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Core–Shell Microspheres of a Catalytically Active Rhodium Complex Bound to a Polyelectrolyte-Coated Latex**

By *Stefan Mecking** and *Ralf Thomann*

Materials constructed by binding transition metal complexes to defined polymeric architectures are a subject of immense interest. A major motivation is their application to catalysis. The high activities and selectivities of homogeneous catalysts based on soluble transition metal complexes[1] are opposed by a usually tedious separation from the products after the reaction, often involving thermal strain on the reactants. Thus, the development of materials combining the advantages of classical homogeneous and heterogeneous catalysts remains a challenge. Most approaches to immobilizing metal complexes have employed microporous organic or inorganic solids.[2] However, a limited diffusion of the substrates within these materials is disadvantageous. Also, the cross-linked copolymers used mostly possess a heterogeneous structure consisting of domains of strongly differing composition.[3]

As a different strategy, binding metal complexes onto structures with dimensions in the range of colloids (1–1000 nm) is finding increasing attention. Structures based on the self-organization of surfactants[4] or surfactant ligands[5] are highly ordered, however due to their dynamic nature aggregation numbers can fluctuate and such structures can be shear sensitive. Very recently, catalytically active metal centers have been bound successfully to dendrimers.[6] However, the well-defined molecular structure of suitable dendrimers requires tedious synthesis.[7] By contrast, polymer lattices are readily obtained by aqueous emulsion polymerization, yielding monodisperse particles in the range of ca. 50–1000 nm in diameter.[8] By microemulsion polymerization, particles as small as 10 nm have already been obtained.[9] Polymer lattices possess an easily accessible outer surface (e.g., for ideal spheres of ∅ 200 nm ca. 30 m^2/g solids). Highly charged lattices stabilized by ionic groups located on the particle surface can bind molecules of opposite charge e. g., the binding of *multiple* layers of synthetic high molecular weight polyelectrolytes to polymer lattices has recently been shown to yield versatile structures of nanometer-scale dimensions.[10]

Simple binding of a polyelectrolyte to a charged particle represents a convenient means of arranging charged moieties

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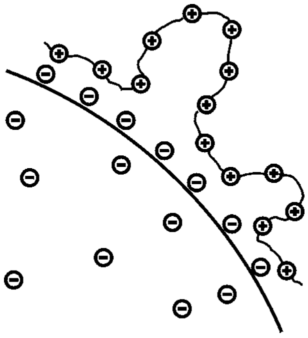
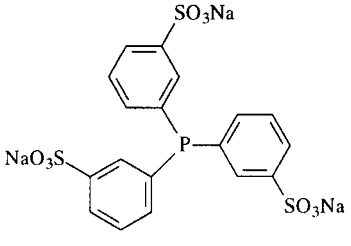
at the particle *surface* (Scheme 1). We report the preparation of structurally well-defined microparticles by the electrostatic binding of a low molecular weight rhodium complex to a polyelectrolyte layer assembled on the surface of a latex particle, and application of the resulting materials to hydroformylation as a catalytic reaction. The core–shell structure of the microspheres is demonstrated by means of electron microscopy. Only a few approaches for binding catalytically active metal complexes to lattices have been reported previously.[11] Most often, a large proportion of the metal centers was located in the interior of the latex.



Scheme 1. Schematic representation of polyelectrolyte adsorption on a charged latex particle.

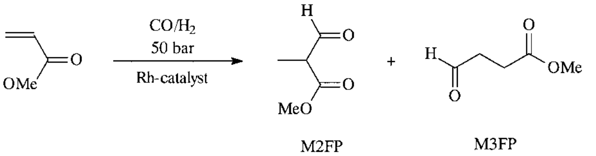
Highly charged monodisperse lattices with particle sizes of 100–400 nm diameter, prepared by copolymerization of styrene and potassium *p*-styrenesulfonate with $K_2S_2O_8$ as an initiator, were utilized.[12,13] Coating with excess poly(diallyldimethylammonium chloride) (PDADMAC), followed by repeated ultracentrifugation/decantation/redispersion cycles, for complete removal of excess PDADMAC and added NaCl electrolyte, yielded coated lattices.[10] Charge inversion of the lattices by coating with the cationic polyelectrolyte is demonstrated by a reversal of the ζ-potential.

To ensure effective binding to the charged latex, an adsorbed molecule should itself be multiply charged. As in catalysis temporary dissociation of a ligand from the metal center can occur, it should be advantageous for each ligand to be multiply charged. For this reason the well-known complex [(H)Rh(CO)(NaTPPTS)$_3$],[14] containing three tri-sulfonated NaTPPTS ligands was employed. In a typical experiment, 3 µmol complex/g latex (solids) were bound to a latex of diameter 280 nm. Complete adsorption is evidenced by atomic absorption spectroscopy (AAS) of supernatant solutions from ultracentrifugation of the complex-loaded lattices (detection limit 0.1 ppm Rh, corresponding to 2 % of the amount of rhodium present). Saturation experiments monitored by AAS revealed that the loading employed corresponds to approximately 50 % of the capacity of the latex. Latex particles were visualized by electron microscopy (Fig. 1, transmission electron microscopy [TEM] image, lower left). Energy-dispersive X-ray analysis (EDX) shows an even distribution of rhodium on the latex particles (Fig. 1, upper left). Microtome cuts of single latex particles embedded in an epoxy resin were investigated. TEM clearly shows that the particle surface is covered by material of high electron density (Fig. 1, lower right). The increased electron density of this layer is due to a large extent to rhodium, as rhodium-specific element specific imaging (ESI; Fig. 1 upper right inset) and also comparison with a rhodium-free latex confirm. Microtome sectioning of spherical particles yields layers of spheres, including caps. A simple visual inspection of the images shown gives a wrong, much too large, impression of the layer thickness if this point is not taken into account. Application of simple geometric principles to the data obtained yields a calculated layer thickness of less than 10 nm (see Experimental section). In the coating and loading procedures, no significant coagulation of the latex was observed. By centrifugation and redispersion cycles, the particles could also be transferred to methanol as a dispersing medium, yielding stable lattices. This is of particular interest as the general applicability to catalytic reactions is greatly expanded, methanol being a much more versatile solvent than water for organic reactants and also gases such as hydrogen.



NaTPPTS

As a first probe for the catalytic activity and stability of the materials prepared, the hydroformylation of methyl acrylate[15] (Eq. 1) was investigated.



M2FP main product   M3FP   (1)

In agreement with literature results[15] and comparative experiments with a non-immobilized catalyst, methyl 2-formylpropionate (M2FP) is obtained as the major product along with small amounts of methyl 4-oxobutyrate (M3FP).[16] In experiments with different reaction times, varying from 1.5–15 h, a steady activity of ca. 30 TO/h (TO = turnovers) was observed.[17,18] By comparison, under the same conditions non-latex bound [(H)Rh(CO)(NaTPPTS)$_3$] displayed an initial activity of 50 TO/h (1.5 h reaction time), decreasing to an average 18 TO/h in a 15 h experiment. These similar rates show that the immobilized catalyst is readily accessible to the substrates. The presence of chloride ions originating from PDADMAC can potentially result in a decrease of catalyst performance in hydroformylation reactions. To this end, the above catalysis experiments revealed no disadvantageous effect.[19] Under the reaction conditions employed, i.e., 60 °C and high-speed stirring (1300 rpm) in methanol as a reaction medium, usually little if any coagulation was observed.[20] Pro-

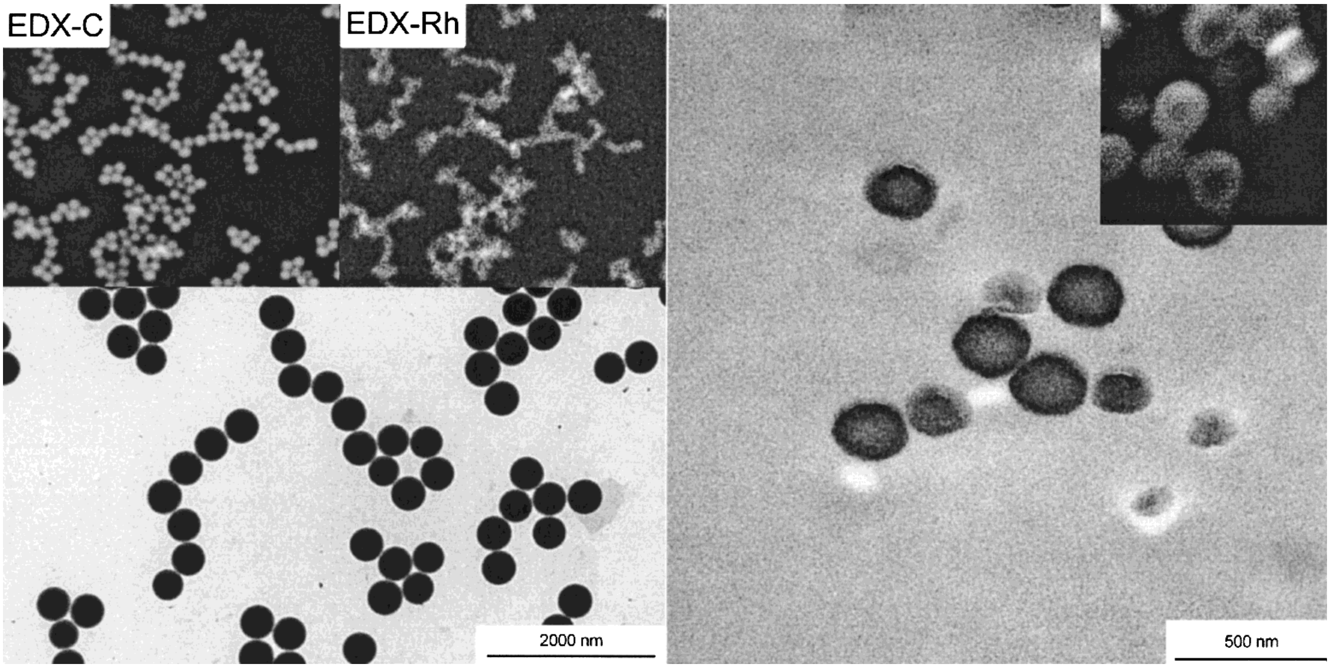


Fig. 1. Electron microscopy imaging of Rh-loaded, PDADMAC-coated latex particles. Lower left: TEM. Insets on upper left: EDX C Kα and Rh Lγ1. Lower right: TEM of microtome cuts. Inset on upper right: ESI of microtome cuts.

ducts were efficiently removed from the latex after the reaction by centrifugation.[21] AAS of the supernatant solutions reveals that with the system described some undesired leaching of rhodium occurs at long reaction times (≤20 %; 1 ppm). Accordingly, in recycling experiments a significantly reduced catalytic activity is observed. However, catalysis occurs by latex-bound metal complexes, as evidenced by the steady catalytic activity observed in experiments over different reaction times (vide supra), independent of any leaching of rhodium.[22] Leaching may occur via loss of phosphine ligands and formation of carbonyl complexes during the catalytic experiment.[23] In accordance with the above, prolonged stirring of the metal-loaded latex under reaction conditions in the absence of substrates caused no leaching to be observed. Whereas leaching in hydroformylation and the relatively low loading of the model system described demand improvement, the good stability achieved under practically relevant conditions and good activity by comparison to reaction in homogeneous solution show the suitability of this approach.

In summary, the adsorption of a catalytically active metal complex on microparticles via electrostatic interactions of sulfonated phosphine ligands with a polycation layer has been demonstrated. Structurally well-defined core–shell particles are obtained by this convenient, versatile approach.

Experimental

Materials and General Considerations: The complex [(H)Rh(CO)(NaTPPTS)$_3$] [14,24] was prepared according to literature procedures. A CO/H$_2$ 1:1 mixture (Messer-Griesheim; H$_2$ 99.999 %, CO 99.994 %) was used as received. Analytical grade methanol, deionized water (Milli-Q plus grade) and all other solvents and reagents were degassed prior to use. Gas chromatographic analyses were performed on a Chrompack 9001 unit equipped with a 25 m CP-Wax 52 CB column. Solids contents of lattices were determined using a Sartorius MA30 moisture analyzer. TEM investigations were carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. For EDX, an Oxford Instruments module was employed. ESI experiments were performed using the five-window method (SIS-software). Sectioning (ca. 40 nm) of the embedded lattices was performed with a Reichert & Jung Ultracut E microtome at ambient conditions. Sectioning of spheres leads to a variety of structures, ranging from small sphere caps to equatorial sections with the same diameter as the original latex. Measuring the thickness of the shell, the three-dimensional character of the sections must be taken into account. Depending on the diameter of the latex and the thickness of the sections, the observed apparent shell thickness is too high. The apparent increase in the shell thickness can be calculated using geometrical sphere equations. It is smallest for equatorial sections; for the equatorial sections prepared it is about 4 nm. To estimate the thickness of the rhodium-containing shell the mean value taken from 100 equatorial sections was determined and corrected with this value. ζ-potentials were measured on a Malvern Mastersizer without additional electrolytes.

Latex Preparation: Anionic lattices were prepared by aqueous emulsion copolymerization of styrene and potassium *p*-styrene sulfonate using K$_2$S$_2$O$_8$ as an initiator according to literature procedures [12]. Optionally, divinylbenzene (5 mol.-%) was added as a crosslinking agent. The resulting lattices were dialyzed against water. For coating with the polyelectrolyte, the latex was reacted with an excess of PDADMAC (Aldrich, average M_w ca. 300 000 g/mol). Typically, a latex was diluted to a solids content of 6 %. PDADMAC and NaCl were added corresponding to a concentration of 5 mM in cationic polyelectrolyte (calculated with respect to monomer units) and 0.3 M in NaCl. The mixture was agitated for 30 min, and then ultracentrifugated (15 000 g), decanted, and the residue redispersed in water. The washing procedure was repeated at least three times, monitoring removal of excess electrolyte.

For adsorption of the metal complex for catalysis experiments, in a typical experiment a solution of 4 µmol [(H)Rh(CO)(NaTPPTS)$_3$] in a few milliliters of water was added to 70 mL of a polyelectrolyte-coated latex (solids content 2.6 %, particle size ∅ 280 nm) with gentle shaking. After 30 min, the latex was ultracentrifugated, the supernatant decanted, and the solid residue was redispersed in methanol.

Hydroformylation Reactions: These were carried out in a 200 mL stainless steel reactor (Büchi AG, Ulster), equipped with a mechanical stirrer and a heating/cooling jacket controlled by a thermocouple dipping into the reaction solution. Immediately after the catalytic reaction, the reaction mixture was ultracentrifugated, and the supernatant was analyzed by gas chromatography using dimethyl succinate as an internal standard. The identity of the products methyl 2-formylpropionate and methyl 4-oxobutyrate was confirmed by ^{1}H and ^{13}C NMR spectroscopy (one-dimensional and 2D correlated spectroscopy) of isolated samples. Blank experiments showed no activation of the steel reactor employed for methyl acrylate hydroformylation.

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[16] *iso*/*n* ca. 30 at 60 °C, 50 bar CO/H_2. In some cases, formation of small amounts of methyl propionate, resulting from the hydrogenation of methyl acrylate, was also observed.

[17] Reaction conditions: methanol as a dispersant (90 mL); 4 μmol rhodium; 115 mmol methyl acrylate; 60 °C; 50 bar combined CO/H_2 (1:1) pressure.

[18] TO ≡ turnovers ≡ mol(aldehydes)/mol(rhodium).

[19] In agreement, ^{31}P and ^{1}H NMR analysis of an aqueous solution of $[(H)Rh(CO)(NaTPPTS)_3]$ in the presence of excess PDADMAC revealed no change in the catalyst precursor complex structure.

[20] In cases where small amounts of coagulate were observed, this was usually found on the stirrer and the upper limit of the liquid level in the reactor. Presumably, it was formed by evaporation of solvent, and thus does not represent an intrinsic problem.

[21] In view of potential applications, filtration on a suitable membrane will be a more convenient method of separation than centrifugation.

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