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Selective Hydrogenation of Unsaturated Aldehydes over Pt Nanoparticles Promoted by Cooperation of Steric and Electronic Effects

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Contents

1. Experimental

1.1 Chemicals

Aluminium isopropoxide, aspartic acid, cinnamyl alcohol, furfural, 3-phenylpropionaldehyde, 3-phenyl-1-propanol, n-decane, succinic acid, ethylenediamine, cinnamaldehyde, α-methyl cinnamaldehyde, 4-fluorocinnamaldehyde, 2-hexenal, 3-methyl-2-butenal, 2-furanacrolein, citral and n-Al_2O_3 were purchased from J&K Scientific Ltd. Pluronic®P123, 3-(p-tolyl)acrylaldehyde and 4-chlorocinnamaldehyde were provided by Energy Chemical. Ethanol, nitric acid, $NaBH_4$, SiO_2, activated carbon, $H_2PtCl_6{\cdot}6H_2O$, $RuCl_3$, $PdCl_2$, $NiCl_2{\cdot}6H_2O$ and $HAuCl_4{\cdot}4H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd. The H_2 (99.99%) and N_2 (99.99%) were provided by Beijing Analytical Instrument Company.

1.2 Preparation of mesoporous Al_2O_3

The mesoporous Al_2O_3 was prepared using the procedures reported [M. S. Aw, G. Dražić, P. Djinović, A. Pintara, *Catal. Sci. Technol.* **2016**, 6, 3797-3805.]. 1 g of Pluronic®P123 (Mw = 5800) was added into 20 mL ethanol. Separately, 2 g of aluminium isopropoxide was added into 16.7 mL ethanol and 1.67 mL of 67% nitric acid and stirred vigorously for 1 h. The two solutions were mixed and stirred vigorously for 5 h. The solution was poured into a crucible and dried at 60 °C for 48 h. The dried sample was calcined in a muffle furnace in static air. The temperature was raised (2 °C min^{-1}) from ambient to 600 °C, followed by further heating (2 °C min^{-1}) to 800 °C. Isothermal steps were maintained for 2 h each.

1.3 Preparation of the catalysts

Pt/n-Al_2O_3: 2 mL H_2PtCl_6 solution (0.0193 mmol/mL) was added into 1 mL ethanol. Subsequently, 200 mg Al_2O_3 and 1 mL ethanol was added into the above solution. The mixture was kept 12 h under vigorous stirring. Fresh aqueous $NaBH_4$ solution (5.0 mL, 0.1081 mmol/mL) was added into the mixture under vigorous stirring. All preparation process was carried out in an ice bath. After stirring for 12 h, Pt-**1a**/n-Al_2O_3 was collected by centrifugation at 5000 rpm for 5 min and washed with ethanol (2 × 10 mL) and water (2 × 10 mL). Then the catalyst was dried in a vacuum oven at 40°C overnight. The Pt/mesoporous-Al_2O_3 was prepared by the same method.

Pt-1a/n-Al_2O_3: 40 mg aspartic acid was dispersed in 1 mL ethanol, and then 2 mL H_2PtCl_6 solution (0.0193mmol/mL) was added into the above solution. The mixture was kept 12 h under vigorous stirring. Subsequently, 200 mg Al_2O_3 and 1 mL ethanol was added into the above solution. The mixture was kept 12 h under vigorous stirring.

A fresh aqueous $NaBH_4$ solution (5.0 mL, 0.1081 mmol/mL) was added into the mixture under vigorous stirring. All preparation process was carried out in an ice bath. After stirring for 12 h, Pt-**1a**/n-Al_2O_3 was collected by centrifugation at 5000 rpm for 5 min and washed with ethanol (2 × 10 mL) and water (2 × 10 mL). Then the catalyst was dried in a vacuum oven at 40°C overnight. The Pt-**1a**/mesoporous-Al_2O_3 was prepared by the same method.

The catalysts with other modifiers, Pt-**1b**/n-Al_2O_3 and Pt-**1c**/n-Al_2O_3 were prepared by the similar method. The procedures for preparing the Ru-**1a**/n-Al_2O_3, Pd-**1a**/n-Al_2O_3, Ni-**1a**/n-Al_2O_3, Au-**1a**/n-Al_2O_3 were the same except that the H_2PtCl_6 solution was changed to $RuCl_3$, $PdCl_2$ $NiCl_2 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$, respectively. The procedures for preparing the Pt/SiO_2, Pt-**1a**/n-SiO_2, Pt/C and Pt-**1a**/C were the same except that the Al_2O_3 was changed to SiO_2 and activated carbon respectively.

1.4 Hydrogenation of α,β-unsaturated aldehydes

All reactions were carried out in a 10 mL stainless steel reaction with a stirrer. In a typical reaction, 30 mg of catalyst and 1 mmol substrates were added in the reactor. Then reactor was flushed three times with H_2, pressurized with H_2 (10 bar), and heated to 30 °C with stirring (500 rpm). After suitable reaction time, the reaction mixture was analysed by GC–MS and GC with n-decane as an internal standard or purified by flash column chromatography on silica gel to afford the desired product was characterized by ^1H NMR and ^{13}C NMR.

1.5 Characterization

Identification of the products was conducted GC/MS analysis on Agilent 7890B GC+ 5977 MSD. The quantitative analysis of the samples was carried out using an Agilent 6820 gas chromatography equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm), Agilent Technologies Singapore (Sales) Pte Ltd., Singapore. The XRD experiment was performed on Rigaku D/max 2500 with nickel filtered Cu-Kα (λ = 0.154 nm) operated at 40 kV and 20 mA. The XPS spectra were obtained using an ESCALab 220I-XL electron spectrometer (VG Scientific) using 300 W Al Kα radiation with a hemispherical energy analyser. The binding energies were calibrated with the C1s level of adventitious carbon at 284.8 eV as the internal standard reference. The TEM and EDS images of the catalysts were obtained using a JEOL-2100F electron microscope operated at 120 kV. The adsorption isotherms of Pt/n-Al_2O_3 and Pt-**1a**/n-Al_2O_3 were determined at 298 K in the pressure range of 0–1 atm on a TriStar II 3020 device (Micromeritics Instrument Corporation, USA). The contents of Pt in the catalysts were analysed by ICP-AES (VISTA-MPX), rf power 1.15 kw, coolant gas flow rate 15 L/min, nebulizer gas flow rate 0.75 L/min, sampling depth 12 mm, auxiliary gas flow rate 1.5 L/min. N_2 adsorption/desorption isotherms were determined using a

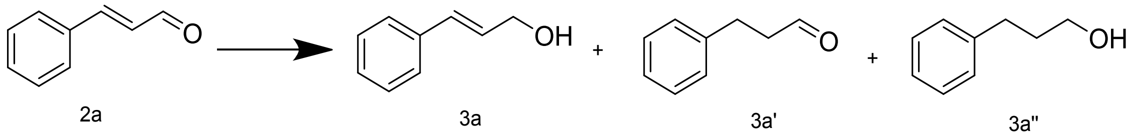
Quadra sorb SI-MP system to evaluated the Brunauer-Emmett-Teller (BET) specific surface area and pore size. The reduction behaviours were studied by H_2-TPR performed in a conventional atmospheric quartz flow reactor (3 mm i.d.) (TriStar II 3020 device). Before the test, the catalyst was heated at 100°C for 30 min under Ar at a flow rate of 50 ml min^{-1}. Then the temperature was reduced to 50°C and a 10% H_2–Ar mixture was flowed through the catalyst at a rate of 30 ml min^{-1}. The temperature was linearly raised from 50 to 400°C at a heating rate of 10°C min^{-1}. The effluent gas was analysed using a thermal conductivity detector (TCD). XAFS experiments were operated at the 1W1B, 1W2B beamline at Beijing Synchrotron Radiation Facility (BSRF). All collected spectra were analysed using Athena and Artemis program within the Ifeffit package. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at ambient temperature in DMSO.

2. Results and Discussion

2.1 Solvents screening

Solvents often affect a reaction significantly. The activity of the catalyst in tetrahydrofuran, toluene, acetonitrile or dioxane was very low. (Table S1, entries 3-6). 99% conversion of cinnamaldehyde could be reached in methanol or ethanol (Table S1, entries 1 and 2). The selectivity to cinnamyl alcohol in methanol was higher. So methanol was the optimum organic solvent.

Table S1. Solvents screening for the hydrogenation reaction of cinnamaldehyde[a]

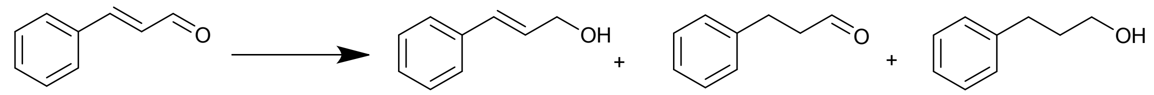


Entry	Solvent	Conversion(%)[b]	Selectivity (%)[c]
1	methanol	99	91
2	ethanol	99	86
3	tetrahydrofuran	29	87
4	toluene	5	90
5	acetonitrile	25	92
6	dioxane	10	89

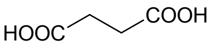
[a] Reaction conditions: cinnamaldehyde 1 mmol, P_{H2} = 10 atm, catalyst 30 mg, solvent 0.5 mL, water 0.1 mL, 30 °C, 3 h. [b] Conversion of **3a** was determined by GC. [c] The selectivity for **3a** was determined by GC using n-decane as the internal standard.

2.2 Catalysts screening

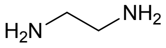
Table S2 The performances of different catalysts for the hydrogenation of cinnamaldehyde[a]



2a **3a** **3a'** **3a"**



1b



1c

Entry	Catalyst	Conversion(%)[b]	Selectivity (%)[c]		
			3a	**3a'**	**3a''**
1	None	0	/	/	/
2	Pt/n-Al_2O_3[d]	30	50	40	10
3	Pt/n-Al_2O_3	68	44	41	15
4	Pt/mesoporous-Al_2O_3[e]	93	0	46	54
5	Pt/mesoporous-Al_2O_3	99	0	29	71
6	Pt/mesoporous-Al_2O_3[f]	99	0	0	99
7	Pd-**1a**/n-Al_2O_3	20	0	40	60
8	Ru-**1a**/n-Al_2O_3	0	/	/	/
9	Au-**1a**/n-Al_2O_3	0	/	/	/
10	Ni-**1a**/n-Al_2O_3	0	/	/	/
11	Pt-**1b**/n-Al_2O_3	56	41	43	16
12	Pt-**1c**/n-Al_2O_3	49	65	27	8
13	Pt/SiO_2	39	75	13	12
14	Pt-**1a**/SiO_2	72	90	4	6
15	Pt/C	99	57	23	20
16	Pt-**1a**/C	81	72	18	10

[a] Reaction conditions: cinnamaldehyde 1 mmol, P_{H2} = 10 atm, catalyst 30 mg, methanol 0.5 mL, water 0.1 mL, 30 °C, 3 h. [b] Conversion of **3a** was determined by GC. [c] Selectivity was determined by GC using n-decane as the internal standard. [d] 1h. [e] 2h. [f] 5h.

2.3 The specific surface areas and pore properties of supports

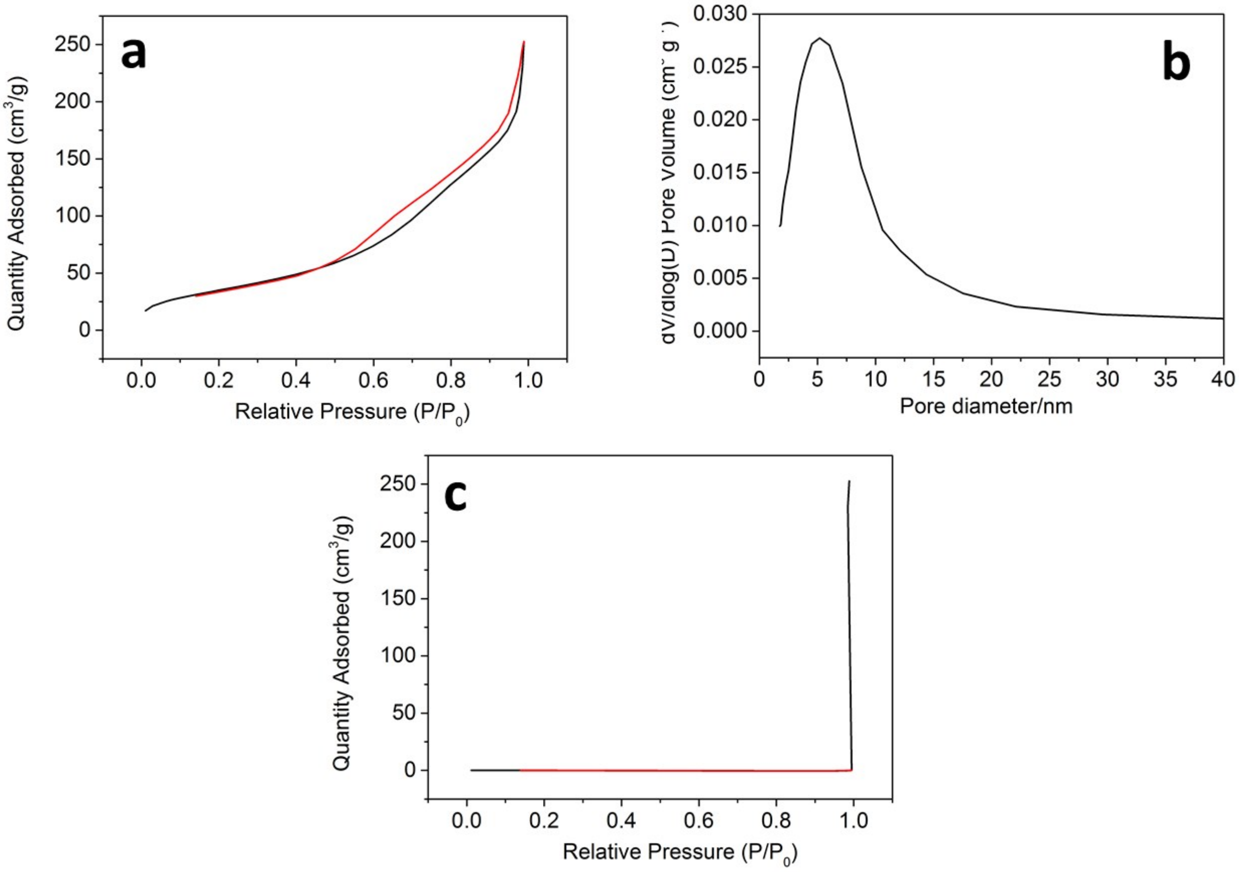


Figure S1. Adsorption–desorption isotherms for mesoporous-Al_2O_3 (a), Pore size distribution obtained from isotherms for mesoporous-Al_2O_3 (b), Adsorption–desorption isotherms for the n-Al_2O_3 (c).

2.4 TEM images of Pt-1a/mesoporous-Al_2O_3 and Pt/mesoporous-Al_2O_3

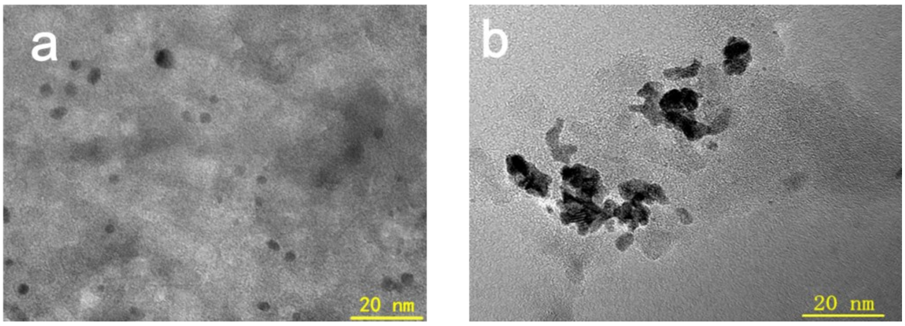


Figure S2.TEM image of Pt-**1a**/mesoporous-Al_2O_3 (a), TEM image of Pt/mesoporous-Al_2O_3 (b).

2.5 XPS spectrums of Pt-1a/n-Al_2O_3 and Pt/n-Al_2O_3

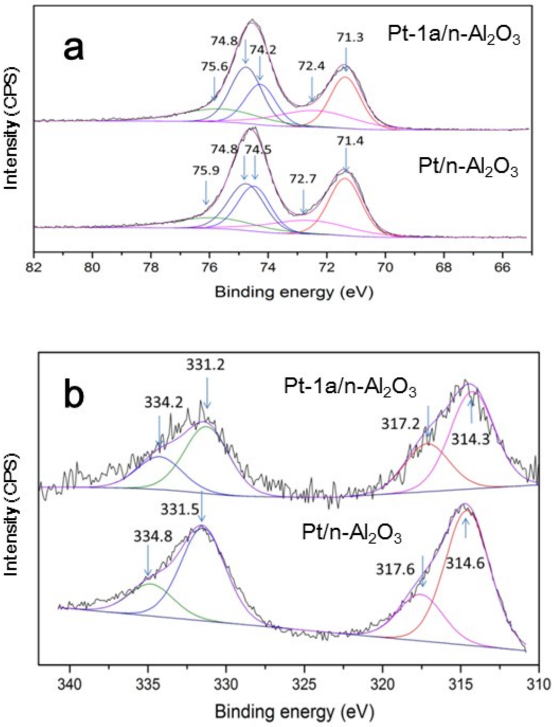


Figure S3. The XPS spectrums of Pt4f of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3 (a), Pt4d of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3 (b).

2.6 FT-EXAFS spectrums of Pt-1a/n-Al_2O_3 and Pt/n-Al_2O_3

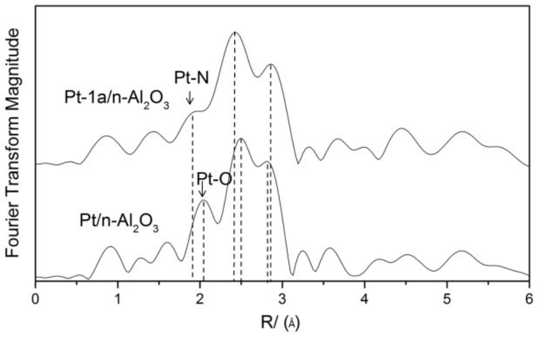


Figure S4.FT-EXAFS spectrums of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3.

2.7 H_2-TPR spectrums of Pt-1a/n-Al_2O_3 and Pt/n-Al_2O_3

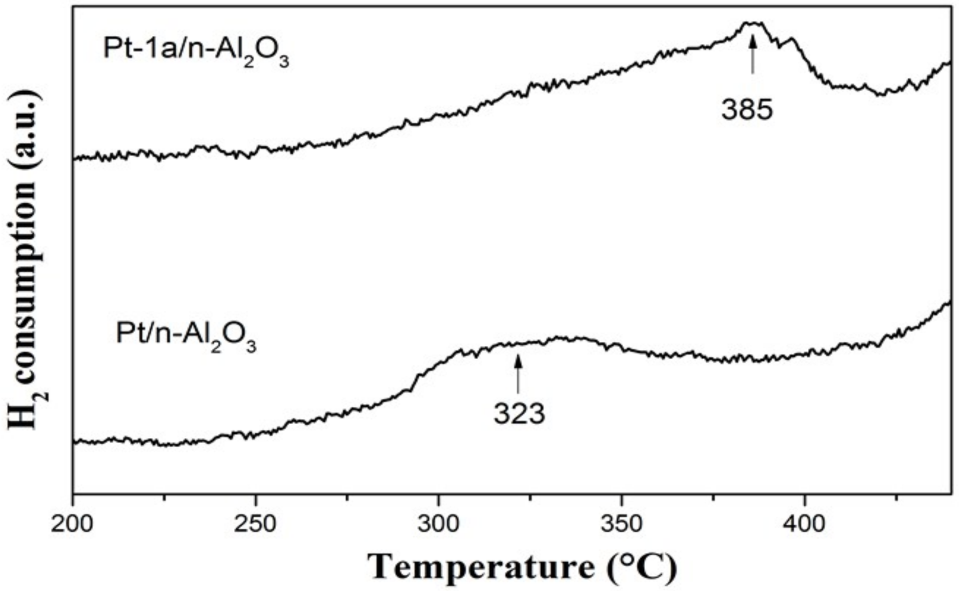


Figure S5.H_2-TPR spectrums of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3.

2.8 XRD spectrums of Pt-1a/n-Al_2O_3 and Pt/n-Al_2O_3

Figure S6 shows the XRD patterns of Pt/n-Al_2O_3 and Pt-**1a**/n-Al_2O_3. The diffraction peaks at 40° can be assigned to the (111) planes of the face-centered cubic Pt particles.

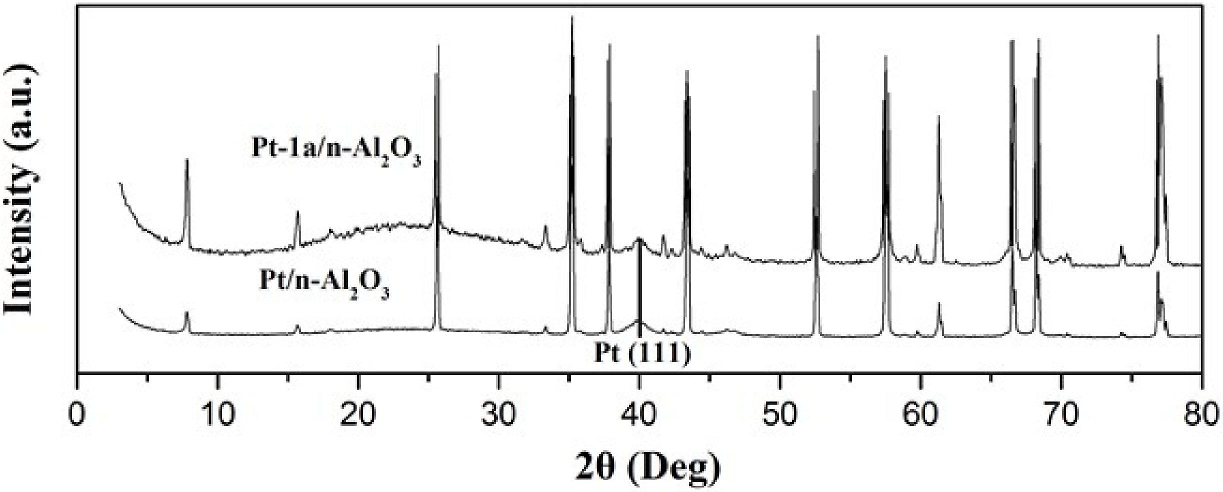


Figure S6.XRD spectrums of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3.

2.9 XANES spectrums of Pt-1a/n-Al_2O_3 and Pt/n-Al_2O_3.

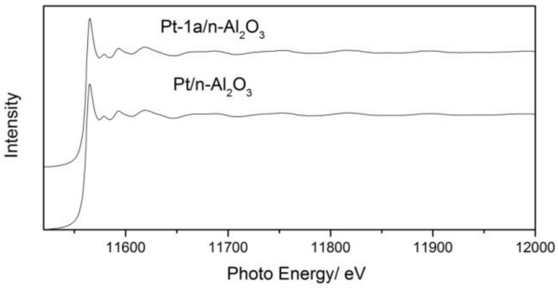


Figure S7.XANES spectrums of Pt-**1a**/n-Al_2O_3 and Pt/n-Al_2O_3.

2.10 Reuse of the Pt-1a/n-Al_2O_3 catalyst.

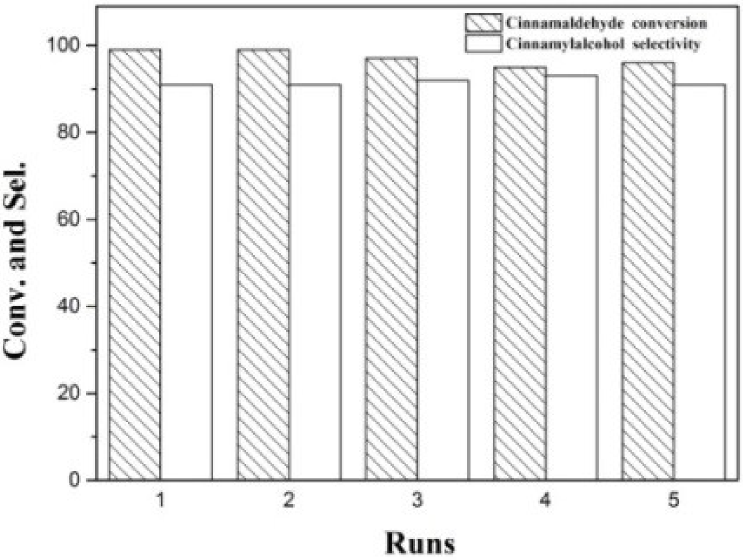
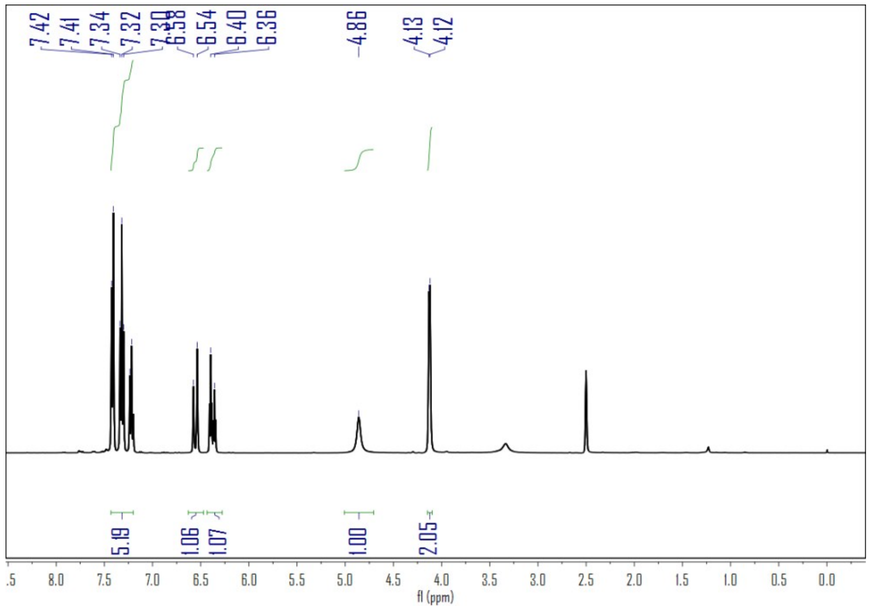
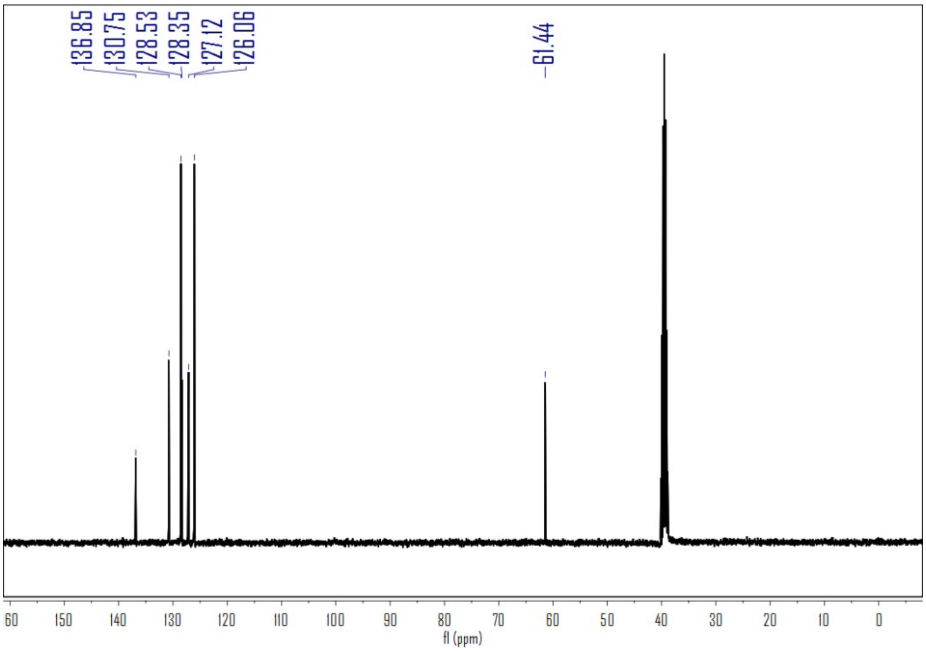


Figure S8. Reuse of the Pt-**1a**/n-Al_2O_3 catalyst. Reaction conditions: cinnamaldehyde 1 mmol, P_{H2} = 10 atm, catalyst 30 mg, methanol 0.5 mL, water 0.1 mL, 30 ^oC, 3 h. Before each cycle, the catalyst was treated by ultrasonic wave.

2.11 NMR data for the 3a.



^{1}H NMR (DMSO, 400 MHz) δ 7.42-7.20 (m, 5H), 6.58-6.54 (m, 1H), 6.41-6.34 (m, 1H), 4.86 (s, 1H), 4.13-4.12 (d, 2H).



^{13}C NMR (DMSO, 100 MHz) δ 136.85, 130.75, 128.53, 128.35, 127.12, 126.06, 61.44.