

Supporting Information

A route to support Pt sub-nanoparticles on TiO₂ and catalytic hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline at room temperature

Shaopeng Li,^{a,b} Youdi Yang,^{a,b} Yanyan Wang,^{a,b} Huizhen Liu,^{*a,b} Jing Tai,^a Jing Zhang,^c and Buxing Han^{*a,b}

a Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics Institute of Chemistry, Chinese Academy of Sciences Beijing 100190 (P.R. China) E-mail:liuhz@iccas.ac.cn, hanbx@iccas.ac.cn

b University of Chinese Academy of Sciences, Beijing 100049, P. R. China

c Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R. China

Experimental Section

Material

Formic acid (A. R. grade), Ethanediamine (A. R. grade) and H₂PtCl₆ (A. R. grade) sodium borohydride were purchased from Sinopharm Chemical Reagent Co. Ltd. H₂ (> 99.99%) was supplied by Beijing Analytical Instrument Company. TiO₂ (P25, 20% rutile and 80% anatase) was purchased from Degussa. All the chemicals were used as received without further purification. N-methyl-N-phenylformamide(ED) was prepared by reaction of ethylenediamine and formic acid. The method was similar to that reported by other authors.^[1] The structure and NMR spectrum of ED is shown in Fig. S10.

Catalyst preparation

In a typical experiment to prepare the ED reduced Pt/TiO₂(Pt/TiO₂-ED), 0.2 g TiO₂ were dispersed in 20 mL of water at room temperature with ultrasound irradiation (150 W) for 30 min. Subsequently, Subsequently, 2.15 mL H₂PtCl₆ aqueous solution (19.308 mmol/L) was added into the above solution with magnetic stirring for 30 min. Then, ED aqueous solution was mixed with TiO₂ suspension under magnetic stirring at 60 °C. After 24 h, the obtained precipitate was separated and washed with deionized water and ethanol three times. The sample was dried in vacuum oven at 70 °C for 6 h. The as-prepared Pt/TiO₂ was then annealed at 300°C under Ar atmosphere for 3 h.

To prepare NaBH₄ reduced Pt/TiO₂ (Pt/TiO₂-NaBH₄), 0.2 g TiO₂ was dispersed in 20 mL of water at room temperature with ultrasound irradiation (150 W) for 30 min. Subsequently, 2.15 mL H₂PtCl₆

aqueous solution (19.308 mmol/L) was added into the above solution with magnetic stirring for 30 min. Then, the fresh NaBH₄ aqueous solution was slowly added into the TiO₂ suspension under magnetic stirring. The obtained precipitate was separated and washed with deionized water and ethanol three times. The sample was dried in vacuum oven at 70 °C for 6 h. The as-prepared Pt/TiO₂ was then annealed at 300 °C under Ar atmosphere for 3 h.

The method to prepare photo reduced Pt/TiO₂ (Pt/TiO₂-Photo) was similar to that reported by other authors.^[2] In a typical experiment, 0.2 g TiO₂ was dispersed in 20 mL of water at room temperature with ultrasound irradiation (150 W) for 30 min. Subsequently, 2.15 mL H₂PtCl₆ aqueous solution (19.308 mmol/L) was added into the above solution with magnetic stirring for 30 min. Then an amount of methanol was added into the solution above. Then, the suspension was irradiated by UV light ($\lambda=365$ nm) for 4 h. The obtained precipitate was separated and washed with deionized water and ethanol three times. The sample was dried in vacuum oven at 70 °C for 6 h. The as-prepared Pt/TiO₂ was then annealed at 300 °C under Ar atmosphere for 3 h.

Characterization

Transmission electron microscopy (TEM) images were obtained on using a JEOL-2100F electron microscope equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 100 kV. The powder X-ray diffraction spectra (Power XRD) measurements were performed on a Philips X' pert MPD instrument using Cu K α radiation (50 kV). The contents of different elements in the Pd/C catalysts were analyzed by ICP-AES (PROFILE. SPEC, Leeman). X-ray photoelectron spectrometry (XPS) study was carried out on an ESCALAB250xi X-ray photoelectron spectrometer using an Al K α source. The EXAFS characterization was performed at the Institute of High Energy Physics of the Chinese Academy of Sciences. The H₂-pulse chemisorption study was performed by using an AutoChem2950 HP Chemisorption Analyzer (Micromeritics).

Reaction

The reaction was carried out in a Teflon-lined stainless steel reactor of 16 mL, which was similar to that used previously.^[3-5] In a typical experiment, 0.1 mmol substrate, 2 mL toluene and the desired amount of catalyst were added into the reactor. The air in the reactor was purged with H₂ for 3 times. Then, the reactor was placed in an air bath of desired temperature, and H₂ was charged to desired pressure. After a certain reaction time, the autoclave was placed in an ice-water mixture and the reaction solution was centrifuged. The reaction mixture was analyzed quantitatively by gas chromatograph (Agilent 6820) equipped with a flame ionization detector (FID).

Identification of the products and reactant was done using a GC-MS (Agilent 7890B 5977A, HP-5MS capillary column (0.25 mm in diameter, 30 m in length)) as well as by comparing the retention time with n-decane which is used as the internal standard in GC traces. The conversion of quinoline and the selectivity of the products were calculated from the GC data. In the catalyst reuse experiment, the solid catalyst was separated by centrifugation and washed with ether for three times, and was used directly for the next run after dried at 60 °C for 6 h under vacuum.

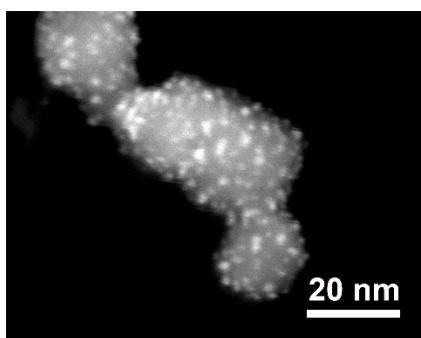


Fig. S1 The HAADF-STEM images of Pt/TiO₂-ED.

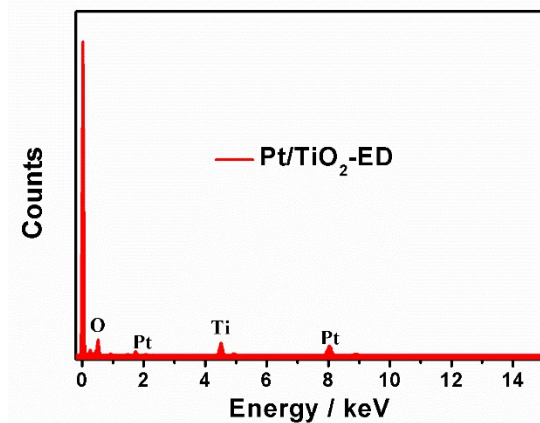


Fig. S2 EDX pattern of Pt/TiO₂-ED.

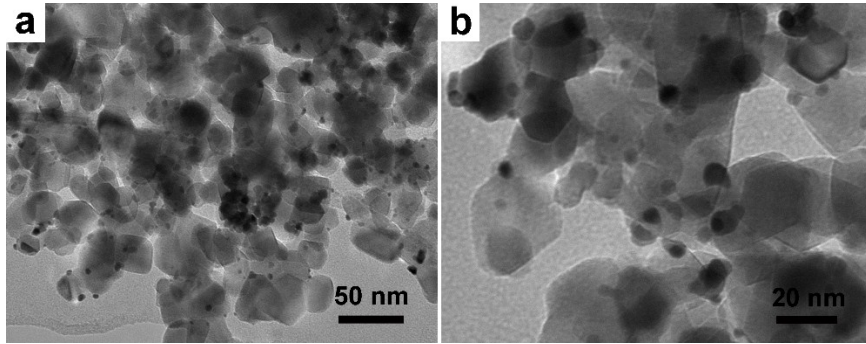


Fig. S3 High-TEM images of the Pt/TiO₂-NaBH₄.

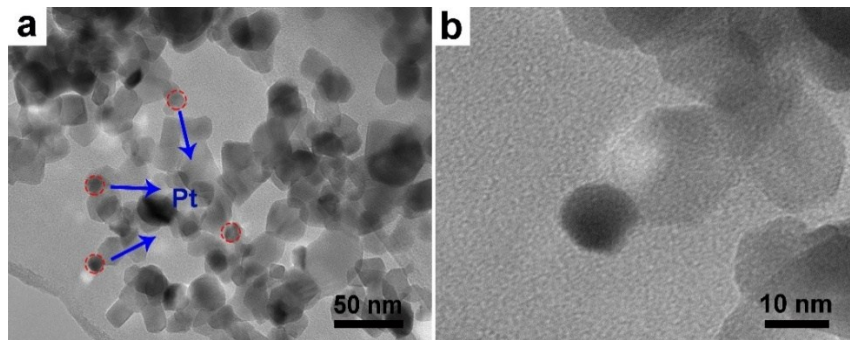


Fig. S4 High-TEM images of the Pt/TiO₂-Photo.

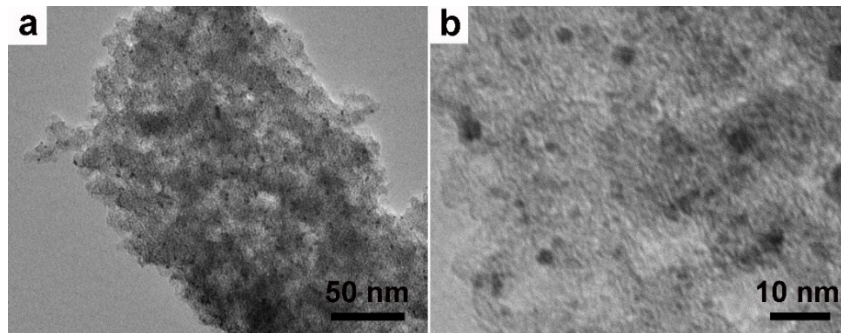


Fig. S5 The TEM images of the commercial Pt/C.

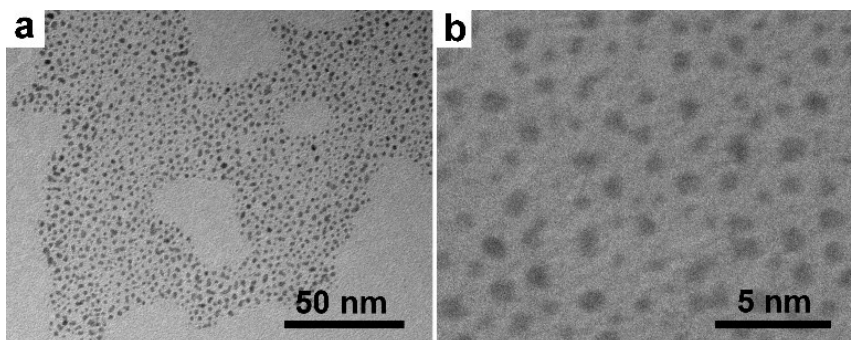


Fig. S6 The TEM images of the Pt-ED nanoparticles.

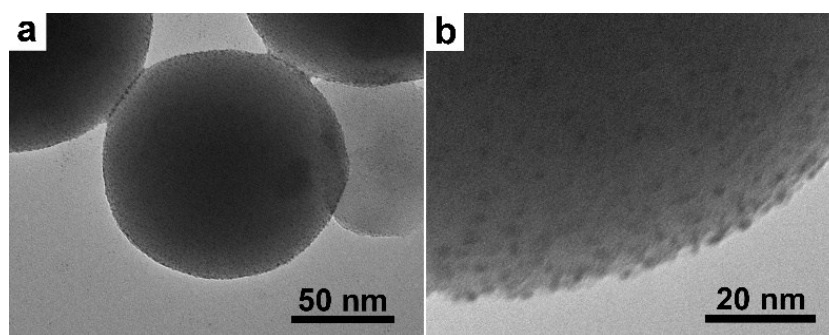


Fig. S7 The TEM images of the Pt/SiO₂-ED.

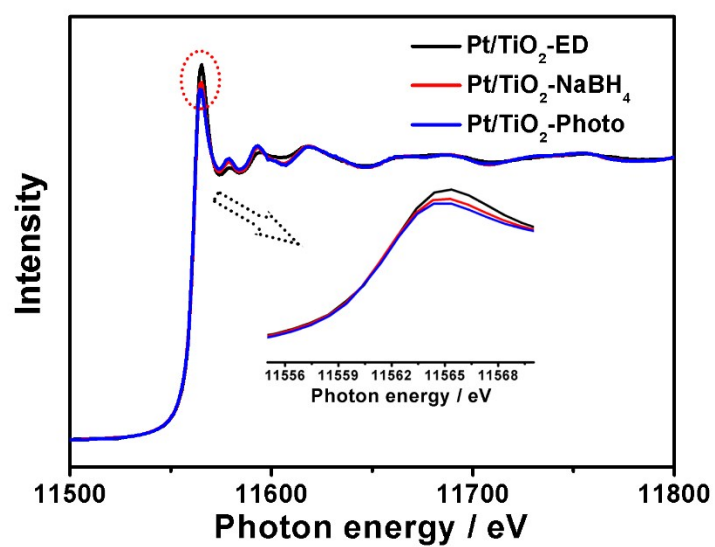


Fig. S8. Pt L-edge XANES.

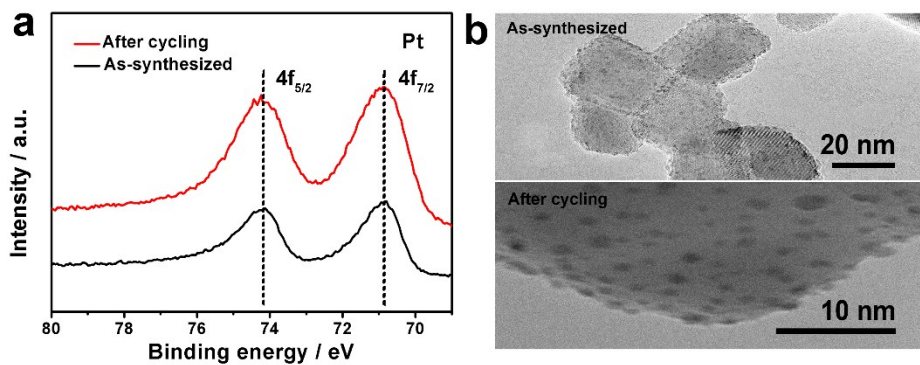


Fig. S9 The XPS and TEM images of the Pt/TiO₂-ED catalyst before and after cycling.

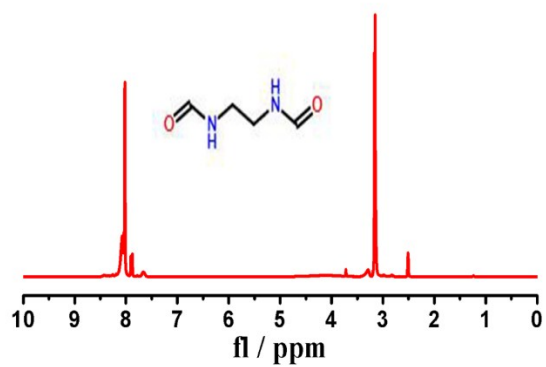


Fig. S10 The structure and ¹H NMR spectrum of N,N'-(ethane-1,2-diyl)diformamide(ED).

Table S1. The inductively coupled plasma mass spectrometry of Pt/TiO₂-x(x=ED, NaBH₄, and Photo)

Entry	Sample	Pt content
1	Pt-ED	3.98%
2	Pt-NaBH ₄	4.02%
3	Pt-Photo	3.87%

Table S2. The effect of solvent and temperature for quinoline hydrogenation*

Entry	Temperature / °C	Solvent	Yield _{THQ} (%)
1	30	n-Hexane	70
2	30	Toluene	99
3	30	Tetrahydrofuran	52
4	30	Methanol	82
5	30	Water	21
6**	30	Toluene	19
7**	50	Toluene	48
8**	70	Toluene	85

* Reaction conditions: quinoline (0.1 mmol), catalyst (20 mg), T (30 °C), H₂ pressure (1 MPa), t (6 h), stirring speed (600 rpm).

** Result of the reaction time 1 hour.

Calculation of turnover frequency (TOF)

$$TOF_{initial} = \frac{n(\text{THQ})}{n(\text{Pt}) * t}$$

Where TOF_{initial} is initial turnover frequency, n(THQ) is mole number of 1,2,3,4-tetrahydroquinoline (THQ) produced after 0.5 h of reaction, n(Pt) is the surface active number of Pt atom, and t is the reaction time of 0.5 h.

References

- 1 Y. Luan, T. Zhang, W. Yao, K. Lu, L. Kong, Y. Lin, M. Ye, *J. Am. Chem. Soc.*, 2017, **139**, 1786.
- 2 M. Shi, D. Bao, B. Wulan, Y. Li, Y. Zhang, J. Yan, Q. Jiang, *Adv. Mater.*, 2017, **29**, 1606550.
- 3 H. Liu, Q. Mei, S. Li, Y. Yang, Y. Wang, H. Liu, L. Zheng, P. An, J. Zhang, B. Han, *Chem. Commun.*, 2018, **54**, 908.
- 4 X. Kang, J. Zhang, W. Shang, T. Wu, P. Zhang, B. Han, Z. Wu, G. Mo, X. Xing, *J. Am. Chem. Soc.*, 2014, **136**, 3768.
- 5 Z. He, H. Liu, Q. Qian, L. Lu, W. Guo, L. Zhang, B. Han, *Sci. China Chem.*, 2017, **60**, 927.