Supporting Information

Selective Extraction of Supported Rh Nanoparticles Under Mild, Non-acidic Conditions with Carbon Monoxide

Malek Y. S. Ibrahim, Scott E. Denmark*

Roger Adams Laboratory, Department of Chemistry, University of Illinois,
Urbana, Illinois, 61801
sdenmark@illinois.edu

Contents

1. Solvents and Chemicals

Leaching solvent acetonitrile (Aldrich, HPLC grade) was distilled over CaH_2 and further dried over 4 Å molecular sieves. Leaching solvent tetrahydrofuran (Fisher, HPLC grade) was dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Leaching solvent toluene (Fisher, ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Leaching solvent *N,N* dimethylformamide (Fisher, ACS grade) was dried by percolation through two columns packed with Linde type 4 Å molecular sieves under a positive pressure of argon and further dried over 4 Å molecular sieves.

$RhCl_3$ hydrate and $RuCl_3$ hydrate were purchased from Pressure Chemcials, and used as received. H_2PtCl_6 hydrate was purchased from Aldrich and used as received. Aluminum oxide, gamma pahse, 20 nm powder was purchased from Alfa Aesar. Titanium oxide P 25 was purchased from Acros and used as recieved. All metal-carbonyl complexes were purchased from Strem, stored and handled in a drybox, and used as received. All other reagents and solvents were purchased from Aldrich, Fisher, Oakwood, or Strem and used as received.

2. Synthesis of Supported Nanoparticles

2.1. RhNP on Al_2O_3

(Samples: *RhA-red, RhA-oxd500, RhA-oxd350, RhA-oxd/red, RhA-aged1, RhA-aged3, RhA-aged/red*)

A solution of the Rh(III) precursor was prepared by dissolving 64.5 mg $RhCl_3.3H_2O$ in 250 mL deionized DI water in a 500 mL round-bottomed flask and the pH was adjusted to 10 using NH_4OH solution (0.2 mL). Five grams of Al_2O_3 powder was added and the pH was readjusted to 10. The slurry was stirred at room temperature for 24 h before stirring was stopped and the slurry was allowed to settle for 1 h. The solid residue was separated by centrifugation and decanting the supernatant then was dried under vacuum (15 mmHg) at room temperature overnight.

Three grams of the dried Rh/Al_2O_3 powder was reduced under hydrogen flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 ^oC/min and held at 500 ^oC for 4 h then cooled to room temperature. The hydrogen flow was gradually reduced to

zero to avoid reheating the sample due to rapid oxidation upon exposure to air. Two grams of the reduced sample was stored under argon atmosphere (*RhA-red*) and 0.5 g of the reduced sample was stored under air for 1 month (*RhA-aged1*) and 3 months (*RhA-aged3*). A 100 mg portion of the (*RhA-aged3*) sample was submitted to a second reduction cycle by hydrogen as described above and stored under argon (*RhA-aged/red*).

One gram of the dried Rh/Al_2O_3 powder was calcined under dry air flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 °C/min and held at 500 °C for 4 h then cooled to room temperature and stored under air (*RhA-oxd500*). A 250 mg portion of sample *RhA-oxd500* was submitted to reduction by hydrogen at 500 °C as described above and stored under argon (*RhA-oxd/red*). Another 500 mg portion of the dried Rh/Al_2O_3 powder was calcined under air at 350 °C the same way as described above and stored under air (*RhA-oxd350*).

2.2. RhNP on TiO_2 (*RhT*)

A solution of the Rh(III) precursor was prepared by dissolving 25.8 mg $RhCl_3.3H_2O$ in 50 mL DI water in a 100 mL round-bottomed flask and the pH was adjusted to 10 by addition of a solution of NH_4OH (0.01 mL). One gram of TiO_2 (P-25) powder was added and the pH was readjusted to 10. The slurry was stirred at room temperature for 24 h before stirring was stopped and the slurry was decanted for 1 h. The solid residue was separated by centrifugation and decantation of the supernatant then was dried under vacuum (15 mmHg) at room temperature overnight.

A 500 mg portion of the dried Rh/TiO_2 powder was reduced under hydrogen flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 °C/min and held at 350 °C for 4 h then cooled to room temperature. The hydrogen flow was gradually reduced to zero to avoid reheating the sample due to rapid oxidation upon exposure to air the stored under argon. Another 500 mg portion of the dried Rh/TiO_2 was calcined under dry air flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 °C/min and held at 350 °C for 4 h then cooled to room temperature and stored under air.

2.3. PtNP on Al_2O_3 (*PtA*)

A solution of the Pt(IV) precursor was prepared by dissolving 13.3 mg $H_2PtCl_6.3H_2O$ in 1 mL DI water in a one-dram vial. The solution was added dropwise to one gram of Al_2O_3 powder with continuous stirring of the powder. The resulting paste was aged at room temperature for 24

h then dried under vacuum (15 mmHg) at room temperature overnight.

The dried Pt/Al_2O_3 powder was calcined under dry air flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 ^{o}C/min and held at 500 ^{o}C for 4 h then cooled to room temperature. The calcined sample was reduced under hydrogen at 500 ^{o}C following the same procedure described above and stored under air (*PtA*)

2.4. RuNP on Al_2O_3 (*RuA*)

A solution of the Ru(III) precursor was prepared by dissolving 12.9 mg $RuCl_3.3H_2O$ in 50 mL DI water in a 100 mL round-bottomed flask and the pH was adjusted to 10 by addition of NH_4OH solution (0.01 mL). One gram Al_2O_3 (P-25) powder was added and the slurry was stirred at room temperature for 24 h before stirring was stopped and the slurry was allowed to settle for 1 h. The solid residue was separated by centrifugation and decantation of the supernatant then was dried under vacuum (15 mmHg) at room temperature overnight.

The dried Ru/Al_2O_3 powder was reduced under hydrogen flowing at 20 mL/min in a tube furnace. The furnace temperature was raised at a rate of 2 ^{o}C/min and held at 650 ^{o}C for 4 h then cooled to room temperature. The hydrogen flow was gradually reduced and the sample was stored under argon atmosphere (*RuA*)

2.5. Commercial Rh and PdNP (*RhA-comm, RhC-comm, PdA-Comm*)

One gram of the densely loaded, commercial samples of Rh NPs supported on alumina (*RhA-comm*) and carbon (*RhC-comm*) in addition to Pd NPs on alumina (*PdA-comm*) were prewashed in 20 mL solution of acetonitrile/water/triethylamine 1/0.2/0.2 v at 70 ^{o}C for 24 h in sealed 20 mL vials then filtered and dried under vacuum (15 mmHg) overnight.

### 3. Characterization of NP

The metal content of the samples was measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, PerkinElmer 2000DV). X-ray Photoelectron Spectroscopy (XPS) was measured by Kratos Axis Ultra XPS with Mg, Al dual anode X-ray source on samples under UHV. The Rh peaks were deconvoluted using three-component analysis for Rh(0), (I) and (III) at ca. 307, 309, 310 (eV) respectively.[1] Treatment of spectra was made with a CasaXPS software. This treatment consists of satellite subtraction, background subtraction using a Shirley-type curve and Rh 3d peak fitting with symmetrical Gauss-Lorentz curves for the

Rh(0), (I), and (II1) states. Percentages for the different oxidation states of Rhodium were estimated from the area of the curves giving the best fitting.[2]

The nanoparticle size was measured using Transmission Electron Microscopy (TEM, JEOL 2010-LaB$_6$, 200 kV, bright field mode, single tilt holder). Prior to TEM imaging, 10 mg of each sample was ground and sonicated in methanol then dispersed on "holey carbon" Cu grids. The diameter of 200 particles was measured and the algebraic mean was determined as the average particle size D in nm.

**Table 1S |** Nanoparticles pretreatment conditions, size, and support metal content

sample	Pretreatment conditions	wt %	D_{avg} nm
RhA-red	H$_2$ at 500 ^{o}C	0.47	1.47
RhA-aged1	RhA-red, 1 month storage in air	0.47	nd
RhA-aged3	RhA-red, 3 month storage in air	0.47	nd
RhA-aged/red	RhA-aged3, H$_2$ at 500 ^{o}C	0.47	nd
RhA-oxd500	air at 500 ^{o}C	0.47	1.76
RhA-oxd350	air at 350 ^{o}C	0.47	nd
RhA-oxd/red500	RhA-oxd500, H$_2$ at 500 ^{o}C	0.47	nd
RhT	H$_2$ at 350 ^{o}C	0.84	<1
RhA-comm	As recieved	4.31	2.66
RhC-comm	MeCN/H$_2$O/Et$_3$N wash at 70 ^{o}C	2.53	1.69
PdA-comm	H$_2$ at 500 ^{o}C	4.83	1.21
PtA	H$_2$ at 500 ^{o}C	0.44	1.63
RuA	H$_2$ at 650 ^{o}C	0.48	1.34
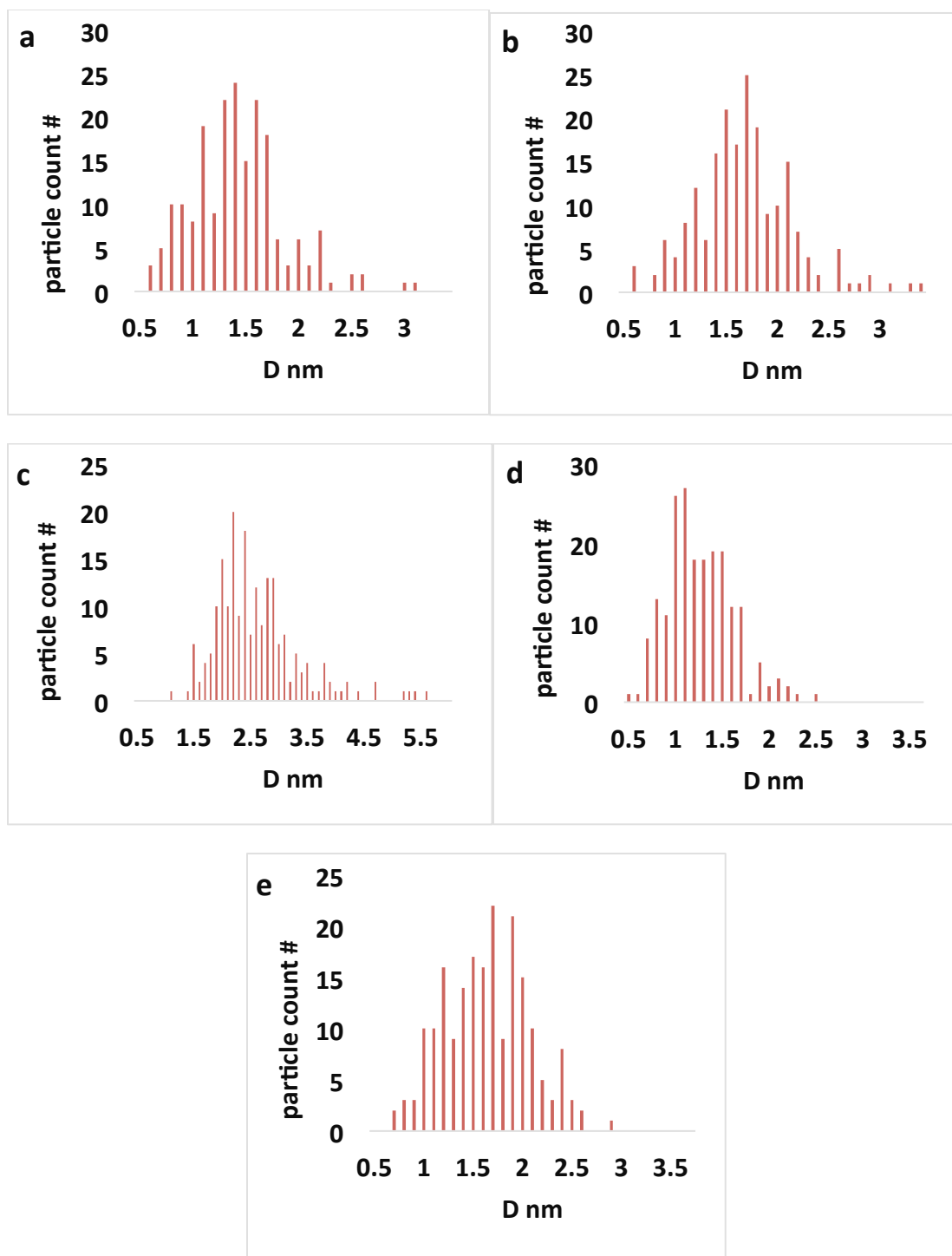
Fig. 1S | Rh NP size distribution by TEM (a) *RhA-red.* (b) *RhA-oxd500.* (c) *RhA-comm.* (d) *RhT.* (e) *RhC-comm.*
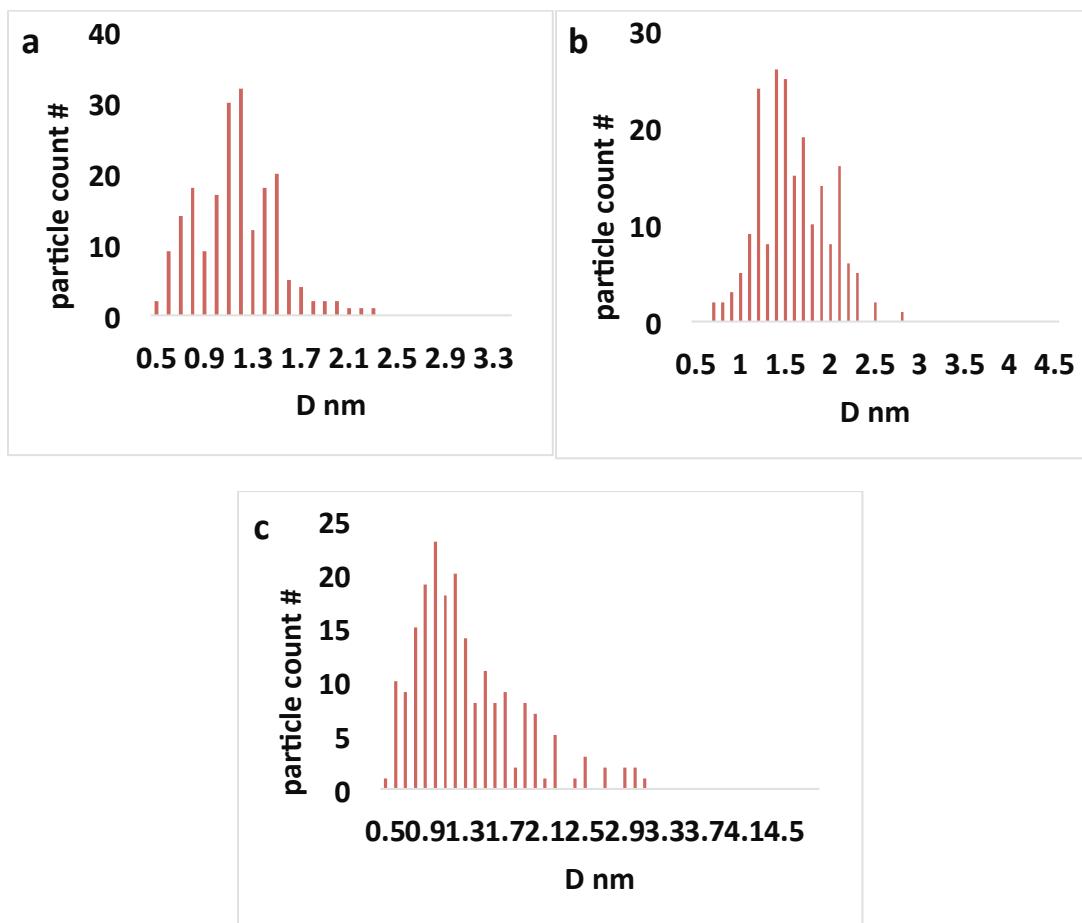
Fig. 2S | Pd, Pt. and Ru metals NP size distribution by TEM (a) *PdA-comm.* (b) *PtA.* (c) *RuA.*
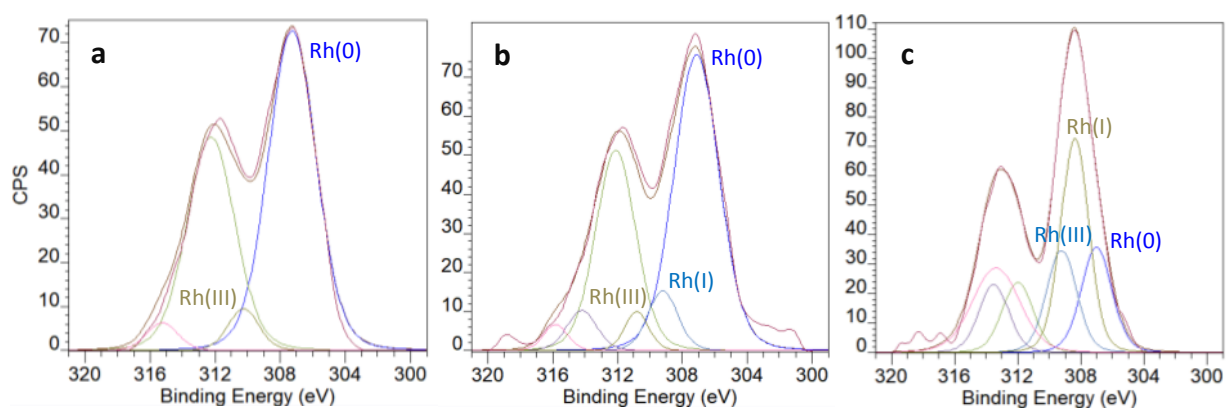
Fig. 3S | XPS Spectra of synthesized Rh NP on alumina (oxidation state distribution from curve fitting) (a) *RhA-red*: 92% Rh(0), 8% Rh(III). (b) *RhA-aged3*: 83% Rh(0), 11% Rh(I), 6% Rh(III). (c) *RhA-oxd500*: 26% Rh(0), 29% Rh(I), 45% Rh(III).

4. Leaching Experiment

Standard leaching experiments were performed by immersing 30 mg of the supported NP sample in a solution containing 2 ml acetonitrile, 0.4 ml triethylamine, and 0.4 ml deionized water in a glass vial with a stir bar. The vial was placed in a stainless-steel, bolted-closure pressure autoclave with a removable top that is fitted with an inlet and outlet needle valves and a pressure gauge. The autoclave was purged with CO three times and then pressurized to the desired CO pressure. The autoclave temperature and stir rate were controlled by a stir plate for 24 h then was cooled to room temperature and depressurized. Under the standard leaching conditions, the solution color remains yellow that turns to dark green upon air exposure. The leaching slurry was filtered under atmospheric air and the residue was rinsed three times with diethyl ether 3X10 ml then dried and sent for metal content measurement by ICP-OES. The leaching efficiency was determined as following:

$$\% \ leaching = \frac{(metal \ wt\% \ before \ leaching - metal \ wt\% \ after \ leaching) \ X \ 100}{metal \ wt\% \ before \ leaching}$$

## 5. Characterization of Post Leaching Solution

Post leaching characterization was done on solutions and residue resulting from leaching *RhA-red* sample at 25 °C for 24 h under 25 barg. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum Two ATR spectrometer using neat sample. Uv-vis spectra were recorded on a a Cary 60 Spectrometer using quartz cuvettes after baseline correction with pure solution of the same composition of the sample. The post leaching spectra were collected after allowing the slurry to settle down for 2 h before CO depressurizing. An aliquot was taken from the CO-saturated clear solution and transferred to the cuvette under atmospheric air directly after depressurizing CO.

6. Additional leaching experiments

6.1. Effect of water and triethylamine addition on leaching of *RhA-red* sample in acetonitrile

Leaching of 30 mg of *RhA-red* sample was performed by immersing 30 mg of the sample in a solution containing 2 ml acetonitrile and 0.2 ml of water, and/or 0.2 ml of triethylamine as indicated in Figure 4S. The post-leaching supernatants were pale violet after venting the CO and slowly turned into green upon exposure to air. UV-vis spectra taken directly after venting CO showed three main peaks at 387, 334, and 277 nm when leaching was performed in dry as well as wet acetonitrile (Figure 4Sa). The spectrum of the acetonitrile/water/triethylamine solution showed a diminished absorbance at 387 and enhanced absorbance at 279 nm when compared to the spectra from the amine-free solutions. The similar absorbance features of dry as well as wet acetonitrile indicates the formation of the same Rh species in both cases. The different absorbance in the triethylamine-containing solution indicates the coordination of the amine with the Rh species. Upon filtration and solvent removal under vacuum, a brown residue was formed that is soluble in triethylamine/water mixture, and insoluble in polar solvents. The UV-vis spectra taken after removal of solvent and redissolving the residue in dry acetonitrile were featureless and exhibited an increasing absorbance at the lower wavelength (Figure 4Sb). The monotonically increasing absorbance at decreasing light wavelength in the re-dissolved residue is characteristic of the formation of metallic Rh NP.[20]
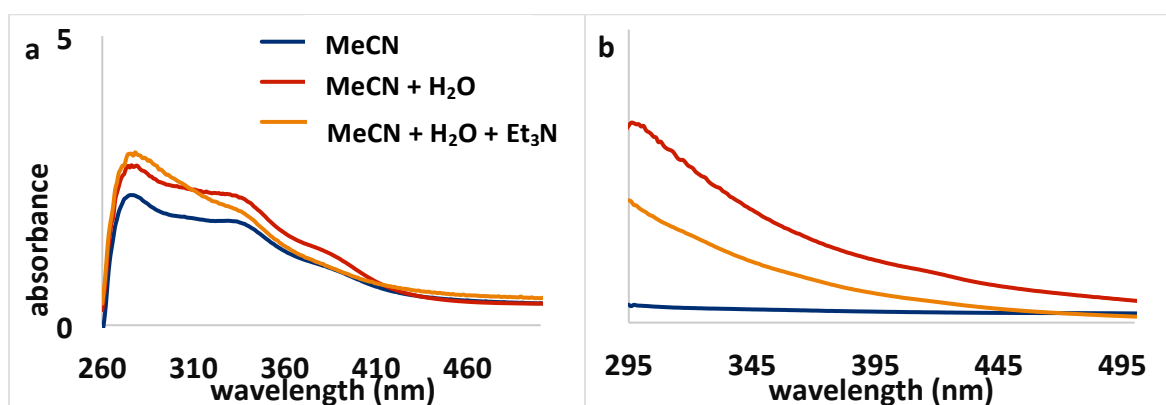
Fig. 4S | (a) UV-vis absorbance of the post leaching solution of sample *RhA-red.* in dry acetonitrile, acetonitrile/water, 5:1 v:v, and acetonitrile/water/triethylamine 5:1:1 v:v:v after 24 h under 20 barg CO pressure at 25 °C (b) UV-vis absorbance after solvent removal under vacuum and re-dissolving of the residues from the three experiments in dry acetonitrile.

Leaching in acetonitrile/water/triethylamine 5:1:1 was repeated on 2 g scale of *Rh/A-red* sample for 36 h. The post leaching slurry was filtered and rinsed with deionized water. The filterate was evacuated under reduced pressure to remove the solvent and the residue was redissolved in

acetone and transferred to a glass boat for hydrogen treatment in a tube furnace. The hydrogen treatment was performed with hydrogen flow at 200 °C for 2 h and the resulting powder was analyzied by ICP-OES which indicated 93.12% Rh content.

6.2. Effect of amine addition on leaching of *RhA-red* sample in dry acetonitrile

Leaching of 30 mg of *RhA-red* sample was performed by immersing 30 mg of the sample in a solution containing 2 ml acetonitrile and 0.4 ml of either triethylamine or piperdine. The CO pressure was set to 20 barg and the leaching was allowed to occur for 24 h at room temperature.

Table 2S. Effect of amine on leaching of *RhA-red* sample in dry MeCN

$$Rh/Al_2O_3 \xrightarrow[\substack{MeCN\ (2\ ml)\\ 25\ °C,\ 24\ h}]{\substack{CO\ (20\ barg)\\ base\ (0.4\ ml)}} Rh + Al_2O_3$$

30 mg
0.47 wt% Rh

base	% leaching
--	41
triethylamine	56
piperdine	21

6.3. Mass Spec. characterization of soluble extracted Rh species

Leaching of 30 mg of *RhA-red* sample was performed by immersing 30 mg of the sample in a solution containing 2 ml acetonitrile and 0.4 ml triethylamine to form a slurry. The CO pressure was set to 20 barg and the leaching was allowed to occur by stirring the slurry for 24 h at room temperature. The stirring was stoped and the slurry was allowed to settle down for 3 hours before venting the pressure vessel. Once CO was vented, a sample was taken from the top clear solvent phase and injected to Waters Q-TOF Ultima Mass Spectrometry Electrospray Ionization (MS-ESI) instrument. Data are reported in the form of *m/z*, Figure 5Sa. The observed mass spectrum indicated the formation of a series of rhodium carbonyl clusters with *m/z* in the range of 700 to 1850. Based on the calculated mass for rhodium carbonyl clusters containg containing 2 to 5 CO atoms/Rh atom, the nuclearity of the observed clusters was estimated to be between 4 to 10 Rh atoms per cluster, Figure 5Sb. The average atomic ratio CO/Rh in the

clusters is estimated to be around 3 based on comparison of the observed masses and those calculated for clusters of different CO/Rh ratios, Figure 5Sc.
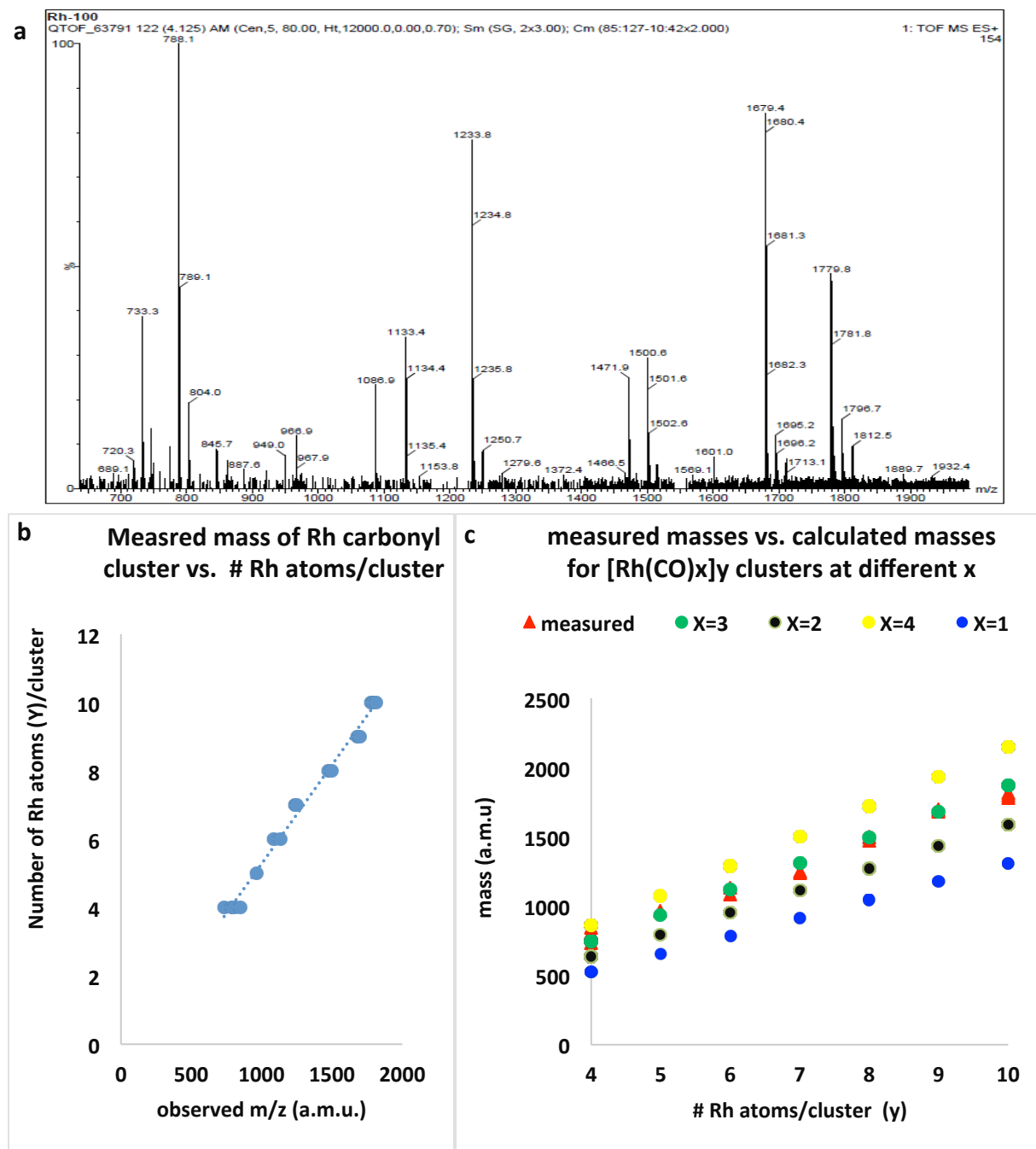
Fig. 5S | (a) MS-ESI of the post leaching solution of sample *RhA-red.* in acetonitrile/water/triethylamine 5:1:1 v:v:v after 24 h under 20 barg CO pressure at 25 °C. (b) assignment of the observed masses to Rh carbonyl clusters with the nearest calculated mass. (c) estimation of the average CO/Rh atomic ratio in the formed clusters by comparing the observed masses (red triangles) to the masses calculated for CO/Rh = 1, 2, 3, 4.

6.4. Effect of inorganic additves on the leaching of *RhA-red* sample in MeCN/Et₃N/H₂O mixture at 25 °C.

Leaching of 30 mg of *RhA-red* sample was performed by immersing 30 mg of the sample in a solution containing 2 ml acetonitrile, 0.4 ml water, and 0.4 ml of triethylamine with 10 mg of either NaCl, or NaOH, or 0.01 ml HCl ACS grade solution. The CO pressure was set to 20 barg and the leaching was allowed to occur for 24 h at room temperature. Slight increase in leaching was observed by the addition of NaOH and NaCl and slight decrease in leaching occurred when HCl was added (Table 3S).

Table 3S. Effect of inorganic additves on the leaching of *RhA-red* sample in MeCN/Et₃N/H₂O mixture at 25 °C.

$$Rh/Al_2O_3 \xrightarrow[\substack{MeCN\ (2\ ml) \\ 25\ °C,\ 24\ h}]{\substack{CO\ (20\ barg) \\ Et_3N\ (0.4\ ml) \\ H_2O\ (0.4\ ml)}} Rh + Al_2O_3$$

30 mg
0.47 wt% Rh
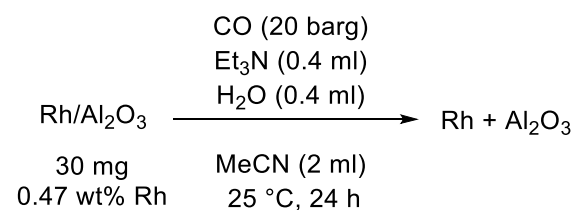
additive	*% leaching*
--	89
NaCl (10 mg)	93
NaOH (10 mg)	90
HCl (0.01 ml)	83

6.5. Leaching of Rh NP supported on titanium oxide

Predominantly-anatase, P-25 titanium oxide-supported Rh NPs *RhT* samples also leach in CO-saturated acetonitrile. As was found with the alumina-supported samples, prereduction enhanced the leaching efficiency and the addition of water and a tertiary amine improved leaching effecicny. Greater than 90% leaching was achieved on the freshly reduced *RhT* sample in a CO-saturated solution containing acetonitrile, water, and amine at room temperature (Table 4S).

Table 4S. Leaching of *RhT* sample at 25 ^{o}C

CO (20 barg)
H$_2$O (X ml)
Me$_2$NEt (Y ml)

Rh/TiO$_2$ $\longrightarrow$ Rh + TiO$_2$

30 mg MeCN (2 ml)
0.84 wt% Rh 25 °C, 24 h

pretreatment gas	*leaching conditions*		*% leaching*
	X ml H$_2$O	*Y ml Me$_2$NEt*	
Air	0	0	42
Hydrogen	0	0	56
Air	0.2	0.2	78
Hydrogen	0.2	0.2	93

6.6. Leaching of Rh NP supported on activated carbon

The standard leaching conditions at 20 barg CO pressure and 70 °C were also effective in extraction of Rh from a commercial, carbon supported sample *RhC-comm* and the Rh content was measured before and after CO leaching for 24 h at 2.53 and 0.67 wt % respectively, i.e. 74% leaching.

6.7. Leaching of non-mixed Pd, Pt, and Ru NPs on alumina at room temperature

Commercial Pd NPs *PdA-comm* sample and synthesized Pt and Ru NPs, *PtA*, and *RuA* all supported on alumina were reduced under hydrogen flow and submitted to the standard leaching conditions at 20 barg CO and room temperature with and without the addition of triethylamine to the acetonitrile/water, 5:1 v:v solution. No observable leaching of any of the three metals was detected without triethylamine, however, the addition of triethylamine caused slight leaching of Pd, and Ru at 15% and 7% respectively (Table 5S).
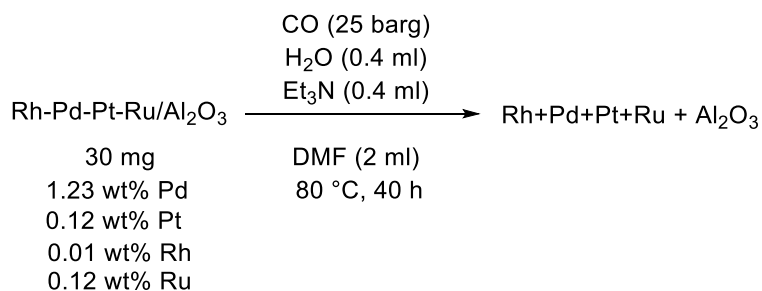
Table 5S. CO-Induced Leaching of *PdA-comm*, *PtA*, and *RuA*

CO (20 barg)
H$_2$O (0.4 mL)
Et$_3$N (X mL)

M/Al$_2$O$_3$ $\xrightarrow{\hspace{3cm}}$ M + Al$_2$O$_3$

30 mg   MeCN (2 mL)
25 °C, 24 h
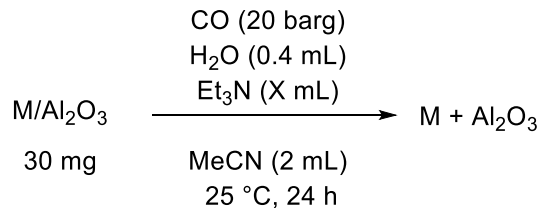
sample	% leaching	
	0 mL Et$_3$N	0.4 mL Et$_3$N
PdA-comm	0	15
PtA	0	0
RuA	0	7

6.8. Effect of additves on the leaching of a mixture of Rh, Pd, Pt, and Ru nanoparticles in DMF at 80 C.

A mixture of nanoparticles of Rh, Pd, Pt, and Ru all supported on alumina was prepared by mixing equal amounts of each individual metal. The resulting powder mixture was homogenized by further grinding and then the sample was reduced under a flow of hydrogen at 500 °C before the leaching experiment to minimize the effect of surface re-oxidation under ambient air. The leaching experiment of the solid mixture was performed at 80 °C in dimethylformamide solution of water and triethylamine 5:1:1 v. The CO pressure was set to 25 barg and the leaching was alowed to go for 40 h to test the leachability of Pd, Pt, and Ru under more forcing conditions. Additives were added to individual experiments as following; 10 mg bipyridyl as an auxilary ligand, 0.4 ml of phenyl iodide as a soruce of halogen ions, and 0.4 ml of tetraethylene diamine TMEDA as an auxiliary ligand.

Addition of phenyl iodide was found to increase the leaching of Pd and Pt indicating the effectiveness of the CO-idncued leaching of these two metals in presence of a source of halogen (Table 6S). TMEDA was found to drastically inhbit leaching of Rh potentially due to the formation of surface stable complex or hindering the formation of the soluble polynuclear carbonyl clusters. Bipyridyl did not have a significant impact on the leaching effecicny or selectivity.

Table 6S. Effect of additves on the leaching of Rh, Pd, Pt, and Ru NP in DMF at 80 ^{o}C.

$$Rh\text{-}Pd\text{-}Pt\text{-}Ru/Al_2O_3 \xrightarrow[\substack{DMF\ (2\ ml)\\ 80\ °C,\ 40\ h}]{\substack{CO\ (25\ barg)\\ H_2O\ (0.4\ ml)\\ Et_3N\ (0.4\ ml)}} Rh+Pd+Pt+Ru + Al_2O_3$$

30 mg
1.23 wt% Pd
0.12 wt% Pt
0.01 wt% Rh
0.12 wt% Ru

additive	*% leaching*			
	Rh	Pd	Pt	Ru
--	77	7	6	60
bipyridyl (10 mg)	80	18	0	55
Phenyl iodide (0.4 ml)	90	43	44	72
tetramethylethylene diamine (0.4 ml)*	20	10	0	45

*no triethylamine added

References:

(1)　H. J. Gysling, J. R. Monnier, G. Apai, *J. Catal.* 1987, **103**, 407-418.

(2)　A. Muñoz, G. Munuera, P. Malet, A. R. González-Elipe, J. P. Espinós, *Surf. Interface Anal.* 1988**, 12**, 247-252.