Electronic Supplementary Information

Rh(0)/Rh(III) core-shell nanoparticles as heterogeneous catalysts for cyclic carbonate synthesis

Younjae Jung, Taeil Shin, Kiseong Kim, Hyeeun Byun, Sung June Cho,* Hyunwoo Kim* and Hyunjoon Song*

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1. General methods

Chemicals. Rhodium(III) acetylacetonate [Rh(acac)₃, 99%], oleylamine (OAm, 70%), *N*-bromosuccinimide (NBS, 99%), *N*-chlorosuccinimide (NCS, >98%) and (diacetoxyiodo)benzene [PhI(OAc)₂] were purchased from Aldrich, and n-hexane (99.5%) and toluene (99.5%) were purchased from Junsei. The chemicals were used as received without further purification.

Preparation of Rh NPs. The Rh NPs were synthesized according to the literature (Y. Feng, X. Ma, L. Han, Z. Peng and J. Yang, *Nanoscale*, 2014, **6**, 6173). Typically, Rh(acac)₃ (100 mg, 0.25 mmol) was dissolved in OAm (10 mL). The mixture was degassed at room temperature for 30 min, heated to 433 K for 20 min under a nitrogen atmosphere, and were allowed to stir for 40 min at 433 K. After the reaction, the reaction mixture was cooled down to room temperature and washed with methanol and hexane twice. The product was precipitated by centrifugation in methanol.

Oxidation and reduction of Rh NPs. For the oxidation process, Rh NPs (3.0 mg) and the oxidants (2 equiv with respect to the Rh NPs) were dissolved in toluene (2.0 mL) in a sealed vial equipped with a stirring bar. The mixture was heated to 413 K and allowed to stir for 1 h at the same temperature. After the oxidation, the mixture was cooled down to room temperature, and washed with hexane and acetone twice. The product was precipitated by centrifugation in ethanol. The reduced Rh NPs were prepared by a mild thermal treatment at 80 °C with a H₂ flow for 6 h.

XPS analysis. Rh NPs were characterized by X-ray photoelectron spectroscopy (XPS) to analyse the surface oxidation states. The Rh NP samples were dispersed in hexane, and were drop-casted on a Si wafer. The resulting wafer was immediately loaded in a UHV chamber. The measurements were performed with the XPS system.

EXAFS analysis. X-ray absorption fine spectroscopy (XAFS) data of the catalysts were collected at Rh K-edge, 23546 eV with ambient condition in Pohang Accelerator Laboratory (7D-XAFS beamline in PLS-II) equipped Si(111) crystal as a monochromator. The beamline energy and ring current were 2.5 GeV and 300 mA, respectively. The step and duration time for X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were 1.0 eV and 2 s, and 0.30 nm⁻¹ and 3 s, respectively. The total number of the points per XAFS spectrum was 500, which were sufficient for the EXAFS analysis. For the EXAFS refinement, after the data processing using Athena, Artemis in Demeter program package (0.9.25) was employed. Using AUTOBK program for $R_{bkg} = 0.1$ nm, the

background removal was performed to extract XAFS signals and subsequently the corresponding XAFS data in *k* space were Fourier transformed with the Kaiser-Bessel window function. The range for Fourier transformation of the Rh samples, Δk , were 30 – 115 nm⁻¹ or 3 – 11.5 Å⁻¹. The phase shifts and amplitude functions of the reference was generated using *Feff* 6. Depending on the samples, the curve fitting ranges were varied in *r* space. The number of independent point of the data for the curve fit, N_{idp} , was dicided from Nyquist theorem, which was always larger than the number of variables, ascribing the enough degree of freedom, N_{var} . The scattering path from the feasible model structure was acquired from the *Feff* calculation. Only the scatterings with large contribution were included in the multi-shell fitting. The many-body reduction factor was procured from a Rh foil under the same condition and was utilized further in the curve fit of the samples.

Zeta potential measurement. The Rh NPs samples (10 mg) were dispersed in toluene (20 mL). The zeta potential was measured via electrophoretic light scattering (ELS) combined with phase analysis light scattering (PALS) (ELS-Z2, Otsuka Japan).

NMR spectroscopy. The ¹H and ¹³C NMR spectra were recorded on a Bruker Ascend 400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer and were reported in ppm, relative to residual protonated solvent peak (CDCl₃).

2. Experimental procedures and spectral data



Fig. S1 XPS spectra in the Rh 3d level for Rh NPs after the treatment with (a) NCS and (b) PhICl₂ at 140 °C.



Fig. S2 XPS spectra in the Rh 3d level for Rh NPs after the treatment with 1, 2, 3, and 5 equiv NBS with respect to the Rh NPs at 140 °C.



Fig. S3 The XPS spectrum in the Br 3d level for the Rh NPs after the oxidation with NBS at 140 °C for 1 h.



Fig. S4 The HRTEM images of the Rh(0)/Rh(III) NPs after the oxidation with NBS.



Fig. S5 (a) TEM image and (b) XPS spectrum in the Rh 3d level of the Rh NPs after H_2 reduction at 80 °C for 6 h.



Fig. S6 The Rh K-edge XANES spectra of the Rh foil reference, pristine, NBS-oxidized, and H₂-reduced Rh NPs, and Rh₂O₃ powders.



Fig. S7 EXAFS spectra and curve fitting in r and q spaces for (a) pristine, (b) NBS-oxidized, and (c) H₂-reduced Rh NPs.

A typical procedure of the coupling of propylene oxide and CO_2 . To an oven-dried stainless steel reactor equipped with a stir bar were added Rh NPs (1.0 mg, 0.010 mmol, 0.10 mol%), NBS (1.8 mg, 0.010 mmol, 0.10 mol%), nBu₄NBr (81 mg, 0.25 mmol, 2.5 mol%), propylene oxide (0.70 mL, 10 mmol), and toluene (0.20 mL). The reactor was charged and discharged with 2.5 bar of CO_2 twice and finally charged with 10 bar of CO_2 . The reactor was stirred at 100 °C for 2 h, and the conversion was determined by the ¹H NMR spectrum of the crude sample.

$$\begin{array}{c} O \\ H_{3}C \end{array}^{1} H NMR (CDCl_{3}, 400 \text{ MHz}) \,\delta \,4.9\text{-}4.8 \,(1\text{H}, \text{m}), 4.55 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.7 \text{ Hz}), 4.02 \,(1\text{H}, \text{dd}, J = 8.4, 7.2 \text{ Hz}), 1.49 \,(3\text{H}, \text{d}, J = 6.2 \text{ Hz}), 1.40 \,(3\text{H}, \text{d}, J = 6.2 \text{ Hz}), 1.30 \,(1100 \,\text{MHz}) \,\delta \,155.1, 73.7, 70.7, 19.4 \,(1100 \,\text{Mz}) \,\delta \,155.1, 75.1,$$

Table S1. The effect of oxidants for the Rh NPs-catalyzed propylene carbonate synthesis

	Rh NPs (0.1 mol%) nBu₄NBr (2.5 mol%) O Oxidant (0.1 mol%)					
	H₃C [^]	(10 bar)	Toluene 100 ^o C, 2 h	H ₃ C		
Entry	Oxidant Conv (%) ^a	Relative surface oxidation state (%) ^b				
		Rh(III)	$Rh(\delta^+)$	Rh(0)		
1	NBS	83	39.5	10.2	50.3	
2	NCS	44	16.6	4.2	79.2	
3	PhICl ₂	28	12.5	6.4	81.1	

^aDetermined by ¹H NMR spectra. ^bDetermined by XPS analysis (Figs. 1d and S1)

Filtration test. To an oven-dried stainless steel reactor equipped with a stir bar were added Rh NPs (1.0 mg, 0.010 mmol, 0.10 mol%), NBS (1.8 mg, 0.010 mmol, 0.10 mol%), nBu₄NBr (81 mg, 0.25 mmol, 2.5 mol%), propylene oxide (0.70 mL, 10 mmol), and toluene (0.20 mL). The reactor was charged and discharged with 2.5 bar of CO₂ twice and finally charged with 10 bar of CO₂. The reactor was stirred at 100 °C for 1 h, and the conversion was determined by the ¹H NMR spectrum of the crude sample. Due to the low boing point of propylene oxide (34 °C), the pressure was released after cooling the reactor to room temperature. The reaction mixture was filtered through a layer of Celite 545 followed by a 0.2 μ m PTFE filter. 0.6 mL of toluene was used for the filtration. The filtrate was transferred to an oven-dried

stainless steel reactor, and then NBS (1.8 mg, 0.010 mmol, 0.10 mol%), nBu₄NBr (81 mg, 0.25 mmol, 2.5 mol%) and propylene oxide (0.70 mL, 10 mmol) were added. The reactor was charged and discharged with 2.5 bar of CO₂ twice and finally charged with 10 bar of CO₂. The reactor was stirred at 100 °C for 2 h, and the conversion was determined by the ¹H NMR spectrum of the crude sample.



Fig. S8 (a) The filtration experiment under the conditions in entry 8. (b) TEM image of the filtered Rh catalyst after the reaction.

Mercury poisoning test. A drop of Hg was added to the Rh NPs-catalyzed coupling reaction of propylene oxide and CO₂. To an oven-dried stainless steel reactor equipped with a stir bar were added Rh NPs (1.0 mg, 0.010 mmol, 0.10 mol%), NBS (1.8 mg, 0.010 mmol, 0.10 mol%), nBu₄NBr (81 mg, 0.25 mmol, 2.5 mol%), propylene oxide (0.70 mL, 10 mmol), and toluene (0.20 mL). Before assembling the pressure reactor, Hg (10 μ L, 0.70 mmol) was dropped to the reaction mixture. The reactor was charged and discharged with 2.5 bar of CO₂ twice and finally charged with 10 bar of CO₂. The reactor was stirred at 100 °C for 2 h, and the conversion was determined by the ¹H NMR spectrum of the crude sample.



Fig. S9. Mercury test for the propylene carbonate synthesis under the conditions in entry 8.

A typical procedure for recycling experiments. To an oven-dried stainless steel reactor equipped with a stir bar were added Rh NPs (1.0 mg, 0.010 mmol, 0.10 mol%), NBS (9.0 mg, 0.0050 mmol, 0.50 mol%), nBu₄NBr (81 mg, 0.25 mmol, 2.5 mol%), propylene oxide (0.70 mL, 10 mmol), and toluene (0.2 mL). The reactor was charged and discharged with 2.5 bar of CO₂ twice and finally charged with 10 bar of CO₂. The reactor was stirred at 100 °C for 2 h. After the reactor was cooled to room temperature, the mixture was transferred to a 1.5 mL centrifuge tube. By the centrifugation for 5 min, the supernatant was decanted, and the precipitates were washed with toluene (0.5 mL) twice by the help of sonication. The supernatant was directly analysed by ¹H NMR spectroscopy. Using the precipitates as the Rh catalyst, the reactions were carried out through the above procedure five times.

3. NMR Spectra

¹H NMR (400 MHz, CDCl₃)

