Electronic Supplementary Material (ESI) for RSC Advances

Catalytic Hydrogenation of Aromatic Rings Catalyzed by Pd/NiO

Yanan Wang,[ab] Xinjiang Cui,[a] Youquan Deng,[a] and Feng Shi*[a]

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000 (China)

[b]University of Chinese Academy of Sciences, Beijing, 100049 (China)

1. Experimental

All solvents and chemicals were obtained commercially and were used as received.

NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GC-MS.

X-ray diffraction (XRD)

XRD patterns of samples were obtained on a STADI P automated transmission diffractometer instrument equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation (40 KV and 40 mA) was used as the X-ray source. The precipitated particles were dried in air and pressed on a glass slide for analysis.

Transmission Electron Microscopy (TEM)

For the prepared catalysts, the particle disperion was diluted by ethanol, and then 10 μL of disperion was cast on the TEM grids with a micorpippet. TEM images were obtained on a Tecnai G2 F30 S-Twin operating at 300 kV.

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar^{+} ion-gun. All spectra were recorded using non-monochromatic Mg Kα (1253.6 eV) radiation.

BET and ICP-AES analysis

Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Pd content of the catalyst was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

Typical procedure for catalyst preparation

The Pd/NiO catalyst was prepared as the method in literature [19]. PVP (18.8 mg) as a stabilizing agent was dissolved in a mixture solvent (16 mL) of water and ethanol (volume ratio = 1:9), 1.2 mL K_2PdCl_4 solution (0.005 g Pd/mL, the molar ratio of Palladium to monomeric unit of PVP = 30) was added to above PVP solution with vigorous stirring. After the mixed solution was refluxed

for 3h at 85 °C, a dark colloid solution was formed. Then, 300 mg NiO was added to the cooled colloid solution and the mixture solution was continued to stir at room temperature for 12 h. Afterwards, the catalyst Pd/NiO was centrifuged, washed with distilled water three times and dried under oven at 100 °C for 6 h. The content of palladium were determined by ICP was 2% in Pd/NiO.

Typical procedure for the hydrogenation of aromatic rings

1.0 mmol substrate, 50 mg catalyst and 2 mL solvent were added into an 80 mL stainless steel autoclave with a glass tube inside equipped with magnetic stirring. Then the air was exchanged with H_2 and 1-5 MPa H_2 was introduced and reacted for 4-36 h at 80-150 °C. Following, the autoclave was cooled to room temperature, the reaction mixture was diluted with acetone and the catalyst was removed by filtration. The filtrate was concentrated in vacuo to give the corresponding hydrogenated product.

Typical procedure for the reuse of the catalyst

1.0 mmol substrate, 50mg catalyst and 2 mL solvent were added into a 80 mL stainless steel autoclave with a glass tube inside equipped with magnetic stirring at the given temperature and pressure. After the reaction, the catalyst was separated by centrifugation and washed with distilled water, followed by drying in air at 100℃ for the next run.

2. Table S1. BET results of the studied catalysts

	Commercial NiO	Pd/NiO
Surface area (m^2/g)	116	98
Pore size (cm^3/g)	0.24	0.20

Figure S1. XRD patterns of (a) NiO, (b) Pd/NiO

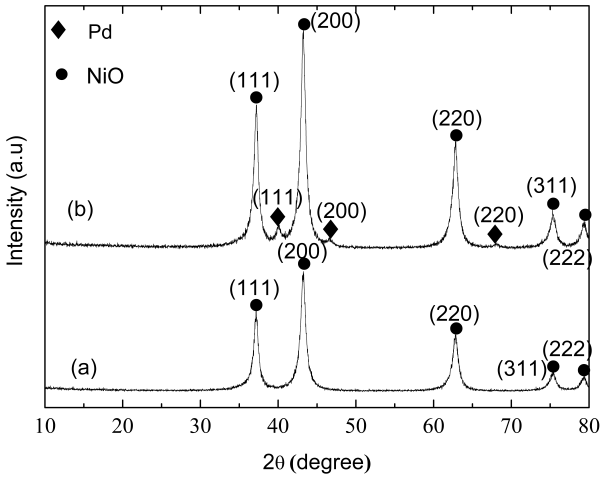
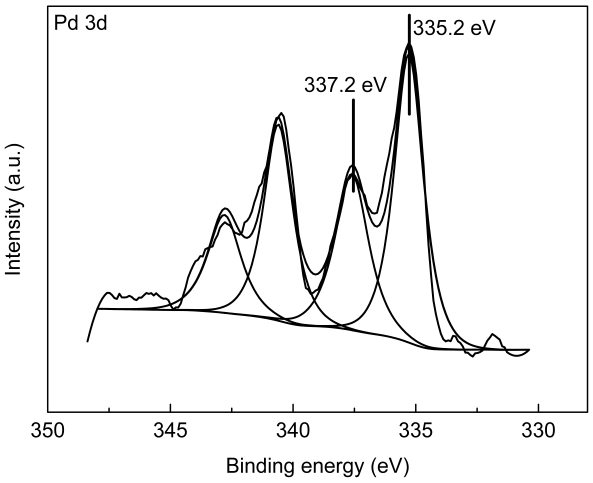
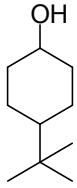


Figure S2. XPS spectra of Pd/NiO

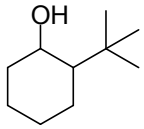


3. NMR characterization

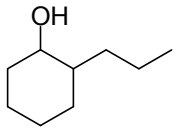


4-tert-butylcyclohexanol: (Table 2, entry 5) (GC purity 98%); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.79-1.13 (m, 9H), 1.16-1.28 (m, 1H), 1.28-1.46 (m, 2H), 1.48-1.52 (m, 1H), 1.71-1.92 (t, 2H), 1.97-2.08 (d, 1H), 3.44-3.62 (m, 1H), 4.04 (s, 1H); ^{13}C NMR (100.6 MHz,

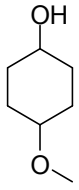
$CDCl_3$): δ = 20.91, 25.62, 27.48, 27.65, 33.40, 36.12, 47.17, 48.03, 65.91, 71.23; MS (E.I., 70 eV) m/z (rel. int.) 41 (31), 55 (20), 57 (100), 67 (39), 80 (22), 81 (67), 82 (33), 83 (31), 99 (23), 123 (34), 138 (23), 156 (1).



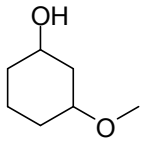
2-tert-butylcycolhexanol: (Table 2, entry 6) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.85-1.03 (d, 9H), 0.86-1.32 (m, 3H), 1.37-1.52 (m,2H), 1.53-1.63 (m, 1H), 1.63-1.87 (m, 2H), 3.43-3.56 (m, 1H), 4.24 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.98, 21.23, 25.18, 26.21, 26.80, 28.61, 29.30, 32.65, 33.07, 35.09，37.95, 50.92, 53.67, 67.98, 73.58; MS (E.I., 70 eV) m/z (rel. int.) 41 (35), 55 (21), 56 (21), 57 (100), 67 (67), 80 (23), 81 (39), 82 (94), 83 (30), 156 (1).



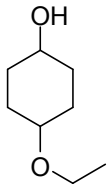
2-propylcycolhexanol: (Table 2, entry 7) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.81-0.98 (t, 3H), 1.02-1.57 (m, 8H), 1.60-1.90 (m, 3H), 1.90-2.04 (m, 1H), 3.16-3.28 (m, 1H), 3.87 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.31, 14.44, 19.63, 20.07, 20.47, 24.84, 25.16, 25.5, 26.53, 30.00, 32.96, 34.14, 34.41, 35.60, 40.92, 44.82, 69.35, 74.65; MS (E.I., 70 eV) m/z (rel. int.) 28 (28), 29 (22), 41 (49), 43 (34), 55 (46), 57 (76), 67 (47), 68 (38), 69 (30), 71 (29), 81 (59), 82 (100), 83 (19), 95 (57), 96 (40), 124 (39), 142 (1).



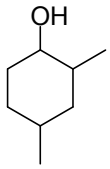
4-methoxycyclohexanol: (Table 2, entry 8) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 1.21-1.42 (m, 2H), 1.50-1.59 (d, 1H), 1.62-1.76 (d, 2H), 1.78-1.88 (m, 1H), 1.89-2.16 (m, 3H), 3.25-3.46 (d, 3H), 3.61-3.86 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.99, 28.85, 30.30, 32.50, 55.41, 55.82, 68.21, 69.47, 75.53, 78.03; MS (E.I., 70 eV) m/z (rel. int.) 41 (21), 57 (20), 58 (25), 71 (36), 72 (100), 73 (36), 112 (25), 130 (6).



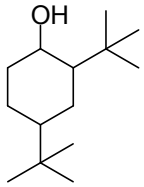
3-methoxycycolhexanol: (Table 2, entry 9) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 1.19-1.34 (m, 1H), 1.45-1.50 (m, 2H), 1.50-1.70 (m, 2H), 1.71-1.98 (m, 2H), 2.02-2.16 (d, 1H), 3.26-3.42 (d, 3H), 3.59 (s, 1H), 3.66-3.82 (m, 1H), 3.96-4.12 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.10, 18.40, 29.25, 29.50, 33.63, 33.75, 38.26, 38.91, 55.15, 55.38, 66.05, 67.82, 75.35; MS (E.I., 70 eV) m/z (rel. int.) 27 (22), 28 (48), 29 (30), 39 (29), 41 (46), 42 (23), 43 (52), 44 (38), 45 (20), 55 (30), 57 (24), 58 (75), 59 (36), 70 (24), 71 (44), 80 (26), 83 (27), 87 (100), 97 (49), 98 (58), 112 (40), 130 (1).



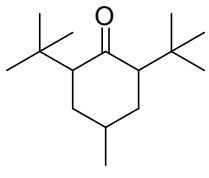
4-ethoxycyclohexanol: (Table 2, entry 10) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.88 (s,1H), 1.15-1.23 (m, 2H), 1.25-1.48 (m, 2H), 1.49-1.88 (m, 3H), 1.85-2.15 (m,1H), 3.15-3.48 (m, 1H), 3.48-3.55 (m, 1H), 3.55-3.68 (s, 1H), 3.68-3.77 (m, 1H), 5.31 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.65, 27.48, 29.57, 30.53, 32.89, 62.89, 63.45, 68.23, 69.78, 73.86, 76.45; MS (E.I., 70 eV) m/z (rel. int.) 29 (17), 41 (19), 43 (16), 44 (14), 55 (15), 57 (68), 58 (39), 59 (16), 69 (10), 72 (10), 81 (19), 85 (36), 86 (100), 87 (23), 98 (19), 126 (14), 144 (1).



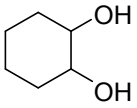
2,4-dimethylcyclohexanol: (Table 2, entry 11) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.82-0.92 (m, 3H), 0.92-1.09 (m, 3H), 1.12-1.57 (m, 3H), 1.60-1.76 (m, 4H), 1.89-2.00 (m, 1H), 3.05-3.15 (m,1H), 3.77 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.19, 18.59, 21.98, 22.55, 26.58, 27.98, 32.10, 32.36, 33.25, 33.70, 35.31, 36.15, 36.79, 39.81, 42.47, 76.47; MS (E.I., 70 eV) m/z (rel. int.) 29 (20), 39 (22), 41 (45), 43 (56), 55 (46), 56 (35), 57 (74), 58 (53), 67 (22), 69 (43), 71 (57), 81 (35), 82 (36), 84 (57), 85 (25), 95 (100), 110 (33), 128 (1).



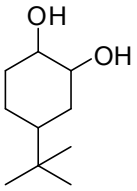
2,4-di-tert-butylcyclohexanol: (Table 2, entry 12) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.81-0.94 (d, 9H), 1.95-1.03 (d, 9H), 1.03-1.24 (m, 4H), 1.25-1.89 (m, 4H), 3.42-3.52 (m, 1H), 4.19 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.87, 22.07, 25.78, 27.64, 28.73, 29.29, 29.64, 32.52, 32.71, 32.82, 33.29, 35.31, 37.85, 47.58, 48.66, 51.3, 53.46, 67.53, 73.60; MS (E.I., 70 eV) m/z (rel. int.) 28 (22), 41 (25), 57 (100), 80 (21), 81 (25), 123 (21), 212 (1).



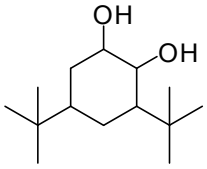
2,6-di-tert-butyl-4-methylcyclohexanone: (Table 2, entry 13) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) : δ = 0.94 (s, 18H), 0.95-0.99 (d, 3H), 1.07-1.32 (m, 2H), 1.86-2.00 (m, 1H), 2.02-2.12 (m, 2H), 2.14-2.18 (d, 1H), 2.18-2.22 (d, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.46, 27.61, 31.74, 32.98, 39.91, 60.51, 215.33; MS (E.I., 70 eV) m/z (rel. int.) 29 (13), 41 (42), 55 (24), 56 (17), 57 (100), 67 (12), 69 (27), 70 (24), 80 (17), 97 (43), 98 (45), 99 (18), 115 (65), 222 (1).



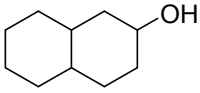
2-hydroxycyclohexane: (Table 2, entry 14) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 1.12-1.45 (m, 3H), 1.46-1.87 (m, 4H), 1.94 (s, 1H), 2.57 (s, 2H), 3.33 (s, 1H), 3.64-3.82 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.42, 24.29, 29.82, 32.81, 70.64, 75.73; MS (E.I., 70 eV) m/z (rel. int.) 29 (14), 41 (25), 42 (21), 44 (22), 69 (24), 70 (100), 83 (37), 98 (38), 116 (13).



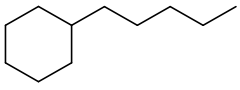
4-methoxycyclohexanol: (Table 2, entry 15) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.77-0.88 (t, 9H), 0.93-1.36 (m, 4H), 1.64-1.79 (s, 1H), 1.93-2.06 (d, 2H), 3.20-3.83 (m, 2H), 3.95 (s, 1H), 4.04 (s,1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.65, 21.43, 25.17, 27.48, 27.51, 27.56, 27.58, 32.94, 33.98, 39.57, 39.89, 46.24, 46.39, 60.46, 75.90, 76.00; MS (E.I., 70 eV) m/z (rel. int.) 29 (12), 41 (31), 57 (100), 80 (25), 81 (24), 82 (20), 95 (15), 123 (21), 138 (15), 155 (8), 193 (1).



1-hydroxyl-3,5-di-tert-butylcyclohexanol: (Table 2, entry 16) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.81-0.94 (d, 9H), 0.95-1.03 (d, 9H), 1.03-1.40 (m, 3H), 1.44-2.06 (m, 4H), 3.09-4.0 (m, 2H), 4.05 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.94, 21.65, 27.56, 27.65, 28.84, 29.25, 29.93, 32.50, 40.34, 41.59, 44.86, 45.98, 49.62, 70.53, 71.00, 71.83, 73.78; MS (E.I., 70 eV) m/z (rel. int.) 29 (13), 41 (35), 43 (17), 55 (20), 57 (100), 69 (22), 70 (29), 83 (22), 97 (98), 98 (26), 111 (32), 153 (33), 154 (49), 228 (1).

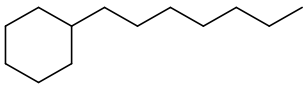


2-hydroxy-decahydronaphthalene: (Table 2, entry 17) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) δ = 0.70-2.12 (m, 16H), 3.30-4.00 (m, 1H), 4.10 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.07, 25.89, 30.55, 31.73, 32.01, 33.27, 34.72, 34.94, 35.42, 35.57, 35.84, 41.23, 42.35, 43.28, 66.99, 70.79, 71.65; MS (E.I., 70 eV) m/z (rel. int.) 29 (9), 41 (27), 55 (33), 67 (39), 79 (33), 81 (32), 93 (27), 94 (76), 95 (53), 107 (30), 121 (46), 136 (100), 154 (1).

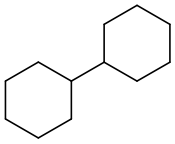


n-pentylcyclohexane: (Table 3, entry 1) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) δ = 0.77-0.98 (m, 5H), 1.13-1.17 (t, 3H), 1.17-1.46 (m, 8H), 1.46-1.92 (m, 5H), 2.54-2.65 (t, 1H); 13C NMR (100.6 MHz, $CDCl_3$): δ = 14.10, 22.75, 26.53, 26.59, 26.85, 32.29,

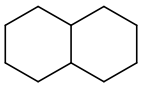
33.54, 37.55, 37.77; MS (E.I., 70 eV) m/z (rel. int.) 29 (9), 41 (26), 55 (58), 83 (100), 97 (6), 154 (33).



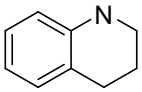
n-heptylcyclohexane: (Table 3, entry 2) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) δ = 0.78-0.94 (m, 5H), 1.07-1.38 (m,16H), 1.57-1.70 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.06, 22.68, 26.48, 26.80, 26.90, 29.38, 29.98, 31.93, 33.49, 37.56, 37.73; MS (E.I., 70 eV) m/z (rel. int.) 29 (8), 41 (25), 55 (51), 82 (80), 83 (100), 97 (7), 111 (2), 125 (1), 182 (24).



bicyclohexyl: (Table 3, entry 3) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$): δ = 0.79-1.47 (m, 12H), 1.48-2.20 (m, 10H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.90, 26.92, 30.21, 43.48; MS (E.I., 70 eV) m/z (rel. int.) 29 (4), 41 (20), 55 (39), 67 (42), 82 (100), 83 (47), 166 (34).



decahydronaphthale: (Table 3, entry 8) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) δ = 0.73-1.00 (m, 3H), 1.00-1.90 (m, 13H), 1.90-2.13 (d, 1H), 2.13-2.48 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.03, 22.60, 29.6; MS (E.I., 70 eV) m/z (rel. int.) 27 (7), 41 (32), 55 (21), 67 (70), 68 (59), 69 (28), 81 (46), 82 (51), 95 (47), 96 (55), 109 (15), 138 (100).



1,2,3,4-tetra-hydroquinoline: (Table 3, entry 9) (GC purity 98%); 1H NMR (400.1 MHz, $CDCl_3$) δ = 1.80-2.20 (m, 2H), 2.55-2.96 (t, 2H), 3.15-3.40 (t, 2H), 3.73 (s, 1H), 6.42-6.52 (d, 1H), 6.54-6.66 (t, 1H), 6.85-7.05 (t, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.23, 27.01, 42.12, 114.20, 116.96, 121.45, 126.73, 129.51, 144.81; MS (E.I., 70 eV) m/z (rel. int.) 51 (7), 65 (6), 77 (12), 78 (7), 91 (7), 104 (9), 117 (20), 118 (21), 130 (15), 132 (100), 133 (77).