Supporting information

Encapsulation of Atomically Dispersed Pt Clusters in Porous TiO₂ for Semi-Hydrogenation of Phenylacetylene

Huibin Wu,^{a,b} Xinchun Yang,^{a,b} Shichao Zhao,^a Liming Zhai,^{a,b} Guofu Wang,^a Bin Zhang,^{*a,b} Yong Qin^{a,b}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Experimental section

1.1 Synthesis of catalysts

All the catalysts were synthesized by the template-assisted atomic layer deposition (ALD) method. The carbon nanofibers (CNFs) were used as the template. The ALD process was performed at a hot-wall closed chamber-type ALD reactor. Before ALD, the CNFs were dispersed on a quarter wafer (8 cm × 8 cm) with the help of ethanol. After the samples were dried at ambient temperature, they were transferred to the ALD chamber. Ultrahigh purity N₂ (99.999%) was used as a carrier gas and the purge gas. TiO₂ deposition was conducted at 250°C with titanium isopropoxide (TTIP) and deionized water as precursors. TTIP was maintained at 80°C to provide enough vapor pressure, while H₂O was kept at room temperature. The ALD of Pt was performed by sequential exposure of samples to trimethyl(methylcyclopentadienyl) platinum (MeCpPtMe₃) and O₃ produced by an ozone generator at 250°C. MeCpPtMe₃ was maintained at 75°C.

Synthesis of CNFs template.

The carbon nanofibers (CNFs) templates were synthesized by chemical vapor deposition using copper nanoparticles as catalysts and acetylene as a feed gas at 280°C. The synthesized samples were carbonized at 900°C in Ar for 2 h. Then the carbonized samples were treated with an HNO₃ aqueous solution (25 wt%) at 100°C for 4 h, followed by filtering, washing, and drying at 120°C in sequence to obtain the CNFs templates.

Synthesis of 1.91%Pt@TiO₂.

The multilayered catalyst 1.91%Pt@TiO₂ was synthesized by multiple sequential depositions of TiO₂ (30 cycles, A) and Pt (1 cycle, B) on the carbon nanofibers (CNFs), followed by calcination at 450°C in the air. Typically, 1.91%Pt@TiO₂/CNFs were prepared after repeated 10 times of A+B procedure, followed by 30 cycles of TiO₂ to cover the Pt layer. Then the 1.91%Pt@TiO₂/CNFs were calcinated in the air to remove the CNFs templates at 450°C for 90 min to obtain the 1.91%Pt@TiO₂. The pulse, exposure, and purge time for TTIP were 1, 8, 20 s, and 0.1, 8, 25 s for H₂O. The pulse, exposure, and purge time for MeCpPtMe₃ were 0.5, 30, 60 s.

Synthesis of 0.57%Pt@TiO₂.

0.57%Pt@TiO₂ was synthesized by multiple sequential depositions of TiO₂ (100 cycles, A) and Pt (1 cycle, B) on the carbon nanofibers (CNFs), followed by calcination at 450°C in the air. Typically, 0.57%Pt@TiO₂/CNFs were prepared after repeated 5 times of A+B procedure followed by 100 cycles of TiO₂ to cover the Pt layer. Then the 0.57%Pt@TiO₂/CNFs were calcinated in the air to remove the CNFs templates at 450°C

for 90 min to obtain the 0.57%Pt@TiO₂. The pulse, exposure, and purge time for TTIP were 1, 8, 20 s, and 0.1, 8, 25 s for H₂O. The pulse, exposure, and purge time for MeCpPtMe₃ were 0.5, 30, 60 s.

Synthesis of 1.63%Pt/TiO₂.

1.63%Pt/TiO₂ was synthesized by deposition of 300 cycles TiO₂ on the CNFs to obtain TiO₂/CNFs. The TiO₂/CNFs powders were then calcinated in the air to remove the CNFs templates at 450°C for 90 min to obtain the TiO₂ nanotubes. Finally, 1 cycle of Pt was deposited on the TiO₂ nanotubes to get 1.63%Pt/TiO₂. The pulse, exposure, and purge time for TTIP were 1, 8, 20 s and 0.1, 8, 25 s for H₂O. The pulse, exposure, and purge time for MeCpPtMe₃ were 3, 60, 120 s and 3, 60, 120 s for O₃, respectively.

Synthesis of 4.12%Pt/TiO₂.

4.12%Pt/TiO₂ was synthesized by deposition of 300 cycles of TiO₂ on the CNFs to obtain TiO₂/CNFs. The TiO₂/CNFs powders were then calcinated in the air to remove the CNFs templates at 450°C for 90 min to obtain the TiO₂ nanotubes. Finally, 3 cycles of Pt were deposited on the TiO₂ nanotubes to prepare 4.12%Pt/TiO₂. The pulse, exposure, and purge time for TTIP were 1, 8, 20 s and 0.1, 8, 25 s for H₂O. The pulse, exposure, and purge time for MeCpPtMe₃ were 3, 60, 120 s and 3, 60, 120 s for O₃, respectively.

1.2 Characterization

The porosity characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at the boiling point of N₂ (-196°C) with Micromeritics ASAP 2500 instruments. Each sample was degassed under vacuum at 90°C for 1 h and 350°C for 8 h prior to the measurement. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) method. And the pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method according to the desorption branches.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250XI multi-technique electron spectrometer (Al K α , 1486.6 eV). The binding energy (BE) is calibrated using the C 1s peak at 284.8 eV. The XPS curves were fitted with the XPSPEAK 4.1 software program.

The catalysts after reaction were dispersed in ethanol solution by ultrasonic agitation, and then the suspension was dropped onto a Lacey Support Film. After the Lacey Support Film was dried at ambient temperature, the samples for TEM measurements were prepared. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL-2100F field emission transmission microscope operated at 200 kV. In addition, aberration-corrected high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were carried out on a Titan Cubed Themis G2 300 (FEI) electron microscope operated at 200 kV. The number of particles for the determination of the size distribution in Figure 1 is 58, 64, and 92 for 1.91%@TiO₂, 1.63%Pt/TiO₂, 4.12%Pt/TiO₂, respectively.

The XAFS results were obtained on the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics, Chinese Academy of Sciences. A Si (111) double-crystal monochromator was used to reduce the harmonic component of the monochrome beam. Pt foil and PtO_2 were used as reference samples. The Pt L₃-edge XANES and EXAFS spectra of the catalysts were measured in fluorescence mode. The X-

ray absorption near edge structure (XANES) and Fourier transform extended X-ray absorption fine structure (FT-EXAFS) data from the XAS analysis were fitted with the ATHENA and ARTEMIS software programs. During curve fittings, the amplitude reduction factor S_0^2 was fixed at the value of 0.78 determined by fitting the data of Pt foil. Fixed coordination number (CNs) of Pt foil is known from the Crystallography Open Database. The metal loading of the catalysts was detected by inductively coupled plasma optical

emission spectrometry (ICP-OES) analysis (Agilent 725, USA). All samples were dissolved in hot aqua regia.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) CO chemisorption measurements were performed on a Bruker spectrometer equipped with an MCT detector and an in-situ reaction cell (Praying Mantis Harrick). The sample was first pretreated in Ar at 200°C for 60 min to remove any contaminant. After cooling the sample to room temperature under Ar, a background spectrum was collected after cooling the sample to room temperature. Then the sample was exposed to 10% CO in Ar at a flow rate of 20 mL/min for about 30 min until saturation. Next, Ar (99.999%) was introduced at a flow rate of 20 mL/min for another 30 min to remove the gas-phase CO, and then the DRIFT spectrum was collected with 256 scans at a resolution of 4 cm⁻¹. Fourier transform infrared (FT-IR) spectroscopy measurements of styrene saturation adsorbed on catalysts were performed to investigate the adsorption behavior of styrene on these catalyst surfaces. The sample was first pretreated in Ar at 200°C for 60 min to remove any contaminant. After cooling the sample to room temperature under Ar, a background spectrum was collected after cooling the sample to room temperature. Then the styrene (heated at 60°C) vapor was pulsed into the reaction cell until saturation. Next, Ar (99.999%) was introduced at a flow rate of 20 mL/min for another 45 min to remove the gas phase styrene, and then the FT-IR spectrum was collected with 256 scans at a resolution of 4 cm⁻¹.

1.3 Catalytic performance

The hydrogenation of phenylacetylene (PA) using ammonia borane (AB) as the hydrogen source was carried out in a 50 mL one-mouth flask. In a typical run, 0.09 mmol of phenylacetylene, 1 mmol of ammonia borane, 10 mg of catalyst, EtOH/H₂O = 10 mL/10 mL were co-added into the flask. The reaction proceeded under magnetic stirring with a rate of 700 rpm at 30°C. The liquid reaction products were analyzed by gas chromatography (Zhejiang Full Chromatogram Analysis, China) equipped with a flame ionization detector. The catalysts were collected by centrifugation, washed three times with ethanol and deionized water, and then dried at 110°C. Then, the dried catalysts were readded to the flask for the next run to test the stability of the catalyst.



Figure S1. Morphology of the catalysts. TEM image of 1.91%Pt@TiO₂ (a), 0.57%Pt@TiO₂ (b), 1.63%Pt/TiO₂ (c) and 4.12%Pt/TiO₂ (d).



Figure S2. (a) N_2 adsorption-desorption isotherms (a) and pore size distribution (BJH method) (b).



Figure S3 Catalytic performance of phenylacetylene semi-hydrogenation over different Ptbased catalysts.



Figure S4. Schematic illustration of the structure of sandwich Pt nanoparticle catalyst $30\text{TiO}_2/\text{Pt/TiO}_2$ and multilayered catalyst $1.91\text{Pt}@\text{TiO}_2$. For $30\text{TiO}_2/\text{Pt/TiO}_2$, the Pt nanoparticles (3.0 nm) are coated by the porous TiO₂ nanolayers, and the exposed Pt sites depend on the pore structure of the TiO₂ nanolayers. Therefore, high selectivity in semi-hydrogenation is obtained by only exposing the Pt species that strongly interacted with the TiO₂ layer to reactants. As a result, most of the Pt atoms of the nanoparticles are inactive due to the inaccessible reactants. In contrast, the Pt atom utilization efficiency on the multilayered catalyst 1.91%Pt@TiO₂ is improved due to the high dispersion of Pt.



Figure S5. Aberration-corrected HAADF-STEM image of 1.91%Pt@TiO₂. (a) fresh sample, (b) After five consecutive runs. Figure S5b shows the aberration-corrected HAADF-STEM images of 1.91%Pt@TiO₂ after five consecutive runs. Figure S5b has confirmed the persistence of the high dispersion of Pt clusters in the majority as in the fresh samples (Figure S5a), indicating its excellent stability.



Figure S6. Hydrolysis of ammonia borane (AB) to hydrogen on 1.91%Pt@TiO₂. (Reaction condition: 1 mmol of ammonia borane, 10 mg of catalyst, EtOH/H₂O = 10 mL/10 mL, 303 K) The rate of ammonia borane (AB) hydrolysis to hydrogen is 2.729 mmol·h⁻¹. On the other hand, the hydrogen consumption rate of the phenylacetylene hydrogenation is about 0.041 mmol·h⁻¹ using H₂ as a hydrogen source and 0.135 mmol·h⁻¹ in tandem reaction. The rate of ammonia borane hydrolysis is about 66 folds higher than that of the hydrogenation of phenylacetylene. Therefore, the rate-determining step of the tandem reaction is the hydrogenation of phenylacetylene.

Table S1 EXAFS fitting parameters at the Pt L_3 -edge for various samples

sample	path	CNs	<i>R</i> (Å)	σ² (Ų×10 ⁻³)	ΔE_0 (eV)
Pt foil	Pt–Pt	12	2.76 ± 0.03	4.2 ± 0.3	7.0 ± 0.3
1.91%Pt@TiO ₂	Pt–O	5.0 ± 0.8	1.95 ± 0.07	2.4 ± 2.5	6.0 ± 1.7
1.63%Pt /TiO ₂	Pt–O	4.5 ± 0.8	1.98 ± 0.06	3.4 ± 2.9	4.7 ± 1.9
4.12%Pt/TiO ₂	Pt–O	4.1 ± 0.6	1.96 ± 0.06	3.4 ± 2.5	5.2 ± 1.6

CNs, coordination numbers; *R*, bonding distance; σ^2 , Debye-Waller factor; ΔE_0 , inner potential shift. Data range $3 \le k \le 12 \text{ Å}^{-1}$, $1.0 \le R \le 2.0 \text{ Å}$.

Catalyst	Pt content	BET surface	BJH pore	CO chemisorption
	(wt%)	area (m²·g⁻¹)	diameter (nm)	(µmol·g⁻¹)
1.63%Pt/TiO ₂	1.63	90.5	1.7	22.4
4.12%Pt/TiO ₂	4.12	94.9	1.7	54.4
1.91%Pt@TiO ₂	1.91	80.5	1.7	19.9
0.57%Pt@TiO ₂	0.57	-	-	-

 Table S2. Physicochemical characteristics of different Pt-based catalysts

Catalyst	Temperature (K)	TOF (h ⁻¹)	Conversion (%)	Styrene selectivity (%)	Yield	Notes
					(%)	
1.91%Pt@TiO ₂	303	657.6ª	93.4	92.9	86.8	This work
1.63%Pt /TiO ₂	303	1463.7ª	92.8	80.7	74.9	This work
4.12%Pt/TiO ₂	303	1875.7ª	92.0	48.2	44.3	This work
30TIO ₂ /Pt/TiO ₂	303	232.4	98.0	95.0	93.1	Ref. ¹
Pt-Ni-Ag _{4.9} NF@CeO ₂	323	187.1	96.8	86.1	83.3	Ref. ²
Pt/PSiO ₂	318	396.0	42.0	88.0	37.0	Ref. ³
Pt-PMA/AC	r. t. ^b	492.0	42.3	80.1	33.9	Ref. ⁴
Pt-Cd-650	353	307.6	94.1	96.3	90.6	Ref.⁵
Pt ₁ Cd _{0.18} -BM	353	3065.6	83.0	85.5	71.0	Ref.⁵
Ru@Pt ₃ /o-CNTs	323	-	88.0	88.0	77.4	Ref. ⁶
Pt/o-CNTs	323	-	99.0	88.0	87.1	Ref. ⁷

Table S3 Catalytic performance of phenylacetylene hydrogenation over different Pt-based catalysts.

^aTOF was calculated based on the number of Pt surface atoms determined by CO chemisorption measurements and the phenylacetylene consumption rate (conversion below 10%). ^b Room temperature.

Table S4 XPS fitting parameters of 1.91% Pt@TiO₂, 1.63% Pt /TiO₂ and 4.12% Pt/TiO₂ after reaction.

catalyst	Pt ⁴⁺ (73.9 eV)		Pt ²⁺ (72.7 eV)		Pt ⁰ (71.5 eV)	
	Area	ratio	Area	ratio	Area	ratio
4.12%Pt/TiO ₂	837.0	15.4%	2278.9	41.8%	2336.6	42.8%
1.63%Pt/TiO ₂	572.0	19.4%	1234.9	41.9%	1140.1	38.7%
1.91%Pt@TiO ₂	268.9	25.6%	591.4	56.2%	191.9	18.2%

Table S5 Hydrogenation of phenylacetylene (PA) on 1.91% Pt@TiO₂ using H₂.

Catalyst	Time	Conversion	Selectivity	Hydrogen consumption rate
	(min)	(%)	(%)	(mmol·h ⁻¹)
1.91%Pt@TiO ₂	15	10.0	84.7	0.041

Reaction condition: 0.09 mmol of phenylacetylene, 0.5 MPa of H₂, 10 mg of catalyst, EtOH/H₂O = 10 mL/10 mL, 303 K

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