Electronic Supplementary Information (ESI) for

A Ni–Mg–Al layered triple hydroxide-supported Pd catalyst for heterogeneous acceptorless dehydrogenative aromatization

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Experimental Section

Instruments and reagents

Gas chromatography (GC) analyses were performed on Shimadzu GC-2014 equipped with a flame ionization detector (FID) and an InertCap-5 or a TC-WAX capillary column. GC mass spectrometry (GC-MS) spectra were recorded on Shimadzu GCMS-QP2010 equipped with an InertCap-5 capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on JEOL JNM-ECA-500 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 495.1 and 124.5 MHz, respectively, using tetramethylsilane (TMS) as an internal reference ($\delta = 0$ ppm). ICP-AES analyses were performed on a Shimadzu ICPS-8100. TEM observations were performed on JEOL JEM-2010HC. XRD patterns were measured on a Rigaku SmartLab diffractometer (Cu$_{K\alpha}$, λ = 1.5405 Å, 45 kV–200 mA). The XPS measurements were carried out on JEOL JPS-9000 using Mg Kα radiation (hν = 1253.6 eV, 8 kV, 10 mA). The binding energies were calibrated by using the Au $4f_{7/2}$ signal at 84.0 eV. Pd/C (Lot. No. 217-024030, NE CHEMCAT), Mg$_3$Al$_1$_LDH (Mg$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O, BET surface area: 51 m^2 g^{-1}, Tomita Pharmaceutical Co., Ltd.), Al$_2$O$_3$ (BET surface area: 160 m^2 g^{-1}, Cat. No. KHS-24, Sumitomo Chemical), and TiO$_2$ (BET surface area: 316 m^2 g^{-1}, Cat. No. ST-01, Ishihara Sangyo Kaisya) were commercially available. Solvents and substrates were obtained from Kanto Chemical, TCI, Wako, or Aldrich (reagent grade), and purified prior to the use if required (See: *Purification of Laboratory Chemicals*, 3rd ed. (Eds.: D. D. Perrin, W. L. F. Armarego), Pergamon Press, Oxford, 1988.).

Preparation of M$_a$Mg$_b$Al$_c$_LTHs

Various M$_a$Mg$_b$Al$_c$_LTHs, such as Ni$_1$Mg$_2$Al$_1$_LTH, were typically prepared as follows. First, a 50 mL aqueous solution of Na$_2$CO$_3$ (0.5 M) was prepared, to which a 100 mL aqueous solution containing Ni(NO$_3$)$_2$ (0.2 M), Mg(NO$_3$)$_2$ (0.4 M), and Al(NO$_3$)$_3$ (0.2 M) was slowly added while maintaining pH at 10.0 ± 0.5 by adding a 3 M NaOH aqueous solution. Then the resulting slurry was vigorously stirred at room temperature for 24 h. The

solid was then filtered off, washed with water until the pH of the filtrate was less than 7, and dried in 80 °C oven for about 5 h. The similar procedure except for the types and amounts of metal precursors was applied to the preparation of other $M_aMg_bAl_c$_LTHs.

Preparation of $Pd(OH)_x/M_aMg_bAl_c$_LTHs

Various $Pd(OH)_x/M_aMg_bAl_c$_LTHs, such as $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH, were typically prepared as follows. First, $Ni_1Mg_2Al_1$_LTH (2.0 g) was added to a 60 mL aqueous solution of $PdCl_2$ (0.83 mM) and KCl (2 equiv with respect to $PdCl_2$, 1.67 mM). The mixture was vigorously stirred at room temperature for 15 min. Then the pH of the mixture was quickly adjusted to 10.0 by adding a 1 M NaOH aqueous solution. The resulting slurry was stirred vigorously at room temperature for 18 h. The solid was then filtered off, washed with water (3 L), and dried in vacuo to afford $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH. The similar procedure was applied to the preparation of other supported Pd hydroxide catalysts. The elemental contents of the catalysts, BET surface areas of the supports, and the average Pd nanoparticle sizes after the dehydrogenation are summarized in Table S1, ESI†.

Catalytic dehydrogenation

A typical procedure for the dehydrogenation: **0.5 mmol-scale**: Into a Schlenk tube (volume: ca. 20 mL) connected to a balloon partially filled with Ar gas, $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (20 mg, Pd: 1 mol %), 4-methylcyclohexanol (0.5 mmol), *N,N*-dimethylacetamide (DMA) (2.0 mL), and a Teflon-coated magnetic stir bar were successively placed, and the reaction mixture was vigorously stirred at 150 °C, in 1 atm of Ar. After the reaction was completed, an internal standard (hexadecane) was added to the reaction mixture, and the conversion of 4-methylcyclohexanol and the yield of 4-methylphenol were determined by GC analysis. The detection of hydrogen in the gas-phase was carried out with gas-phase MS analysis. The quantification of hydrogen gas formation was performed by measurement of the evolved gas volume. **10 mmol-scale**: Into a Schlenk tube (volume: ca. 50 mL) connected to a balloon partially filled with Ar gas, $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (100 mg, Pd: 0.25 mol %), 4-methylcyclohexanol (10 mmol), *N,N*-dimethylacetamide (DMA) (20 mL), and a Teflon-coated magnetic stir bar were successively placed, and the reaction mixture was vigorously stirred at 150 °C for 72 h, in 1 atm of Ar. After the reaction, the catalyst was filtered off (>90 % recovery). Then, EtOAc (30 mL) and *n*-hexane (10 mL) were added to the filtrate, which was washed with brine (20 mL) 5 times. The organic phase was dried with Na_2SO_4, and evaporated to remove solvents. The crude product was subjected to column chromatography on silica gel (using *n*-hexane/acetone as the eluent), giving the pure product. The product was identified by GC-MS and NMR (^{1}H and ^{13}C) analyses. The retrieved catalyst was washed with water and ethanol before being used for the reuse experiment.

Consecutive Diels-Alder/dehydrogenation reaction

Sn–W mixed oxide (50 mg), 2,3-dimethyl-1,3-butadiene (0.75 mmol), 1,4-naphthoquinone (0.5 mmol), dichloromethane (1 mL), and a Teflon-coated magnetic stir bar were successively placed in a Pyrex glass reactor (volume: ca. 20 mL). The reaction mixture was vigorously stirred at room temperature for 5 h. After the reaction completed, the catalyst was filtered off and the filtrate was moved to a Schlenk tube (volume: ca. 20 mL). Then dichloromethane was evaporated, and $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (100 mg, Pd: 5 mol %), styrene

(2.0 mmol), *N,N*-dimethylacetamide (DMA) (2.0 mL), and a Teflon-coated magnetic stir bar were successively placed to the Schlenk tube, and the reaction mixture was vigorously stirred at 130 °C, in 1 atm of Ar. After the reaction, the catalyst was filtered off, and DMA was evaporated. The crude product was subjected to column chromatography on silica gel (using *n*-hexane/acetone as the eluent), giving the pure product. The product was identified by GC-MS and NMR (^{1}H and ^{13}C) analyses.

Product data
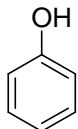
(CAS number: 108-95-2)

phenol: MS (EI): *m/z* (%) : 94 (100) [M^+], 66 (17), 65 (13), 55 (4).
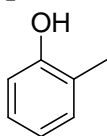
(CAS number: 95-48-7)

2-methylphenol: MS (EI): *m/z* (%) : 108 (100) [M^+], 107 (80), 90 (19), 89 (11), 80 (12), 79 (26), 77 (23).
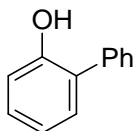
(CAS number: 90-43-7)

2-phenylphenol: MS (EI): *m/z* (%) : 170 (100) [M^+], 169 (66), 142 (13), 141 (36), 139 (12), 115 (30), 89 (8), 77 (4), 63 (6), 51 (4).
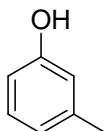
(CAS number: 108-39-4)

3-methylphenol: MS (EI): *m/z* (%) : 108 (100) [M^+], 107 (87), 90 (10), 80 (10), 79 (25), 77 (21).
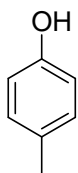
(CAS number: 106-44-5)

4-methylphenol: MS (EI): *m/z* (%) : 108 (90) [M^+], 107 (100), 80 (10), 79 (21), 77 (27), 53 (11), 51 (12).
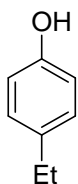
(CAS number: 123-07-9)

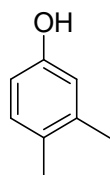**4-ethylphenol:** MS (EI): *m/z* (%) : 122 (40) [*M*⁺], 107 (100), 77 (14).
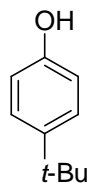
(CAS number: 98-54-4)

4-*t*-buthylphenol: MS (EI): *m/z* (%) : 150 (22) [*M*⁺], 136 (10), 135 (100), 107 (38), 95 (13), 91 (9), 77 (9), 65 (6), 51 (3).
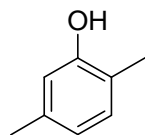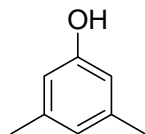

(CAS number: 95-87-4)

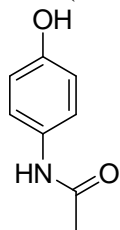**2,5-dimethylphenol:** MS (EI): *m/z* (%) : 122 (100) [*M*⁺], 121 (36), 107 (90), 91 (16), 79 (15), 77 (22).

(CAS number: 95-65-8)

3,4-dimethylphenol: MS (EI): *m/z* (%) : 122 (86) [*M*⁺], 121 (42), 107 (100), 91 (12), 77 (18).

(CAS number: 108-68-9)

3,5-dimethylphenol: ¹H NMR (495.1 MHz, CDCl₃, TMS): δ 2.26 (s, 6H), 4.69 (brs, 1H), 6.46 (s, 2H), 6.58 (s, 1H). ¹³C{¹H} NMR (124.5 MHz, CDCl₃, TMS): δ 21.39, 113.14, 122.68, 139.68, 155.50. MS (EI): *m/z* (%) : 122 (100) [*M*⁺], 121 (34), 107 (76), 91 (9), 77 (14).

(CAS number: 103-90-2)

4-acetamidophenol: MS (EI): *m/z* (%) : 151 (31) [*M*⁺], 109 (100), 108 (14), 81 (19), 80 (28), 53 (17), 52 (12).
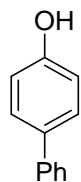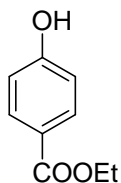

(CAS number: 92-69-3)

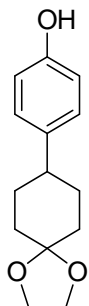**4-phenylphenol:** MS (EI): *m/z* (%) : 171 (13), 170 (100) [*M*⁺], 141 (25), 115 (18).
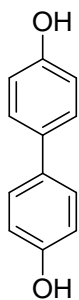
(CAS number: 92-88-6)

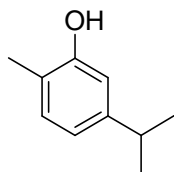**4,4'-dihydroxybiphenyl:** MS (EI): *m/z* (%) : 187 (13), 186 (100) [M^+], 157 (12), 128 (6), 93 (8).

(CAS number: 120-47-8)

4-(ethoxycarbonyl)phenol: MS (EI): *m/z* (%) : 166 (24) [M^+], 138 (26), 122 (11), 121 (100), 93 (14), 65 (8).
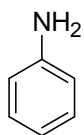

(CAS number: 142256-87-9)

4-(1,4-dioxaspiro[4.5]dec-8-yl)phenol: MS (EI): *m/z* (%) : 234 (11) [M^+], 133 (2), 120 (18), 107 (3), 100 (6), 99 (100), 91 (2), 87 (9), 86 (7), 77 (1), 55 (5).
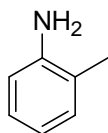

(CAS number: 499-75-2)

5-isopropyl-2-methylphenol: MS (EI): *m/z* (%) : 150 (36) [M^+], 136 (10), 135 (100), 115 (8), 107 (12), 91 (14), 77 (6).
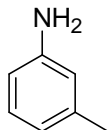

(CAS number: 62-53-3)

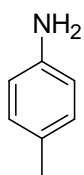**aniline:** MS (EI): *m/z* (%) : 93 (100) [M^+], 92 (11), 66 (38), 65 (16).

NH₂ structure

(CAS number: 95-53-4)

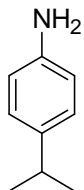**2-methylaniline:** MS (EI): *m/z* (%) : 107 (83) [*M*⁺], 106 (100), 79 (13), 77 (14).

(CAS number: 108-44-1)

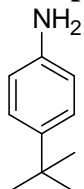**3-methylaniline:** MS (EI): *m/z* (%) : 107 (100) [*M*⁺], 106 (98), 79 (16), 77 (15).

(CAS number: 106-49-0)

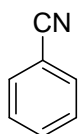**4-methylaniline:** MS (EI): *m/z* (%) : 107 (76) [*M*⁺], 106 (100), 77 (11).

(CAS number: 99-88-7)

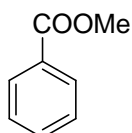**4-isopropylaniline:** MS (EI): *m/z* (%) : 135 (39) [*M*⁺], 120 (100), 91 (6), 77 (4).

(CAS number: 769-92-6)

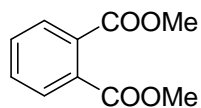**4-*t*-butylaniline:** MS (EI): *m/z* (%) : 149 (30) [*M*⁺], 135 (10), 134 (100), 106 (18), 94 (13), 91 (4), 77 (4).

(CAS number: 100-47-0)

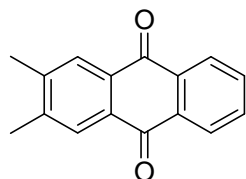**benzonitrile:** MS (EI): *m/z* (%) : 103 (100) [*M*⁺], 76 (28).

(CAS number: 93-58-3)

methylbenzoate: MS (EI): *m/z* (%) : 136 (47) [*M*⁺], 105 (100), 77 (44), 51 (11).

(CAS number: 131-11-3)

dimethylphthalate: MS (EI): m/z (%) : 194 (9) [M^+], 164 (10), 163 (100), 138 (16), 137 (10), 79 (14), 77 (15).


(CAS number: 6531-35-7)

2,3-dimethylanthraquinone: ^{1}H NMR (495.1 MHz, CDCl$_3$, TMS): δ 2.42 (s, 6H), 7.75−7.78 (m, 2H), 8.02 (s, 2H), 8.25−8.29 (m, 2H). ^{13}C{^{1}H} NMR (124.5 MHz, CDCl$_3$, TMS): δ 20.37, 127.17, 128.27, 131.57, 133.74, 133.96, 144.19, 183.41. MS (EI): m/z (%) : 237 (17), 236 (100) [M^+], 235 (15), 221 (17), 208 (19), 193 (17), 178 (11), 165 (26).

Table S1 Characterization data for various supported Pd hydroxide catalysts

| Entry	Catalysts	Pd content (mmol/g)	Ratios of metals in the supports	BET surface area of the supports (m^2/g)	Average Pd particle sizes after the dehydrogenation (nm), $N = 200$
1	Pd(OH)$_x$/Mg$_3$Al$_1$_LDH	0.25	Mg:Al = 3.4:1	51	3.3 ($\sigma = 0.8$)
2	Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH	0.25	Ni:Mg:Al = 1.0:2.3:1.1	86	2.7 ($\sigma = 0.6$)
3	Pd(OH)$_x$/Co$_1$Mg$_2$Al$_1$_LTH	0.25	Co:Mg:Al = 1.0:2.1:1.0	35	2.8 ($\sigma = 0.7$)
4	Pd(OH)$_x$/Fe$_1$Mg$_2$Al$_1$_LTH	0.29	Fe:Mg:Al = 1.0:2.1:1.0	209	2.3 ($\sigma = 0.9$)
5	Pd(OH)$_x$/Ni$_{1.5}$Mg$_{1.5}$Al$_1$_LTH	0.23	Ni:Mg:Al = 1.5:1.3:1.0	68	2.3 ($\sigma = 0.9$)
6	Pd(OH)$_x$/Ni$_2$Mg$_1$Al$_1$_LTH	0.25	Ni:Mg:Al = 2.0:0.6:1.0	62	2.8 ($\sigma = 0.8$)
7	Pd(OH)$_x$/Ni$_3$Al$_1$_LDH	0.24	Ni: Al = 3.1:1	106	2.1 ($\sigma = 0.7$)
8	Pd(OH)$_x$/Al$_2$O$_3$	0.24	–	160	3.6 ($\sigma = 1.4$)
9	Pd(OH)$_x$/TiO$_2$	0.25	–	316	3.0 ($\sigma = 0.8$)
10	Pd/C	–	–	–	4.3 ($\sigma = 1.1$)

Table S2 Acceptorless dehydrogenation of 4-methylcyclohexanol (**1a**) to 4-methylphenol (**2a**) with various catalysts[a]
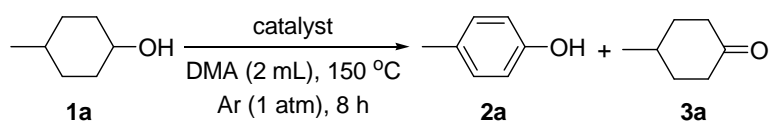
Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	**3a**
1	Pd(OH)$_x$/Mg$_3$Al$_1$_LDH	6	nd	3
2	Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH	97	94	3
3	Pd(OH)$_x$/Co$_1$Mg$_2$Al$_1$_LTH	91	72	18
4	Pd(OH)$_x$/Fe$_1$Mg$_2$Al$_1$_LTH	74	16	54
5	Pd(OH)$_x$/Ni$_{1.5}$Mg$_{1.5}$Al$_1$_LTH	98	94	4
6	Pd(OH)$_x$/Ni$_2$Mg$_1$Al$_1$_LTH	97	93	4
7	Pd(OH)$_x$/Ni$_3$Al$_1$_LDH	98	94	3
8	Pd(OH)$_x$/Al$_2$O$_3$	1	nd	1
9	Pd(OH)$_x$/TiO$_2$	12	9	2
10	Pd/C	<1	nd	nd
11	Ni$_1$Mg$_2$Al$_1$_LTH	1	nd	1

[a]Reaction conditions: **1a** (0.5 mmol), catalyst (Pd: 1 mol%), DMA (2 mL), 150 °C, Ar (1 atm), 8 h. Conversions and yields were determined by GC analysis using *n*-hexadecane as the internal standard. DMA = *N,N*-dimethylacetamide. nd = not detected.

Table S3 Solvent effect on acceptorless dehydrogenation of 4-methylcyclohexanol (**1a**) to 4-methylphenol (**2a**)[a]
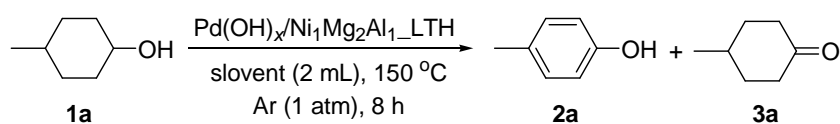
| Entry	Solvent	Conv. (%)	Yield (%)	
			2a	**3a**
1	DMA	97	94	3
2	DMF	5	nd	nd
3	DMSO	7	nd	nd
4	*o*-dichlorobenzene	35	nd	8
5	mesitylene	83	23	47
6	diglyme	77	49	19

[a]Reaction conditions: **1a** (0.5 mmol), catalyst (Pd: 1 mol%), solvent (2 mL), 150 °C, Ar (1 atm), 8 h. Conversions and yields were determined by GC analysis using *n*-hexadecane as the internal standard. DMA = *N,N*-dimethylacetamide, DMF = *N,N*-dimethylformamide. DMSO = dimethylsulfoxide. diglyme = diethylene glycol dimethyl ether. nd = not detected.

Table S4 Acceptorless dehydrogenation of 4-methylcyclohexanone (**3a**) to 4-methylphenol (**2a**) with various catalysts[a]
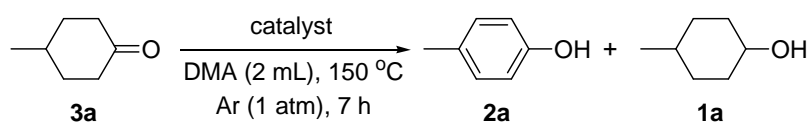

Entry	Catalyst	Conv. (%)	Yield (%)	
			2a	**1a**
1	Pd(OH)$_x$/Mg$_3$Al$_1$_LDH	94	93	1
2	Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH	98	96	1
3	Pd(OH)$_x$/Co$_1$Mg$_2$Al$_1$_LTH	72	61	11
4	Pd(OH)$_x$/Fe$_1$Mg$_2$Al$_1$_LTH	41	27	4
5	Pd(OH)$_x$/Ni$_{1.5}$Mg$_{1.5}$Al$_1$_LTH	98	91	1
6	Pd(OH)$_x$/Ni$_2$Mg$_1$Al$_1$_LTH	94	88	4
7	Pd(OH)$_x$/Ni$_3$Al$_1$_LDH	94	89	4
8	Pd(OH)$_x$/Al$_2$O$_3$	60	50	nd
9	Pd(OH)$_x$/TiO$_2$	50	39	nd
10	Pd/C	25	10	nd
11	Ni$_1$Mg$_2$Al$_1$_LTH	5	nd	nd

[a]Reaction conditions: **1a** (0.5 mmol), catalyst (Pd: 1 mol%), DMA (2 mL), 150 °C, Ar (1 atm), 7 h. Conversions and yields were determined by GC analysis using *n*-hexadecane as the internal standard. DMA = *N,N*-dimethylacetamide. nd = not detected.
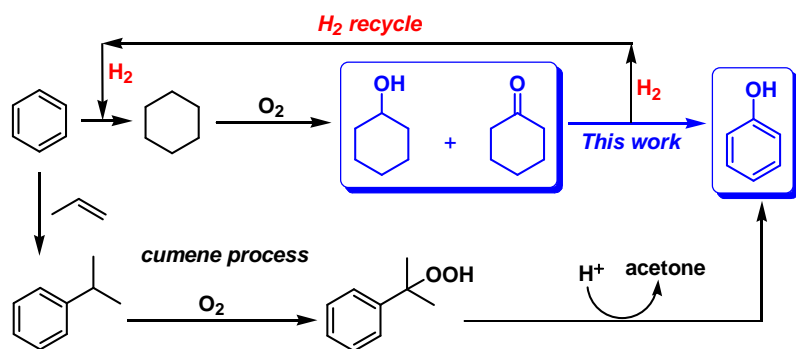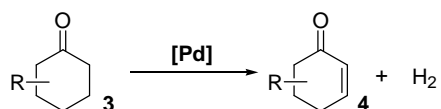
Scheme S1 Synthesis of phenol.

91%
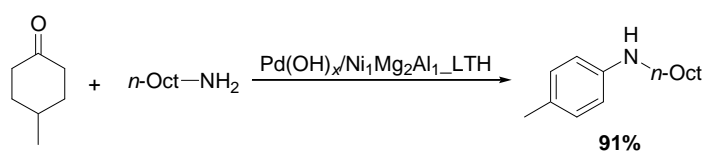
Scheme S2 Synthesis of 4-methyl-*N*-octylaniline from 4-methyl cyclohexanone (**3a**) and *n*-octylamine. Reaction conditions: **3a** (1.0 mmol), *n*-octylamine (0.5 mmol), Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH (1 mol%), DMA (2 mL), 150 ℃, Ar (1 atm), 20 h. Yield was determined by GC analysis using *n*-hexadecane as the internal standard.
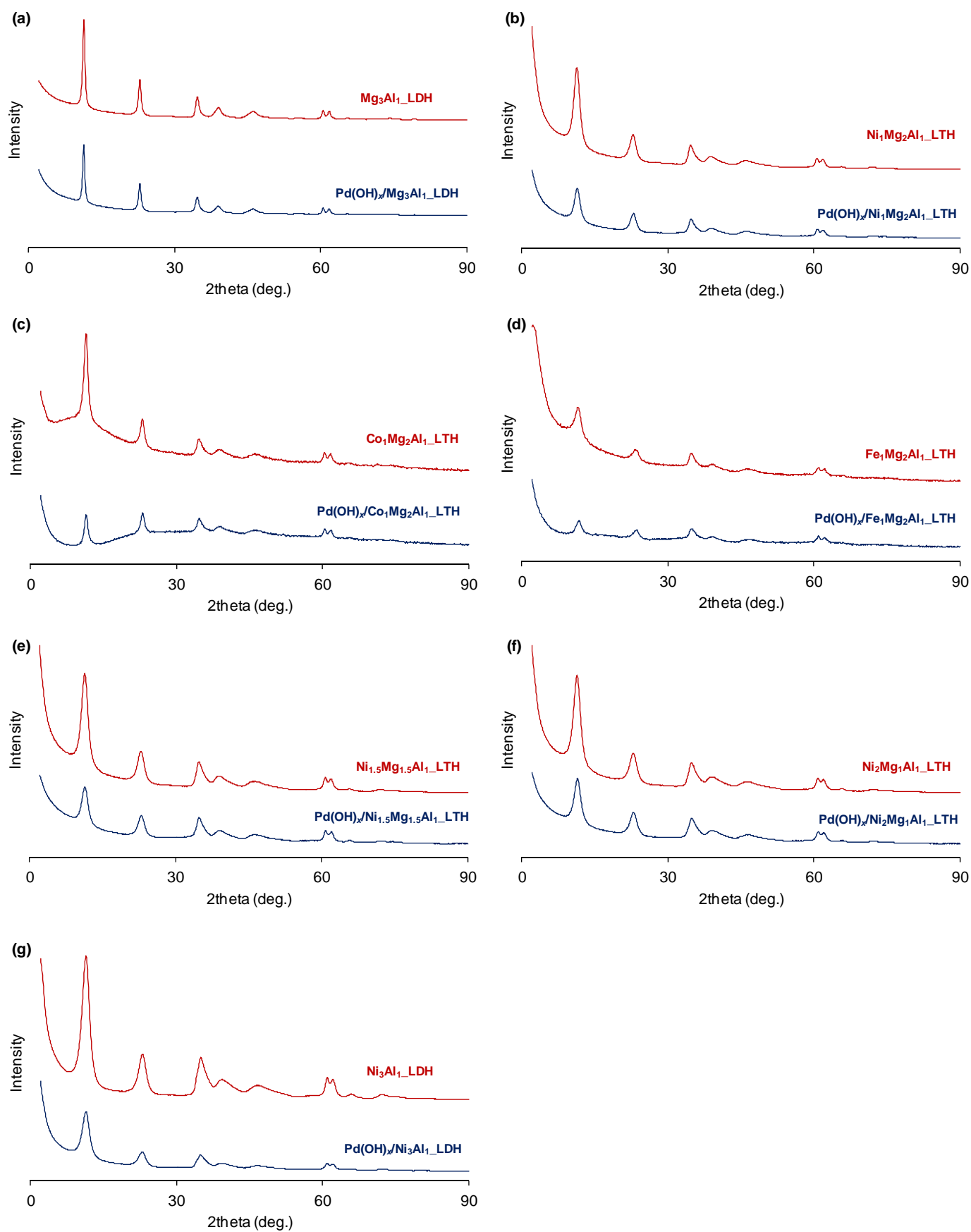
(a) cyclohexanones to cyclohexenones
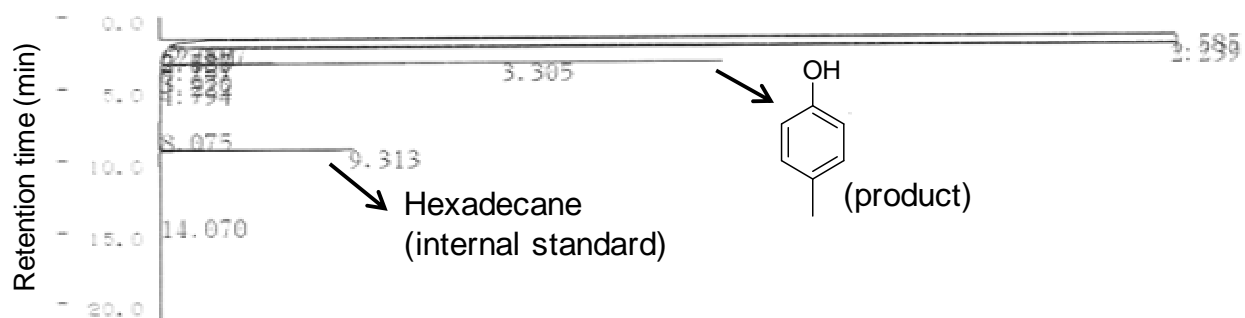

(b) cyclohexenones to phenols
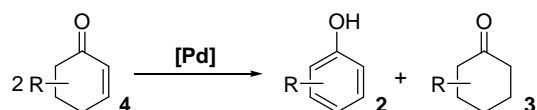
Scheme S3 Reaction paths for the Pd(OH)$_x$/Mg$_3$Al$_1$_LDH-catalyzed dehydrogenation of **3** to **2**.
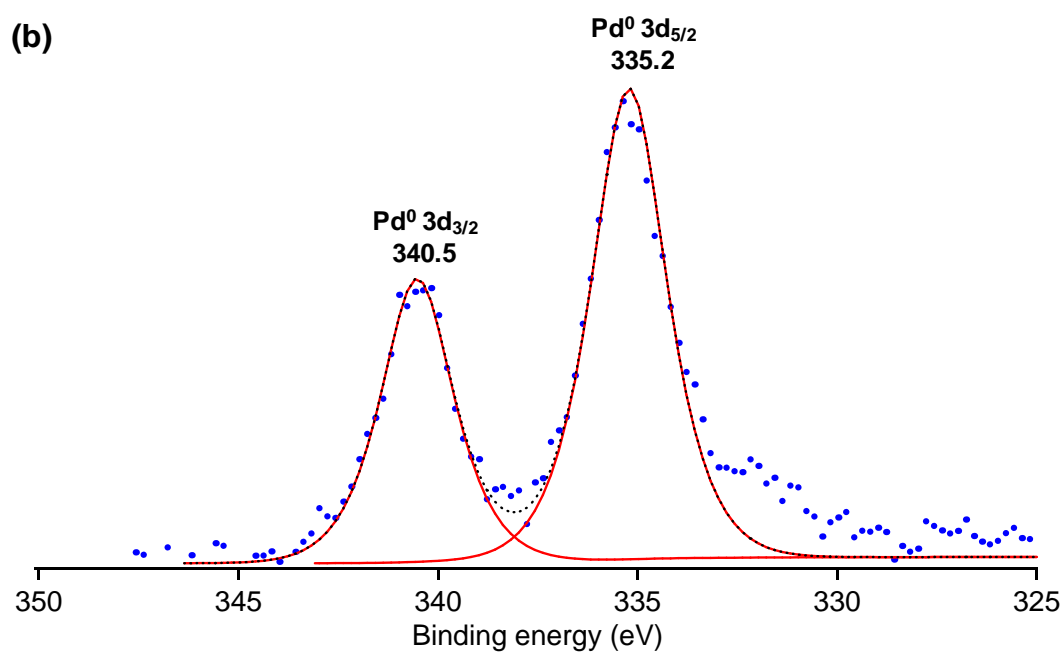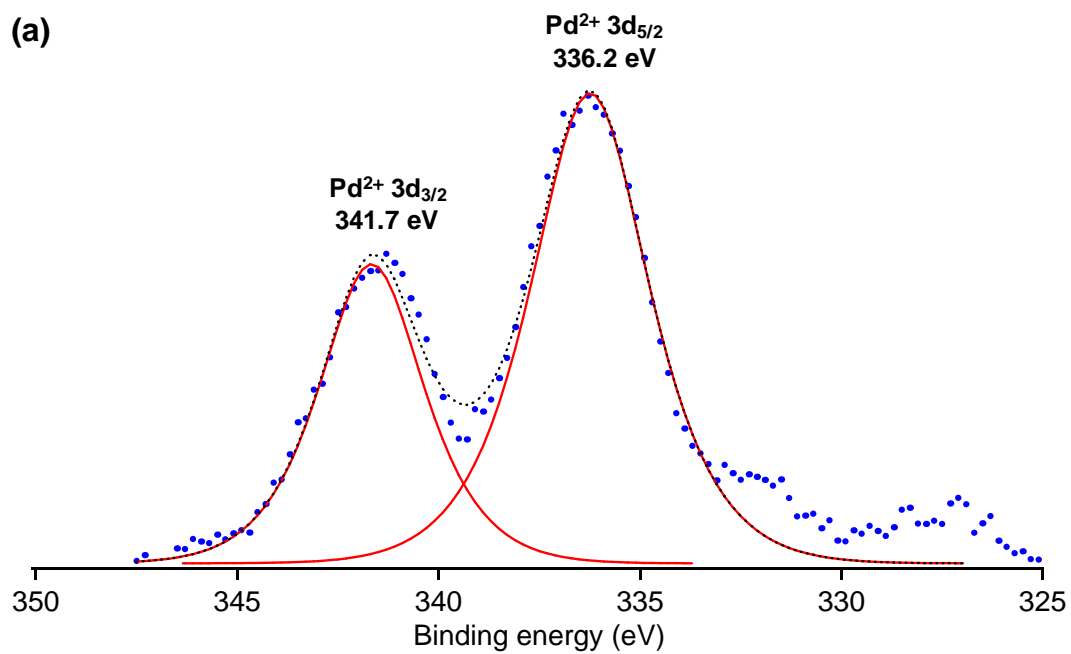
Fig. S1 XRD patterns of various M$_a$Mg$_b$Al$_c$_LTHs and Pd(OH)$_x$/M$_a$Mg$_b$Al$_c$_LTHs.

Fig. S2 The reactor used in this study. The balloon was partially filled with Ar gas.

Fig. S3 GC chart of the reaction solution after the dehydrogenation of **1a** to **2a** by Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH for 10 h. Reaction conditions are shown in Table S2.

(a)

Pd^{2+} 3d$_{5/2}$
336.2 eV

Pd^{2+} 3d$_{3/2}$
341.7 eV

Binding energy (eV)

(b)

Pd^{0} 3d$_{5/2}$
335.2

Pd^{0} 3d$_{3/2}$
340.5

Binding energy (eV)

Fig. S4 XPS spectra of the Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH catalyst around Pd 3d components: (a) the freshly prepared catalyst; (b) after using the catalyst for the reaction of **1a** for 1 h. The blue dots indicate the data points. The red solid and black broken lines indicate the deconvoluted signals and the sum of the deconvoluted signals, respectively.

(a)

(b)
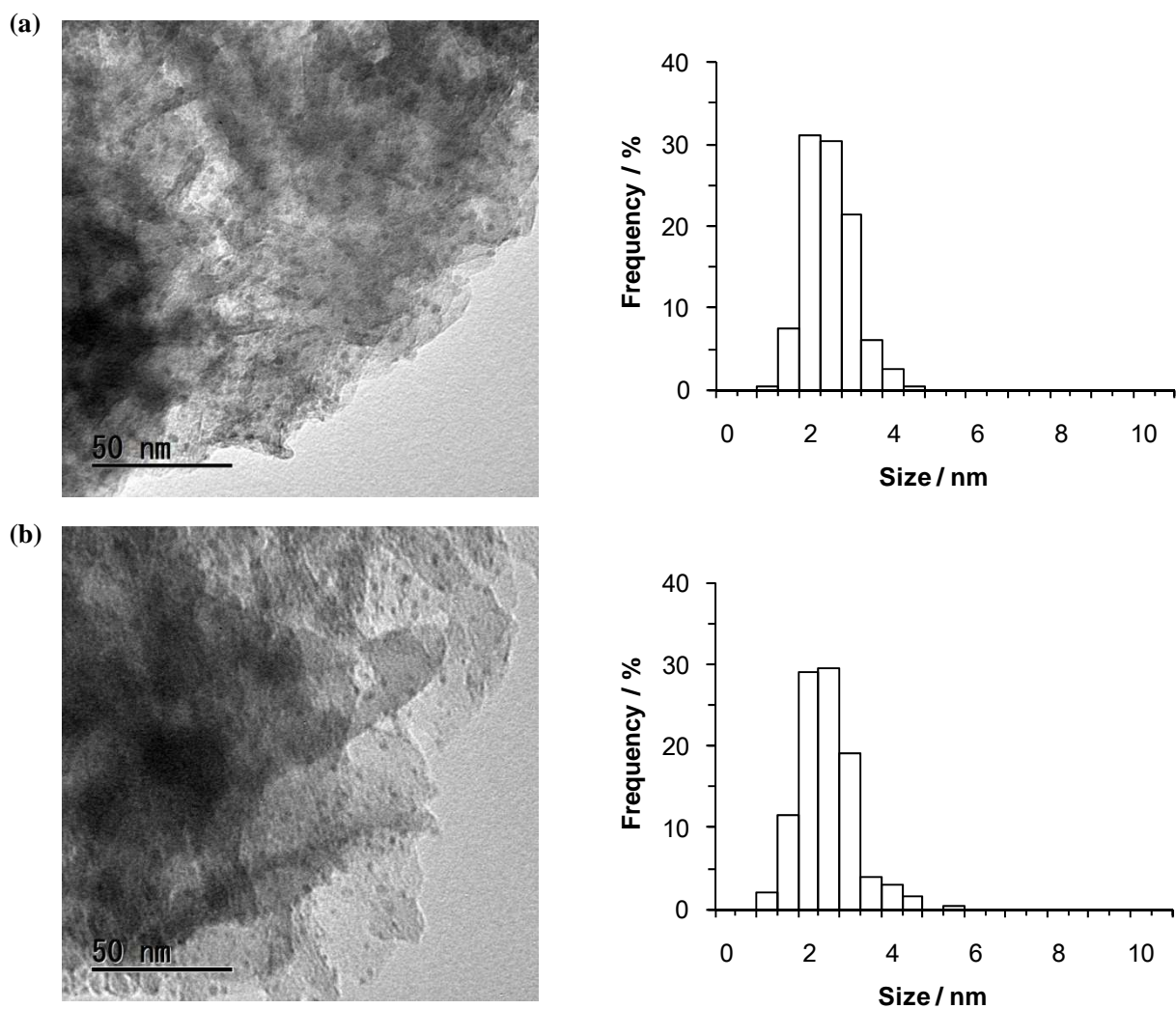
Fig. S5 TEM images and Pd nanoparticle size distributions of (a) the Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH catalyst after the first use (average: 2.7 nm, σ: 0.6 nm) and (b) Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH after the 5th reuse experiment (average: 2.6 nm, σ: 0.7 nm). The size distributions were determined using 200 particles.
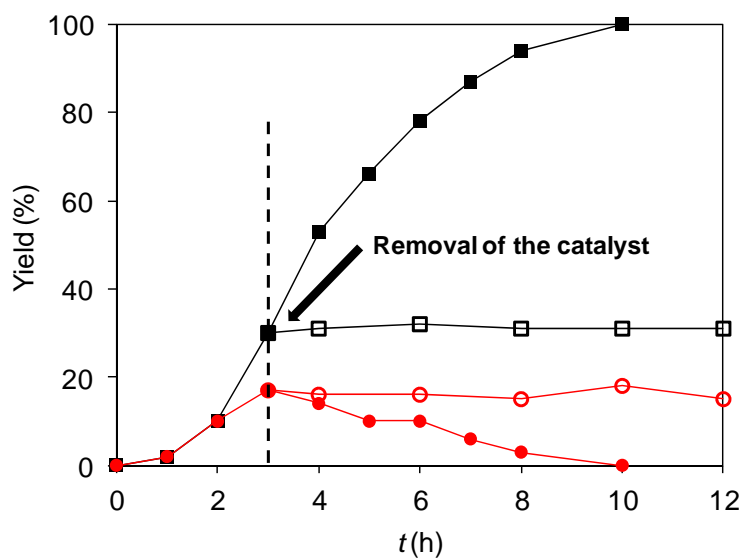
**Fig. S6** Effect of removal of the Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH catalyst on the dehydrogenation of **1a**. The reaction conditions were the same as those described in Table 1. GC yields using *n*-hexadecane as the internal standard are shown here. Closed squares and circles indicate the yields of **2a** and **3a**, respectively, without removal of the catalyst; open squares and circles indicate the yields of **2a** and **3a**, respectively, after removal of the catalyst.
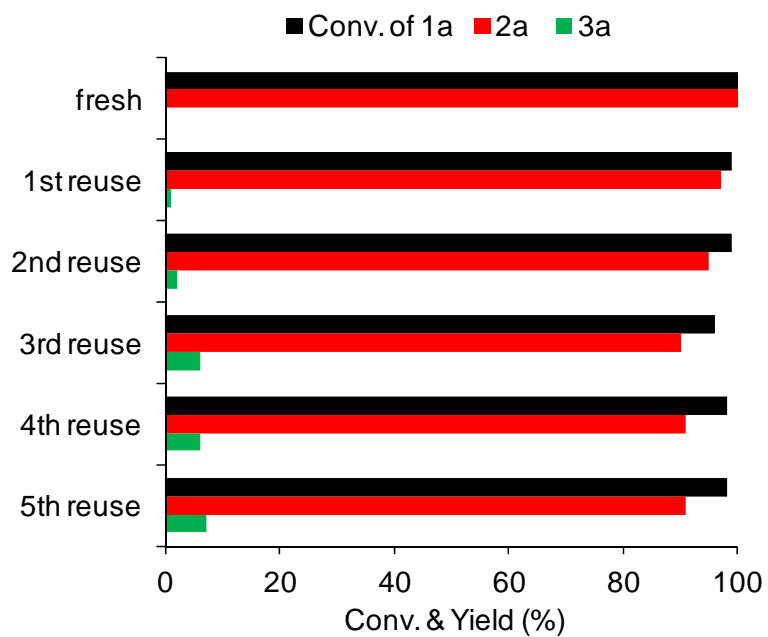
Fig. S7 Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH reuse experiments. The reaction conditions were the same as those described in Table 1. Conversions and yields were determined by GC analysis using *n*-hexadecane as the internal standard. The yields of **2a** for the initial, 1st reuse, 2nd reuse, 3rd reuse, 4th reuse, and 5th reuse experiments were >99%, 97%, 95%, 90%, 91%, and 91%, respectively.
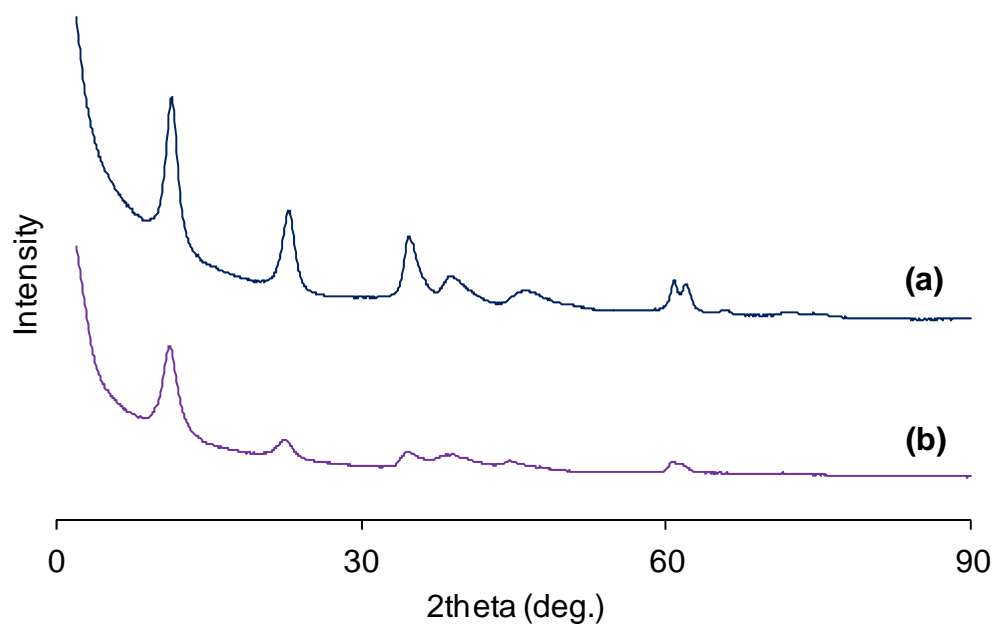
Fig. S8 XRD patterns of (a) the fresh Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH catalyst and (b) Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH after the 5th reuse experiment.
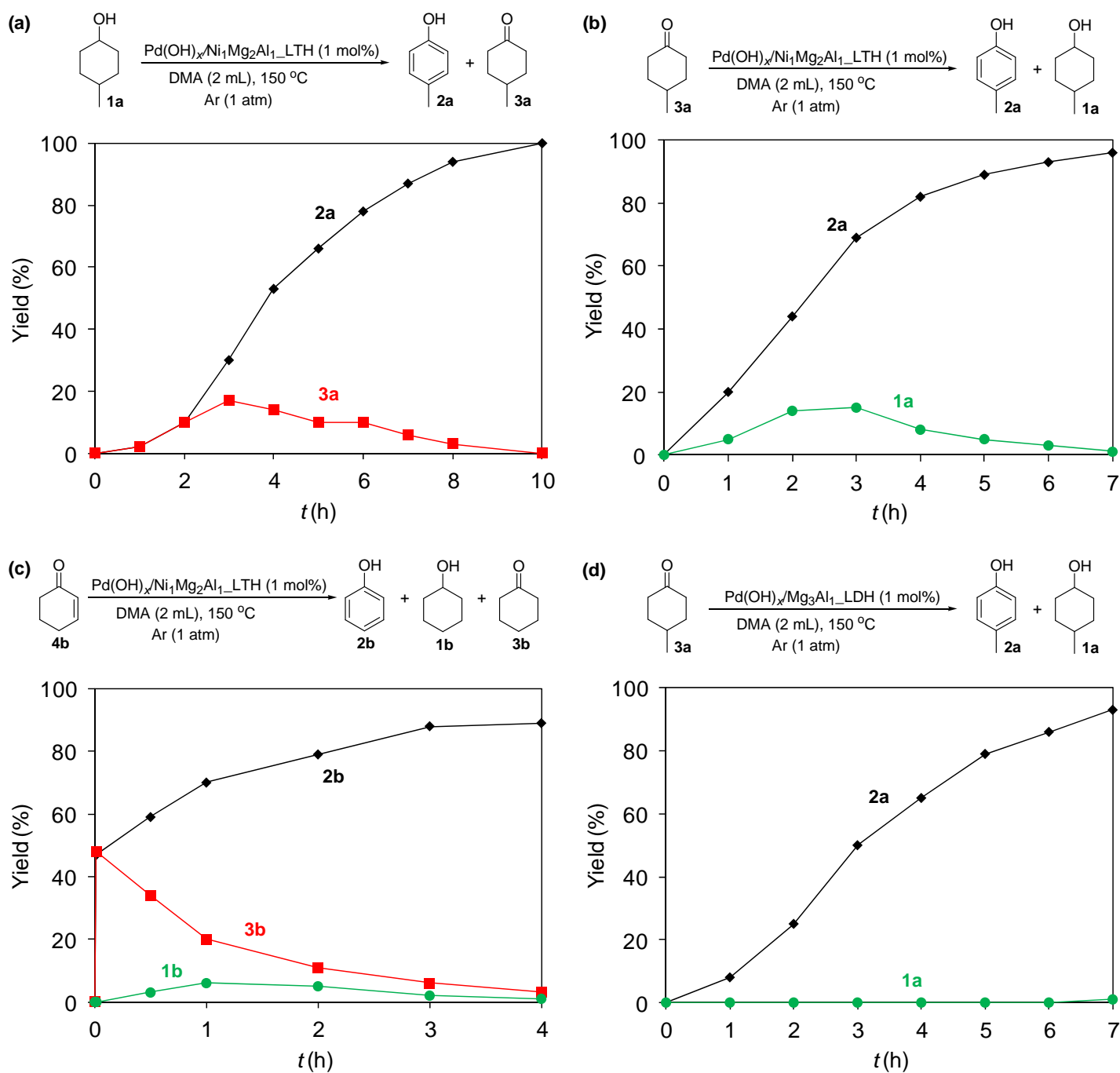
Fig. S9 Reaction profiles of dehydrogenations with Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH starting from (a)**1a**, (b) **3a**, (c) **4b**, and (d) **4b** using Pd(OH)$_x$/Mg$_3$Al$_1$_LTH as the catalyst. Reaction conditions: substrates (0.5 mmol), catalysts (Pd: 1 mol%), DMA (2 mL), 150 °C, Ar (1 atm). GC yields using *n*-hexadecane as the internal standard are shown here.
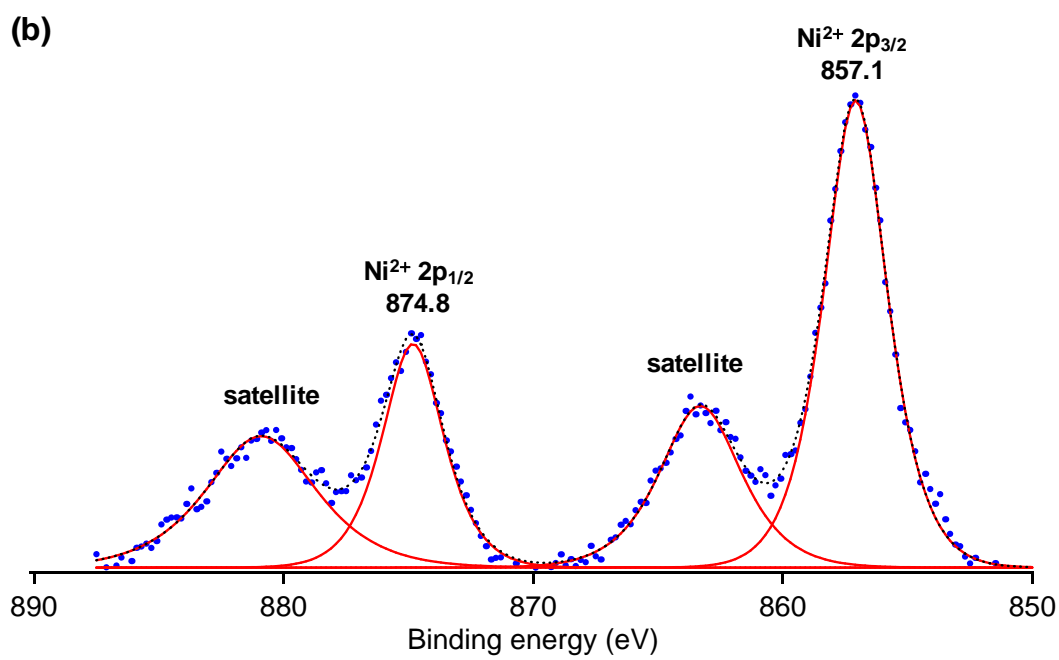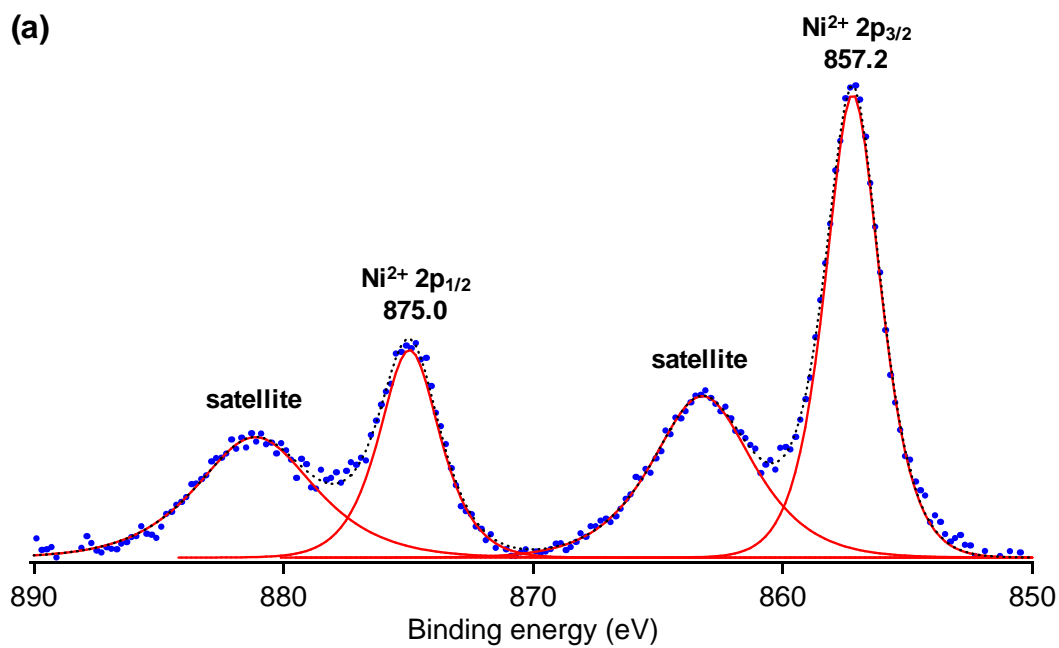
Fig. S10 XPS spectra of the Pd(OH)$_x$/Ni$_1$Mg$_2$Al$_1$_LTH catalyst around Ni 2p components: (a) the fresh catalyst; (b) after 8 h of the dehydrogenation. The blue dots indicate the data points. The red solid and black broken lines indicate the deconvoluted signals and the sum of the deconvoluted signals, respectively.