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Palladium nanoparticles-confined pore-engineered urethane-linked thiol-functionalized covalent organic frameworks: a high-performance catalyst for the Suzuki Miyaura cross-coupling reaction†

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Covalent organic frameworks (COFs) are potential templates for the synthesis of nanomaterials owing to the versatility of their structure. Most of the reported COFs comprise imine linkages. Herein, we report for the first time the synthesis of a urethane-linked COF (UCOF) using monoformylphloroglucinol and 1,4-phenylene diisocyanate as monomers. Furthermore, the UCOF was functionalized with cysteamine to introduce free dangling thiol groups into the cavity. The latter played a critical role in fixing the active metal efficiently and facilitating the confined growth of small metal nanoparticles (~4–6 nm) with a high surface area leading to a pore-engineered heterogeneous Pd catalyst (PdNPs@UCOF-SH). The COF and Pd catalyst were characterized using various analytical techniques such as CP-MAS NMR, FTIR, PXRD, BET, FEG-SEM, HRTEM, XPS, TGA, and ICP-AES. The as-prepared UCOF-SH-supported Pd nanoparticles showed excellent catalytic activity in the Suzuki Miyaura cross-coupling reaction under mild conditions with low catalyst loading and eco-friendly solvents. The scope was extended to various aryl boronic acids and aryl halides (I, Br, and Cl). The halo-substituted and non-halo biaryl derivatives were obtained in good to excellent yields, within a shorter reaction time, avoiding the homocoupling of aryl boronic acid. The pore-engineered COF-derived catalyst is selective and easily recycled up to 10 runs without significant loss of catalytic activity. This reveals the robust nature of the PdNPs@UCOF-SH catalyst and the sustainability of the process which opens a new frontier for several catalytic applications.

1 Introduction

The chemical industry relies heavily on organic transformations. Among them, Suzuki Miyaura, Heck, Negishi, Stille, Kumada, Sonogashira, and other cross-coupling reactions have been widely used in synthetic organic chemistry due to their high potency for forming new carbon–carbon bonds.[1] The implementation of cross-coupling reactions in synthetic organic chemistry adds incomparable advantages to developing a prosperous society. Among various coupling reactions, the Suzuki Miyaura cross-coupling reaction has drawn a lot of attention due to its enormous versatility in the formation of C–C bonds. The SMC reaction is environmentally friendly and relatively simple to carry out. The organoborane reactants used in this reaction possess thermal stability, inertness to water and oxygen, and tolerance of diverse functional groups.[2] Suzuki–Miyaura cross-coupling (SMC) of aryl boronic acids and aryl halides is a promising and potent method for synthesizing biaryl derivatives, which are used as building blocks in a variety of medicines, agrochemicals, polymers, and natural products.[3,4] To date, advancements in catalysis related to the SMC reaction have been of great importance to researchers as it is a very important reaction for designing synthetic protocols for the preparation of pharmacophores and drug molecules.[5] In particular, various palladium (Pd)-based catalysts have been employed and gradually developed by researchers to assist in the SMC reaction.

Traditionally, homogeneous palladium catalysts utilized for SMC reactions typically experience the ill effects of critical recovery issues, which leads to the wastage of valuable metal assets and additionally causes heavy metal contamination in the products. To overcome these issues, the development of productive, selective, and efficient heterogeneous palladium catalysts is exceptionally alluring.[6] To heterogenize palladium nanoparticles, various supports have been developed by researchers such as silica, carbon materials, metal–organic frameworks (MOFs), metal oxides, polymers, graphene, *etc.*, and they are employed for catalytic applications. Despite their

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