Supporting Information

Enhancing the Catalytic Properties of Ruthenium Nanoparticle-SILP Catalysts by Dilution with Iron

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1. Experimental

Safety Warning

High-pressure experiments with compressed $H_{2(g)}$ must be carried out only with appropriate equipment and under rigorous safety precautions.

1.1. General

The supported ionic liquid phase (SILP) was synthesized as previously reported.¹ If not otherwise stated, the synthesis of the SILP and FeRu NPs immobilized on SILPs (FeRuNPs@SILP) were carried out under an inert atmosphere using standard Schlenk techniques or within a glovebox. After synthesis, SILPs and FeRuNPs@SILPs were stored under an inert atmosphere. Furfuralacetone and benzylideneacetone were purified by sublimation prior to use. Catalyst solutions and substrates were prepared under an inert atmosphere. Furfuralacetone and the SILP were synthesized according to known literature methods. {Fe[N(Si(CH₃)₃)₂]₂} and [Ru(cod)(cot)] were obtained from NanoMePS. Mesitlyene (from VWR Prolabo, 99%) was dried over alumina desiccant and degassed *via* freeze-pump-thaw cycling. All other chemicals and solvents were purchased from commercial sources and used without purification.

1.2. Analytics

Solution-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300, 400 or 600 MHz spectrometer. ¹H and ¹³C NMR spectra were calibrated to TMS using the residual solvent signal. High-pressure experiments were performed using in-house engineered 10 and 20 mL stainless steel finger autoclaves. Catalytic reactions were performed in glass inlets using a magnetic stirbar (500 rpm) and an aluminum heating block. Gas chromatography (GC) was performed on a Thermo Scientific Chromatograph Tace GC Ultra equipped with a CP-Wax 52 CB column from Agilent. Brunauer-Emmett-Teller (BET) measurements were performed on a Quadrasord SI automated Surface Area and Pore Size Analyzer from Quantachrome Instruments and the data analysis using QuadraWin 5-04. Transmission electron microscopic (TEM) images were collected using a JEOL JEM 1400 operated at 120kV and using a tungsten filament. The NP size and distribution was determined from the measurement of >150 spherical particles chosen in arbitrary areas of enlarged micrographs. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) was performed on a JEOL JSM 7800F operated at 10 kV with a thermally-assisted Schottky electron gun and equipped with a Bruker XFlash[®] 6|60 detector (silicon drift detector technology). Scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM/EDS) was obtained on a Hitachi S-5500 ultrahighresolution cold field emission scanning microscope with a Thermo Scientific NORAN System 7 X-ray Microanalysis unit at an acceleration voltage of 30 kV. X-ray absorption fine structure (XAFS) measurements were carried out on the CLÆSS beamline of the ALBA synchrotron facility (Barcelona, Spain).

2. Synthesis of Supported Ionic Liquid Phases and Bimetallic Catalysts

2.1 Synthesis of Supported Ionic Liquid Phase



Scheme S1: Synthesis of the supported ionic liquid phase

[1-butyl-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (5.49 g, 8.80 mmol) were combined and dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO₂ (10.0 g in 50.0 mL toluene). After stirring for 15 min at rt, DCM was removed *in vacuo* and the resulting mixture was refluxed for 18h. Upon removal of the organic phase, the SILP was washed with DCM (3x25 mL) and dried *in vacuo*. The organic phases were combined and solvent removed to determine the residual quantity of IL not grafted onto the dehydroxylated SiO₂ (Total IL Loading = Theoretical Loading – Recovered Residual IL). Total IL Loading = 0.732 mmol IL/g SiO₂. BET Surface Area = 211 m²/g and Pore Radius = 35.7 Å.

2.2 Characterization of Iron-Ruthenium Nanoparticles Immobilized a Supported Ionic Liquid Phase (FeRuNPs@SILP)

2.2.1 Characterization of FeRuNPs@SILP Before Catalysis

Catalyst	Metal Ra	itio (%)ª	Metal Loading	TEM NP Size	
	Fe	Ru	(%) ^b	(nm)	
Fe ₁₀₀	99±1	1±1	0.9±0.3	3.3±0.5	
Fe ₆₀ Ru ₄₀	61±4	39±4	1.1 ± 0.4	3.2±0.5	
Fe33Ru67	33±5	67±5	1.0 ± 0.4	2.9±0.5	
Fe25Ru75	24±4	76±4	1.0 ± 0.4	3.4±0.5	
Fe20Ru80	19±3	81±3	1.0±0.3	3.5±0.5	
Ru ₁₀₀	1±1	99±1	0.8±0.4	3.4±0.6	

Table S1: SEM/EDX and TEM data for FeRuNPs@SILP

^a Determined by SEM/EDS, Metal ratio = [(metal atomic counts)/(Fe atomic counts + Ru atomic counts)]×100. ^b Determined by SEM/EDS, Metal loading = [(Fe atomic counts + Ru atomic counts)/(total atomic counts)]×100.



Figure S1: Transmission electron microscopic images for (a) $Fe_{60}Ru_{40}NPs@SILP$, (b) $Fe_{33}Ru_{67}NPs@SILP$, (c) $Fe_{25}Ru_{75}NPs@SILP$, (d) $Fe_{20}Ru_{80}NPs@SILP$, (e) $Ru_{100}NPs@SILP$ and (f) $Fe_{100}NPs@SILP$ before catalysis.



Figure S2: Transmission electron microscopic histograms for (a) Fe₆₀Ru₄₀NPs@SILP, (b) Fe₃₃Ru₆₇NPs@SILP, (c) Fe₂₅Ru₇₅NPs@SILP, (d) Fe₂₀Ru₈₀NPs@SILP, (e) Ru₁₀₀NPs@SILP and (f) Fe₁₀₀NPs@SILP before catalysis.

2.2.2 Characterization of FeRuNPs@SILP After Catalysis

Catalyst	Surface area	Pore Radius	Metal Ra	tio (%) ^a	Metal Loading	NP Size (nm)	
	(m ² ·g ⁻¹)	(Å)	Fe	Ru	(%) ^b		
Before Catalysis	201	33.2	24±4	76±4	1.0 ± 0.4	3.4±0.5	
After Catalysis	198	33.1	25±5	75±5	0.7±0.4	3.2±0.5	

Table S2: Characterization data for Fe₂₅Ru₇₅NPs@SILP after catalysis

^a Determined by SEM/EDX, Metal ratio = [(metal atomic counts)/(Fe atomic counts + Ru atomic counts)] *100. ^b Determined by SEM/EDX, Metal loading = [(Fe atomic counts + Ru atomic counts)/total atomic counts] *100.



Figure S3: Transmission electron microscopic (a) image and (b) histogram for Fe₂₅Ru₇₅NPs@SILP after one cycle of catalysis.

2.2.3 Characterization of FeRuNPs@SILP using X-ray Absorption Spectroscopy

X-ray Absorption Fine Structure (XAFS) Measurements

FeK (7111 eV) and RuK (22117 eV) XAFS measurements were carried out on the CLÆSS beamline of the ALBA synchrotron facility. Si (111) and Si (311) double crystal monochromators were used for the energy scan along with Rh-coated toroid mirror for unwanted harmonics elimination. The spectra were recorded in the fluorescence mode at ambient temperature. For the measurements, 2-mm thick PTFE spacer rings were filled with the sample powders under inert atmosphere and sealed with Kapton tape. Spectra were measured simultaneously with the reference spectrum foil placed between the second and third ionization chambers, so that the absolute energy calibration was performed. All spectra were measured two times to ensure their reproducibility.

XAFS Data Analysis

Standard procedures were followed to analyze the XAFS data. First, the raw absorption spectrum in the pre-edge region was fitted to a straight line and the background above the edge was fitted with a cubic spline. The EXAFS function, $\chi(E)$, was obtained by subtracting the post-edge background from the overall absorption and then normalized with respect to the edge jump. The normalized $\chi(E)$ was transformed from energy space to k-space, where k is the photoelectron wave vector. The $\chi(k)$ data were multiplied by k^2 to compensate the damping of EXAFS oscillations in the high k-region. Subsequently, k²-weighted $\chi(k)$ data in the k-space ranging from 2.8 to 13.8 Å⁻¹ for the Ru *K*-edge and from 2.8 to 13.1 Å⁻¹ for the Fe *K*-edge were Fourier transformed (FT) to r-space to separate the EXAFS contributions from the different coordination shells. A non-linear least-squares algorithm was applied to the curve fitting of an EXAFS in the r-space between 1.3 and 3.2 Å (without phase correction) for Ru and between 1.2 and 2.9 Å for Fe. All of the manipulations were performed in the VIPER program [Klementiev K. V., VIPER for Windows; www.cells.es/Beamlines/CLAESS/software/viper.html]² with the backscattering amplitude and the phase shift for the specific atom pairs being theoretically calculated by using FEFF8 code.³ From EXAFS analysis, structural parameters, such as coordination numbers (CN), bond distance (R), the Debye-Waller factor (σ^2), and inner potential shift (ΔE_0) were calculated.



Figure S4. Normalized Fe *K*-edge XANES spectra of Fe reference compounds, α -Fe₂O₃ (black), FeO (red) and Fe foil (blue), where the pre-edge and absorbance edge have been marked as **P** and **A**, respectively.



Figure S5. Fe *K*-edge EXAFS spectra of Fe reference compounds, Fe foil (blue) and α -Fe₂O₃ (black)



Figure S6: Ru K-edge spectra of the (a) XANES and (b) EXAFS regions for a Ru foil reference (black), Fe₂₅Ru₇₅NPs (after catalysis) (orange), Fe₂₅Ru₇₅NPs (oxidized) (light green), Fe₂₅Ru₇₅NPs (red) and a RuO₂ reference (light blue)



Figure S7. Fe K-edge spectra of the (a) XANES and (b) EXAFS regions for Fe₁₀₀NPs@SILP (blue), Fe₁₀₀NPs@SILP (oxidized) (dark green), Fe₂₅Ru₇₅NPs (after catalysis) (orange), Fe₂₅Ru₇₅NPs (oxidized) (light green) and Fe₂₅Ru₇₅NPs (red)



Figure S8. Modelling of the Fe K-edge EXAFS spectrum of $Fe_{25}Ru_{75}NPs@SILP$ with contributions of Fe-O, Fe-Fe and Fe-Ru backscattering, (a) absolute value of FT (r-space), (b) experimental spectrum in k-space and (c) reverse FT in k-space (BFT, within r = 0.6 ... 3.5 Å), model and contributions of individual shells to model. The model results from superposition of the contributions in k-space, not in r-space.

Table S3. Total coordination numbers, pairing factors and alloy extent for Fe and Ru in bimetallicFeRu@SLIP catalysts estimated from EXAFS spectra

Sample	Coordination Numbers (CN)				Pairing Factors (P _{observed})		Alloy Extent (%)		Structure	
	Fe-Ru	Fe-i	Ru-Fe	Ru- <i>i</i>	Fe	Ru	J _{Fe}	J _{Ru}		
Fe ₆₀ Ru ₄₀ NPs@SILP	4.10	10.49	4.38	9.68	0.39	0.45	98	75	Homophilic	
Fe ₂₅ Ru ₇₅ NPs@SILP	2.67	4.06	1.52	7.89	0.66	0.19	93	77	Homophilic	
Fe ₂₅ Ru ₇₅ NPs@SILP (after catalysis)	2.73	3.91	1.13	7.15	0.70	0.16	93	63	Homophilic	
Fe25Ru75NPs@SILP (oxidized)	4.18	5.51	1.57	7.21	0.76	0.22	101	87	Homophilic	

3. Catalytic Data for the Selective Hydrogenation of Substituted Aromatic using FeRuNPs@SILP

Table S4. Influence of exposure of $Fe_{25}Ru_{75}NPs@SILP$ to atmospheric conditions prior to catalysis in the hydrogenation of furfural acetone (6)^a

Experimental Details		Product Yield (%) ^b					
	6a	6b	6c	6d			
Without exposure to atmosphere	0	0	94	6			
With exposure to atmosphere ^[c]	0	0	60	40			

^a Reaction conditions: $Fe_{25}Ru_{75}NPs@SILP$ (40 mg, 0.016 mmol total metal loading), Mesitylene (0.5 mL), Furfuralacetone (0.4 mmol), H₂ (20 bar), 100°C, 18h, magnetically stirred at 600 rpm. ^b Conversion = >99% as determined by GC using tetradecane as an internal standard. ^[d] Reaction mixture was exposed to the atmosphere for 1h prior to catalysis.



Figure S9. Kinetic data for the C=O reduction of intermediates **6a** and **6c** within the reaction network for the hydrogenation of furfuralacetone catalyzed by (a) Fe₂₅Ru₇₅NP@SILP and (b) Ru₁₀₀NPs@SILP, respectively.

4. References

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