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PAPER

Organic carbonates as stabilizing solvents for transition-metal nanoparticles†

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Biodegradable, non-toxic, “green” and inexpensive propylene carbonate (PC) solvent is shown to function as a stabilizing medium for the synthesis of weakly-coordinated transition-metal nanoparticles. Kinetically stable nanoparticles (M-NPs) with a small and uniform particle size (typically $<5 \pm 1$ nm) have been reproducibly obtained by easy, rapid (3 min) and energy-saving 50 W microwave irradiation under an argon atmosphere from their metal–carbonyl precursors in PC. The M-NP/PC dispersions are stable for up to three weeks according to repeated TEM studies over this time period. The rhodium nanoparticle/PC dispersion is a highly active catalyst for the biphasic liquid–liquid hydrogenation of cyclohexene to cyclohexane with activities of up to and 1875 (mol product) (mol Rh)⁻¹ h⁻¹ and near quantitative conversion at 4 to 10 bar H₂ and 90 °C. From the PC dispersion the M-NPs can be coated with organic capping ligands such as 3-mercaptopropionic acid or trioctylphosphine oxide for further stabilization.

Introduction

Organic carbonates, such as dimethyl carbonate, diethyl carbonate, ethylene carbonate or propylene carbonate (PC) (Fig. 1) are polar solvents which are available in large amounts and at low prices, have a large liquid temperature range (for PC mp. -49 °C, bp. 243 °C), are of only low (eco)toxicity and are completely biodegradable.¹ Propylene carbonate (PC) is an aprotic, highly dipolar solvent, which has a low viscosity^{2,3} and is considered a *green* solvent because of its low flammability, volatility and toxicity.⁴

Organic carbonates are recognized as solvents in industrial applications such as cleaning, degreasing, paint stripping, gas treating, and textile dyeing.⁵ Yet, so far organic carbonates are used primarily for extractive applications and as solvents in electrochemistry.¹ PC is used as a solubilizer and co-solvent in cosmetics,⁶ in the FLUOR process for the removal of carbon dioxide from natural gas streams in the oil industry,⁷ in lacquer⁸ and BASF is using PC for waste removal in the copper wire-coating process.⁹ PC is also investigated for Li-ion battery research.^{10,11}

Here we show that PC can function as a solvent for metal nanoparticle synthesis and stabilization without the need for additional capping ligands. Metal nanoparticles (M-NPs) are of

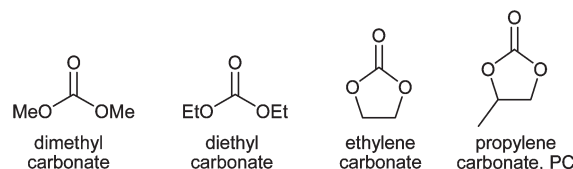


Fig. 1 Selected organic carbonates.

significant interest for technological applications in several areas of science and industry, especially in catalysis due to their high activity.^{12–15} The controlled and reproducible synthesis of defined and stable M-NPs with a small size distribution is important.^{16–20} Very small M-NPs tend to aggregate because of their high surface energy and large surface area. To avoid this agglomeration, M-NPs need to be stabilized either by organic donor ligands,^{21–24} ionic liquids^{15,25–27} or by deposition on solid supports.^{28–30}

Reports on metal nanoparticles in organic carbonates are rare and appear to be of accidental coincidence for Pd-NPs.^{31–34} Here we demonstrate that PC can generally stabilize small M-NPs (<5 nm).

Results and discussion

M-NP synthesis and characterization

The metal carbonyl Mo(CO)₆, W(CO)₆, Re₂(CO)₁₀, Fe₂(CO)₉, Ru₃(CO)₁₂, Os₃(CO)₁₂, Co₂(CO)₈, Rh₆(CO)₁₆ or Ir₄(CO)₁₂ was dissolved/suspended under an argon atmosphere in dried and deoxygenated propylene carbonate (PC). Complete decomposition by microwave irradiation of the metal carbonyl in PC was

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achieved after only 3 min using a low power of 50 W under argon (Fig. 2).

The resulting orange-red Os-, yellow Mn- and W-, and dark-brown to black Mo-, Re-, Ru-, Co-, Rh- and Ir-NP dispersions were reproducibly obtained through the microwave decomposition route. Complete $M_x(CO)_y$ decomposition from short, 5 min microwave irradiation was verified by infrared spectroscopy with no (metal-)carbonyl bands between 1800 and 2000 cm^{-1} being observed any more after the microwave treatment (Fig. 3).

The resulting M-NPs were analyzed by transmission electron microscopy (TEM; Fig. 4–6), selected area electron diffraction (SAED), and dynamic light scattering (DLS) for their size and

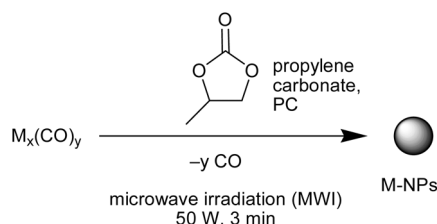


Fig. 2 Microwave decomposition of metal carbonyls to M-NPs in PC.

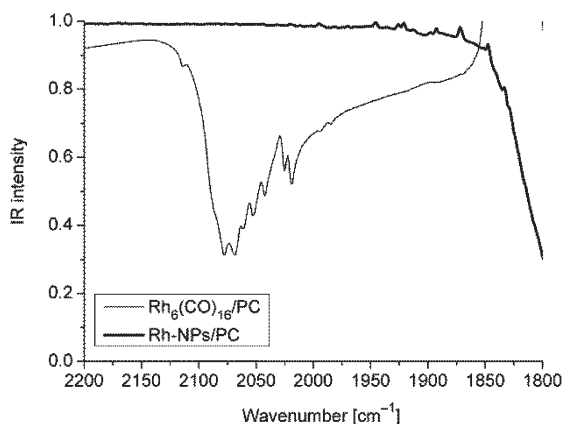


Fig. 3 IR-spectra of $\text{Rh}_6(\text{CO})_{16}/\text{PC}$ (light curve) and the resulting Rh-NP (0.5 wt%)/PC-dispersion (bold curve) after microwave treatment (50 W, 3 min).

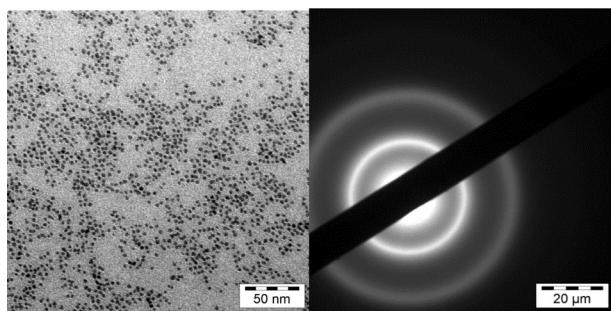


Fig. 4 TEM (left) and SAED (right) of Ru-NPs in PC from $\text{Ru}_3(\text{CO})_{12}$ (entry 5 in Table 1). The black bar is the beam stopper. The diffraction rings at (\AA) 2.10 (very strong), 1.61, 1.26, 1.15 (all weak) match with the d-spacing of the Ru-metal diffraction pattern (see Table S3†).

size distribution (Table 1). SAED patterns do not show reflections indicative of a very crystalline material. We therefore conclude that the particles obtained from the synthesis are amorphous M-NPs stabilized by PC. Still the diffraction rings match the known d-spacing of the respective metal diffraction pattern (see Tables S3–S5 in ESI†).

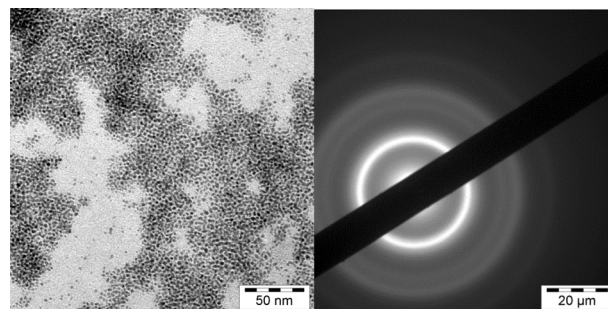


Fig. 5 TEM (left) and SAED (right) of Rh-NPs in PC from $\text{Rh}_6(\text{CO})_{16}$ (entry 8 in Table 1). The black bar is the beam stopper. Diffraction rings at (\AA) 2.23 (very strong), 1.94 (strong), 1.39, 1.17 and 0.89 (weak) match the d-spacing of the Rh-metal diffraction pattern (see Table S4†).

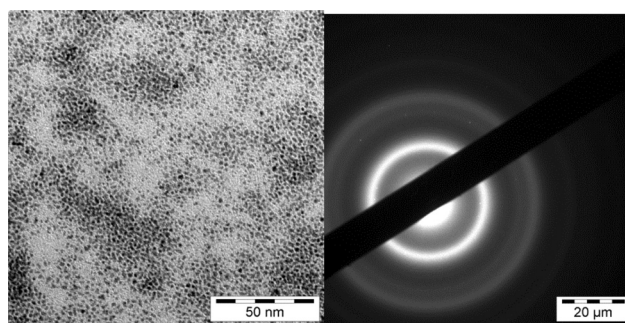


Fig. 6 TEM (left) and SAED (right) of Ir-NPs in PC from $\text{Ir}_4(\text{CO})_{12}$ (entry 10 in Table 1). The black bar is the beam stopper. The diffraction rings at (\AA) 2.25 (strong), 1.38 and 1.20 (weak) match with the d-spacing of the Ir-metal diffraction pattern (see Table S5†).

Table 1 M-NP size and size distribution in PC^a

Entry	Metal carbonyl	TEM $\bar{\phi}$ (σ) ^b [nm]	DLS $\bar{\phi}$ (σ) ^b [nm]
1	$\text{Mo}(\text{CO})_6$	2.2 (± 0.5)	3.5 (± 1.1)
2	$\text{W}(\text{CO})_6$	2.9 (± 0.6)	3.7 (± 1.4)
3	$\text{Re}_2(\text{CO})_{10}$	<1	1.4 (± 0.5)
4	$\text{Fe}_2(\text{CO})_9$	2.4 (± 0.9)	3.2 (± 0.8)
5	$\text{Ru}_3(\text{CO})_{12}$	2.7 (± 0.5)	2.6 (± 0.8)
6	$\text{Os}_3(\text{CO})_{12}$	3.0 (± 1.5)	4.0 (± 1.2)
7	$\text{Co}_2(\text{CO})_8$	6.1 (± 7.4)	6.7 (± 2.2)
8	$\text{Rh}_6(\text{CO})_{16}$	2.1 (± 0.6)	2.4 (± 0.8)
9	$\text{Rh}_6(\text{CO})_{16}^c$	3.2 (± 1)	—
10	$\text{Ir}_4(\text{CO})_{12}$	1.3 (± 0.5)	6.0 (± 1.6)
11	$\text{Ir}_4(\text{CO})_{12}^c$	1.5 (± 0.4)	—

^a 0.5 wt% M-NP/PC dispersions obtained by MWI with 50 W for 3 min unless noted otherwise. ^b Median diameter ($\bar{\phi}$) and standard deviation (σ). See experimental section for TEM and DLS measurement conditions. ^c 1 wt% M-NP/PC dispersion by MWI with 50 W for 5 min; see Fig. S1 and S2 in ESI for TEM pictures.

The hydrodynamic radius from DLS is roughly two to three times the size of the pure kernel cluster. For very small M-NPs (<1 nm) the size of the hydrodynamic radius was measured to be more than three times the radius found from TEM. The median M-NP diameter for the microwave-synthesized Mo-, W-, Re-, Ru-, Os-, Rh- and Ir-NPs at 0.5 wt% of M-NPs in PC was between <1 and 3.0 nm, with a narrow size distribution (TEM data in Table 1). No extra stabilizers or capping molecules are needed to achieve this small particle size. It is, at present, not trivial to routinely and easily prepare uniform nanoparticles in the size range between <1 and 3 nm without strong capping ligands. For the magnetic Fe-NPs and Co-NPs the median diameter was somewhat larger with 2.4 and 6.1 nm, respectively. For Rh- and Ir-NPs also 1 wt% M-NP dispersions were prepared and by comparison the higher metal concentrations give larger particles. The M-NP/PC dispersions are stable for up to three weeks according to repeated TEM measurements over this time period.

Less-noble M-NPs in PC will be oxidized when exposed to air whereas noble M-NPs (Rh, Ir) can be air stable, as seen before for M-NPs in ionic liquids.^{25c-e}

Hydrogenation of cyclohexene and 1-hexyne

Organic carbonates have recently been used as solvents in catalysis, e.g., for platinum-catalyzed hydrosilylation of unsaturated fatty acid esters³⁵ in Pd-catalyzed substitution reactions,³⁶ regioselective rhodium-catalyzed hydroformylation³⁷ and in the asymmetric iridium-catalyzed hydrogenation of olefins.^{2,38} Palladium colloids in PC were used to hydrogenate dienes and alkynes^{31,32} and for Heck-reactions.³³ The weak interactions between a nanoparticle and organic carbonates could be of interest to develop more efficient catalyst processes.

Here we tested the Rh-NP/PC dispersions for their catalytic activity in the biphasic liquid–liquid hydrogenation of cyclohexene to cyclohexane (Fig. 7, Table 2). The low miscibility of substrates and products with the PC phase allows for easy separation by simple decantation of the hydrophobic phase. Cyclohexene was chosen as a substrate since it presents a challenge because of

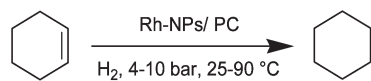


Fig. 7 Hydrogenation of cyclohexene to cyclohexane with Rh-NPs.

Table 2 Hydrogenation of Rh-NPs/PC with different substrates^a

Entry	Substrate	<i>t</i> [min]	<i>p</i> _{H2} [bar]	<i>T</i> [°C]	Conversion [%]	Activity [mol product × (mol Rh) ⁻¹ × h ⁻¹]
1	Cyclohexene	108	4	75	95 ^c	590
2	Cyclohexene	34	4	90	95 ^c	1875
3	Cyclohexene	61	10	25	95 ^c	1045
4	1-Hexyne ^b	104	10	25	88	51
5	Cyclohexene ^d	1440 (= 24 h)	4	90	0	0

^a 10 mL (0.1 mol) cyclohexene or 1.0 mL (1.8 mmol) 1-hexyne; 0.75 mL of the Rh-NP/PC dispersion with 1 wt% Rh (9 mg, 8.8 × 10⁻⁵ mol Rh).
^b 1 mL *n*-decane was added to provide a biphasic liquid–liquid catalytic system. No *n*-hexene detected by GC analysis see experimental section. ^c The reaction was intentionally stopped at 95 or 88% conversion as thereafter the decrease in cyclohexene concentration lowered the reaction rate (see Fig. S7 in ESI). ^d Hydrogenation was carried out with Rh/SR-NPs (see Table 3, entry 3).

its low solubility in PC and is an intermediate in the hydrogenation of benzene to cyclohexane.^{39,40}

For activity comparison Tables S6 and S7 in ESI† summarize related hydrogenation activities for cyclohexene and 1-hexyne with M-NPs in ILs and on supports from the literature. Activities for cyclohexene hydrogenations with Rh-NPs/PC were twice as good than for Ru- or Rh-NP catalysts in ILs,^{26,41,42} but not as good as for Rh-NPs on supports^{30,43,44} (Table S5 in ESI†). The lower hydrogenation activities of Ru- and Rh-NPs in ILs are traced to the IL diffusion barrier for H₂ and the substrate. Ligand-free NPs on supports have a lower diffusion barrier, hence, higher activity.³⁰

Rh- and Ru-NPs surface capping

The addition of an organic ligand to the bare M-NP surface is generally described as a surface functionalization. However derivatization, coating or capping are better terms.⁴⁵ The post synthetic introduction of an organic capping ligand on the dispersed M-NPs in PC is possible. Surface capping of Rh- or Ru-nanoparticles dispersed in the propylene carbonate was carried out here with 3-mercaptopropionic acid, HS-(CH₂)₂-COOH or trioctylphosphine oxide (TOPO). Both 3-mercaptopropionic acid⁴⁵ and TOPO^{46,47} are well-known stabilizing reagents and both are soluble in propylene carbonate. The transformation of M-NP/PC to M-NP/HS-(CH₂)₂-COOH or M-NP/TOPO was done by treating the M-NP/PC dispersion with an excess of HS-(CH₂)₂-COOH or TOPO at room temperature over night. The strong affinity between the thiol (-SH) or phosphine oxide (-P=O) group and the rhodium or ruthenium nanoparticles replaces the PC protective layer. The ligand-capped nanoparticles are significantly larger (Table 3, Fig. 8 and 9, see Fig. S3–S6 in ESI† for additional TEM pictures).

The use of a protic organic thiol ligand and the unpolar TOPO ligand more than doubles the size of the resulting capped metal nanoparticles (Table 3). The aggregation is a result of the introduction of the capping ligands into the polar PC network. Subsequently the stabilizing property of propylene carbonate towards the M-NPs is weakened and results in further M-NP agglomeration which is driven by the surface–surface interactions.

Conclusion

We describe here a simple, reproducible, and broadly applicable microwave-induced metal carbonyl decomposition for the

Table 3 Ligand capped M-NP size and size distribution

Entry	Metal	Ligand	M-NP/PC original size from TEM [nm]	M-NP/ligand in PC	
				TEM $\bar{\phi}$ (σ) ^a [nm]	DLS $\bar{\phi}$ (σ) ^{a,b} [nm]
1	Rh	HS-(CH ₂) ₂ -COOH	2.1 (\pm 0.6)	9 (\pm 5)	24 (\pm 17) ^c
2	Rh	TOPO		10 (\pm 5)	30 (\pm 14) ^d
3	Ru	HS-(CH ₂) ₂ -COOH	2.7 (\pm 0.5)	13 (\pm 4)	6.0 (\pm 1.5) ^c
4	Ru	TOPO		13 (\pm 5)	37 (\pm 12) ^d

^a Median diameter ($\bar{\phi}$) and standard deviation (σ). See experimental section for TEM and DLS measurement conditions. ^b Hydrodynamic radius, median diameter from the measurements at 633 nm. The resolution of the DLS instrument is 0.6 nm. ^c Measurement performed in ethanol. ^d Measurement performed in chloroform.

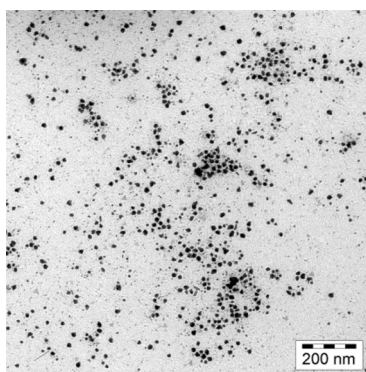


Fig. 8 TEM of Rh-NP/HS-(CH₂)₂-COOH from propylene carbonate after thiolation with 3-mercaptopropionic acid, centrifugation and re-dispersion in ethanol.

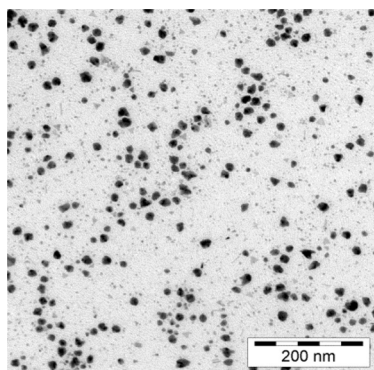


Fig. 9 TEM of Rh-NP/TOPO from propylene carbonate after stabilization with TOPO, centrifugation and re-dispersion in chloroform.

synthesis of common transition-metal nanoparticles in propylene carbonate, PC. The M-NP sizes of about 1 to 3 nm for most of these transition-metal nanoparticles are very small and uniform with no extra stabilizers or capping molecules needed to achieve this small particle size in a stable M-NP/PC dispersion. Polar organic carbonates are susceptible for microwave irradiation which, thus, provides a very simple and reproducible way for the rapid (3 min) and energy-saving (50 W power) synthesis of defined and very small M-NPs from their binary metal-carbonyl complexes in PC. The obtained Rh-NP/PC dispersions can be used – without further treatment – as highly active hydrogenation catalysts. In comparison to ionic liquids, PC and other organic

carbonates are established industrial and low-priced solvents.⁴ PC appears as an attractive alternative for weakly coordinated, albeit sufficiently stabilized metal nanoparticles.

Experimental section

Materials and instrumentation for M-NP synthesis: Mo(CO)₆, W(CO)₆, Re₂(CO)₁₀, Fe₂(CO)₉, Ru₃(CO)₁₂, Os₃(CO)₁₂, Co₂(CO)₈, Rh₆(CO)₁₆, and Ir₄(CO)₁₂ were obtained from Strem and Aldrich, racemic propylene carbonate (PC) from Sigma-Aldrich (purity 99.7%, H₂O free). Cyclohexene (>99%), 1-hexyne (>97%), 3-mercaptopropionic acid (>99%), *n*-decane (p.a., purity >99.5%) and trioctylphosphine oxide (99%) were obtained from Sigma-Aldrich and used without further purification. All synthesis experiments were carried out with Schlenk techniques under argon since the metal carbonyls are hygroscopic and air sensitive. The PC was dried under high vacuum (10⁻³ mbar) for several days.

FT-IR (Fourier transform infrared) measurements were carried out on a Bruker TENSOR 37 IR spectrometer in a range from 4000 to 500 cm⁻¹ in a KBr cuvette (thickness 0.05 mm).

Transmission electron microscopy (TEM) photographs were taken at room temperature on a Zeiss LEO 912 TEM operating at an accelerating voltage of 120 kV. Samples were deposited on 200 μ m carbon-coated copper grids. TEM was operated in combination with selected area electron diffraction, SAED (also known as transmission electron diffraction, TED) which gives information concerning compound phase(s) and crystallinity, similar to X-ray powder diffraction.

A Malvern Zetasizer Nano-ZS was used for the *dynamic light scattering (DLS) measurements* working at 633 nm wavelength. Care was taken for choosing the right parameters, such as the index of refraction of the transition metals at their wavelength (Table S2†). Samples were prepared by dissolution of 0.05 or 0.1 mL of the 0.5 wt% metal/PC dispersion in acetone (99% p.a.; particle free) in a glass cuvette before measurement. Acetone is also capable of stabilizing nanostructured metal clusters.^{48,49}

Metal nanoparticle (M-NP) synthesis

Decomposition by means of microwave irradiation was carried out under argon. In a typical reaction, the fine metal carbonyl powder M_x(CO)_y (M = Mo, W, Re, Fe, Ru, Os, Co, Rh, Ir; 19.8

to 8.8 mg, respectively; see Table S1 in ESI†) was dissolved/suspended (≈ 1 h) under an argon atmosphere at room temperature in dried and deoxygenated PC (density: 1.19 g mL^{-1} , 1 mL , 1.19 g) for a 0.5 wt% M-NP/PC dispersion. For the synthesis of a 1 wt% M/PC dispersion the metal carbonyl $M_x(\text{CO})_y$ ($M = \text{Rh } 15.5 \text{ mg}$; $M = \text{Ir } 12.9 \text{ mg}$) was suspended/dissolved (≈ 1 h) under an argon atmosphere at room temperature in dried and deoxygenated PC (0.75 mL , 0.9 g). For the synthesis, the mixture was placed in a microwave (CEM, Discover) under an inert argon atmosphere and the conversion was finished within 3 min at a power of 50 W. For the 1 wt% dispersions a time of 5 min and a power of 50 W were chosen. Each decomposition reaction was carried out at least twice. Decomposition reactions to produce the Rh-NPs that were used in the catalysis in this work were carried out ten or more times.

Catalysis

The hydrogenation reactions with Rh-NPs/PC were carried out in stainless steel autoclaves connected with an online hydrogenation–consumption monitoring system (Büchi pressflow gas controller, bpc). The autoclave was conditioned by evacuation and re-filling with nitrogen. All autoclave loading was carried out under nitrogen. Each autoclave was equipped with a glass inlay, to eliminate any catalytic influence of the stainless steel surface on the reaction process. A typical experiment used 0.75 mL of the Rh-NP/PC dispersion with 1 wt% Rh (9 mg , $8.8 \times 10^{-5} \text{ mol}$ Rh) and 10 mL of cyclohexene (0.1 mol , density 0.811 g mL^{-1} , $M = 82.14 \text{ g mol}^{-1}$) or 1.0 mL of 1-hexyne (1.8 mmol , density 0.72 g mL^{-1} , $M = 82.14 \text{ g mol}^{-1}$). The autoclave was heated to the desired temperature and set to the desired pressure of H_2 which was kept constant over the reaction time. After this time the reactor was depressurized, and the volatile organic components condensed under vacuum (15 min) into a clean cold trap (liquid nitrogen cooled). The Rh-NP/PC dispersion was left behind. The conversions were investigated by gas chromatography using a Perkin Elmer headspace GC HS6 with a DB 5 column ($60 \text{ m} \times 0.32 \text{ mm}$ film thickness $25 \mu\text{m}$) oven temperature $40 \text{ }^\circ\text{C}$, N_2 carrier flow 120 L min^{-1}) and a flame ionization detector (FID, $250 \text{ }^\circ\text{C}$ detector temperature). The conversion was analyzed by adding a drop of the mixture into a GC sample vial with 1 mL of water. The addition of water as a non-electrolyte can enlarge the activity coefficient of organic components, thereby increase their detection sensitivity through the increase in peak area. The FID does not detect the water itself.⁵⁰ Kinetic stabilization of M-NPs in PC is not as high as in ionic liquids. Catalytic conditions lead to visible nanoparticle aggregation already after one run. Hence, no recycling experiments were carried out.

Preparation of ligand-capped M-NP in PC

The obtained Rh- and Ru-NPs/PC (0.4 mL , $0.5 \text{ wt}\%$) were stirred with 3-mercaptopropionic acid (2 mL , $3.5 \times 10^{-5} \text{ mol}$) or TOPO (14 mg , $3.5 \times 10^{-5} \text{ mol}$) over night. The ligand-capped M-NPs were collected by centrifugation (2000 rpm , 15 min) and decantation of the clear propylene carbonate phase. The capped

M-NPs were dried for several days under high vacuum to remove the PC solvent.

Acknowledgements

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