

Abstract

The Tsuji–Trost allylation is an important reaction in homogenous organic synthesis due to its versatility, selectivity, and broad applicability in forming carbon–carbon (C–C) and carbon–heteroatom (C–X) bonds. Heterogeneous catalysts for the Tsuji–Trost allylation are desirable for tunable activity and selectivity. Moreover, they are much easier to separate from the reaction mixture, which improves cost-effectiveness, simplifies the removal of heavy metals from the products, and enables catalyst recyclability, contributing to enhanced sustainability.

This thesis investigates zeolite-supported Pd catalysts for the Tsuji–Trost allylation of malonates and chemically similar nucleophiles. Three catalysts: Pd@USY, Pd@deAl-USY, and Pd@lay-MFI were synthesized and thoroughly analyzed. Among them, Pd@USY displayed superior catalytic activity, Pd@deAl-USY showed moderate activity, while Pd@lay-MFI remained inactive. These observed trends correlate with Pd NP sizes (2.2 nm, 2.5 nm, and 24 nm, respectively), as confirmed by STEM and PSD analysis.

Reaction conditions were optimized to improve selectivity and efficiency. Using dichloromethane as solvent and K_2CO_3 as base gave the best results, with full conversion reached in just two hours in the model reaction of diethyl malonate with allyl acetate. Fine-tuning the reactant ratio to 1.5 equivalents of malonate minimized di-substitution. A range of substrates was tested, revealing that nucleophilicity and α -substitution played significant roles in determining reactivity. Bulky substituents on adjacent chains appeared to hinder conversion and product yield, likely by limiting substrate diffusion within the zeolite's micropores.

Despite high initial performance, catalyst reusability was limited, with noticeable deactivation after just two cycles. This loss of activity was not attributed to leaching, oxidation, or byproduct poisoning, as confirmed by multiple control experiments. Instead, the evidence points towards an unexpected role of supports acidity. This hypothesis is supported by several findings: the reduced activity of Pd@deAl-USY (less acidic), the complete inactivity of more acidic Pd@USY (Si/Al = 2.6), the poor performance of Na^+ ion exchanged Pd@USY, and the gradual deactivation observed when Pd@USY was in prolonged contact with the base. Together, these results suggest that an optimal acidity window is crucial for maintaining catalytic efficiency. Notably, catalyst regeneration was able to restore activity, indicating that deactivation is reversible, with the main limiting factor being moderate sintering of Pd NPs.

In summary, Pd@USY demonstrated excellent performance as a heterogeneous alternative to homogeneous catalyst for the Tsuji–Trost allylation under mild conditions, offering broad substrate scope and straightforward preparation. Although the cause of deactivation remains a challenging task for the future, the catalyst exhibits good stability, selectivity, and handling properties, making it a promising candidate for further development.

Keywords: Catalysis, zeolites, palladium, nanoparticles, Tsuji–Trost allylation