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

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In the presence of a Ni–Mg–Al layered triple hydroxide-supported Pd catalyst, acceptorless dehydrogenative aromatization of a wide range of cyclohexanols/cyclohexanones and cyclohexylamines efficiently proceeded to give the corresponding phenols and anilines, respectively, in moderate to high yields with liberation of molecular hydrogen.

Dehydrogenative aromatization has recently emerged as an attractive method for the synthesis of various arenes from ubiquitous saturated six-membered carbocyclic compounds.[1] For example, it has been reported that phenols,[2] substituted anilines,[3] and aryl ethers[4] could be synthesized by employing Pd-catalyzed dehydrogenative aromatization of cyclohexanones or cyclohexylimines as the key reactions. Generally, these reactions require stoichiometric amounts of oxidants (hydrogen acceptor), such as 1-octene, styrene, *tert*-butyl peroxybenzoate, 2,3-dichloro-5,6-dicyanobenzoquinone, and molecular iodine, or molecular oxygen.[1–4] On the other hand, acceptorless dehydrogenative aromatization, which generates molecular hydrogen as the sole co-product, represents a more environmentally friendly and economical method for the synthesis of arenes because of its high atom efficiency, but has been much less studied until now.

Phenols and anilines are very important commodity chemicals and also key structural moieties in numerous pharmaceuticals, agrochemicals, electronic materials, plastics, and resins.[5] In bulk chemical industry, millions tons of phenol are annually produced by the well known cumene process.[6] However, the cumene process has several shortcomings, such as the formation of acetone co-product and the involvement of explosive cumene hydroperoxide (Scheme S1, ESI†).[6] The acceptorless dehydrogenative aromatization of a cyclohexanol/cyclohexanone mixture, namely KA oil, should be an attractive alternative to produce phenol from benzene, because KA oil is industrially produced by the well established two-step procedure involving hydrogenation of benzene to cyclohexane followed by aerobic auto-oxidation of cyclohexane (Scheme S1, ESI†).[7] In addition, molecular hydrogen produced in the dehydrogenative aromatization step is possibly recycled to the hydrogenation of benzene (Scheme S1, ESI†). Thus, overall aerobic oxidation of benzene to phenol should be formally achieved by these sequential processes. In fine chemical industry, numerous prominent synthetic methods for substituted phenols and anilines have been developed, such as electrophilic substitution and cross-coupling reactions.[8] The acceptorless dehydrogenative aromatization of cyclohexanols/cyclohexanones and cyclohexylamines can be especially useful for the synthesis of substituted phenols and anilines, respectively, because the easy availability of cyclohexanols/cyclohexanones and cyclohexylamines with various substituted patterns on cyclohexyl rings through several established chemical transformations.

Recently, homogeneous Ir- and heterogeneous Pd nanoparticle-catalyzed acceptorless dehydrogenative aromatization of cyclohexanones to phenols have been developed.[9] However, they have several drawbacks, such as the need of rather sophisticated ligands and/or base additives and difficulties in reuse of the catalysts. Moreover, to the best of our knowledge, there are virtually no useful catalytic systems for the acceptorless dehydrogenation of cyclohexanols to phenols and cyclohexylamines to anilines. Therefore, the development of easily separable and reusable heterogeneous catalysts for the acceptorless dehydrogenative aromatization under ligand- and additive-free conditions is highly desirable from the practical, economical, and environmental points of view.

Quite recently, we have reported that the Mg–Al layered double hydroxide (LDH)-supported Au–Pd alloy nanoparticles could efficiently promote the oxidation of cyclohexanols/cyclohexanones to phenols using molecular oxygen as the terminal oxidant.[2d] In a continuation of our interest in the layered hydroxide-supported metal catalysts[10] for dehydrogenation catalysis, herein, we report for the first time that a Ni–Mg–Al layered triple hydroxide (LTH)-

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[b] *Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.*

† Electronic Supplementary Information (ESI) available: Experimental details, spectral data of products, Tables S1–S4, Figs. S1–S10, and Schemes S1–S3. See DOI: 10.1039/x0xx00000x

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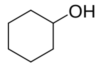
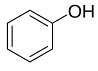
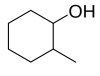
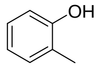
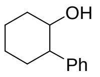
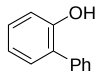
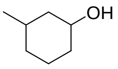
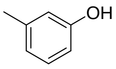
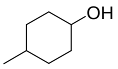
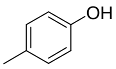
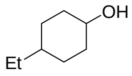
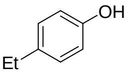
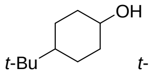
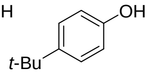
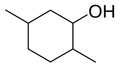
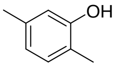
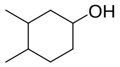
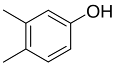
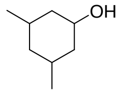
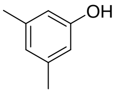
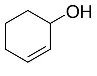
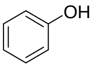
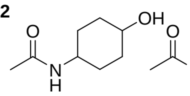
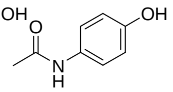
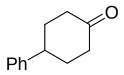
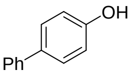
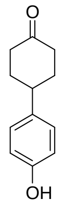
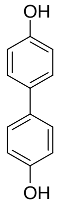
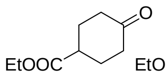
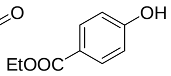
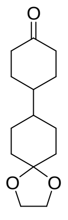
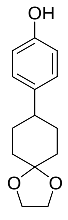
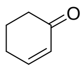
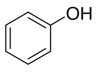
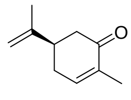
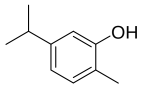
supported Pd catalyst can efficiently promote the ligand- and additive-free acceptorless dehydrogenative aromatization of cyclohexanols/cyclohexanones to phenols and cyclohexylamines to anilines via a consecutive triple-dehydrogenation process. The catalysis was intrinsically heterogeneous, and the catalyst could be reused several times with keeping its catalytic performance.

Initially, we prepared various M–Mg–Al layered triple hydroxides (M = Ni, Co, Fe, $M_aMg_bAl_c$_LTH, M/Mg/Al = *a*/*b*/*c*) by the simple co-precipitation method. Then, $M_aMg_bAl_c$_LTH supported Pd hydroxide catalysts were prepared by deposition-precipitation method ($Pd(OH)_x/M_aMg_bAl_c$_LTH, see the Experimental section in ESI† for their preparation and characterization, Table S1 and Fig. S1, ESI†).[11] These catalysts were directly applied to the acceptorless dehydrogenative aromatization of 4-methylcyclohexanol (**1a**) to 4-methylphenol (**2a**) in *N,N*-dimethylacetamide (DMA) at 150 °C under 1 atm of Ar (Tables S2 and S3, Figs. S2 and S3, ESI†).[12] Although $Pd(OH)_x/Mg_3Al_1$_LDH showed almost no catalytic activity for the dehydrogenation (Table S2, entry 1, ESI†), $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH could efficiently promote the reaction and gave the desired **2a** in 94% yield (Table S2, entry 2, ESI†); we also confirmed that *ca*. three equivalents of molecular hydrogen with respect to **1a** were formed during the reaction. The color of the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst was changed from initial light brown to black within less than 1 min. The XPS spectrum of the freshly prepared $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst showed the binding energies of Pd $3d_{3/2}$ and $3d_{5/2}$ at 341.7 eV and 336.2 eV, respectively, which indicate that the oxidation state of the Pd species is +2 (Fig. S4a, ESI†). After the catalyst was utilized for the reaction of **1a** for 1 h, the binding energies of Pd $3d_{3/2}$ and $3d_{5/2}$ were changed to 340.5 eV and 335.2 eV, respectively (Fig. S4b, ESI†). These results suggest that the Pd^{2+} species were reduced by the substrate to Pd^0 species during the reaction. In addition, the transmission electron microscope (TEM) analysis of $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH after the reaction revealed that Pd^0 nanoparticles were formed on the surface of $Ni_1Mg_2Al_1$_LTH (average size of the nanoparticles = 2.7 nm, Fig. S5a, ESI†). The $Ni_1Mg_2Al_1$_LTH support alone did not promote the dehydrogenation (Table S2, entry 11, ESI†). Although the dehydrogenative aromatization also proceeded in the presence of $Pd(OH)_x/Co_1Mg_2Al_1$_LTH and $Pd(OH)_x/Fe_1Mg_2Al_1$_LTH (Table S2, entries 3 and 4, ESI†), the performance of these catalysts were inferior to that of $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH. The effect of the Ni/Mg/Al molar ratio of the support was not significant (Table S2, entries 5–7, ESI†). $Pd(OH)_x/Al_2O_3$, $Pd(OH)_x/TiO_2$, and Pd/C were not effective for the dehydrogenation (Table S2, entries 8–10, ESI†).

To verify whether the observed catalysis for the dehydrogenative aromatization was intrinsically heterogeneous or not, the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst was removed by hot filtration when the conversion of **1a** was about 50%, and then the reaction was carried out under the same reaction conditions with the filtrate. By the removal of the catalyst, the reaction was completely stopped (Fig. S6, ESI†). Furthermore, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the filtrate revealed that Pd species were not present in the filtrate (below detection limit, Pd: <0.2%). These experimental results suggest that the catalysis was not derived from leached Pd species, and the observed catalysis was intrinsically heterogeneous.[13] The $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst could be easily retrieved from the reaction mixture by simple filtration with >90% recovery, and could be reused at least five times for the reaction of **1a** with keeping its high catalytic performance (Figs. S5, S7, and S8 ESI†).[14]

With the optimized reaction conditions in hand, we next investigated the substrate scope of the present acceptorless dehydrogenative aromatization using $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH as

Table 1 Substrate scope for the acceptorless dehydrogenation of cyclohexanols/cyclohexanones to phenols with $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH^a

Entry	Substrate	Product
1		 12 h, 89%
2		 12 h, 92%
3		 8 h, 76%
4		 12 h, 95%
5		 10 h, >99%
6		 10 h, 97%
7		 12 h, 93%
8		 10 h, 94%
9		 8 h, 97%
10		 0.5 mmol scale: 8 h, 97% 10 mmol scale: 72 h, 88(79)%^{b}
11		 10 h, 86%
12		 16 h, 83%
13		 2 h, 98%
14		 5 h, 87%
15		 7 h, 52%
16		 10 h, 90%
17		 4 h, 89%
18		 0.5 h, >99%

^{a}Reaction conditions: Substrate (0.5 mmol), $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (Pd: 1 mol%), DMA (2 mL), 150 °C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as the internal standard. ^{b}Substrate (10 mmol), $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (Pd: 0.25 mol%), DMA (20 mL), 150 °C, Ar (1 atm), 72 h. The value in parenthesis is the yield of isolated product.

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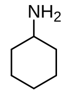
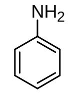
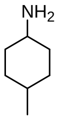
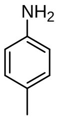
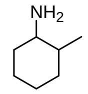
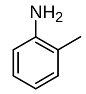
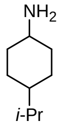
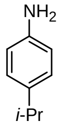
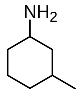
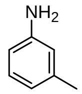
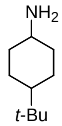
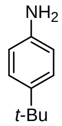
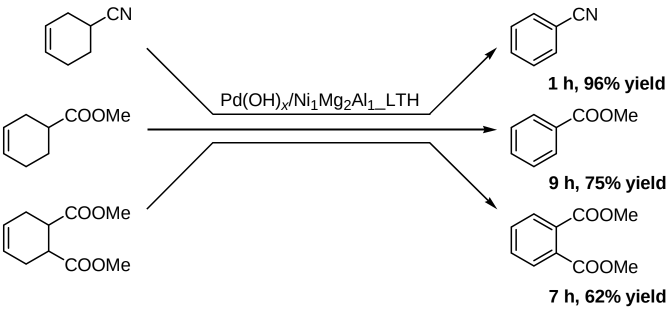
the catalyst. Various alkyl and phenyl substituted cyclohexanols were efficiently converted into the corresponding phenols in high yields (Table 1, entries 2–10). A 10 mmol-scale dehydrogenation of 3,5-dimethylcyclohexanol was also successful; the amount of the catalyst could be reduced to 0.25 mol%, and the corresponding phenol was obtained in 79% isolated yield (Table 1, entry 10). 2-Cyclohexen-1-ol was also an effective substrate for the dehydrogenation (Table 1, entry 11). The amide functionality was tolerated in the present dehydrogenation (Table 1, entry 12). Besides cyclohexanols, cyclohexanones were also efficiently dehydrogenated into the corresponding phenols in high yields (Table 1, entries 13–16). Cyclohexanones possessing ester and alkoxy groups were dehydrogenated without hydrolysis of these functional groups (Table 1, entries 15 and 16). Enones, such as 2-cyclohexen-1-one and carvone, were also dehydrogenated efficiently, but the double bond hydrogenation occurred in the case of carvone (Table 1, entries 17 and 18).

The acceptorless dehydrogenation of cyclohexylamines also efficiently proceeded in the presence of $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH. Cyclohexylamines substituted with various alkyl groups on the 2-, 3-, and 4-positions selectively gave the corresponding anilines in high yields (Table 2).[15] Encouraged by the dehydrogenation catalysis of $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH, we then attempted the dehydrogenation of substituted cyclohexenes to arenes (Scheme 1). Cyclohexenes with cyano and ester groups were efficiently dehydrogenated to the corresponding arenes in moderate to high yields.[16] We also successfully performed the consecutive two-step Diels-Alder/dehydrogenation reaction for the synthesis of an arene from a diene and a dienophile (Scheme 2); the Diels-Alder reaction of 2,3-dimethyl-1,3-butadiene and 1,4-naphthoquinone was carried out using the heterogeneous Sn–W mixed oxide catalyst developed previously by our group,[17] and then the dehydrogenation of the resulting cyclohexene gave 2,3-dimethylathraquinone in 80% overall yield based on 1,4-naphthoquinone. Furthermore, 4-methyl-*N*-octylaniline was succesfully synthesized from 4-methylcyclohexanone and *n*-octylamine by using the present acceptorless dehydrogenative aromatization strategy (Scheme S2).

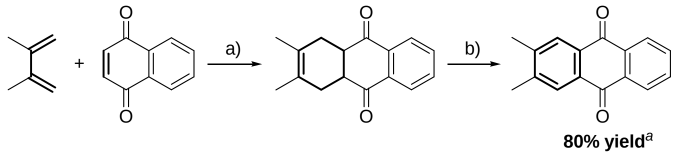
Table 2 Substrate scope for the acceptorless dehydrogenation of cyclohexylamines to anilines with $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH[a]

Entry	Substrate	Product	Entry	Substrate	Product
1		 **10 h, 76%**	4		 **10 h, 81%**
2		 **10 h, 83%**	5		 **8 h, 95%**
3		 **10 h, 88%**	6		 **8 h, 89%**

[a] Reaction conditions: Substrate (0.5 mmol), $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (Pd: 1 mol%), DMA (2 mL), 150 °C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as the internal standard.



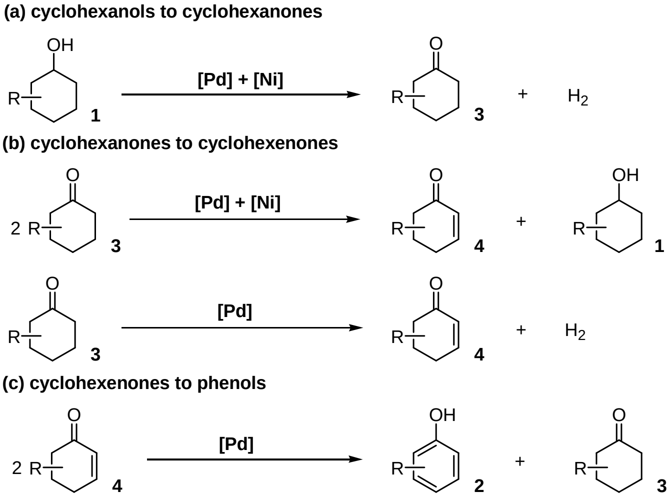
Scheme 1 Dehydrogenation of substituted cyclohexenes catalyzed by $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH. Reaction conditions: Substrate (0.5 mmol), $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (Pd: 5 mol%), styrene (2.0 mmol), DMA (2 mL), 130 °C, Ar (1 atm). Yields were determined by GC analysis using *n*-hexadecane as the internal standard.



Scheme 2 Consecutive Diels-Alder/dehydrogenation reaction. Reaction conditions: a) Sn–W mixed oxide (50 mg), 2,3-dimethyl-1,3-butadiene (0.75 mmol), 1,4-naphthoquinone (0.5 mmol), dichloromethane (1 mL), rt, 5 h. b) $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH (Pd: 5 mol%), styrene (2.0 mmol), DMA (2 mL), 130 °C, Ar (1 atm), 1 h. [a]Isolated yield based on 1,4-naphthoquinone.

The reaction profile for the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH-catalyzed acceptorless dehydrogenation of **1a** showed that 4-methylcyclohexanone (**3a**) was initially formed, followed by the dehydrogenation to give **2a** (Fig. S9a, ESI†). When the dehydrogenation of **3a** was carried out, **1a** was formed as the intermediate, which suggests that **3a** partially works as the hydrogen acceptor (Fig. S9b, ESI†). The dehydrogenation starting from 2-cyclohexen-1-one (**4b**) indicated that phenol (**2b**) was produced through the very fast disproportionation of **4b** (Fig. S9c, ESI†). Based on the above results, the present acceptorless dehydrogenative aromatization proceeds through (a) acceptorless dehydrogenation of cyclohexanols (**1**) to cyclohexanones (**3**) (Scheme 3a), (b) disproportionation or simple dehydrogenation of **3** to cyclohexenones (**4**) (Scheme 3b), and (c) disproportionation of cyclohexenones to give phenols (**2**) (Scheme 3c).

The dehydrogenation of **3a** to **2a** with various $Pd(OH)_x/M_aMg_bAl_c$_LTH catalysts were generally more efficient than $Pd(OH)_x/Al_2O_3$, $Pd(OH)_x/TiO_2$, and Pd/C (Table S4, ESI†), which indicates that the basicity of $M_aMg_bAl_c$_LTHs plays a very important role for the present dehydrogenation likely via promoting deprotonative coordination of **3** to the active metal (Pd) centers. $Pd(OH)_x/Mg_3Al_1$_LDH, which is inactive for the dehydrogenation of **1a** to **2a**, showed almost the same activity as $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH for the dehydrogenation of **3a** to **2a** (Table S4, entries 1 and 2, ESI†). Therefore, the high activity of $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH for the dehydrogenation of **1** to **2** is likely originated from its high efficiency for the alcohol dehydrogenation from **1** to **3** (Scheme 3a). In addition, as mentioned above, $Ni_1Mg_2Al_1$_LTH did not promote the dehydrogenation of **1a** to **3a** (Table S2, entry 11, ESI†). Thus, we consider that both Pd and Ni



Scheme 3 Possible reaction paths for the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH-catalyzed acceptorless dehydrogenative aromatization of cyclohexanols.

species are indispensable for the dehydrogenation of **1** to **3** (Scheme 3a). The XPS spectrum of the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst after the dehydrogenation of **1a** revealed that Ni species were not reduced during the reaction and maintained its oxidation state as +2 (Fig. S10, ESI†). Therefore, Ni^{2+} species likely assist the Pd-catalyzed dehydrogenation of **1** to **3**. The reaction profile for the dehydrogenation of **3a** to **2a** with $Pd(OH)_x/Mg_3Al_1$_LDH showed that **1a** was not formed as the intermediate (Fig. S9d, ESI†). In addition, $Pd(OH)_x/Mg_3Al_1$_LDH did not promote the dehydrogenation of **1a** to **3a**, as mentioned above (Table S2, entry 1, ESI†). Thus, the simple dehydrogenation of **3** to the corresponding **4** proceeds in the case of $Pd(OH)_x/Mg_3Al_1$_LDH-catalyzed reaction without occurrence of the disproportionation of **3** (Scheme S3, ESI†). The above results also indicate that Ni^{2+} species in the $Ni_1Mg_2Al_1$_LTH plays an essential role for the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH-catalyzed disproportionation of **3** (Scheme 3b). On the other hand, it is likely that Pd species alone are contributed to the simple dehydrogenation of **3** to **4** and the disproportionation of **4** (Scheme S3, ESI†).

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11 The X-ray diffraction (XRD) analysis of $Pd(OH)_x/M_aMg_bAl_c$_LTH catalysts revealed that the layered structure of the supports was maintained after the deposition of Pd hydroxide species (Fig. S1, ESI†).
12 Among the various solvents examined, such as DMA, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *o*-dichlorobenzene, mesitylene, and diglyme, DMA was the most suitable solvent for the present dehydrogenation (Table S3, ESI†).
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14 The XRD and TEM analyses of the $Pd(OH)_x/Ni_1Mg_2Al_1$_LTH catalyst after the 5th reuse experiment revealed that the $Ni_1Mg_2Al_1$_LTH structure and the average size of the Pd nanoparticles were almost unchanged compared to the catalyst after the 1st dehydrogenation experiment (after the 1st dehydrogenation experiment: 2.7 nm, after the 5th reuse experiment: 2.6 nm) (Figs. S5 and S8, ESI†).
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16 In these cases, however, styrene was required as the hydrogen acceptor. Otherwise, the disproportionation of cyclohexenes proceeded and gave a 2:1 mixture of cyclohexanes and arenes.
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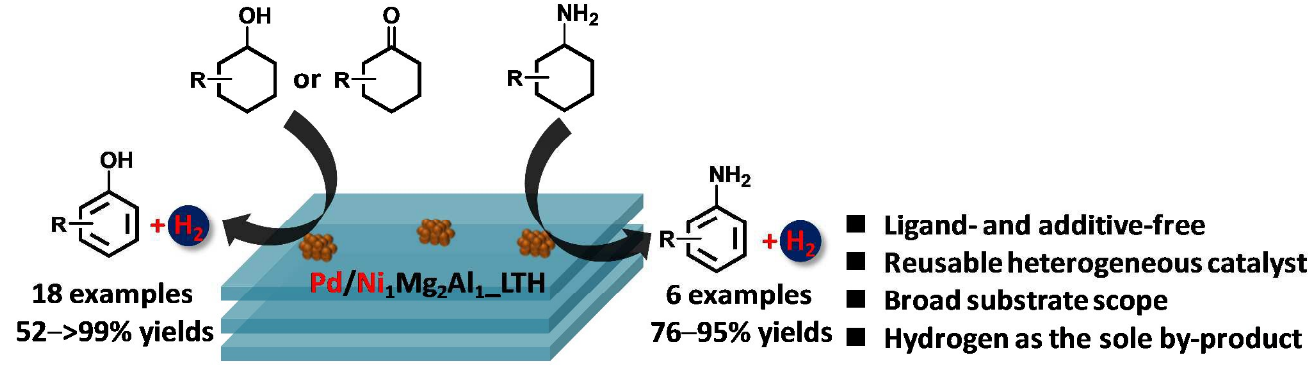
Graphic abstract



In the presence of a Ni–Mg–Al layered triple hydroxide-supported Pd catalyst, acceptorless dehydrogenative aromatization of a wide range of substrates efficiently proceeded with liberation of molecular hydrogen.