

Supporting Information

Bimetallic RuPd nanoparticles in ionic liquids: Selective catalysts for the hydrogenation of aromatic compounds

Gabriel Abarca,^{a,b} Wellington D. G. Gonçalves,^a Brunno L. Albuquerque,^a Jairton Dupont,^{*a} Martin H. G. Prechtl^{*c,d} and Jackson D. Scholten^{*a}

^aInstituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Agronomia, CEP 91501-970, Porto Alegre-RS, Brazil.

^bUniversidad Bernardo O'Higgins, Escuela de Obstetricia y Puericultura, Centro Integrativo de Biología y Química Aplicada (CIBQA), Santiago 8370993, Chile.

^cUniversität zu Köln, Department of Chemistry, Greinstr. 6, D-50939 Köln, Germany.

^dInstituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001, Lisboa, Portugal.

*Corresponding authors

E-mail: jairton.dupont@ufrgs.br; martin.prechtl@uni-koeln.de; jackson.scholten@ufrgs.br

Experimental

General methods

All manipulations involving the metal complexes were carried out under an argon atmosphere by using Schlenk or glovebox techniques. [Ru(COD)(2-methylallyl)₂] was obtained from Sigma-Aldrich and used without further purification. BMI.PF₆,¹ [Pd₂(dba)₃]² and the Ru⁰ and Pt⁰ NPs^{3,4} were prepared according to reported procedures. Benzene was degassed and stored under argon prior to use. All the other chemicals were purchased from commercial sources and used without further purification.

GC and GC-MS

GC analyses were run with an Agilent Technologies GC System 6820 with a FID detector and a DB-17 column (T injector=250 °C; P=103 kPa; T program=10 min at 40 °C, 10 °C min⁻¹ until 250 °C, then 10 min at 250 °C). GC-MS analyses were run with a Shimadzu QP50 with a Rtx-5MS column; T injector=250 °C; P=103 kPa; T program=10 min at 40 °C, 10 °C min⁻¹ until 250 °C, then 10 min at 250 °C; EI=70 eV).

Preparation of RuPd NPs

In a standard reaction, a Fischer-Porter bottle was loaded in the glove box with the precursor *Bis*(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II) [Ru(COD)(2-methylallyl)₂] (35.9 mg, 0.112 mmol) and BMI.PF₆ (1 mL). The system was stirred under vacuum for 20 min and heated to 75 °C. Then, 4 bar of hydrogen was added to the system, which was kept reacting for 18 h at 75 °C. The obtained black suspension was evacuated to remove the volatiles. Then, to the formed Ru nanoparticles, the precursor [Pd₂(dba)₃] (51.5 mg, 0.056 mmol) was added. After 24 h, the black suspension was placed under vacuum to remove the volatiles. The RuPd (1:9) and (9:1) NPs were prepared by fixing the Ru content and adding the desired amount of Pd, following the same procedure. For characterization analysis, the black suspension was washed with acetone (3x20 mL) followed by centrifugation. The isolated nanoparticles were dried under vacuum and stored under argon at -20 °C. The nanoparticles were analyzed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and temperature-programed reduction (TPR).

TEM

TEM analysis was performed by using a JEOL JEM 1200 ExII operating at 80 kV (CMM-UFRGS, Brazil). The samples were prepared by dropping the acetone-diluted solution of the isolated RuPd NPs onto a copper grid. Particle size distributions were determined from the digital images obtained with a CCD camera. The diameters of the particles in the micrographs were measured using the software ImageJ and the histograms were performed with OriginPro 2016.

XPS

For the XPS measurements, the powder of the RuPd NPs was spread out over the carbon tape and introduced into the analysis chamber at the D04A-SXS beam-line endstation at LNLS⁵. The spectra were collected by using an InSb (111) double crystal monochromator at fixed photon energies of 1840 and 3000 eV. The hemispherical electron analyzer (PHOIBOS HSA3500 150 R6) was set at a pass energy of 30 eV, and the energy step was 0.1 eV, with an acquisition time of 100 ms/point. The overall resolution was around 0.3 eV. The base pressure used inside the chamber was around 5.0×10^{-9} mbar. The monochromator photon energy calibration was done at the Si K-edge (1839 eV). An additional calibration of the analyzer's energy was performed by using a standard Au foil (Au 4f_{7/2} peak at 84.0 eV). The XPS measurements were obtained at a 45° take off angle at room temperature. Analysis of the Ru 3d, Pd 3d, O 1s and C 1s envelopes was performed and peak-fitted after subtraction of a Shirley background using Gaussian–Lorentzian (30%) peak shapes obtained from the Casa XPS software package.

XRD

XRD analyses were carried out using a Philips X'Pert MPD diffractometer with Bragg-Brentano geometry using a graphite curved-crystal with the Cu K α X-ray radiation (1.5406 Å). For comparison, Ru (ICSD 40354) and Pd (ICSD 76148) patterns were used.

TPR

TPR analysis were measured in Hiden analytical CATLAB-PCS combined microreactor and mass spectrometer under 20 mL.min⁻¹ H₂ 5%/Ar flow at temperatures between room temperature and 500 °C with a heating rate of 5 °C.min⁻¹.

ICP-OES

ICP measurement was performed in a Perkin Elmer Optima 2000 DV ICP-OES.

Hydrogenation reactions

In a typical experiment, a Fischer-Porter bottle loaded with freshly prepared RuPd NPs in IL (see above) was mixed with benzene or phenol as the substrate (substrate/catalyst ratio see Table 1). The mixture was stirred under a constant pressure of hydrogen gas (4 bar) at 60 °C for the indicated times (Table 1). A sample was taken from the reaction mixture every 20 min. After the desired reaction time, the reactor was cooled to room temperature and depressurized. GC and GC-MS analysis of the samples were used to determine the conversions and selectivities.

Table S1 XPS signals at Ru 3d and Pd 3d region observed for the different photon energies

Photon energy ^a	Catalyst	Ru 3d _{5/2} ^a		Pd 3d _{5/2} ^a		
		Ru(IV)	Ru(0)	Pd-X	Pd(II)	Pd(0)
1840	RuPd	282.1(58) ^b	279.8(42)	340.8(38)	338.5(39)	334.7(23)
3000	RuPd	281.4(26)	280.5(74)	-	-	334.5(100)

^a (eV); ^b in parenthesis is described the percentage of each oxidation state.

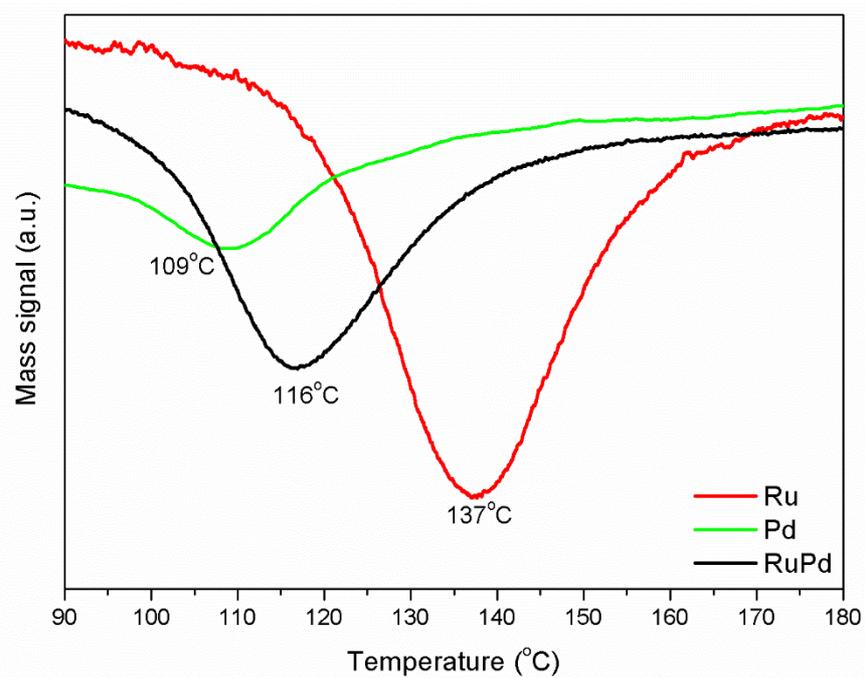


Fig. S1 TPR analysis of the catalysts.

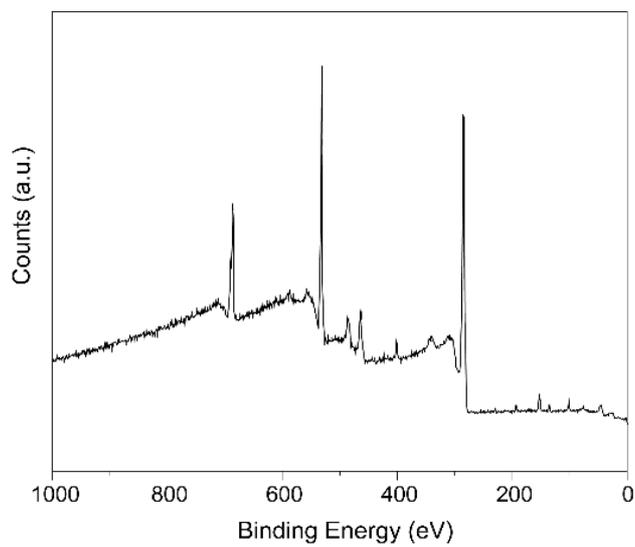


Fig. S2 Wide-scan XPS analysis of the RuPd (1:1) NPs.

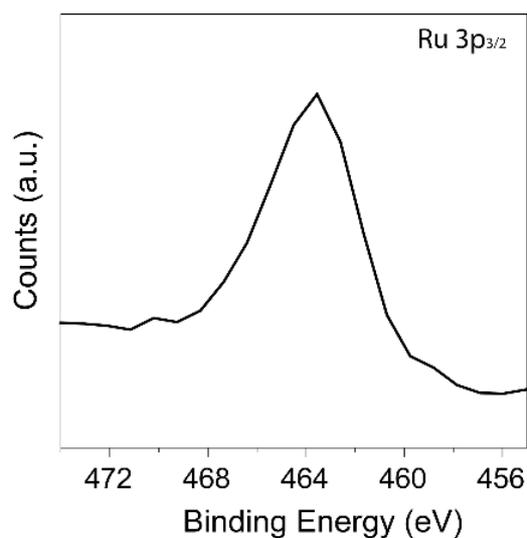


Fig. S3 XPS analysis of the RuPd (1:1) NPs showing the Ru 3p_{3/2} region.

References

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