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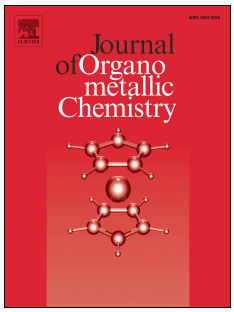

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Synthesis of 3-sulfenylindoles by Pd (II) nanoclusters confined within metal−organic framework fibers in aqueous solution

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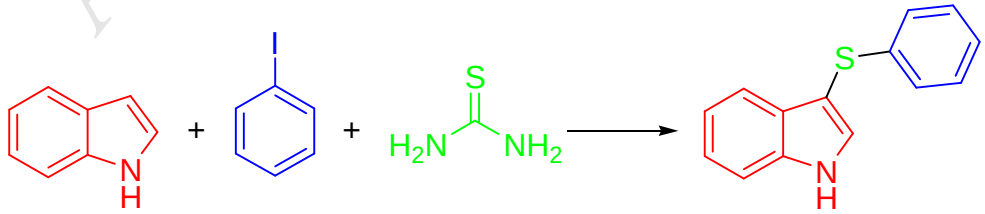
Abstract
We have found that fibrous nanosilica (KCC-1) can used as a excellent support for the synthesis of highly sparse nanoparticles. KCC-1 has high surface area that was functionalized with 1,3-bis(dimethylthiocarbamoyloxy)benzene groups acting as the strong performers so that the Pd (II) was complex without aggregation on the fibers of the KCC-1 microspheres (KCC-1/BTB/Pd). For synthesis of 3-sulfenylindoles from aryl iodide, indoles, and thiourea used from the KCC-1/BTB/Pd NPs as a catalyst that showed excellent catalytic activities under green conditions. Compared with the traditional substrate, KCC-1/BTB/Pd substantially increases protection and the accessibility of the nanoparticle sites due to its three dimensional hierarchical structure.

Keywords: KCC-1, Nano catalyst, One-pot synthesis, Green chemistry

Introduction

The metal complex have strong catalytic activities that for this property has been a topic of research.[1–5] Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their catalysis related properties, which can be leveraged in various usage. Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their catalysis related properties, which can be leveraged in various usage such as Sonogashira [6-8], Suzuki-Miyaura [9-11], Heck [12-14], Hiyama [15-17], Larock heteroannulation [18-21], degradation of pollutants,[22] hydrogenation,[23] and fuel cells. [24] In recent years, it has been proved that the use of complex functional groups either grafted or smeared on the solid supports played an important role in preventing the aggregation of metal catalysts.[25-34] Fibrous nano-silica (KCC-1), which possibilities a high surface area and easy availability through its fibers is reported by Polshettiwar et al. .[35] This would be an ideal catalyst support troth for the making of noble metal based catalysts that represent high availability of active sites and excellent catalytic activity. [36-44]
Sulfenylated indoles consist of an important class of indole derivatives and have been discovered as scaffolds possessing versatile biological relevance. According to known results, The development of general protocol for 3-sulfenylindoles formation has received significant attention because of their therapeutic value in the treatment of cancer,[45] HIV,[46] allergies,[47] heart disease,[48] and bacterial infection.[49] Various sulfenylating agents such as sulfonium salts,[50] quinone mono-O,S-acetals,[51] sulfonyl hydrazides,[52] sulfinates,[53] disulfides,[54] sulfenyl halides,[55] N-thioimides,[56] thiols[57] and arylsulfonyl chlorides[58] were smoothly coupled with indoles. These processes, though efficient, have several drawbacks including unstable and expensive reagents, lower reaction yields, unpleasant odors, uncommon solvents, requirement of inert atmosphere and excess reagent loadings as well as long reaction times. Moreover, most of these methods need preparation steps of the thiolating agent. Therefore, there is still a growing demand to develop an efficient method for the synthesis of 3-sulfenylindoles from suitable and readily available precursors. Herein, we report the synthesis of KCC-1 supported 1,3-bis(dimethylthiocarbamoyloxy)benzene-Pd(II) complex (KCC-1/BTB/Pd) and its application for investigate the one-pot synthesis of 3-sulfenylindoles from aryl iodide, indoles, and thiourea. We enthusiasm to report cross-couplings between aryl iodide, indoles, and thiourea for first time (Scheme 1).



Scheme 1 Synthesis of 3-Sulfenylindoles from aryl iodide, indoles, and thiourea in the presence of KCC-1/BTB/Pd NPs.

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