CHAPTER 1

Hybrids from Polymer Colloids and Metallic Nanoparticles: A Novel Type of “Green” Catalyst

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Metallic nanoparticles have interesting perspectives in the application of catalysis as they exhibit unusual chemical and physical properties differing from the bulk material. However, for all practical applications, metallic nanoparticles must be stabilized in solution in order to prevent aggregation. Here we have reviewed our recent studies on metallic nanoparticles encapsulated in spherical polyelectrolyte brushes (SPBs) and thermosensitive core–shell microgels, respectively. SPB particles consist of a poly(styrene) (PS) core onto which long chains of polyelectrolyte brushes are densely grafted by a grafting-from technique. In the case of thermosensitive microgels, the core consists of PS whereas the network consists of poly(N-isopropylacrylamide) (PNIPA) crosslinked by N,N’-methylenebisacrylamide (BIS). Both polymeric particles present as excellent carrier systems for applications in catalysis. More importantly, the composite systems of metallic nanoparticles and polymeric carrier particles allow us to do “green chemistry,” that is, low temperature, easy removal of the catalyst and low leaching of heavy metal into the product. The chemical reactions can be conducted in a very efficient way. In addition, in the case of using microgels as the carrier system, the reactivity of composite particles can be adjusted by the volume transition within the thermosensitive networks. Hence, this chapter gives clear indications on how carrier systems for metallic nanoparticles should be designed to adjust their catalytic activity.
1.1. INTRODUCTION

Metal nanoparticles have attracted a lot of attention, because they may exhibit unusual chemical and physical properties differing strongly from the bulk material,\textsuperscript{1–3} which are due to three major factors: high surface-to-volume ratio, quantum size effect, and electrodynamic interactions.\textsuperscript{4} Metallic nanoparticles have interesting perspectives in the applications as catalysts,\textsuperscript{5–8} sensors,\textsuperscript{9} and electronics. However, the high specific surface area of the metal nanoparticles often leads to the common tendency of agglomeration, and usually requires their immobilization in mesoscopic carriers to prevent precipitation. Using suitable polymeric systems, such as microgels,\textsuperscript{10–12} dendrimers,\textsuperscript{13–16} and block copolymer micelles\textsuperscript{17–19} as carriers or “nanoreactors,” metal nanoparticles can be immobilized and handled in an easier fashion. Metallic nanoparticles immobilized in such systems can then be used for catalysis in various media.\textsuperscript{20} Moreover, the concept of green chemistry has become a top priority item for catalysis industry, that is, low temperature, easy removal of the catalyst and low leaching of heavy metal into the product.\textsuperscript{21, 22} This requires a carrier system that should allow separation (e.g., via filtration), have long-term stability, be easy to handle, and prevent the metallic nanoparticles from coagulating. Moreover, no stabilizing agent that may alter or block the surface of the nanoparticles should be used. The carrier systems should also be sufficiently stable during recycling of the catalyst.

In this chapter, we review recent work on two special types of polymeric carrier systems, namely, the spherical polyelectrolyte brushes (SPBs) and thermosensitive core–shell microgels, which have been used successfully for the immobilization of metal nanoparticles. Figure 1.1a gives a schematic representation of the SPB particles: Long linear polyelectrolyte chains are grafted densely to a colloidal core particle.\textsuperscript{23, 24} The term brush implies that the grafting of the chains is sufficiently

![Figure 1.1](attachment:image1.png)

**Figure 1.1.** (a) Structure of the spherical polyelectrolyte brushes having cationic polyelectrolyte chains on their surface. The core consists of poly(styrene) and has diameters of approximately 100 nm. The chains are densely grafted to the surface of these cores by a grafting-from technique (“photoemulsion polymerization,” cf. Ref. 24). (b) The core–shell microgel particles shown in a schematic fashion: The core consists of poly(styrene) (PS) whereas the network consists of poly(N-isopropylacrylamide) (PNIPA) crosslinked by \(N, N'\)-methylenebisacrylamide (BIS).
dense; that is, the linear dimensions of the polyelectrolyte chains are much larger than the average distance between two neighboring chains on the surface. These positively charged polyelectrolyte chains form a dense layer on the surface of the core particles and can bind metal ions. Reduction leads to metallic nanoparticles. Figure 1.1b depicts core–shell microgels that consist of a solid core of polystyrene and a shell of crosslinked poly(N-isopropylacrylamide) (PNIPA). The metal ions are localized within the network because of complexation between the metal ions and the nitrogen atoms of PNIPA. Reduction of these ions leads to nearly monodisperse metallic nanoparticles that are only formed within the polymer layer.

The focus of this chapter is the use of both the spherical polyelectrolyte brushes and microgel particles as carrier systems for novel metal nanoparticles, which can be used for catalysis in aqueous media, that is, under very mild conditions. Thus, the composite systems of metallic nanoparticles and polymeric carrier particles allows us to do “green chemistry” and conduct chemical reactions in a very efficient way. This approach can open new possibilities for catalytic application of metal composite particles in different reactions and represents a typical example of “mesotechnology”: Nanoscopic objects with catalytic properties are judiciously combined with polymeric carriers to serve for a given, well-defined purpose.

1.2. SPHERICAL POLYELECTROLYTE BRUSH BASED METALLIC NANOPARTICLES

Often, nanoparticles are stabilized by alkyl chains attached through thiol bonds to the surface of the metal. However, the strong interaction of the thiol group with the surface of the nanoparticles may profoundly alter the catalytic properties of the metal. The same problem may occur when immobilizing nanoparticles on solid substrates.

Recently, we reported that the SPBs are excellent carriers for various metal nanoparticles. In particular, we demonstrated that the composites of metal nanoparticles and SPBs are very stable. This fact can be understood when considering the synthesis of the composites in detail. Figure 1.2 shows the synthesis of Au nanoparticles (NPs) on a cationic SPB. The AuCl$_4^-$ ions are introduced as counterions of the brush layer and all metal ions not firmly bound in this layer are flushed away by ultrafiltration. Hence, only the reduction of these immobilized AuCl$_4^-$ ions will lead to well-defined Au NPs. All stages of nanoparticle formation within the brush layer can be followed easily by dynamic light scattering (DLS), which determines the hydrodynamic radius ($R_H$) of the particles. Since the radius $R$ of the core particles is exactly known, the thickness $L$ of the surface layer can be obtained by $L = R_H - R$ throughout all stages of the synthesis of the particles. We found that even low concentrations of AuCl$_4^-$ ions lead to a considerable shrinking of the polyelectrolyte layer on the surface of the core particles from 71 to 59 nm. This shrinking of the surface layer is due to partial crosslinking of the polyelectrolyte chains by the AuCl$_4^-$ ions.

The AuCl$_4^-$ ions are partially complexed by the polyelectrolyte chains. In this way the AuCl$_4^-$ ions create a densely crosslinked mesh of polyelectrolyte chains. Thus, the local concentration of AuCl$_4^-$ ions is therefore enlarged considerably.
In the next step the reducing agent NaBH$_4$ is added, which results in a collapse of the surface layer to a thickness of 21 nm. The micrographs of the resulting composite particles obtained by cryo-TEM are shown in Figure 1.3. It demonstrates that small Au NPs have been formed in this step.

A possible reason for the decrease of the hydrodynamic radius may be sought in a degradation of the polyelectrolyte layers by cleavage or other side reactions. However, this explanation can easily be refuted by dissolution of the Au NPs upon addition of NaCN in the presence of O$_2$. This process leads to $L = 69$ nm, which is identical to the starting value of 71 nm within the limits of error. Hence, the polyelectrolyte chains of the brush layer are condensed by the Au NPs as shown schematically in Figure 1.2. After the dissolution of the Au NPs the chains stretch again and assume their previous conformation. Hence, the Au NPs formed by reduction within the brush layer lead to an additional crosslinking of the polyelectrolyte chains that extend far beyond the crosslinking effect of the AuCl$_4^-$ ions. This attractive interaction could be related to the negative charge of the Au NPs. Thus, the Au NPs crosslink the polyelectrolyte chains by ionic interaction.

The advantages of generating metallic nanoparticles using this method are obvious: Because of the confinement of the counterions, nanoparticles are only
generated within the polyelectrolyte layer. Stabilization of the nanoparticles against aggregation is effected by the colloidal carrier particles. Because the metal nanoparticles carry no group stabilizing their surface, they exhibit a high catalytic activity. Thus, these systems can be used for catalysis of various chemical reactions that proceed in aqueous solution or in two-phase systems. In the following we review the main applications established so far.

1.2.1. SPB Based Au, Pt, and Pd Nanoparticles for Catalysis in Two-Phase Systems

In 1912, Paul Sabatier received the Nobel Prize for chemistry for his investigations into the use of finely divided metals in hydrogenation reactions. Since then, heterogeneous catalysis in organic chemistry has been developed extensively. During our research, we examined the hydrogenation of butyraldehyde to 1-butanol catalyzed by platinum nanoparticles supported on SPB particles. All reactions were carried out in aqueous solution at 40 °C and 70 bar hydrogen pressure. Product extraction was accomplished using a second (organic) liquid phase. The reactant and product concentrations (butyraldehyde and 1-butanol) were monitored by gas chromatography (GC). Excellent recyclability was observed concerning the catalytic performance and the product extraction, as shown in Figure 1.4. The catalyst system was used for 10 reactions, and the products extracted with ether after each reaction. It was found that the efficiency of the catalyst remains unaltered in nine consecutive reactions. The catalyst was stable against aggregation during the reactions and the workup procedure. Moreover, our previous work showed that platinum and palladium nanoparticles prepared by the same method can be used as catalysts for the degradation of 4-nitrophenol using NaBH₄. It is interesting to note that palladium was more effective than platinum, but their catalytic activities were in the same magnitude when normalized to the surface of metal particles. However, the hydrogenation...
activities of palladium nanoparticles were orders of magnitude smaller than those observed for the platinum system.

1.2.2. Pd-Nanoparticles Immobilized on SPBs for the Heck and Suzuki Coupling

The palladium-catalyzed Heck\textsuperscript{36, 37} and Suzuki\textsuperscript{38, 39} reactions (cobalt nanospheres are also able to catalyze these reactions\textsuperscript{40}) between aryl halides and alkenes or boronic acids are well-established tools for C=C bond formation in organic synthesis, respectively.\textsuperscript{41, 42} Such reactions are traditionally catalyzed using many different kinds of phosphine-based palladium catalysts and phosphine-free palladium catalysts such as Pd(PPh\textsubscript{3})\textsubscript{4}, Pd(Oac)\textsubscript{2}, [(n\textsubscript{3}-C\textsubscript{3}H\textsubscript{5})PdCl]\textsubscript{2}, and Pd\textsubscript{2}(dba)\textsubscript{3}C\textsubscript{6}H\textsubscript{6}.\textsuperscript{43}

Recently, there have been many reports on the use of palladium nanoparticles as catalysts.\textsuperscript{44, 45} A convenient route for cross-coupling reactions involves reusable palladium nanoparticles that promote these reactions in organic solvents or in water.\textsuperscript{46, 47} However, the handling of the nanoparticles may impose problems during workup unless the particles are immobilized on suitable carriers. Recently, we reported that Pd nanoparticles immobilized in cationic spherical polyelectrolyte brushes (SPBs) present a composite system that can be used as an efficient catalyst for the Heck and Suzuki coupling reactions, as shown in Figure 1.5.\textsuperscript{48} Figure 1.6 shows the typical test reactions for the Suzuki- and Heck-type cross-coupling reactions using palladium nanoparticles as catalyst. We demonstrate that both reactions can be carried out under mild conditions and low temperatures (Suzuki reaction: 50 °C; Heck reaction: 70 °C). Pd loadings of 0.09 mol% (Suzuki) and 0.029 mol% (Heck) were used. For the Suzuki reaction the boronic acid gave rise to homocoupling products in 14% yield under the above-mentioned mild reaction conditions. Hetero-coupling was observed for bromides ( conversions of 80–90%) and iodides (around
However, chlorides resulted in low yields (ca. 6%). Additionally, substituents in the ortho and meta positions resulted in lower yields (due to steric hindrance) than para-substituted arenes. Selected results are listed in Table 1.1.

The Heck-type reaction (see Figure 1.6 and Table 1.2) using palladium nanoparticles as a catalyst was investigated using eight different aryl halides. With a
catalyst loading of 0.029 mol% Pd a variety of aryl iodides showed almost complete conversion, whereas aryl bromides were unreactive under the conditions employed. Under such mild conditions in water it is not possible to expand the scope of the Heck reaction to bromides or chlorides.

The reproducibility was found to be very good for palladium nanoparticles as catalyst of both Suzuki- and Heck-type reactions. In four runs the products were removed by ether and new starting materials were added to the water phase. We found that Pd@SPB could be used repeatedly without loss of activity. After these four runs

TABLE 1.1. Suzuki-Type Cross-coupling Using Palladium Nanoparticles Stabilized in SPB Particles as Catalyst

<table>
<thead>
<tr>
<th>Halide</th>
<th>Product</th>
<th>GC Conversion</th>
<th>Homocoupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>[image]</td>
<td>83%</td>
<td>4%</td>
</tr>
<tr>
<td>MeO-Br</td>
<td>[image]</td>
<td>79%</td>
<td>5%</td>
</tr>
<tr>
<td>MeO-B</td>
<td>[image]</td>
<td>15%</td>
<td>6%</td>
</tr>
<tr>
<td>NO2-B</td>
<td>[image]</td>
<td>22%</td>
<td>1%</td>
</tr>
<tr>
<td>O2N-Br</td>
<td>[image]</td>
<td>50%</td>
<td>1%</td>
</tr>
</tbody>
</table>

*Yields were determined by GC; hcp = homocoupling product (biphenyl)。“
cycles the nanoparticles were filtered off and investigated by cryo-TEM in order to
detect possible changes in the number and morphology of the nanoparticles.
We found that the nanoparticles are still embedded in the SPB support. Hence,
the present Pd@SPB catalyst system could easily be recycled and reused.

The excellent reproducibility can be explained by the robustness of the catalyst
system during catalysis and workup.

### TABLE 1.2. Heck Reaction Promoted by Pd@SPB in Aqueous Media$^a$

<table>
<thead>
<tr>
<th>Iodide</th>
<th>Product</th>
<th>GC Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Iodide" /></td>
<td><img src="image2" alt="Product" /></td>
<td>97%</td>
</tr>
<tr>
<td><img src="image3" alt="Iodide" /></td>
<td><img src="image4" alt="Product" /></td>
<td>98%</td>
</tr>
<tr>
<td><img src="image5" alt="Iodide" /></td>
<td><img src="image6" alt="Product" /></td>
<td>96%</td>
</tr>
<tr>
<td><img src="image7" alt="Iodide" /></td>
<td><img src="image8" alt="Product" /></td>
<td>98%</td>
</tr>
<tr>
<td><img src="image9" alt="Iodide" /></td>
<td><img src="image10" alt="Product" /></td>
<td>96%</td>
</tr>
</tbody>
</table>

$^a$ One mL of catalyst solution leads to a loading of 0.029 mol% Pd; the catalytic reactions were carried out at 70 °C for 24 h.\(^{48}\)
1.2.3. SPB-Based Nanoalloys of Noble Metals

Recently, we developed a method for the immobilization of Au–Pt nanoparticles into spherical polyelectrolyte brushes. Figure 1.7 a shows the method of synthesis employed here: First, AuCl$_4^-$ ions are immobilized as counterions within the surface layer of cationic polyelectrolyte chains. Because we know the total number of charges on the surface of the core particles, the number of AuCl$_4^-$ ions can be adjusted precisely in order to replace only a certain fraction of the Cl$^-$ counterions. After ultrafiltration, PtCl$_6^{2-}$ ions are introduced in the same manner. Any excess of metal ions is flushed away by ultrafiltration. Finally, reduction by NaBH$_4$ leads to Au–Pt alloy nanoparticles of a given composition. Figure 1.7b displays the HR-TEM of Au$_{73}$Pt$_{27}$. The crystal lattice is observed throughout the entire particle. Moreover, electron diffraction (inset of Figure 1.7b) demonstrates the crystalline state of the nanoparticles. Wide-angle X-ray scattering (WAXS) studies demonstrated that these alloys present solid solutions; that is, the particles consist of a random mixture of both types of metal atoms. Therefore, the lattice constants measured for the alloys vary continuously between the values found for the pure metals (Vegard-type).

The catalytic oxidation of alcohols to aldehydes has been applied to investigate the catalytic activity of these Au–Pt alloy particles. All reactions were carried out at room temperature using aerobic conditions. Notably, no phase transfer catalyst is needed for this reaction and the reaction conditions are very mild. GC revealed that no by-product is obtained under these conditions. We find full conversion within the limits of error. Hence, water is the only product formed by this reaction (besides the aldehyde or ketone). We find that systems containing pure Au nanoparticles are much less stable than the alloy particles. Substrates containing phenyl groups lead to considerable leaching of gold and even coagulation. This may result from the strong interaction of Au with the phenyl groups, as determined by Miyamura et al.

![Figure 1.7](image-url)
However, alloy nanoparticles turned out to be fully stable under the same conditions. This finding is corroborated by an analysis of the composite particles before and after catalysis by cryogenic TEM. No change or leaching of the nanoparticles is observed. Moreover, repeated use of the composite particles as catalysts did not lead to a noticeable decrease of catalytic activity. Hence, spherical polyelectrolyte brushes present a system that allows us to generate and to utilize alloy nanoparticles that exhibit properties widely differing from the properties of the respective bulk alloys.

Faceted, well-defined Pt single nanocrystals (NCs) with a typical size of 2–3 nm can be obtained by partial dissolution of nanoalloys of Pt and Au as shown in Figure 1.8.51 The dealloying of the Au–Pt nanoalloy proceeded surprisingly smoothly. The colloidal stability of the composite particles was not lost during the reaction with the cyanide ions, and coagulation of the NPs on the surface of the carrier particles was not observed during this process. The structure of the Pt NPs was analyzed by combining high-angle annular dark-field scanning TEM (HAADF-STEM) and HR-TEM with electron diffraction (ED) and WAXS. A low-magnification HAADF-STEM micrograph of the PS spheres on the supporting holey carbon film is shown in Figure 1.9a, and Figure 1.9b (from the same area at higher magnification) shows the uniform distribution of the Pt NPs on the PS spheres. In order to avoid any disturbance of this analysis by the core particles, only NPs sitting on the periphery of the carrier spheres were analyzed by HR-TEM (Figure 1.9c–f). The HR-TEM shows that the Pt NPs contain no grain boundaries and are single crystals. In several cases, the facets can be indexed because the NCs are aligned by chance; in Figure 1.9e, f, the electron diffraction shows directly the hexagonal symmetry of the cubic crystal.

The catalytic reduction of 4-nitrophenol to 4-aminophenol has been used for the analysis of the catalytic activity of the Pt NPs. The Pt NCs exhibit a high catalytic activity and turnover numbers as high as $1580 \pm 50$, which is among the highest turnover numbers measured for this reaction.26, 35, 52 Hence, the composite particles consisting of the SPBs and the Pt NCs present a system with high colloidal stability that may be used for catalysis in an aqueous environment.

The composite particles of metal nanoparticles and spherical polyelectrolytes present robust systems that can be employed in catalysis.53 More importantly, such metal nanoparticles can be used as effective catalysts in a “green” fashion, that is, low temperature, easy removal of the catalyst, and low leaching of heavy metal into the product.

1.3. MICROGEL-BASED METALLIC NANOPARTICLES

Microgels may have several important advantages over other systems, namely, stability, ease of synthesis, good control over particle size, and easy functionalization for stimulus-responsive behavior (e.g., change in volume in response to a change in pH, ionic strength, or temperature).55 It is clear that this kind of materials holds great promise for nanotechnology.56 Moreover, microgel-stabilized metal nanoparticles are kind of “quasi-homogeneous” nanoparticle catalysts, which have advantages of
both homogeneous and heterogeneous catalysts, such as high activity and easy separation for reuse.\textsuperscript{31}

Most of these systems are poly(N-isopropylacrylamide) or related copolymers.\textsuperscript{57} In aqueous media, PNIPA exhibits a lower critical solution temperature (LCST) at about 32 °C, which is close to the physiological temperature.\textsuperscript{58–60} Below the LCST, the polymer chains are soluble in water due to formation of hydrogen bonds between the water molecules and the amide side chains. When the temperature increases, the polymer undergoes a volume phase transition. Water is expelled from the microgel interior, thus causing a drastic decrease in volume above the LCST of the polymer. Antonietti et al.\textsuperscript{61, 62} were the first to employ microgels as “exotemplates” for the preparation of metal nanoparticles. Recently, Kumacheva and co-workers\textsuperscript{63} introduced polymer microgels as carrier systems for nanoparticles. They showed that semiconductors, metal, and magnetic NPs with

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**Figure 1.8.** Synthesis scheme of Pt NCs by dealloying of an Au–Pt nanoalloy. The carrier particles are SPBs that consist of a solid PS core ($R_h = 50$ nm) onto which cationic polyelectrolyte chains of 2-aminoethylmethacrylate (2-AEMH) are attached. In a first step, the chloride counterions were exchanged against AuCl$_4^-$ ions; in a second step the rest of Cl$^-$ ions were exchanged against PtCl$_4^{2-}$ ions. Bimetallic Au$_{45}$Pt$_{55}$ nanoalloy particles were generated by reduction of the mixture of these ions by NaBH$_4$. The composition of the resulting nanoalloy can be adjusted by the ratio of the metal ions in the brush layer. In the final step, cyanide ions and oxygen were used to leach out the Au atoms from the nanoalloy under very mild conditions. This procedure leads to faceted Pt NCs with a few nanometers in diameter embedded in the surface layer of polyelectrolyte chains. (See Ref. 51.)
Figure 1.9. (a, b) HAADF-STEM micrographs of the Pt NPs (bright spots) embedded and uniformly dispersed on a surface layer of the spherical polyelectrolyte. (c) HR-TEM micrograph of nanoparticles on the surface of two adjacent carrier particles. (d) HR-TEM micrograph of several NCs. (e, f) HR-TEM micrographs of two different Pt single NCs of sizes 4.6 and 2.8 nm, respectively, showing well-defined facets. All micrographs were acquired at 300 keV. (Insets) The Fourier transforms of the images. (See Ref. 51.)
predetermined size, polydispersity, and optical and magnetic properties can successfully be synthesized using polymer microgels as a template, which will have promising applications in catalysis, biolabeling, and chemical and biological separation. Pich et al.\(^{64}\) have used temperature-sensitive polyvinylcaprolactam-based microgels as containers for the deposition of catalytic active silver nanoparticles. Biffis and Sperotto\(^{65}\) have studied the application of microgel–stabilized metal nanoclusters as catalysts for different reactions and confirmed the enhanced catalytic activity of Pd nanoclusters in Heck reaction of activated aryl bromides, which was attributed to the smaller size of the metal nanoclusters.

Recently, we have successfully used thermosensitive core–shell microgel particles as a template for the deposition of metal nanoparticles (Ag, Au, Pd, Pt, and Rh)\(^{25, 31, 66, 67}\). These microgel particles consist of a PS core onto which a shell of PNIPA has been affixed in a seeded emulsion polymerization.\(^{68, 69, 70}\) The synthesis of metallic nanoparticles in the presence of microgel particles was performed at room temperature via the addition of NaBH\(_4\), and could be followed optically by the color change of the suspension. The immobilization of metal nanoparticles may be due to the strong localization of the metalate ions within the network, which is probably caused by a complexation of the metalate ions by the nitrogen atoms of the PNIPA.\(^{71, 72}\) Both negatively charged and positively charged microgel particles can be used as the template. Their charges are introduced by the anionic initiator (K\(_2\)S\(_2\)O\(_8\)) and cationic initiator (V50), respectively, and not by anionic or cationic comonomers. Figures 1.10 and 1.11 display the cryo-TEM images of different metal nanoparticles embedded in microgel particles with negative charge and positive charge, respectively. From cryo-TEM images, the dark spherical area indicates the PS core, whereas the light corona around the dark core represents the PNIPA shell of the particles. The metal nanoparticles are seen as small black dots. It is evident that most of the metal nanoparticles are homogeneously immobilized inside the PNIPA networks affixed to the surface of the core particles. The analysis revealed that the size of metal nanoparticles is different. This may be due to the difference of the complexation of the metal ions with the functional groups of the microgels. Furthermore, Figures 1.10 and 1.11 show another important point: All particles have a well-defined distance to their neighboring particles. This is due to the electrostatic repulsion that originates from the charges affixed to the core particles. These charges keep the entire suspension stable even above the volume transition where the steric repulsion between the particles breaks down. This point will become important further below when considering the catalytic activity of the composite particles above the volume transition.\(^{69}\)

Moreover, investigations by DLS measurements of composite particles indicated that the original thermosensitive properties of the PNIPA network are not suppressed by the incorporation of metal particles into the network. The metal nanoparticles do not alter the volume transition within the network. Such a microgel system can work as an “active carrier” for the metal nanoparticles that allows us to modulate the catalytic activity of nanoparticles by a thermodynamic transition that takes place within the carrier system.\(^{25, 26, 73}\) The principle is shown in Figure 1.12: Metallic nanoparticles embedded in such a network are fully accessible by the reactants at low
temperature. Above the transition, however, the marked shrinking of the network should be followed by a reduction in the diffusion of the reactants within the network. Thus, the rate of reactions catalyzed by the nanoparticles should also be reduced. In this way, the network could act as a “nanoreactor” that can be opened or closed to a certain extent.

1.3.1. Catalytic Activity for Reduction of 4-Nitrophenol

The catalytic activity of microgel-based metal nanoparticles was investigated by monitoring photometrically the reduction of 4-nitrophenol by an excess of NaBH₄. We assumed that reduction rates were independent of the concentration of NaBH₄ because it was in excess compared to 4-nitrophenol. Moreover, the apparent rate constant, $k_{\text{app}}$, was found to be proportional to the surface $S$ of the metal nanoparticles present in the system.

$$-\frac{dc_t}{dt} = k_{\text{app}}c_t = k_1Sc_t$$

Figure 1.10. Cryo-TEM images of negatively charged microgel particles embedded with different metal nanoparticles: (a) with Ag ($d$: 8.5 ± 1.5 nm), (b) with Au ($d$: 2.0 ± 0.5 nm), and (c) with Pd ($d$: 3.8 ± 0.6 nm) nanoparticles. (See Ref. 25.)
Figure 1.11. Cryo-TEM images of (a,b) Au ($d$: 4.8 ± 1.2 nm), (c) Pt ($d$: 2.8 ± 1.3 nm), and (d) Rh ($d$: 4.5 ± 1.5 nm) nanocomposite particles embedded in positively charged microgel particles, respectively. (See Ref. 31.)

Figure 1.12. Schematic representation of composite particles consisting of thermosensitive core–shell particles in which metallic nanoparticles are embedded. The composite particles are suspended in water, which swells the thermosensitive network attached to the surface of the core particles. In this state the reagents can diffuse freely to the nanoparticles, which act as catalysts. At higher temperatures ($T > 32^\circ C$) the network shrinks and the catalytic activity of the nanoparticles is strongly diminished.
where \( c_t \) is the concentration of 4-nitrophenol at time \( t \) and \( k_1 \) is the rate constant normalized to \( S \), the surface area normalized to the unit volume of the system. Figure 1.13 gives a typical curve for the influence of the temperature on the rate constant \( k_{\text{app}} \) of the catalytic reaction, which does not follow a typical Arrhenius-type dependence on temperature. When the reaction temperature is low, the PNIPA network is swollen. In this case, metal nanoparticles, which have been embedded in the network, can be accessed by the reactants of the catalytic reduction. So the rate constant \( k_{\text{app}} \) will exhibit a linear relation of \( \ln k_{\text{app}} \) with \( T^{-1} \). However, when the temperature increases further, the PNIPA network shrinks markedly, which is followed by reduction in the diffusion of reactants within the network. This in turn will lower the rate of reaction catalyzed by the metal nanoparticles. It is obvious that the increase of \( k_{\text{app}} \) by the rise of temperature is overcompensated by the diffusional barrier. Hence, the reaction rate must reach its minimum at the transition temperature. If the increase of temperature continues, the PNIPA network will not shrink any more and the density within the network stays constant. Now the strong increase of \( k_{\text{app}} \) with \( T \) will be predominant and the reaction rate will rise again. This demonstrates that the volume transition within a thermosensitive network can be used as a switch: Figure 1.13 shows that the catalytic activity of the metallic nanoparticles can be tuned down by more than one order of magnitude. In the case of the SPB-based metallic system, that is, the SPB-30-Pd9, the rate constant \( k_{\text{app}} \) is fully described by a conventional Arrhenius expression. Therefore, the \( S \)-curve seen in the Arrhenius plot in Figure 1.13 must solely be due to the diffusional barrier for the reactants if the

![Figure 1.13. Dependence of the rate constant \( k_1 \) on the temperature \( T \) for different systems: Arrhenius plot of \( k_1 \) measured in the presence of the composite particles SPB-30-Pd9 (filled squares; system 1; [Pd composites]: 0.00063 g/L). In the case of the Microgel-1-Pd9 system (open squares; system 2; [Pd composites]: 0.00128 g/L), we obtained an \( S \)-curve, which is similar to that of silver nanoparticles (filled circles; data taken from Ref. 66; [Ag composites]: 0.0063 g/L). The concentrations of the reactants were as follows: [4-nitrophenol]: 0.1 mmol/L; [NaBH\(_4\)]: 10 mmol/L. (See Ref. 26.)](image-url)
network is shrinking with increasing temperature. This phenomenon has also been proved by other groups for thermosensitive polymer-based metal nanoparticles.\textsuperscript{76, 77} Li et al.\textsuperscript{78} have observed a similar behavior for the hydrogenation of a hydrophobic alkene.

### 1.3.2. Catalytic Activity for Oxidation of Alcohol

The polarity of the gel also changes with the volume phase transition of the microgel from hydrophilic to hydrophobic. As shown in Figure 1.14, at low temperatures ($T < 32 \, ^\circ\text{C}$) the network is swollen in water, and hydrophilic. Above the volume transition ($T > 32 \, ^\circ\text{C}$), the network becomes hydrophobic and can thus accumulate hydrophobic reactants. From this point of view, the catalytic activity of metal–microgel composite particles at high temperatures will be affected both by the volume transition of the microgel (as shown in Figure 1.12) and by the change of polarity of the microgel (as shown in Figure 1.14). Oxidation reaction of alcohols to the corresponding aldehydes or ketones\textsuperscript{79–82} has been used to investigate the catalytic behavior of microgel-based metal nanoparticles at different temperatures. It is worth noting that the reaction conditions are very mild and no phase transfer catalyst is needed. Microgel-based metal nanocomposites can efficiently catalyze the aerobic oxidation of benzyl alcohol at room temperature, which demonstrates that composite [Figure 1.14](#).

**Figure 1.14.** Schematic presentation of catalytic oxidation of benzyl alcohol in the presence of metal nanoparticles immobilized in thermosensitive core–shell microgels at different temperatures. At lower temperatures ($T < 32 \, ^\circ\text{C}$), the microgel network is hydrophilic and swollen in water, while at high temperatures ($T > 32 \, ^\circ\text{C}$), the network shrinks and becomes hydrophobic. Thus, microgel particles embedding the metal catalyst will move to the oil phase, which will be favorable for the uptake of hydrophobic benzyl alcohol into the metal–microgel composite. Therefore, the catalytic activity of the metal–microgel composites will be affected by both the volume transition and the polarity change of the microgel. (See Ref. 31.)
microgels represent robust catalysts. No by-products have been detected by GC after
the reaction and water is the only product formed besides the aldehyde.

Figure 1.15 shows the influence of temperature on the catalytic activity in an
Arrhenius plot of the turnover frequency (TOFs). These data can now be compared to
data obtained for the reduction of 4-nitrophenol with an excess of NaBH₄ in presence
of the metal nano-composite particles. From Figure 1.15 a nonlinear relation between
ln(TOF) and 1/T can be seen. The TOFs increase more than exponentially when
increasing the temperature. Only in the immediate vicinity of the LCST is a
significantly smaller TOF monitored.

In principle, there are two factors that will influence the catalytic activity: First, the
collapsed PNIPA layer presents a steric barrier for benzyl alcohol molecules to
diffuse from bulk aqueous dispersion to the surface of Au nanoparticles, causing the
reaction to slow down, as shown in Figure 1.12. Second, with the increase of
temperature, water-soluble hydrophilic PNIPA networks will become oil-soluble and
hydrophobic, which will be favorable for the diffusion of hydrophobic benzyl alcohol
onto the Au nanoparticle surface (as shown in Figure 1.14). Thus, the catalytic
activity of Au composite particles should increase with increasing temperature.
Figure 1.15 demonstrates that the second effect prevails in most of the temperature
range; the TOF value observed at 40 °C is much higher than the value from
conventional Arrhenius kinetics. This is different from the behavior that we
found for the reduction reaction of 4-nitrophenol. The results demonstrate that
the catalytic activity of oxidation reaction of benzyl alcohol is more sensitive to the
change of polarity than the diffusional barrier brought about by the volume transition
of a crosslinked PNIPA network. It should be noted that the selectivity of the reaction
is lower when the reaction temperature is higher than 30 °C. Under these conditions
benzoic acid was detected as a by-product by GC, which is in accord with the
phenomenon found by Hutchings and co-workers⁷⁹ and Biffis et al.⁸²

![Figure 1.15. TOF versus 1/T for the oxidation of benzyl alcohol in the presence of
microgel–Au nanocomposite particles (1 atm air, 1 mmol K₂CO₃, [microgel–Au] = 3.68 ×
10⁻⁵ mol/L). The broken lines are guide lines for the reader. (See Ref. 31.)](image-url)
CONCLUSION

Here we have reviewed our recent studies on metallic nanoparticles encapsulated in spherical polyelectrolyte brushes and thermosensitive core–shell microgels, respectively. Both polymeric particles present excellent carrier systems for applications in catalysis. The composite systems of metallic nanoparticles and polymeric carrier particles allow us to do “green chemistry” and conduct chemical reactions in a very efficient way. Moreover, in the case of using microgels as the carrier system, the reactivity of composite particles can be adjusted by the volume transition within the thermosensitive networks. Hence, the present chapter gives clear indications on how carrier systems for metallic nanoparticles should be designed to adjust their catalytic activity.

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