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Solvent-free selective hydrogenation of chloronitrobenzene to chloroaniline over a robust Pt/Fe₃O₄ catalyst

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1. Experimental details

1.1 Reagents and characterization

Hydrogen (99.999%) was supplied by Beijing Gases Company. Pt/C (1.0 wt%) was purchased from ACROS. *o*-CNB (ACROS, 99%), *m*-CNB (Alfa, 98%), *o*-BNB (Alfa, 99%) were used after recrystallization from ethanol. Methanol (HPLC grade, 99.9%) was purchased from Fisher. Other reagents used in this work were of analytical grade. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were taken on a FEI Tecnai G²F20 transmission electron microscope. The sample was prepared by ultrasonically dispersing the Pt/Fe₃O₄ catalyst in ethanol for several minutes. A drop of the dilute suspension was placed onto a copper grid covered with a carbon film and ethanol in the sample was removed by evaporation. The particle size distribution histogram was obtained on the basis of the measurements of 500 particles. X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAX-PC 2500 diffractometer with monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at an accelerating potential of 40 kV and a tube current of 300 mA. The specific surface area of the

catalyst was measured by an ASAP 2010 volumetric sorption analyzer. An inductively coupled plasma atomic emission spectrometer (ICP-AES, Leeman Corp.) was used to analyze the composition of the Pt/Fe₃O₄ catalyst. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker-500 MHz NMR spectrometer. FT-IR spectra of samples in KBr pellets were recorded on a Nicolet 750 FT-IR spectrometer. High-resolution mass spectra (HRMS) were measured on a Bruker Apex IV FTMS spectrometer. Elemental analysis was performed on a vario EL elemental analyzer.

1.2 Preparation of the Pt colloidal solution

A glycol solution of NaOH (50 ml, 0.26 M) was added dropwise into a glycol solution of H₂PtCl₆·6H₂O (50mL, 20 g/L) under stirring. The mixture was stirred vigorously for 30 minutes and then heated at 160 °C by microwave for 5min under nitrogen atmosphere. A dark-brown Pt colloid (Pt: 3.7 g/L) was obtained.¹

1.3 Preparation of the Fe₃O₄ support

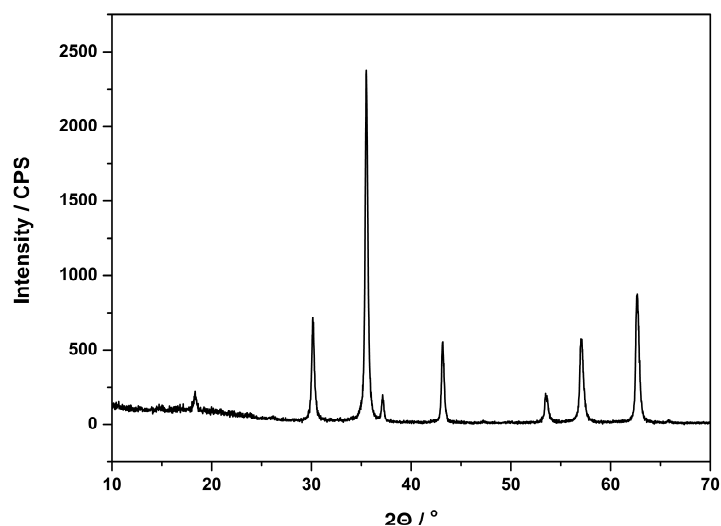


Fig. S1 XRD pattern of the Fe₃O₄ support.

FeCl₃·6H₂O (50 g) and urea (50 g) were dissolved in 300 ml of glycol. The obtained solution was heated until an orange precipitate was generated. After being washed with water and ethanol, the precipitate was dried by infrared lamp. The resulting yellow powder was calcined at 400 °C under nitrogen atmosphere for three

hours to generate black Fe₃O₄ powder.²

The specific surface area of the prepared Fe₃O₄ support was 23 m²/g. Figure S1 shows the XRD pattern of the prepared Fe₃O₄ support which matches well with that of Fe₃O₄ (JCPDS, 19-0629).

1.4 Catalyst preparation

16.4 ml of the prepared Pt colloid solution was added dropwise into a suspension containing 6 g of the Fe₃O₄ support and 200 ml of ethanol under stirring. After stirring vigorously for an hour, the precipitate was collected by an applied magnetic field and washed with water, and dried at 80 °C for one day to obtain the Pt/Fe₃O₄ (1.0 wt% Pt) catalyst as a black powder.

1.5 Solvent-free hydrogenation of halonitrobenzene

Solvent-free hydrogenation of halonitrobenzene was performed in a 300 ml titanium autoclave equipped with a thermowell, a cooling coil and a mechanical agitator. Typically, 1.2 g of Pt/Fe₃O₄ and 50 ml of methanol were added into the autoclave. Then the autoclave was sealed and flushed with H₂ three times to remove the air. The catalyst was pre-activated at room temperature and 2.0 MPa for an hour. After pre-activation, a mechanical vacuum pump was used to remove methanol in the autoclave by evaporation. Then 97.0 g of halonitrobenzene was melted and added into the autoclave, and the air in the autoclave was replaced by H₂ again as aforementioned. The autoclave was heated up to 50 °C and charged with H₂ up to 2.0 MPa. The hydrogenation reaction was carried out under mechanical agitation (1000 rpm) and the temperature was controlled by cooled ethanol flowing in the cooling coil and an external electrical heater. During the reaction, H₂ of 2.0 MPa was continuously supplied to the autoclave by a steel cylinder. After the reaction, the organic product and biphenyl as an internal standard substance were dissolved in methanol to form a

solution which was quantitatively analyzed by a gas chromatographer (Shimadzu GC-2010), equipped with a flame ionization detector and an Rtx-5MS capillary column (ϕ 0.25 mm \times 60 m). Reactants and products are identified by comparison with authentic samples or GC-MS coupling (Agilent 7980A).

Platinum and iron contents in the products were measured by ICP-AES after digesting the samples in concentrated nitric acid (GR) under heating. For the separation of 2-chloro-N-cyclohexylaniline (CCHA) and N-cyclohexylaniline (CHA) from the reaction products formed in the hydrogenation of *o*-CNB over Pt/C, most of *o*-CAN in the oil phase was removed by vacuum distillation at 130 °C. Then the residue was purified by silica gel column chromatography with a mixture of petroleum ether and ethyl acetate (v/v: 50:1) as the eluent, followed by recycling high-pressure liquid chromatography (LC-9101) with methanol as the eluent.

CHA was characterized by ^1H NMR spectrum and GC-MS. Figure S2 shows the MS spectrum of formed CHA in GC-MS which matches well with that of CHA standard sample (NIST, 270961). ^1H NMR of CHA (500 MHz, CDCl_3 , TMS): δ (ppm) 1.16-1.40 (m, 6H), 1.74-1.78 (m, 2H), 2.05-2.08 (m, 2H), 3.22-3.28 (m, 1H), 4.23 (br s, 1H), 6.64 (d, $J = 7.5$ Hz, 2H), 6.69 (t, $J = 7.0$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 2H).

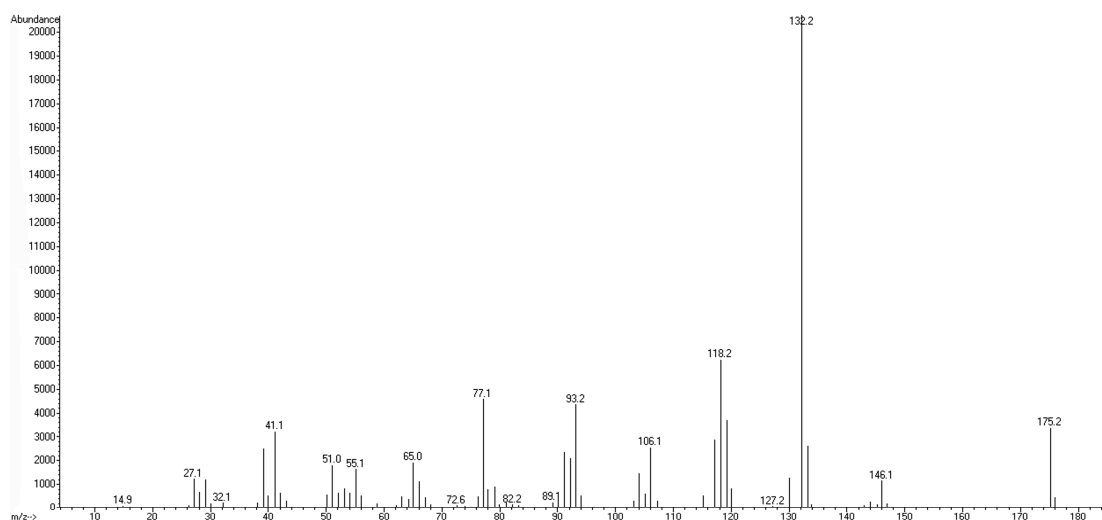


Fig. S2 MS spectrum of CHA in GC-MS.

As a new compound, CCHA formed in the hydrogenation over Pt/C was identified by GC-MS, ^1H NMR, ^{13}C NMR, IR, and HRMS spectroscopy, as well as elemental analysis. ^1H NMR of CCHA (500 MHz, CDCl_3 , TMS): δ_{H} (ppm) 1.20-1.30 (m, 4H), 1.34-1.43 (m, 2H), 1.75-1.79 (m, 2H), 2.03-2.06 (m, 2H), 3.28-3.32 (m, 1H), 4.22 (br s, 1H), 6.56 (t, $J = 7.0$ Hz, 1H), 6.66 (d, $J = 8.0$ Hz, 1H), 7.09 (m, 1H), 7.22 (dd, $J = 1.0, 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} (ppm) 143.16, 129.27, 127.70, 119.02, 116.56, 111.69, 51.46, 33.20, 25.88, 24.89. HRMS (ESI, m/z): $[\text{M}-\text{H}]^+$ calc.: 210.1044; found: 210.1039. Anal. calcd for $\text{C}_{12}\text{H}_{16}\text{ClN}$: C, 68.7; H, 7.7; N, 6.7. Found: C, 68.8; H, 7.6; N, 6.8%. Figure S3 and Figure S4 show the FT-IR spectrum and MS spectrum in GC-MS of CCHA, respectively. All the characterization data confirmed that CCHA formed as a by-product in the solvent-free hydrogenation of *o*-CNB over the Pt/C catalyst.

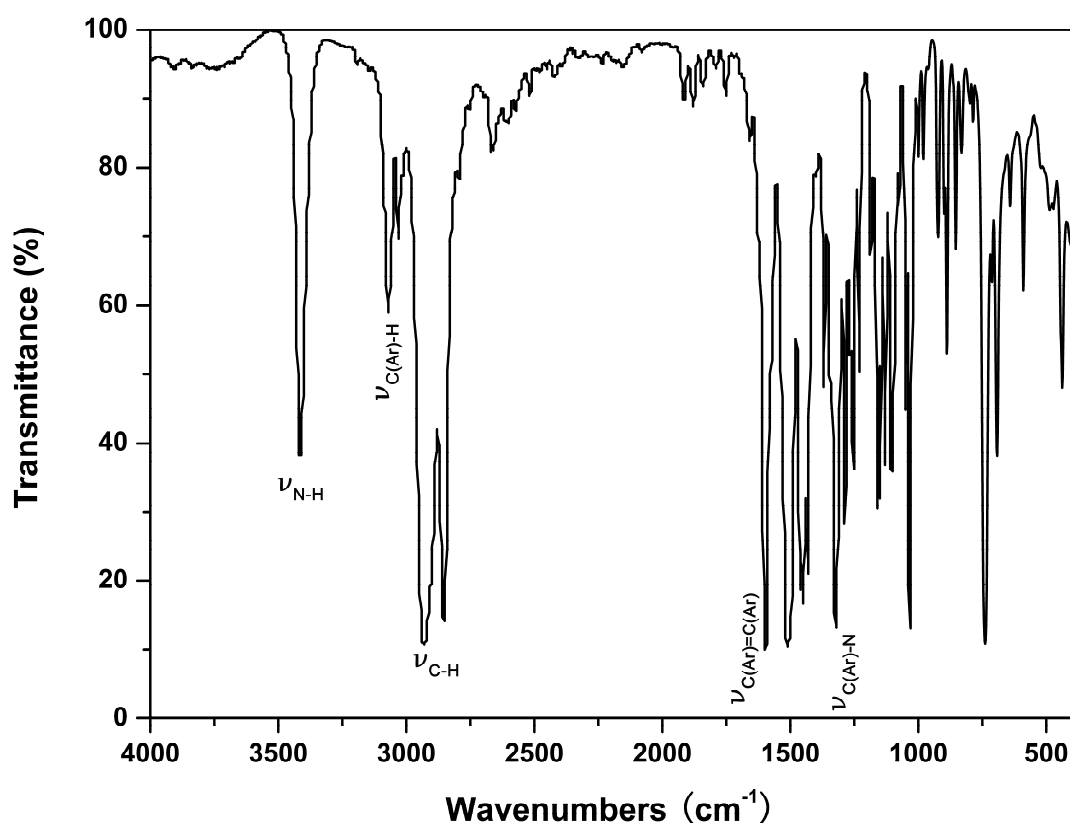


Fig. S3 FT-IR spectrum of CCHA.

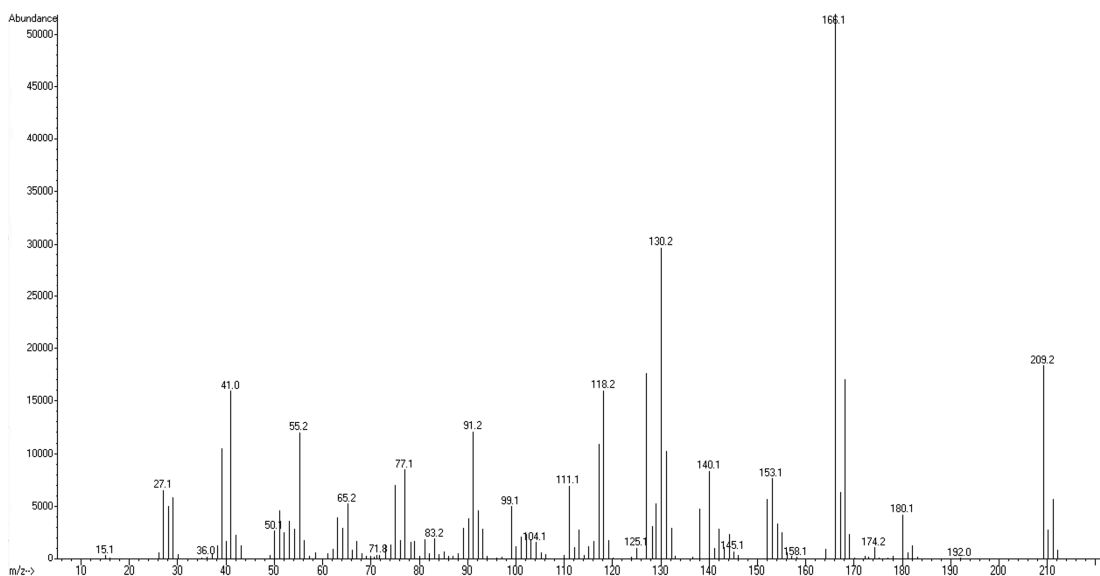
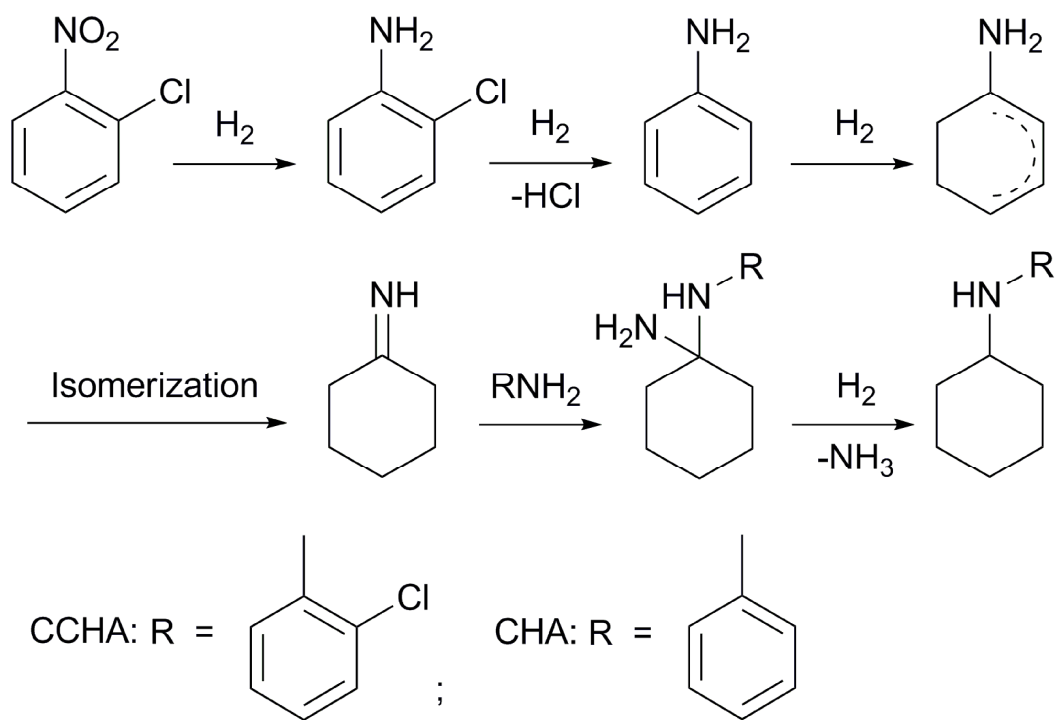


Fig. S4 MS spectrum of CCHA in GC-MS.



Scheme S1 The side reaction pathway for the formation of main high-boiling byproducts over Pt/C.

References

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- 2 L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song and L. J. Wan, *Adv. Mater.*, 2006, **18**, 2426.