Selective Synthesis of *m*-Phenylenediamine Derivatives through Catalytic Dehydrogenative Aromatization

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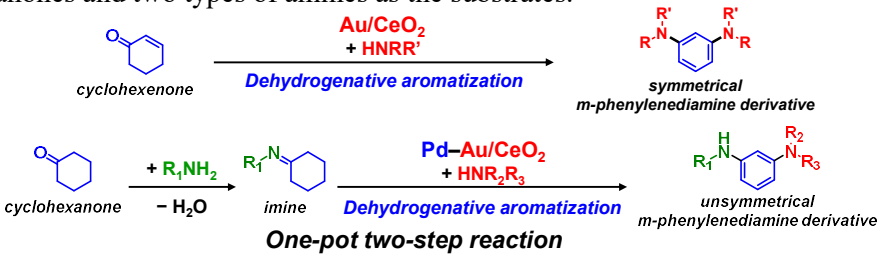
Keywords: dehydrogenative aromatization; Au nanoparticle catalysts; palladium catalysts; aerobic oxidation; *m*-phenylenediamine

Dehydrogenative aromatization is an environmentally friendly reaction that enables the synthesis of various aromatic compounds from cyclohexanones, which are relatively easy to functionalize regioselectively.[1] However, the synthesis of *m*-phenylenediamine derivatives via dehydrogenative aromatization, in which two amine nucleophiles can be introduced simultaneously at the *m*-position, has not been achieved because it was difficult to control the product selectivity due to irreversible formation of byproducts such as phenols and anilines. Here, we have achieved the selective synthesis of symmetric *m*-phenylenediamine derivatives through dehydrogenative aromatization using cyclohexenones and secondary amines as the substrates, using a CeO_2-supported Au nanoparticle (Au/CeO_2) catalyst for the first time.[2] Furthermore, detailed analysis revealed that the key points of this reaction are: (i) specific multi-site adsorption of the intermediates onto Au nanoparticles, (ii) promotion of O_2 utilization by the CeO_2 support, (iii) facilitation of 1,2/1,4-addition of secondary amines to cyclohexenones on the CeO_2 support.

However, this reaction system presented two issues: (i) it could not be applied to the synthesis of unsymmetrical *m*-phenylenediamine derivatives using two types of amines as the nucleophiles, and (ii) cyclohexenones were more difficult to obtain and synthesize than cyclohexanones. In this study, further investigation revealed that these issues could be resolved by employing a composite catalyst system combining Au/CeO_2 with Pd exhibiting α,β-dehydrogenation activity.[3] This approach enabled the selective one-pot two-step synthesis of *m*-phenylenediamine derivatives, including the unsymmetrical ones, using cyclohexanones and two types of amines as the substrates.



1) Y. Izawa, C. Zheng, S. S. Stahl, *Angew. Chem. Int. Ed.* **2013**, *52*, 3672. 2) H. Kimura, T. Yatabe, K. Yamaguchi, *J. Am. Chem. Soc.* **2025**, *147*, 27238. 3) a) D. Takei, T. Yatabe, X. Jin, T. Yabe, N. Mizuno, K. Yamaguchi, *ACS Catal.* **2020**, *10*, 5057. b) D. Takei, T. Yatabe, T. Yabe, R. Miyazaki, J. Hasegawa, K. Yamaguchi, *JACS Au* **2022**, *2*, 394.