Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Precise regulation of selectivity of supported nano-Pd catalysts using polysiloxane coatings with tunable surface wettability

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Contents

1. General information and experimental section

General Information:

Field-emission scanning electron microscope was carried out by using a JSM-6701F, (JEOL). TEM was carried out by using a Tecnai G2 F30 S-Twin transmission electron microscope operating at 300 kV. For TEM investigations, the catalysts were dispersed in ethanol by ultrasonication and deposited on carbon-coated copper grids. XRD measurements were conducted by using a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator with CuK_{a1} radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-90 ^{o}. XPS were obtained using a VG ES-CALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar^{+} iron gun. The electron binding energy was referenced to the C1s peak at 284.8 eV. The background pressure in the chamber was less than 10-7 Pa. The BET surface area measurements were performed on a Quantachrome IQ_2 at the temperature of 77 K. The pore size distribution was calculated from the adsorption-desorption isotherm by using the Barrett, Joyner, and Halenda (BJH) method. Prior to measurements, the samples were degassed at 100 ^{o}C for 12 h, at a rate of 10 $^{o}C \bullet min^{-1}$. Measurements of CAs were performed with a Contact Angle System OCA20 (Dataphysics, Germany) equipped with a tilting table. The syringe was positioned in a way that the water droplets (5 μL) could contact surface of the samples before leaving the needle. Tilting angle of the table was adjustable (0 °– 70 °) and the subsequent measurement of the SAs was allowed at the same position on the sample. A minimum of six readings were recorded for each sample, and the average values with standard errors were reported.

Experimental Section:

All solvents and chemicals were obtained commercially and were used as received. The TiO_2 support used in this work is Aeroxide® P25 which was purchased from Acros corporation.

2. Typical procedure for catalyst preparation:

Synthesis of Pd/TiO_2 sample:

The supported Pd/TiO_2 sample was prepared with deposition−precipitation method. TiO_2 (0.5 g, P25, J&K Scientific, anatase/rutile = 80/20) was dispersed in deionized water (25 mL), and a K_2PdCl_4 aqueous solution (1.0 mL, [Pd] 5.0 mg/mL) was added into the solution under vigorous stirring. The pH value was adjusted to about 10 by using 0.2 M NaOH, and the solution was stirred for another 3 h at room temperature. Then 4.0 mL of hydrazine solution ($V_{hydrazine} : V_{water} = 1 : 3$) was added to the solution and stirred for 4 h. The solid sample was recovered by centrifugation and washed with water. After drying at 80 °C for 12 h, a gray solid sample was obtained and denoted as Pd/TiO_2.

Synthesis of Pd/TiO_2@ POS coating

The Pd/TiO_2 (100 mg) was charged into the mixture of ethanol, ammonia (1 mL), and deionized water (5 mL) in a 100 mL conical flask. The suspension was stirred for 10 min and then ultrasonicated for 30 min. After that, different volumes of HDTMS and TEOS (4.12 mL) were injected slowly into the solution under magnetically stirred, and consequently reacted at room temperature under magnetic stirring for 4 h. The mixture was filtered, washed with water and ethanol, respectively, and dried in an oven overnight at 60 °C. A gray solid sample was obtained and denoted as Pd/TiO_2@ POS coating.

3. Typical procedure for catalytic reactions

Typical procedure for catalytic hydrogenation of phenylacetylene

A mixture of phenylacetylene (102 mg, 1.0 mmol), catalyst (0.009 mol%), and EtOH (4 mL) was added to a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with H_2 (1.0 atm) three times. The reaction mixture

was stirred at 50 °C for 2 h. Then, the autoclave was cooled to room temperature. Subsequently, the reaction mixture was analyzed by GC-MS (Agilent 7890B/5977A) and GC-FID (Agilent 7890A).

Typical procedure for reductive amination of aniline with paraformaldehyde

A mixture of aniline (93 mg, 1.0 mmol), paraformaldehyde (30 mg, 1.0 mmol), catalyst (0.009 mol%), and 1,4-dioxane (4 mL) was added to a glass tube which was placed in an 100 mL autoclave. Then, the autoclave was purged and charged with H_2 (1.0 atm) three times. The reaction mixture was stirred at 80 °C for 4 h. Next, the autoclave was cooled to room temperature. Subsequently, the reaction mixture was analyzed by GC-MS (Agilent 7890B-5977A).

4. Characterization results of catalysts

Table S1 The physical properties of catalysts

Entry	Catalyst	CA_{water} [a]	Pd (wt%) [b]	SA (m^2 g^{-1}) [c]	APR (nm) [c]	PV (cm^3 g^{-1}) [c]
1	Pd/TiO_2	22.9 °	0.50%	55.325	20.460	0.5660
2	Pd/TiO_2@POS-0	41.8 °	0.19%	24.701	5.01	0.0636
3	Pd/TiO_2@POS-1	44.5 °	0.22%	37.548	8.692	0.1632
4	Pd/TiO_2@POS-2	66.2 °	0.07%	24.116	7.725	0.0931
5	Pd/TiO_2@POS-3	110.8 °	0.03%	25.587	7.335	0.0938
6	Pd/TiO_2@POS-4	144.3 °	0.04%	27.182	7.560	0.1027
6	Pd/TiO_2@POS-5	154.5 °	0.07%	11.932	8.717	0.0520

a. Measured by contact angle system OCA20; b. Determined by ICP-AES; c. Determined by an IQ_2 automated gas sorption analyser; SA: BET surface area; APR: average pore radius; PV: pore volume.

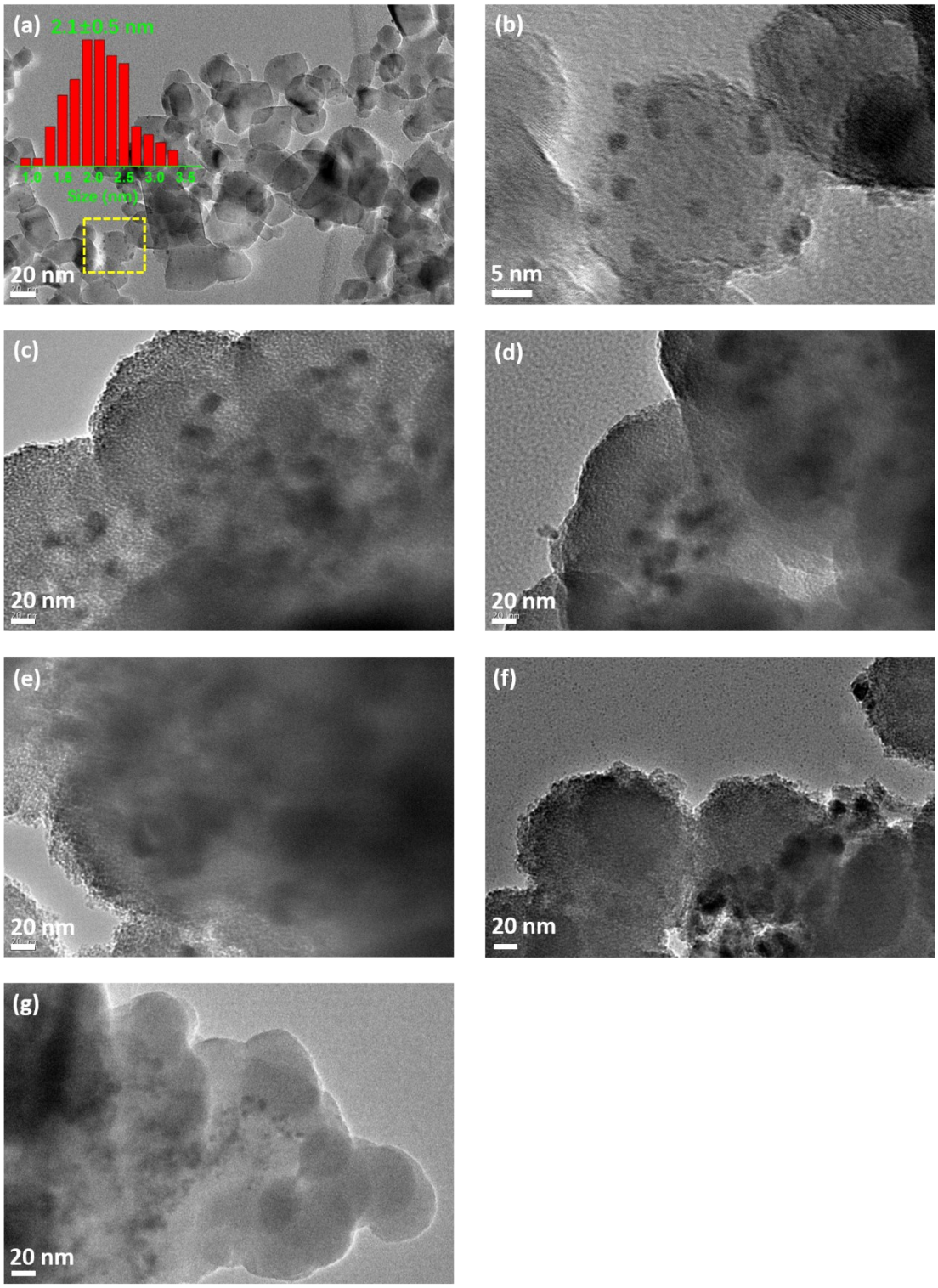


Fig. S1 TEM of samples. (a) Pd/TiO_2, (c) Pd/TiO_2@POS-1, (d) Pd/TiO_2@POS-2, (e) Pd/TiO_2@POS-3, (f) Pd/TiO_2@POS-4, (g) Pd/TiO_2@POS-5. HR-TEM image of (b) Pd/TiO_2 [(b) is a magnified picture of a region from (a)].

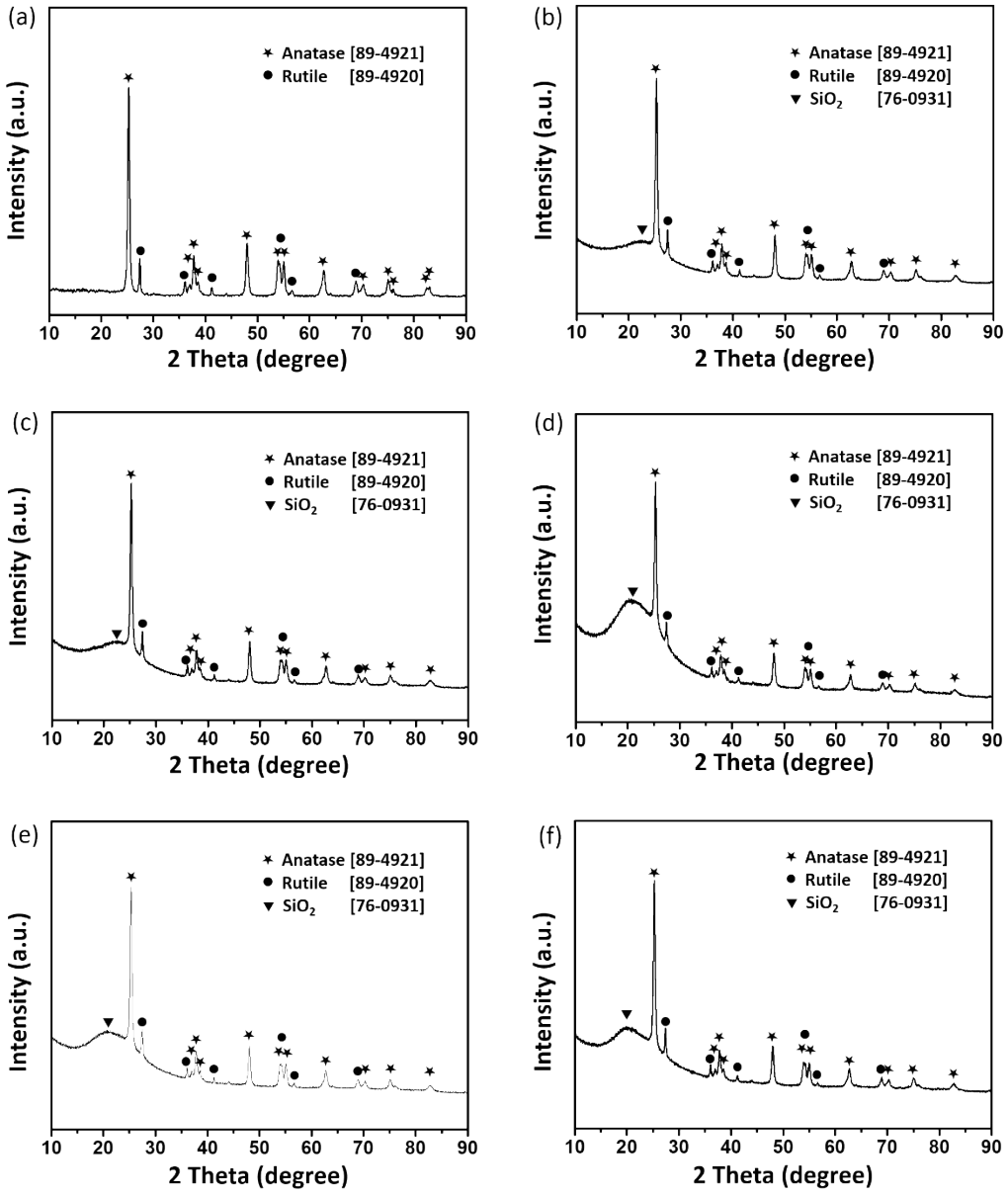


Fig. S2 XRD patterns of samples. (a) Pd/TiO_2, (b) Pd/TiO_2@POS-1, (c) Pd/TiO_2@POS-2, (d) Pd/TiO_2@POS-3, (e) Pd/TiO_2@POS-4, (f) Pd/TiO_2@POS-5.

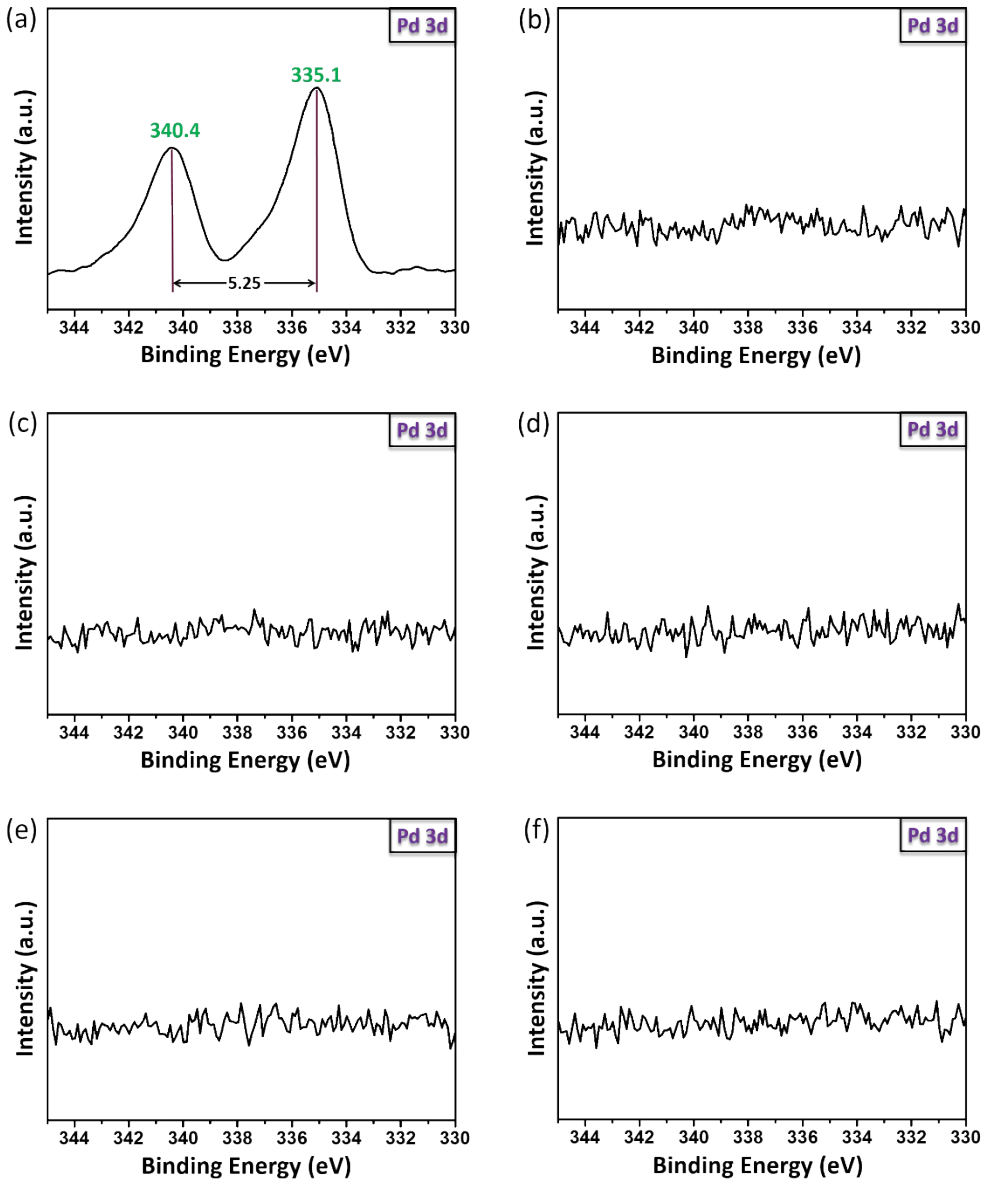


Fig. S3 XPS spectra of samples. (a) Pd/TiO_2, (b) Pd/TiO_2@POS-1, (c) Pd/TiO_2@POS-2, (d) Pd/TiO_2@POS-3, (e) Pd/TiO_2@POS-4, (f) Pd/TiO_2@POS-5.

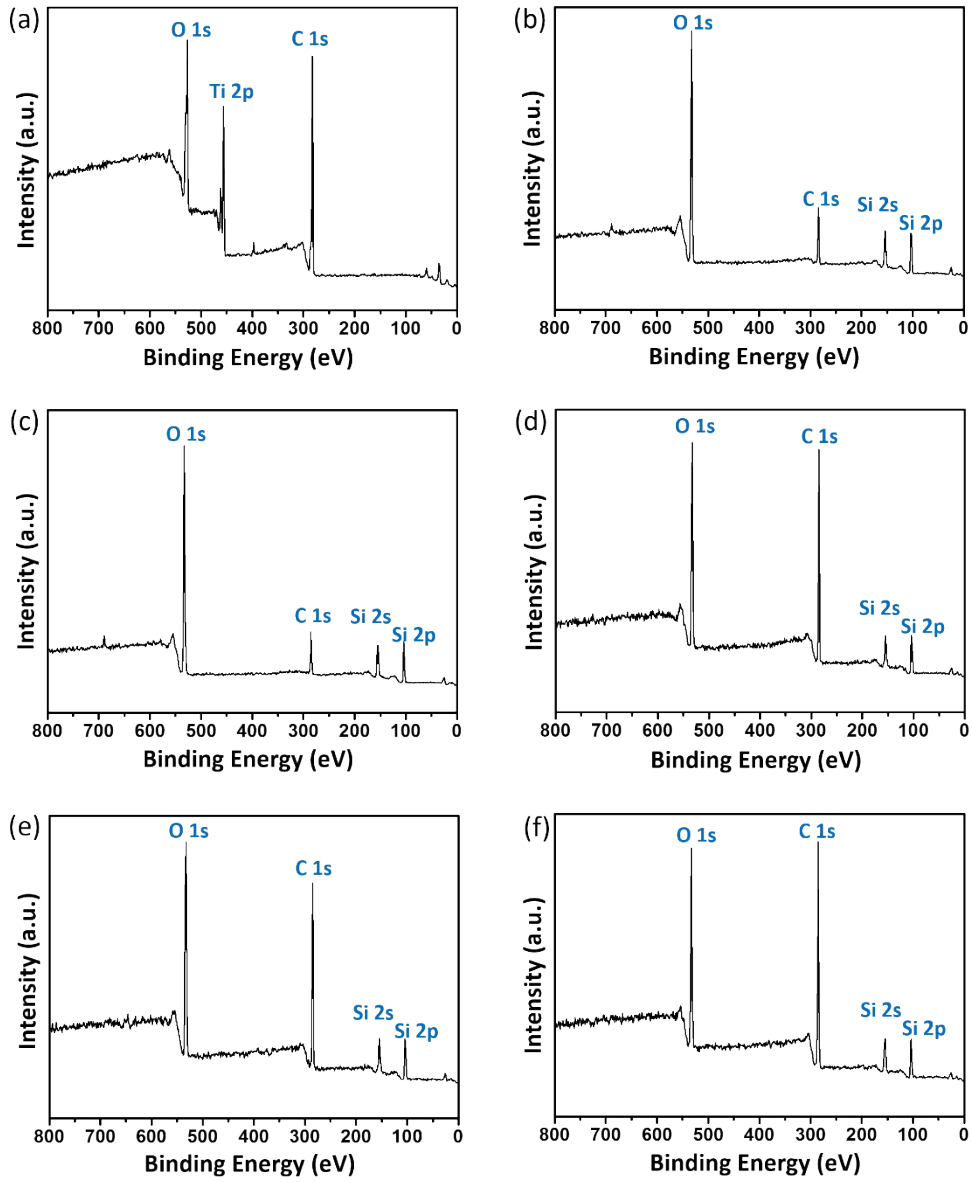


Fig. S4 XPS survey spectra of samples. (a) Pd/TiO_2, (b) Pd/TiO_2@POS-1, (c) Pd/TiO_2@POS-2, (d) Pd/TiO_2@POS-3, (e) Pd/TiO_2@POS-4, (f) Pd/TiO_2@POS-5.

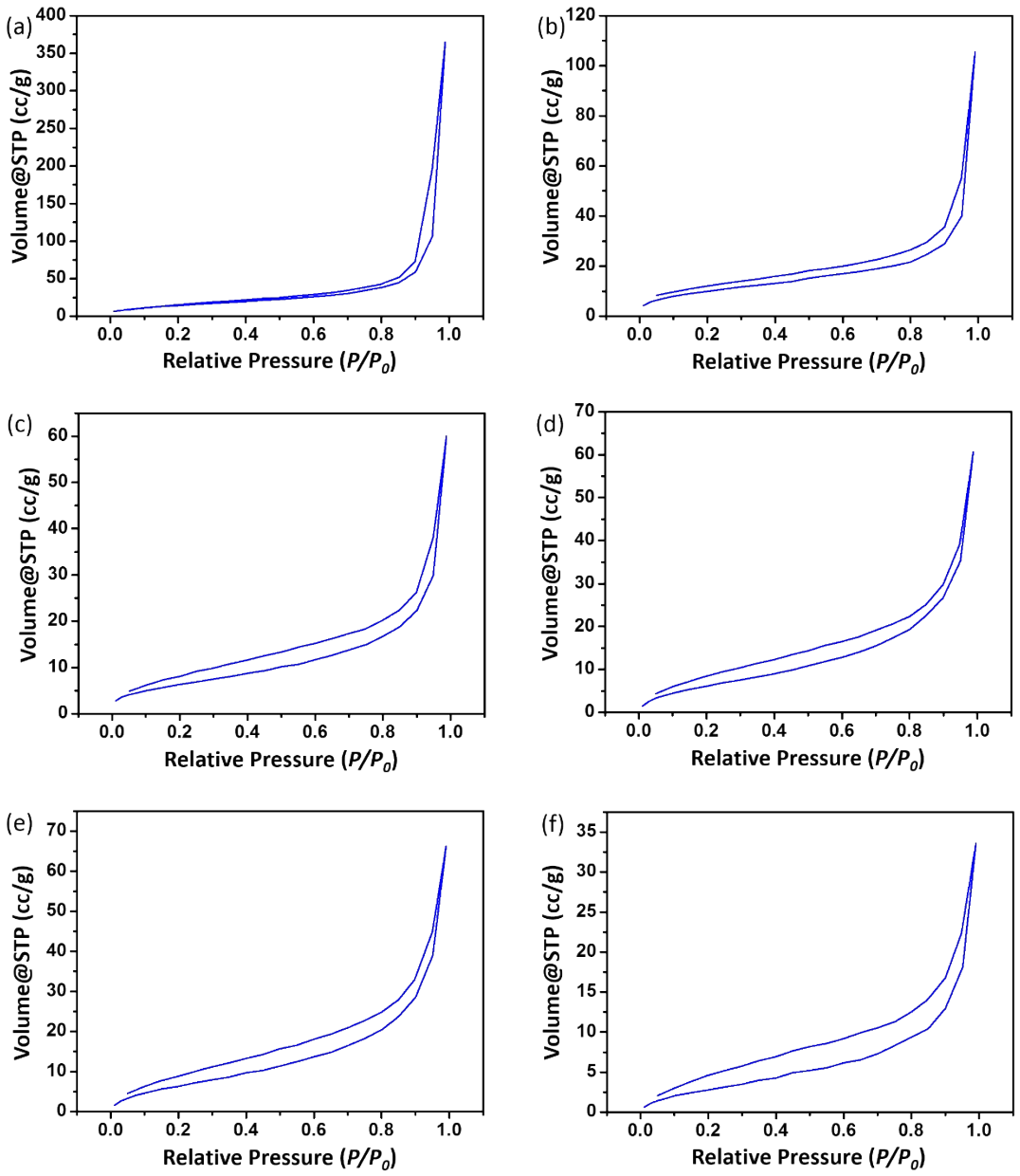
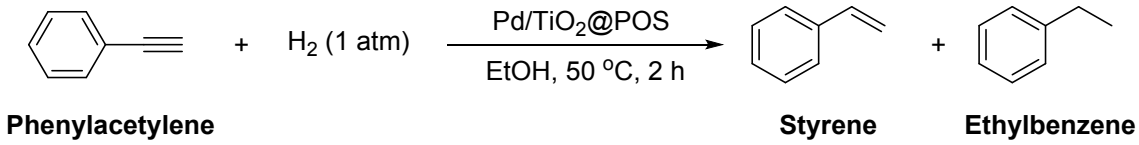


Fig. S5 N_2 adsorption-desorption isotherm of samples. (a) Pd/TiO_2, (b) Pd/TiO_2@POS-1, (c) Pd/TiO_2@POS-2, (d) Pd/TiO_2@POS-3, (e) Pd/TiO_2@POS-4, (f) Pd/TiO_2@POS-5.

5. Catalytic performance of catalysts

Table S2 Catalytic data in hydrogenation of phenylacetylene [a]

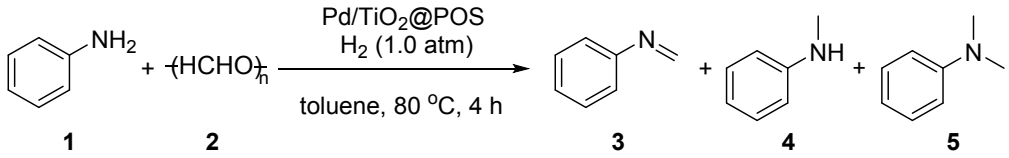


Phenylacetylene **Styrene** **Ethylbenzene**

Entry	Surface properties	Cat.	CA_{water}(°)	Conv.[b](%)	Yield [c](%)	Sel.[d] (%)	
						Styrene	Ethyl benzene
1	Hydrophilic	Pd/TiO_2	22.9	>99	99	67.9	32.2
2		Pd/TiO_2@POS-0	41.8	16	15	94.2	5.8
3		Pd/TiO_2@POS-1	44.5	20	17	91.7	8.3
4		Pd/TiO_2@POS-2	66.2	83	74	91.7	8.3
5	Hydrophobic	Pd/TiO_2@POS-3	110.8	>99	98	--	>99
6		Pd/TiO_2@POS-4	144.3	>99	98	--	>99
7		Pd/TiO_2@POS-5	154.5	>99	97	--	>99

a. Reaction conditions: phenylacetylene (1.0 mmol), H_2 (1.0 atm), catalyst (0.009 mol%), EtOH (4.0 mL), 50 ℃, 2 h; b. Determined by GC-MS; c. Combined yield of styrene and ethylbenzene was determined by GC-FID using biphenyl as the internal standard material; d. Determined by GC-FID.

Table S3 Catalytic data in reductive amination of aniline with paraformaldehyde[a]



1 **2** **3** **4** **5**

Entry	Surface properties	Cat.	CA_{water} (°)	Conv.[b](%)	Sel.[c] (%)		
					3	4	5
1	Hydrophilic	Pd/TiO_2	22.9	86	60.7	26.0	13.3
2		Pd/TiO_2@POS-0	41.8	83	98.7	1.3	--
3		Pd/TiO_2@POS-1	44.5	84	90.1	9.9	--
4		Pd/TiO_2@POS-2	66.2	91	78.9	17.8	3.3
5	Hydrophobic	Pd/TiO_2@POS-3	110.8	81	19.5	65.3	15.1
6		Pd/TiO_2@POS-4	144.3	87	6.0	69.6	24.4
7		Pd/TiO_2@POS-5	154.5	89	39.9	51.8	9.3

a. Reaction conditions: aniline **1** (1.0 mmol), paraformaldehyde **2** (1.0 mmol,), catalyst (0.009 mol%), H_2 (1.0 atm), toluene (4.0 mL), 80 ℃, 4 h; b. Determined by GC-MS; c. Determined by GC-MS.

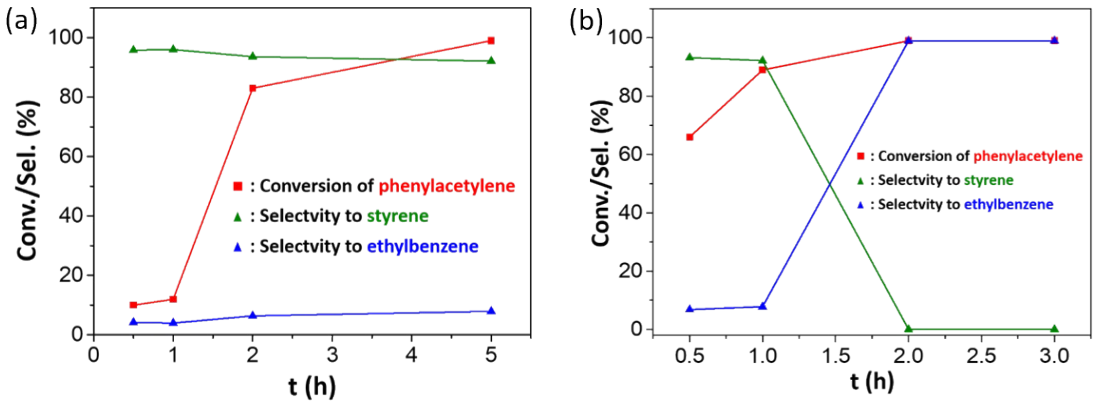


Fig. S6 Products distribution during the hydrogenation of phenylacetylene. (a) Pd/TiO_2@POS-2 as catalyst; (b) Pd/TiO_2@POS-4 as catalyst. Reaction conditions: phenylacetylene (1.0 mmol), H_2 (1.0 atm), catalyst (0.009 mol%), EtOH (4.0 mL), 50 ℃.

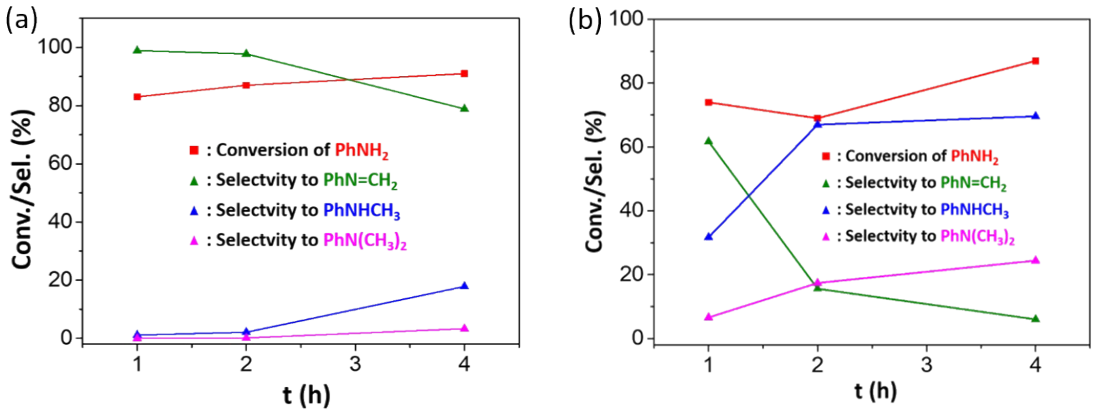


Fig. S7 Products distribution during the reductive amination of aniline with paraformaldehyde. (a) Pd/TiO_2@POS-2 as catalyst; (b) Pd/TiO_2@POS-4 as catalyst. Reaction conditions: aniline (1.0 mmol), paraformaldehyde (1.0 mmol,), catalyst (0.009 mol%), H_2 (1.0 atm), toluene (4.0 mL), 80 ℃.