

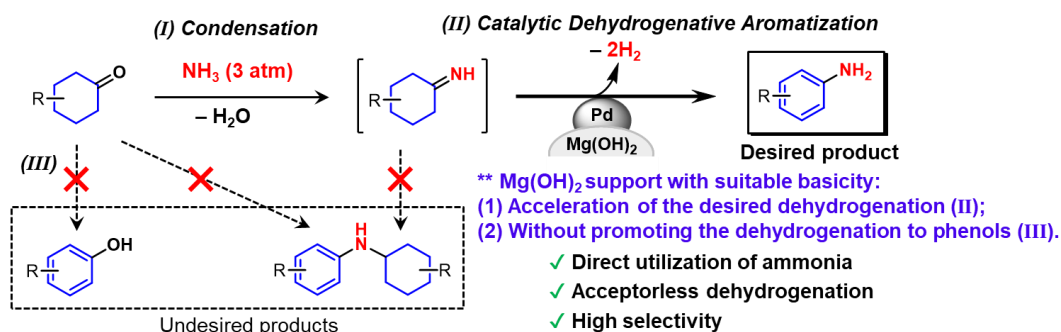
Selective Synthesis of Primary Anilines Using NH_3 as a Nitrogen Source *via* Acceptorless Dehydrogenative Aromatization

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Although synthetic methods of primary anilines including reduction of nitrobenzenes, aromatic substitution, and cross-coupling reactions were reported, there are still several disadvantages such as the multi-step synthesis which does not directly utilize NH_3 , inevitable pre-functionalization of substrates, and/or the limitation of specific *ortho/meta/para* selectivity in those processes. Moreover, the cross-coupling reactions require a stoichiometric amount of base and produce halogen-containing byproducts.¹ Recently, a new method, phenol-to-aniline amination, was also reported, yet it tolerates a narrow substrate scope.² On the other hand, our group has successfully developed a process for the synthesis of primary anilines from a variety of cyclohexanones using NH_3 as a direct nitrogen source *via* Pd nanoparticle-catalyzed dehydrogenative aromatization.³ However, this reaction requires a stoichiometric amount of styrene as the hydrogen acceptor. Overall, as far as we know, there is virtually no general and efficient heterogeneous catalytic system for this conversion without using any acceptor.

In this study, we have developed a novel method for the selective synthesis of primary anilines in high yields from cyclohexanones by utilizing NH_3 as the nitrogen source directly *via* acceptorless dehydrogenative aromatization in the presence of an $\text{Mg}(\text{OH})_2$ -supported Pd nanoparticle catalyst. Various experimental results suggested that the basic sites on $\text{Mg}(\text{OH})_2$ could effectively accelerate the desired dehydrogenation of cyclohexylimine intermediates formed by the condensation of cyclohexanones and NH_3 , which suppressed the formation of the undesired *N*-cyclohexylanilines. In addition, the undesirable formation of phenols by direct cyclohexanone dehydrogenation hardly proceeded because of the suitable basicity of $\text{Mg}(\text{OH})_2$.



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