

Supplementary Material

Reductive amination of phenol over Pd-based catalysts: Elucidating the role of the support and metal cluster size

Maray Ortega^a, David Gómez^b, Raydel Manrique^a, Guillermo Reyes^c, Julieth Tatiana García-Sánchez^d, Víctor Gabriel Baldovino Medrano^{d,e}, Romel Jiménez^b, Luis E. Arteaga-Pérez^{a,f*}

^a Laboratory of Thermal and Catalytic Processes (LPTC), Wood Engineering Department, Faculty of Engineering, Universidad del Bio-Bio, Concepción, Chile. Email: larteaga@ubiobio.cl Twitter: @LptcUbb

^b Carbon and Catalysis Laboratory (CarboCat), Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile.

^c Biobased Colloids and Materials, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FI-00076, Espoo, Finland.

^d Centro de Investigaciones en Catálisis (CICAT), Universidad Industrial de Santander, Colombia

^e Laboratorio Central de Ciencia de Superficies (SurfLab), Universidad Industrial de Santander, Colombia

^f Universidad de Concepción, Unidad de Desarrollo Tecnológico, UDT, Coronel, Chile

Catalysts

Synthesis and pre-treatments

The synthesis of the catalysts was carried out by incipient wet impregnation using PdCl₂ (59%, Sigma Aldrich) as the Pd precursor, with the addition of triethanolamine (TEA, ≥ 99.0%, Merck) and hydrochloric acid (HCl (aq.) ≥ 37.0% Merck). The addition of triethanolamine (mol (TEA)/mol (Pd) = 4) allows the amino groups to act as a coordination site for metallic Pd. The Al₂O₃ (CAS 44740-22) and SiO₂ (CAS 43855-30) were purchased from Alfa-Aesar (Chile) as pellets, thus they were dried at 100 °C for 24 h, crushed, and sieved to particle sizes <75 μm before use.

After impregnation, the catalyst's precursors were dried at 60 °C for 48 h in static air in a drying oven (Lab Tech, LDO-150F) and then calcined at 500 °C for 2 h (2 °C/min) in a muffle (Nabertherm). After calcination, the precursors were placed in a U-shaped reactor (18 mm ID) and treated under a constant flow of H₂ (99.999%, 40 mL/min) at 400 °C (2 h dwell time), using a heating rate of 2 °C/min. The metal loading (1 – 10%wt. Pd) over Al₂O₃ and the heating ramp for reduction were varied for generating four different Pd cluster sizes (denoted as Pd/Al₂O₃-D1, Pd/Al₂O₃-D2, Pd/Al₂O₃-D3, and Pd/Al₂O₃-D4, here D1 to D4 indicates the increasing particle sizes).

Surface characterization by Pyridine FTIR

The nature of surface acid sites (Lewis or Brønsted) was inspected by infrared spectroscopic investigation of the pyridine (C₅H₅N, J.T. Baker, >99.9%) adsorption and desorption tests. Samples were pressed (2 tons, 1 min) on 13 mm discs (10 mg) and mounted inside a flow cell, equipped with ZnSe windows and a vacuum system (Pfeiffer Hicube Eco Turbo). The samples were outgassed at 10⁻⁴ Pa and 450 °C (5 °C/min) for 10 hours. Then the spectrum of the outgassed samples was taken as a baseline, and the adsorption of pyridine was initiated at 150 °C for 30 min. Subsequently, desorption was carried out at 25, 140, 250, and 400 °C for 30 min each. The IR spectra corresponding to each of the desorption temperatures were collected with a Nicolet iS50 (ThermoScientific) using an MCT detector, 32 scans with a resolution of 4 cm⁻¹. Pyridine adsorbed at Lewis (L-Py) and Brønsted (PyH⁺) acid sites exhibits bands at around 1445–1460 cm⁻¹ and 1540–1548 cm⁻¹, respectively. The bands of hydrogen-bonded pyridine (hb-Py) are in similar ranges of 1440–1447 cm⁻¹ and 1590–1600 cm⁻¹.

Surface characterization by SEM-EDX

Scanning electron microscopy (SEM) measurements were recorded after the reduction of the precursors. This analysis was performed, in a Hitachi SU3500 microscope operated at an accelerating voltage of 20kV and coupled to a Bruker XFlash 610M energy-dispersive X-ray (EDX) accessory. Figure M3 shows the SEM micrograph and EDX signals of the Pd catalysts supported on C, SiO₂, and Al₂O₃. The recorded images showed a uniform distribution of the metal particles along the surface of the three catalysts indicating that the anchoring of the metal during impregnation was successful.

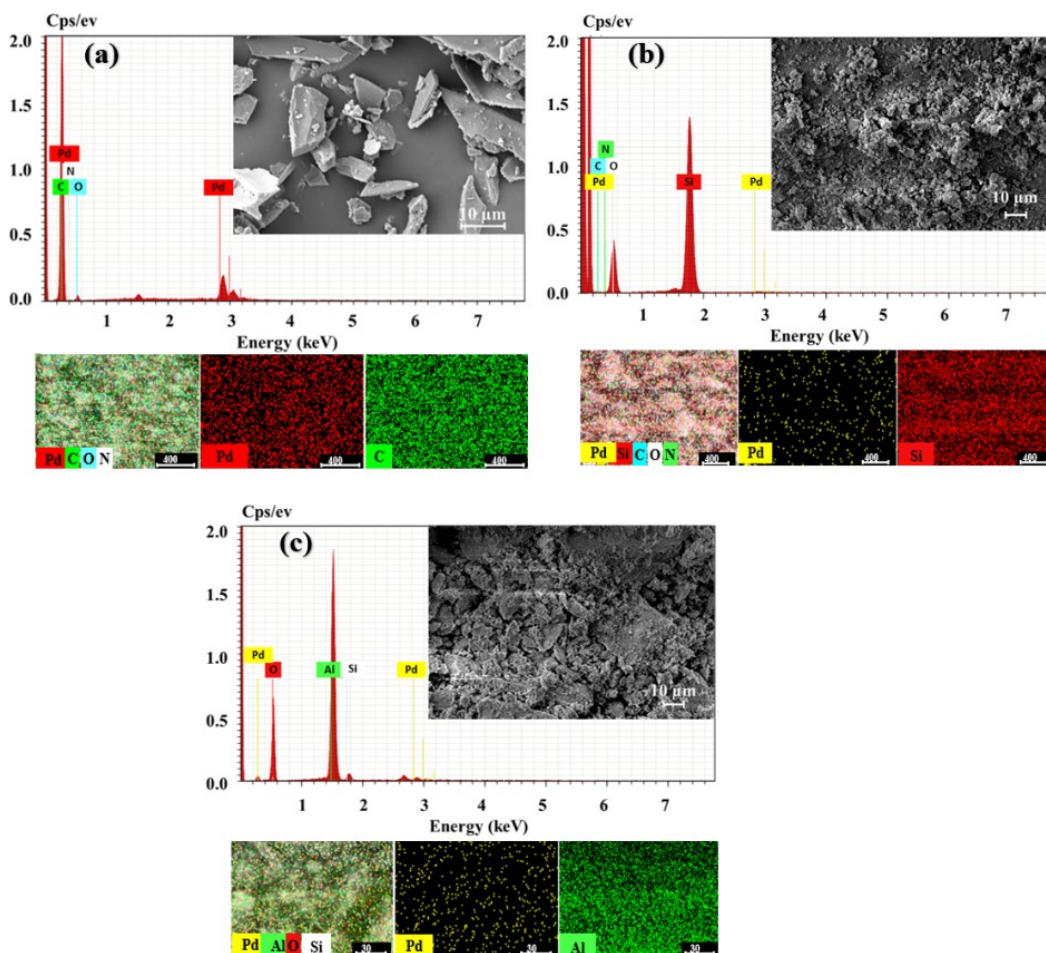


Figure E1. SEM-EDX characterization of the corresponding spatial distribution of (a) Pd/C, (b) Pd/SiO₂, (c) Pd/Al₂O₃ catalysts.

Table E1. Results from the chemical characterization of catalysts.

Catalyst	Metal content by AAS* (nm)	Metal content by SEM-EDX (nm)
Pd/C	9.37±0.6	10.8±0.4
Pd/SiO ₂	9.35±0.08	8.7±0.07
Pd/Al ₂ O ₃ -D3	8.95±0.6	10.1±0.07
Pd/Al ₂ O ₃ -D4	8.95±0.6	n.d.
Pd/Al ₂ O ₃ -D2	4.87±0.13	n.d.
Pd/Al ₂ O ₃ -D1	1.09±0.01	1.08±0.07

* The composition by AAS was used for the estimation of TOF.

Surface characterization by NH₃-TPD

The bulk surface acidity of the Pd catalysts supported on C, SiO₂ and Al₂O₃ were inspected by temperature-programmed desorption of ammonia (NH₃-TPD). The experiments were carried out using the 3FLEX (Micromeritics) apparatus equipped with a TCD combined with a mass spectrometer (Cirrus 2, MKS Spectra Product). Before analysis, samples (~30 mg) were pre-treated 30 min under a He flow (50 mL/min) at 350 °C (10 °C/min) up to baseline stabilization. The adsorption of NH₃ was carried out at 100 °C for 15 min (30 mL/min). Once the surface was saturated, the weakly adsorbed NH₃ was removed by flowing He (100 mL/min) at 100 °C for 0.5 h. Subsequently, desorption was carried out using a linear heating rate of 10 °C/min from 100 to 550 °C. Products formed during the TPD-NH₃ treatment were identified by a mass spectrometer by following specific fragments, m/z 17, 18, 28 corresponding to the m/z of NH₃, H₂O, and N₂, respectively. All desorption profiles were normalized per gram of catalyst (Figure M2), and the density of acid sites ($\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{cat}}$) was obtained from the ponderation of total acidity by the surface area (m^2/g). The strength of the acid sites was ascribed to the temperature-relative position of peaks (weak <250 °C, medium 250 – 450 °C, and strong >450 °C).

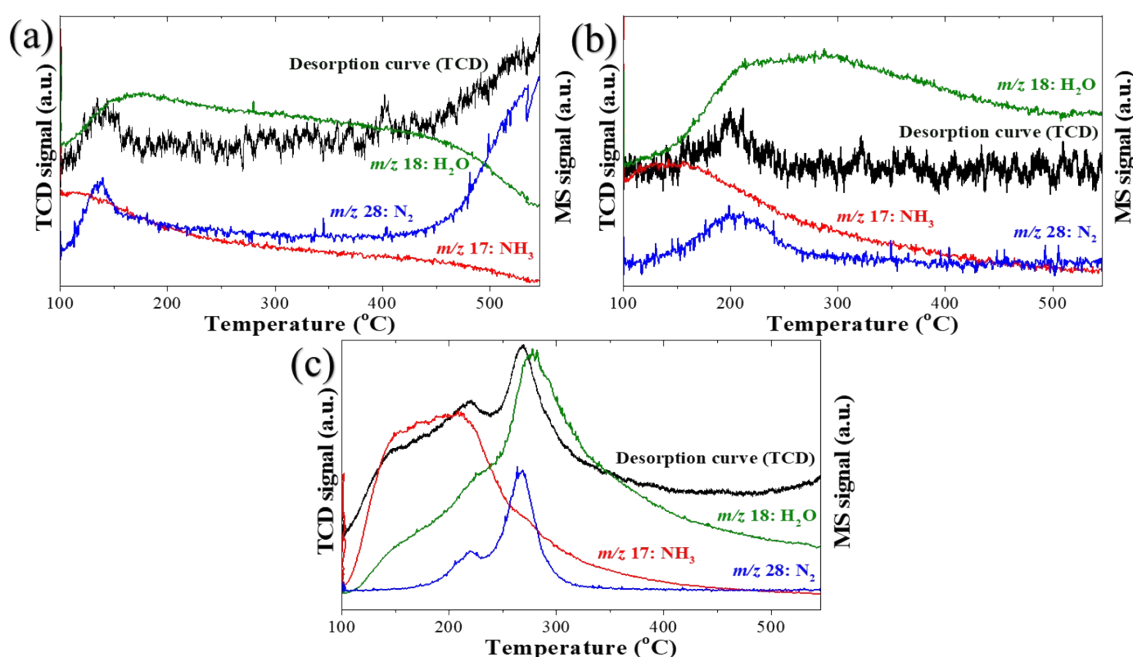


Figure E2. NH₃-TPD profiles of the supported Pd catalysts: (a) Pd/C, (b) Pd/SiO₂ and (c) Pd/Al₂O₃-D3

Experimental design

Prior to the activity test and kinetic measurements, the absence of mass transfer limitations is inspected. To guarantee that the catalytic activity tests are carried out under a regimen of kinetic control, the quantitative parameters of Mears and Weisz-Prater [11] were calculated and the mass balance closure was verified.

Products identification and quantification

Identification

An aliquot of the reaction products (100 μL) obtained according to the previous procedure and stored at -40 °C, is transferred to amber GC Vials along with 500 μL of solvent. Then these samples are analyzed by gas chromatography coupled to mass spectrometry for the identification of analytes. The analysis is performed in a Clarus 690 (Perkin Elmer) chromatograph equipped with a quadrupole mass detector (SQ8S, Perkin Elmer). The compounds are separated in an Elite 1701 column (30 m \times 0.25 mm \times 0.25 μm) by heating from 45 to 280 °C at 2.5 °C min^{-1} . The MS is operated at 70 eV, and a sweep of m/z between 30 and 600 Da is performed. The identification is done by comparing the ionization patterns of the identified species with the NIST mass spectra MS library using a Match cut-off above 85%.

The complete data of the compound's identification for the phenol amination with cyclohexylamine, and for the auto-condensation of the cyclohexylamine are provided in the files ESI-2.xls and ESI_3.xls, respectively.

Quantification

The reaction mixtures are analyzed by ex-situ gas chromatography (GC) using n-nonane as internal standard. The samples are then analyzed by ex-situ gas chromatography in an SRI chromatograph (Model 8610) equipped with an on-column injection port, a flame ionization detector (FID) and a MTX-5 column (30 m X 0.25 mm X 0.1 μm). Retention time's assignment is done by injecting solvent-pure products samples prior to samples analysis.

Table. E2. Reaction conditions for phenol amination with cyclohexylamine. Solvent = tert Amyl Alcohol, and Pd/C (10 wt.%). Second section is referred to the conditions for the kinetic experiments.

Run	Phenol Concentration (mol/L)	CyA (Eqv)	Catalyst	Run	Phenol Concentration (mol/L)	CyA (Eqv.)	Catalyst
1	0.2	1.4	None	7	0.2	1.4	Pd/C
2	0.2	1.4	Al ₂ O ₃	8	0.2	1.4	Pd/ SiO ₂
3	0.2	1.4	C	9	0.2	1.4	Pd/Al ₂ O ₃ -D1
4	0.2	1.4	SiO ₂	10	0.2	1.4	Pd/Al ₂ O ₃ -D2
5	None	1.4	Pd/C	11	0.2	1.4	Pd/Al ₂ O ₃ -D3
6	0.2	None	Pd/C	12	0.2	1.4	Pd/Al ₂ O ₃ -D4

Evaluation of mass transfer limitations

The Weisz-Prater criterion was used to rule out the influence of internal limitations while the Mear's criterion was applied to evaluate the importance of external mass transfer limitations.

$$\text{Weisz-Prater: } \Phi_{WP} = \frac{r_{obs} * R_p^2}{C_{s,i} * D_{eff}}$$

$$\text{Mears: } Cm = \frac{-r_{obs} * \rho_b * R_p * n}{k_c * C_s}$$

Here r_{obs} is the initial reaction rate, R_p is the mean radius of the catalyst particle, D_{eff} is de effective diffusivity of the reactant in the solvent, and C_s is the substrate concentration.

The initial rates (r_{obs}^0 , mol_i/L min) were calculated by polynomial regression, and differentiation of the C_i vs time curves extrapolated to zero-time for conversion below 20%.

$$r_i^0 = \left[\left(\frac{dC_i}{dt} \right) \right]_{t=0}$$

Table E3. Application of the Mears's criterion to the reaction system. calculated from the initial reaction rate at agitation rates of 900 rpm on Pd/C, Pd/SiO₂ and Pd/Al₂O₃ catalysts. **Reaction conditions:** T = 140 °C, P_{H2}= 1.5 bar, C⁰PhOH = 0.2 mol/L, m_{cat} (Pd/C; Pd/SiO₂; Pd/Al₂O₃) = 0.3 g, VR = 15 mL.

Catalysts	Parameter	Phenol	Cyclohexylamine
General	<i>Re</i>	81818.2	81818.2
	<i>Sc</i>	144.3	544.8
	<i>Sh</i>	658.5	1019.8
<i>Pd/C</i>	<i>k_c (m/s)</i>	0.0335	0.0137
	<i>ρ_b (g/cm³)</i>	0.225	0.225
	<i>R_p (m)</i>	0.000050	0.000050
	<i>r_{obs} (mol/s g_{cat})</i>	7.92*10 ⁻⁷	7.92*10 ⁻⁷
	<i>Cm</i>	2.54*10⁻⁶	6.19*10⁻⁶
<i>Pd/SiO₂</i>	<i>k_c (m/s)</i>	0,0096	0,0039
	<i>ρ_b (g/cm³)</i>	0.140	0.140
	<i>R_p (m)</i>	0.000175	0.000175
	<i>r_{obs} (mol/s g_{cat})</i>	1.63*10 ⁻⁷	3.26*10 ⁻⁷
	<i>Cm</i>	3.98*10⁻⁶	1.94*10⁻⁵
<i>Pd/Al₂O₃ – D3</i>	<i>k_c (m/s)</i>	0,0096	0,0039
	<i>ρ_b (g/cm³)</i>	0.310	0.310
	<i>R_p (m)</i>	0.000175	0.000175
	<i>r_{obs} (mol/s g_{cat})</i>	9.01*10 ⁻⁷	1.22*10 ⁻⁶
	<i>Cm</i>	4.86*10⁻⁵	1.61*10⁻⁴

Table E4. Application of the Weisz-Prater criterion to the reaction system, calculated from the initial reaction rate on Pd/C, Pd/SiO₂ and Pd/Al₂O₃ catalysts. **Reaction conditions:** T = 140 °C, P_{H2}= 1.5 bar, C⁰PhOH = 0.2 mol/L, m_{cat} (Pd/C; Pd/SiO₂; Pd/Al₂O₃) = 0.3 g, VR = 15 mL, agitation rates = 900 rpm.

Catalysts	Parameter	Phenol	Cyclohexylamine
<i>Pd/C</i>	<i>λ</i>	0,232	0.245
	<i>D_{eff} (cm²/s)</i>	9.87*10 ⁻⁶	1.54*10 ⁻⁶
	<i>r_{obs} (mol/s cm³)</i>	1.78*10 ⁻⁷	1.78*10 ⁻⁷
	<i>φ_{WP}</i>	0.0022	0.0138
<i>Pd/SiO₂</i>	<i>λ</i>	0.040	0.042
	<i>D_{eff} (cm²/s)</i>	4.48*10 ⁻⁵	7.35*10 ⁻⁶
	<i>r_{obs} (mol/s cm³)</i>	2.28*10 ⁻⁸	4.56*10 ⁻⁸
	<i>φ_{WP}</i>	0.0007	0.0090
<i>Pd/Al₂O₃ – D3</i>	<i>λ</i>	0.060	0.064
	<i>D_{eff} (cm²/s)</i>	3.57*10 ⁻⁵	5..80*10 ⁻⁶
	<i>r_{obs} (mol/s cm³)</i>	2.79*10 ⁻⁷	3.78*10 ⁻⁷

 ϕ_{WP} **0.0114****0.0950**
