N- and P-Doped Carbon-Supported Platinum Catalysts for Selective Reductive Coupling of Nitro Compounds with Aldehydes to Nitrones

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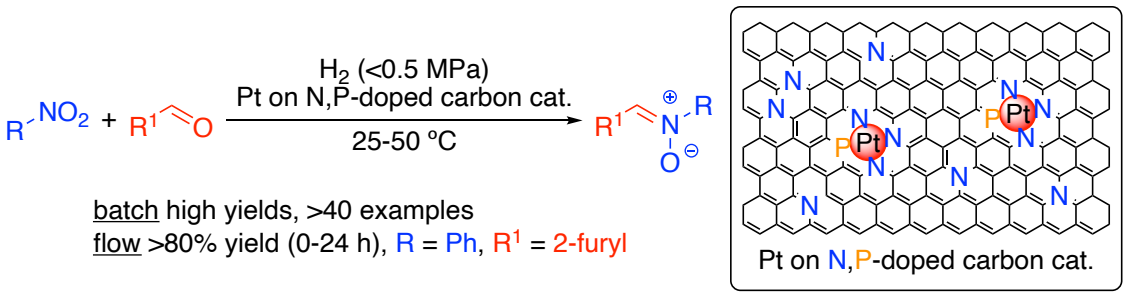
Single-atom catalysts (SACs) are easily separable and recyclable heterogeneous catalysts with well-defined active centers.[1)] SACs incorporate the advantages of both homogeneous and heterogeneous systems, enabling sustainable and efficient reactions. SACs-catalyzed hydrogenations are known to proceed via an unconventional mechanism; a hydrogen molecule is activated by heterolytic dissociation at single-atomic sites, as opposed to homolytic activation by nanoparticle species.[1)] Nevertheless, studies that exploit the unique features of SACs for selective hydrogenation reactions remain scarce.

The reductive coupling of nitro compounds and aldehydes using hydrogen gas and heterogeneous catalysts is an environmentally friendly synthetic method for nitrones, with water as the only byproduct.[2)] However, control of side-reductions poses a significant challenge. Therefore, we hypothesized that the selectivity could be manipulated by fine-tuning of the catalyst structure, such as coordination sites.

We prepared nitrogen- and phosphorus-doped carbon-supported platinum catalysts as SACs based on a recent report.[3)] The platinum catalysts showed remarkable selectivity in the target coupling reactions over commercial platinum nanoparticle catalysts. Possible side-reactions such as hydrogenation of nitrone products, hydroxylamine intermediates to primary amines, and aldehydes to alcohols were suppressed. In addition, phosphorus dopants on the carbon support enhanced the catalytic activity for the conversion of nitro compounds compared to nitrogen-doped carbon-supported catalysts. As a result, the desired nitrones were afforded in high yields and selectivity. Moreover, the method was applicable to a wide range of substrates and continuous-flow reactions, which have never been achieved before. Further details will be discussed in the presentation.



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