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## Accepted Article

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# One-pot Synthesis of Rh Nanoparticles in Polycationic-shell, Triphenylphosphine Oxide-functionalized Core-crosslinked Micelles for Aqueous Biphasic Hydrogenation

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## Abstract

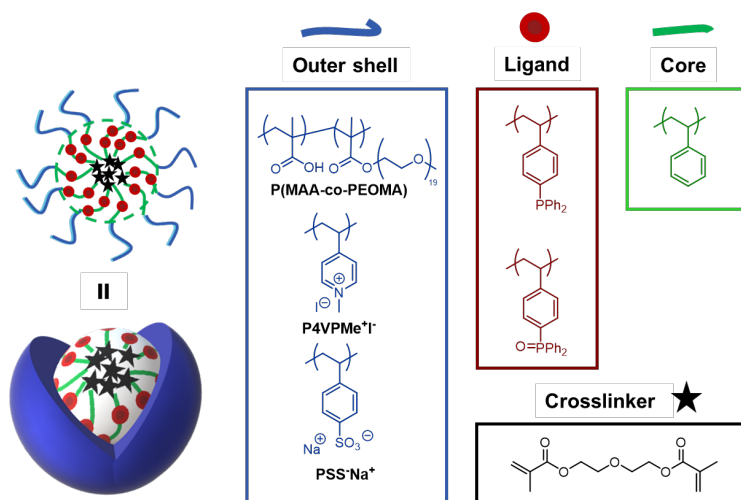
Cationic-shell core-crosslinked micelles (CCM-C) with rhodium nanoparticles (RhNPs) anchored to core-linked triphenylphosphine oxide (TPPO) ligands were synthesized by a facile one-pot approach by the reduction of  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2/\text{toluene}]$  in the presence of an aqueous TPPO@CCM-C latex. The resulting RhNP-TPPO@CCM-C latex showed to be performant for the aqueous biphasic

hydrogenation of styrene with an average corrected turnover frequency (cTOF) up to 23600 h<sup>-1</sup> based on the RhNP surface atoms. The catalyst system also proved reusable in multiple catalytic runs without any visible RhNP loss during the recycling process as well as applicable to the hydrogenation of other selected alkenes, alkynes and carbonyl substrates (average cTOF of 1000–3200 h<sup>-1</sup>), thus demonstrating a high versatility.

## Introduction

Liquid/liquid biphasic catalysis is a convenient approach for catalyst recovery and recycling,<sup>[1]</sup> and the use of an aqueous catalytic phase is attractive for a large-scale implementation.<sup>[1–3]</sup> For the conversion of organic substrates, the catalyzed reaction usually takes place either in the aqueous phase, in the substrate/product phase (*e.g.*, thermomorphic systems<sup>[4]</sup>), or at the water/organic interface depending on the solubility properties of catalyst and substrate.<sup>[2]</sup> An alternative, and less developed approach, involves stable aqueous dispersions (latexes) of micelles that host the catalyst within the hydrophobic micellar core. Here, each micelle operates as an individual catalytic nanoreactor and the reaction occurs within the homogeneous environment of the micellar core in which both catalyst and substrate have a high local concentration. This induces fast reaction kinetics, while the catalyst remains confined within the water phase inside the micelles, enabling easy separation and recovery after the reaction by a simple decantation.

Although copolymer micelles are relatively persistent objects with low critical micellar concentrations (CMCs) and slow micelle/free chain dynamics,<sup>[5–12]</sup> additional advantages in terms of stability and recyclability can be achieved by crosslinking. Such crosslinked micelles can be fabricated by first allowing amphiphilic linear chains to self-assemble in micellar form and then by chain crosslinking either at the outer shell, at the inner core,<sup>[13–20]</sup> or within an intermediate shell<sup>[21–23]</sup> to form catalytic unimolecular nanoreactors.<sup>[24]</sup> Some of us have developed different families of core-crosslinked micelle (CCM) nanoreactors with a polystyrene core, diethylene glycol dimethacrylate as core-crosslinker, and either neutral (CCM-N),<sup>[25–33]</sup> cationic (CCM-C)<sup>[34–37]</sup> or anionic (CCM-A)<sup>[38,39]</sup> hydrophilic shells (Figure 1) by convergent reversible addition fragmentation chain-transfer (RAFT) polymerization. The CCM shells consist of random poly(ethylene oxide) methyl ether methacrylate (PEOMA) and methacrylic acid copolymer blocks for CCM-N, poly(4-vinyl-*N*-methylpyridinium iodide) blocks for CCM-C or poly(sodium *p*-toluenesulfonate) blocks for CCM-A.



**Figure 1.** TPP- and TPPO-functionalized CCMs previously used as supports for RhNPs in aqueous biphasic hydrogenation catalysis.

After loading the CCMs with molecular metal precatalysts such as  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$  (COD: 1,5-cyclooctadiene) or  $[\text{Rh}(\text{CO})_2(\text{acac})]$  (acac: acetylacetonate), they were applied as catalytic nanoreactors in aqueous biphasic olefin hydrogenation<sup>[31,33,35–37,39]</sup> and olefin hydroformylation.<sup>[25,27,30,32,40]</sup> Moreover, CCMs-containing core-linked triphenylphosphine (TPP) ligands (TPP@CCM-C)<sup>[36]</sup> or triphenylphosphine oxide (TPPO) ligands (TPPO@CCM-C)<sup>[37]</sup> allowed to confine Rh nanoparticles (RhNPs) that were generated either *in-situ* by reduction of core-anchored molecular complexes under  $\text{H}_2$ ,<sup>[31,33,35,36,39]</sup> or *ex-situ* in the presence of stabilizers (TPP/pyridine mixture)<sup>[41,42]</sup> and then transferred to the CCMs cores.<sup>[37]</sup> The RhNP-TPP@CCM-C catalyst proved very active for the hydrogenation of styrene, 1-octene and acetophenone, but RhNPs leaching occurred when reaction mixtures were extracted with diethyl ether for product isolation.<sup>[36]</sup> The presence of TPPO ligands in the CCM cores immobilized the RhNPs much better, enabling the RhNP-TPPO@CCM-C catalyst to display high initial catalytic activity in styrene hydrogenation and withstand RhNPs leaching upon diethyl ether solvent extraction.<sup>[37]</sup> Nevertheless, the activity of the catalyst decreased gradually upon reuse converging to a low value, which was attributed to the removal of surface-bound RhNP stabilizers during the extraction protocol altering the stability and activity of the RhNPs. These results clearly suggest that an alternative synthesis approach without stabilizers is needed to obtain RhNP-TPPO@CCM-C nanoreactors that maintain their catalytic performance upon recycling.

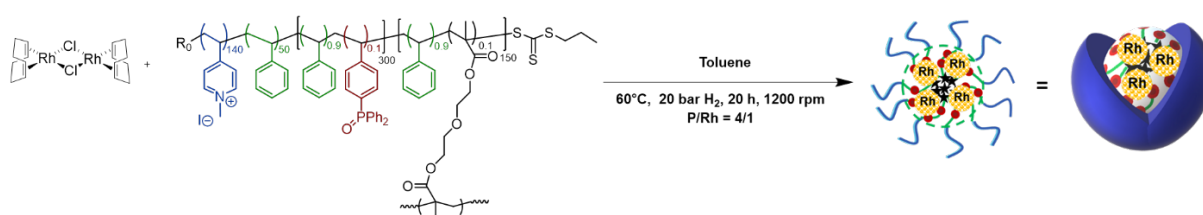
In this work, a new one-pot synthesis approach is described to obtain the RhNP-TPPO@CCM-C catalyst with narrow-sized RhNPs without the use of auxiliary stabilizers. The resulting catalyst was thoroughly characterized and applied in the aqueous biphasic hydrogenation of styrene, where it demonstrated superior performance with respect to both activity, catalyst/product phase separation as well as recyclability relative to previous RhNPs@CCM catalyst systems.<sup>[36,37]</sup> The versatility of the catalyst system was also shown for the hydrogenation of other alkenes, alkynes and carbonyl substrates.

## Results and Discussion

### One-pot synthesis and characterization of RhNP-TPPO@CCM-C

RhNPs embedded in the hydrophobic cores of a stable latex of TPPO@CCM-C were synthesized in a single step by heating a biphasic mixture containing the aqueous TPPO@CCM-C white latex and a yellow toluene solution of  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$  under  $\text{H}_2$  pressure (Scheme 1). Toluene was used to dissolve the Rh precursor and to swell the TPPO@CCM-C core.  $\text{H}_2$  was applied for reducing  $\text{Rh}^{\text{I}}$  to  $\text{Rh}^0$ , which only occurred upon heating, whereas the TPPO functions in the core of the polymer particles served to stabilize and anchor the formed RhNPs. This could be performed without any additional stabilizer or base additive (Table 1, Entry 1), and without the need of preliminary *ex-situ* synthesis of the RhNPs as previously reported.<sup>[37]</sup> Comparative syntheses were also carried out in the presence of a base such as pyridine or  $\text{NEt}_3$

(Table 1, Entries 2 and 3), which can aid the reaction by trapping the HCl produced during the reduction of Rh<sup>I</sup> to Rh<sup>0</sup>, in addition to potentially contribute to the RhNP stabilization.<sup>[36,37]</sup> After the synthesis and phase separation, all three produced RhNP-TPPO@CCM-C latexes were black, and the toluene solution turned colorless and transparent, signaling the successful formation and confinement of RhNPs in the core of the CCMs.



**Scheme 1.** Synthesis of RhNP-TPPO@CCM-C by a single step procedure.

**Table 1.** Syntheses of RhNP-TPPO@CCM-C.<sup>a</sup>

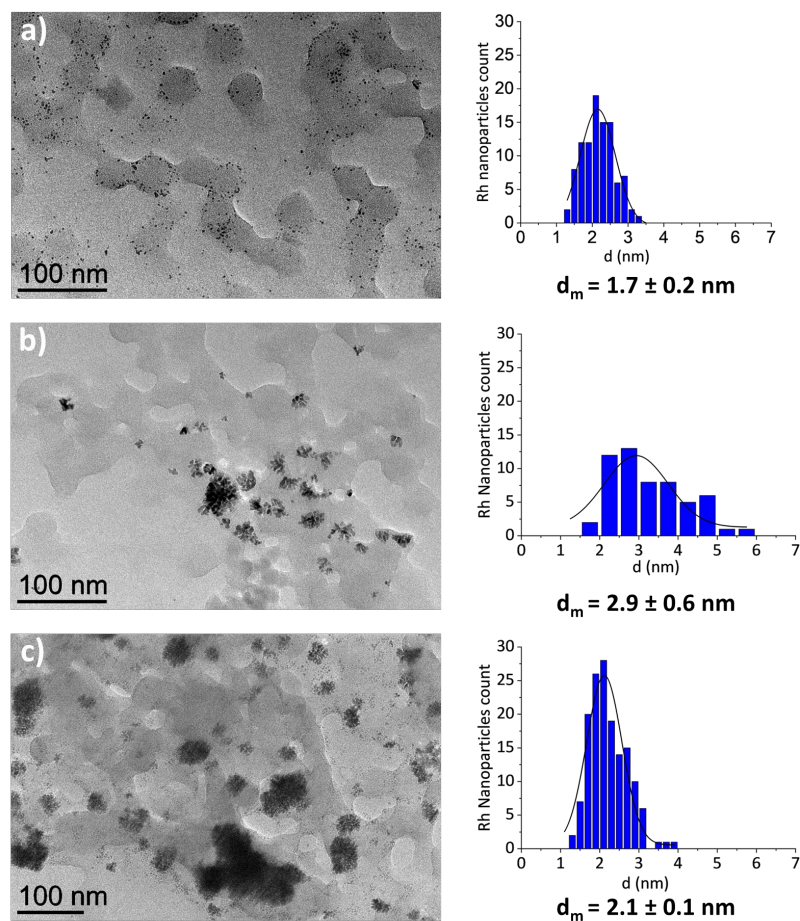
Entry	Base	Molar TPPO/Rh/Base ratio	RhNPs average size (nm)	
			Before catalysis	After catalysis
1	-	4/1/0	1.7 ± 0.2	1.9 ± 0.6
2	Pyridine	4/1/4	2.9 ± 0.6	3.1 ± 0.1
3	NEt <sub>3</sub>	4/1/4	2.1 ± 0.1	1.8 ± 0.2

<sup>a</sup> Reaction conditions: 20 bar H<sub>2</sub>, 20 h, 60 °C, toluene, 1200 rpm.

Transmission electron microscopy (TEM) analyses confirmed the successful incorporation of the RhNPs in the TPPO@CCM-C cores in all cases (Figure 2). The RhNPs synthesized without base (Entry 1) were well-dispersed and showed a narrow size distribution with a mean diameter ( $d_m$ ) of  $1.7 \pm 0.2$  nm. On the other hand, the RhNPs formed in the presence of pyridine or NEt<sub>3</sub> (Entries 2 and 3), were agglomerated and had larger average diameters ( $d_m = 2.9 \pm 0.6$  nm and  $d_m = 2.1 \pm 0.1$



nm, respectively). When using only molecular TPPO (*i.e.*, not linked to the CCM support) as stabilizer under the same reaction conditions (toluene, TPPO/Rh = 4/1, 20 bar H<sub>2</sub>, 20 h, 60 °C, 1200 rpm) and no base additive, a black colloidal suspension of RhNPs was also obtained. These RhNPs were also found to have slightly larger average diameter ( $d_m = 2.4 \pm 0.2$  nm) than those embedded in the TPPO@CCM-C latex obtained without a base and were quite well dispersed (SI, Figure S1). Furthermore, when treating a [Rh(COD)( $\mu$ -Cl)]<sub>2</sub> solution in toluene under H<sub>2</sub> pressure in the absence of any polymer, stabilizer and base, only large agglomerates were produced under the same reaction conditions (SI, Figure S2).



**Figure 2.** TEM images (left) and corresponding RhNP size distribution (right) of the three one-pot synthesized RhNP-TPPO@CCM-C latexes obtained (a) without base, (b) with pyridine and (c) with NEt<sub>3</sub>.

The smaller size of the RhNPs in the TPPO@CCM-C obtained from the base-free procedure may result from a more efficient stabilization in the polymer, due to the combined interaction with the oxygen lone pairs of the TPPO ligands in the CCM-C core and  $\pi$ -electrons of the phenyl groups of the polystyrene chains. The confinement effect may also provide an improved rate of nucleation, resulting in a greater number of NPs and a consequent decrease of their average size.<sup>[42–50]</sup> In principle, the nucleation may predominantly occur either within the CCM cores or in the bulk toluene phase, followed by migration and anchoring within the CCM cores. Since small-sized RhNPs ( $d_m = 2.4 \pm 0.2$  nm) were generated in the presence of molecular TPPO in the toluene phase, even without base, whereas large agglomerates were generated in toluene without stabilizer, it seems likely that faster nucleation occurred within the CCM-C cores that contain TPPO ligands. The reason for the agglomeration of the core-confined RhNPs synthesized in the presence of a base is presently not understood. Anyhow, the best performing latex is the one obtained by the simpler base-free procedure.

Thermogravimetric/differential scanning calorimetry (TG/DSC) analyses of the TPPO@CCM-C and RhNP-TPPO@CCM-C polymers were further performed under N<sub>2</sub> to examine their relative thermal stability (SI, Figure S3). The TPPO@CCM-C showed an initial decomposition peak at 239 °C (*ca.* 20 wt.% loss), followed by a gradual weight loss at higher temperatures with a peak at 413 °C (total weight loss *ca.* 88 wt.%). On the other hand, the RhNP-TPPO@CCM-C exhibited initial degradation at a higher

temperature (peak at 264 °C, ca. 50 wt.% loss) and a lower total weight loss (77 wt.%) with a second peak at 403 °C, suggesting an effect of the RhNPs on the polymer decomposition.

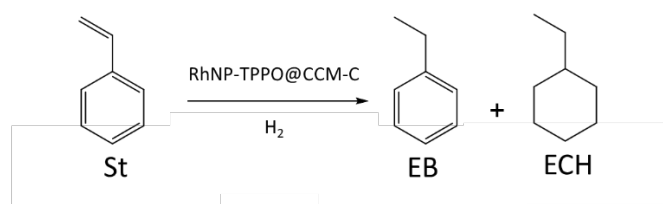
The thermal stability of the RhNP-TPPO@CCM-C was insufficient to perform further investigations of the RhNPs by conventional techniques such as carbon monoxide temperature-programmed desorption (CO-TPD), which requires high temperatures for the CO desorption.<sup>[51,52]</sup> However, X-ray photoelectron spectroscopy (XPS) analyses were performed on the TPPO@CCM-C and RhNP-TPPO@CCM-C systems (SI, Figures S4-S6 and Table S1). Comparison of the two systems indicated a shift in binding energies for the RhNP-TPPO@CCM-C system, which is particularly notable for the O1s excitation ( $\Delta E = 0.58$  eV). This supports the existence of RhNP-polymer interaction in RhNP-TPPO@CCM-C. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of TPPO@CCM-C and RhNP-TPPO@CCM-C were further compared to that of TPPO to examine the RhNPs-polymer interactions (SI, Figure S7). The strong P-C stretching band of TPPO<sup>[53]</sup> at 1120 cm<sup>-1</sup> was visible in both TPPO@CCM-C and in the broad envelope band (1120-1182 cm<sup>-1</sup>) for RhNP-TPPO@CCM-C. The strong P=O stretching band of TPPO<sup>[53]</sup> (1182 cm<sup>-1</sup>) was also quite evident in TPPO@CCM-C and in the RhNP-TPPO@CCM (TPPO/Rh = 4/1). However, a new band (1156 cm<sup>-1</sup>) was also observed in the case of RhNP-TPPO@CCM-C, likely corresponding to a redshifted P=O stretching band of the TPPO bound to the RhNPs surface as also previously

observed for other metal-coordinated TPPO compounds.<sup>[54,55]</sup> This corroborated the existence of interaction between the RhNPs and the core-linked TPPO ligands.

## **Aqueous biphasic hydrogenation with RhNP-TPPO@CCM-C**

### **Hydrogenation of styrene without base additive**

Using the RhNP-TPPO@CCM-C latex produced in the absence of base, an initial series of catalytic runs with different reaction times were carried out with a styrene/Rh ratio of 5000/1 at 25 °C, 20 bar of H<sub>2</sub> and stirring of 1200 rpm to limit external mass transfer (SI, Figure S8). A complete conversion of styrene was reached after 2 h corresponding to an average TOF of 3000 h<sup>-1</sup> (cTOF of 4300 h<sup>-1</sup> based on the RhNP surface atoms). Additional catalytic runs with a fixed reaction time of 0.25 h and different styrene/Rh ratios yielded the results reported in Table 2, Entries 1-3. The system showed excellent selectivity (>99%) towards the formation of ethylbenzene (EB) with formation of only trace amounts of the fully saturated product ethylcyclohexane (ECH). Similar high selectivities were also previously described for styrene hydrogenation using other RhNP-CCM catalysts<sup>[36,37]</sup> and attributed to ultrasmall NPs and extensive RhNP ligand coverage. Moreover, phase separation was fast in all reactions (< 3 min) facilitating product separation and catalyst recovery, in line with observations from other aqueous biphasic catalytic applications featuring CCM nanoreactors with a cationic shell.<sup>[35-37]</sup>



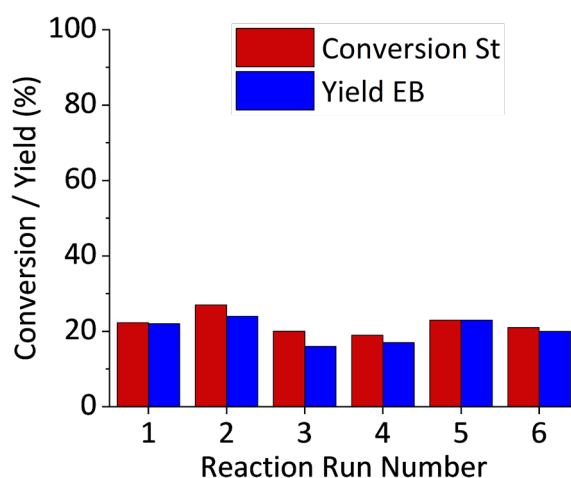
**Table 2.** Hydrogenation of styrene using RhNP-TPPO@CCM-C synthesized without base.<sup>a</sup>

Entry	Molar styrene/Rh ratio	T (°C)	Conversion (%)	Selectivity (%)		TOF / <i>c</i> TOF <sup>b</sup> (h <sup>-1</sup> )
				EB	ECH	
1	2000/1	25	82	>99	<0.1	7800 / 11500
2	5000/1	25	21	>99	<0.1	4500 / 6500
3	10000/1	25	8	>99	<0.1	3000 / 4450
4	5000/1	30	35	>99	<0.1	8000 / 11600
5	5000/1	35	58	>99	<0.1	11200 / 16400
6	5000/1	45	65	>99	<0.1	12900 / 19000
7	5000/1	55	83	>99	<0.1	16100 / 23600

<sup>a</sup> Reaction conditions: 20 bar H<sub>2</sub>, 0.25 h, 1200 rpm. <sup>b</sup> Corrected average TOF (*c*TOF) calculated by considering only the surface Rh atoms (see SI). EB = ethylbenzene, ECH = ethylcyclohexane.

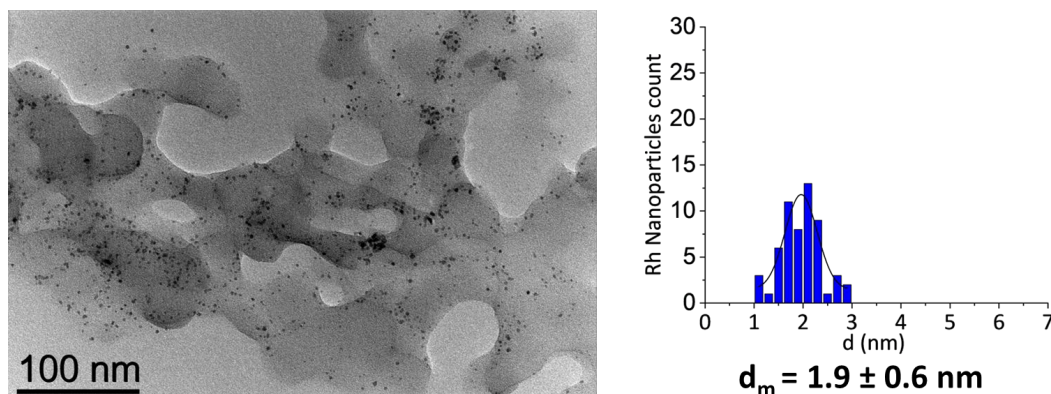
The hydrogenation of styrene was also performed with the same RhNP-TPPO@CCM-C latex at higher temperatures (30–55 °C) with a styrene/Rh ratio of 5000/1 (Table 2, Entries 4–7). At 55 °C, a conversion of 83% was obtained corresponding to a very high average TOF of 16100 h<sup>-1</sup> (*c*TOF of 23600 h<sup>-1</sup>). The more moderate conversions obtained in the 25–35 °C range allowed to estimate an apparent reaction activation energy (*E*<sub>a</sub>) of 69 ± 6 kJ/mol from an Arrhenius plot (SI, Figure S9), which is comparable to the *E*<sub>a</sub> obtained for the gas-phase hydrogenation of styrene.<sup>[56]</sup> However, at higher reaction temperatures the apparent *E*<sub>a</sub> decreased to 4 ± 1 kJ/mol indicating diffusion limitations (internal mass transfer).<sup>[57,58]</sup>

The recycling of the RhNP-TPPO@CCM-C latex was further evaluated for a series of reaction runs (styrene/Rh ratio of 5000/1, 0.25 h) with intermediate product extraction by diethyl ether (Figure 3). The extraction procedure was similar to that previously applied to recycle the RhNP-TPP@CCM-C and RhNP-TPPO@CCM-C latexes,<sup>[35–37]</sup> as well as the latex of the molecular Rh<sup>I</sup>-TPP@CCM.<sup>[35,36]</sup> A rather constant styrene conversion of *ca.* 21%, corresponding to an average TOF of ~4500 h<sup>-1</sup> (cTOF of 6500 h<sup>-1</sup>), was obtained over six consecutive reaction runs when the recovered catalyst system was reactivated with H<sub>2</sub> (20 bar, 1 h, 25 °C) prior to the addition of new batches of substrate. In contrast, erratic results were obtained if recycling was performed without the reactivation treatment possibly because of passivation of the RhNPs by a surface oxide layer formed during the recycling procedure.<sup>[37,42,59]</sup> Notably, the found catalytic activity was significantly higher than previously obtained for the aqueous biphasic hydrogenation of styrene using an analogous *ex-situ* catalyst system (average cTOF of 1440 h<sup>-1</sup>).<sup>[37]</sup>



**Figure 3.** Reuse of RhNP-TPPO@CCM-C in six catalytic runs of styrene hydrogenation with intermediate H<sub>2</sub> treatment (20 bar H<sub>2</sub>, 25 °C, 1 h, 1200 rpm) and product extraction by diethyl ether. Reaction conditions: Styrene/Rh = 5000/1, 20 bar H<sub>2</sub>, 25 °C, 0.25 h, 1200 rpm.

TEM analysis of the recovered latex after the sixth reaction runs (Figure 4) confirmed that the RhNPs remained well-dispersed with a similar mean size ( $d_m = 1.9 \pm 0.6$  nm) as prior to catalysis (see Table 1). Likewise, the inductively coupled plasma mass spectrometry (ICP-MS) analysis conducted on an identical latex (*ex-situ* prepared) after recycling revealed a mere cumulative loss of approximately 2% in catalyst inventory.<sup>[37]</sup> Together, this clearly emphasize the positive effect obtained from the superior interaction between RhNPs and TPPO in comparison to analogous CCM systems such as, e.g., TPP@CCM-C.<sup>[36]</sup>



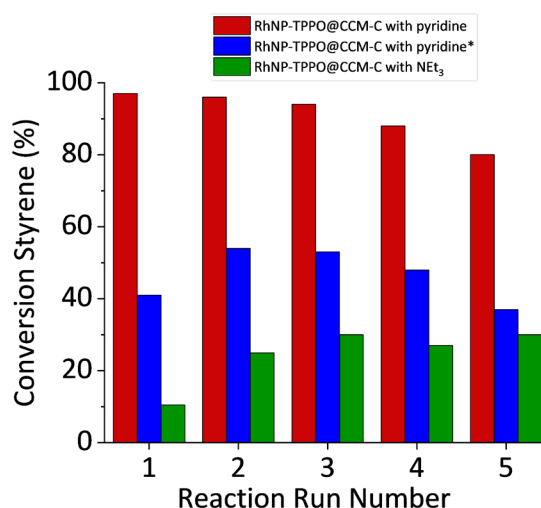
**Figure 4.** TEM image (left) and the corresponding RhNP size distribution ( $d_m = 1.9 \pm 0.6$  nm) (right) of RhNP-TPPO@CCM-C latex after six catalytic runs of styrene hydrogenation with intermediate  $H_2$  treatment and product extraction by diethyl ether (same conditions as Figure 3).

A reference hydrogenation experiment was carried out under the same conditions (styrene/Rh = 10000/1, 20 bar  $H_2$ , 25 °C, 0.25 h) using a toluene phase of the TPPO-stabilized RhNPs as catalyst. This resulted in a styrene conversion of 53% (average TOF of  $\sim 20000$  h<sup>-1</sup>, cTOF of 21500 h<sup>-1</sup>) with >99% of EB selectivity. Using EB as substrate under the same reaction conditions yielded only 0.6% of ECH, confirming the high selectivity of the TPPO-stabilized RhNPs under these mild reaction conditions. The

cTOF decreased from  $\sim 21500 \text{ h}^{-1}$  for the reaction carried out with the RhNP-TPPO/toluene catalytic system to  $\sim 6500 \text{ h}^{-1}$  for that conducted with the RhNP-TPPO@CCM-C/biphasic system, which indicated that the latter was influenced by internal mass transport restrictions of the styrene substrate and/or the EB product.

### Hydrogenation of styrene with base additive

The RhNP-TPPO@CCM-C latexes obtained in the presence of pyridine (Table 1, Entry 2) or  $\text{NEt}_3$  (Table 1, Entry 3) were also evaluated for styrene hydrogenation, after extensive prewashing with diethyl ether prior to the first catalytic run (Figure 5).



**Figure 5.** Reuse of the RhNP-TPPO@CCM-C latexes prepared with base additives in styrene hydrogenation with intermediate  $\text{H}_2$  treatment (20 bar  $\text{H}_2$ , 25 °C, 0.25 h, 1200 rpm) as well as product extraction by diethyl ether. Reaction conditions: Styrene/Rh = 5000/1 (\*6500/1), 20 bar  $\text{H}_2$ , 25 °C, 0.25 h, 1200 rpm.

When using the RhNP-TPPO@CCM-C latex prepared with  $\text{NEt}_3$ , the first catalytic run yielded a styrene conversion of  $\sim 10\%$ , but the subsequent runs converged to a stable conversion of ca. 25-30%. Similar difference between the first and consecutive reaction runs were reported for the RhNP-TPPO@CCM-C latex obtained by transfer of *ex-situ*



synthesized RhNPs<sup>[37]</sup> as well as other studies using NEt<sub>3</sub>.<sup>[42]</sup> This can be attributed to an induction time, possibly resulting from restructuring of the RhNP surface under catalytic conditions, which produced more catalytically active sites and consequently led to higher conversions. On the other hand, the RhNP-TPPO@CCM-C latex prepared with pyridine showed a much higher activity (conversion of *ca.* 97%), with an average TOF of ~18200 h<sup>-1</sup> (cTOF of 40000 h<sup>-1</sup>) in the first run. However, the activity steadily decreased over the subsequent runs, most likely as a consequence of the continuous removal of adsorbed pyridine from the RhNP surface during the successive recycling extractions with diethyl ether. This result is analogous to that of the RhNP-TPPO@CCM-C latex obtained by incorporating the *ex-situ* synthesized RhNPs with stabilization by TPP and pyridine,<sup>[37]</sup> thus confirming that the presence of pyridine has a beneficial effect on the catalytic activity of the RhNPs. The reason for this promotion effect is currently unknown. Interestingly, when the catalyst recycling was performed with a higher styrene/Rh ratio of 6500/1, the activity dropped in the first run (as expected) to an average TOF of ~10000 h<sup>-1</sup> (cTOF of 23000 h<sup>-1</sup>), and the system proved less stable compared to the RhNP-TPPO@CCM-C synthesized in one-pot without base (Figure 5). Additionally, TEM analyses of the recovered latexes synthesized in the presence of pyridine or NEt<sub>3</sub> (SI, Figure S10) showed dispersions and RhNP size distributions after the fifth catalytic runs ( $3.1 \pm 0.1$  nm with pyridine,  $1.8 \pm 0.2$  nm with NEt<sub>3</sub>) similar to those observed prior to the first catalytic runs ( $2.9 \pm 0.6$  nm with pyridine,  $2.1 \pm 0.1$  nm with NEt<sub>3</sub>) (see Figure 2).

## Hydrogenation of styrene in the presence of Hg

To validate that RhNPs were the only catalytically active species in the RhNP-TPPO@CCM-C latex, a styrene hydrogenation experiment was also conducted in the presence of a substantial excess of Hg (styrene/Hg/Rh = 5000/500/1, 20 bar H<sub>2</sub>, 25 °C, 0.25 h, 1200 rpm), as the metal is known to poison and deactivate RhNPs both not Rh<sup>I</sup> species.<sup>[60]</sup> As expected, the observed styrene conversion was negligible (< 0.1%) confirming the absence of catalytically active Rh<sup>I</sup> species in the TPPO@CCM-C core.

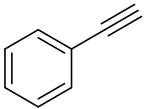
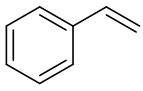
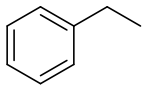
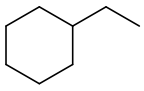
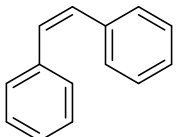
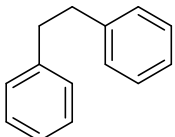
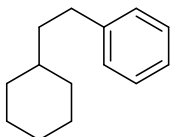
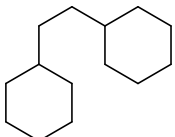
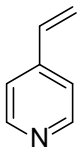
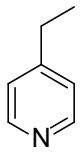
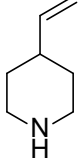
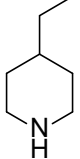
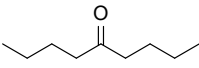
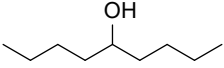
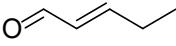
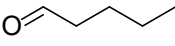
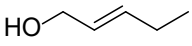
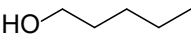
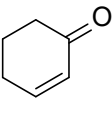
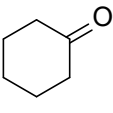
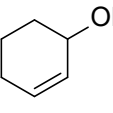
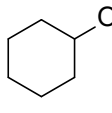
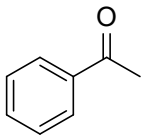
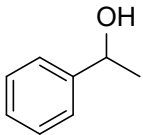
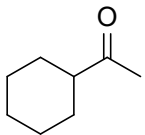
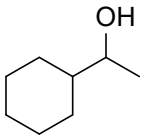
TEM analysis of the recovered latex after the catalytic run with Hg (Figures S11 and S12) still showed the presence of small RhNPs in the polymer, but with a larger average diameter ( $d_m = 2.7 \pm 0.1$  nm) than prior to catalysis ( $1.7 \pm 0.2$  nm) along with much larger particles (average size  $16 \pm 5$  nm) that can be attributed to nanoscopic Hg droplets. The increase in apparent size of the RhNPs could result from the formation of a Hg-Rh amalgam at the RhNP surface.<sup>[60,61]</sup> In line with this showed high-resolution (HR) TEM analyses coupled with energy-dispersive X-ray spectroscopy (EDX) on the spent latex after the poisoning the presence of Hg along with RhNPs and well-identified signals for P and I from the polymer (SI, Figure S12). This result also substantiates that Hg is able to cross the CCM hydrophilic shell.

## Hydrogenation of other substrates

Lastly, the applicability of the RhNP-TPPO@CCM-C latex synthesized without base was screened for the aqueous biphasic hydrogenation of other substrates, including aromatics, alkenes, alkynes and carbonyl compounds. The screening conditions for

the alternative substrates were selected to align with the full conversion of styrene (substrate/Rh = 5000/1, 20 bar H<sub>2</sub>, 25 °C, 2 h, 1200 rpm) with neat substrate and not optimized (Table 3). This approach served to assess the catalyst efficacy with respect to different substrate within a consistent experimental framework.

**Table 3.** Aqueous biphasic hydrogenation of aromatics, alkenes, alkynes and carbonyl substrates using Rh-TPPO@CCM-C.<sup>a</sup>

Entry	Substrate / Conversion (%) <sup>b</sup>	Products / Selectivity (%) <sup>b</sup>				$\epsilon$ TOF (h <sup>-1</sup> )
1	 30	 77.6	 22.4	 <0.1	1100	
2	 <0.1	 nd	 nd	 nd	2.5	
3	 79	 96.8	 nd	 nd	3200	
4	 <0.1	 nd				2.5
5	 <0.1	 nd	 nd	 nd	2.5	
6	 27	 1.4	 34.9	 63.7	1000	
7	 86	 >99	 <0.1	 <0.1	3000	

<sup>a</sup> Reaction conditions: Substrate/Rh = 5000/1, 20 bar H<sub>2</sub>, 25 °C, 2 h, 1200 rpm. <sup>b</sup> Conversions and selectivities determined by GC-FID. Product identification confirmed by <sup>1</sup>H NMR (Entries 4 and 5) and GC-MS (Entry 3). nd = not detected.

The results confirmed a rather high hydrogenation activity (average TOFs of 1100-3200 h<sup>-1</sup>) and high chemoselectivity towards the reduction of both double and triple carbon-carbon bonds in phenylacetylene (Entry 1) and 4-vinylpyridine (Entry 3). The catalytic activity was, however, significantly lower than for styrene under similar reaction conditions (cTOF of 4300 h<sup>-1</sup>; see Table 1) and for this reason the product selectivity towards EB (22.4%) in the former reaction was also lower than found for the reaction with styrene (>99%, Figure S8). The lower activity of the catalyst may reflect a relatively stronger interaction of the alkyne substrate to the surface of the RhNP hampering access of styrene to the active sites. Highly sterically hindered *Z*-stilbene (Entry 2) and the aliphatic  $\alpha,\beta$ -unsaturated substrate (*E*)-hex-2-enal (Entry 5) were only hydrogenated to a low extent under the applied conditions. Also, the carbonyl group of the aliphatic compound 5-nonanone (Entry 4) was hardly hydrogenated, whereas the cyclic (and activated)  $\alpha,\beta$ -unsaturated substrate 2-cyclohexen-1-one (Entry 6) yielded a good conversion (cTOF of 1000 h<sup>-1</sup>) with high selectivity (63.7%) to cyclohexanol, and acetophenone (Entry 7) showed an even higher conversion (cTOF of 3000 h<sup>-1</sup>), with a nearly quantitative selectivity toward phenylethanol (>99%). Notably, no significant hydrogenation of the aromatic ring was observed in any of the reactions.

Overall, the outcomes of the screening, albeit non-optimized, distinctly highlight the capacity of the RhNP-TPPO@CCM-C catalyst synthesized without base, for the hydrogenation of unsaturated substrates beyond styrene. Nonetheless, variations in

catalyst activity may be influenced by differences in substrate solubility in the polystyrene core and their adsorption on the RhNPs surface, but comprehensive investigation into these factors exceeds the scope of the current study.

## Conclusions

A RhNP-TPPO@CCM-C latex was successfully synthesized by one-pot reduction of  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]/\text{toluene}$  in the presence of an aqueous TPPO@CCM-C latex in absence of additional stabilizers and base. The produced RhNPs were smaller in size ( $d_m = 1.7 \pm 0.2$  nm) than their analogs synthesized under similar conditions but in the presence of only TPPO as stabilizer ( $d_m = 2.4 \pm 0.2$  nm). This difference underlines the positive confinement effect on the RhNPs size, which leads to smaller NPs. The RhNP-TPPO@CCM-C catalyst demonstrated under mild conditions (20 bar  $\text{H}_2$ , 25-55 °C) higher catalytic activity for aqueous biphasic styrene hydrogenation (cTOFs of 4500-16000  $\text{h}^{-1}$ ) than what was previously reported for RhNP in CCMs along with complete selectivity towards EB. The catalyst was also applicable to the hydrogenation of other unsaturated substrates under similar reaction conditions, including alkynes and carbonyl compounds. Importantly, the facile one-pot synthesis procedure and the stable anchoring of the RhNPs to the core TPPO ligands circumvented RhNP leaching during product separation by diethyl ether extractions as reported earlier,<sup>[36]</sup> thus making the RhNP-TPPO@CCM-C latex highly attractive for aqueous biphasic catalysis with catalyst recycling. Further investigations will focus on understanding

and improving the hydrogenation performance of this RhNP-TPPO@CCM-C catalytic system (*e.g.*, by employing vectorizing solvents), and on expanding the scope to the confinement of other metal NPs and to the hydrogenation of other substrates.

## Experimental section

### Materials and methods

Chloro(1,5-cyclooctadiene)rhodium(I) dimer ( $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$ , >98%, Sigma-Aldrich), triphenylphosphine oxide (TPPO, >98%, Sigma-Aldrich), pyridine (anhydrous, >99.8%, Sigma-Aldrich), triethylamine ( $\text{NEt}_3$ , >99.5%, Sigma-Aldrich), toluene (99%, Sigma-Aldrich; dried on SPS), styrene (St, >99%, Sigma-Aldrich), mercury (Hg, 99.9999 Suprapur®, Sigma-Aldrich; note: Hg should be handled with the utmost care, using proper safety precautions), phenylacetylene (98%, Sigma-Aldrich), *cis*-stilbene (96%, Sigma-Aldrich), 4-vinylpyridine (95%, Sigma-Aldrich), 5-nonanone (98%, Sigma-Aldrich), *trans*-2-hexen-1-al (98%, Sigma-Aldrich), 2-cyclohexan-1-one ( $\geq 95\%$ , Sigma-Aldrich) and  $\text{H}_2$  (99.999%, Air Liquid Denmark) were used as received.

The TPPO@CCM-C latex ( $\text{R}_0\text{-(4VPMe}^+\text{I)}_{140}\text{-}b\text{-St}_{50}\text{-}b\text{-(St}_{0.9}\text{-CO-SDPPO}_{0.1})_{300}\text{-}b\text{-(St}_{0.9}\text{-CO-DEGDMA}_{0.1})_{150}\text{-SC(S)SnPr}$ ) was synthesized as described previously<sup>[37]</sup> from 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) or  $\text{R}_0\text{-SC(S)SnPr}$  ( $\text{R}_0 = \text{C}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{COOH}$ ), 4-vinylpyridine, and (4-styryl)diphenylphosphine oxide (SDPPO) (51.1  $\mu\text{mol}$  of TPPO per mL of latex), and had a polymer content of 12.3 wt.%.

The autoclaves used for the RhNP syntheses and for the hydrogenation catalyses had a volume of 15 mL and were homebuilt. All catalytic reactions were performed under an inert atmosphere of dry argon (99.999%, Air Liquide Denmark), and the results reproduced within  $\pm 5$  %.

## Characterization and analysis techniques

Morphological analyses of the copolymer nanomaterials and of the RhNP latexes were carried out by TEM on a JEOL JEM 1400 transmission electron microscope working at 120 kV (Centre de Microcaractérisation Raimond Castaing, UAR 3623, Toulouse, France). Diluted aqueous samples were dropped on a formvar/carbon-coated copper grid and dried under vacuum for 24 h before analysis.

XPS analyses of the RhNP latexes were performed using a Thermo Scientific system at room temperature using AlK $\alpha$  radiation (1484.6 eV) and a spot size of 400  $\mu\text{m}$ . A flood gun was used to reduce sample charging effects and the obtained spectra were further corrected by setting the C 1s binding energy at 284.8 eV. Data processing was done using the Avantage 5.948 software.

TG analysis and DSC of samples were carried out on a Mettler Toledo TGA/DSC 3+ instrument under an N<sub>2</sub> gas flow. Freeze-dried samples were placed into an alumina crucible and then heated from 25 to 800 °C at a heating rate of 10 °C/min.

FTIR spectra of freeze-dried samples were measured using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with diamond ATR mode. Each measurement consisted of an average of two scans ( $600\text{--}4000\text{ cm}^{-1}$ ) with background correction.

Liquid nuclear magnetic resonance (NMR) spectra were recorded in 5 mm diameter tubes at 25 °C on Bruker Avance III 300 or 400 MHz spectrometers. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were determined using the residual peak of the deuterated solvent as internal standard and are reported in ppm ( $\delta$ ) relative to tetramethylsilane.

Quantitative determination of products and residual substrates in the organic phases after catalysis were conducted by gas chromatography (GC) using an Agilent 6890N gas chromatograph equipped with a HP-5MS capillary column ( $30\text{ m} \times 250\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$ ) and a flame ionization detector (FID), using He (99.999%, Air Liquide Denmark) as carrier gas. The peak assignments were assisted by independent gas chromatography-mass spectrometry (GC-MS) analyses using an Agilent 6850-5975C system.

## One-pot synthesis of RhNP-TPPO@CCM-C

### Synthesis without added base

The TPPO@CCM-C latex<sup>[37]</sup> (1 mL, 51.1  $\mu\text{mol}$  of TPPO ligands) was dispersed in water (4 mL). Then toluene was added (4 mL) and the suspension was vigorously stirred for 15 min to swell the CCM-C cores. Afterwards, a toluene solution (3.2 mL) with  $[\text{Rh}(\text{COD})(\mu\text{-Cl})_2]$  (3.6 mg, 7.43  $\mu\text{mol}$ ) was added, and the mixture was magnetically



stirred (1200 rpm) for 5 min before transferring to a glass vial (40 x 20 mm), which was placed into an autoclave. The autoclave was then charged with 20 bar of H<sub>2</sub> and positioned in an aluminum heating block at 60 °C. After stirring for additionally 20 h, the autoclave was carefully depressurized and the colorless transparent toluene (top phase) removed from the vial by decantation. The remaining aqueous black latex was then used for catalysis.

### **Syntheses with added base**

Identical procedures to that of the previous section were carried out with the addition of [Rh(COD)(μ-Cl)]<sub>2</sub> (3.6 mg, 7.43 μmol) and either pyridine (2.9 mg, 37 μmol) or triethylamine (3.71 mg, 37 μmol) after the CCM-C core swelling. The resulting latexes were washed with diethyl ether (3 × 1 mL) prior to catalysis.

### **Hydrogenation catalysis**

#### **Aqueous biphasic hydrogenation with RhNP-TPPO@CCM-C**

To the prepared RhNP-TPPO@CCM-C latexes (1 mL, 10.1 μmol of TPPO ligands, 1.8 μmol of Rh) were added the desired amounts of substrate (see Results and Discussion section) and decane (internal standard) in glass vials. The vials were placed inside an autoclave that was charged with 20 bar of H<sub>2</sub> and positioned in an aluminum heating block at the desired temperature with magnetic stirring (1200 rpm) using a cross bar. After the set time, the stirring was stopped and the autoclave slowly vented. Then, the vials were removed and the reaction mixture allowed to phase separate. After

complete phase separation (ca. 1 min) and removal of the top organic phase, the latex was extracted with diethyl ether ( $3 \times 0.3$  mL), applying 5 min of stirring (1200 rpm) followed by 5 min for phase separation without stirring for each extraction (these operations were carried out in air). Lastly, the combined organic phases were analyzed by GC and the catalyst activity was calculated as turnover frequency (TOF) and as corrected TOF (cTOF), the latter being based on the Rh surface atoms only (see SI for details).

### Catalyst recycling experiments

After the extraction treatment that followed each hydrogenation run, the vials containing the RhNP-TPPO@CCM-C latex were charged with a new batch of substrate for a next catalytic run (see the Results and Discussion section for the reaction conditions and stoichiometries). Afterwards, the product recovery and analysis were done according to the protocol described above for the hydrogenation experiments.

### Catalyst poisoning experiment

Mercury (Hg) was added to a reaction vial containing the RhNP-TPPO@CCM-C latex (1 mL, 10.1  $\mu\text{mol}$  of TPPO ligands, 1.8  $\mu\text{mol}$  of Rh) in a large excess (Hg/Rh = 500/1) and stirred (1200 rpm) at 25 °C for 5 h. Afterwards, the vial was charged with styrene (St/Rh = 5000/1) under argon and placed in the autoclave. Then, the autoclave was charged with 20 bar of H<sub>2</sub> and positioned in an aluminum heating block at 25 °C and stirred (1200 rpm, cross bar) for 0.25 h. After the set time, the product recovery and

analysis were carried out according to the same protocol described above for the hydrogenation experiments.

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## Contribution of Authors

**Chantal J. Abou-Fayssal:** Investigation, Visualization, Writing - Original Draft.

**Leonhard Schill:** Investigation, Writing - Review & Editing. **Rinaldo Poli:** Funding acquisition, Conceptualization, Writing - Review & Editing. **Eric Manoury:**

Conceptualization, Resources, Supervision, Writing - Review & Editing. **Karine**

**Philippot:** Conceptualization, Resources, Supervision, Writing - Review & Editing.

**Anders Riisager:** Conceptualization, Methodology, Resources, Supervision, Writing - Review & Editing.

## Conflicts of Interest

The authors declare no conflict of interest.

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