pi A/L^2
\]

\[
c...circularity
\]

\[
L...perimeter
\]

\[
A...particle~area
\]

### 2.10 Asymmetric flow-field flow fractionation

Fractionation of Pd NPs/C\(_r\)-amine was carried out using an AF4 system (AF2000 Postnova Analytics, Landsberg, Germany). The used channel is 29 cm long with a maximum width of 5 cm, a spacer with the height of 500 \( \mu \)m, and a regenerated cellulose membrane with a 5-kDa cutoff.
The flows were provided by two separate HPLC pumps and the cross-flow was realized by a separate syringe pump. The toluene used as eluent was degassed by an inline degasser. The detector flow was kept at 0.3 mL/min. The output from the channel was connected to an on-line UV/Vis spectrometer set at 300 nm wavelength for the detection of the Pd NPs.

3 Results and discussion

After the synthesis of the Pd NPs (see the Experimental section), a few intermediate steps are necessary before starting the separation. In order to remove the polymer stabilizer, which may be detrimental for a later application of the NP, the PVP has to be substituted by a molecular stabilizer that does not hinder the free movement of the NP like PVP does [53]. Dodecyl amine was chosen because the amines are weak coordinating stabilizers that can easily be substituted after separation when interfering with the application [54–56]. The phase transfer procedure is explained in the Experimental section. The TEM image of the C₁₂-amine-stabilized Pd NPs (Figure 1A) shows a rather wide size distribution between 2 and 10 nm and, also, the differences in the morphology of the particles. The sample consists of spherical, peanut-like, and rod-like particles, respectively. By comparing the TEM images of the Pd NPs in ethylene glycol with those obtained after the phase transfer to toluene, it is assumed, that the more complex structures derive from agglomeration of the spheres during the phase transfer.

The SAXS profile (Figure 1B) was fitted using the IFT method (see Experimental section) assuming that the solution contains spherical Pd NPs with different particle sizes. Figure 2A compares the results obtained by the TEM and SAXS. The average diameter of the volume-weighted particle size distribution function obtained from the TEM image using the program ImageJ (see the Experimental section) is about 4.0 nm. For a better comparability of the results, the rods were assumed as quasi spheres. Therefore, ImageJ calculated the circle equivalent diameter (see the Experimental section). The maximum of the volume-weighted size distribution obtained by fitting the SAXS profile with the IFT method is at 2.8 nm (2Rₘₐₓ).

Figure 2B shows fractograms of the multiple AF4 runs of the dodecyl amine-stabilized Pd NPs. The runs were carried out with toluene as the solvent. Toluene was chosen because the stabilizing effects of dodecyl amine in other solvents like ethanol seem to be too weak during the focus phase so the NPs can interact with each other and with the membrane. Both effects lead to the deterioration of the separation, visible as a strong loss of material and problems with the reproducibility. For toluene, it can be seen that there is a high reproducibility of the fractionation (Figure 2B). One major advantage of the AF4 method, in contrast to the other separation techniques, is that also impurities can be removed from the system during the separation process. In order to transfer the NPs from the water to the toluene phase, a molar excess of dodecyl amine (5:1) was necessary. It is assumed that the dodecyl amine, which is not directly bound to the NP surface, pass the membrane during the AF4 run. To prove this assumption, the C₁₂ amine stabilized Pd NPs (8 mg) obtained after the evaporation of toluene were dissolved in d₆-benzene and examined by NMR before and after the AF4 separation. The corresponding H-NMR results are shown in Figure 3. Spectrum a shows the NMR signals of pure dodecyl amine. While the initial Pd-C₁₂ amine solution (curve b) clearly shows the NMR signals from dodecyl amine, the signals of the Pd NPs after the AF4 separation are much weaker, indicating that the dodecyl amine has been removed from the NP surface.

![Figure 1](image1.png)  TEM image of the dodecyl amine-stabilized Pd NPs after the phase transfer to toluene (scale bar 20 nm) (A) and the scattering profile of the initial sample (black) and the fit using the IFT method (red) (B).
amine, such signals were not observed for the sample collected after the AF4 fractionation (curve c). Therefore, it is assumed that most of those C12-amine molecules, which are not directly used for NP stabilization, permeate the membrane during the separation process. So the sample contains, after the separation, only such amount of C12-amine necessary to stabilize the NPs in solution in contrast to the auxiliary electrolytes in electrophoresis.

For further analysis of the separation process, the retentate was fractionated in nine different fractions. Each fraction was collected within a time interval of 30 s. As the solution volume of a single fraction was low, the sampling procedure was repeated 20 times.

The size, shape, and size distribution of the Pd NPs in each fraction were determined by the SAXS and TEM analyses. The corresponding SAXS profiles are given in Figure 4A. For the NP fractions with higher retention times, the particle scattering decreased faster with increasing q-values, indicating a larger particle size. The SAXS data were further evaluated using the Guinier approximation and IFT technique. The corresponding results are presented in Figure 4B and Table 1. Figure 4B shows the Guinier plots of the Pd NPs. For the fractions collected between 8.5 to 9 min (sample B) and 9.5 to 10 min (sample D), the Guinier plots show a linear behavior over a wide q range, which indicates that the Pd NPs have a relatively narrow size distribution. This is not the case for the fractions of longer
The obtained Guinier radii are summarized in Table 1.

The TEM images of the Pd NPs from the different fractions with the corresponding particle size distribution are shown in Figure 5. In order to compare the different-shaped particles regarding their size, the rod-like particles were regarded as quasi circular (see the Experimental section). The corresponding diagrams (right from TEM) also compare

<table>
<thead>
<tr>
<th>Sample</th>
<th>Retention time/(min)</th>
<th>HRTEM Øa/(nm)</th>
<th>σ/(nm)</th>
<th>Circularity</th>
<th>Shape</th>
<th>2×Rg&lt;(a)/(nm)</th>
<th>2×R&lt;max(DV, R)/(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Initial 4</td>
<td>1.4 (35%)</td>
<td>0.88</td>
<td>S+P+R</td>
<td></td>
<td>8.0</td>
<td>2.7</td>
</tr>
<tr>
<td>B</td>
<td>8.5–9</td>
<td>3.2</td>
<td>0.4 (13%)</td>
<td>0.95</td>
<td>Spheres (S)</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>D</td>
<td>9.5–10</td>
<td>3.5</td>
<td>0.89</td>
<td>S</td>
<td></td>
<td>3.7</td>
<td>2.7</td>
</tr>
<tr>
<td>F</td>
<td>10.5–11</td>
<td>4.6</td>
<td>0.7 (16%)</td>
<td>0.68</td>
<td>S+P</td>
<td>5.0</td>
<td>3.5</td>
</tr>
<tr>
<td>H</td>
<td>11.5–12</td>
<td>6.2</td>
<td>0.8 (13%)</td>
<td>0.58</td>
<td>Peanut-like (P)</td>
<td>5.9</td>
<td>–</td>
</tr>
<tr>
<td>J</td>
<td>12.5–13</td>
<td>7.2</td>
<td>1 (14%)</td>
<td>0.49</td>
<td>Rods (R)</td>
<td>7.3</td>
<td>–</td>
</tr>
</tbody>
</table>

*a* The average volume-weighted particle diameter.

*b* The Guinier radius; the values that are not given in the table are not available for this method.

Figure 5 TEM images (B–J) and the corresponding particle size distribution from the TEM and from the fit of the SAXS profiles (see also Figure 8; B, D, F) using the IFT method (scale bar is 10 nm).
the number-weighted distribution from the TEM with the volume-weighted particle size distribution obtained from the SAXS data analysis. The images B and D show the NPs with almost spherical shape, while F shows a mixture of the bigger spheres and peanut-like particles. On Image H, most of the Pd particles are peanut-like and only some rods are visible, and on Image J, there are only rods. The results of the TEM and SAXS are summarized in Table 1.

The results of both methods (Table 1) show that the Pd NPs were separated regarding their particle size and/or shape. The size distributions from the SAXS were obtained by the fitting of the scattering curves using the IFT method assuming that the shape of the particles is spherical. For the samples collected at 8.5 and 9.5 min (sample B and D), the main particle diameter determined from the TEM increases from 3.2 to 3.5 nm. The high value of circularity for these samples indicates a nearly spherical shape (see the Experimental section, equation 3). The Guinier radius of these fractions increases from 1.45 to 1.85 nm and is slightly larger than the maximum of the volume-weighted particle radii distribution (Rmax in Table 1). The polydispersity of the particle size for these both fractions is lower than 15%, and the results of the TEM and SAXS data evaluation are in good accordance. The sample collected at 10.5 min (F) gives a circularity of 0.68, which is much lower than that obtained for the initial solution (0.88). Like the initial sample, this fraction contains both spherical particles and aggregates. The ratio of the spherical particles to the aggregated particles is much lower than that of the initial solution (ratio between the spheres and coalesced particles was about 6 to 1). The fit of the scattering curve using the IFT method, assuming the spherical particle shape, gives again to the small particle sizes as already observed for the initial solution. The Guinier radius of this fraction is in good accordance with the mean particle diameter determined from the TEM analysis. At longer retention times, the collected fractions (H and J) contain only aggregated Pd NPs, which are composed of spheres similar in size like samples B, D, and F.

Owing to the low Pd concentration and the more complex structures of the NPs, the IFT method was not applied for samples H and J. The Guinier radius derived from the SAXS was in reasonable accordance with the mean diameter obtained from the TEM.

In Figure 6, the mean retention times of the different Pd NP fractions are plotted against the mean diameter derived from the TEM.

The linear relationship between both variables was expected from equation 4 [57], which gives a rough estimation for the development of the retention time in dependence of the particle radius or diameter. The factor K contains the Boltzmann constant, temperature, solvent density, height of the AF4 channel, and the ratio between the flows in the AF4. All these parameters can be assumed to be constant for the single separation experiment. The summand L is the product of K and the thickness of the ligand shell, which can also be assumed to be approximately constant.

$$t_r = K r_{np} + L$$

The finding of the linear relationship between the particle diameter and the retention time is also considered as a strong indication that the single dodecyl amine-stabilized NP move in the separation channel nearly independently from each other and that the interaction between the single particles can be neglected.

In addition to the Pd NPs, also results of spherical Rh NPs (1.5±0.4 nm, 2.3±0.2 nm, 4.0±0.4 nm) using identical separation conditions are shown in Figure 6. The implementation of the Rh NPs in this diagram, which are stabilized by the same ligand C12-amine and which fit the linear relationship of the Pd NPs demonstrates that the separation via AF4 in the applied size range (below 10 nm) is not limited to one special element.

This is a major advantage of the AF4. As long as the particle surface is similar and the particles can be stabilized in the same way, this method can be used for the NP separation of any element or compositions of elements. Compared to most other techniques, the AF4 separates only due to the hydrodynamic size, which is, in contrast to the density and permittivity, not element specific. A disadvantage is that the AF4 is hardly robust against the changing of the conditions. To enable a good separation performance, interactions between the NPs and the membrane must be excluded, according to the flow field theory [53]. This means that the stabilizer, the solvent, and
the membrane type, must fit the separation problem. The problem occurs during the short time after the injection of the sample when it is focused on the membrane because high concentrations of the NPs are reached close to the surface of the membrane. The stabilizer has to protect the NP well, so the particles do not aggregate and, at the same time, do not stick to the membrane. When the stabilizer is not able to suppress the interactions of the NPs with the membrane, it leads to a loss of the material upon separation. This phenomenon is visible as an increase of the signal intensity for the successive injections and particularly strong when using a new membrane [58]. Such a behavior was not observed for Pd/C12-amine (Figure 2) or for Rh/C12-amine. Other separation techniques like continuous flow electrolysis and size exclusion chromatography do not have this problem because a concentration step is missing.

Additionally, the stabilizer should not have an own size distribution like polymers or form superstructures because this leads to a superimposition of the size distribution of the NPs and thus to a decrease in resolution. Most advantageous for a preparative application of the AF4 is the cleaning of the sample because the other techniques with a comparable resolution (continuous flow electrolysis, size exclusion chromatography) need auxiliary materials (like electrolytes, buffer), which are hardly removable without changing the size distribution of the separated samples.

After proving the concept of separation, a larger amount of the Pd NPs was separated for the preparation of the supported nanopalladium catalysts by further increasing the number of the AF4 runs. The conditions of the sample collection were adjusted to reach that in each fraction one of the three different shapes (S, P, R) dominates. The results of the characterization by the TEM are summarized in Table 2.

For the preparation of the supported catalyst with comparable Pd loading, the amount of Pd in the different fractions has to be known. To estimate the concentration of Pd, the UV/Vis spectroscopy was used. Figure 7 shows the UV/Vis spectra of the different Pd NP fractions. The Pd concentrations were roughly determined from the UV/Vis intensity after comparing it with that of a sample with a known NP concentration.

For the preparation of the catalyst, the colloidal deposition method was used (Experimental section) [59]. The excess solution was checked after centrifugation via UV/Vis for complete deposition. To determine the amount of Pd on the support, the material was pulped in acid, and the Pd concentration was determined by the atomic absorption spectrometry (AAS). The results are summarized in Table 3.

For the catalytic testing of the different-sized and -shaped Pd NP based materials, the hydrogenation of HMF was chosen (see the Experimental section). This reaction not only offers the possibility of measuring the activity but also the possibility to compare the selectivity of the catalysts. The reaction scheme is very complex [60] so Figure 8 shows only a simplified one with the two desired products.

The results of the catalytic test are summarized in Table 3. The activity is related to the amount of conversed HMF, the time, and the molar amount of Pd in the reaction.

The activity of the Pd NPs for the hydrogenation of HMF decreases with their increasing size. For Cat-a to Cat-c, there is only a slight decrease from 128.4 to 97.1 mol h⁻¹ mol⁻¹. This loss of activity can be explained by the lower surface area of the rods toward the spheres due to the aggregation. The reason for the subsequent abrupt drop of the activity for Cat-d is presently unknown. Surprisingly, a gain in the selectivity to the target products from Cat-a (44%) to Cat-c (94%) can be observed. As such Pd structures have not yet been isolated and studied before, no explanation for this behavior can be found in literature. Most of the possible side products result from the ring opening of the furan; it might be assumed that these reactions are effectively suppressed by such aggregated structures.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Retention time/(min)</th>
<th>HRTEM Ø/(nm)</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>8.25–9.25</td>
<td>2.7</td>
<td>S</td>
</tr>
<tr>
<td>b</td>
<td>9.75–10.75</td>
<td>3.3</td>
<td>P</td>
</tr>
<tr>
<td>c</td>
<td>11.25–12.25</td>
<td>5.7</td>
<td>R</td>
</tr>
<tr>
<td>d</td>
<td>12.75–13.75</td>
<td>7.4</td>
<td>R</td>
</tr>
</tbody>
</table>

Figure 7 The UV/Vis spectra of the collected fractions.
Conclusion

The AF4 technique can be used to separate the NPs regarding the particle size in the sub-10-nm range with a very high rate of reproducibility and good resolution. To separate such small NPs, the stabilizing agent has to be molecular, and the interaction between the stabilizer molecules, which are bonded to the particle surface has to be excluded, e.g., by the choice of the appropriate solvent. The stabilizers that meet the above requirements are alkyl amines like dodecyl amine. An advantage of the AF4 method is that no further separation agents such as electrolytes are necessary, which might be important for later applications. In contrast to the other separation techniques, the NP-containing solution is also purified. Although the organic and inorganic impurities and excess stabilizer are removed during the separation process, the separated solutions are stable, and the NPs do not agglomerate.

The first catalytic tests of the materials prepared by the AF4 separation shows that the single fractions of the particles derived from the same batch synthesis show a different catalytic behavior. Especially, the synthesis of the NPs with a certain degree of agglomeration might allow the preparation of the materials with specific catalytic properties, which can be hardly formed by other methods.

Acknowledgements: The authors thank the Leibniz-Gemeinschaft for the financial support.

Received December 14, 2012; accepted March 14, 2013; previously published online April 26, 2013

References


Jens Baumgard studied Chemistry at the University of Rostock, where he graduated in 2009. Since 2009 to date, he has been a PhD candidate in the group of Prof. Udo Kragl at the Leibniz Institute for Catalysis in Rostock, where he has been working on the synthesis of metallic nanoparticles and their catalytic application.

Marga-Martina Pohl is a senior scientist at the Department of Analytical Services of the Leibniz Institute for Catalysis in Rostock. Her general research is focused on aberration-corrected scanning transmission electron microscopy (STEM) including high-resolution HAADF. Her interests include the characterization of nanostructured materials mainly heterogeneous catalysts from the noble metal catalysts to multicomponent systems.
Udo Kragl studied Chemistry at the University of Bonn. He finished his PhD thesis in 1992 in the field of Biochemical Reaction Engineering. After a postdoc at Ciba-Geigy International Research Laboratories in Japan, he returned to the Juelich Research Center for his habilitation. Having finished, he immediately gained a position as full professor for Chemical Reaction Engineering at the University of Rostock. Since 2007, he is the Dean of the Faculty for Interdisciplinary Research at the same university. He taught Industrial Chemistry at the National University of Singapore as a visiting professor in 2007. He is active in the German Society of Catalysis (GeCats). His research interests are in the field of novel reactor concepts for chemo- and biocatalysis, the application of ionic liquids and membrane processes for downstream processing, and catalyst recycling.

Norbert Steinfeldt studied Chemistry at the University Leipzig. Upon completion of his PhD degree at the Humboldt University (Berlin) in 1995, he joined the chemical faculty at the University of Limerick as a postdoc. Afterward, he joined the Leibniz Institute for Catalysis, where he was dealing with different projects in the field of microreaction technology and high-throughput experimentation. Presently, his research focuses on the development and application of nanostructured material for catalytic reactions and water cleaning.