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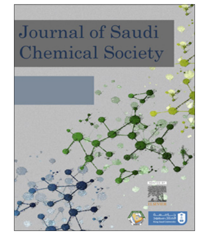

ORIGINAL ARTICLE

Heck-type olefination and Suzuki coupling reactions using highly efficient oxacalix[4]arene wrapped nanopalladium catalyst

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Heck reaction

Abstract A simple one-pot method is used for the synthesis of water dispersible and stable palladium nanoparticles (PdNps) where oxacalix[4]arene dihydrazide (OXDH) is used as both a reducing and capping agent. The OXDH-PdNps have been characterized by UV–Visible spectroscopy, Fourier transform infrared (FT-IR), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The OXDH-PdNps are spherical in shape with an average size of 3–4 nm and well crystallized in a face centered cubic structure. The capping of the OXDH ligand on the nanoparticles surface was evaluated using FT-IR. The OXDH-PdNps have been used in carbon–carbon coupling reactions, namely, the Suzuki–Miyaura and Mizoroki–Heck reactions. Both of the reactions are carried out under phosphine-free conditions to provide better yields. The nanocatalyst can be easily recovered and reused for six consecutive catalytic cycles without any significant loss in its catalytic activity.

1. Introduction

The field of nanoscience and nanotechnology is growing enormously due to the wide range of applications by nanomaterials with a size of 1–100 nm. The synthesis and use of noble metal nanoparticles, such as gold [1], silver [2], platinum [3] and palladium [4,5], have achieved fascinating heights in almost all interdisciplinary fields. In particular, the unique and favorable properties of metal nanoparticles, which are primarily less than 10 nm in size with a high surface area to volume ratio, has enabled their use for catalytic applications [6,7]. Nanoparticles

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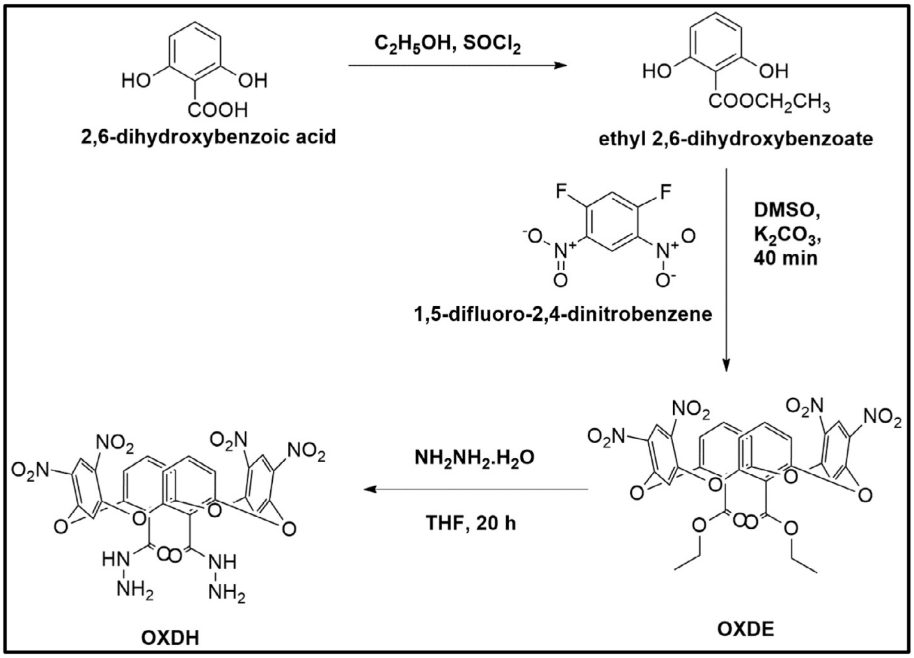


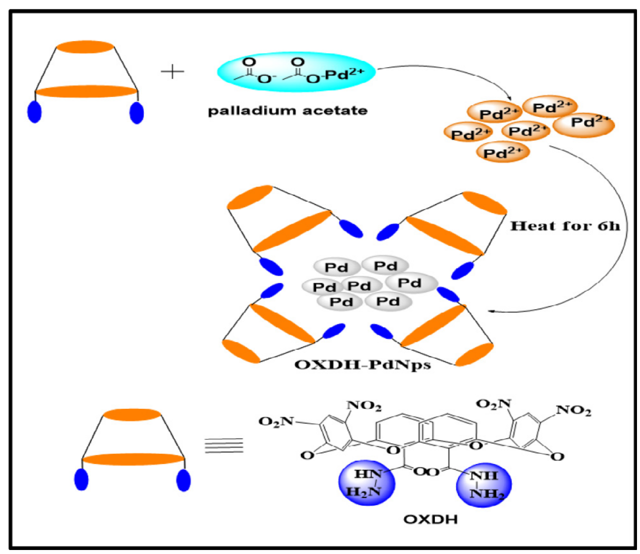
Scheme 1 Synthetic route for oxacalix[4]arene dihydrazide (OXDH).

as catalysts have been used to promote and accelerate several chemical reactions, such as hydrogenation, oxidation [8,9], reduction [10], carbon–carbon, and carbon–nitrogen coupling [11] reactions, resulting in a high yield of products.

To function as efficient catalysts, nanoparticles should meet certain requirements, i.e., they should be of small size, well dispersed and uniform in nature and they should possess a large surface area. Our considerable interest in using palladium nanoparticles for catalysis is due to its wide utility as a catalyst in industrial processes [12,13], fuel cells [14,15] and organic synthesis [16,17]. Literature has also demonstrated the use of palladium compounds and their nanoform to catalyze the Suzuki [18], Heck [19], Sonogashira [20], Stille [21], Hiyama [22] and Ullmann-type [23] coupling reactions. These C–C coupling reactions catalyzed by palladium nanoparticles are of extreme importance in organic transformation reactions, which have great industrial potential for the synthesis of therapeutic drugs and their intermediates [24]. Thus, a significant use of palladium nanoparticles is observed in the field of organic chemistry [25].

The preparation of metal nanoparticles by the chemical reduction method involves the reduction of metal ions to their zero oxidation states. To prevent aggregation, after the reduction in the metallic salt, the formed nanoparticles are stabilized by adding a different stabilizing agent, such as polymers and dendrimers [26]. Therefore, the preparation of metal nanoparticles in which the reactant itself acts as both the reducing and stabilizing agent is ideal to yield stable metal nanoparticles. Different types of stabilizers and reducing agents have been used to synthesize PdNps of different sizes.

Calixarenes [27] are large macrocycles with an inherent hollow cavity and a web-like structure, which can be used to cap the nanoparticles [28]. Our research group has recently reported a method of using different calixarene platforms as both the reducing and stabilizing agents in the preparation of metal nanoparticles [29–36]. There are very few reports in the literature on the use of calixarenes-functionalized PdNps



Scheme 2 Schematic illustration of the formation of PdNps reduced and stabilized by OXDH.

[37]. Oxacalixarenes are hetera-calixarenes with oxygen atoms that replace the methylene bridge [38]. Oxacalixarenes are still at an early development stage in the field of nanoscience and are yet to be explored in a wide range of applications [39–41]. The use of oxacalixarenes to synthesize palladium nanoparticles and, in particular, in the field of catalysis may inspire further exploration by researchers.

To the best our knowledge, only our group has reported the use of the oxacalix[4]arene dihydrazide derivative (DHOC) as both a reducing and capping agent for the formation of PdNps in water [35]. The adopted method is a simple one-pot approach, which does not require a nitrogen atmosphere and

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