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

Kazuya Yamaguchi*
Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
**Corresponding author: +81-3-5841-7197, kyama@appchem.t.u-tokyo.ac.jp*

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 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 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

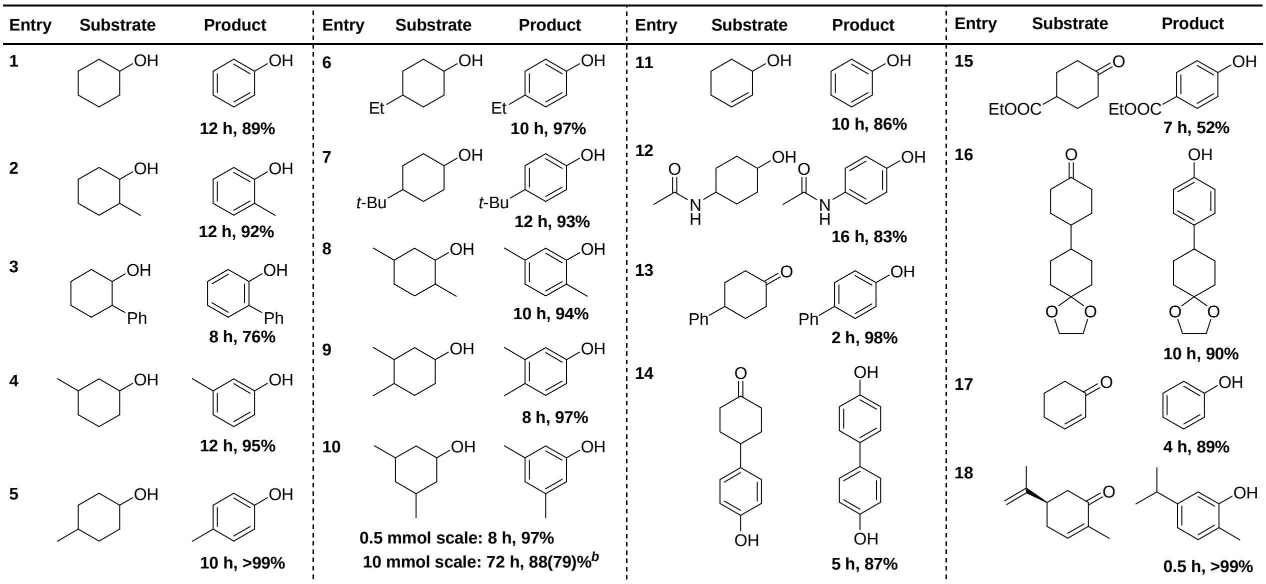
We prepared various M–Mg–Al layered triple hydroxides (M = Ni, Co, Fe, $M_aMg_bAl_c$-LTH, M/Mg/Al = $a/b/c$) by the simple co-precipitation method. Then, $M_aMg_bAl_c$-LTH supported Pd hydroxide catalysts ($Pd(OH)_x/M_aMg_bAl_c$-LTH) were prepared by deposition-precipitation method. A typical procedure 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 H_2 in the gas-phase was carried out with gas-phase MS analysis. The quantification of H_2 formation was performed by measurement of the evolved gas volume.

3. Results and discussion

As-prepared $Pd(OH)_x/M_aMg_bAl_c$-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 $Pd(OH)_x/Mg_3Al_1$-LDH showed almost no catalytic activity for the dehydrogenation, $Pd(OH)_x/Ni_1Mg_2Al_1$-LTH could efficiently promote the reaction and gave the desired **2a** in 94% yield; we also confirmed that *ca*. three equivalents of H_2 gas 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. 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 $Ni_1Mg_2Al_1$-LTH support alone did not promote the dehydrogenation. 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, the performance of these catalysts was much 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. $Pd(OH)_x/Al_2O_3$, $Pd(OH)_x/TiO_2$, and Pd/C were not effective for the dehydrogenation.

As shown in Table 1, in the presence of the $Pd(OH)_x/Ni_1Mg_2Al_1$-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.

Table 1. Acceptorless dehydrogenation of cyclohexanols/cyclohexanones to phenols with $Pd(OH)_x/Ni_1Mg_2Al_1$-LTH[a]



[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.

Furthermore, we successfully realized, for the first time, the efficient conversion of cyclohexanone oximes to anilines by utilizing $Pd(OH)_x/Mg_3Al_1$-LDH catalyst under hydrogen-acceptor-free conditions.[2] 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

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