

Supporting Information

Wettability-Driven Palladium Catalysis for Enhanced Dehydrogenative Coupling of Organosilanes

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1. Chemicals and materials

Triethylsilane (Et₃SiH, 99 wt %), diethylsilane (Et₂SiH₂, 99 wt %), triisopropylsilane (*i*-Pr₃SiH, 98 wt %), tributylsilane (*n*-Bu₃SiH, 98 wt %), dimethylphenylsilane (PhMe₂SiH, 97 wt %), methyldiphenylsilane (Ph₂MeSiH, 98 wt %), triphenylsilane (Ph₃SiH, 98 wt %), trimethoxy(propyl)silane (C₆H₁₆O₃Si, 98 wt %), deuterium oxide (D₂O, 99.9 % D), methanol (MeOH, 99.5 wt %), ethanol (EtOH, 99.5 wt %), isopropanol (*i*-PrOH, 99.7 wt %), 1-butanol (*n*-BuOH, 99.5 wt %), benzyl alcohol (C₇H₈O, 99 wt %), ethylene glycol (C₂H₆O₂, 99.5 wt %), glycerol (C₃H₈O₃, 99 wt %), *n*-butylamine (C₄H₁₁N, 99 wt %), aniline (C₆H₇N, 99.5 wt %), morpholine (C₄H₉NO, 99.5 wt %), ethylbenzene (C₈H₁₀, 99 wt %), bibenzyl (C₁₄H₁₄, 99 wt %), naphthalene (C₁₀H₈, 99 wt %), palladium chloride (PdCl₂, Pd ≥ 60.0 wt %), rhodium chloride hydrate (RhCl₃ · xH₂O, Rh ≥ 38.5 wt %), chloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O, Pt ≥ 37.5 wt %), ruthenium chloride hydrate (RuCl₃ · xH₂O, Ru ≥ 37.5 wt %), and iridium chloride (H₂IrCl₆, Ir ≥ 35.0 wt %) were supplied by J&K Chemicals and used without further purification.

Vulcan XC-72, BP2000, M800 and 660R carbon blacks were purchased from Cabot. TiO₂ (P25), SiO₂ (Aerosil 380) and Al₂O₃ (Aeroxide Alu C) were supplied by Evonik. Graphite powder, HNO₃ (70 wt %), H₂SO₄ (98 wt %), NaOH (99 wt %), NaBH₄ (99.5 wt %), NaNO₃ (99 wt %), KMnO₄ (98 wt %), H₂O₂ (30 wt %) and HCl (38 wt %) were purchased from Aladdin.

2. Catalyst preparation

2.1 Preparation of XC-72-HNO₃ material: XC-72-HNO₃ was prepared by chemical oxidation treatment. 10 g XC-72 carbon black was stirred in HNO₃ solution (100 mL, 7.2 mol L⁻¹) and refluxed for 8 h. After filtered and washed with distilled water until the pH of filtrate was 7, the sample was dried

in air at 100 °C to give a fine XC-72-HNO₃ powder.

2.2 Preparation of graphite oxide (GO): GO was prepared by a modified Hummers method.^[S1] Briefly, 2.0 g as-received graphite powders was stirred in concentrated H₂SO₄ (46 mL) at 25 °C, and NaNO₃ (1.0 g) was added. After over continuous stirring for over 2 h, the mixture was cooled to 0 °C and KMnO₄ (6.0 g) was slowly added to the suspension under vigorous stirring. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension (should be < 10 °C). After that, the mixture was stirred at 25 °C for 1 h, followed by further stirring at 35 °C for 3 h. Then distilled water (92 mL) was slowly added to the reaction vessel. The diluted suspension was stirred for an additional 15 min and further diluted with distilled H₂O (280 mL) and then H₂O₂ (20 mL, 30 wt %) was added. After filtered and washed with 5% HCl aqueous solution, the resulting gel-like material was dried in air at 65 °C to give a fine dark brown GO powder.

2.3 Preparation of XC-72-T-Ar, XC-72-HNO₃-T-Ar, CNTs-T-Ar, AC-T-Ar and r-GO-T-Ar materials: These materials were prepared via calcination of XC-72 carbon black or XC-72-HNO₃ in Argon atmosphere at different temperature for 2 h with a ramping rate of 5 °C min⁻¹, wherein the T in prepared materials denotes the calcination temperature.

2.4 Preparation of hydrophobically-modified TPS-Al₂O₃ and TPS-TiO₂: 1 g Al₂O₃ or TiO₂ (P25) was introduced into 50 mL toluene, then 2.4 mL trimethoxy(propyl)silane (TPS) was added into the solution and refluxed for 6 h. After filtered and washed with toluene and acetone, the sample was dried at 25 °C in vacuum for 12 h. The obtained white powder was denoted as TPS-Al₂O₃ or TPS-TiO₂.

2.5 Preparation of Pd/XC-72-T-Ar catalyst: Series Pd/XC-72-T-Ar catalysts with the Pd loading of 0.5-8.9 wt % (based on ICP bulk chemical analysis) were prepared via a facile wet chemical reduction method. Firstly, 0.5 g XC-72-T-Ar was introduced into 200 mL distilled H₂O (or ethanol-water solution when T ≥ 700 °C, V_{ethanol}/V_{H₂O} = 1/5) and dispersed by ultrasonic at 25 °C for 2 h. Then the XC-72-T-Ar solution was stirred at 25 °C meanwhile 0.1 M NaOH was slowly added for adjusting the pH at the constant value of 9.5. After stirring for 24 h, an appropriate amount of PdCl₂ solution (6 g L⁻¹) was added into the solution at a fixed pH (9.5). After stirring for 1 h, the calculated amount of NaBH₄ solution (freshly prepared, n_{NaBH₄}/n_{Pd} = 15/1) was rapidly added into the solution under vigorous stirring. The mixture was aged for 6 h at 25 °C under stirring, after which the suspension was filtered and extensively washed with distilled water until it was free of chloride ions. The sample was dried in air at 100 °C for 12 h to give a black Pd/XC-72-T-Ar catalyst.

2.6 Preparation of Pd/XC-72, Pd/BP2000, Pd/M800, Pd/660R, Pd/XC-72-HNO₃, Pd/XC-72-HNO₃-T-Ar, Pd/CNTs, Pd/AC, Pd/r-GO, Pd/CNTs-T-Ar, Pd/AC-T-Ar, Pd/r-GO-T-Ar, Pd/XC-72-700-Ar, Ru/XC-72-700-Ar, Rh/XC-72-700-Ar and Ir/XC-72-700-Ar catalysts: Metal loading of all the catalysts was 1.0 wt % (based on ICP bulk chemical analysis). In analogy to the case of Pd/XC-72-T-Ar, these catalysts were prepared by the procedure of wet chemical reduction.

2.7 Preparation of Pd/Al₂O₃, Pd/P25, Pd/ZrO₂, Pd/SiO₂, hydrophobically-modified Pd/TPS-Al₂O₃ and Pd/TPS-P25 catalysts: These catalysts were prepared using the wet chemical reduction method. Pd loading of all the catalysts was 1.0 wt % (based on ICP bulk chemical analysis). Firstly, 0.5 g Al₂O₃ or

P25 or ZrO₂ or SiO₂ or TPS-Al₂O₃ or TPS-P25 was introduced into 200 mL distilled H₂O (or ethanol-water solution for TPS-Al₂O₃ and TPS-P25 supports, $V_{\text{ethanol}}/V_{\text{H}_2\text{O}} = 1/5$) and dispersed by ultrasonic at 25 °C for 2 h, and the solution was stirred at 25 °C for 24 h. Then an appropriate amount of PdCl₂ solution (6 g L⁻¹) was added into the solution. After stirring for 1 h, the calculated amount of NaBH₄ solution (freshly prepared, $n_{\text{NaBH}_4}/n_{\text{Pd}} = 15/1$) was rapidly added into the solution under vigorous stirring. The mixture was aged for 6 h at 25 °C under stirring, after which the suspension was filtered and extensively washed with distilled water until it was free of chloride ions. The sample was dried in air at 100 °C for 12 h to give a catalyst.

3. Supplementary data

Table S1. Hydrolysis of **1a** by 1.0 wt % Pd/XC-72-700-Ar at different temperature.^[a]

$$\text{Et}_3\text{Si-H (1a)} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Et}_3\text{Si-OH (1b)}$$

Entry	Temperature [°C]	Reaction time [s]	Et ₃ Si-OH yield [%]	TOF [h ⁻¹] ^[b]
1	17	96	>99	384400
2	21	74	>99	496400
3	25	57	>99	645300
4	29	49	99	752900
5	33	41	97	894500

[a] Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=10000, air atmosphere. [b] Based on total Pd atoms.

Table S2. Activity of other carbon nanostructures supported Pd for hydrolysis of **1a**.^[a]

$$\text{Et}_3\text{Si-H (1a)} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Et}_3\text{Si-OH (1b)}$$

Entry	Catalyst ^[b]	Reaction time [min]	Et ₃ Si-OH yield [%]	TOF [h ⁻¹] ^[c]
1	Pd/CNTs	10	95	14400
2	Pd/AC	11	94	12940
3	Pd/r-GO	150	90	910
4	Pd/CNTs-400-Ar	5.5	99	27520
5	Pd/AC-400-Ar	7	96	20790
6	Pd/r-GO-400-Ar	82	91	1682

[a] Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=2500, air atmosphere, 25 °C. [b] Pd loading was 1.0 wt %. [c] Based on total Pd atoms.

Table S3. BET surface area and adsorption ability of various carbon supports for **1a**, *n*-hexane and H₂O at 25 °C.

Support	BET surface area [m ² g ⁻¹]	Adsorption amount of 1a [mmol g ⁻¹]	Adsorption amount of <i>n</i> -hexane [mg g ⁻¹]	Adsorption amount of H ₂ O [mg g ⁻¹]
XC-72	254	1.05	604 (2.38) ^[a]	84 (0.33)
BP2000	1207	0.81	2204 (1.83)	404 (0.33)
M800	251	0.92	545 (2.17)	58 (0.23)
660R	125	0.54	216 (1.73)	30 (0.24)
XC-72-300-Ar	243	1.12	681 (2.80)	61 (0.25)
XC-72-700-Ar	187	1.28	726 (3.88)	16 (0.09)
XC-72-900-Ar	186	1.20	709 (3.81)	13 (0.07)
XC-72-HNO ₃	262	0.13	223 (0.85)	441 (1.68)
XC-72-HNO ₃ -400-Ar	240	0.27	283 (1.18)	218 (0.91)
CNTs	210	0.091	196 (0.93)	65 (0.31)
AC	802	0.090	729 (0.91)	1412 (1.76)
r-GO	128	0.052	76 (0.59)	313 (2.45)

[a] Numbers in parentheses are the corresponding surface area-based adsorption capacity referred to mg m⁻².

Table S4. Kinetic isotope study for hydrolysis of **1a** over Pd/XC-72-700-Ar and Pd/XC-72-HNO₃.^[a]

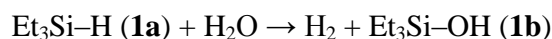
Entry	Catalyst ^[b]	Silane	Oxidant	TOF [h ⁻¹] ^[c]	KIE ^[d]	Fraction	
						Et ₃ SiOH	Et ₃ SiOD
1	Pd/XC-72-700-Ar	Et ₃ SiH	H ₂ O	645300	-	100	0
2	Pd/XC-72-700-Ar	Et ₃ SiH	D ₂ O	529000	1.2	0	100
3	Pd/XC-72-HNO ₃	Et ₃ SiH	H ₂ O	35260	-	100	0
4	Pd/XC-72-HNO ₃	Et ₃ SiH	D ₂ O	31700	1.1	0	100

[a] Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=2500, air atmosphere, 25 °C. [b] Pd loading was 1.0 wt %. [c] Based on total Pd atoms. [d] KIE = TOF (entry 1 or 3)/TOF (entry 2 or 4).

Table S5. BET surface area and adsorption ability of solid oxide supports for **1a**, *n*-hexane and H₂O at 25 °C.

Support	BET surface area [m ² g ⁻¹]	Adsorption amount of 1a [mmol g ⁻¹]	Adsorption amount of <i>n</i> -hexane [mg g ⁻¹]	Adsorption amount of H ₂ O [mg g ⁻¹]
Al ₂ O ₃	106	0.073	103 (0.97) ^[a]	205 (1.93)
P25	57	0.098	140 (2.46)	196 (3.44)
ZrO ₂	186	0.077	112 (0.60)	240 (1.29)
SiO ₂	380	0.1	132 (0.35)	316 (0.83)
TPS-Al ₂ O ₃	61	0.37	364 (5.97)	3 (0.05)
TPS-P25	32	0.52	306 (9.56)	4 (0.13)

[a] Numbers in parentheses are the corresponding surface area-based adsorption capacity referred to mg m⁻².

Table S6. Activity of various catalysts for hydrolysis of **1a**.^[a]

Entry	Catalyst ^[b]	Particle size [nm] ^[c]	Reaction time [min]	Et ₃ Si-OH yield [%]	TOF [h ⁻¹] ^[d]
1	Pt/XC-72-700-Ar	2.2	60	79	2688
2	Ru/XC-72-700-Ar	2.8	60	0	0
3	Rh/XC-72-700-Ar	3.1	60	66	2243
4	Ir/XC-72-700-Ar	2.4	60	0	0
5	Pd/Al ₂ O ₃	2.7	57	78	2778
6	Pd/P25	3.0	10	94	19150
7	Pd/ZrO ₂	2.9	53	81	3099
8	Pd/SiO ₂	2.6	25	93	7541
9	Pd/TPS-Al ₂ O ₃	2.9	17	99	11890
10	Pd/TPS-P25	3.2	2.4	98	83210

[a] Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=2500, air atmosphere, 25 °C. [b] metal loading was 1.0 wt %. [c] Evaluated by TEM. [d] Based on total metal atoms.

Table S7. Production of various silylamines via aminolysis of **1a**.^[a]

Entry	Amine	Reaction time [min]	Et ₃ Si-NR ¹ R ² yield [%]	TOF [h ⁻¹] ^[b]
1	<i>n</i> -BuNH ₂	15	93	13950
2	PhNH ₂	14	98	15750
3	morpholine	21	99	10607
4 ^[c]	<i>n</i> -BuNH ₂	40	80	4500

[a] Reaction conditions: 5 mmol **1a**, 5 mmol amine, 5 mL dried THF, 1.0 wt % Pd/XC-72-700-Ar, S/C=2500, Ar atmosphere, 60 °C. [b] Based on total Pd atoms. [c] 1.0 wt % Pd/XC-72-HNO₃.

Table S8. Comparison of different catalytic systems reported for the hydrolysis of organosilanes.

Catalyst (S/C)	Silane	Time	Silanol yield [%]	TOF [h ⁻¹] ^[a]	Ref. ^[b]
Pd/XC-72-700-Ar (10000)	Et ₃ SiH	57 s	>99	654300 ^[c] (1686000) ^[d]	This work
	PhMe ₂ SiH	3 min	99	213200	
Pd/AlO(OH) (1000)	Et ₃ SiH	10 min	98	5880	10a
Pd/C-100Hox (20000)	Et ₃ SiH	1 h	>99	20000	10b
Au/HAP (120)	Et ₃ SiH	2 h	>99	60	10d
AuNPore (100)	Et ₃ SiH	2 h	94	5029 ^[d]	10e
AuCNT (20000)	Et ₃ SiH	1 h	90	18000	10f
Au/SiO ₂ (250)	Et ₃ SiH	2 min	>99	29700 ^[d]	10g
Au-2/o-CNT (1000)	Et ₃ SiH	15 min	99	3960	10h
Au ₃₄ Ag ₂₈ (PA) ₃₄ /XC-72 (7130) ^[e]	Et ₃ SiH	12 min	>99	35650	10i

Pt/GO (3300)	Et ₃ SiH	1 h	99	3270	10n
Au@PPX (115)	PhMe ₂ SiH	3.5 h	99	33	10j
Au/ONT (2000)	PhMe ₂ SiH	2.5 h	96	768	10k
Ag/HAP (33)	PhMe ₂ SiH	15 min	99	131	10l
AgPd NSs (20)	PhMe ₂ SiH	1 h	>99	20	10m
Ru ₂ (CO) ₆ Cl ₄ (2000)	Et ₃ SiH	5 min	94	22560	9c
[Fe(C ₆ H ₅ N ₂ O)-(CO)(MeCN) ₃][PF ₆] (10000)	Et ₃ SiH	15 min	>99	40000	9g
(TPA)Rh-I (250)	PhMe ₂ SiH	1.5 h	95	158	9i

[a] TOF was calculated by the following equation: TOF (h⁻¹) = mmol of the product/mmol of the catalyst/time (h). [b] References in the article. [c] These values were obtained based on the silane conversion at 15 %. [d] These values were obtained based on surface metal atoms. [e] Based on Au atoms.

Table S9. Comparison of different catalytic systems reported for the alcoholysis of organosilanes.

Catalyst (S/C)	Silane	Alcohol	Time	Silanol yield [%]	TOF [h ⁻¹] ^[a]	Ref. ^[b]
Pd/XC-72-700-Ar (10000)	Et ₃ SiH	MeOH	1 min	>99	619300 ^[c]	This work
		<i>n</i> -BuOH	3 min	>99	208100 ^[c]	
Au/HAP _{nano} (667)	Et ₃ SiH	<i>n</i> -BuOH	1 h	93	620	14d
[Au]-SMAP-Rh (75000)	PhMe ₂ SiH	EtOH	16 h	80	3750	14b
10Dod-Au NP array	PhMe ₂ SiH	<i>n</i> -BuOH	1 h	83	55000 ^[d]	14c
Cu-(B)G (200)	PhMe ₂ SiH	<i>n</i> -BuOH	24 h	>99	8.3	14e
Cu ₃ (BTC) ₂	PhMe ₂ SiH	<i>n</i> -BuOH	1 h	98	167	14f
[RuCl ₂ (<i>p</i> -cymene)] ₂ (1000)	Et ₃ SiH	MeOH	<1 min	>99	367000	14h
CpFe(CO) ₂ Me (100)	Et ₃ SiH	EtOH	24 h	21	0.875	14k

[a] TOF was calculated by the following equation: TOF (h⁻¹) = mmol of the product/mmol of the catalyst/time (h). [b] References in the article. [c] These values were obtained based on the silane conversion at 15 %. [d] These values were obtained based on surface metal atoms.

Table S10. Comparison of different catalytic systems reported for the aminolysis of organosilanes.

Catalyst (S/C)	Silane	Amine	Time	Silylamine yield [%]	TOF [h ⁻¹] ^[a]	Ref. ^[b]
Pd/XC-72-700-Ar (2500)	Et ₃ SiH	<i>n</i> -BuNH ₂	15 min	93	13950 ^[c]	This work
		PhNH ₂	14 min	98	15750 ^[c]	
Pd/G (20)	Et ₃ SiH	<i>n</i> -BuNH ₂	7 h	87	2.5	19b
Au/HAP (120)	Et ₃ SiH	<i>n</i> -BuNH ₂	12 h	99	12	19c
Yb{η ² -Ph ₂ CN(C ₆ H ₃ Me ₂ -2,6)}(hmpa) _n (33)	Et ₃ SiH	<i>n</i> -BuNH ₂	3 h	21	2.3	19e
Ru ₃ (CO) ₁₂ (100)	Et ₃ SiH	PhNH ₂	4 h	>99	25	19i
Ba{CH(SiMe ₃) ₂ } ₃ (THF) (400)	Ph ₃ SiH	pyrrolidine	5 min	75	3600	19j

[a] TOF was calculated by the following equation: TOF (h⁻¹) = mmol of the product/mmol of the catalyst/time (h). [b] References in the article. [c] These values were obtained based on the silane conversion at 15 %.

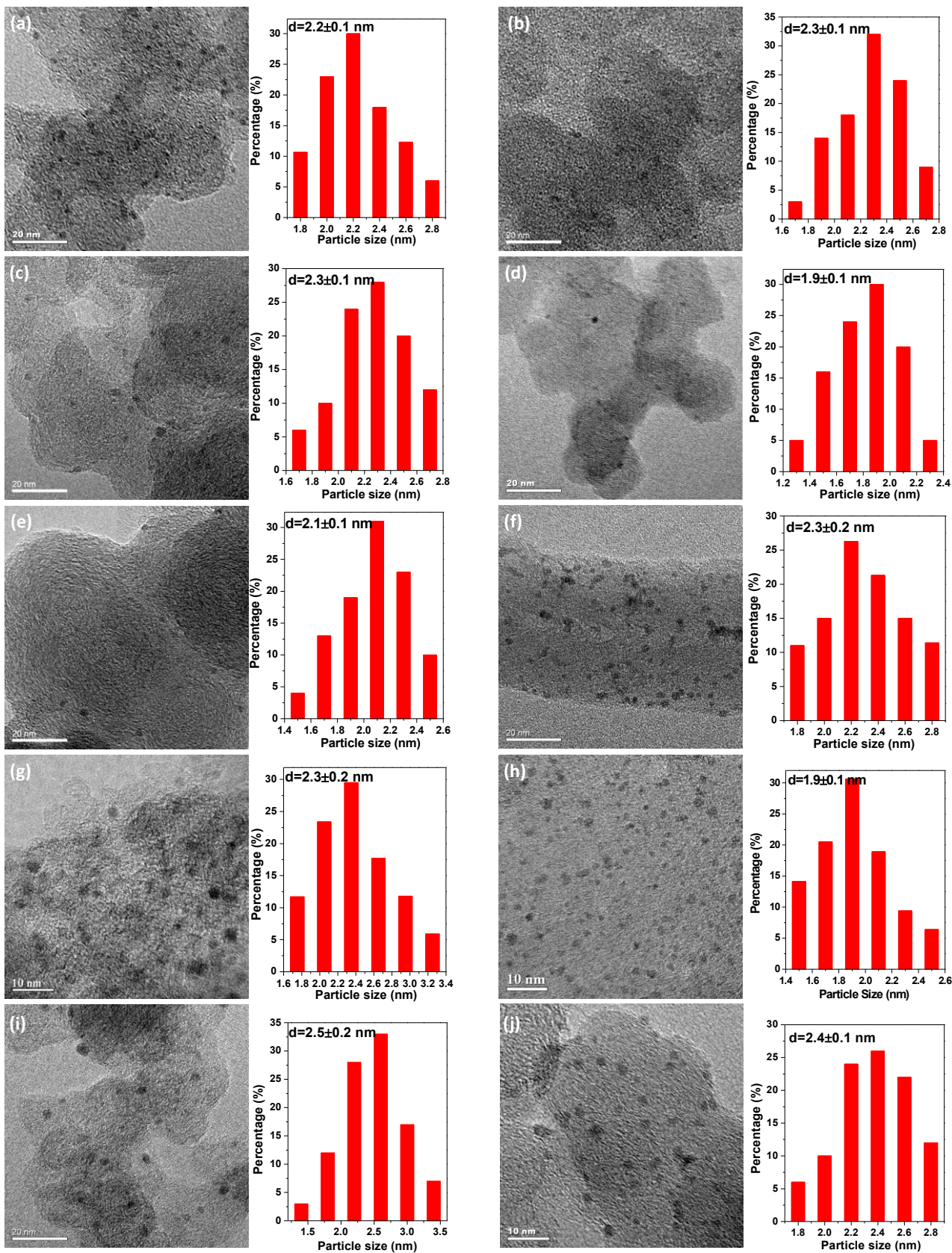


Figure S1. Transmission electron microscopy (TEM) images and particle size distributions of 1 wt % Pd catalyst. (a) Pd/BP2000, (b) Pd/M800, (c) Pd/660R, (d) Pd/XC-72-300-Ar, (e) Pd/XC-72-900-Ar, (f) Pd/CNTs, (g) Pd/AC, (h) Pd/r-GO (i) Pd/XC-72-HNO₃-400-Ar and (j) reused 1.0 wt % Pd/XC-72-700-Ar after ten times.

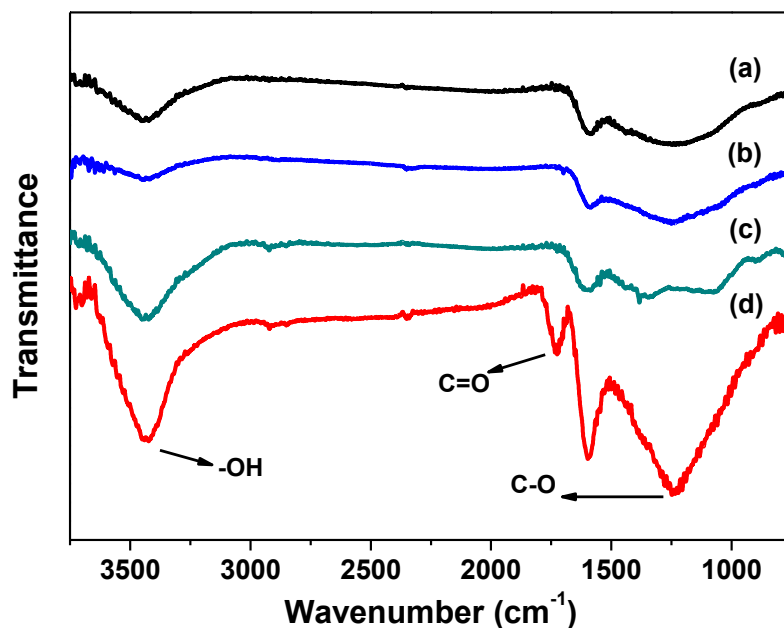


Figure S2. Fourier transform infrared spectroscopy (FT-IR) spectra of (a) XC-72, (b) XC-72-700-Ar, (c) Pd/XC-72-HNO₃-400-Ar and (d) XC-72-HNO₃.

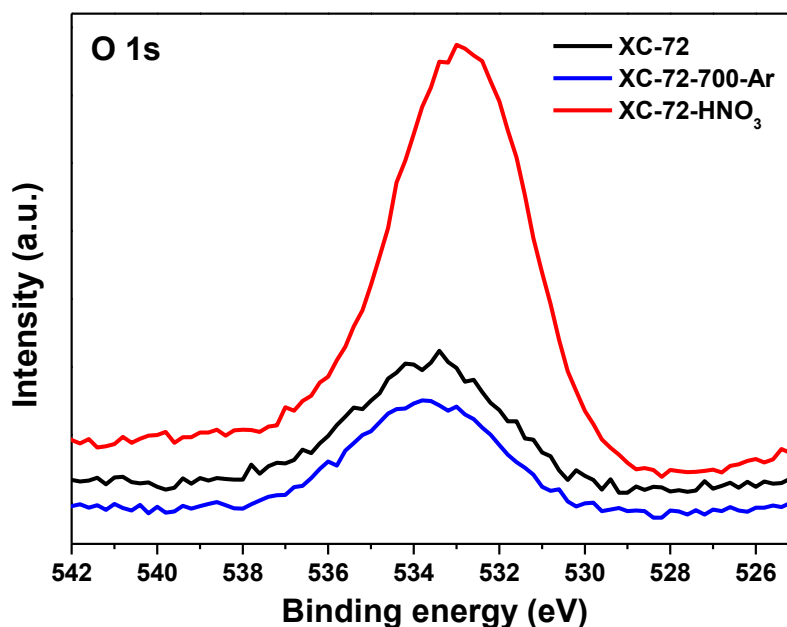


Figure S3. O 1s X-ray photoelectron (XP) spectra of XC-72, XC-72-700-Ar and XC-72-HNO₃.

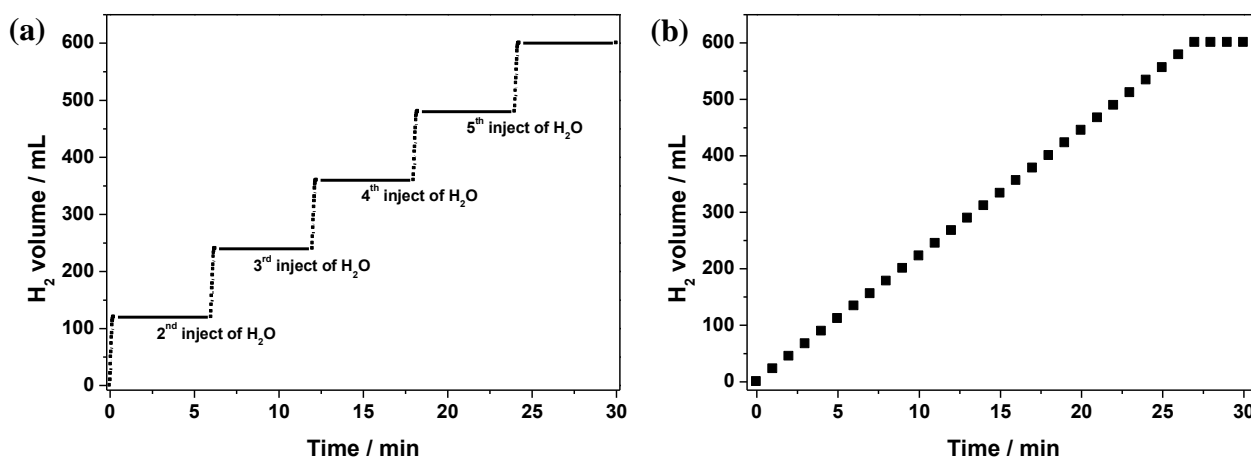


Figure S4. Generation of hydrogen on-demand using 1.0 wt% Pd/XC-72-700-Ar. (a) via sequential injection of **1a** at intervals; and (b) via slowly and continuously injecting **1a** into a THF-H₂O solution.

Reaction conditions: 25 mmol **1a**, 2.5 mL water, 50 mL THF, S/C = 2500, air atmosphere, 25 °C.

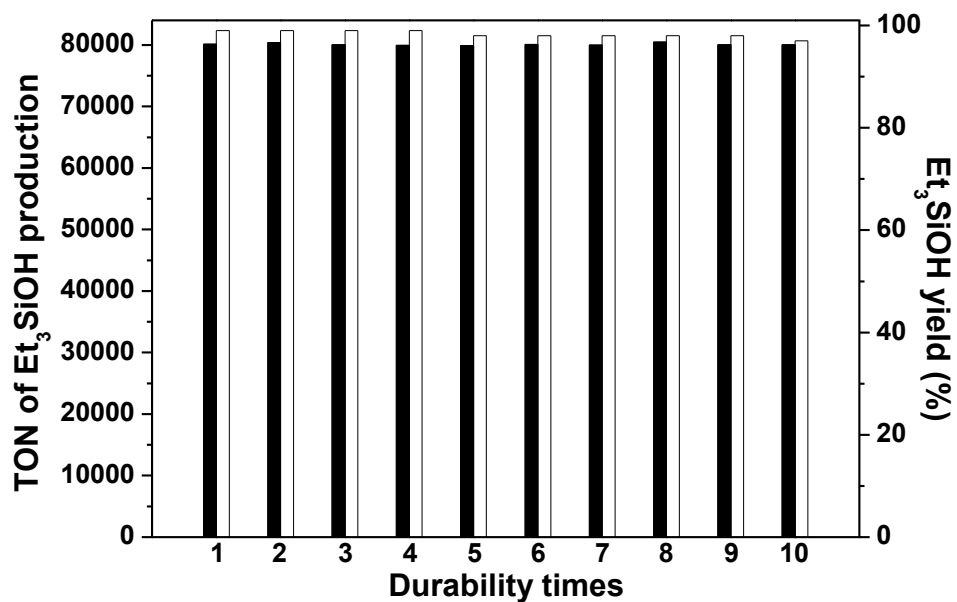


Figure S5. Large-scale durability of 1.0 wt % Pd/XC-72-700-Ar for **1b** production via hydrolysis of **1a**. Reaction conditions: 50 mmol **1a**, 5 mL water, 100 mL THF, S/C = 80000, air atmosphere, 25 °C.

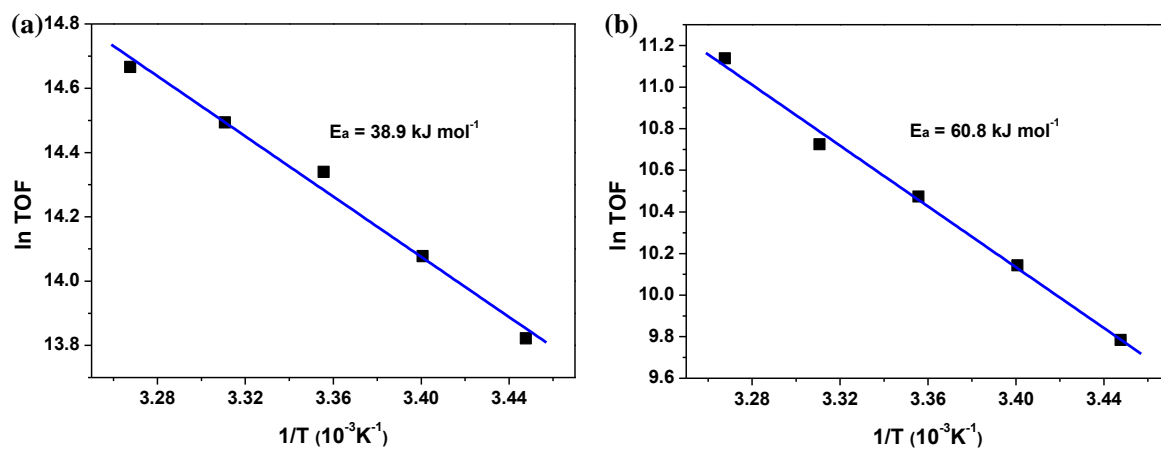


Figure S6. Arrhenius plot for hydrolysis of **1a** over (a) 1.0 wt % Pd/XC-72-700-Ar and (b) 1.0 wt % Pd/XC-72-HNO₃.

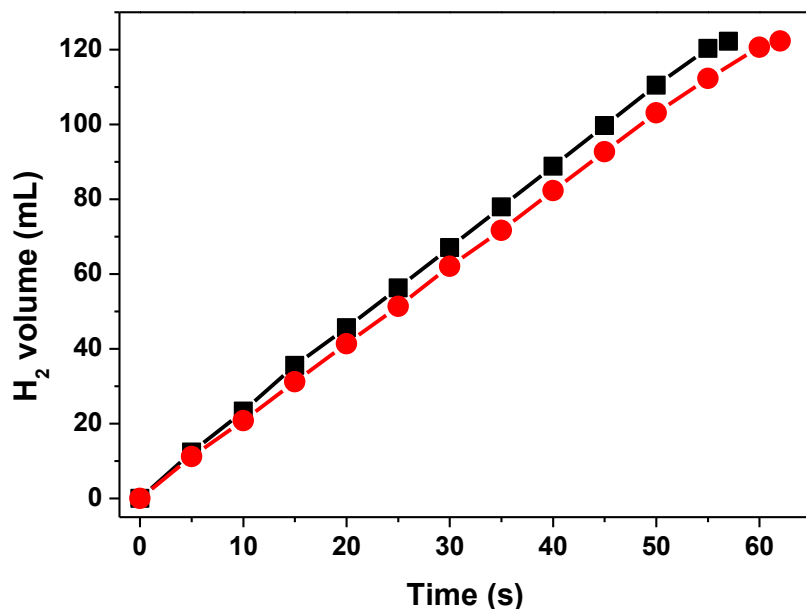


Figure S7. Air-stability of 1.0 wt % Pd/XC-72-700-Ar. Compared to the fresh one (black line), Pd/XC-72-700-Ar stored for two years (red line) at 25 °C can still complete the reaction in ca. 1min. Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=10000, air atmosphere.

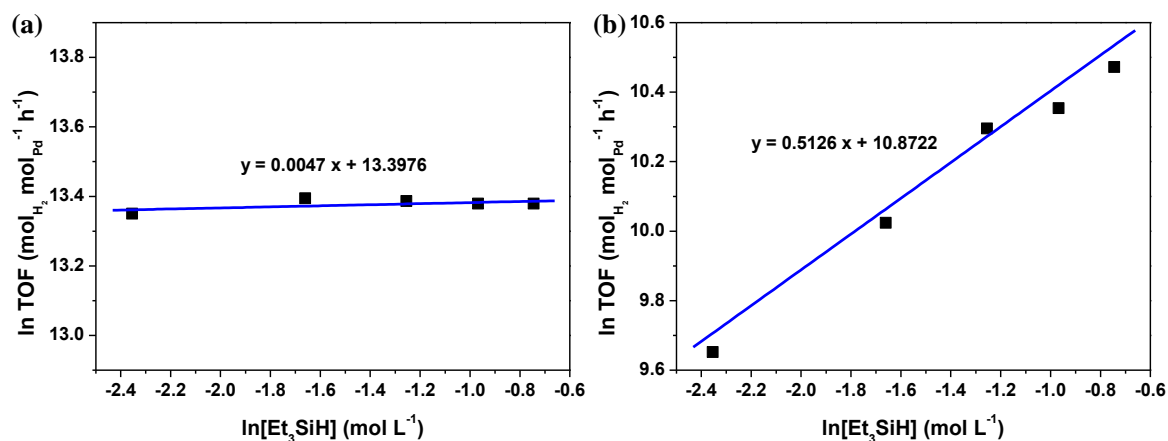


Figure S8. Dehydrogenative coupling rate as a function of **1a** concentration over (a) 1.0 wt % Pd/XC-72-700-Ar and (b) 1.0 wt % Pd/XC-72-HNO₃. Reaction conditions: 2-6 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=10000, air atmosphere, 25 °C.

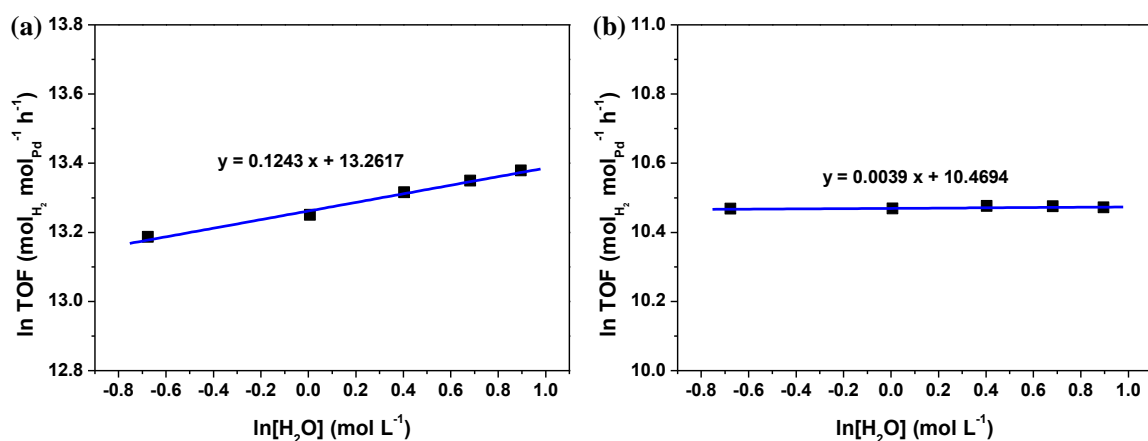


Figure S9. Dehydrogenative coupling rate as a function of H₂O concentration over (a) 1.0 wt % Pd/XC-72-700-Ar and (b) 1.0 wt % Pd/XC-72-HNO₃. Reaction conditions: 5 mmol **1a**, 0.1-0.5 mL

water, 10 mL THF, S/C=10000, air atmosphere, 25 °C.

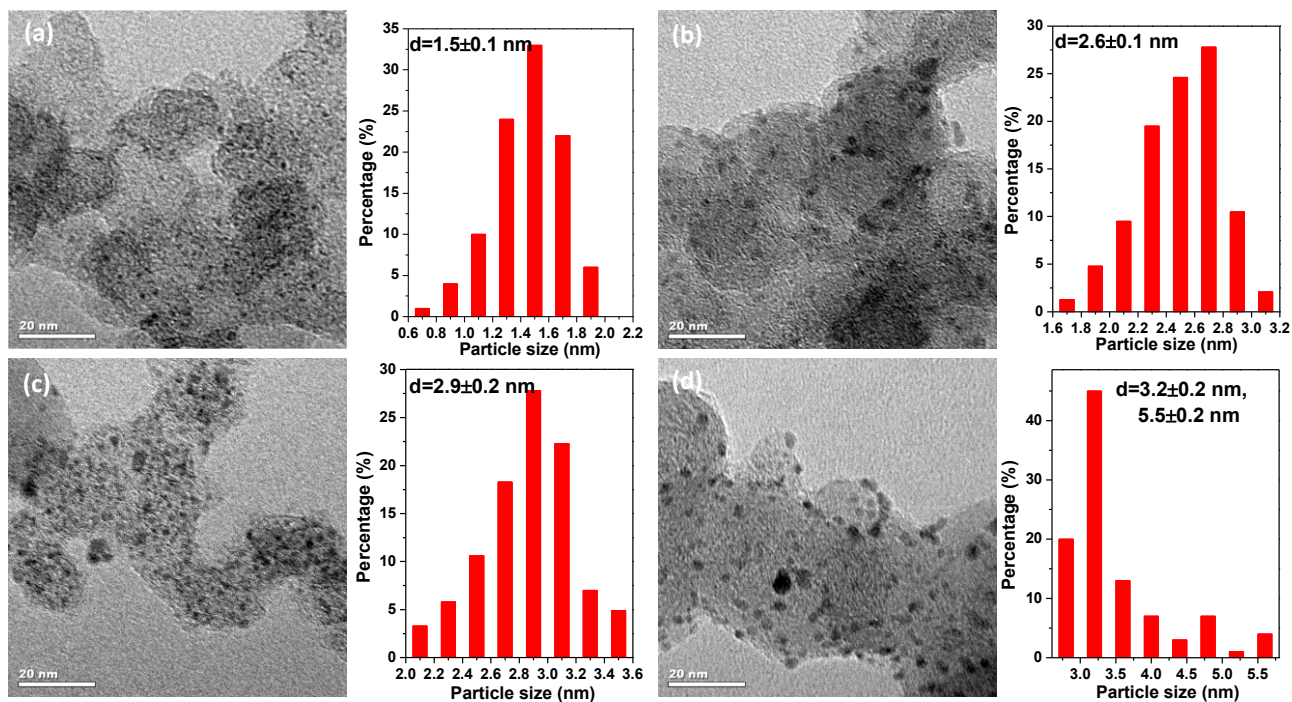


Figure S10. TEM images and particle size distributions of Pd/XC-72-700-Ar with the Pd loading of (a) 0.5, (b) 2.1, (c) 4.6 and (d) 8.9 wt %.

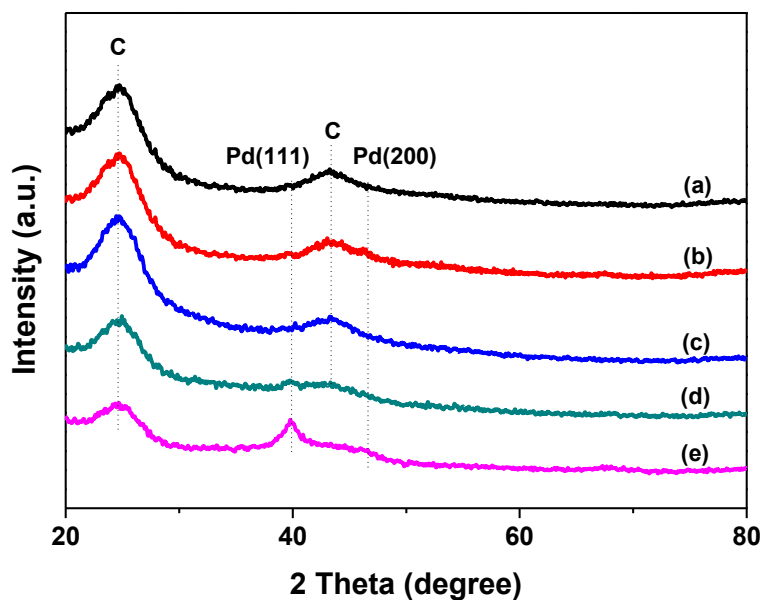


Figure S11. X-ray diffraction (XRD) patterns of Pd/XC-72-700-Ar with Pd loading of (a) 0.5, (b) 1.0, (c) 2.1, (d) 4.6 and (e) 8.9 wt %.

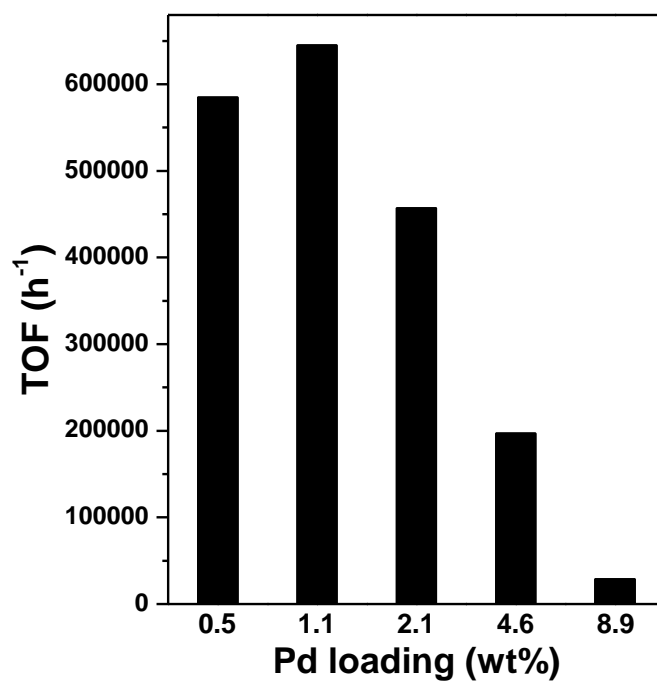


Figure S12. Hydrolysis of **1a** over Pd/XC-72-700-Ar as a function of Pd loading. Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C=10000, air atmosphere, 25 °C.

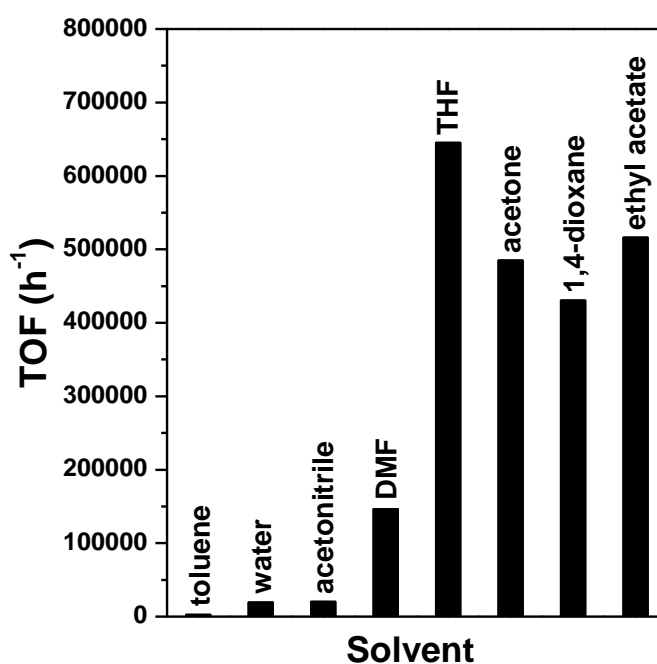


Figure S13. Hydrolysis of **1a** over 1.0 wt % Pd/XC-72-700-Ar as a function of solvent. Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL solvent, S/C=10000, air atmosphere, 25 °C.

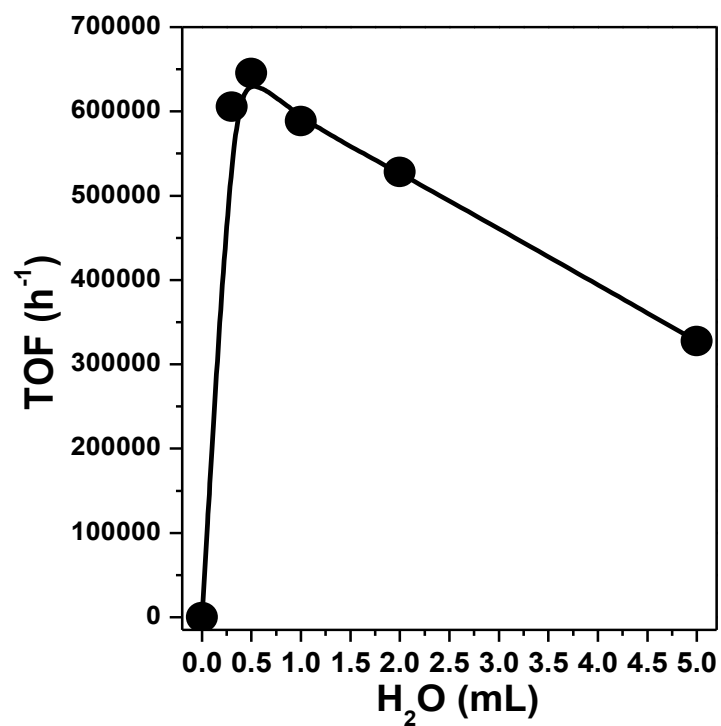


Figure S14. Hydrolysis of **1a** over 1.0 wt % Pd/XC-72-700-Ar as a function of water amount. Reaction conditions: 5 mmol **1a**, 10 mL THF, S/C=10000, air atmosphere, 25 °C.

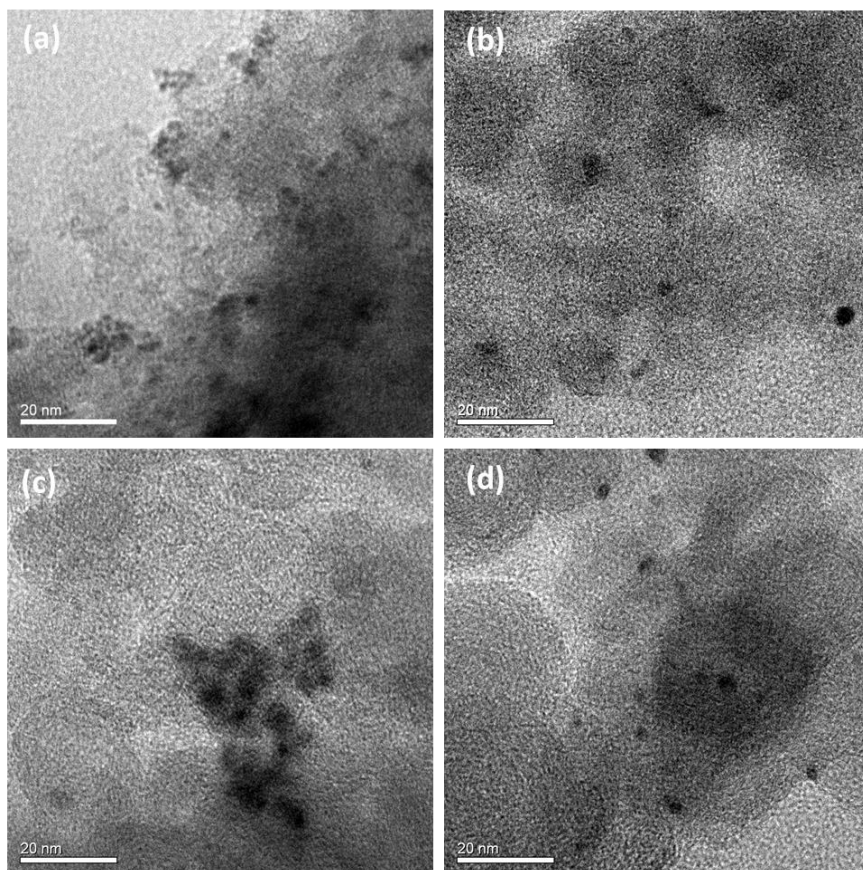


Figure S15. TEM images of (a) Pt/XC-72-700-Ar, (b) Ru/XC-72-700-Ar, (c) Rh/XC-72-700-Ar, (d) Ir/XC-72-700-Ar.

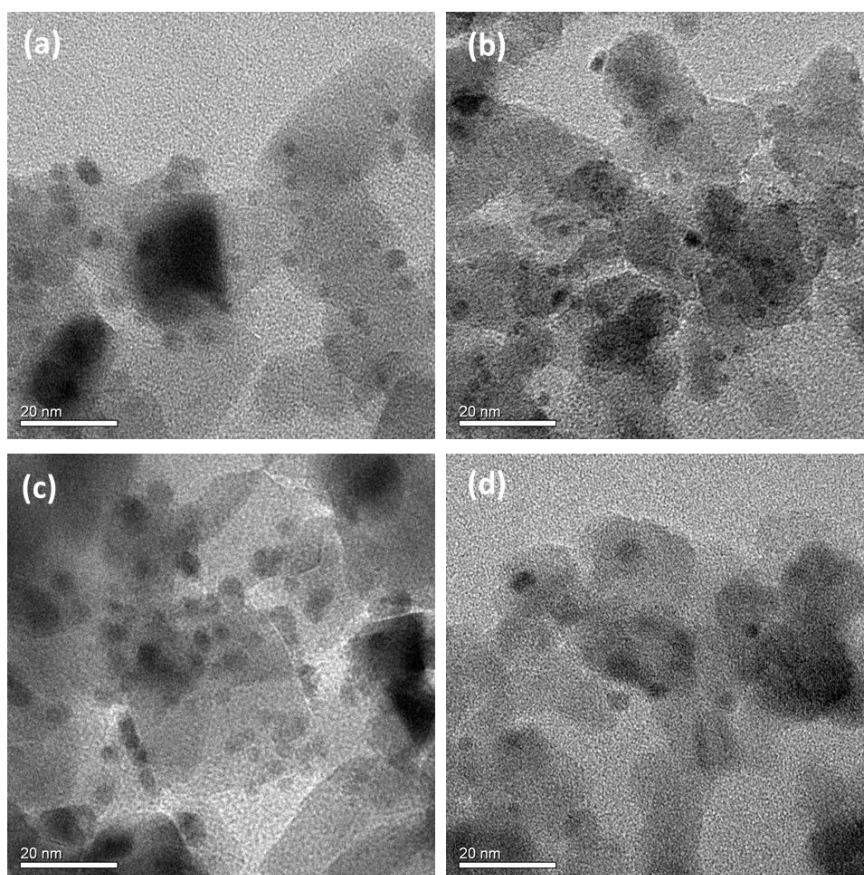


Figure S16. TEM images of (a) Pd/Al₂O₃, (b) Pd/P25, (c) Pd/TPS-Al₂O₃, (d) Pd/TPS-P25.

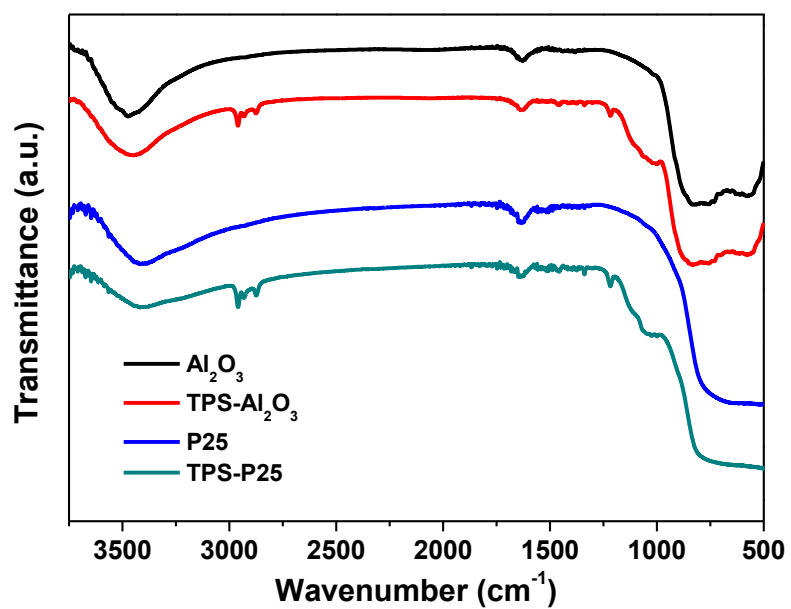


Figure S17. FT-IR spectra of Al₂O₃, TPS-Al₂O₃, P25 and TPS-P25.

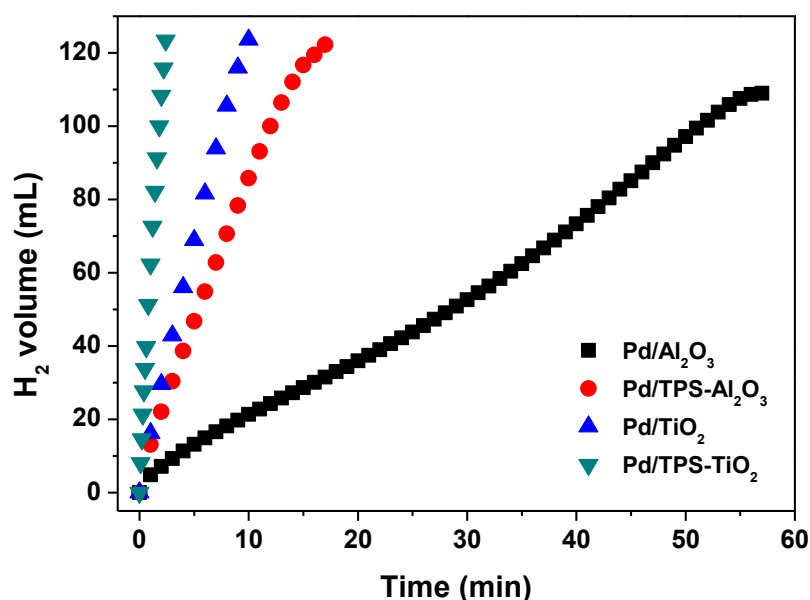
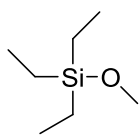
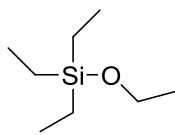


Figure S18. Hydrolysis of **1a** over hydrophobically-modified and unmodified catalysts.

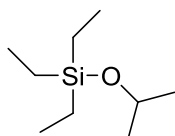
4. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of products



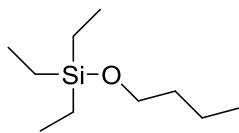
(Table 3, entry 1).[S2] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.47 (s, 3H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.62 (q, $J = 8.0$ Hz, 6H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 50.6, 6.6, 4.0.



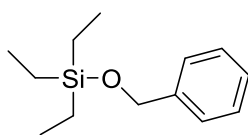
(Table 3, entry 2).[S3] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.69 (q, $J = 7.2$ Hz, 2H), 1.19 (t, $J = 7.2$ Hz, 3H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.61 (q, $J = 8.0$ Hz, 6H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 58.3, 18.6, 6.7, 4.4.



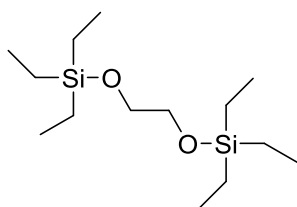
(Table 3, entry 3).[S3] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.99 (hept, $J = 6.0$ Hz, 1H), 1.16 (d, $J = 6.0$ Hz, 6H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.60 (q, $J = 8.0$ Hz, 6H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 64.7, 25.8, 6.8, 4.8.



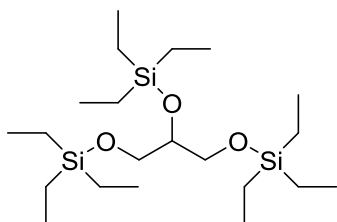
(Table 3, entry 4).[S4] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.61 (t, $J = 6.8$ Hz, 2H), 1.55-1.48 (m, 2H), 1.40-1.31 (m, 2H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.91 (t, $J = 7.6$ Hz, 3H), 0.60 (q, $J = 8.0$ Hz, 6H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 62.6, 35.1, 19.0, 13.9, 6.7, 4.4.



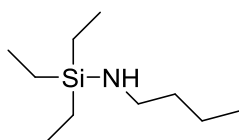
(Table 3, entry 5).[S3] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.34-7.19 (m, 5H), 4.73 (s, 2H), 0.98 (t, $J = 8.0$ Hz, 9H), 0.65 (q, $J = 8.0$ Hz, 6H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 141.3, 128.2, 126.9, 126.2, 64.7, 6.7, 4.5.



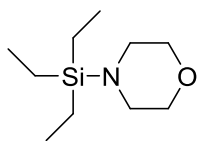
(Table 3, entry 6).[S5] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.68 (s, 4H), 0.96 (t, J = 8.0 Hz, 18H), 0.61 (q, J = 8.0 Hz, 12H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 64.2, 6.7, 4.4.



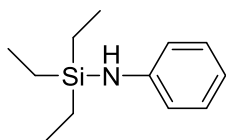
(Table 3, entry 7). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.72 (quint, J = 5.6 Hz, 1H), 3.62 (q, J = 5.2 Hz, 2H), 3.51 (q, J = 5.2 Hz, 2H), 0.96 (t, J = 8.0 Hz, 27H), 0.65-0.57 (m, 18H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 74.4, 64.6, 6.8, 6.7, 4.9, 4.4.



(Scheme 1, entry 1).[S6] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 2.70 (q, J = 6.8 Hz, 2H), 1.41-1.26 (m, 4H), 0.95-0.88 (m, 12H), 0.51 (q, J = 7.2 Hz, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 41.8, 37.2, 20.0, 13.9, 7.1, 4.7.



(Scheme 1, entry 2).[S6] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.55 (t, J = 4.4 Hz, 4H), 2.87 (t, J = 4.4 Hz, 4H), 0.93 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 68.7, 45.9, 7.1, 3.7.



(Scheme 1, entry 3).[S6] $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.11 (t, J = 8.0 Hz, 2H), 6.70-6.64 (m, 3H), 3.31 (br s, 1H), 0.97 (t, J = 8.0 Hz, 9H), 0.75 (q, J = 8.0 Hz, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 141.7, 129.2, 117.3, 116.0, 7.0, 4.6.

Supplementary references:

[S1] Hummers JR., W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

[S2] Ojima, Y.; Yamaguchi, K.; Mizuno, N. *Adv. Synth. Catal.* **2009**, *351*, 1405-1411.

[S3] Park, S.; Brookhart, M. *Organometallics* **2010**, *29*, 6057-6064.

[S4] Mitsudome, T.; Yamamoto, Y.; Noujima, A.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Eur. J.* **2013**, *19*, 14398-14402.

[S5] Yang, J.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2008**, *130*, 17509-17518.

[S6] Blandez, J. F.; Esteve-Adell, I.; Alvaro, M.; Garcia, H. *Catal. Sci. Technol.* **2015**, *5*, 2167-2173.

