



Review

Optimal exploitation of supported heterogenized Pd nanoparticles for C-C cross-coupling reactions

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ARTICLE INFO

Keywords:

Nanomaterials
Heterogeneous catalysis
Transition metal catalysis
Cross-coupling reactions
Heck reaction
Sonogashira reaction
Suzuki-Miyaura coupling reaction

ABSTRACT

The fine chemicals, materials, and pharmaceutical industries have been intrigued by the cross-coupling reactions wherein palladium (Pd) has traditionally garnered maximum attention as it catalyzes a variety of C–C cross-coupling reactions, particularly Sonogashira, Heck, and Suzuki reactions besides being employed for various other cross-coupling reactions, namely C–N, C–O, among others. Due to the expensive and rare nature of Pd, synthetic chemists have been forced to develop techniques that drastically reduce its amount deployed in catalytic processes, facilitating its recovery and reuse for multiple appliances and reducing the processing cost in industrial-scale processes. Pd nanoparticles (NPs), immobilized on nanostructured materials, afford catalytic systems that are far more superior to unsupported ones. Herein, three pioneering reactions, namely Heck, Sonogashira, and Suzuki-Miyaura coupling reactions involving sustainable use of the Pd nanocatalysts adorned on various nanomaterial supports encompassing inorganic carbonaceous materials. The supports comprise silica and other metal oxide-based hybrid materials, biopolymers and other organic polymeric hybrids, and magnetic nanostructured-based entities. The concepts and reasoning underlying the improvement of stability, efficiency, substrate selectivity, reusability, reduced deactivation, sintering and leaching, better catalytic environment and support-nano catalyst synergy are explained through the management of composition, structure, surface area, porosity, pore volume, pore dimensions and surface functionalities etc. The article also details the rational design, synthetic strategies, and developments in the use of nanomaterials as support for immobilizing Pd nano catalysts and highlighting their need, importance and the key role played by them in heterogeneous catalysis. It is anticipated that this effort will not only help the organic, inorganic, and material chemists in designing competent heterogeneous catalysts for achieving a plethora of industrial processes but will also provide new model nano catalysts to fast-track the fundamental understanding of the catalytic mechanisms.

1. Introduction

The transition metal (TM) mediated C–C coupling reactions are key synthetic approaches among organic reactions and have become an integral part of synthetic endeavors. These reactions have become an innovative tool kit for organic chemists to construct complex organic molecules that are inconceivable by the conventional organic reactions. [1,2] Among the TM catalysts, palladium (Pd)-catalysts have a special

place as the unique characteristics of Pd, such as partially filled d orbitals and moderate atomic size, allow them to both accept and donate electrons as well as contribute to the stability and the catalytic action of the Pd nanocatalysts (Figs. 1–3). [3] Košmrlj and co-workers studied the mechanism of copper-free Sonogashira reaction, revealing through both experimental evidence and computational analysis that the mechanism involves transmetalation between different palladium species (Fig. 2). [4] The Pd-catalyst is not only used for C–C coupling reactions like Heck,

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