



Rhodium-catalyzed aqueous biphasic hydrogenation of alkenes with amphiphilic phosphine-containing core-shell polymers

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ABSTRACT

The biphasic aqueous hydrogenation reaction of styrene and 1-octene could be efficiently carried out using phosphine-containing core-shell water-soluble polymers used as nanoreactors in presence of $[\text{Rh}(\text{COD})\text{Cl}]_2$. The catalytic aqueous phase could be successfully recycled up to six times.

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1. Introduction

Hydrogenation is clearly a major reaction in organic synthesis both at the laboratory and industrial scale. It has been reported that at least one catalytic hydrogenation step is included in around 25% of all chemical processes [1]. Hydrogenation is applied at the very large scale such as, for instance, for the desulfurization of fuels [2,3], but is also largely used for the production of fine chemicals [4], including chiral ones [5–8]. As a way to improve the efficiency of chemical processes [9] in economic and environmental terms, biphasic aqueous catalysis is an elegant approach because it simplifies the catalyst separation by simple decantation and its subsequent recycling. This operational mode has found large scale industrial implementation in hydroformylation [10–12], but has also been used for hydrogenation reactions [13]. Within this approach, the catalyst is usually confined in the aqueous phase [14] while substrates and products are in the water-immiscible organic

phase. The (pre)catalysts may be water-soluble complexes [15–23] or metal nanoparticles dispersed in water [24–33].

We have recently reported a new approach in aqueous biphasic catalysis, which consists of using stable latexes of unimolecular polymeric nanoreactors, characterized by a well-controlled core-shell structure with a narrow size distribution around 100 nm and a spherical morphology [34,35]. They were synthesized by controlled RAFT polymerization in water, yielding stable dispersions with a 25–30% polymer content in weight in a one-pot procedure. The polymeric nano-objects remain confined in the aqueous phase by virtue of their hydrophilic shell but contain a phosphine-functionalized core where the (pre)catalyst is covalently bound. The hydrophobic cores are swollen very rapidly by various organic compounds [36]. We have shown that the $[\text{Rh}(\text{acac})(\text{CO})_2]$ pre-catalyst can be coordinated inside the polymer core [36–38] and the resulting metal-loaded nanoreactors were successfully used in the aqueous biphasic hydroformylation of 1-octene with excellent activity, low metal leaching, facile catalyst recovery and efficient recycling [36,39–41]. We have also shown that other metal complexes, notably $[\text{RhCl}(\text{COD})_2]$, can be incorporated inside the polymer core, but the resulting objects were only studied in terms of coordination chemistry and interparticle metal migration dynamics and mechanism [37,38]. In the present contribution, we report the first application of these amphiphilic core-shell polymers to the biphasic aqueous hydrogenation of alkenes.

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2. Experimental

2.1. General considerations

Chloro(1,5-cyclooctadiene)rhodium(I) dimer, (98%, Strem), 1-octene (99+%, Acros), 1-nonanol (>99%, Alfa TCI), *n*-decane (99%, Aldrich), *n*-dodecane (99%, Acros), toluene (99%, Acros) and anisole (99.0%, Fluka) were used as received. Styrene (99%, Acros) was purified by passing it through a column of active basic aluminum oxide to remove the stabilizer. Dihydrogen was obtained from Linde Gas. The triphenylphosphine (TPP) containing core cross-linked micelles, TPP@CCM1 [34] and TPP@CCM2 [40], were synthesized as described in our previous contributions and stored under an inert atmosphere.

2.2. Catalytic tests

2.2.1. General procedure for the hydrogenation of styrene or 1-octene under biphasic conditions

In a Schlenk tube under argon was added 1 mL of latex (for TPP@CCM1): 0.12 mmol of TPP; (for TPP@CCM2: 0.063 mmol of TPP) and 2 mL of H₂O. Toluene (0.2 mL) was then added to swell the particles and the reaction mixture was stirred for 1 min. Then, a solution of [Rh(COD)Cl]₂ (for TPP@CCM1): 15.4 mg (0.03 mmol; P:Rh=2); for TPP@CCM2: 3.77 mg (0.0078 mmol; P:Rh=4) in toluene (0.3 mL) was added and the reaction mixture was stirred for 10 min at RT. The aqueous phase became yellow while the toluene phase became colorless.

Separately, a stock organic phase was prepared with the substrate (for styrene: 3.17 g, 30 mmol; for 1-octene: 3.37 g, 30 mmol) and decane (1.26 g, 9 mmol) as internal standard in 40 mL of the desired solvent to obtain a substrate concentration of 0.75 mmol/mL. For the reaction without solvent, a mixture containing 0.823 g of styrene (7.9 mmol) and 0.766 g of decane (5.38 mmol) was prepared.

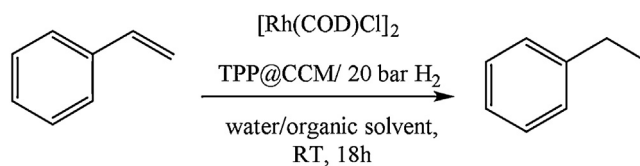
In a vial containing a magnetic stirrer under argon was added 0.5 mL of the aqueous phase containing the core cross-linked micelles and the rhodium precursor (see above) and 1 mL of the organic stock solution (see above). The vial was placed in a steel reactor, which was then charged with 20 bar of dihydrogen. The reaction mixture was then stirred at RT for 18 h with magnetic stirring set at a speed of 1200 rpm. After stopping the stirring and an additional 4 h decantation under dihydrogen pressure, the reactor was vented and then flushed with argon. The organic layer was then withdrawn by syringe and the aqueous phase was extracted by two portions of 0.5 mL of diethylether, all these operations being conducted under argon. The combined organic solutions were then analyzed by GC.

For the recycling experiments, a new portion of the substrate stock solution was added to the vial under argon and the reaction was carried out as described above.

2.2.2. Kinetic studies

The investigations under biphasic conditions were carried out as described in the previous section, using several identical vials. The reaction in each vial was stopped at a different reaction time before the GC analysis.

For the homogenous catalytic reactions, triphenylphosphine (39.3 mg, 0.15 mmol), styrene (1.56 g, 15 mmol) [Rh(COD)Cl]₂ (18.5 mg, 0.0375 mmol), and dodecane as GC standard (0.66 mg, 3.75 mmol) were dissolved in deoxygenized anisole (17.6 g) and used as stock solution. Several different vials with 2 mL each of the stock solution were used as described above.



Scheme 1. Hydrogenation of styrene under biphasic conditions. Solvent = toluene or 1-nonanol. Styrene/P/Rh = 200/2/1.

2.2.3. High resolution ICP-MS

The rhodium catalyst leaching to the organic phase was measured using high resolution ICP-MS on a XR Thermo Scientific Element. For the sample preparation, the recovered organic phase was diluted into water using a 10⁵ volumetric dilution factor. In practice, a 1 L volumetric flask was filled at ~2/3 with milli-Q water, then 10 μL of the organic product phase were introduced using a Gilson P20 precision pipette. Borders were rinsed and the flask was introduced into an ultrasound bath for 1 h. The solution was left overnight and the dilution was then completed with milli-Q water to the 1 L mark. Standards were prepared using solutions of Rh(acac)(CO)TPP in nonanol at various weight fractions of Rh in the (0.001–0.5)·10^{−9} range (1–500 ppt).

3. Results and discussion

3.1. Preliminary catalytic tests

Two different polymer samples, TPP@CCM1 and TPP@CCM2, prepared as described in a previous report [36,37], have been used in this study. They contain unimolecular nanoreactors in which the spherical polymer particles are characterized by three distinct zones (see Fig. 1): a hydrophilic shell with an average of 30 monomers (50:50 mixture of methacrylic acid, MAA, and poly(ethylene oxide) methyl ether methacrylate, PEOMA) per chain, linear hydrophobic chains in the intermediate zone with an average of 300 monomer units per chain consisting of a mixture of styrene and diphenylphosphinostyrene (DPPS), and an inner cross-linked core with additional styrene and the cross-linking monomer, diethylene glycol dimethacrylate (DEGDMA) in a 90:10 ratio for a total of 100 monomers per chain. The two samples differ in the DPPS content in the intermediate hydrophobic layer: 10% for CCM1 and 5% for CCM2.

The TPP@CCM1 sample was first used in the hydrogenation of styrene with toluene as organic solvent, after charging the polymer particles with the [Rh(COD)Cl]₂ precatalyst as described in the Experimental part [38]. This first test was carried out under the conditions depicted in Scheme 1 with a substrate/P/Rh ratio of 200/2/1. After 18 h at RT under H₂ pressure, although the transformation of styrene to ethylbenzene was complete, the decantation process proved very problematic: only a small portion of the organic phase was observed at the top of the reaction vial, while the aqueous phase and most of the organic materials had formed a stable dense phase with the aspect of a gel. The failure of the mixture to properly decant obviously precludes an efficient product recovery and the recycling of the aqueous catalytic phase.

3.2. Hydrogenation reactions of styrene in 1-nonanol

We imagined that the behavior observed in the above preliminary test may result from interparticle coupling with formation of a macrogel. This hypothesis comes from our previous finding of rapid and reversible (in the absence of chemical reaction) interpenetration of the particles, involving core-core contact [37]. This was proven by the irreversible particle aggregation in the presence of reactions leading to products in which the metal centers binds

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