

SUPPLEMENTARY INFORMATION

Thiol functionalised supports for controlled metal nanoparticle formation for improved C-C coupling

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Experimental

Synthesis: “Thiol-SiO₂” was synthesised by mixing 0.2 g of 3-mercaptoptrimethoxysilane, 100 mL of toluene and 5.0 g of mesoporous 150 Å Davison Silica Gel with 60 – 200 mesh size (“Bare SiO₂”). This was stirred at 70 °C for 24 hours, and then filtered and washed sequentially with 500 mL of toluene, hexane and ethanol. The system was then dried overnight at 70 °C.

“Pd-Thiol-SiO₂ AS” and “Pd-SiO₂ AS” were synthesised by mixing 1.0 g of either “Thiol-SiO₂” or “Bare SiO₂” respectively, with 20 mL of methanol and 0.033 g of K₂PdCl₄. This was stirred at room temperature for 24 hours, then subsequently filtered with 100 mL of methanol and dried overnight at 70 °C.

“Pd-Thiol-SiO₂ Red” and “Pd-SiO₂ Red” were formed by activating either “Pd-Thiol-SiO₂ AS” or “Pd-SiO₂ AS” (respectively) at 300 °C, under a flow of 200 mL/min of 5% H₂ in N₂, at a ramp rate of 1 °C/min.

Nitrogen physisorption: Nitrogen physisorption were performed at 77 K, on a sample dried under 20 mTorr of vacuum at 120 °C overnight. Analysis was performed on a Micromeritics Gemini 2375 surface area analyser. Surface area was calculated using the BET model,^[S1] and the pore width distributions was determined using the BJH method.^[S2]

Metal content: Pd and Si were measured using ICP-AES, whilst C, H, N and S elemental analysis was obtained through MEDAC as a commercial service.

Solid state NMR: Samples were packed into 3.2 mm Bruker rotors, for a total sample weight of 14 mg, in all cases. Samples were acquired at a spinning rate of 20 kHz in double resonance mode, using a Bruker Avance Neo Spectrometer with a 9.4 T widebore magnet, in air. The sample ¹H T₁ was assessed using a saturation recovery pulse technique, which was used for ¹³C cross-polarization with ramped amplitude on the ¹H channel^[S3] and SPINAL64 1H decoupling.^[S4] ¹³C chemical shift was calibrated using adamantane as indirect chemical shift reference.^[S5]

UV/Vis: Perkin Elmer Lambda 35 spectrophotometer was used to collect the reflectance UV/Vis spectra of powdered samples. BaSO₄ was used as a reference solid material.

TEM: TEM micrographs were obtained with the FEI Tecnai T12 instrument at Biomedical Imaging Unit, University Hospital Southampton.

XPS: XPS was measured at Harwell XPS, an EPSRC national facility for X-ray photoelectron spectroscopy. The obtained spectra were calibrated against C1s peak at 285 eV. The data was fitted using the CasaXPS software.^[S6]

Catalysis: 0.115 g (0.94 mmol, Limiting reagent) of phenylboronic acid, 0.12 g (0.86 mmol) of naphthalene (internal standard), 0.12 g (0.87 mmol) of anhydrous potassium carbonate, 0.05 g of catalyst (total mass) and 1.22 mmol of halogenated benzene substrates (all purchased from Sigma Aldrich, with > 99 % purity) were mixed with 15 mL of ethanol and stirred at 40 °C for 8 hours. Samples were taken every 2 hours, and the liquid reaction mixture was centrifuged before being injected into a Clarus 480 GC equipped with an Elite-5 column and a Flame-Ionized Detector, which used the areas of halogenated benzene (reagent), naphthalene (internal standard) and biphenyl (product) to convert peak areas to moles, using relative response factors, derived from calibrations (Figure S1). Similar calibrations were also performed for chlorobenzene, bromobenzene, 1-iodo-4-nitrobenzene and 4-nitrobiphenyl.

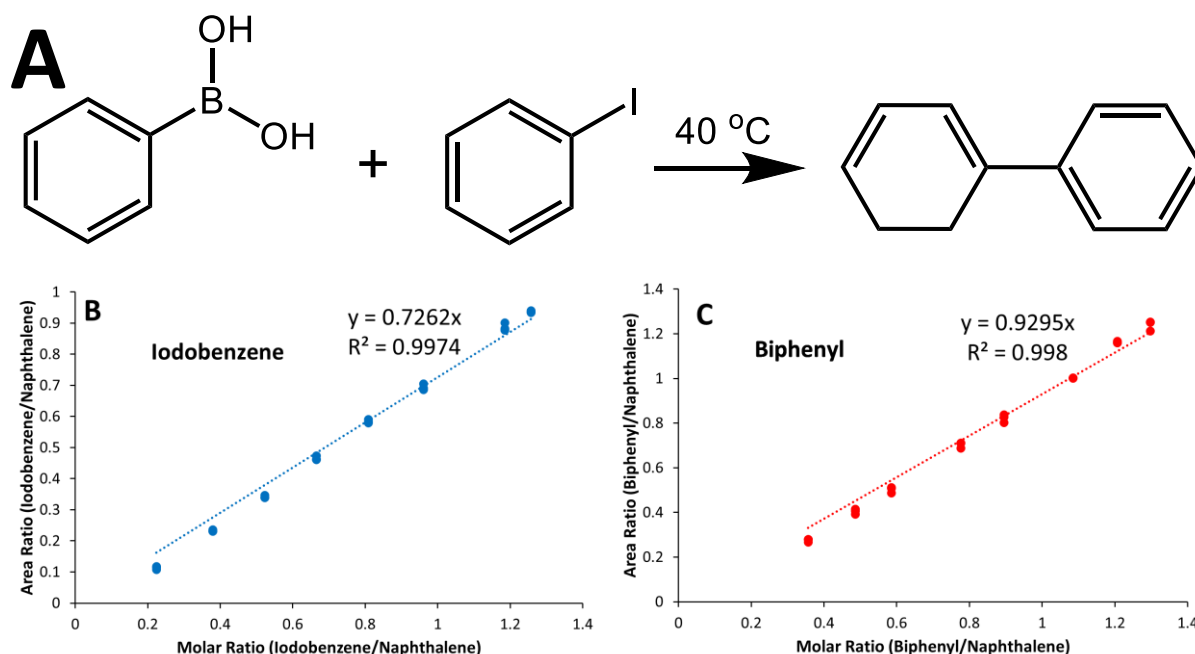


Figure S1: A) Reaction scheme of the Suzuki coupling reaction with associated calibration data, yielding the relative response factors of 0.7262 and 0.9295 for iodobenzene (B) and biphenyl (C), relative to the naphthalene internal standard.

The biphenyl yield (relative to the limiting reagent, Phenylboronic acid), turnover number (TON) and turnover frequency were calculated thus:

$$\text{Biphenyl Yield (mol\%)} = \frac{100\% \times \text{Biphenyl Moles (mol)}}{\text{Initial Phenylboronic Acid Moles (mol)}}$$

$$\text{Turnover Number (molmol}^{-1}\text{)} = \frac{\text{Biphenyl Moles (mol)}}{\text{Moles of Pd (mol)}}$$

$$\text{Turnover Frequency (hr}^{-1}\text{)} = \frac{\text{Turnover Number (molmol}^{-1}\text{)}}{\text{Time (hr)}}$$

And the mass balance (which was constantly between 95-105 mol%), was also calculated as:

$$\text{Mass Balance (mol\%)} = 100\% \times \frac{\text{Biphenyl Moles (mol)} + \text{Iodobenzene Moles (mol)}}{\text{Initial Iodobenzene Moles (mol)}}$$

Catalyst recycling was performed by filtering off the used catalyst, reactivating it at 300 °C, under a flow of 200 mL/min of 5% H₂ in N₂, at a ramp rate of 1 °C/min. After this the catalyst was tested in a fresh system.

Characterising thiol-SiO₂ systems

Table S1: Elemental analysis and metal loadings for thiol-grafted SiO₂ systems.

System	Elemental loadings (wt%)			C/S Molar ratio
	C	S	Pd	
Thiol-SiO ₂	1.15	0.97	N/A	3.16
Pd-Thiol-SiO ₂ AS	1.29	0.83	0.72	4.15
Pd-Thiol-SiO ₂ Red	0.82	0.69	0.76	3.17

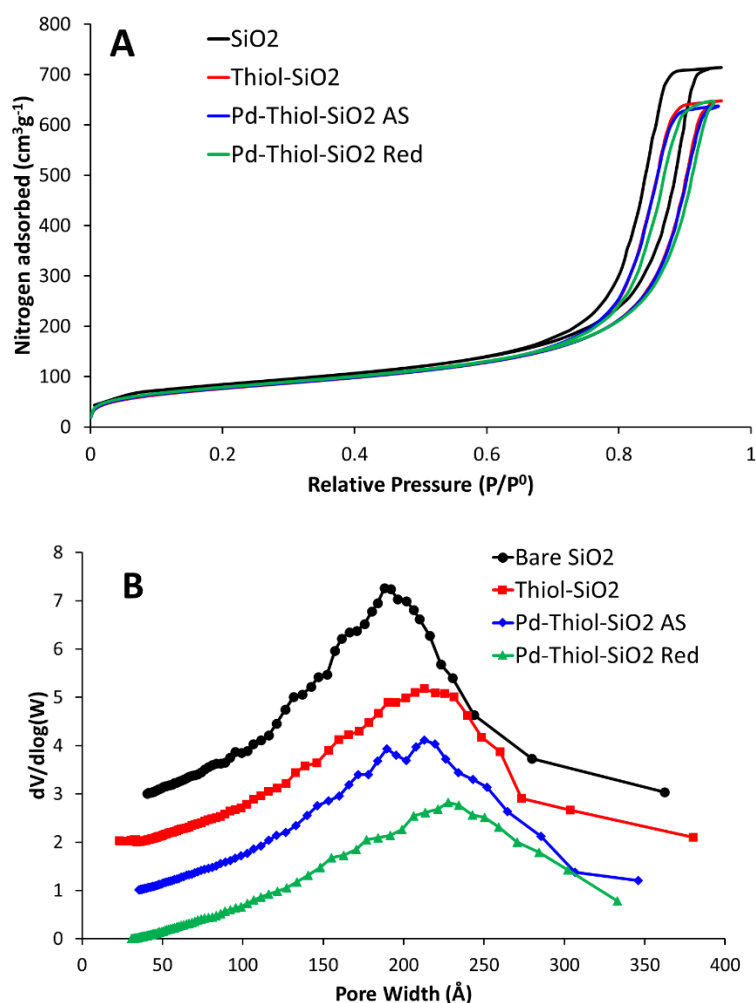


Figure S2: Comparing the porosity of thiol-grafted SiO₂ systems, showing slight differences on grafting (A) to the isotherm, with a slight shift to higher pore widths (B) using the BJH distribution.

Table S2: Porosity measurements for thiol-grafted SiO₂ systems.

System	BET Surface Area (m ² g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)	Average Pore Width (Å)
Bare SiO ₂	295	1.10	188
Thiol-SiO ₂	276	1.00	213
Pd-Thiol-SiO ₂ AS	279	0.99	213
Pd-Thiol-SiO ₂ Red	283	1.00	228

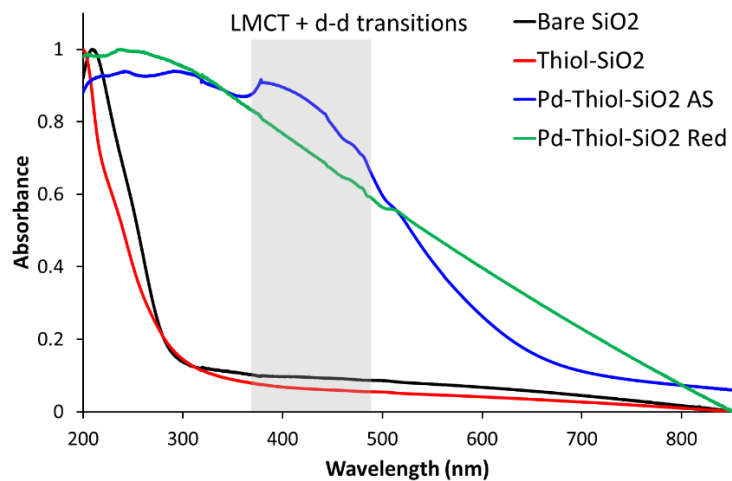


Figure S3: UV/Vis spectra of thiol-grafted SiO₂ systems and the influence of Pd.

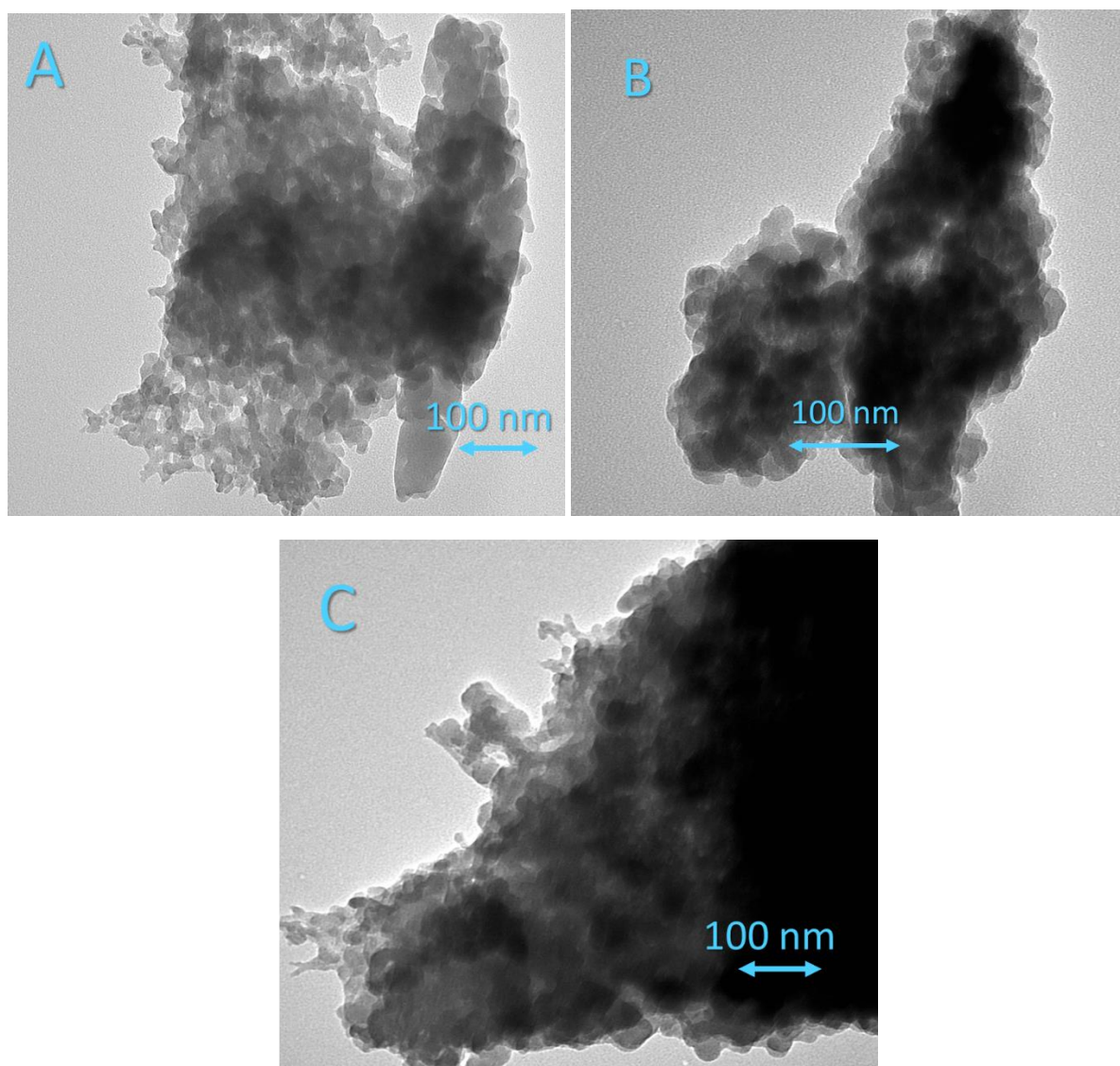


Figure S4: TEM images of Pd-Thiol SiO₂ AS showing no metal nanoparticles or clusters.

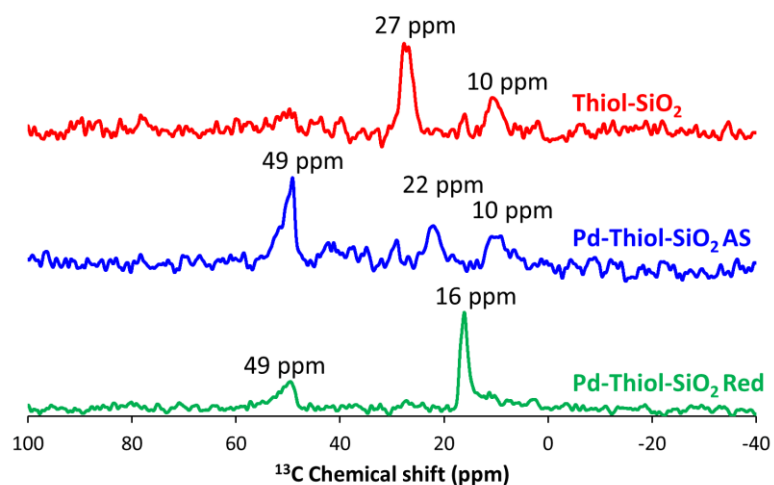
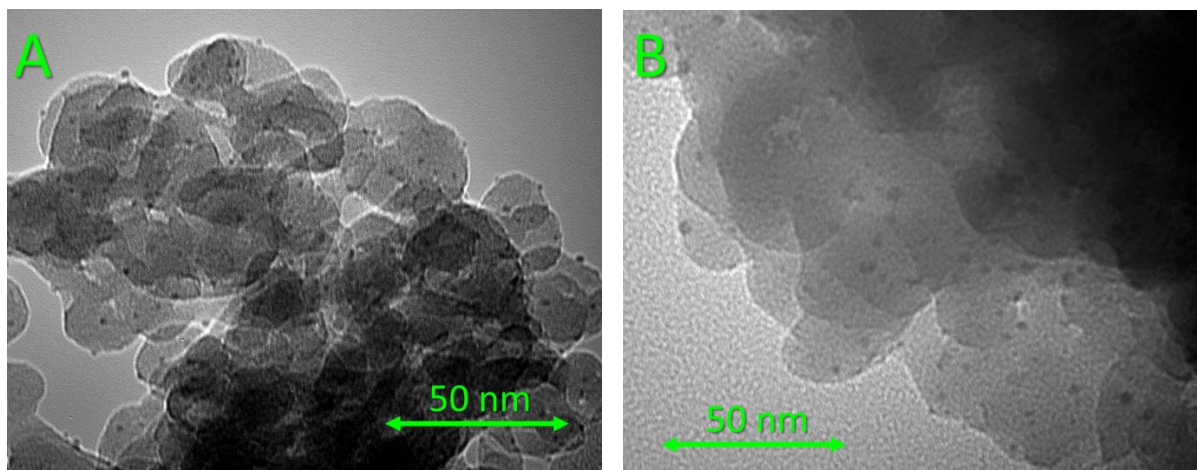


Figure S5: ^{13}C NMR spectra confirming the thiol grafted onto the silica surface (Thiol-SiO₂), and the variation in carbon environment on introducing Pd into the system (Pd-Thiol-SiO₂ AS), and reduction of the system (Pd-Thiol-SiO₂ Red).



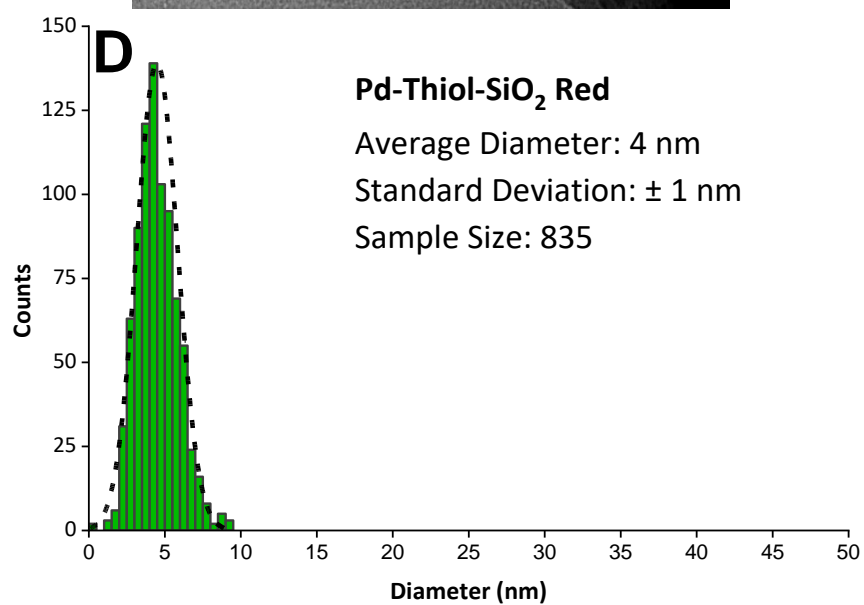
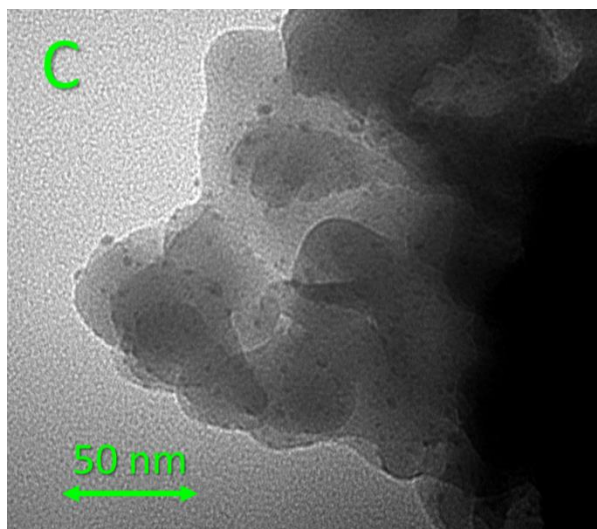


Figure S6: A range of TEM images (A-C) of Pd-Thiol-SiO₂ Red, showing small uniform Pd nanoparticles, with the accompanied nanoparticle size distribution plot (D).

Characterising non-thiol SiO₂ systems

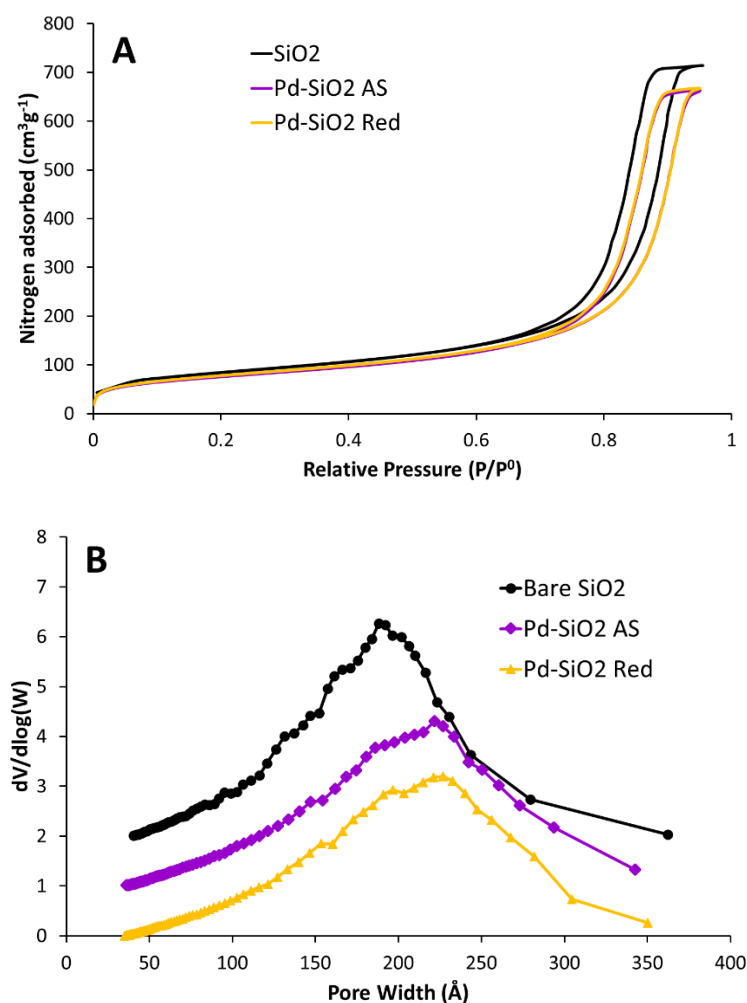


Figure S7: Comparing the porosity of non-thiol-grafted SiO₂ systems, showing slight differences on grafting (A) to the isotherm, also with a slight shift to higher pore widths (B) using the BJH distribution.

Table S3: Porosity measurements for non-thiol-grafted SiO₂ systems.

System	BET Surface Area (m ² g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)	Average Pore Width (Å)	Pd loading (wt%)
Bare SiO ₂	295	1.10	188	N/A
Pd- SiO ₂ AS	273	1.02	227	0.96
Pd- SiO ₂ Red	278	1.03	227	0.96

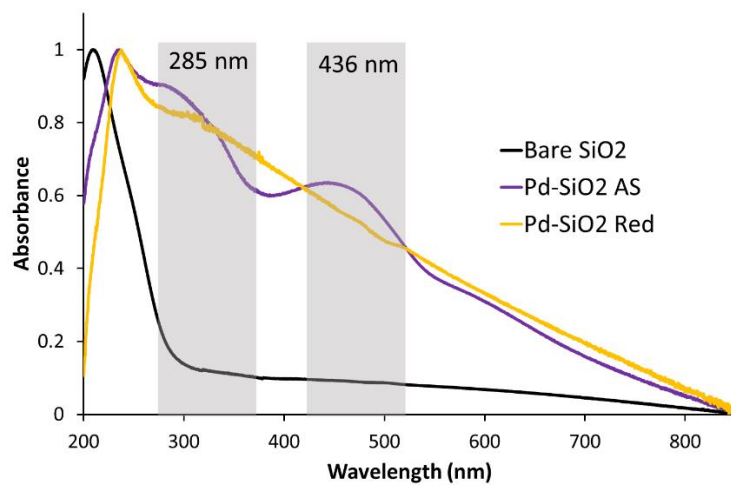
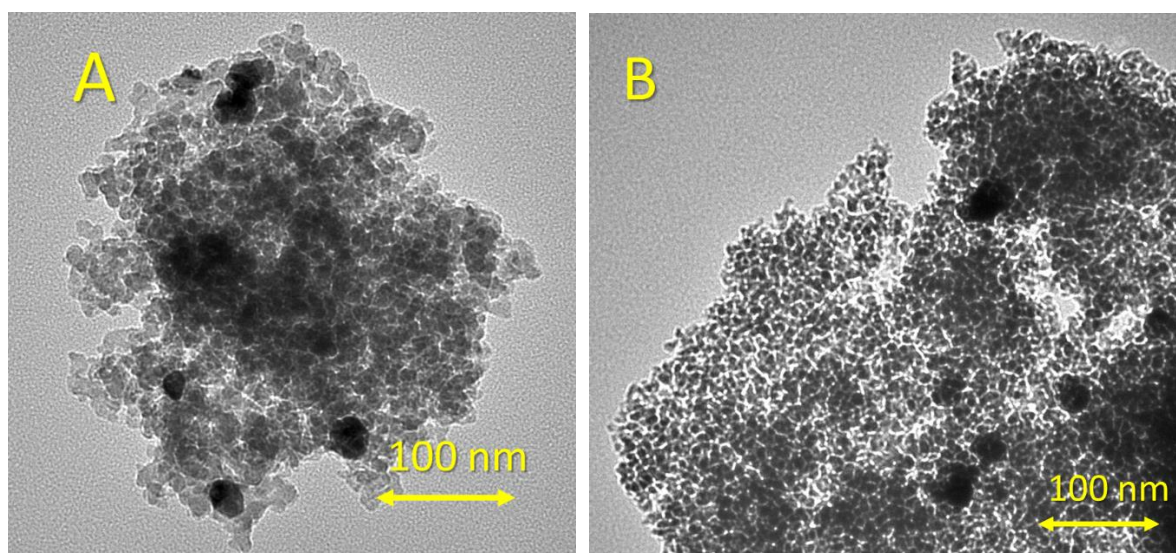


Figure S8: UV/Vis spectra of non-thiol-grafted SiO₂ systems and the influence of Pd.



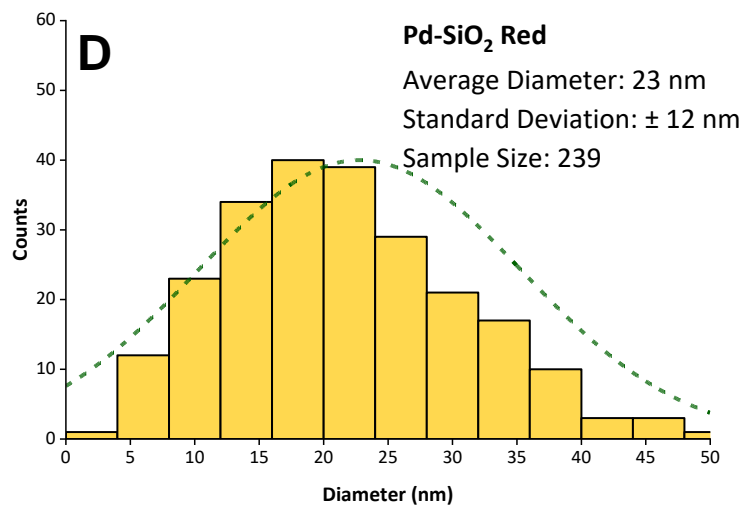
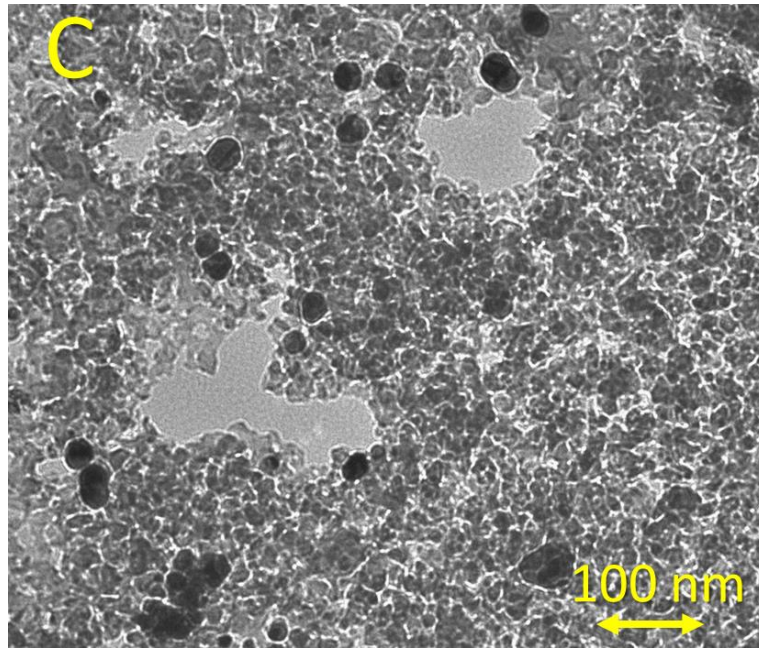


Figure S9: A range of TEM images (A-C) of Pd- SiO₂ Red, showing large, varied Pd nanoparticles, with the accompanied nanoparticle size distribution plot (D).

Analysing the Suzuki coupling reaction

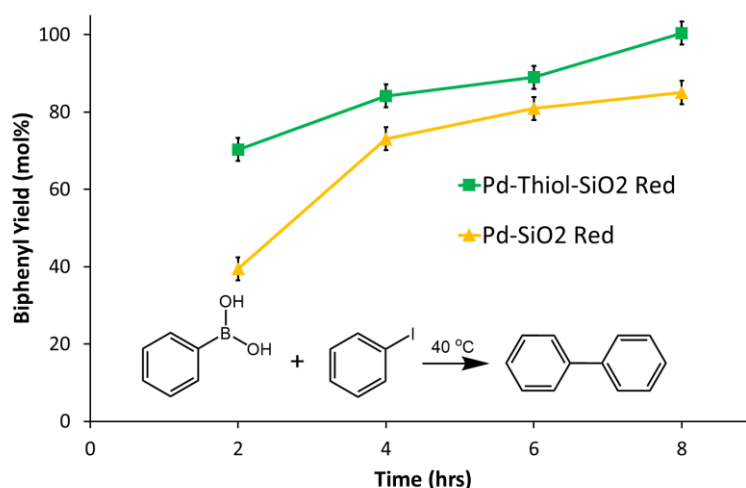


Figure S10: Biphenyl yield as a function of time, showing the influence of added thiol-groups on the catalytic Suzuki coupling of iodobenzene and phenylboronic acid. Reaction conditions: 40 °C, 50 mg of catalyst, 0.94 mmol of phenylboronic acid, 0.86 mmol of naphthalene (internal standard), 0.87 mmol of anhydrous K_2CO_3 , 1.22 mmol of Iodobenzene and 15 mL of ethanol.

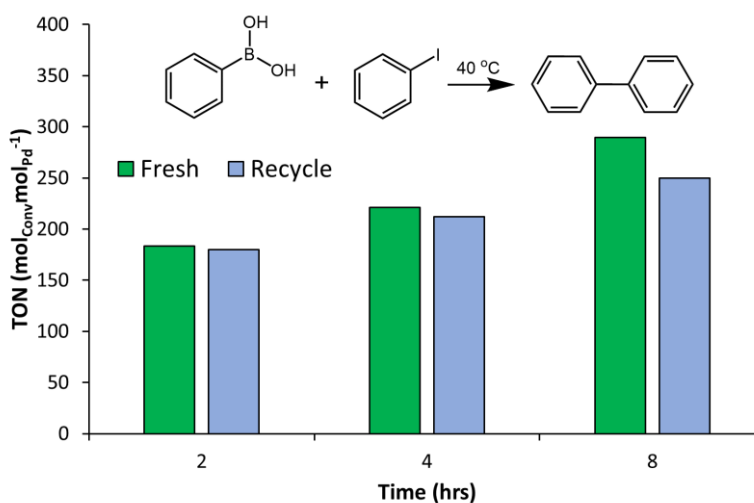


Figure S11: Showing the catalyst stability, comparing the TON of a fresh “Pd-Thiol-SiO₂ Red” catalyst with a recycled, reactivated catalyst on the catalytic Suzuki coupling of iodobenzene and phenylboronic acid. Reaction conditions: 40 °C, 50 mg of catalyst, 0.94 mmol of phenylboronic acid, 0.86 mmol of naphthalene (internal standard), 0.87 mmol of anhydrous K_2CO_3 , 1.22 mmol of Iodobenzene and 15 mL of ethanol.

Table S4: Recent literature findings on the Suzuki Coupling of iodobenzene and phenyl boronic acid to form biphenyl with Pd-based systems.

Pd-System	Temp (°C)	Time (hrs)	Yield (mol%)	TOF (hr^{-1})	Ref
Pd-SAs/3DOM-CeO ₂	25	4	92	232	S7

Pd _{1.0} /CeO ₂	25	4	78	346	S7
5 wt% Pd/C	25	4	80	71	S7
Pd@COF-QA	35	1	61	36	S8
Pd-Thiol-SiO ₂ -Red	40	2	70	92	This work
Pd-SiO ₂ -Red	40	2	39	38	This work
Pd-Ni(20)/RGO	45	3	99	1111	S9
Pd(II)-NHC-SiO ₂	65	18 mins	100	3333	S10
SBA/di-urea/Pd	70	20 mins	>99	1283	S11
Fe ₃ O ₄ @C-Pd-550	75	30 mins	100	244	S12
Pd@meso-SiO ₂	80	3 mins	99.5	2664	S13
GO-2N-Pd(II)	80	30 mins	100	400	S14
Pd-isatin-boehmite	80	50 mins	97	39	S15
Pd@APGO	80	6	96	68	S16
Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -Pd(0)	80	6	98	218	S17
Pd-CoFe ₂ O ₄ MNPs	80	12	81	42	S18
Pd/FeO _x @SiO _{2-x} 500	85	20 mins	100	3756	S19
m-4,4'-Me ₂ bpy-MOF-Pd	85	12	75	6.3	S20
HGR-Py-Pd	100	5 mins	100	1000	S21
NDG@Pd	100	25 mins	100	~200	S22
Pd/CeZrO _{4-x}	100	3	81	N/A	S23
MOF-253-0.05PdCl ₂	100	8	98	53	S24
Pd@CC-SO ₃ H-NH ₂	100	24	96	N/A	S25
Pd@g3Amino-Si(HDPE)	115	3	100	141	S26

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