Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rhodium Nanoparticle Catalysts Stabilized with a Polymer that Enhances Stability without Compromising Activity

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1. Materials and Methods

THF was obtained from a solvent drying system and was stored with 4 Å molecular sieves. Diisopropylamine was refluxed with Na wire and distilled prior to use. N-vinyl-2-pyrrolidone (NVP) was distilled under reduced pressure prior to use. Hydrogen (99.999%), $RhCl_3 \cdot nH_2O$ (AR grade), poly(N-vinyl-2-pyrrolidone) (PVP, K30) and other chemicals were obtained commercially and used without further purification. All organic reactions were performed using standard Schlenk techniques under N_2. Dialysis was performed with a Spectra/Por Dialysis Membrane with a molecular weight cutting off (MWCO) of 1000.

NMR spectra were recorded at 20 °C on a Bruker DMX 400 instrument with TMS as an internal standard. IR spectra were recorded on a Fourier transform infrared spectrophotometer (Tensor 27, Perkin Elmer) with a resolution of 2 cm^{-1}. GC was performed on a Varian Chrompack CP-3380 using nitrogen as the carrier gas. Freeze drying was carried out on a Christ Alpha 1-2 LD Freeze dryer (Germany).

Size-exclusion chromatography (SEC) was performed on a Waters Alliance GPCV 2000 system equipped with refractive index (RI), differential viscometer and light scattering (90, RALLS) detectors. Separation was carried out at 60 °C with TSK-Gel Alpha 3000 + 4000 columns using DMF + 0.5 g L^{-1} LiCl as eluent at a flow rate of 0.6 ml min^{-1}. Molecular weights were determined relative to narrow polydispersity poly(methyl methacrylate) (PMMA) standards. Results were calculated with the Empower Pro multidetection GPC software (V. 5.00).

X-ray photoelectron spectrometry (XPS) was performed on an Axis Ultra spectrometer (Kratos, UK). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out using a Philips Tecnai F30 transmission electron microscope operating at 300 keV. Zeta potentials were measured on a Zetasizer nano ZS90 (Malvern) equipped with a microprocessor unit. TGA were recorded on a Thermal Analysis SDT2960 simultaneous differential thermal analyzer with a heating

rate of 10 °C min^{-1} under nitrogen or air.

2. Synthesis of the polymers

2.1 Synthesis of 3,3-di(ethoxycarbonyl)-1-vinylpyrrolidin-2-one (DEVP) and poly(3,3-di(ethoxycarbonyl)-1-vinylpyrrolidin-2-one) (PDEVP)

These two compounds were prepared according to a literature method.[1] Their ^{1}H and ^{13}C NMR spectra were in excellent agreement with the literature data. Since PDEVP was synthesized using free radical polymerization the M_W was slightly different from the literature value: GPC (DMF): M_n = 59000, M_w = 15000, d = 2.5.

2.2 Synthesis of sodium poly(1-vinylpirrolidin-2-one-3-carboxylate) ***1***

The synthesis of **1** was reported previously,[1] but a modified procedure was applied in this study. PDEVP (1 g) was dispersed in a mixture of NaOH aqueous solution (3 M) and ethanol (60 ml, 1:1). The dispersion was stirred for 2 h at 50 °C. The ethanol was then removed under vacuum and the residue was dialyzed against water through a membrane (MWCO: 1000) at room temperature for 48 h, during which water in the beaker was refreshed every 8 h. The mixture was then freeze dried to afford a white powder. Yield: 625 mg, 90 %. ^{1}H NMR (400MHz, D_2O): 1.65 (br, 2H), 2.05 (br, 1H), 2.22 (br, 1H), 3.13-3.22 (br, 3H), 3.58 (br, 1H). ^{13}C NMR (100.5 MHz, D_2O): 23.3, 34.6, 41.4, 44.5, 46.1, 52.4, 174.4, 177.5. IR (cm^{-1}): 1652 ($\nu_{C=O}$ N-C=O), 1575 ($\nu_{C=O}$ O-C=O).

2.3 Synthesis of 1-methyl-3-octylimidazolium poly(1-vinylpirrolidin-2-one-3-carboxylate) ***2***

1 (50 mg, 0.3 mmol based on the repeating unit), [omim]Cl (76 mg, 0.33 mmol) and water (4 ml) were stirred at room temperature for 12 h during which time an insoluble material accumulated in the flask. The water was removed by decantation and the residue was washed with water (2 × 2 ml) and dried under vacuum, affording a waxy solid. Yield: 42 mg, 42 %. ^{1}H NMR (400MHz, d_4-methanol): 0.91 (t, 3H, J = 7.2 Hz), 1.33 (m, 10H), 1.70 (br, 2H), 1.90 (m, 2H), 2.21 (br, 2H), 3.19 (br, 3H), 3.78 (br, 1H), 4.00 (s, 3H), 4.28 (t, 2H, J = 7.4 Hz), 7.69 (d, 1H, J = 2.0 Hz), 7.73 (d, 1H, J = 1.9 Hz).

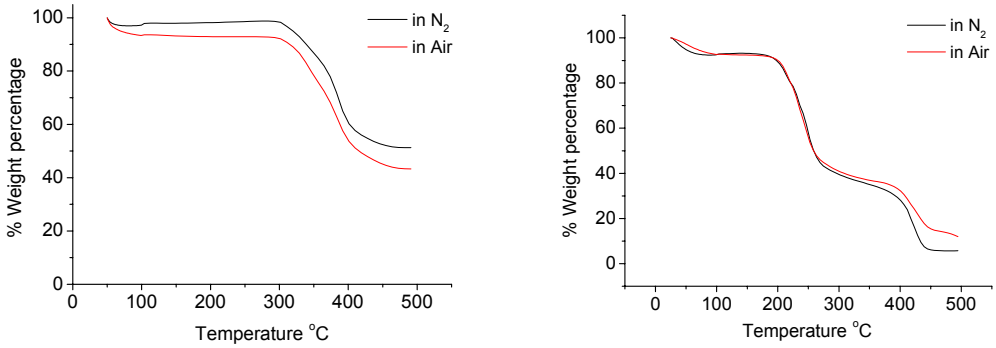


Figure S1. TGA curves of **1** (left) and **2** (right) under N_2 and air.

3. Synthesis and characterization of the rhodium nanoparticles (Rh NPs)

3.1 Synthesis of the polymer protected Rh NPs

An aqueous solution of $RhCl_3 \cdot 3H_2O$ (10 mM, 1 ml) was mixed with the solution of PVP (150 mM based on pyrolidone monomer, 1.35 ml), **1** (100 mM, 2.0 ml) or **2** (100 mM, 2.0 ml). $NaBH_4$ was rapidly added to the mixture with vigorous stirring to afford a black solution. The mixture was stirred for 1 h and then diluted with water to 10.00 ml to give the polymer protected Rh NP solutions termed PVP-Rh and **1**-Rh. For Rh NPs with a stabilizer ratio of 2 instead of 20, the same procedure was applied except reduced amount of **1** or PVP were used.

3.2 Synthesis of unprotected Rh NPs

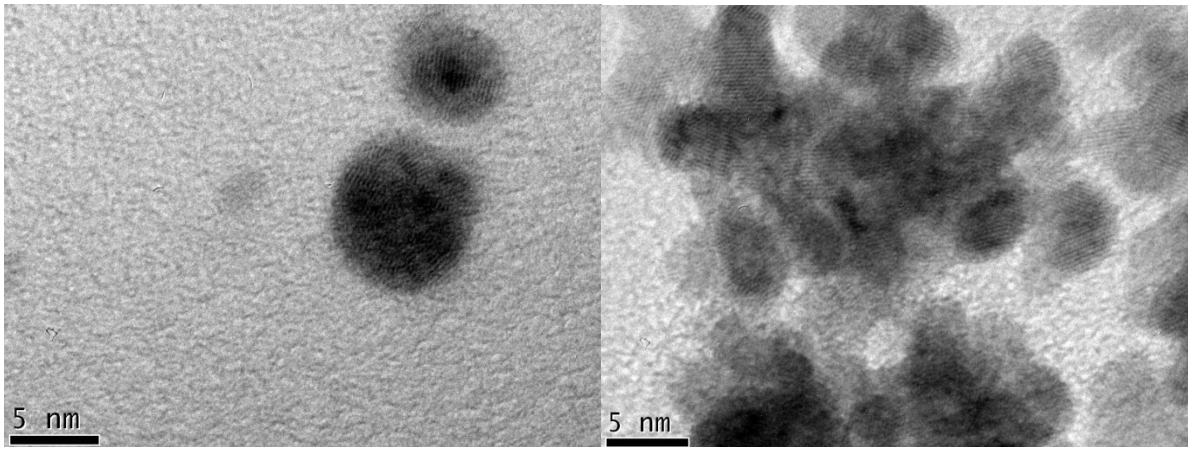
Unprotected Rh NPs were prepared accordingly to a literature procedure.[2] An aqueous solution of $RhCl_3 \cdot nH_2O$ (400 mg, 1.5 mmol in 5 ml water) and NaOH (500 mg, 12.5 mmol in 5 ml water) were sequentially added into glycol (100 ml) with stirring, affording a transparent orange solution. The solution was heated at 160 °C for 3 h, with an nitrogen flow passing through the system to remove water and volatile organic by-products. After cooling to room temperature, additional glycol was added to the solution to a volume of 100 ml. A transparent dark-brown solution of the Rh NPs (15 mM) in glycol was obtained.

3.3 Coating of unprotected Rh NPs with the polymers

The Rh NPs in glycol (4 ml, 0.06 mmol Rh), described in section *3.2*, were mixed with an aqueous solution of PVP or **1** (8 ml, 150 mM, 1.2 mmol repeating unit). The mixture was transferred into a membrane bag (MWCO: 1000) and was dialyzed for 48 h using deionized water to remove glycol. The water in the beaker was changed every 8 h. Complete removal of glycol was confirmed by NMR spectroscopy. Finally the mixture inside the membrane bag was diluted to 100 ml with deionized water, which gave a transparent dark brown solution.

3.4 TEM analysis

The solutions of polymer protected Rh NPs (0.1 ml) were diluted with methanol (1 ml). After sonication for 1 h, one drop of the solution was placed on a copper grid coated with carbon film, dried in a desiccators filled with N_2, and analyzed by TEM and HRTEM.



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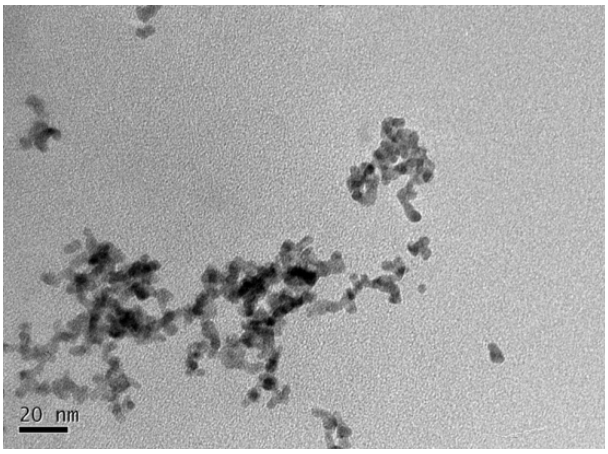

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Figure S2. a) HRTEM for PVP-Rh; b) HRTEM for **1**-Rh; c) TEM for **1**-Rh after heating at 200 °C for 2 h.

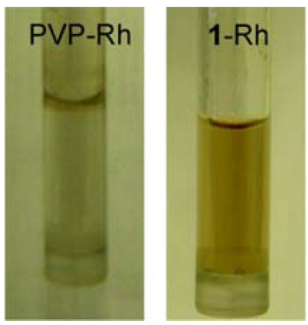

Figure S3. Photographs of the Rh NP solutions prepared by coating preformed Rh NPs with PVP (left) or **1** (right) after heating at 200 °C for 2 h.

3.5 XPS analysis

For XPS analysis the ratio of Rh:polymer was increased to 1:5. The solutions of the polymer protected Rh NPs were freeze dried prior to analysis. The spectra of the C, N, O and Rh core level were measured using a Mg $K\alpha_{1,2}$ X-ray source (photon energy = 1253.6 eV).

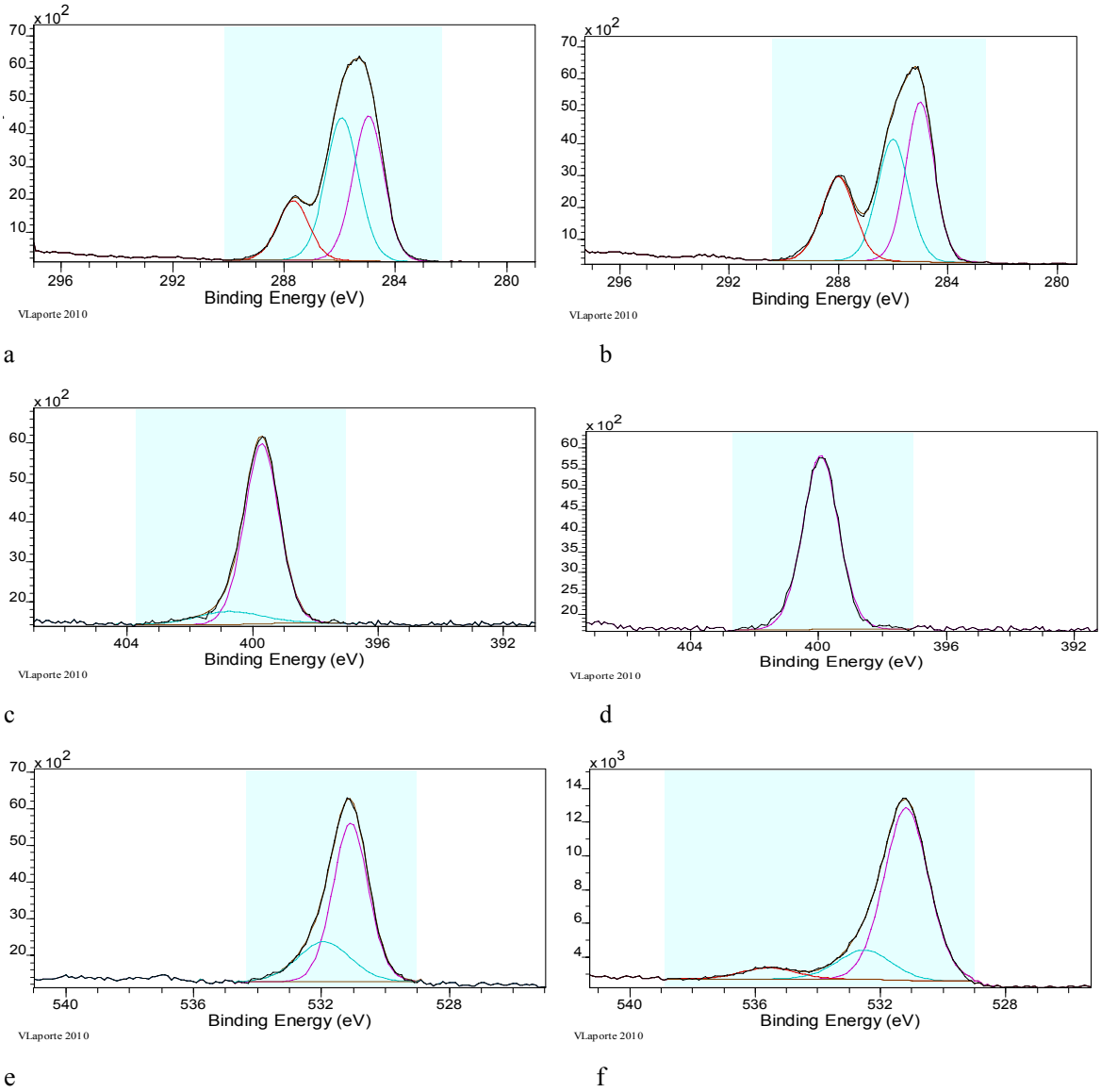

Figure S4. XPS spectra for a) PVP-Rh (C 1s region); b) **1**-Rh (C 1s region); c) PVP-Rh (N 1s region); d) **1**-Rh (N 1s region); e) PVP-Rh (O 1s region); f) **1**-Rh (O 1s region).

3.5 IR spectroscopy

The samples were prepared as described in section 3.1 except with a polymer to Rh ratio of 2. Prior to analysis the samples were freeze dried and further dried at 140 °C under vacuum for 2 h. The change in ν_{CO} at ca. 1600 cm^{-1} for the polymer when used to stabilize the Rh NPs indicates that the carboxylate group interacts with the NP surface.

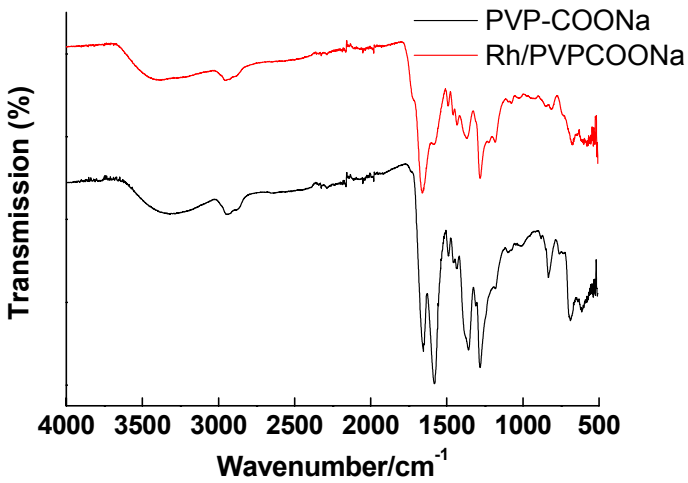

Figure S5. FT-IR spectra of **1** (black) and **1**-Rh NPs (red).

3.6 Zeta potential measurements

The zeta potentials of the Rh NPs were measured on a Zetasizer nano ZS90 (Malvern) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation.[3] The concentration of the Rh NPs was fixed at 0.5 mM (based on Rh). A polymer (repeating unit) to Rh ratio of 20:1 was used for all the measurements. The solution was equilibriated at 25 °C for 10 min before analysis and an average of 32 measurements was taken to represent the measured potential. The data are shown in Figure 4 in the manuscript. As a control, Rh NPs coated by PAA was also prepared for zeta potential measurement. The preparation is the same as that described in *section 3.1* except PAA was used as the stabilizer.

4. Catalytic studies

Hydrogenation reactions were performed in an autoclave equipped with heating/cooling system. The solution of the appropriate Rh NPs (1 mM, 2 ml) and the substrate (1.0 mmol, to give a Rh content of 0.2% with respect to the substrate), was placed in the autoclave. The system was purged with hydrogen and then filled to 20 atm. The mixture was stirred at 60 °C for 2 h. Then the autoclave was cooled to below 25 °C within 15 min and the hydrogen was released and the products were extracted with diethyl ether (2×2 ml). The combined organic layers were analyzed by GC ananlysis with octane as internal standard. For recycling experiments the resulting reaction mixture was stirred for 10 h under a flow of nitrogen to remove the remaining ether and fresh substrate was then added.

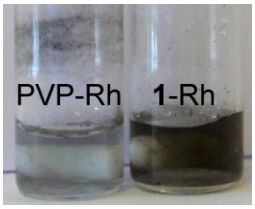

Figure S6. Photograph of the Rh NPs in aqueous phase after 5 batches of reaction. (left: PVP-Rh; right **1**-Rh).

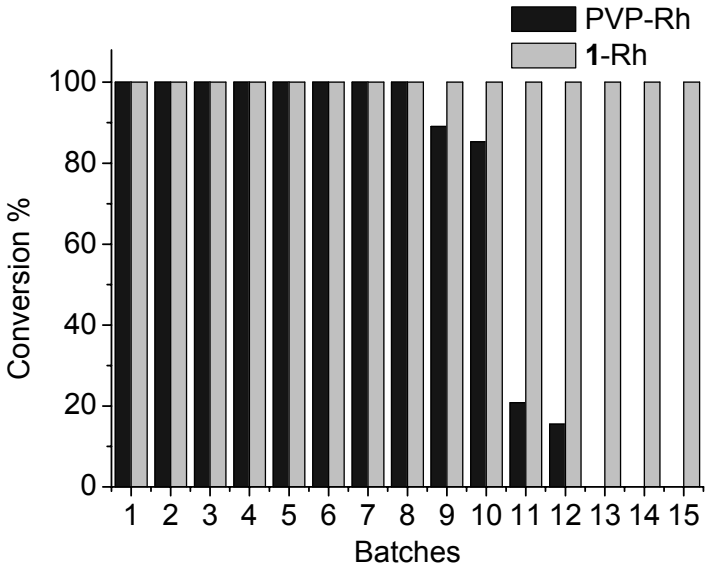

Figure S7. Recycling of phenol hydrogenation catalyzed by **1**-Rh and PVP-Rh (reaction conditions: reactant 1 mmol, 1×10^{-3} mmol of Rh NPs (Rh:Stabilizer = 1:20) in 2 ml water, H_2 20 atm, 60 °C, 2 h.)

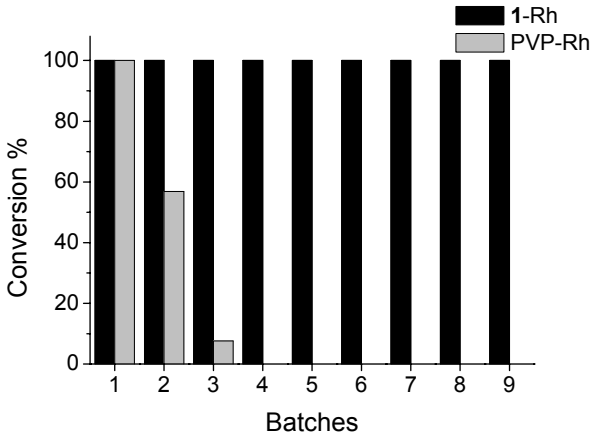

Figure S8. Recycling of toluene hydrogenation catalyzed by **1**-Rh and PVP-Rh (reaction conditions: reactant 1 mmol, 1×10-3 mmol of Rh NPs (Rh:Stabilizer = 1:2) in 2 ml water, H_2 20 atm, 60 °C, 2 h.)

1 M. Bencini, E. Ranucci, P. Ferruti, C. Oldani, E. Licandro, S. Maiorana, *Macromolecules* **2005**, *38*, 8211.
2 Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang, *Chem. Mater.* **2000**, *12*, 1622.
3 R. J. Hunter, *Zeta Potential in Colloid Science*, Academic Press, New York, **1981**.