Synthesis of phenols and anilines through acceptorless dehydrogenative
aromatization catalysis over supported Pd nanoparticles

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Abstract: In the presence of layered hydroxide-supported Pd catalysts, acceptorless dehydrogenative
aromatization of a wide range of cyclohexanols/cyclohexenols/cyclohexanones/cyclohexenones
and cyclohexylamines efficiently proceeded to give the corresponding phenols and anilines, respectively, with
liberation of \( \text{H}_2 \).

Keywords: Acceptorless dehydrogenative aromatization, Phenols, Anilines.

1. Introduction

Dehydrogenative aromatization has recently emerged as an attractive method for the synthesis of
various arenes from ubiquitous saturated six-membered carbocyclic compounds. For example, it has been
reported that phenols, substituted anilines, and aryl ethers 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). On the other hand,
acceptorless dehydrogenative aromatization, which generates \( \text{H}_2 \) 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 key structural moieties in numerous pharmaceuticals, agrochemicals, electronic materials,
plastics, and resins. The acceptorless dehydrogenative aromatization can be useful for the synthesis of
substituted phenols and anilines because the easy availability of saturated six-membered carbocyclic
compounds with various substituted patterns on cyclohexyl rings through several established chemical
transformations. In this study, we have successfully realized the efficient acceptorless dehydrogenative
aromatization of a wide range of substrates to their corresponding phenols and anilines by utilizing layered
hydroxide-supported Pd catalysts.¹

2. Experimental

We prepared various \( M\text{–Mg–Al} \) layered triple hydroxides (\( M = \text{Ni, Co, Fe, M}_a\text{Mg}_b\text{Al}_c\text{-LTH, M/Mg/Al} = a/b/c \)) by the simple co-precipitation method. Then, \( M_a\text{Mg}_b\text{Al}_c\text{-LTH supported Pd hydroxide catalysts
(Pd(OH)}/M_a\text{Mg}_b\text{Al}_c\text{-LTH) were prepared by deposition-precipitation method. A typical procedure for the
dehydrogenation: Into a Schlenk tube connected to a balloon partially filled with Ar gas, catalyst, substrate,
solvent, and a Teflon-coated magnetic stir bar were successively placed, and the reaction mixture was
vigorously stirred at reaction temp. in 1 atm of Ar. The substrate conversion and product yield were
periodically determined by GC analysis. The detection of \( \text{H}_2 \) in the gas-phase was carried out with gas-phase
MS analysis. The quantification of \( \text{H}_2 \) formation was performed by measurement of the evolved gas volume.

3. Results and discussion

As-prepared Pd(OH)}/M_aMg_bAl_c-LTH 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. Although Pd(OH)}/Mg_bAl_c-LDH showed almost no
catalytic activity for the dehydrogenation, Pd(OH)}/Ni_1Mg_bAl_c-LTH could efficiently promote the reaction
and gave the desired 2a in 94% yield; we also confirmed that ca. three equivalents of \( \text{H}_2 \) gas with respect to
1a were formed during the reaction. The color of the Pd(OH)}/Ni_1Mg_bAl_c-LTH catalyst was changed from
initial light brown to black within less than 1 min. The XPS spectrum of the freshly prepared Pd(OH)$_2$/Ni$_{1}$Mg$_{2}$Al$_{1}$-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. 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. These results suggest that the Pd$^{2+}$ species were reduced by the substrate to Pd$^{0}$ species during the reaction. The Ni$_{1}$Mg$_{2}$Al$_{1}$-LTH support alone did not promote the dehydrogenation.

Although the dehydrogenative aromatization also proceeded in the presence of Pd(OH)$_2$/Co$_{1}$Mg$_{2}$Al$_{1}$-LTH and Pd(OH)$_2$/Fe$_{1}$Mg$_{2}$Al$_{1}$-LTH, the performance of these catalysts was much inferior to that of Pd(OH)$_2$/Ni$_{1}$Mg$_{2}$Al$_{1}$-LTH. The effect of the Ni/Mg/Al molar ratio of the support was not significant. Pd(OH)$_2$/Al$_{2}$O$_3$, Pd(OH)$_2$/TiO$_2$, and Pd/C were not effective for the dehydrogenation.

As shown in Table 1, in the presence of the Pd(OH)$_2$/Ni$_{1}$Mg$_{2}$Al$_{1}$-LTH catalyst, various kinds of substrates (cyclohexanols, cyclohexenols, cyclohexanones, and cyclohexenones) could be converted into their corresponding phenols. Moreover, the transformation of cyclohexylamines to their corresponding anilines was also successful. The observed catalysis was truly heterogeneous, and the catalyst could be reused for these transformations with keeping its high catalytic performance.

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*Reaction conditions: Substrate (0.5 mmol), Pd(OH)$_2$/Ni$_{1}$Mg$_{2}$Al$_{1}$-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. *Substrate (10 mmol), Pd(OH)$_2$/Ni$_{1}$Mg$_{2}$Al$_{1}$-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.

Furthermore, we successfully realized, for the first time, the efficient conversion of cyclohexanone oximes to anilines by utilizing Pd(OH)$_2$/Mg$_3$Al$_1$-LDH catalyst under hydrogen-acceptor-free conditions. The substrate scope was very broad with respect to cyclohexanone oximes, which gave the corresponding primary anilines in high yields with high selectivities.

4. Conclusions

We have successfully developed the novel efficient acceptorless dehydrogenative aromatization of a wide range of substrates to their corresponding phenols and anilines by utilizing layered hydroxide-supported Pd catalysts. The substrate scope was very broad, and these reaction theoretically produce H$_2$ (and water) as the by-product(s), which features the environmentally-friendly nature of these reactions.

References