

Supporting information

Proper aggregation needed as highly active Pt/Al₂O₃ for hydrogenation of chloronitrobenzene

*Rongtian Gu, Deming Meng, Minyi She, Yibo Wang, Hua Yang, Xiangke Guo,
Nianhua Xue, Weiping Ding**

Key Lab of Mesoscopic Chemistry of Ministry of Education, School of Chemistry
and Chemical Engineering, Nanjing University, Nanjing 210023, China

*Email: Dingwp@nju.edu.cn

Materials and Methods

Synthesis of γ -Al₂O₃

Two types of alumina are used in this article. 1) A0: a commercial γ -Al₂O₃ with mainly external {110} facet, obtained by the direct roasting dehydration of boehmite (Aluminum Corporation Shandong). 2) A1: a γ -Al₂O₃ porous nanorods with higher energy {111} facet, synthesized using a method similar to our previous report¹.

Synthesis of Pt₁/A1

The sample of Pt₁/A1, with 0.8 wt.% platinum species dispersed atomically on the surface of the A1, was prepared by the incipient wetness impregnation method. Typically, 0.1 mL of aqueous hex-chloroplatinic acid solution (80 mg Pt/mL) was diluted to 0.65 mL using deionized water, then the solution was dropped into 0.992 g of corresponding A1 (γ -Al₂O₃{111}) powder, and kept the mixture at room temperature for 12 h before drying at 80°C. The as-prepared sample was grinded and calcined at 550 °C for 3 h in air.

Synthesis of Pt_n/A1

The Pt_n/A1, with aggregated platinum particles supported on A1, was obtained by a similar treatment except that A1 was pretreated by olic acid (OA). Typically, dispersed 1g OA in 20 mL ethanol, then added 1 g A1 to the solution, stirred for 5 hours, filtered, washed with ethanol 3 times and dried at 80 °C to obtain OA-coated alumina (A1@OA). Then 0.8 wt.% Pt was impregnated on the A1@OA. Similarly, the as-prepared sample was calcined at 550 °C for 3 h in air.

The modification of A1 with OA here helps to weaken the interaction between platinum and support.

Synthesis of xPt/A1 and xPt/A0

In addition to the above-mentioned A1 support, we also selected another alumina A0

(γ -Al₂O₃{110}) with a different morphology and specific surface area as the support. A series of samples with different platinum content were also prepared by a similar impregnation method, denoted as xPt/A1(A0), where x represents the percentage of Pt mass content.

Instruments and measurements

The content of platinum species was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. The specific surface areas of catalysts were measured by N₂-sorption at 77 K using Micromeritics ASAP 3020 apparatus and calculated by the Brunauer-Emmett-Teller (BET) method.

High resolution transmission electron microscopy (HRTEM) measurements were taken with a JEOL JEM-2100 instrument operated at 200 kV. The high angle annular dark field-scanning transition electron microscopy (HAADF-STEM) images were obtained using a FEI TITAN operated at 300 kV.

The X-ray diffraction (XRD) analyses were performed on a Phillips X'Pro diffractometer with Cu K α radiation operated at 40 kV and 40 mA.

The X-ray photoelectron spectroscopy (XPS) were conducted on a Thermo Scientific Escalab 250Xi system equipped with a monochromatic Al K α (h ν = 1486.6 eV) X-ray exciting source. The test spectra were corrected with binding energy of C 1s (284.6 eV).

The *in-situ* Fourier transform infrared (FTIR) of CO absorption was measured by a Bruker Tensor 27 infrared spectrophotometer. The catalysts were pretreated in pure Ar at 200 °C for 1 h to remove the water and other surface adsorbed species, and the IR background was collected after cooling to room temperature. Then 5 vol.% CO/Ar was introduced into the cell for 30 minutes to saturate the CO adsorption at room temperature (~ 20 °C). Subsequently, the atmosphere was switched to pure Ar to clear the physically adsorbed CO, and the IR spectra were recorded every 15 s

simultaneously until there was no signal for gas phase CO.

Hydrogen temperature-programmed reduction (H₂-TPR) and CO temperature-programmed desorption (CO-TPD) experiments were performed using Xianquan 5000 apparatus.

- 1) H₂-TPR: 100 mg catalyst were pretreated in helium (99.999%) at 200 °C for 1 h, then placed in a dry ice-ethanol bath (-72 °C), switched to 5 vol.% H₂/N₂ mixture and recorded baseline. The system was removed from the dry ice-ethanol bath and allowed to warm to room temperature (25 °C), followed by heating to 700 °C at rate of 10 °C/min, and the hydrogen consumption was recorded with a thermal conductivity detector.
- 2) CO-TPD: 100 mg catalyst were pretreated in helium (99.999%) at 200 °C for 1 h, then adsorbed CO for 1 h under a 5 vol.% CO/Ar mixture at -72 °C (dry ice-ethanol bath), followed by helium purging and baseline recording. Then the system was removed from the dry ice bath and allowed to warm to room temperature (25 °C), and the CO desorption was recorded with a thermal conductivity detector.

H/D exchanges was taken by a Dycor Dymaxion Mass Spectrometer (AMETEK Process Instruments). The as-prepared sample (100 mg) was pretreated under pure Ar (20 mL/min) at 200 °C for 1 h, and then cooled under the same atmosphere to -72°C (dry ice-ethanol bath). Introduce 10 vol.% H₂/Ar into the system at this low-temperature for 1 h to enrich the surface of the sample with hydrogen. Subsequently, the atmosphere was switched to pure Ar to scavenge physically adsorbed H₂, and the system was removed from the dry ice-ethanol bath under 10 vol.% D₂/Ar and the HD signal was recorded while warming to room temperature.

Catalytic test

The catalytic performances of all the samples for the selective hydrogenation of *o*-

Chloronitrobenzene (CNB) were evaluated under mild conditions in a 50 ml high-pressure autoclave with a magnetic stirrer (600 rpm). Typically, the reactant (CNB, 0.5 mL), catalyst (0.05 g), and solvent (ethanol, 10 mL) were mixed in the reactor, and then pure H₂ was introduced and kept at 8 bars, and the reaction system was heated to a given temperature (measured with a thermometer in the autoclave). After the reaction, solid catalyst was separated from the liquid products, and the reactant and products were analyzed by gas chromatography (GC9560) equipped with a flame ionized detector and an SE-54 column.

TOFs is defined as the number of converted molecular of reactant per hour per mole of Pt.

Table S1 List of Pt/Al₂O₃ catalyzes hydrogenations in the literature.

Entry	Temp. (°C)	Conv. (%)	Sel. (%)	Ref.
1	80	15.1	>99	2
2	45	82.6	77.7	3
3	40	87.3	27.8	4
4	40	95.0	60.2	
5	40	91.6	40.8	5
6	40	90.5	6.1	
7	160	100	0	
8	160	85	82	6
9	30	>99	>95	this work
10	60	>98	>99	this work

Table S2 Platinum content and Brunauer–Emmett–Teller (BET) surface areas of typical catalysts

Catalyst	Pt content (wt.%)	A _{BET} (m ² /g)
A1	-	154.5
Pt ₁ /A1	0.78	150.1
Pt _n /A1	0.75	151.2
A0	-	249.8

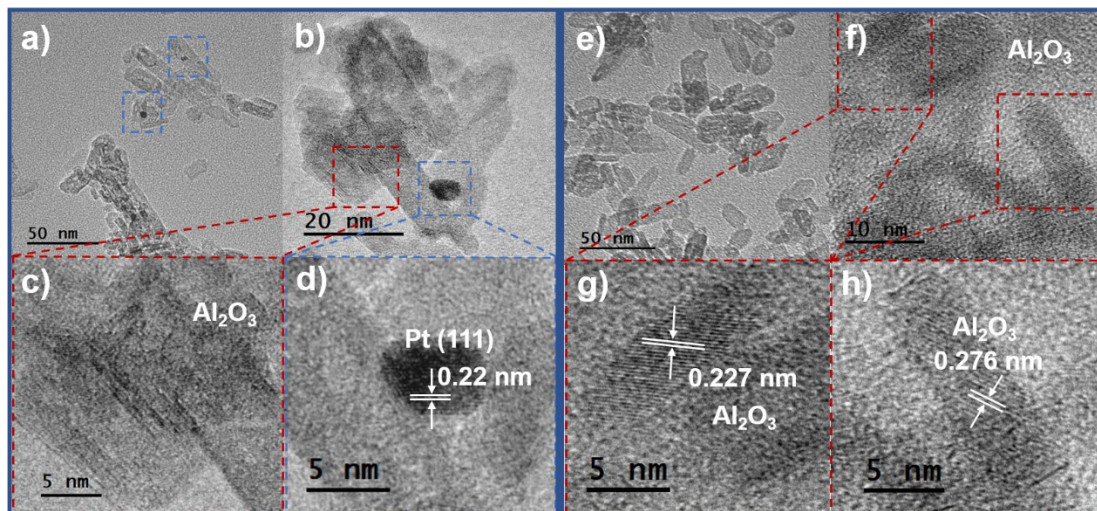


Fig. S1 Morphologies of samples. HRTEM images of a-d) $Pt_n/A1$ and e-h) $Pt_1/A1$.

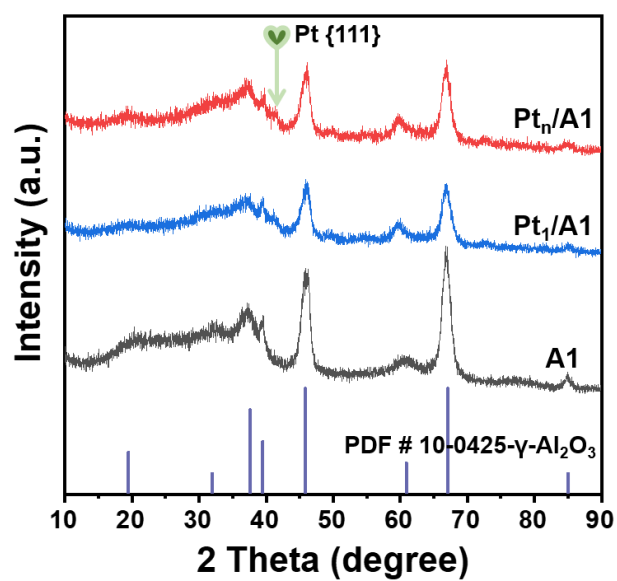


Fig. S2 XRD patterns of typical samples (Pt: PDF # 04-0802)

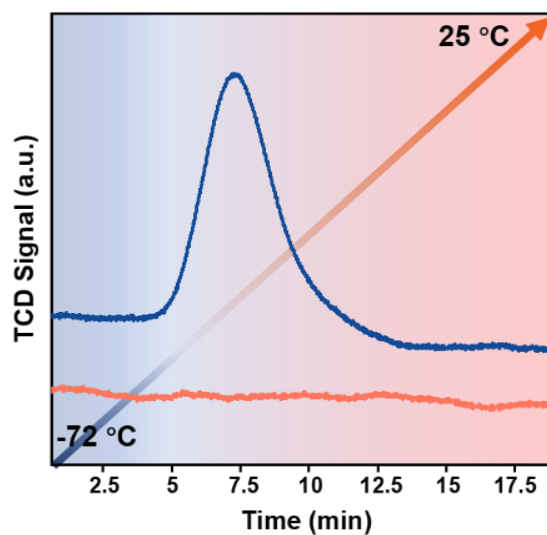


Fig. S3 CO-TPD curves of samples, where the gradation of the image background from blue (left) to red (right) represents the rise in temperature.

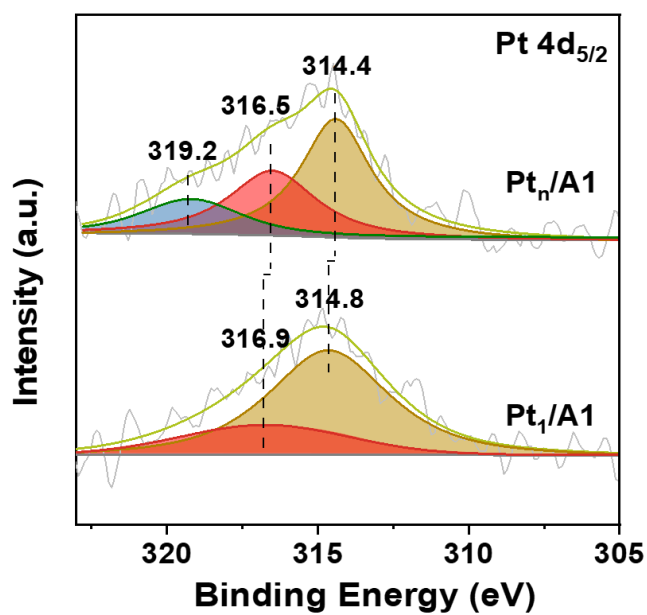


Fig. S4 Pt 4d XPS spectra of the samples.

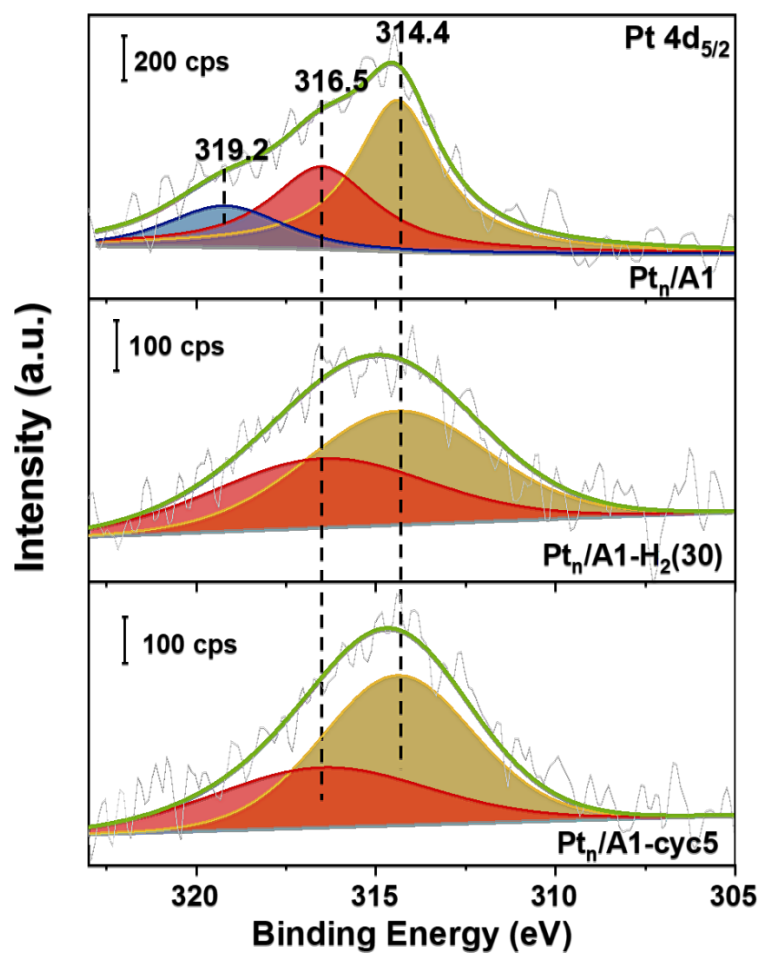


Fig. S5 Pt 4d XPS spectra of the samples, where Pt_n/A1-H₂(30) indicates the sample of Pt_n/A1 under 5 vol.% H₂/N₂ treatment at 30 °C for 1h, and Pt_n/A1-cyc5 indicates the sample of Pt_n/A1 after the fifth cycle of *o*-chloronitrobenzene hydrogenation tests.

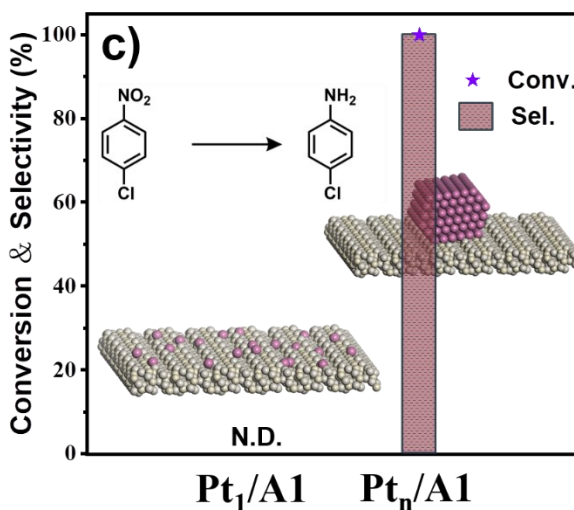
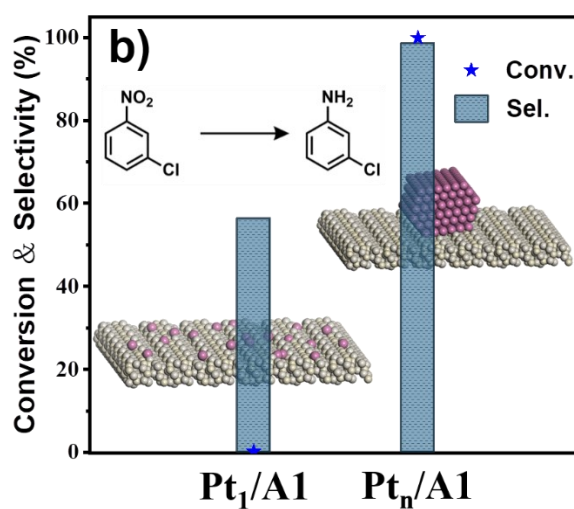
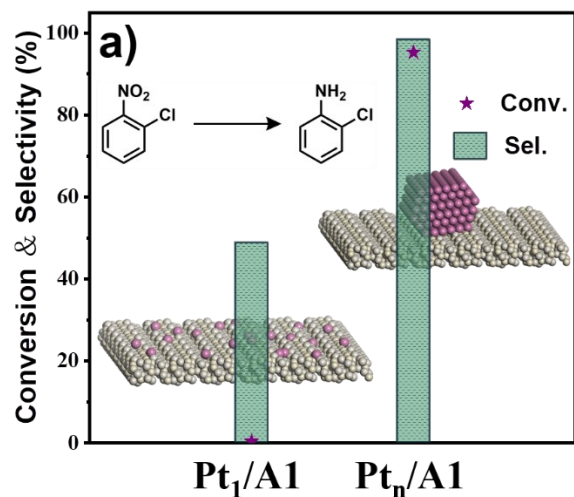


Fig. S6 Hydrogenation performance of a) *ortho*-, b) *meta*-, c) *para*-chloronitrobenzene on Pt₁/A1 and Pt_n/A1. Reaction conditions: 0.05 g catalyst, 0.5 g substrate, 10 mL ethanol, 8 bar H₂, 1 h, 30 °C.

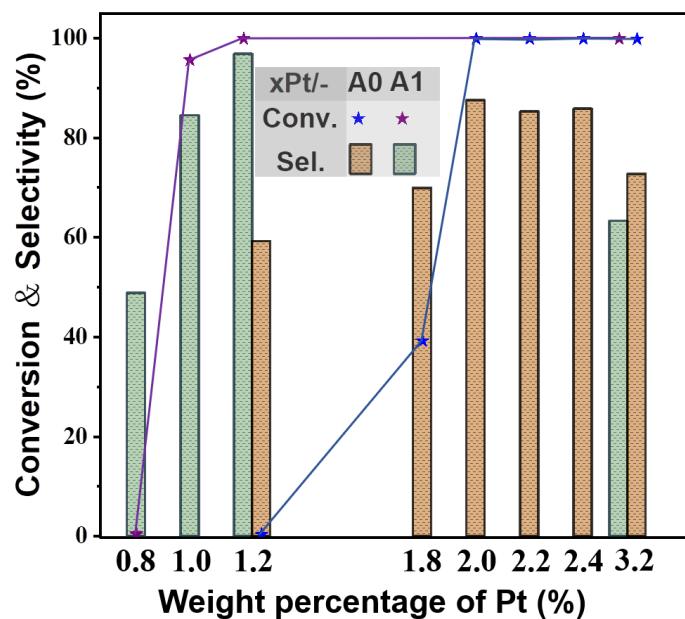


Fig. S7 Hydrogenation performance of *o*-CNB over xPt/A0 and xPt/A1 catalysts, where “x” represents the percentage of Pt mass content. Except for *o*-CAN, the other products are nitrobenzene and aniline. Reaction conditions: 0.05 g Cat., 0.5 g *o*-CNB, 10 mL ethanol, 8 bar H₂, 1 h, 60 °C.

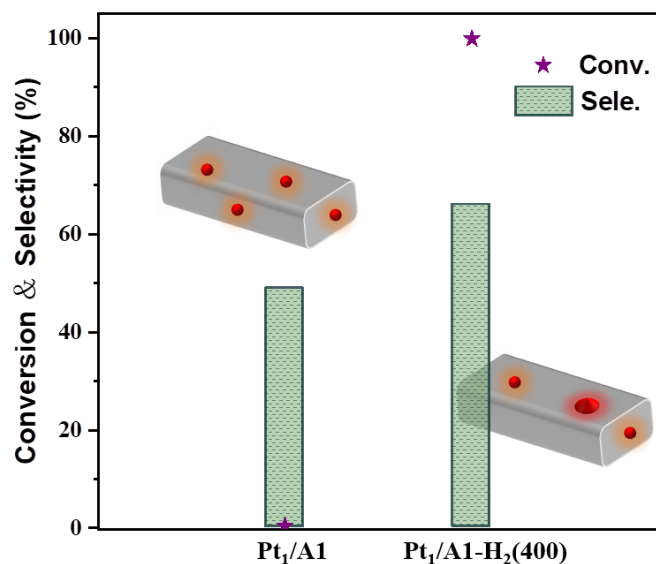


Fig. S8 Hydrogenation performance of *o*-CNB to *o*-CAN, where Pt₁/A1-H₂(400) indicates the sample of Pt₁/A1 under 5 vol.% H₂/N₂ treatment at 400 °C for 1h.

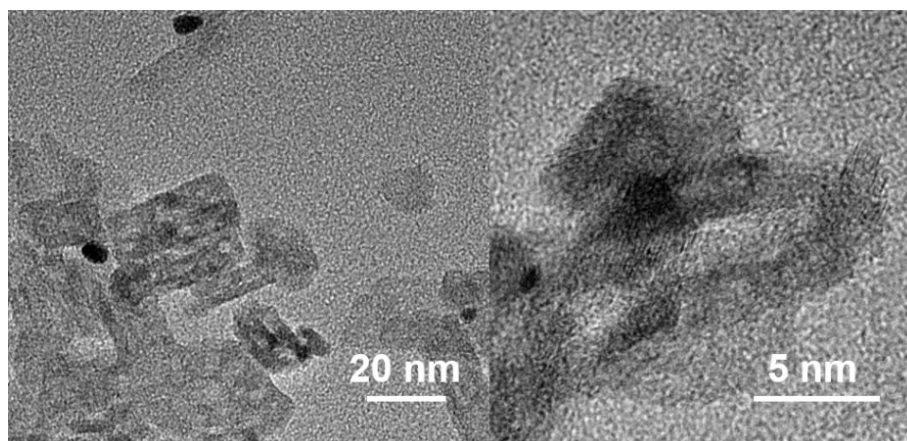


Fig. S9 HRTEM images of sample 3.2Pt/A1, in which irregularly shaped and unevenly sized particles were formed.

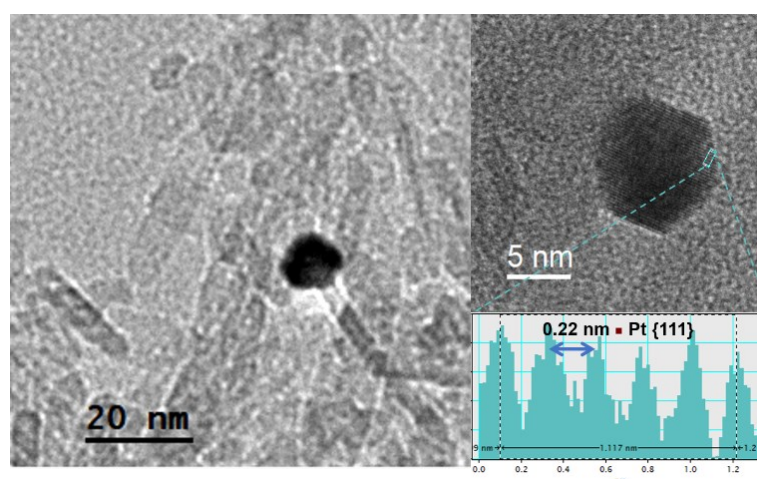


Fig. S10 HRTEM images of Pt₁/A1-H₂(400), of which the big size Pt particles formed.

References

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