Rhodium nanoparticles inside well-defined unimolecular amphiphilic polymeric nanoreactors: synthesis and biphasic hydrogenation catalysis†

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Rhodium nanoparticles (Rh NPs) embedded in different amphiphilic core-crosslinked micelle (CCM) latexes (RhNP@CCM) have been synthesized by [RhCl(COD)(TPP@CCM)] reduction with H₂ (TPP@CCM = core-anchored triphenylphosphine). The reduction rate depends on temperature, on the presence of base (NEt₃) and on the P/Rh ratio. For CCMs with outer shells made of neutral P(MAA-co-PEOMA) copolymer chains (RhNP@CCM-N), the core-generated Rh NPs tend to migrate toward the hydrophilic shell and to agglomerate depending on the P/Rh ratio and core TPP density, whereas the MAA protonation state has a negligible effect. Conversely, CCMs with outer shells made of polycationic P(4VPMe⁺I⁻) chains (RhNP@CCM-C) maintain core-confined and well dispersed Rh NPs. All RhNP@CCMs were used as catalytic nanoreactors under aqueous biphasic conditions for acetophenone, styrene and 1-octene hydrogenation. Styrene was efficiently hydrogenated by all systems with high selectivity for vinyl reduction. For acetophenone, competition between benzene ring and carbonyl reduction was observed as well as a limited access to the catalytic sites when using CCM-C. Neat 1-octene was also converted, but the activity increased when the substrate was diluted in 1-nonanol, which is a better core-swelling solvent. Whereas the molecular Rh⁺ center was more active than the Rh⁰ NPs in 1-octene hydrogenation, the opposite trend was observed for styrene hydrogenation. Although Rh NP migration and agglomeration occurred for RhNP@CCM-N, even at high P/Rh, the NPs remained core-confined for RhNP@CCM-C, but only when toluene rather than diethyl ether was used for product extraction before recycling.

Introduction

Although metal nanoparticles (NPs) have been known for a long time, their controlled generation has attracted keen interest only recently,1–4 because of growing awareness that their characteristics such as size and morphology strongly influence their physical and chemical properties. Much effort is currently devoted to the synthesis of very precisely defined metal nanoparticles, up to the atomic precision level.5–7 In addition to fundamental aspects, the particular properties that the metal NPs display relative to bulk metals and molecular complexes make them very attractive for applications in diverse domains, particularly in catalysis. Nanocatalysis is now a well-recognized discipline at the frontier between homogeneous and heterogeneous catalyses.8–9 Metal NPs are highly attractive because of their high surface-volume ratio, especially for diameters of one nanometer or below (subnanoparticles), thus providing a high number of potential active sites (>90% of surface atoms). Therefore, developing synthetic tools that enable the production of ultra-small NPs is of prime importance. In terms of catalytic performance, in addition to the metal nature and particle size, other important parameters are the crystalline structure, the nature and relative amounts of the exposed faces, edges and corners and the composition and architecture (e.g. core–shell) for multimetallic NPs. However, the performance in catalysis may also be influenced or even oriented by the surrounding stabilizer or by the support.20–22

The choice of the stabilizing agent is critical as it controls both the NP size and dispersion and provides long-term stability during the catalytic process.23–26 Contrarily to heterogeneous catalysis where calcination is usual to suppress organic contaminants and liberate the active sites, but like in molecular catalysis, metal–ligand interactions are of paramount
importance as they may improve the activity or even promote more interesting chemoselectivities. The challenge is to find capping ligands that at the same time stabilize the metal NPs and allow access to the metal surface for the catalytic transformation. Ligand-stabilized metal NPs may be involved in catalysis as colloidal suspensions in water, polyols or organic solvents and several strategies have been developed to facilitate the catalyst recovery.

Among the available strategies for catalyst recovery and recycling, aqueous biphasic catalysis is particularly attractive when the catalyst can be confined in the aqueous phase, because the organic reaction products can be easily separated by decantation. However, the reaction may be severely limited by mass transport if the catalyst is totally insoluble in the organic reactant/product phase and if the reactants are totally insoluble in water, limiting the productive process to the organic/water interface. In this respect, the use of surfactants or micellar systems able to increase the organic/water interphase has been shown beneficial. Increased rates have indeed been obtained upon anchoring catalytic NPs on the hydrophilic shell of micelles. Thermoregulated processes, where the catalyst is anchored on thermosensitive macromolecules (hydrophilic at low temperature and hydrophobic at high temperature) have also been implemented in metal NP catalysis. An alternative solution is to anchor the catalyst to the hydrophobic core of micelles. This allows the reaction to take place with high local concentrations of both catalyst and substrates and each individual micelle operates as an independent nanoreactor. This strategy has been implemented for a few molecular catalysts, but examples with metallic nanoparticles are not available to the best of our knowledge. One limitation of self-assembled micelles is the disaggregation equilibrium with the individual amphiphilic molecular components, resulting in catalyst losses. However, this phenomenon may be blocked by making the object unimolecular by crosslinking. In this respect, dendrimers such as poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) have been used as unimolecular nanoreactors to embed catalytic NPs of various metals. However, one limiting factor for the application of dendrimers is their multistep synthesis, which may be rather time consuming, particularly for the higher generations.

Some of us have recently developed unimolecular amphiphilic star polymers with a triphenylphosphine-functionalized polystyrene core and a hydrophilic shell, thus ensuring a stable aqueous dispersion (latex). We have therefore named this polymeric architecture core-crosslinked micelles (CCM). These polymers, the general structure of which is shown in Fig. 1, were obtained by a convergent polymerisation procedure, using the reversible addition–fragmentation chain-transfer (RAFT) strategy. The procedure is particularly straightforward (three-step-one-pot) for the polymers with the neutral P(MAA-co-PEOMA) outer shell (CCM-N). The first step involved polymerisation of the water-soluble monomers to yield hydrophilic individual chains corresponding to the outer blocks of the final particles. These were extended with a hydrophobic block in the second step, which involved polymerisation-induced self-assembly (PISA) and yielded micelles. The triphenylphosphine (TPP) ligand was introduced during this step via copolymerisation of 4-diphenylphosphinostyrene (DPPS) as a comonomer of styrene. Finally, the third step linked all the micellar chains together at the core level by further chain extension with a crosslinking monomer (diethylene glycol dimethacrylate – DEGDMA). The synthesis of the polymer with a cationic P4VPMe+I− shell (CCM-C) presented a few obstacles, which required the introduction of additional steps. Anyhow, for both types of polymers, the good control ensured by the RAFT polymerisation method led to spherical polymer particles with quite narrow size distributions and average diameters in the 100–150 Å range. Versions of these polymers with a different TPP content, for both CCM-N and CCM-C, could be produced by using styrene–DPPS comonomer mixtures during the hydrophobic block chain growth (5–25% molar ratio of DPPS). Variants of this polymeric scaffold (different core ligand or polymer architecture) have also been synthesized, but the most intensively investigated polymers have so far been those with the CCM architecture and core-anchored TPP ligands and the present contribution also focuses on the use of these polymers. They will be referred as CCM-N-x and CCM-C-x, where N and C refer to the type of hydrophilic shell (neutral and cationic, respectively) and x stands for the molar fraction of ligand-functionalized styrene in the hydrophobic core.

In our previous work, all these polymers were charged with either [Rh(acac)(CO)₂] (acac = acetylacetone) or [RhCl(COD)] (COD = 1,5-cyclooctadiene), which coordinated to the core-anchored triphenylphosphine ligands (referred to as TPP@CCM) by either CO replacement or Cl-bridge splitting to yield [Rh(acac)(CO)[TPP@CCM]] or [RhCl(COD)[TPP@CCM]], respectively. The resulting metal-loaded polymers were subsequently used in Rh-catalysed aqueous biphasic olefin hydroformylation or hydrogenation showing excellent performance and recyclability with sub-ppm catalyst losses. In further exploratory investigations, the [RhCl(COD)[TPP@CCM]] precatalyst was also applied to the hydrogenation of acetoephone. However, contrarily to the observed behaviour in styrene hydrogenation, the catalytic mixture unexpectedly turned black, suggesting that the molecular Rh precatalyst was reduced to the metallic state under these conditions, with the possible formation of metal NPs. We reasoned that, in a phosphate-poor environment (P : Rh ratios of 1 : 1 or 2 : 1 were initially used),
styrrene might protect the Rh$_1$ centre from reduction by H$_2$ because of its $\pi$-acidity as a ligand, contrarily to acetophenone. We report herein a systematic investigation of the [RhCl(COD)][TPP@CCM] reduction and of the effect of various parameters on the size and morphology of the produced Rh NPs. Finally, the performance of the resulting catalytic nano-reactors in acetophenone, styrene and 1-octene hydrogenation will be described, also in terms of catalyst stability and recycling, providing useful new information about the Rh NP stabilisation and mobility in the amphiphilic polymer environment.

Results and discussion

Generation of rhodium nanoparticles in the CCM-N polymers

A first application of the [RhCl(COD)]$_2$-loaded CCM-N latex$^{81}$ to the aubic biphasic catalysed hydrogenation of acetophenone (90 °C, 20 bar of H$_2$) led to an unexpected colour change of the initially pale cream latex to black, suggesting metal reduction, and to a low extent of substrate reduction (see catalytic results below). On the other hand, previous work had demonstrated very efficient aubic biphasic styrene or 1-octene hydrogenation with no colour change using the same protocol.$^{79}$ Metallic rhodium, in the form of small NPs, has previously been obtained by reduction of several molecular Rh$_1$ and Rh$_{11}$ precursors$^{82}$ including [RhCl(COD)].$^{81-85}$ A black latex was again obtained when neat toluene, without any added acetophenone, was used to swell the polymer core, showing that acetophenone is not essential for the metal reduction. When the [RhCl(COD)][TPP@CCM] reduction was carried out at 25 °C (either with or without acetophenone), the latex only turned light grey, suggesting that the reduction may be incomplete under these conditions. However, a black latex was again obtained at 60 °C. Reasoning that the reduction of a Rh$_{11}$Cl complex by H$_2$ also generates an equivalent amount of HCl per Rh atom, the procedure was then repeated in the presence of excess NEt$_3$ ($\geq$5 equiv.). Under these conditions, a black latex was obtained even at 25 °C. These initial studies were carried out with a fully metal-loaded (P/Rh = 1 : 1) CCM-N-0.1 latex, in which each polymer chain contains on average 30 TPP ligands in the hydrophobic PS block and 15 PEOMA/15 MAA monomers in the hydrophilic P(MAA-co)-PEOMA block. Therefore, the PEOMA/Rh ratio is ca. 0.5. It should also be pointed out that the NEt$_3$ excess leads to the transformation of the neutral shell into an anionic one, containing triethylammonium carboxylate functions, $\text{–COO}^-$NEt$_3^+$. The amount of NEt$_3$ used is sufficient for the neutralisation of all generated HCl and all the shell carboxylic functions.

The transmission electron microscopy (TEM) analyses of the recovered latexes, Fig. 2(a–c), besides confirming the formation of metal NPs, highlighted a few interesting phenomena. While the grey latex obtained in the absence of base contains isolated small size (<5 nm) NPs, see Fig. 2(a), the black latex obtained in the presence of base contains few individual small NPs together with a dominant fraction of NP agglomerates, Fig. 2(b). These agglomerates appear to accumulate mostly on the polymer particle surface (hydrophilic shell). A similar behaviour is observed for the NPs formed in the absence of base at 60 °C.

![TEM images of CCM-N-x polymer latexes (x = 0.1, (a)–(c): 0.05, (d) and (e) after loading with [RhCl(COD)]$_2$ (P/Rh = 1 : 1) and treatment with H$_2$ (20 bar) under different conditions for 20 h.](image)

Fig. 2 TEM images of CCM-N-x polymer latexes (x = 0.1, (a)–(c): 0.05, (d) and (e) after loading with [RhCl(COD)]$_2$ (P/Rh = 1 : 1) and treatment with H$_2$ (20 bar) under different conditions for 20 h.

In separate experiments, the Rh NPs were also generated at 25 °C, both in the absence and presence of NEt$_3$, using the fully loaded CCM-N-0.05, all other conditions being the same (H$_2$ pressure, NEt$_3$/Rh ratio, reaction time). The behaviour was qualitatively identical: grey and black latexes in the absence and presence of base, respectively. The TEM images of these products are shown in Fig. 2(d) and (e), respectively. The former looks rather similar to the RhNP@[CCM-N-0.1] latex obtained under the same conditions, with dispersed individual Rh NPs and no aggregates. The latter shows a few large NP aggregates located near a few polymer particles, while most other polymer particles are NP-free and there are no visible individual NPs. Fig. 2(e) also shows a few Rh NP agglomerates located outside of the CCM particles, most probably resulting from mechanical detachment from the CCM outer shells during the preparation of the TEM grid. Since the CCM-N-0.05 particles contain on average only 15 TPP functions per chain, these are located farther from each other and the PEOMA/TPP ratio is twice that of the CCM-N-0.1 particles. The observed trends suggest that while the Rh NPs start to form as small individual particles in the CCM core, the core TPP and the shell PEO functions subsequently compete under the influence of the PEO/TPP ratio. For comparison, we have generated Rh NPs by reduction of [RhCl(COD)]$_2$ toluene solutions in the presence of either the
PEOMA monomer or the macroRAFT chains R<sub>P</sub>-MAA<sub>15</sub>-co-PEOMA<sub>15</sub>-SC(S)SPr (macroRAFT-N), at various PEO/Rh ratios. The macroRAFT-N polymer, where R<sub>P</sub>-SC(S)SPr is the CTPPA trithiocarbonate used as RAFT agent for the polymer synthesis (see Experimental Procedures in the ESI†), is the intermediate obtained after the first step of the CCM-N synthesis as pointed out in the Introduction. The TEM images reveal particle agglomerates very much like those of Fig. 2(c) and (e), see ESI, Fig. S1.† In particular, at equivalent PEO/Rh ratios, stabilisation by the macroRAFT chains produces smaller agglomerates than the free PEOMA monomer, and the agglomerates are smaller when using a greater PEO/Rh ratio, as may be expected. The results of the experiments with the CCM in Fig. 2 also indicate mobility for the Rh NPs, with migration from the core to the shell and from one polymer particle to another. In previous work, we demonstrated that the molecular Rh<sup>1</sup> complex can rapidly migrate between different particle cores via reversible interpenetration with core–core contact, in combination with phosphine exchange reactions.<sup>83</sup> This principle can therefore be extended to the metallic NPs.

When using an incompletely Rh-loaded CCM-N latex (P/Rh = 4), no Rh<sup>1</sup> reduction occurred at 25 °C, even in the presence of excess NEt<sub>3</sub>. This suggests that the excess phosphine ligand exerts a protective action against reduction to the metallic state, like the styrene and 1-octene substrates in our previous catalysed hydrogenation study,<sup>77</sup> and confirms the principle that only a coordinatively unsaturated Rh<sup>1</sup> centre, such as that obtained from [RhCl(COD)][TPP@CCM] after removal of the COD ligand by hydrogenation in the absence of additional TPP, may be readily reduced by H<sub>2</sub>. When the same procedure was carried out at 60 °C, however, Rh NPs were once again generated. In the absence of base, NPs formed only upon warming to 90 °C. In this case, the TEM characterisation shows small NPs in all polymer particles, although they appear to be located mostly near the surface of the polymer particles rather than homogeneously dispersed in the core, see Fig. S2.† Therefore, the NPs obtained under these conditions have either reduced mobility or increased thermodynamic stability relative to the particles stabilized by the shell PEO chains. The same comparative experiments with P/Rh ratios of 1 : 1 and 4 : 1 were also carried out for the [RhCl(COD)]<sub>2</sub>-loaded CCM-N-0.2 latex (for which TPP/PEO = 4), in the presence of NEt<sub>3</sub>, yielding similar results. Large agglomerates, even larger than those obtained with the CCM-N-0.1 and 0.05 latexes, were produced when using a 1 : 1 P/Rh ratio at 25 °C (Fig. S3(a)†), whereas using a 4 : 1 ratio at 60 °C led to better dispersed and very small NPs, Fig. S3(b).† These results indicate that the Rh NP migration is strongly affected by the P/Rh ratio but not by the PEO/Rh ratio.

For comparison, Rh NPs were also generated by [RhCl(COD)]<sub>2</sub> reduction from a homogeneous toluene solution in the presence of PPh<sub>3</sub>, using P/Rh ratio of 1 and 4, and in the presence of ≈5 equiv. of NEt<sub>3</sub>. The reduction rate followed the same trend as observed for the RhNP@CCM-N synthesis: rapid at 25 °C for a P/Rh ratio of 1 : 1 and no reduction at all for a 4 : 1 ratio, but the latter mixture yielded NPs at 60 °C. The RhNP@PPh<sub>3</sub> obtained at 60 °C with P/Rh = 4 are significantly smaller, more narrowly dispersed, and less aggregated than those obtained at 25 °C with P/Rh = 1, see Fig. S4.† Their size is quite similar to RhNP@PPh<sub>3</sub> previously obtained from [Rh([η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub>])<sub>2</sub>]<sup>86,87</sup> Additional control experiments carried out in the absence of H<sub>2</sub> and in the presence of 10 equiv. of NEt<sub>3</sub> per Rh showed no colour change over 20 h at 60 °C, whether the P/Rh ratio is 1 or 4, indicating that the amine does not act as a reducing agent for the Rh<sup>2</sup> complex and that H<sub>2</sub> is essential to accomplish the Rh NP formation. The conclusions to be drawn from these investigations are that using a low P/Rh ratio (or no phosphine at all) leads to agglomerated Rh NPs, whereas higher P/Rh ratios yield better dispersed ones. For the experiments with the Rh-loaded CCM polymers, the lower P/Rh ratio leads to extensive NP migration and accumulation as aggregates in the PEO-rich areas.

Generation of rhodium nanoparticles in the CCM-C polymers

The formation of Rh NPs has also been investigated using the cationic-shell CCM particles (CCM-C) as stabilizing matrix. The charged nature of the shell in CCM-C (see Fig. 1) stops the interpenetration of the polymer particles and the interparticle migration of the molecular Rh<sup>1</sup> complexes.<sup>88</sup> Hence, we anticipated that the Rh NP migration may also be stopped. In addition, the chemical nature of the CCM-C outer shell is not expected to strongly stabilize metal NPs, although we cannot discard a potential role of the iodide counterions.

Under the same conditions (P/Rh ratios, temperature, H<sub>2</sub> pressure, base and reaction time) the Rh NP generation in the CCM-C-0.1 latex followed the same reactivity trend as in the CCM-N latexes: reduction at 25 °C when P/Rh = 1 and only upon warming to 60 °C when P/Rh = 4. However, as anticipated, the Rh NPs remained confined in all cases within the polymer core, see Fig. 3. The amount of used base (0, 1 or 5 equiv. per Rh for P/Rh = 1) did not affect the NP morphology or their dispersion within the polymer particles, see Fig. S5.† In order to evaluate the potential of the outer shell as a stabilizer for the generation of Rh NPs, the reduction of [RhCl(COD)]<sub>2</sub> was also carried out in the presence of the amphiphilic diblock macroRAFT agent R<sub>P</sub>- (4VPMe<sup>1</sup>–I<sup>−</sup>)<sub>140</sub>b-S<sub>50</sub>-SC(S)SPr (macroRAFT-C), using MeOH as a solvent and equivalent amounts (4VPMe<sup>1</sup>–I/Rh) ratios to those of the syntheses with the CCM-C polymer. This macroRAFT-C polymer is an intermediate of the CCM-C synthesis.<sup>74,80</sup> The resulting Rh NPs are highly agglomerated with agglomerate sizes that are essentially independent on the macroRAFT-C/Rh ratio, in the 10–50 nm range (Fig. S6†).

Fig. 3 TEM images of the CCM-C-0.1 polymer latex after loading with [RhCl(COD)]<sub>2</sub> and reduction with H<sub>2</sub> (20 bar) in the presence of NEt<sub>3</sub> (5 equiv. per Rh) for 20 h. (a) P/Rh = 1 : 1, 25 °C. (b) P/Rh = 4 : 1, 60 °C.
Catalysed hydrogenation of acetophenone

The TEM characterisation of the RhNP@CCM shows that the P/Rh ratio and the type of CCM shell (neutral, cationic) affect the NP location (core vs. shell), whereas the presence or absence of NEt₃ does not appear to induce significant changes on the synthesized NP morphology and location. The NPs are stabilized by either core-anchored TPP for the CCM-N nanoreactors at high P/Rh ratios and for the CCM-C nanoreactors under any conditions, or by the shell PEO chains for the CCM-N nanoreactors at low P/Rh ratios. Therefore, in order to properly evaluate the catalytic performance of the RhNP@CCM systems, control experiments were run with related Rh NPs, namely RhNP@PPh₃, RhNP@PEOMA, RhNP@macroRAFT-N and RhNP@macroRAFT-C, generated in the presence of the corresponding stabilizers under homogeneous conditions. The catalytic experiments with the RhNP@CCM latexes were carried out under aqueous biphasic conditions using the ‘as synthesized’ latex, diluted with water, as catalyst phase and toluene as the organic carrier phase. The control runs with RhNP@PPh₃, RhNP@PEOMA, RhNP@macroRAFT-N were carried out in toluene without any water phase, whereas methanol was used as a compatible solvent for the control runs with RhNP@macroRAFT-C. All results are collected in Table 1.

The partial reduction products 1-phenylethanol (2, carbonyl reduction) and methyl cyclohexyl ketone (3, arene ring reduction) and the fully reduced 1-cyclohexylethanol (4) were observed in variable proportions, depending on the stabilizer and conditions (Scheme 1). A certain amount of methylcyclohexane (MeCy), produced by the ring reduction of the toluene solvent, was also observed (see Table 1). The arene ring reduction is not surprising, because arene hydrogenation is well-known to be promoted by metal NPs, particularly those of Rh.⁵⁸,⁹₄,¹₀² A most relevant precedent is the reported biphasic acetophenone (and other functionalized arenes) hydrogenation using buffered water, benzene or cyclohexane as organic phase, and cetyltrimethylammonium bromide or tetrabutylammonium hydrogen sulphate as phase transfer catalyst, which also produced mixtures of all the possible products 2–4.¹⁰⁰ Although the authors of that contribution wrote “we are not certain

![Scheme 1 Products resulting from the hydrogenation of acetophenone catalysed by Rh NPs.](image)

Table 1  Acetophenone hydrogenation catalysed by Rh NPs

| Entry | NP stabilizer | P/Rh | PEOMC/Rh | 4VPMeT−/Rh | T/°C | Conv./% | TON 2 | TON 3 | TON 4 | TON MeCy |
|-------|--------------|------|----------|------------|------|--------|--------|--------|--------|----------|
| 1     | CCM-N-0.1    | 1⁻   | 0.5      | —          | 25   | 21.0   | 31.0  | 9.5    | 2.0    | 22.5     |
| 2     | 15          | 60   | 4.4      | 61.8       | 13.4  | 7.0    |        |        |        |          |
| 3     | 10          | 90   | 100.0    | 162.1      | 16.9  | 29.1   |        |        |        |          |
| 4     | 4⁻         | 25   | 43.5     | 63.2       | 20.8  | 8.6    |        |        |        |          |
| 5     | 60          | 60   | 100.0    | 118.6      | 33.5  | 63.8   |        |        |        |          |
| 6     | CCM-C-0.1    | 1⁻   | 0.5      | —          | 25   | 94.8   | 150.5 | 24.5   | 19.7   |          |
| 7     | PPh₃        | 1⁻   | —        | —          | 60⁻  | 97.2(3.7) | 146.4(7.9) | 7.6(3.1) | 44.3(13.4) | 23.9(7.7) |
| 8     | 4⁻         | 60⁻  | 78.8(6.8) | 138.3(13.2) | 0.5(0.8) | 1.3(2.1) | 2.8(0.2) |        |        |          |
| 9     | PEOMA       | 0.5⁻ | —        | —          | 60⁻  | 93.6(0.5) | 75.3(17.4) | 7.9(6.5) | 106.5(54.7) | 4.3(0.9) |
| 10    | 2           | 60⁻  | 93.6(4.7) | 152.3(11.9) | 17.5(4.5) | 19.5(2.4) | 29.5(14.0) |        |        |          |
| 11    | 8           | 60⁻  | 96.0(0.8) | 109.9(26.7) | 21.1(4.0) | 33.0(10.8) | 3.4(0.1) |        |        |          |
| 12    | macroRAFT-N | 0.5⁻ | —        | —          | 60⁻  | 98.8(1.5) | 93.0(22.0) | 42.4(2.5) | 62.5(25.6) | 10.7(3.5) |
| 13    | 2           | 60⁻  | 98.8(0.1) | 107.2(19.4) | 34.1(8.7) | 58.9(11.2) | 2.4(0.4) |        |        |          |
| 14    | 0.5         | 60⁻  | 97.1(0.3) | 112.4(4.0) | 49.6(2.1) | 133.3(3.5) | 21.6(4.3) |        |        |          |
| 15    | 2           | 60⁻  | 96.4(1.0) | 25.0(6.6)  | 59.1(13.8) | 109.7(4.8) | 11.7(2.4) |        |        |          |
| 16    | CCM-C-0.1    | 1⁻   | 4.7      | —          | 25   | 12.9   | 10.2  | 4.2    | 0.0    | 1.0      |
| 17    | 60          | 60   | 9.1      | 14.0       | 4.1   | 0.0    |        |        |        | 60.5     |
| 18    | 90          | 90   | 86.5     | 154.0      | 9.2   | 7.2    |        |        |        |          |
| 19    | 4⁻         | 18.7 | 25       | 11.3       | 0.0   | 0.0    |        |        |        | 10.3     |
| 20    | 60          | 60   | 18.0     | 25.3       | 10.6  | 0.0    |        |        |        | 21.1     |
| 21    | 90          | 90   | 23.5     | 49.8       | 0.0   | 0.0    |        |        |        |          |
| 22    | macroRAFT-C | —    | 4.7      | 60⁻        | 20.9(6.5) | 32.0(10.0) | 6.9(1.9) | 3.2(1.5) | 2.0(0.1) |          |
| 23    | 18.8        | 60⁻  | 12.5(6.9) | 17.0(7.4)  | 3.8(3.5) | 2.5(1.8) | 2.0(0.2) |        |        |          |

a Unless otherwise stated, the Rh NPs were synthesized at 60 °C in the presence of NEt₃ (10 equiv. per Rh) and the indicated support prior to catalysis. b Standard conditions: acetophenone/Rh = 200; 0.4 mL of latex, 0.5 mL of toluene; p[H₂] = 20 bar; 20 h. The figures are averages, with standard deviations in parentheses, when multiple runs were carried out. c 8.07 μmol of Rh. d 1.70 μmol of Rh. e Average and standard deviation from 3 parallel runs. f Average and standard deviation from 4 parallel runs. g No NEt₃ was used in the NP synthesis. h The volatility of methylcyclohexane led to escape of the product from the reaction vials and prevented a reliable measurement of its amount at the end of the reaction. i 5.09 μmol of Rh. j 1.29 μmol of Rh.
whether the phase-transfer process described herein involves a soluble or insoluble rhodium catalyst\textsuperscript{a*}, their molecular precursor \{[RhCl\{1,5-hexadiene\}]\} and catalytic conditions were quite similar to those used here. The acetoephonone hydrogenation catalysed by Rh NPs has previously been reported for NPs stabilized by polyvinylpyrrolidone (RhNP@PVP)\textsuperscript{104} and by phosphine ligands, including PPh\textsubscript{3}.\textsuperscript{46} There are also a few reports on the Rh NP-catalysed transfer hydrogenation of acetophenone by isopropanol, focusing on enantioselectivity, but the observed conversions were very poor, except at the highest temperature for P/Rh = 1 (entry 18). These results may indicate poor mass transport of the substrate towards the CCM core and suggest that the Rh NPs remain trapped within the CCM core under catalytic conditions, contrary to the RhNP@CCM-N latex examined above. A TEM analysis of the latex after catalysis (Fig. 5) confirms this conclusion. These results may seem puzzling, because both CCM-N and CCM-C previously showed excellent performance in olefin hydrogenation (notably styrene and 1-octene) by molecular Rh\textsuperscript{1@CCM-N}, which is confined within the CCM core.\textsuperscript{79,80} Indeed, the CCM-C nanoreactors performed equally well (or better) than CCM-N. Since toluene is a good solvent for polystyrene and efficiently swells the CCM core, it can vectorize substrates toward the catalyst, even those like 1-octene that do not have themselves

Confined in the hydrophobic core, the most interesting comparison is between entries 5 and 8. While the activity compares favorably, the large selectivity difference (large amounts of arenne reduction products for entry 5, traces in entry 8) suggests a different catalyst organisation, raising questions about the stability of the core confinement in RhNP@CCM-N. TEM images for this catalyst recorded after catalysis revealed large NP aggregates outside of the CCM particles, Fig. 4. Given this result, we can conclude that the CCM-N scaffold is not an appropriate support for the Rh NP confinement under these catalysis conditions.

Moving to the cationic CCM latex (RhNP@CCM-C, entries 16–21), the substrate conversions were very poor, except at the highest temperature for P/Rh = 1 (entry 18). These results may indicate poor mass transport of the substrate towards the CCM core and suggest that the Rh NPs remain trapped within the CCM core under catalytic conditions, contrary to the RhNP@CCM-N latex examined above. A TEM analysis of the latex after catalysis (Fig. 5) confirms this conclusion. These results may seem puzzling, because both CCM-N and CCM-C previously showed excellent performance in olefin hydrogenation (notably styrene and 1-octene) by molecular Rh\textsuperscript{1@CCM-N}, which is confined within the CCM core.\textsuperscript{79,80} Indeed, the CCM-C nanoreactors performed equally well (or better) than CCM-N. Since toluene is a good solvent for polystyrene and efficiently swells the CCM core, it can vectorize substrates toward the catalyst, even those like 1-octene that do not have themselves

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high affinity for polystyrene. Control experiments run with RhNP@macroRAFT-C (entries 22–23) gave equally poor conversions. In this catalyst, the Rh NPs are possibly stabilized by interaction with the iodide anions associated to the polycationic P4VPMe⁺ chains. Therefore, the only possible way to rationalize these results is that the polycationic nature of the CCM-C and macroRAFT-C, although not affecting the mass transport of the organic solvent (toluene), have a negative effect on the mass transport of the acetophenone substrate, perhaps as a consequence of electrostatic interactions between the 4VPMe⁺ ions and the substrate carbonyl group. This hypothesis is supported by the results obtained for the hydrogenation of styrene (*vide infra*).

### Catalysed hydrogenation of styrene

These reactions were carried out under conditions identical to those of the acetophenone hydrogenation (notably, styrene/Rh NP catalysis). But in this case, since styrene is the primary product, the second reaction is effectively the hydrogenation of the vinyl group. However, as discussed above, these reactions were carried out under conditions identical to those used for the acetophenone hydrogenation (Scheme 2) and the organic solvent. The second one is to compare the results with those of the previously published molecular hydrogenations, where 1-nonanol was also used as continuous organic phase.79,80 The Rh NP-catalysed hydrogenation of styrene has only been addressed in one recent report, with NPs stabilized by a phosphine ligand.81 Additional contributions have addressed the hydrogenation of other arenes and aromatic heterocycles with Rh NPs stabilized by PEOM,96,97 cyclic iminium salts108 or phosphines.98,109 All our new results are collected in Table 2.

Since the RhNP@CCM-N catalytic efficiency is very high (entries 24–27), experiments were carried out only up to 60 °C. Full substrate conversion was already achieved in 20 h at 25 °C, with high selectivity for the vinyl group hydrogenation. Only traces of the final product 7 were observed at 25 °C for the NPs produced with P/Rh = 1 (entry 24) and this increased only slightly when operating at 60 °C (entry 25). The RhNP@PPh₃ performed equally well (entries 28–29), with a slightly greater arene hydrogenation, particularly when P/Rh = 1. The RhNP@PEOM also gave full conversion and similar selectivity (entries 31–33). The RhNP@macroRAFT-N also gives full conversions and an even greater proportion of 7, particularly for the sample obtained with PEO/Rh = 0.5 (entry 34). Clearly,

![Scheme 2](image-url)

**Scheme 2** Products resulting from the hydrogenation of styrene catalysed by Rh NPs.

### Table 2 | Styrene hydrogenation catalysed by Rh NPs

| Entry | NP stabilizer | P/Rh | PEO/Rh | 4VPMe⁺I⁻/Rh | Styrene/Rh | T°C | 5°/% | 6°/% | 7°/% |
|-------|--------------|------|--------|-------------|------------|-----|-----|-----|-----|
| 24    | CCM-N-0.1    | 1    | 0.5    | —           | 200        | 25  | 0.1 | 99.3| 0.6 |
| 25    |              | 60   | 0.1    |             | 200        | 25  | 0   | 100 | 0   |
| 26    |              | 2    | —      | —           | 200        | 60  | 0.1 | 97.0| 3.0 |
| 27    |              | 60   | 0      |             | 200        | 25  | 0   | 100 | 0   |
| 28    | PPh₃         | 1    | —      | —           | 200        | 60  | 0   | 100 | 0   |
| 29    |              | 60   | 0      | —           | 200        | 60  | 0.1 | 93.1| 6.9 |
| 30    |              | 4    | —      | —           | 200        | 200 | 0.1 | 19.2| 80.9|
| 31    | PEOMA        | 0.5  | —      | —           | 200        | 60  | 0   | 88.0| 12.0|
| 32    |              | 2    | —      | —           | 200        | 60  | 0.5 | 90.6| 9.4 |
| 33    |              | 8    | —      | —           | 200        | 60  | 0   | 54.6| 45.4|
| 34    | macroRAFT-N  | 0.5  | —      | —           | 200        | 60  | 0   | 19.1| 80.9|
| 35    |              | 2    | —      | —           | 200        | 60  | 0   | 93.7| 6.3 |
| 36    |              | 0.5  | —      | —           | 200        | 60  | 5.1 | 36.5| 91.4|
| 37    |              | 2    | —      | —           | 200        | 60  | 2.8 | 19.9| 77.3|
| 38    | CCM-C-0.1    | 1    | —      | 4.7         | 200        | 25  | 0   | 99.0| 1.0 |
| 39    |              | 60   | 0.1    | —           | 200        | 25  | 0   | 99.6| 0.3 |
| 40    |              | 200  | 0      | —           | 200        | 25  | 0   | 100 | 0   |
| 41    |              | 60   | 0      | —           | 200        | 25  | 0   | 99.8| 0.2 |
| 42    |              | 4    | —      | 18.7        | 200        | 25  | 0   | 100 | 0   |
| 43    |              | 60   | 0      | —           | 200        | 25  | 0   | 100 | 0   |
| 44    |              | 200  | 0      | —           | 200        | 25  | 0   | 100 | 0   |
| 45    |              | 60   | 0      | —           | 200        | 25  | 0   | 99.9| 0.1 |
| 46    | macroRAFT-C  | —    | —      | 4.7         | 200        | 60  | 0   | 99.0| 1.0 |
| 47    |              | 18.8 | —      | —           | 200        | 60  | 0   | 99.9| 0.1 |
| 48    |              | 19.2 | —      | —           | 200        | 60  | 6.3 | 93.7| 0   |

*Unless otherwise stated, the Rh NPs were synthesized at 60 °C in the presence of NEt₃ (10 equiv. per Rh) and the indicated support prior to catalysis. Standard conditions: 0.4 mL of latex, 0.5 mL of 1-nonanol; p(H₂) = 20 bar; 20 h. The figures are averages, with standard deviations in parentheses, when multiple runs were carried out. Average and standard deviation from 3 parallel runs. Average and standard deviation from 4 parallel runs. Pure styrene was used as organic phase. No NEt₃ was used in the NP synthesis. Average and standard deviation from 4 parallel runs. Average and standard deviation from 5 parallel runs.
a greater amount of stabilizer (either the phosphine or the ethylene oxide functions) negatively affects the ring hydrogenation, probably by reducing the surface accessibility. For the RhNP@macroRAFT-N catalyst, additional runs were carried out in the absence of NEt₃ (both in the NP synthesis and in catalysis; same batch used for the acetoephene hydrogenation; entries 36–37). Like for the acetoephene hydrogenation, the absence of base increases the rate of ring hydrogenation. It is also interesting to compare the much lower extent of ring hydrogenation for styrene (Table 2) relative to acetoephene (Table 1). For instance, runs 1 and 24 for RhNP@CCM-N-0.1 at 25 °C and P/Rh = 1 show 27% of ring-hydrogenated products (3 + 4) for acetoephene vs. only 0.6% (7) for styrene. Likewise, these fractions are 60% and 12%, respectively, for runs 9 and 31 involving RhNP@PEOMA at 60 °C and PEO/Rh = 0.5. This difference may result from the action of the carbonyl function in acetoephene and the hydroxyl function in the phenylethanol intermediate in keeping the substrate more strongly anchored to the RhNP surface. However, because of the Rh NP migration under catalytic conditions, as already demonstrated in the previous section, interest in using this latex is limited. Indeed, a TEM analysis of the CCM-N-0.1 catalyst after styrene hydrogenation with P/Rh = 4 (run 27), shown in Fig. S7, reveals a very similar morphology change to that observed after the acetoephene hydrogenation under the same conditions (Fig. 4(c)).

The RhNP@CCM-C catalyst also shows excellent performance (entries 38–45), like the RhNP@CCM-N catalyst, with full substrate conversion (up to 2000 equiv. vs. Rh) at both 25 and 60 °C within 20 h. This is in stark contrast with the poor performance in acetoephene hydrogenation, confirming the hypothesis of a severe mass transport limitation for the latter. High activities were also observed for the RhNP@macroRAFT-C control runs (entries 46–48). The fraction of ring-hydrogenated product is even lower than that observed for the RhNP@CCM-N-0.1 and RhNP@macroRAFT-N systems. Since neat styrene is a good solvent for polystyrene, the hydrogenation was also carried out in bulk (styrene/Rh = 2000), yielding once again full conversion in 20 h at both 25 and 60 °C for both P/Rh ratios (entries 49–51 and 49–47). High activities for the hydrogenation of neat styrene were also observed for the RhNP@PPh₃ (run 30) and RhNP@macroRAFT-C (run 48) control runs.

In order to better assess the catalyst performance, a series of experiments were also carried out using shorter reaction times with the RhNP@CCM-C-0.1 (P/Rh = 4) catalyst, see Table 3. When operating in 1-nonanol (styrene/Rh = 200), quantitative conversion to ethylbenzene was still achieved down to 1 h (runs 49–53). Lowering the temperature to 25 °C and using neat styrene (conditions identical to those of entry 44 in Table 2) gave again full conversion after 2 and 1.75 h (runs 54–55). Only for shorter reaction times of 1.5, 1 and 0.5 h (runs 56–58), incomplete conversions were witnessed. From runs 55–58, average TOF values over the entire catalytic runs of 1143, 1020, 994 and 1056 h⁻¹ can be calculated from the TON/time ratios, for an overall average of 1053 ± 46 h⁻¹.

In order to assess the possible effect of the TPP concentration in the hydrophobic CCM core, two additional hydrogenations of neat styrene were carried out using a reaction time of 0.5 h under otherwise identical conditions, with RhNP@CCM-C-0.05 and RhNP@CCM-C-0.2 (runs 59–60). The results are quite comparable, indicating that the TPP concentration does not significantly affect the NP catalytic activity. All experiments in Table 3 show perfect selectivity in favor of the ethylbenzene product. In comparison with the only published example of styrene hydrogenation with Rh NPs (complete conversions in 24 h at R.T and 30 bar of H₂ in isopropanol with TON up to 756), the activity appears much greater. However, that investigation did not report runs with shorter reaction time or greater substrate/Rh ratios. It is also of interest to compare these results with the recently reported ones carried out under the same conditions (aqueous biphasic, neat styrene, 25 °C, 20 bar of H₂) with the molecular Rh³ system embedded in the same CCM support, where a TOF of ca. 300 h⁻¹ was obtained. Thus, the catalytic activity of the Rh NPs appears superior to that of the molecular system.

| Entry | NP stabilizer | P/Rh | 4VPMₑ⁻¹ /Rh | Styrene/Rh | T°C | Time/h | 5% | 6% | 7% |
|-------|--------------|------|-------------|------------|-----|--------|----|----|----|
| 49    | CCM-C-0.1    | 3.93 | 18.3        | 200        | 60  | 15     | 0  | 99.6| 0.4|
| 50    |              | 10   | 0           | 100        | 0   |
| 51    |              | 5    | 0           | 100        | 0   |
| 52    |              | 2    | 0           | 100        | 0   |
| 53    |              | 1    | 0           | 100        | 0   |
| 54    | 4.05         | 18.9 | 200²        | 25         | 2   | 0      | 100| 0  |
| 55    |              | 1.75 | 0           | 100        | 0   |
| 56    |              | 1.5  | 23.5        | 76.5       | 0   |
| 57    |              | 1    | 50.3        | 49.7       | 0   |
| 58    |              | 0.5  | 73.6        | 26.4       | 0   |
| 59    | CCM-C-0.05   | 4.04 | 18.8        | 200²       | 0.5 | 58.3  | 41.7| 0  |
| 60    | CCM-C-0.2    | 4.09 | 19.0        | 200²       | 0.5 | 56.1  | 43.9| 0  |

a The Rh NPs were synthesized at 60 °C in the presence of NEt₃ (10 equiv. per Rh) and the indicated support prior to catalysis. Standard conditions: 0.4 mL of latex; 0.5 mL of 1-nonanol (if used); p(H₂) = 20 bar.  b 0.96 μmol of Rh. c 2.43 μmol of Rh. d 0.45 μmol of Rh. e 1.89 μmol of Rh. f Neat styrene (no 1-nonanol).
Finally, the hydrogenation of neat styrene was repeated under the same conditions of entry 58 of Table 3 (P/Rh = 4, 25 °C, 0.5 h, 20 bar of H₂) with catalyst recovery and recycling. In a first series of experiments, the product recovery involved extraction of the latex phase (after decanting off the organic layer) with diethyl ether, in order to remove all product and residual substrate from the polymer hydrophobic core prior to the addition of a new substrate charge for the next catalytic run (see Experimental section). This extraction procedure is identical to that used in all individual runs of the above tables, as well as to that used for the recycling experiments with the molecular Rh⁰ catalyst embedded in the CCM. The results are shown in Fig. 6(a). Again, the selectivity was 100% in favor of ethylbenzene, with no trace of ethylcyclohexane. While the first run gave a higher conversion (66.4%) relative to entry 58 of Table 3, the subsequent runs indicated significant loss of activity, with a continuous drop of the conversion to less than 5% after the 5th recycle. This decrease cannot be related to metal leaching or to mechanical losses during the separation phase, because the decantation phase was rapid yielding a colourless and transparent organic phase and a sharp interface. In a separate recycle series (Fig. 6(b)), a catalyst regeneration step was operated after the 1st recycle, consisting of H₂ treatment (20 bar, 80 °C, 2 h) in the absence of substrate. The activity was partially recovered in the 2nd recycle. However, it dropped again in the 3rd recycle. This suggests a NP surface deactivation process, which was only incompletely corrected by the regeneration phase. The TEM analysis of the latex recovered after the 6th recycle (first series), Fig. 6(c), reveals large Rh NP agglomerates and empty polymer particles. Therefore, the irreversible (i.e. not recovered by regeneration) activity loss can be attributed at least in part to the loss of Rh NP active surface associated to the agglomeration.

The Rh NP extraction from the CCM core can be associated to the use of diethyl ether for the product separation. Indeed, the Rh NPs can be expected to interact similarly with Et₂O and with the PEO functions of the CCM-N shell. In order to substantiate this hypothesis, a final series of catalytic runs with recycling was carried out using toluene instead of Et₂O for product extraction, in combination with periodical NP surface regeneration. The results are shown in Fig. 7(a). A first catalyst regeneration, conducted immediately after the 1st run, led to greater activity relative to the original one (ca. 80% conversion). Without any additional regeneration, the high activity was maintained for the next two recycles and then gradually fell to ca. 20% in the 5th recycle. At this point, a second catalyst regeneration led again to a full activity recovery to ca. 80% conversion for the next two cycles. The TEM analysis of the recovered latex after the 8th recycle clearly showed that the Rh NPs remained well dispersed inside the CCM particles, see e.g. Fig. 7(b). The comparison of the activity trend for the recycles with ether and toluene washings and the TEM images of the recovered catalyst in Fig. 6 and 7 constitutes indirect proof of the Rh NP confinement in the CCM-C hydrophobic core. A precise comparison of the Rh NP size before and after catalysis is difficult, but the TEM image clearly evidences the absence of NP agglomeration. The observed behaviour confirms the surface deactivation phenomenon during the catalytic runs at 25 °C and the full reactivation by H₂ treatment at 80 °C. Clearly, no surface deactivation would be expected if the catalytic hydrogenations are conducted directly at higher temperatures.

The marked difference in behaviour between the recycle results with diethyl ether and toluene washings provides useful information about the relative aptitude of different NP stabilizers. This difference is in line with the different NP migration behaviour observed for the RhNP@CCM-N and RhNP@CCM-C systems. Although the phosphine P lone pairs bind Rh⁰ much more tightly than the O lone pair in ethers, the same is definitely not true for the Rh⁰ atoms on the Rh NP surface. Thus, while diethyl ether washings did not lead to any significant Rh⁰ leaching from the supported molecular Rh⁰@CCM (N or C) systems,⁷⁹ the Rh NPs could be maintained in the stabilizing environment of the CCM core only in the absence of large concentrations of O-based donor stabilizers. The Rh NP extraction from the CCM-C core observed during the recycles with Et₂O washings, leading to agglomeration and loss of catalytic activity, is certainly facilitated by the large diethyl ether.
concentration. A determination of the relative P- and O-donor affinity with respect to the Rh NP surface would require more detailed quantitative study, which is beyond the scope of the present study.

**Catalysed hydrogenation of 1-octene**

The main objective of these experiments was to gather additional evidence for the Rh NPs confinement in the CCM-C core. Since 1-octene is not a good solvent for polystyrene, its mass transport to the polymer core is limited unless vectorized by a good solvent such as toluene or 1-nonanol. Indeed, a previously described NMR investigation did not evidence any core 1-octene incorporation when added as a neat phase to a CCM-N latex, whereas this was confirmed after core swelling by toluene. All subsequent investigations of the biphasic 1-octene hydrogenation with the molecular [RhCl(COD)(TPP@CCM)] precatalyst (CCM = CCM-N or CCM-C) were carried out with 1-nonanol as vectoring solvent.

The experiments were only carried out with the CCM-C-0.1 latex, using both the in situ-activated [RhCl(COD)(TPP@CCM-C)] precatalyst and the RhNP-containing system, RhNP@CCM-C (see Table 4). Before catalysis implementation, the latexes were freeze-dried in order to completely remove toluene (previously used as swelling solvent to load the molecular Rh precursor) and avoid any 1-octene mass transport assistance. The experiment with the molecular catalyst (run 61) unexpectedly yielded a rather efficient hydrogenation. Since this molecular catalyst is unambiguously core-confined, this result demonstrates the occurrence of 1-octene mass transport to the polystyrene core. Consequently, the previously reported absence of 1H and 31P NMR signatures (of incorporated 1-octene and core-anchored TPP ligands, respectively) after equilibration of the CCM-N particles with neat 1-octene cannot be attributed to the absence of 1-octene in the core. Rather, the 1-octene amount (a poor polystyrene solvent) at equilibrium is evidently too small to confer sufficient mobility to the polymer and the correlation times remain too long for NMR observation. A new NMR investigation has confirmed the absence of 1H and 31P resonances for core-incorporated 1-octene and core-anchored TPP after equilibrating the TPP@CCM-C-0.1 latex with neat 1-octene.

As shown in entry 62, the Rh NPs also catalysed the hydrogenation of 1-octene, but the yield was ca. half that of run 61, suggesting that the Rh NPs have lower activity than the molecular catalyst for the hydrogenation of this substrate. This is opposite to the observed trend in styrene hydrogenation. This difference may be rationalized by a different relative affinity of 1-octene and styrene to bind to and be activated by a coordinatively unsaturated monometallic Rh center versus the surface of a Rh NP. Finally, the activity was greater (full conversion after 3 h) when 1-octene hydrogenation was carried out in the presence of 1-nonanol (run 63). This phenomenon is clearly related to an increased 1-octene mass transport, resulting from the vectorizing effect of 1-nonanol. This more than compensates the expected negative effects of substrate dilution on the kinetics and the possible 1-nonanol competition for NP surface binding. Thus, these catalysis results provide additional evidence in support of the Rh NP confinement in the CCM-C hydrophobic core environment.

**Conclusions**

We have extended the nanoreactor application of triphenylphosphine-functionalized core-crosslinked micelle latexes, for the first time, to metal nanoparticle catalysis. These latexes, with either neutral P(MAA-co-PEOMA) or polycationic P(4VPMe+I)PEO71#91#93 chains on the micelle surface (CCM-N and CCM-C, respectively) and loaded with a Rh precatalyst, [RhCl(COD)(TPP@CCM)], were previously used to support molecular catalysts. We have now shown that Rh NPs can be synthesized from these precursors by H2 reduction in the absence of olefins. For fully loaded (P/Rh = 1) latexes, the core-anchored complexes were readily reduced to Rh NPs by H2 (20 bar) at 25 °C in the presence of NEt3, whereas heating to 60 °C is needed in the absence of base. Partially loaded latexes (P/Rh = 4) yield Rh NPs only upon heating and in the presence of excess NEt3. The TEM analysis reveals migration of the produced NPs from the core to the shell for RhNP@CCM-N latexes, due to competition between the core TPP ligands and the shell PEO chains as stabilizing functions. During the catalytic applications, even the phosphine-richer (P/Rh = 4) RhNP@CCM-N latexes led to NP migration and agglomeration away from the CCM particles, invalidating the CCM-N strategy for catalyst confinement. For the cationic-shell latexes, on the other hand, the Rh NPs remained well-dispersed and core-confined for all P/Rh ratios after catalysis, but only when toluene, which displays poorer stabilizing power towards the Rh NPs than the core-anchored triphenylphosphines, was used for product recovery/catalyst recycling. These RhNP@CCM-C latexes are therefore of interest for the catalytic application of Rh NPs under aqueous biphasic conditions with catalyst recycling. The catalytic studies presented here show high activity for the reduction of styrene in bulk (TOF greater than 1000 h⁻¹ at 25 °C and 20 bar of H2) and also of 1-octene, although the activity in the latter case is improved when the substrate is vectorized to the CCM core by 1-nonanol, which is a better polystyrene solvent. On the other hand, the polycationic nature of the CCM shell introduced mass transport limitations in the hydrogenation of acetophenone, blocking access to the catalytic NPs. Further investigations are necessary to establish the origin of this blocking effect. It should be possible to implement aqueous biphasic
nanocatalysis under a wider array of experimental conditions through the development of nanoreactors with different core functions, i.e. ligands that can better stabilize the metal NPs than TPP while allowing substrate access to the NP surface.

Author contributions

H. Wang: investigation, data curation; A. M. Fiore: investigation; C. Fliedel: supervision; E. Manoury: funding acquisition, validation; K. Philippot: conceptualisation, validation, writing – review & editing; M. M. Dell’Anna: supervision; P. Mastrorilli: resources, writing – review & editing; R. Poli, conceptualisation, validation, writing – original draft.

Conflicts of interest

There are no conflicts to declare.

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