Catalysis with Soluble Hybrids of Highly Branched Macromolecules with Palladium Nanoparticles in a Continuously Operated Membrane Reactor

Rafael Sablong,[a] Ulf Schlotterbeck,[b] Dieter Vogt,[a,*] Stefan Mecking[b,*]

[a] Schuit Institute of Catalysis, Eindhoven University of Technology, STW 3.29, PO Box 513, 5600MB Eindhoven, Netherlands
E-mail: d.vogt@tue.nl
[b] Institute for Macromolecular Chemistry and Freiburg Materials Research Center, Albert-Ludwigs-University Freiburg, Stefan-Meier-Str. 31, 79104 Freiburg, Germany
Fax: (+49)-761-203-6319, e-mail: stefan.mecking@makro.uni-freiburg.de

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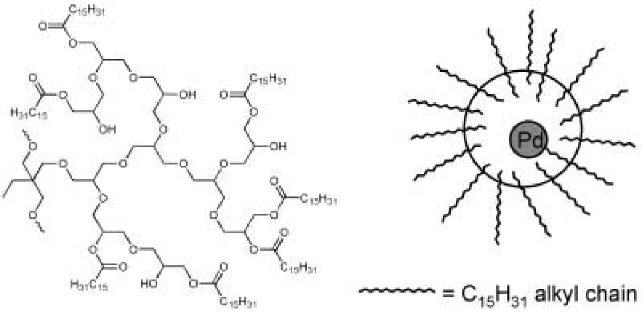
Abstract: The continuous recovery and recycling of soluble metal nanoparticles by means of ultrafiltration is described, employing hybrids of palladium nanoparticles with highly branched amphiphilic polyglycerol as a catalyst for cyclohexene hydrogenation as a model reaction. In a continuously operated membrane reactor a productivity of 29000 TO over 30 exchanged reactor volumes was observed for nanoparticles of 2.2 nm size, with a maximum rate of 1200 TO h^{-1}. Catalysis by soluble metal complexes can be excluded. After 30 hours of operation, some decrease in activity is observed which is due to deposition of palladium on the ultrafiltration membrane, however this material does not contribute to catalytic activity.

Keywords: colloids; hydrogenation; polymers; recycling; ultrafiltration

Transition metal clusters and colloids with particle sizes in the range of one to ten nanometers are of widespread interest.[1] From a fundamental perspective, the transition from the properties of the bulk to those of individual molecules occurs in this size range. A transition metal cluster of 2 nm diameter consists of a few hundred atoms, the majority of which are located at the surface of the cluster. Thermodynamically favored aggregation must be prevented by electrostatic and/or steric stabilization, most often brought about by adsorption of low-molecular-weight surfactants or polar linear polymers on the nanoparticle surface.[1] More recently, motivated by the concept of particle size control by means of synthesis in a confined environment[1b, d] and the challenge of efficient nanoparticle stabilization, hybrids of dendrimers with metal nanoparticles have been investigated.[2] The tedious syntheses of dendrimers are, however, prohibitive for many applications. In contrast to perfectly branched monodisperse dendrimers[3] (degree of branching for an ideal dendrimer 100%), randomly branched hyperbranched macromolecules[4] with narrow molecular weight distributions (degree of branching *ca.* 60%) can be accessible in one-pot reactions. Amphiphilic modification of hyperbranched polyglycerol[5] or polyethyleneimine[6] by partial esterification or, respectively, amidation with fatty acids results in macromolecules with an apolar shell and a polar core. Metal nanoparticles are stabilized efficiently by these materials, the polar moieties being responsible for adsorption to the particle surface and the apolar region conveying solubility also in apolar organic solvents.[6,7]

Colloidal nanoparticles are now recognized to occupy a decisive role in various synthetically important reactions, in which they can represent the catalytically active species or be in equilibrium with the latter.[8] The recovery of soluble nanoparticles after a catalytic reaction represents a challenge, however, which has received little attention to date. Biphasic techniques, intensely investigated for the recovery of soluble metal complexes, are often restricted to substrates with a relatively narrow range of solubility with respect to the catalyst phase, or they suffer from a partial miscibility of phases which can result in losses of solvent.[9] As the majority of organic substrates is soluble in aprotic organic solvents,



Scheme 1. Structure of partially esterified hyperbranched polyglycerol and schematic respresentation of hybrids with metal nanoparticles.

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for catalytic organic syntheses carrying out reactions in such media – or in the neat reagents – is desirable. Nanofiltration with solvent-stable membranes can represent a versatile technique for catalyst recovery in organic reaction media.[10] We now report on catalysis with palladium nanoparticles stabilized by a hyperbranched amphiphilic polymer in a continuously operated membrane reactor.[11]

As a simple and straightforward model reaction, we have chosen the hydrogenation of cyclohexene. A stirred membrane reactor module equipped with a solvent-stable Koch MPF-50 membrane[12] was operated at 40 atm. The reaction mixture was drawn continuously from the reactor *via* the membrane (trans-membrane pressure 10 atm), that is the reactor was operated in dead-end mode. Cyclohexene (neat or as a toluene solution) and a hydrogen solution were metered *via* HPLC pumps. The saturated hydrogen solutions were supplied from a stirred 1-L steel vessel pressurized with hydrogen to 40 atm. Flow rates were usually adjusted such that starvation neither in hydrogen nor in cyclohexene occurred, that is the reaction was run at limited conversion. The reactor being under steady state flow conditions, the catalyst solution was injected *via* a port in one of the substrate feeds. After exchange of a few reactor volumes a steady conversion is achieved, e.g., 30% cyclohexene conversion for the example shown in Figure 1, corresponding to a catalytic activity of 1200 TO h^{-1} (TO = turnovers, i.e., moles of cyclohexane formed per mole of palladium; calculated with respect to the entire amount of Pd present in the nanoparticles, i.e., the activity of the significant surface atoms will be higher). Over 30 exchanged reactor volumes, corresponding to a time of operation of 30 hours, a productivity of a total of 29,000 turnovers was observed. The observed moderate decrease in activity over this period can be related to colloidal destabilization and deposition of small portions of the metal nanoparticles into the membrane. It is known that in dead-end operation mode of stirred cells, an insufficient cross-flow can result in polarization of the membrane, i.e., the particles are 'swept' onto the membrane. It can be noted that this is not an intrinsic problem as membrane polarization can be overcome by a turbulent flow parallel to the membrane surface, e.g., in a loop reactor.[13,14]

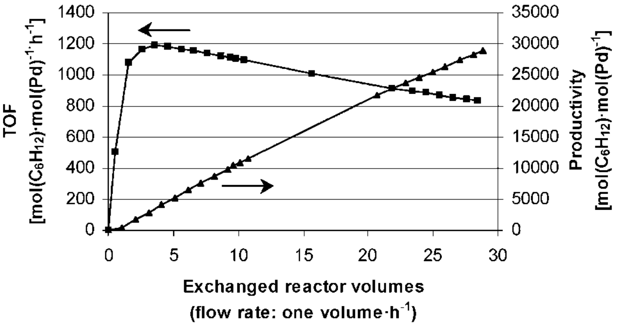

Figure 1. Hydrogenation of cyclohexene in a continuously operated membrane reactor catalyzed by soluble hybrids of palladium nanoparticles with highly branched amphiphilic polyglycerol. Conditions, see Table 1 (particle size 2.2 ± 0.5 nm).

Table 1. Continuous hydrogenation with colloids of different particle size.[a]

Average particle size	Exchanged reactor volumes n (duration of run)	Activity during n^{th} volume [TO h^{-1}][b]
2.2 ± 0.5 nm	4	1190
	10	1100
	25	870
4.9 ± 1.3 nm	4	710
	10	620
	25	350

[a] Temperature: 23 °C; 1.78 μmol Pd in 20 mL reactor volume; flow rate: one reactor volume per hour; feed: 0.33 M in cyclohexene, *ca.* 0.12 M in H_2.

[b] Activity calculated with respect to the entire amount of palladium present, i.e., activity of the significant surface atoms will be higher.

In some cases, analysis of the filtrate by AAS revealed very small amounts of palladium (<1% of the total amount of Pd, corresponding to < 0.03% average loss per exchanged reactor volume), which also do not bear any correlation with observed catalytic activities. Thus, any significant involvement of conceivable catalytically active soluble metal complexes can be excluded. Rather, these observations can be related to defects in the membrane. Transmission electron microscopy reveals no strong changes in size of the soluble metal nanoparticles within experimental error, e.g., 4.7 ± 1.2 nm after catalysis *vs.* 4.9 ± 1.3 nm for the starting colloid employed, that is, no larger aggregates are involved in catalysis (formation of colloidally unstable aggregates which do not contribute significantly to catalytic activity most likely occurs to a small extent, *vide infra*).

The aforementioned small portion of palladium deposited on the membrane does not contribute considerably to the catalytic activity. After a catalytic hydrogenation experiment in the membrane reactor, the colloid solution was flushed from the cell, and the membrane washed briefly with toluene. In a blank experiment, pumping cyclohexene and hydrogen solution through the reactor equipped with the used membrane without addition of metal nanoparticle solution, no conversion was observed. In accordance with this, analysis of a used membrane after a hydrogenation catalyzed by a colloid afforded an amount of palladium on the membrane corresponding to 22% of the total amount of palladium nanoparticles added, which is in reasonable agreement with the loss in activity over the entire previous hydrogenation run (29%). Thus, catalysis indeed occurs solely by the metal nanoparticles in solution.

Comparing colloids with different average particle sizes, an increase in particle size and thus decrease in the number of surface atoms results in a decrease in catalytic activity for a given amount of palladium, as expected (Table 1). The loss in activity over a catalytic run is more pronounced for the large particles, which can be ascribed to a lower colloidal stability under the conditions of the recycling experiments.

In summary, hybrids of macromolecules with metal nanoparticles can be employed as soluble catalysts in a continuously operated membrane reactor. An observed slow loss in activity with prolonged reaction times may be related to the dead-end operation mode employed, and recovery in a loop-reactor is currently being investigated.

Experimental Section

Hyperbranched polyglycerols [degree of branching (DB) of 60%] with a trimethylolpropane core and average molecular weights M_n ranging from 2000 to 6000 g mol^{-1} as determined by ^{13}C NMR, $M_w/M_n \leq 1.6$ from GPC *vs.* poly(proplyene oxide) standards were supplied by hyperpolymers GmbH.[15] Amphiphilic modification was carried out according to ref.[16] In brief, to a solution of a hyperbranched polyglycerol and catalytic amounts of *N*-methylimidazole in anhydrous pyridine, a solution of freshly distilled palmitoyl chloride in anhydrous toluene was added slowly. After refluxing overnight the solution was cooled to room temperature and K_2CO_3 was added. Solvent removal and addition of fresh toluene was repeated several times, the inorganic salts were filtered off from the toluene solution and the polymer was purified by dialysis (benzoylated cellulose membrane, cut-off $\leq$ 1200 g mol^{-1}) or ultrafiltration in toluene. Polymers with degrees of esterification between 71 and 78% as determined from ^{1}H NMR were obtained in good yields (70–90% after dialysis).

Colloids were prepared and characterized according to ref.[7]. In brief, partially esterified hyperbranched polyglycerol (250 mg) and palladium acetate (7.5 mg, 33.4 μmol) were dissolved in 25 mL of toluene and heated to 60 °C overnight, affording a dark brown colloid solution.

A custom-made, stainless steel, magnetically stirred, 20-mL membrane reactor was used (for a detailed description of the membrane reactor see ref.[17]). The solvent-stable multilayer asymmetric membrane utilized (MPF-50, Koch Industries) has a nominal cut-off of 700 dalton in methanol. This figure should be taken as an order of magnitude only, as the actual cut-off will depend on the solvent and solute employed.

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