Supporting Information

Rare Earth Oxide Anchored Platinum Catalytic Site Coated Zeolitic Imidazolate Frameworks toward Enhancing Selective Hydrogenation

Liangmin Ning,[†] Shengyun Liao,[‡] Caiqiao Dong,[†] Mingtao Zhang,[†] Wen Gu,[†,*] and Xin Liu [†,*]

Dedicated to the 100th anniversary of Nankai University

[†] College of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), Tianjin Key Laboratory of Metal and Molecule Based Material Chemistry, Collaborative Innovation Centre of Chemical Science and Engineering, Nankai University, Tianjin, 300071, China.

[‡] Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, 300384, China.

[*] E-mail: liuxin64@nankai.edu.cn; guwen68@nankai.edu.cn

Chemicals and reagents

All solvents are of analytical grade and used after purchase with no purification. $Gd(NO_3)_3·6H_2O$, urea, $H_2PtCI_6·6H_2O$, poly(sodium-p-styrenesulfonate) (PSS), $Zn(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, 2-methylimidazole, cinnamaldehyde, Citral, benzaldehyde, furfural, acetophenone, cyclohexanone, cyclopentanone, nitrobenzene, dimethyl 2-nitroterephthalate, 4-nitrophenol and 2-nitrophenol were purchased from Aladdin.

The catalytic hydrogenation of CAL

High-pressure hydrogenation reactions were carried out using 100 mL Parr reactor. In a typical procedure, 25 mg of catalyst powder was dispersed in 10 mL of ethanol. Then, 132 mg (1 mmol) of *trans*-cinnamaldehyde (CAL) were introduced. Subsequently, the solution was transferred into a Teflon-lined stainless steel autoclave, the autoclave was purged with Ar and H_2 for 3 times, respectively. Then, the final H_2 pressure of the autoclave was set at 2.0 MPa. During the catalytic process, the reaction solution was magnetically stirred with the speed of 600 rpm at 100 ^{o}C for a certain time. After that, the catalysts were separated by centrifugation and the obtained reaction solution was filtered through a filter membrane (0.22 μm) and then was analyzed by gas chromatography (GC, Agilent, GC 6890N, column: HP-5, 30 m × 0.25 mm × 0.25 μm) and gas chromatography-mass spectrometry (GC-MS, Agilent, GC 6890N, MS 5973, column: HP-5MS, 30 m × 0.25 mm × 0.25 μm).

The catalytic hydrogenation of 4-NP

High-pressure hydrogenation reactions were carried out using 100 mL Parr reactor. In a typical procedure, 25 mg of catalyst powder was dispersed in 20 mL of H_2O. Then, 139 mg (1 mmol) of 4-nitrophenol (4-NP) were introduced. Subsequently, the solution was transferred into a Teflon-lined stainless steel autoclave, the autoclave was purged with Ar and H_2 for 3 times, respectively. Then, the final H_2 pressure of the autoclave was set at 2.0 MPa. During the catalytic process, the reaction solution was magnetically stirred with the speed of 600 rpm at 120 ^{o}C for a certain time. After that, the catalysts were separated by centrifugation and the obtained reaction solution was filtered through a filter membrane (0.22 μm) and then was analyzed by UV (RAYLEIGH UV-2200).

Recycling test

After the reaction, the catalyst was separated by magnetic separation technology, then washed with ethanol (6×30 ml) for three times, and dried overnight at 80 ^{o}C in vacuum. The regenerated catalyst is directly used in the next step of catalytic reaction. Finally, the catalyst was characterized by XRD, HRSEM and HRTEM after the eight cycle.

Characterization

X-ray powder diffraction (XRD) intensities of the different samples were measured on a Rigaku D/max-IIIA diffractometer (CuKα, λ =1.54056 Å). IR spectra were recorded in the range of 4000-400 cm^{-1} on a Bruker Tensor37 spectrometer with KBr pellets. TGA experiments were performed in flowing N_2 on a NETZSCH TG 209 instrument with a heating rate of 10 °C/min. The BET surface areas and pore volumes were measured by N_2 adsorption-desorption at 77 K on a Micromeritics ASAP 2020 instrument at -196 °C.The quantitative analyses of the products were determined on a GC apparatus with FID detector or on the Agilent 6890/5973 Gas Chromatograph-Mass Spectrometer (GC-MS) instrument. The Pt contents of all the samples were quantitatively determined by the inductively coupled plasma optical emission spectrometry (ICP-OES: Varian 700-ES). The morphology of catalytic materials was obtained by high resolution scanning electron microscope (HRSEM: MERLIN Compact 6164, ZEISS) and high resolution transmission electron microscopy (HRTEM: FEI Talos F200X G2 AEMC) at 200 kV. X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIS 165 with a dual X-ray anode (Mg and Al) and all XPS spectra were recorded using the MgKα line. All the structures discussed here were optimized from various initial conformations at the M06-2X/6-311G+(d, p).

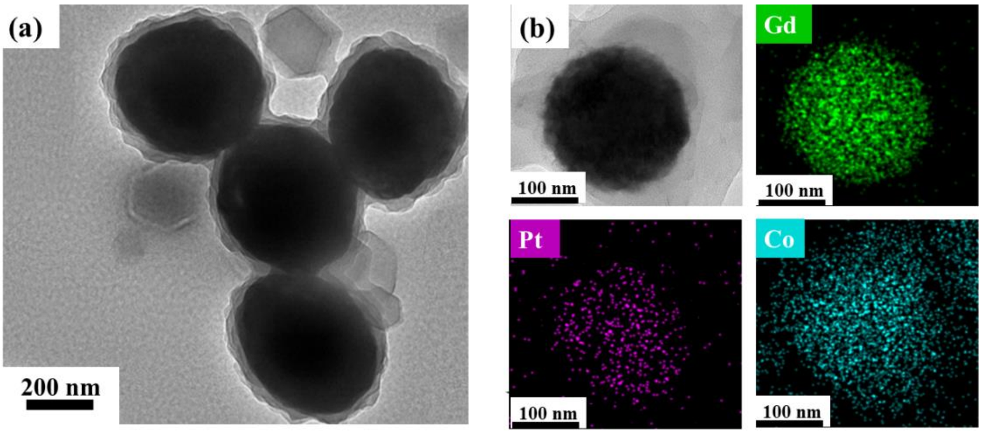

Figure S1. (a) HRTEM and (b) elemental mapping images of Gd_2O_3@Pt@ZIF-67 (Gd: green, Pt: purple, Co: light blue).

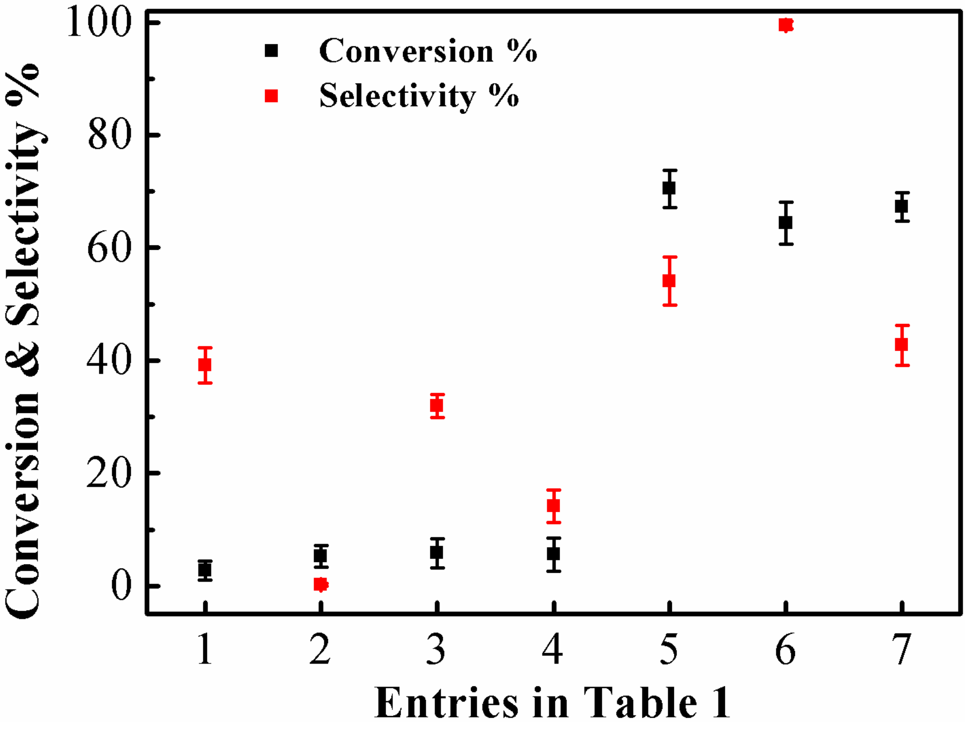

Figure S2. Error limits on data (conversion and selectivity) in Table 1.

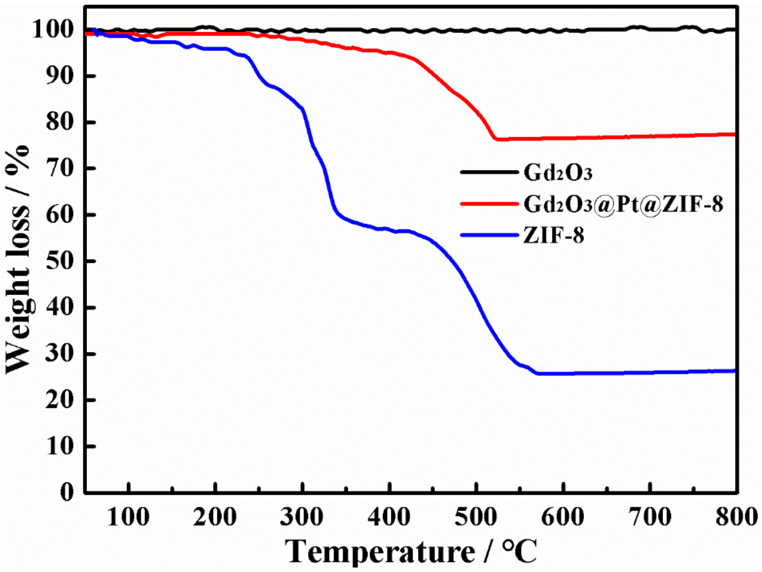

Figure S3. (a) TGA plots of Gd_2O_3 (black line), ZIF-8 (blue line) and Gd_2O_3@Pt@ZIF-8 (red line).

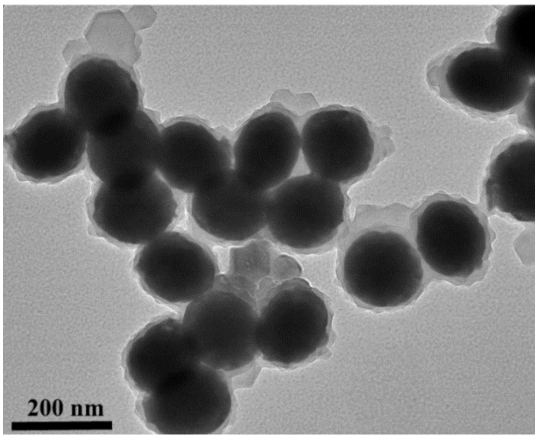

Figure S4. HRTEM images of used Gd_2O_3@Pt@ZIF-8

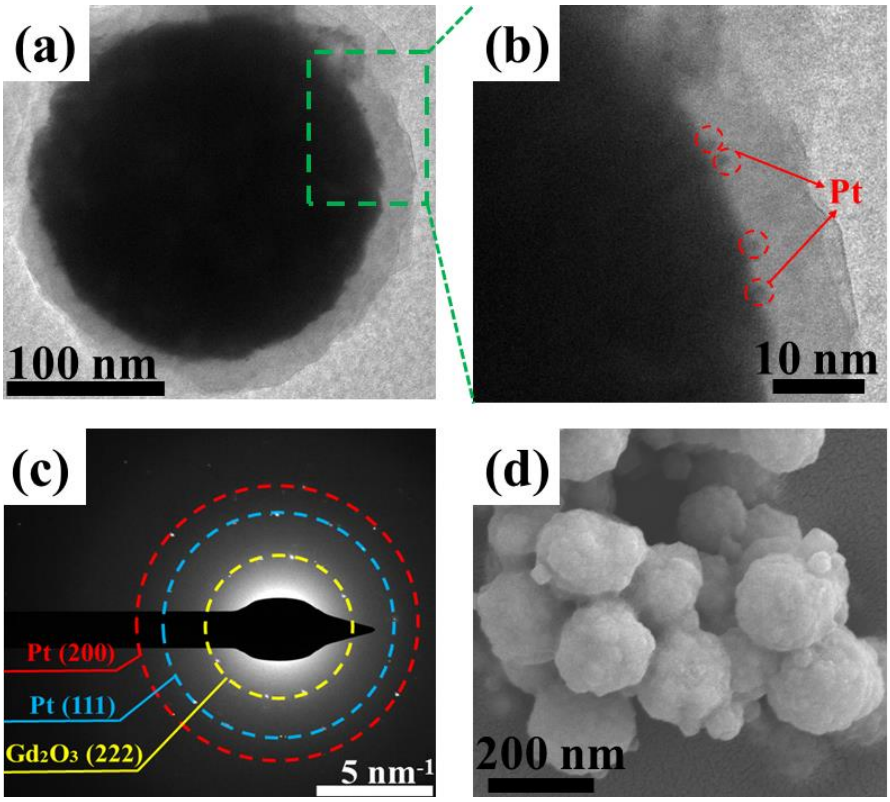

Figure S5. HRTEM images (a-b), SAED pattern (c), and HRSEM images (d) of used Gd_2O_3@ZIF-8 after five recycles.

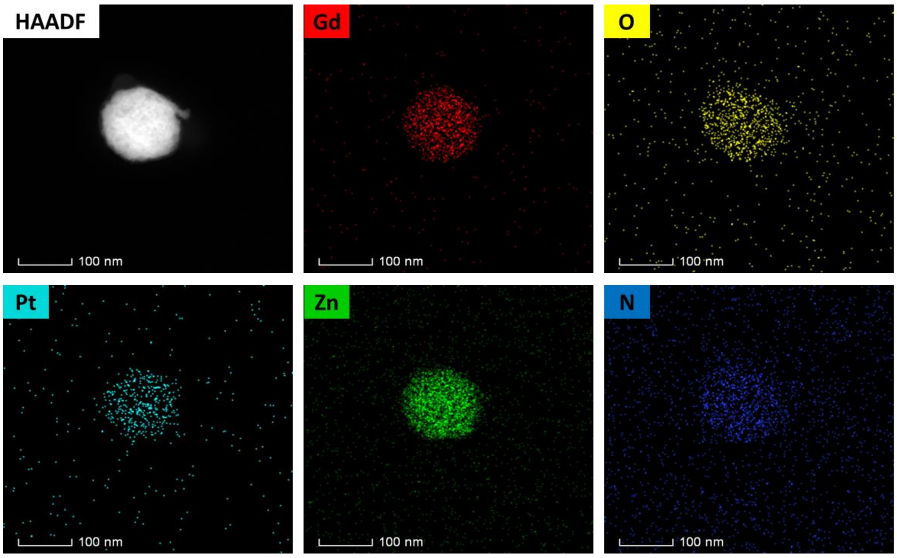

Figure S6. HAADF-STEM images and elemental mapping for used Gd_2O_3@Pt@ZIF-8 (Gd: red, O: yellow, Pt: light blue, Zn: light green, N: blue).

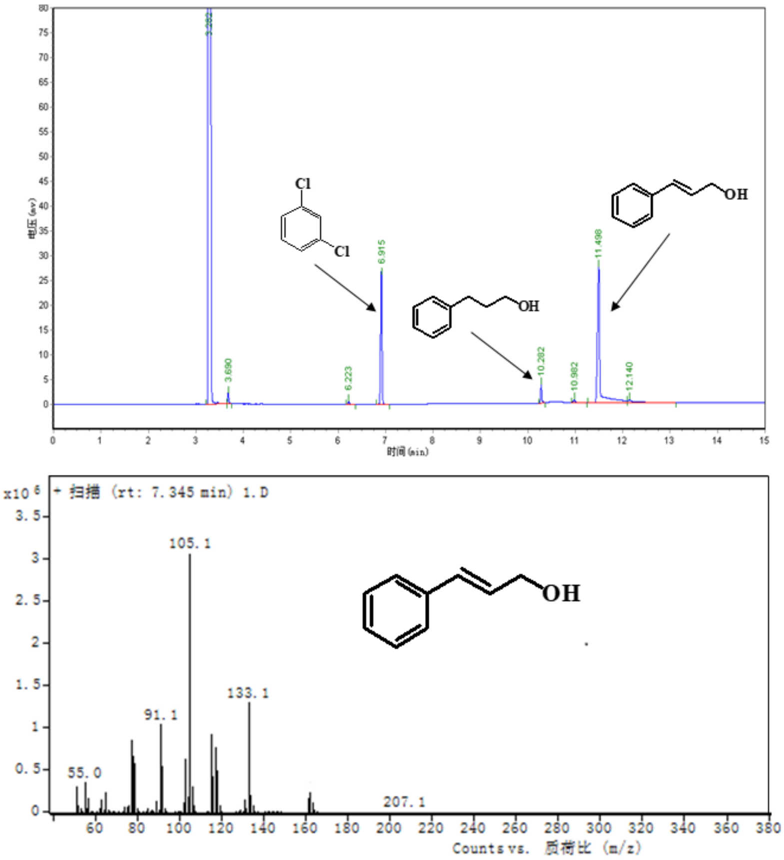

Figure S7. GC and GC-MS analysis for the hydrogenation products of cinnamaldehyde.

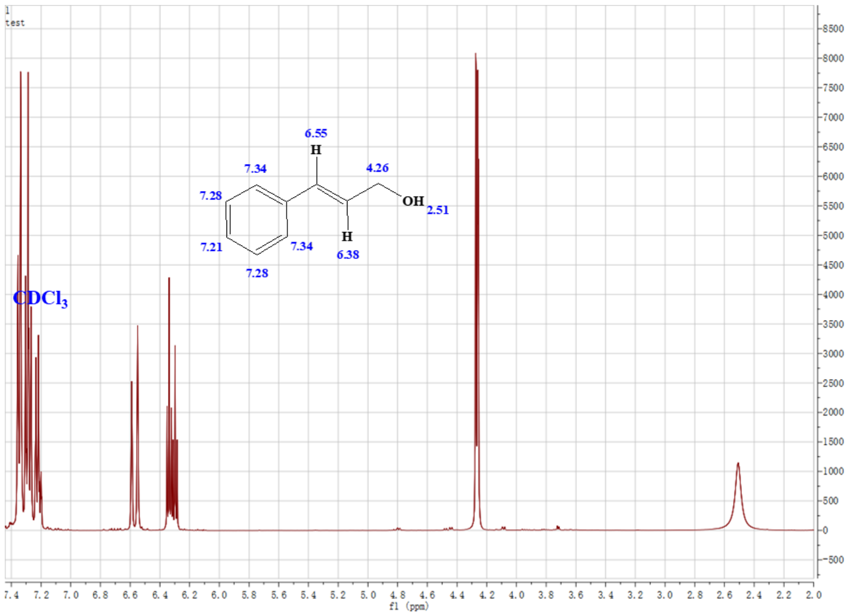

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) for the hydrogenation products of cinnamaldehyde.

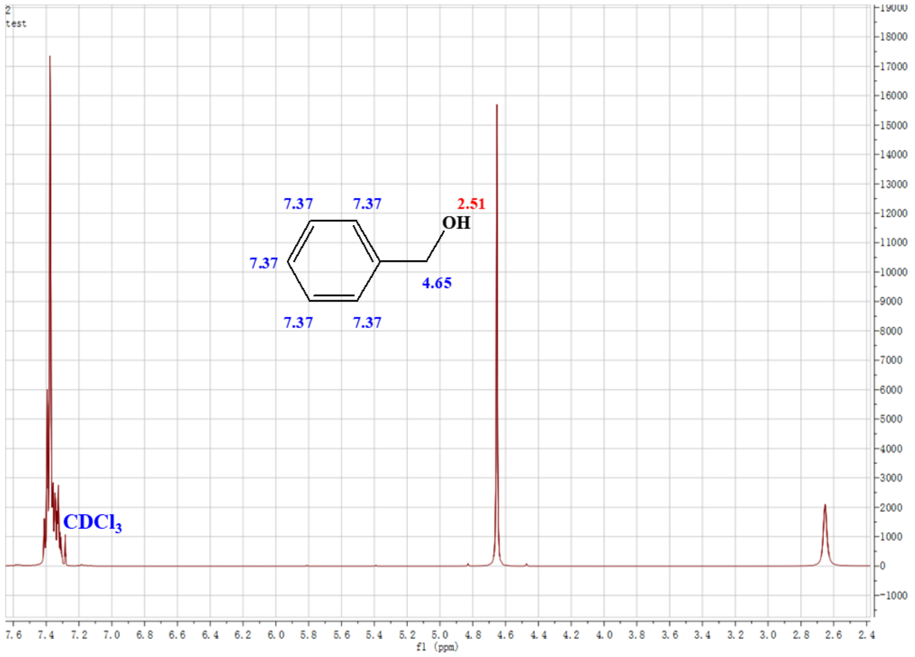

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) for the hydrogenation products of benzaldehyde.

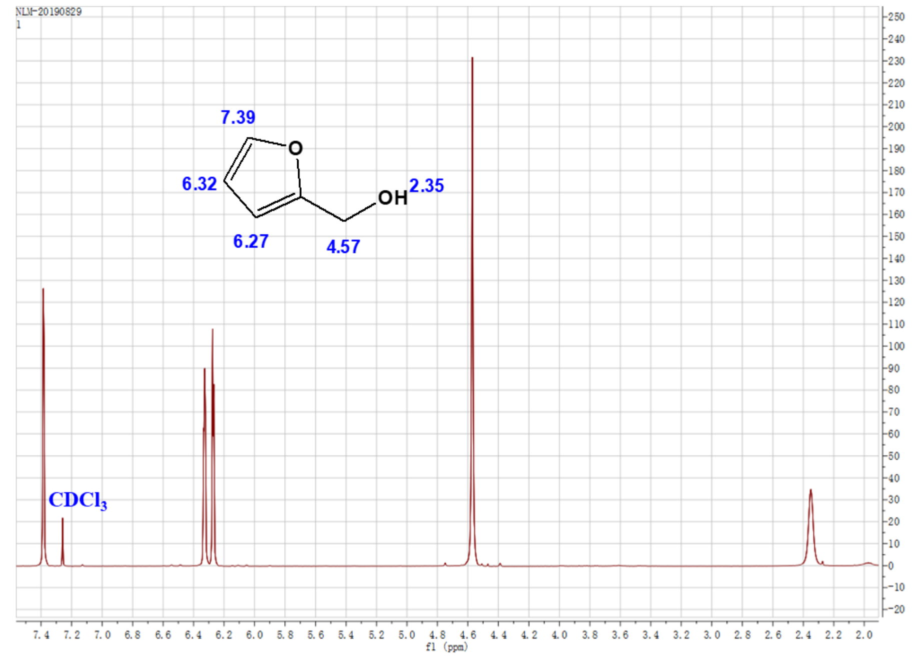

Figure S10. ^{1}H NMR (400 MHz, CDCl$_3$) for the hydrogenation products of furfural.

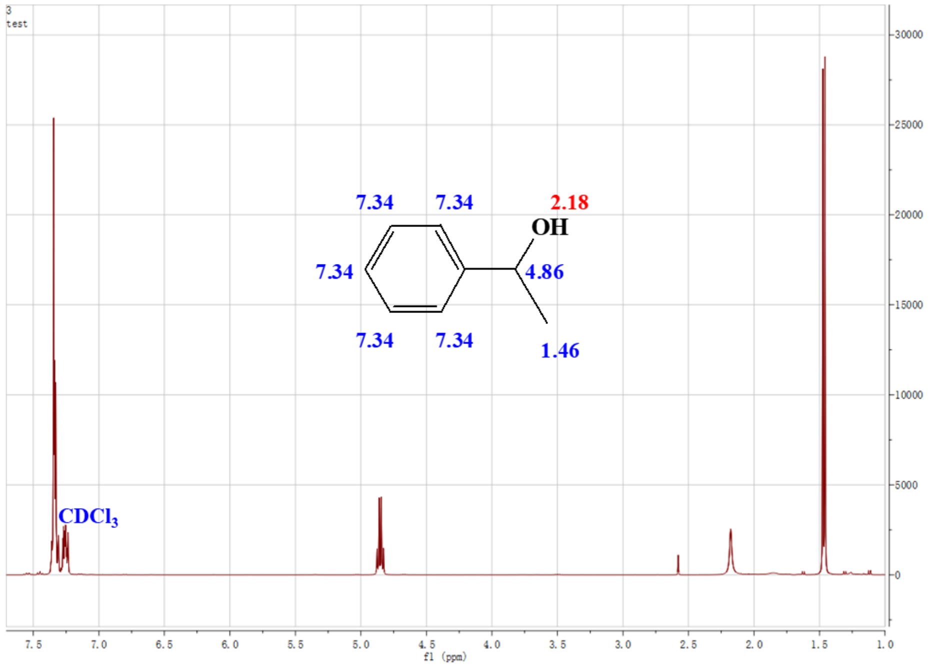

Figure S11. ^{1}H NMR (400 MHz, CDCl$_3$) for the hydrogenation products of acetophenone.

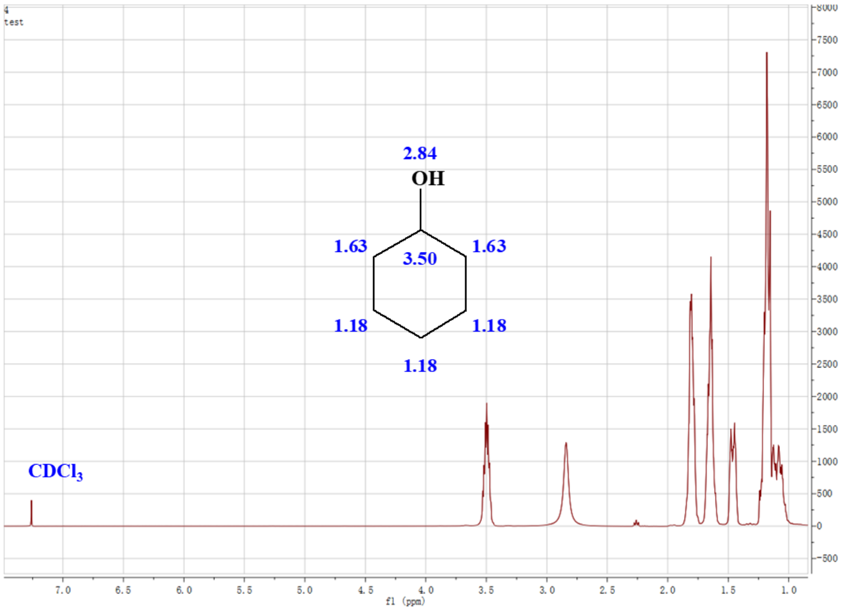

Figure S12. ^{1}H NMR (400 MHz, CDCl$_3$) for the hydrogenation products of cyclohexanone.

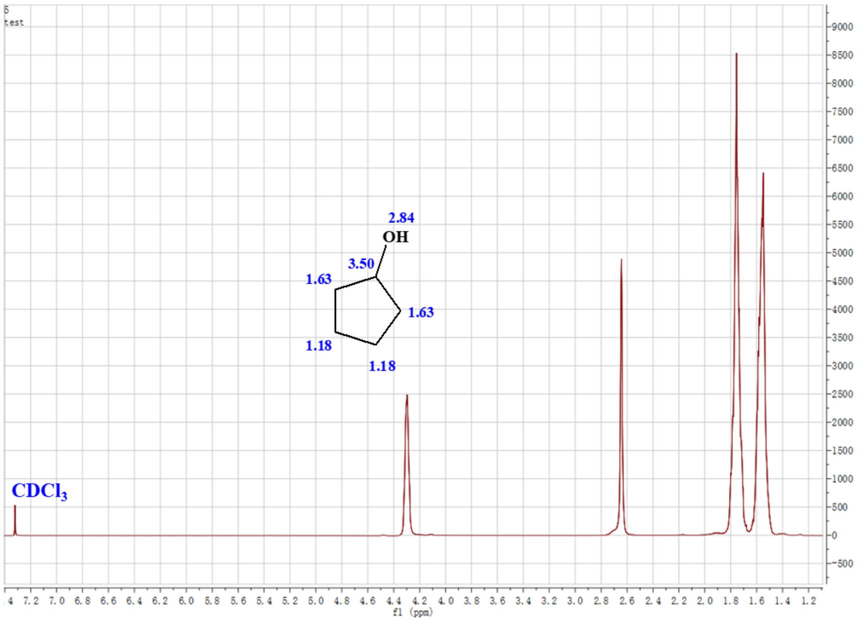

Figure S13. ^{1}H NMR (400 MHz, CDCl$_3$) for the hydrogenation products of cyclopentanone.

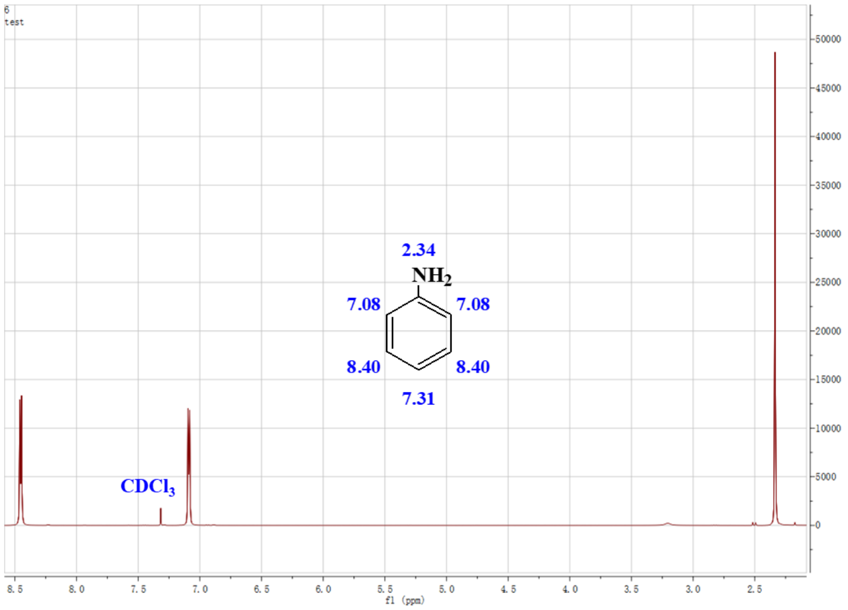

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) for the hydrogenation products of nitrobenzene.

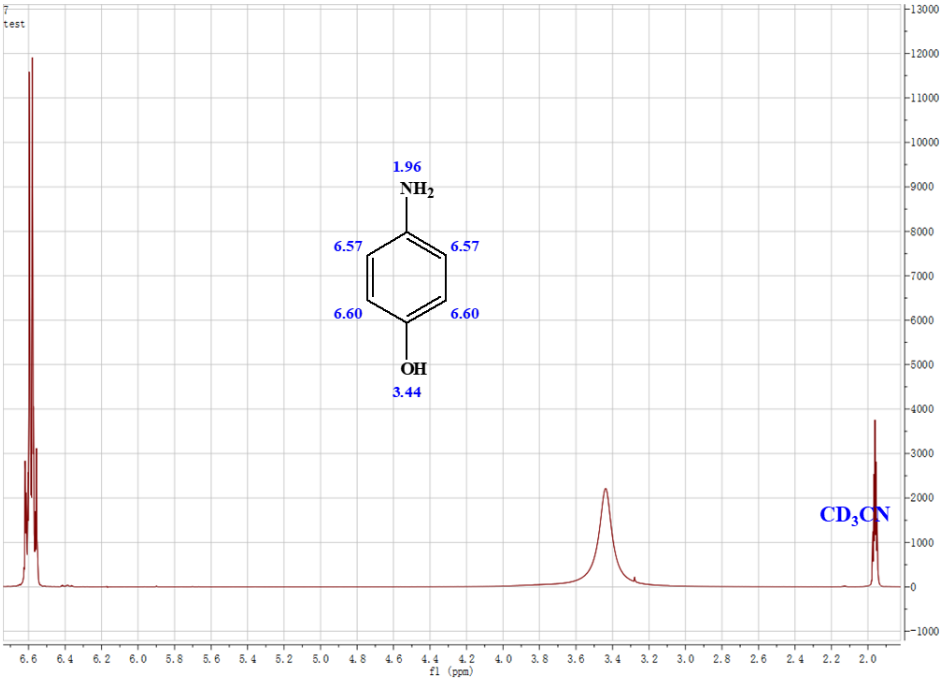

Figure S15. ^{1}H NMR (400 MHz, CD_3CN) for the hydrogenation products of 4-nitrophenol.

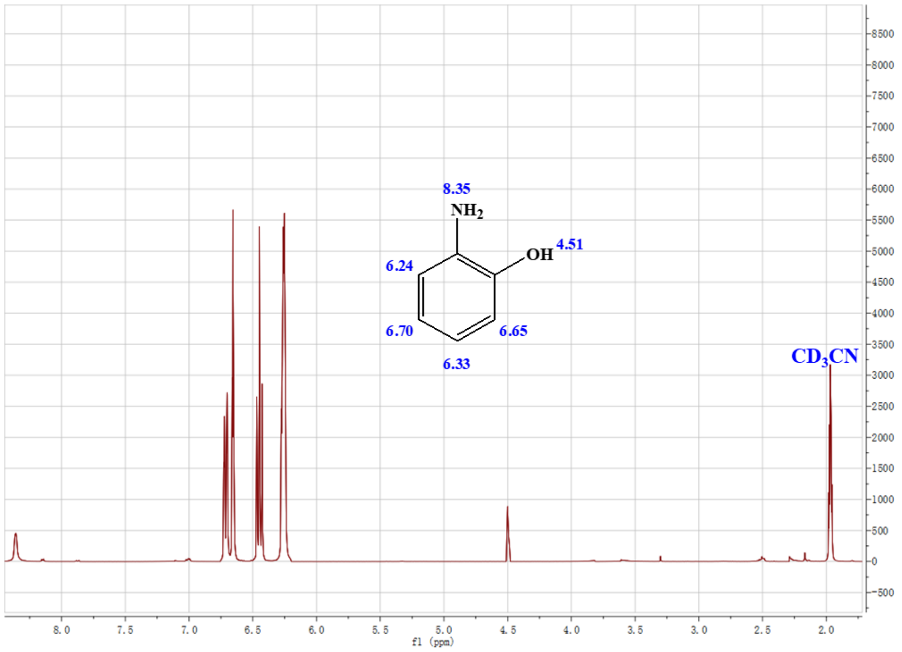

Figure S16. ^{1}H NMR (400 MHz, CD_3CN) for the hydrogenation products of 2-nitrophenol.

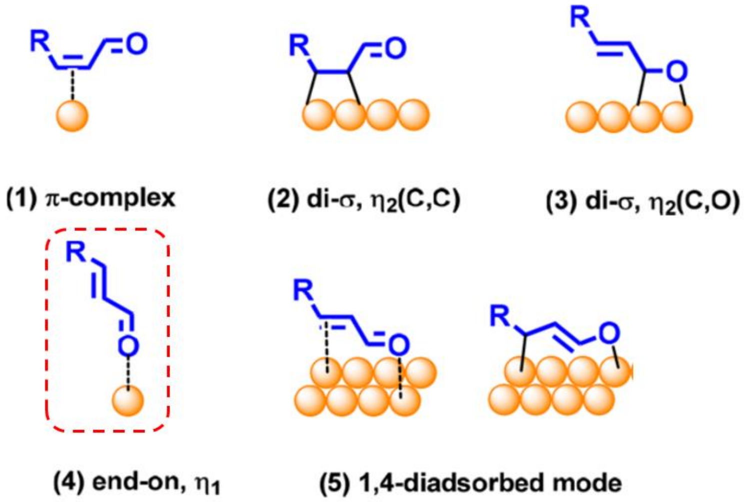

Figure S17. Adsorption patterns of α, β-unsaturated aldehydes on metal nanoparticles and single atoms. Adapted with permission from ref 51 in article. Copyright 1995 Elsevier.

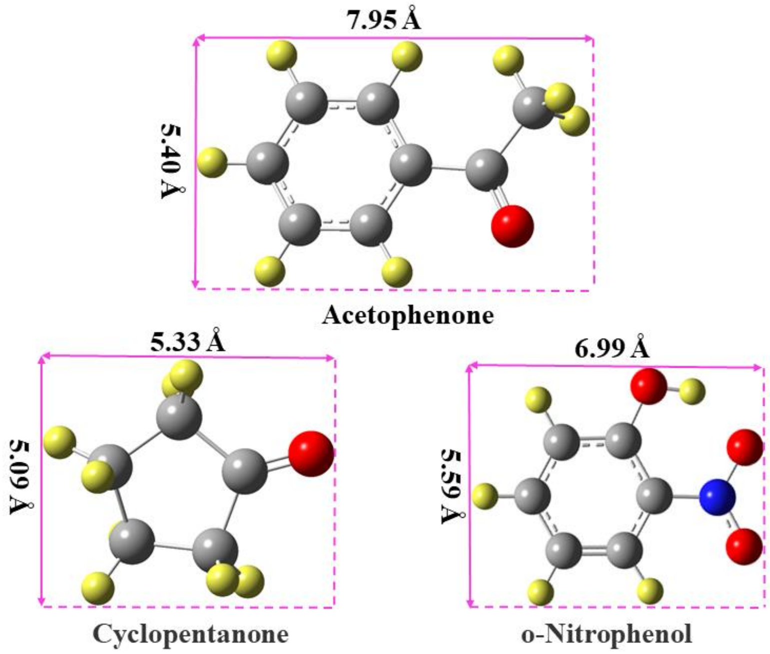

Figure S18. The spatial distance of substrate molecules is measured by Gaussian after structure optimization.