Support-enhanced selective aerobic alcohol oxidation over Pd/silicas

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Experimental

SBA-15 Synthesis

Pluronic P123 (10 g) was dissolved in water (75.5 ml) and hydrochloric acid (2 M 291.5 ml) with stirring at 35 °C. Tetramethoxysilane (15.5 ml) was added and left for 20 h with agitation. The resulting gel was aged for 24 h at 80 °C without agitation. The solid was filtered, washed with water (1000 ml) and dried at room temp before calcination at 500 °C for 6 h in air (ramp rate 1 °C min^{-1}).

SBA-16 Synthesis

Pluronic F127 (10 g) was dissolved in water (75.5 ml) and hydrochloric acid (2 M 291.5 ml) with stirring at 25 °C. Tetramethoxysilane (15.5 ml) was added and left for 20 h with agitation. The resulting gel was aged for 48 h at 80 °C without agitation. The solid was filtered, washed with water (1000 ml) and dried at room temperature before calcination at 500 °C for 6 h in air (ramp rate 1 °C min^{-1}).

KIT-6 Synthesis

Pluronic P123 (10 g) was dissolved in water (361.6 ml), Butan-1-ol (12.3 ml) and hydrochloric acid (35% 16.7 ml) with stirring at 35 °C. Tetramethoxysilane (15.6 ml) was added and left for 20 h with agitation. The resulting gel was aged for 24 h at 80 °C without agitation. The solid was filtered, washed with water (1000 ml) and dried at room temperature before calcination at 500 °C for 6 h in air (ramp rate 1 °C min^{-1}).

Palladium impregnation

Mesoporous SBA-15, SBA-16 and KIT-6 supports (1.5 g) were wetted with aqueous tetraamine palladium(II) nitrate solution (12 ml with nitrate precursor concentrations adjusted to achieve nominal Pd loadings of 0.05-5 wt% wt%). Resulting slurries were stirred for 18 h at room temperature before heating to 50 °C. After 5 h, agitation ceased and the solids were left at 50 °C for 24 h to dry to a powder. These powders were calcined at 500 °C for 2 h in air (ramp rate 1 °Cmin^{-1}) prior to reduction at 400 °C for 2 h (ramp rate 10 °Cmin^{-1}) under flowing hydrogen (10 cm^3min^{-1}). Commercial silica (SiO_2) (1.5g Sigma, 220 m^2g^{-1}) was likewise wetted with aqueous tetraamine palladium(II) nitrate solution (8 ml with varying nitrate conentrations to span 0.05- 3 wt% nominal loadings)., and the slurry treated as above (dried, calcined and reduced).

Aerobic selective alcohol oxidation

Catalyst screening was performed using Radleys Starfish carousel batch reactors on a 10 ml scale at 90 °C under atmospheric pressure of air. Catalysts (100 mg for Pd loadings <0.5 wt%, and 50 mg for nominal Pd loadings >0.5 wt%) were added to reaction mixtures containing 8.4 mmol of either crotyl (0.603 g) or cinnamyl (1.123 g) alcohol, an internal standard (mesitylene, 0.1 ml) and toluene solvent (10 ml) at 90 °C under stirring. The absolute Pd level varied between 0.47 μmol (0.05 wt% catalysts) and 19.5 μmol (for the highest loading 4.14 wt% Pd/SiO_2 tested), corresponding to substrate:catalyst ratios ranging from 17872 (0.05 wt%) down to 430 (4.14 wt%). Reactions were sampled periodically for kinetic profiling by off-line gas chromatography using a Varian 3900GC with 8400 autosampler fitted with a (15 m x 0.25 mm x 0.25 μm) CP-Sil5 CB column.

Characterisation

Nitrogen porosimetry was undertaken on a Quantachrome Nova 1200 porosimeter, and analysed using NovaWin 2 version 2.2 software. Samples were degassed at 120 °C for 2 hours prior to analysis by nitrogen adsorption at -196 °C. Adsorption/desorption isotherms were recorded for all parent and Pd-impregnated silicas. BET surface areas were calculated over the relative pressure range 0.01-0.2. Pore diameters and volumes were calculated applying the BJH method to the desorption isotherm for relative pressures >0.35.

Low and wide angle XRD patterns were recorded on either a PANalytical X'pertPro diffractometer fitted with an X'celerator detector and Cu K_α (1.54Å) source or a Bruker D8 Advance diffractometer fitted with a LynxEye high-speed strip detector and Cu K_α (1.54Å) source. Both instruments were calibrated against either Si (PANalytical) or SiO_2 (Bruker) standards. Low angel patterns were recorded for 2θ = 0.3-8° with a step size of 0.01°. Wide angle patterns were recorded for 2θ = 25-75° with a step size of 0.02°. The Scherrer equation was used to calculate volume-averaged Pd particle sizes.

High resolution S/TEM images were recorded on an FEI Tecnai F20 field emission gun (FEG-)TEM operating at 200 kV equipped with a Gatan Orius SC600A CCD camera. Samples were prepared for TEM by dipsersing in methanol and drop-casting onto a copper grid coated with a holey carbon support film (Agar Scientific Ltd). Images were analysed in ImageJ 1.41.

XPS was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutraliser and magnetic focusing lens employing Al K_α monochromated radiation (1486.7 ev). Spectral fitting was performed using CasaXPS version 2.3.14. Binding energies were corrected to the Si 2p peak at 103.4 eV. Pd 3d XP spectra were fitted using a common asymmetric peak shape determined from palladium oxide and foil standards. Errors were estimated by varying the Shirley background-subtraction procedure across reasonable limits and re-calculating the component fits.

Pd metal surface areas were measured via CO pulse chemisorption on a Quantachrome chemBET 3000 system. Samples were outgassed at 150 °C under flowing He (20 ml min^{-1}) for 1 h, prior to reduction at 100 °C under flowing hydrogen (20 ml min^{-1}) for 1 h before analysis at room temperature.[33] Note, this reduction protocol is more mild than that employed during Pd impregnation, and thus does not induce additional particle sintering.

Structural and catalytic properties of silicas and Pd/silicas

Parent silica supports

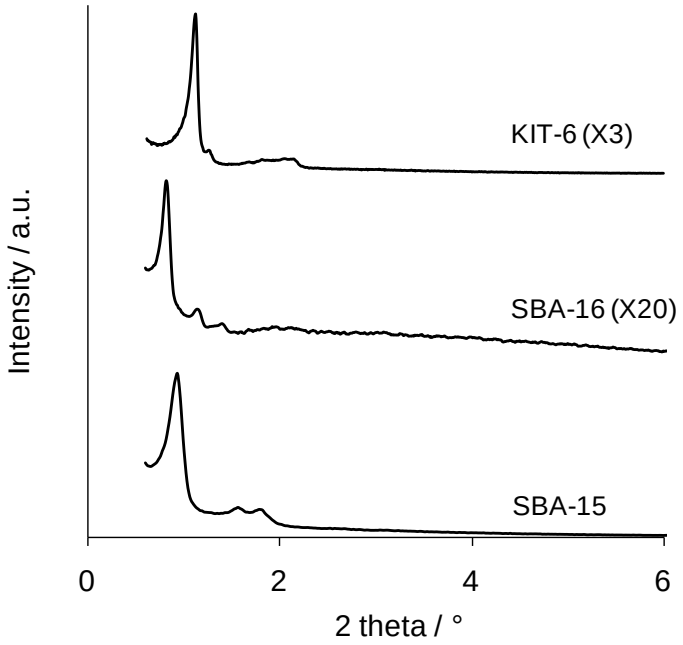


Figure S1. Low Angle XRD patterns for parent mesoporous silica supports.

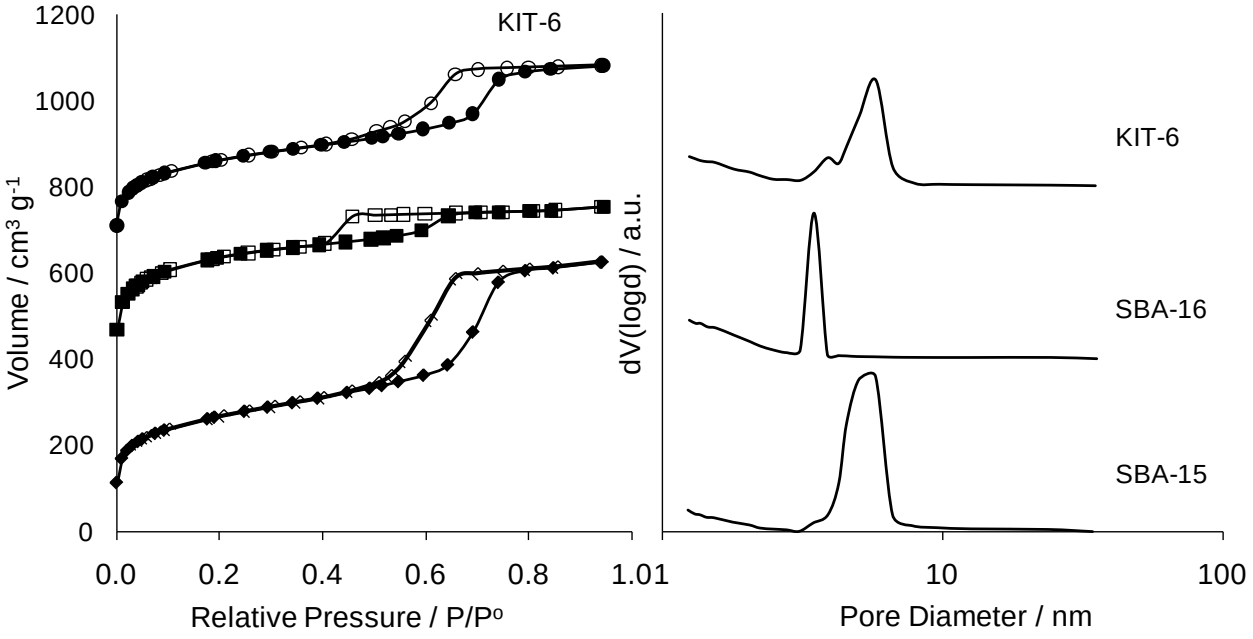


Figure S2. Nitrogen adsorption-desorption isotherms and associated BJH pore size distributions for parent mesoporous silica supports.

Table S1. Textural properties of parent silica supports

Sample	Surface area $m^2 g^{-1}$[a]	External surface area $m^2 g^{-1}$[b]	Mesopore Diameter nm[c]	Cell parameter nm[d]
SiO_2	207.2	169.7	n/a	n/a
SBA-15	949.7	47.4	5.7	9.4
SBA-16	819.6	30.1	3.4	13.7
KIT-6	935.8	26.4	5.7	19.3

[a] N_2 BET

[b] N_2 BET of as-synthesised support (surfactant template present in-pore)

[c] BJH desorption isotherm

[d] Low angle XRD

Pd-impregnated silica supports

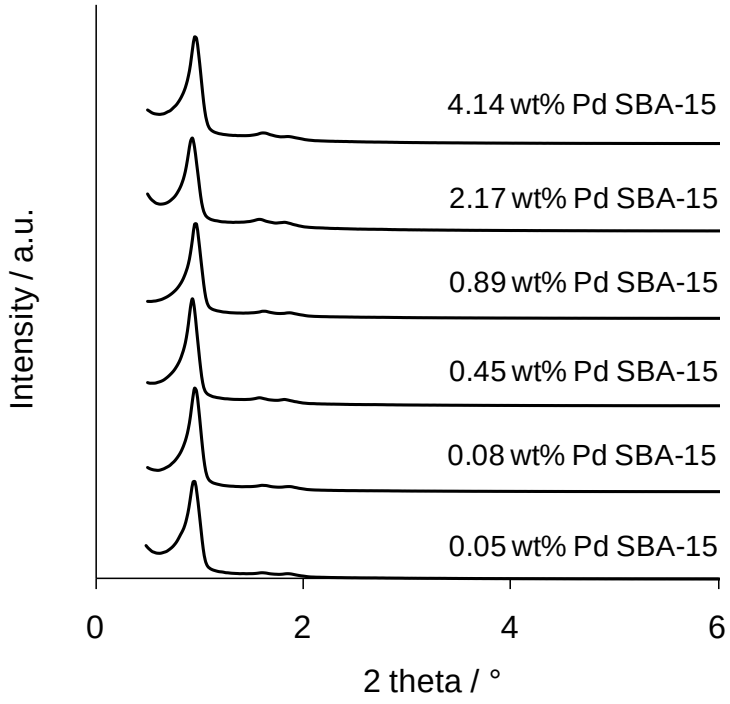


Figure S3. Low angle XRD for Pd-impregnated SBA-15. Pore structure is preserved following impregnation.

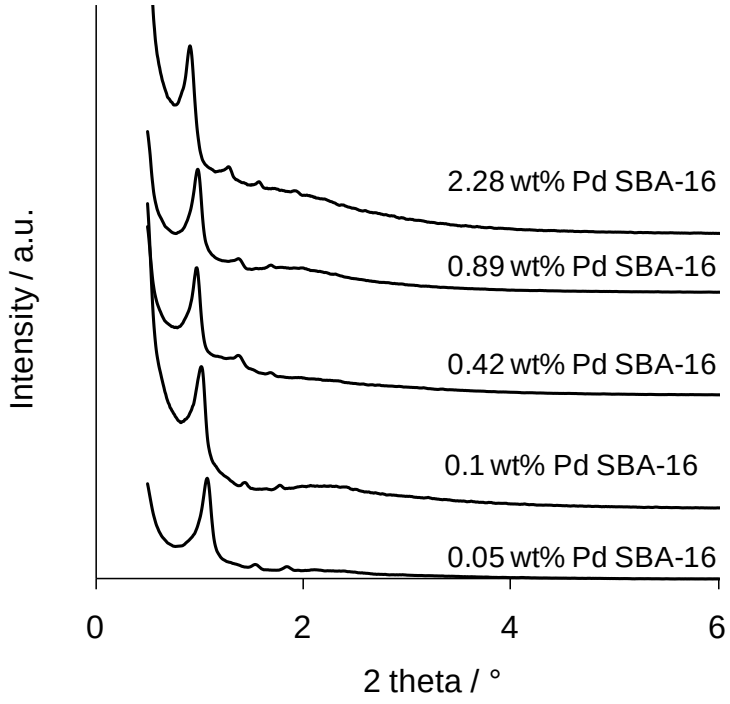


Figure S4. Low angle XRD for Pd-impregnated SBA-16. Pore structure is preserved following impregnation.

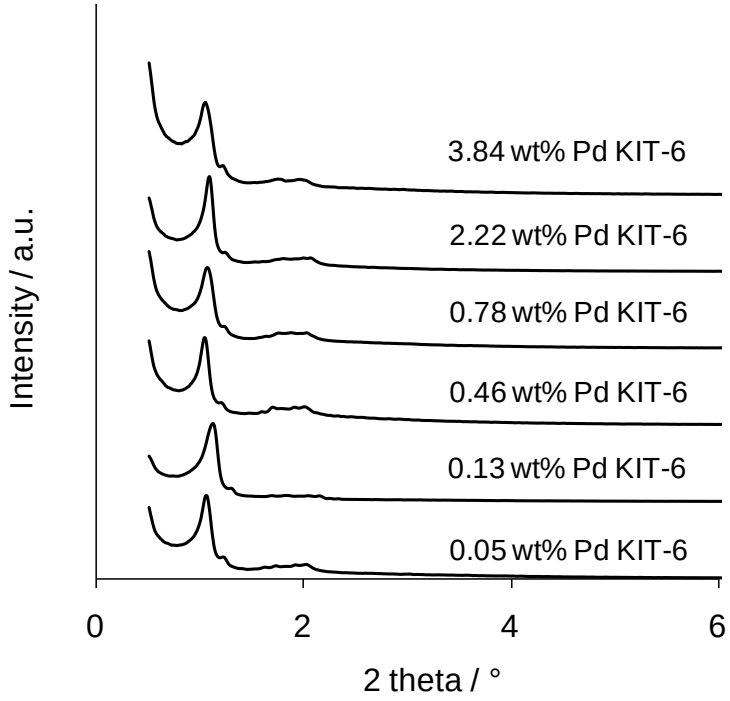


Figure S5. Low angle XRD for Pd-impregnated KIT-6. Pore structure is preserved following impregnation.

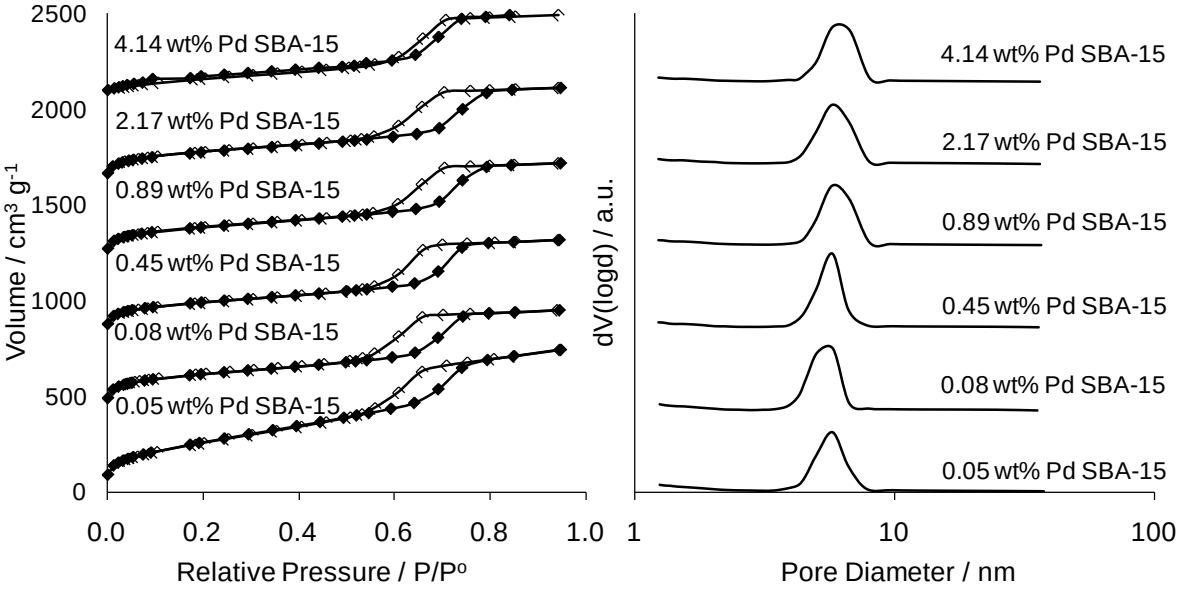


Figure S6. Nitrogen adsorption-desorption isotherms and associated BJH pore size distributions for Pd-impregnated SBA-15. Porosity is preserved following impregnation.

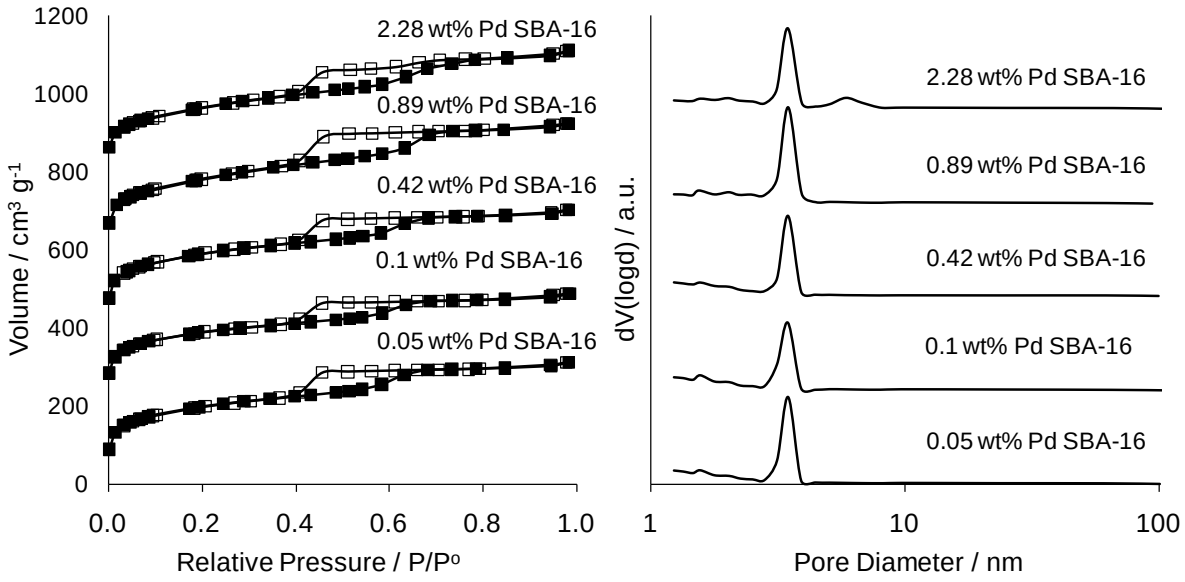


Figure S7. Nitrogen adsorption-desorption isotherms and associated BJH pore size distributions for Pd-impregnated SBA-16. Porosity is preserved following impregnation.

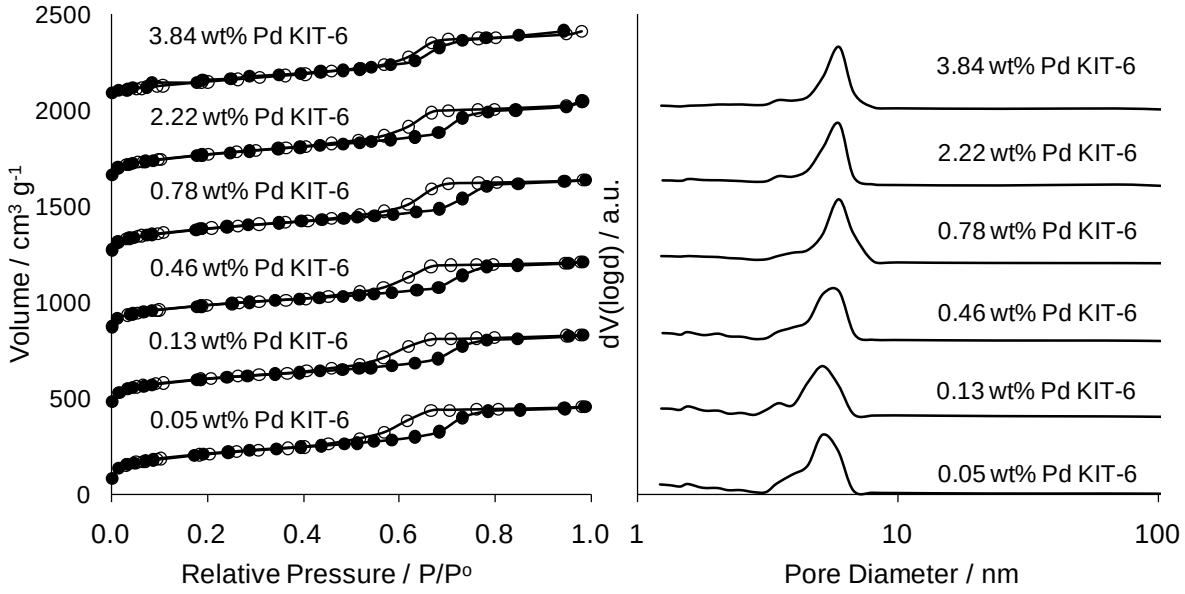


Figure S8. Nitrogen adsorption-desorption isotherms and associated BJH pore size distributions for Pd-impregnated KIT-6. Porosity is preserved following impregnation.

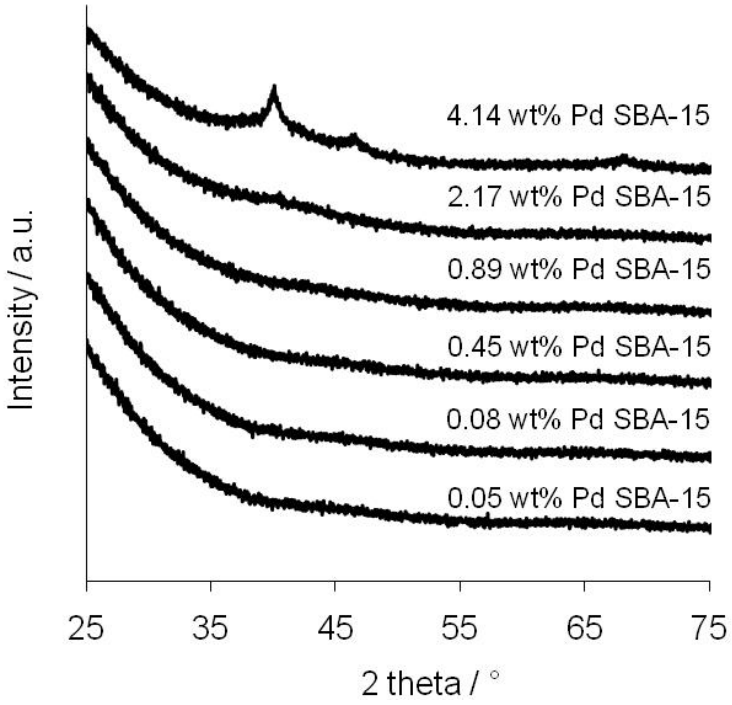


Figure S9. Wide angle XRD patterns for Pd-impregnated SBA-15.

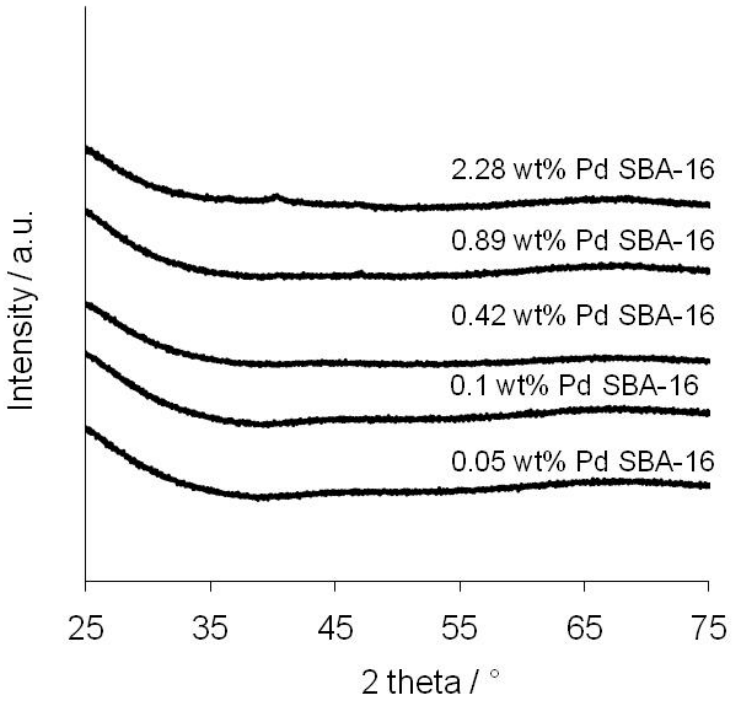


Figure S10. Wide angle XRD patterns for Pd-impregnated SBA-16.

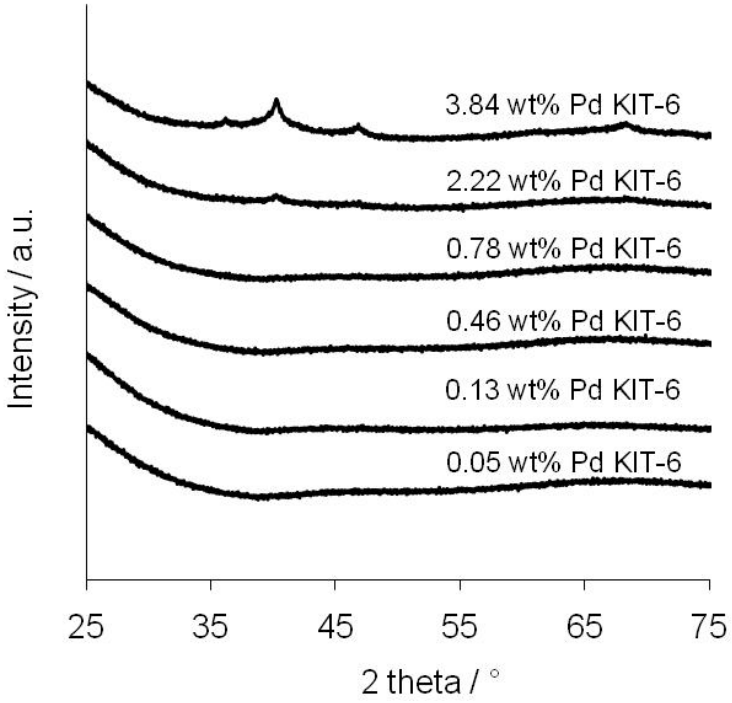


Figure S11. Wide angle XRD patterns for Pd-impregnated KIT-6.

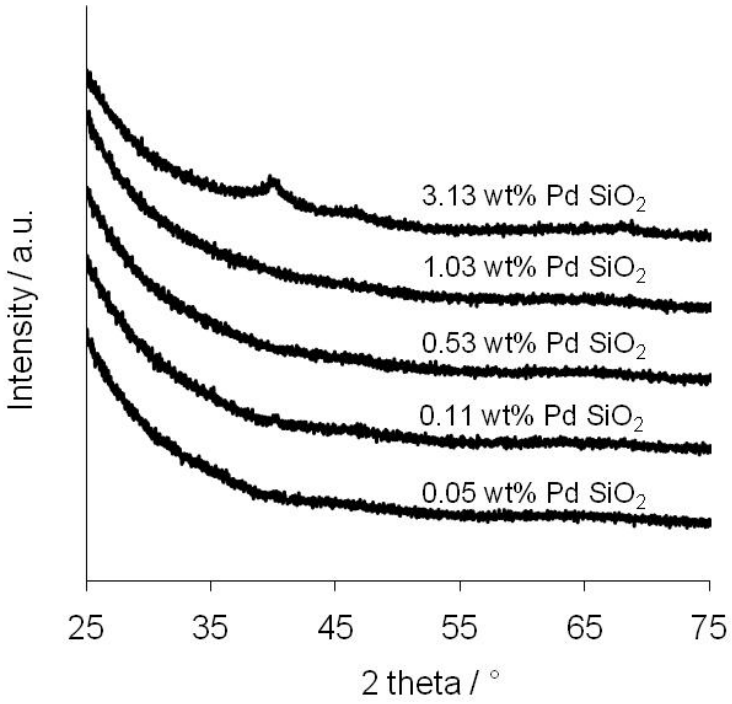
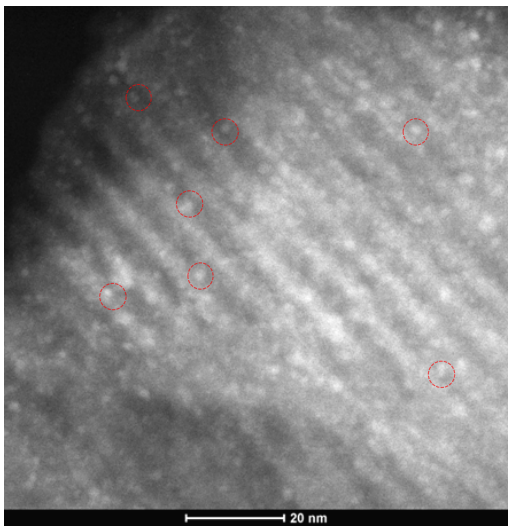
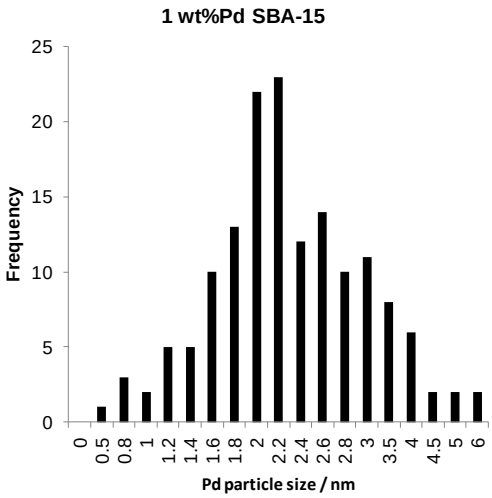
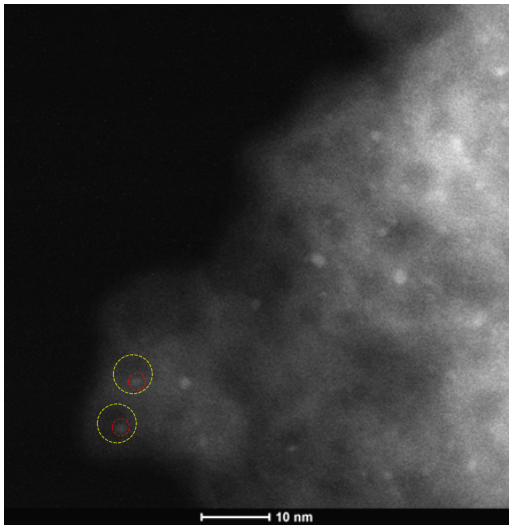
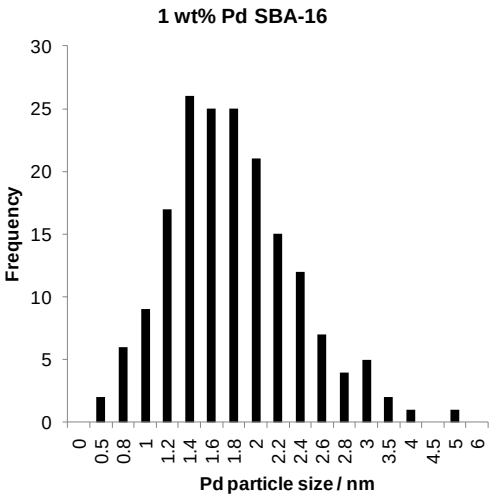


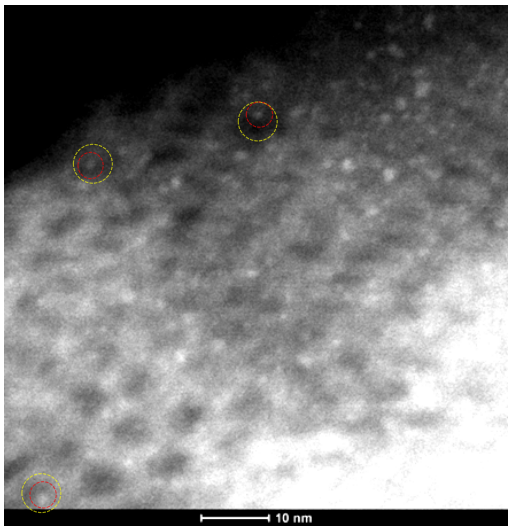
Figure S12. Wide angle XRD patterns for Pd-impregnated commercial silica.











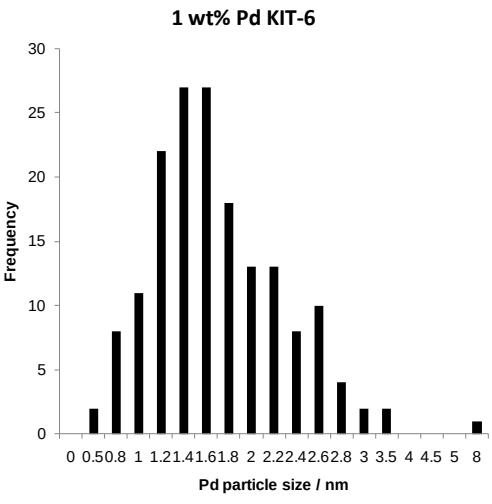


Figure S13. HAADF-STEM images and associated particle size distributions for Pd-impregnated mesoporous silicas; yellow circles highlight mesopores, and red circles highlight in-pore Pd nanoparticles. Analyses based upon ~100-150 particles.

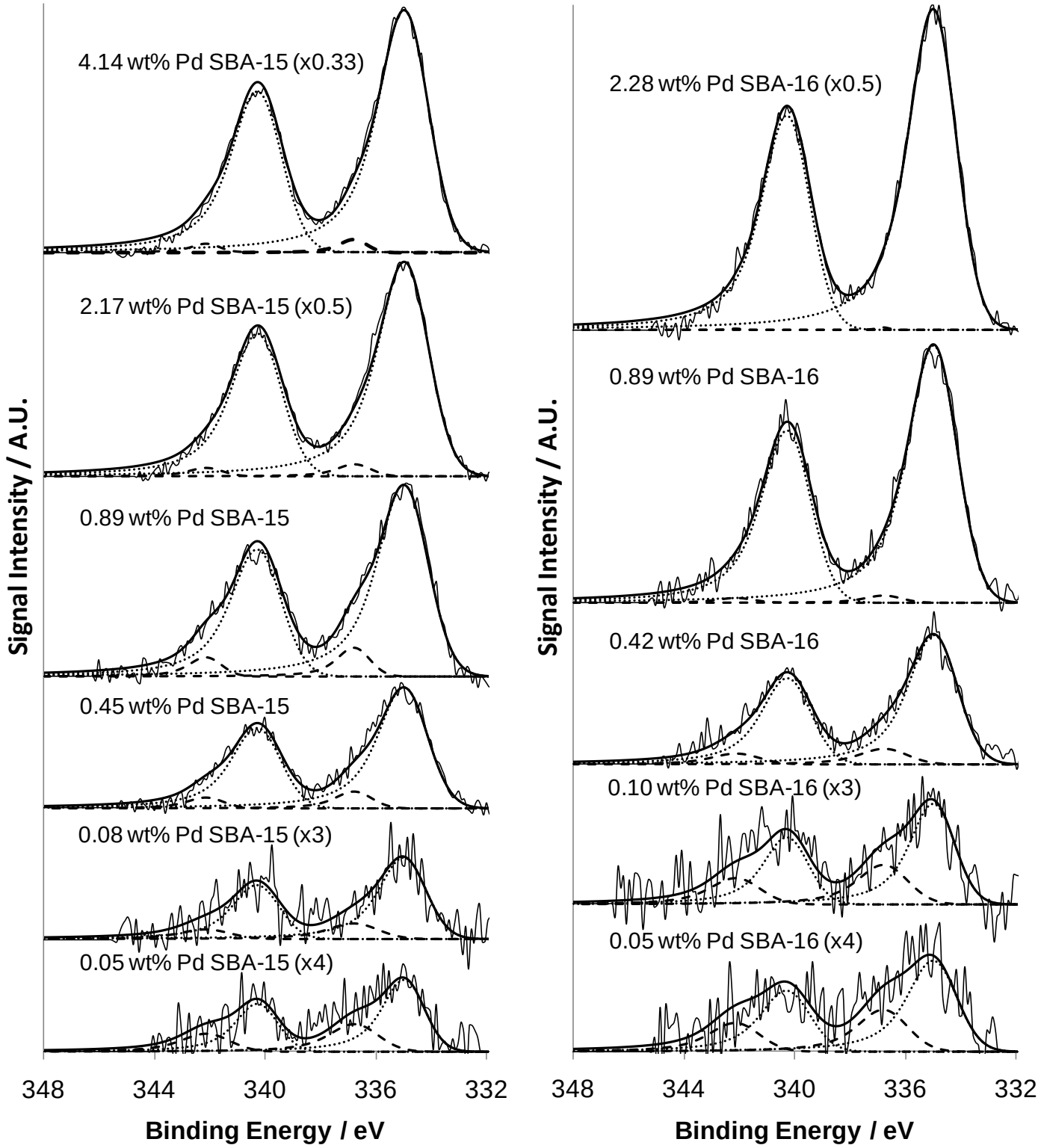


Figure S14. Fitted Pd 3d XP spectra for (a) Pd/SBA-15 series, (b) Pd/SBA-16 series

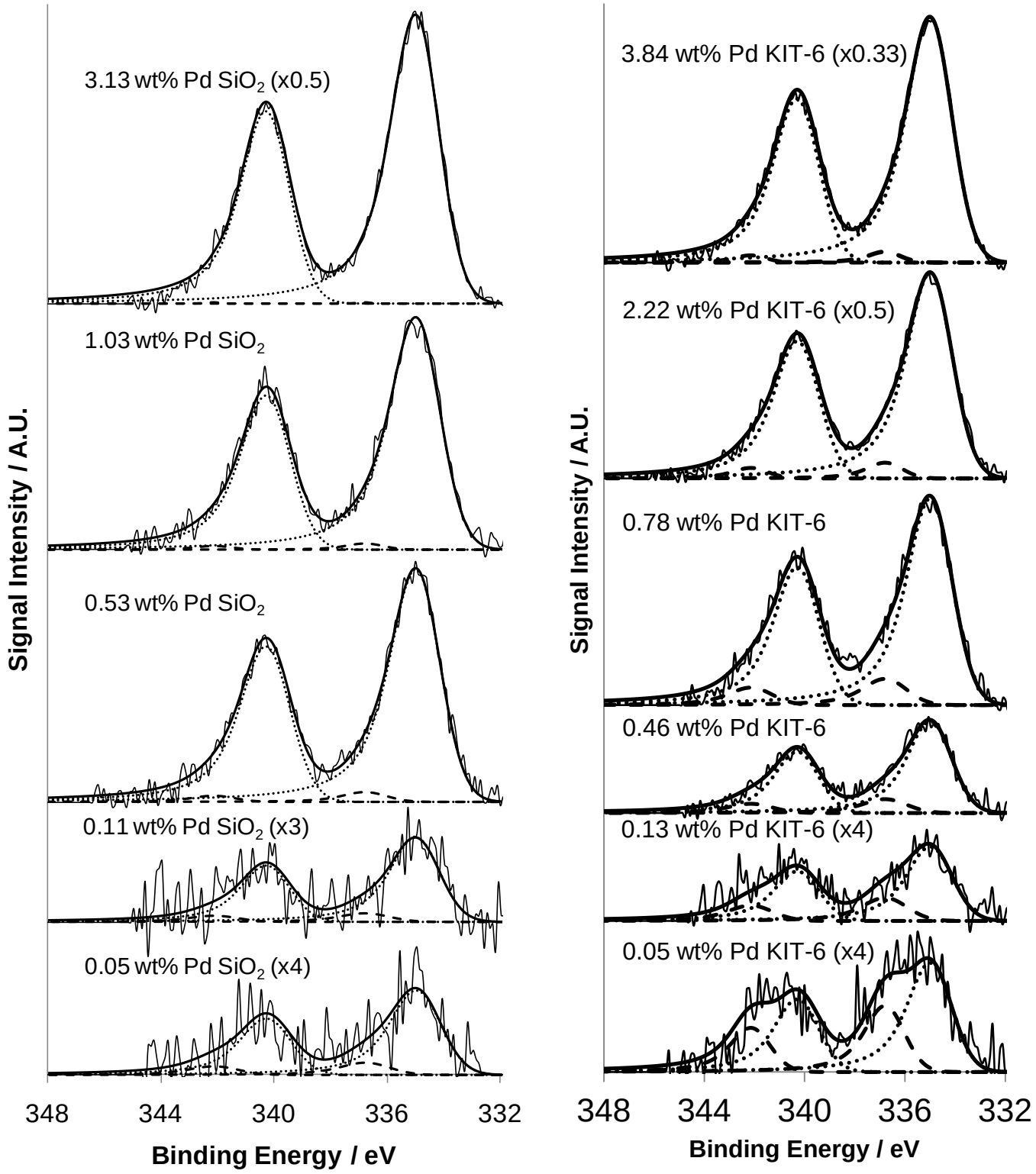


Figure S15. Fitted Pd 3d XP spectra for for (a) Pd/SiO_2 and (b) Pd/KIT-6 series.

Table S2. Physico-chemical properties of Pd/silicas

Support	Pd loading / wt%[a]	Pd dispersion / %[b]	Pd particle size / nm[c]	PdO content / atom%[d]	Surface area / $m^2\ g^{-1}$[e]	Mesopore diameter / nm[f]	Cell dimension / nm[g]
SiO_2	3.13	28.20	4.0 (3.0)	0.25	187.7	n/a	n/a
SiO_2	1.03	40.30	2.8	1.53	186.7	n/a	n/a
SiO_2	0.53	44.50	2.5	4.36	191.2	n/a	n/a
SiO_2	0.11	56.16	1.9	10.56	199.9	n/a	n/a
SiO_2	0.05	67.79	n/a	15.09	192.9	n/a	n/a
SBA-15	4.14	37.34	2.9 (2.9)	2.36	573.2	5.7	9.3
SBA-15	2.17	43.30	2.6	3.80	630.8	5.7	9.5
SBA-15	0.89	52.00	2.3	6.04	652.6	5.7	9.1
SBA-15	0.45	56.90	1.9	8.81	673.5	5.7	9.5
SBA-15	0.08	64.04	1.7	18.45	768.9	5.7	9.3
SBA-15	0.05	78.05	n/a	25.41	740.5	5.7	9.2
SBA-16	2.28	64.10	1.7	3.50	587.5	3.5	13.7
SBA-16	0.89	71.00	1.6	10.69	646.8	3.5	12.7
SBA-16	0.42	79.24	1.4	11.92	678.9	3.5	12.7
SBA-16	0.10	82.08	1.4	27.79	670.4	3.5	12.3
SBA-16	0.05	87.99	n/a	34.07	702.8	3.5	12
KIT-6	3.84	44.14	2.5 (2.4)	2.81	525.8	5.9	20.6
KIT-6	2.22	62.10	1.8	7.33	604.6	5.9	19.8
KIT-6	0.78	71.46	1.6	11.28	658.4	5.9	20.2
KIT-6	0.46	79.42	1.4	14.66	652.8	5.1	20.7
KIT-6	0.13	85.56	1.3	26.70	714.6	5.1	19.2
KIT-6	0.05	88.25	n/a	33.44	743.6	5.1	20.4

[a]ICP or XRF

[b]from CO chemisorption assuming a CO:$Pd_{surface}$ stoichiometry of 1

[c]Mean particle diameter from Pd dispersion (or XRD via Scherrer analysis)

[d]XPS

[e]N_2 BET

[f]BJH desorption isotherm

[g]Low angle XRD

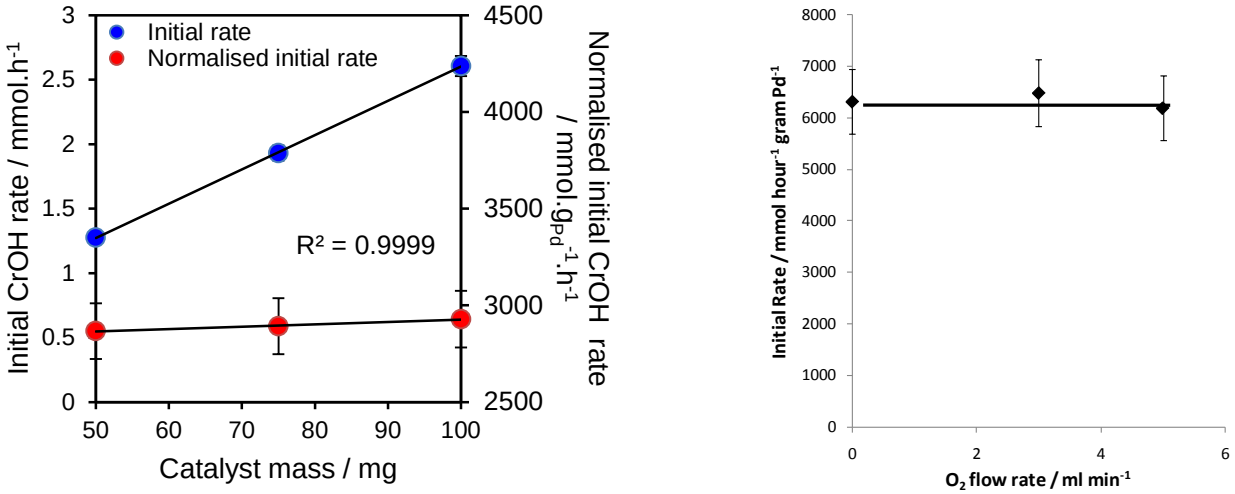


Figure S16. Influence of catalyst:substrate ratio (**left**) and O_2 flow rate (**right)** on CrOH initial reaction rate over 1 wt% Pd/SBA-15 and 0.46 wt% Pd/KIT-6 catalysts respectively.

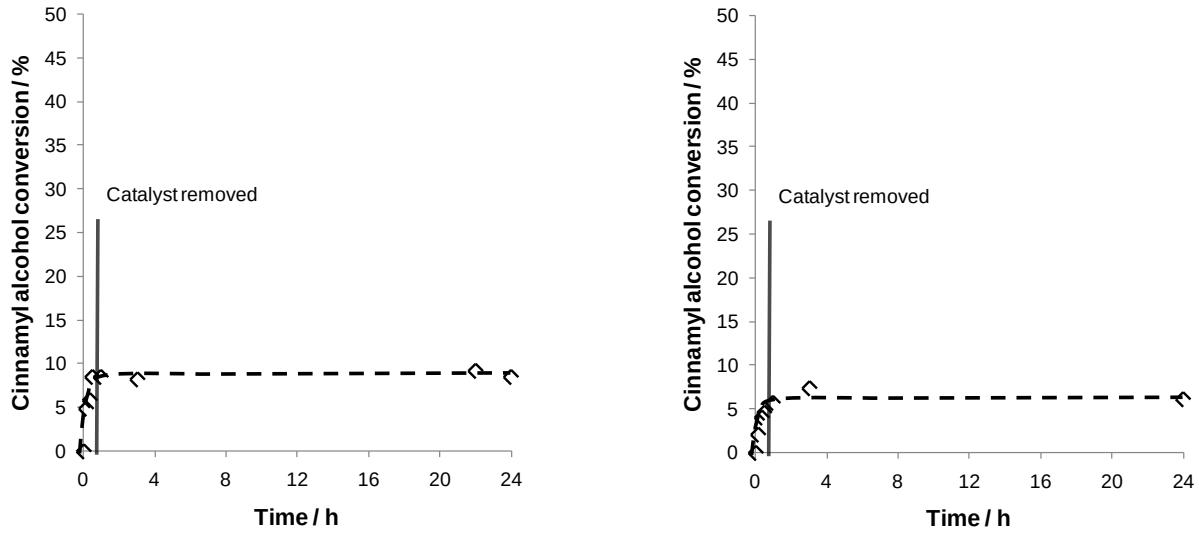


Figure S17. Hot filtration test to assess Pd leaching in CinnOH selox over (**left**) 0.5 wt% Pd/KIT-6 and (**right)** 0.5 wt% Pd/SBA-15. Removal of catalyst at 30 min instantly stops reaction, showing negligible leaching.

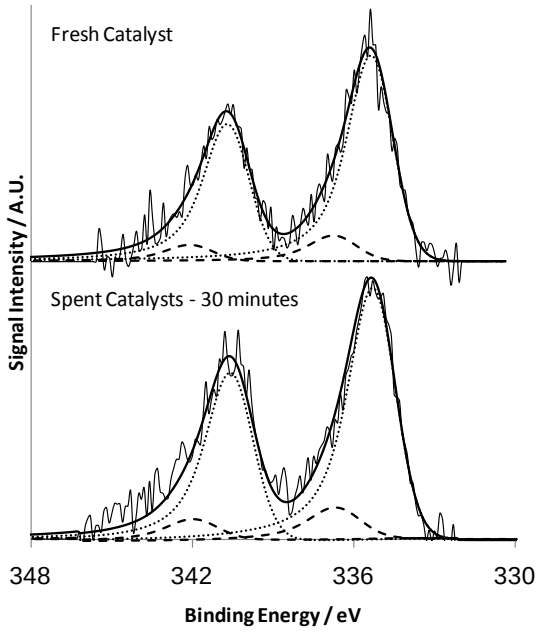


Figure S18. Pd 3d XP spectra of 0.5 wt% Pd SBA-16: as-prepared (**top**) and hot filtered after 30 min CinnOH selox (**bottom**) evidencing negligible oxide reduction during the initial reaction period.

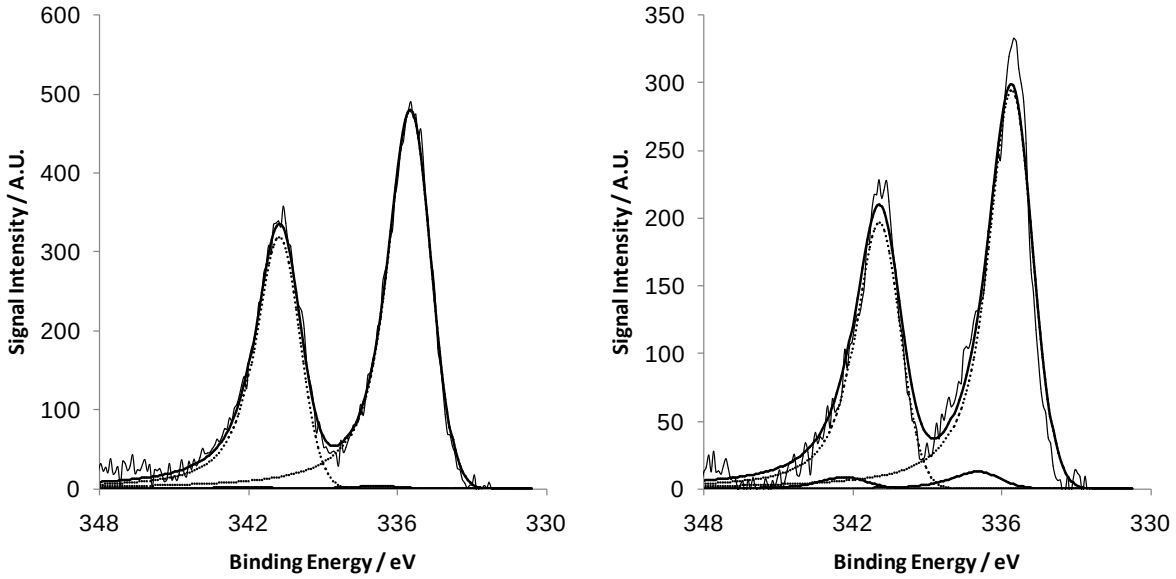
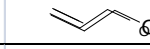
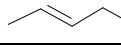
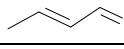
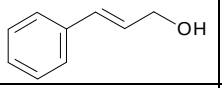
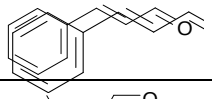
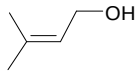
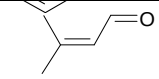
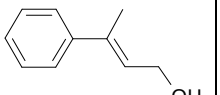
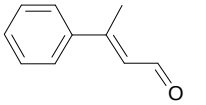
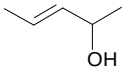
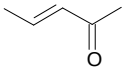
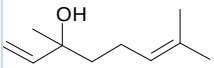
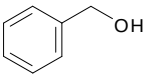
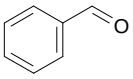
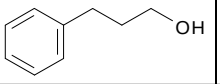
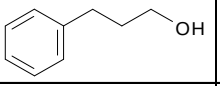
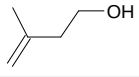
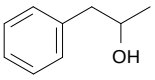


Figure S19. Pd 3d XP spectra of spent 2.22 wt% Pd/KIT-6 showing (**left**) complete reduction to Pd metal after 24 h CinnOH selox under conventional conditions, and (**right**) how flowing O_2 during helps retain initial surface PdO.

Table S4. Pd 3d XP analysis of fresh and spent (after 24 h CinnOH selox) 0.3 wt% Pd/silicas.

Support phase	Pd content (fresh) / wt% ±0.05	Pd content (spent) / wt% ±0.05
SBA-15	0.3	0.39
SBA-16	0.25	0.27
KIT-6	0.25	0.28

Table S4. Selox performance 0.5 wt% Pd/KIT-6 against allylic and saturated alcohols at 90 °C.

Alcohol		Primary Product	Conversion / %	Selectivity / %	TOF / h^{-1}
Allyl Alcohol [a]			47	70	1580
Crotyl Alcohol [b]			60	64	1190
Cinnamyl Alcohol [b]			76	59	980
Prenol Alcohol [c]			27	90	920
Trans-2-methyl-3-phenyl-2-propen-1-ol [c]			28	76	710
3-buten-2-ol [a]			70	66	3550
3-penten-2-ol [c]			30	70	1050
Linalool Alcohol [c]		n/a	0	0	0
Benzyl Alcohol [c]			61	96	1120
Hydrocinnamyl Alcohol [c]		n/a	0	0	0
Hydrocinnamyl Alcohol [d]		n/a	0	0	0
3-methyl-3-buten-1-ol [c]		n/a	0	0	0
1-phenylpropen-2-ol [c]		n/a	0	0	0

[a]Catalyst mass 0.025g; T = 90°C, [Alcohol] = 8.4mmol; conversion and selectivity reported after 3 h; TOF after 30 min.

[b]Catalyst 0.05g; T = 90°C; [Alcohol] = 8.4mmol; conversion and selectivity reported after 24 h, TOF after 30 min.

[c]Catalyst 0.025g ; T = 90°C, [Alcohol] = 8.4mmol; conversion and selectivity reported after 24 h, TOF after 30 min.

[d]Catalyst 0.025g; T = 90°C, [Alcohol] = 8.4mmol; 1 bar flowing O_2 at 3 $ml.min^{-1}$; conversion and selectivity after 3 h; TOF after 30 min.