



## Review

## Nanocatalysis: Recent advances and applications in boron chemistry

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## ABSTRACT

Considerable progress has been made in the application of transition metal nanoparticles (NP)-based catalysts in boron chemistry. These offer the advantages of high efficiency and good recyclability. Existing drawbacks need to be addressed before use in industrial applications. This review updates the latest progress in the area of nano-catalysis in boron chemistry, such as catalytic break-down and formation of C–B bonds in arenes (e.g., Suzuki–Miyaura cross-coupling reaction), isotopic exchanges in H–B, B–B and I–B containing molecules, and dehydrogenation of boron compounds.

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## 1. Introduction

Transition metal nanoparticles (NPs) are materials consisting of millions of metal atoms in varying morphologies, such as polyicosahedral and rod-shaped, less than 10 nm in size. The metal atom composites may be either homometallic species or nanoparticles of

mixed bi- or multimetals. The preparation and characterization of, and applications for transition metal NPs in organic synthesis have been well documented in several reviews [1–9]. Although considerable progress has been made in applying metal NPs as catalysts in different types of organic reactions, there is still room for expansion in this specialized area.

Transition metal nanoparticles are currently prepared by reduction (including wet hydrogen and electrochemical reduction), thermal decomposition, sonic-chemical decomposition, ion implantation, biomineralization, photolysis, UV photolysis, microwave irradiation, metal–vapor deposition and mechanochemical synthesis

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[1–11]. The preparation process plays a key role in controlling the size and morphology of the particles, and is thus closely related to catalyst performance [1–11]. In general, nanoparticles are analyzed by X-ray absorption spectroscopy (XAS), inductively coupled plasma (ICP) spectroscopy, UV–vis spectroscopy, X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray microanalysis (EDX, EDS), X-ray and electron diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscope (SEM) to obtain information on their size, morphology, qualitative chemical composition, elemental oxidation states, structure, crystallinity, lattice spacing, and so on [1–11]. Extensive reports have been published and reviewed on the applications of transition metal nanoparticle-catalyzed organic transformations. This review focuses on the latest developments in the area of transition metal NP-catalyzed reactions involving boron-containing species.

## 2. Progress in Suzuki–Miyaura cross-coupling reactions

Application of nanoscale transition metal nanoparticles in chemical transformations involving boron compounds has a very long history. Examples include the well-known palladium nanoparticles (Pd-NPs)-catalyzed Suzuki–Miyaura C–C cross-coupling reactions utilizing commonly available and less toxic arylboronic acid reagents. This example is a well-recognized, highly successful and important coupling reaction and, therefore, this area has been thoroughly investigated; important findings, such as developments in homogeneous catalysis, have been published in reviews [12–18] (Eq. (1)). A large body of literature has appeared in the past few years, so much so that it is difficult to include all the references here. We have attempted to include as many examples as possible where they are necessary for the discussion. Palladium complex-based homogeneous catalysts were the first to be used, and were well-explored in the course of catalyst development and Suzuki–Miyaura cross-coupling reactions [19–22]. In this well-established reaction mechanism, the active Pd metal center breaks the C–B bond in arylboronic acid to form new C–C and X–B (where X = Cl, Br, I) bonds [12–18]. Therefore palladium-NP-based catalysts were introduced as homogeneous catalysts into the stock of catalytically active species, and the resulting catalytic system was highly active for this type of reaction [12–18].

Since the pioneering work on catalytic Suzuki–Miyaura cross-coupling reactions reported by Reetz and co-workers [12,13], palladium NPs with different morphologies – spherical, cubic and polyhedral – have been prepared and mounted on various supports with a range of pore sizes and surface areas, such as micro-, meso- and macroporous carbon-based materials, metal oxides and polymers [12–18]. Most of the Pd-NPs in supported or colloidal composite morphologies have been reported to be spherical or nearly-spherical in shape. This type of Pd-NP often produces a high catalytic performance and reasonable recyclability in coupling reactions involving boronic acid derivatives [12–18]. Pd-NPs in other shapes, such as nanorods and branched star NPs (Fig. 1) etc. [23,24], have also been prepared and utilized in Suzuki–Miyaura coupling reactions.



Advanced synthesizing techniques have led to the design and effective control of the NP sizes, shapes and morphologies. In the presence of hydrochloric acid, the shape of Pd NPs evolved from nanocubes bounded by Pd [100] facets to octahedra bounded by [111] facets (Fig. 2) [25]. In particular, for palladium NP-catalyzed Suzuki–Miyaura C–C cross-coupling reactions, the sequence of activity occurs in the same order as the aryl halide used: aryl iodide > aryl bromide > aryl chloride. In similar reaction conditions, greater activity has been observed with

smaller Pd-NPs [24,26]. Collins and co-workers prepared Pd-NPs with cubic, cuboctahedral and octahedral morphologies and examined their activity in Suzuki–Miyaura cross-coupling reactions [27]. The activity of the Pd-NPs reportedly follows the trend cube > cuboctahedron > octahedron. In addition, shape-dependent activity is reported to be directly correlated with the presence of Pd [100] surface facet [27].

In addition, catalyst supports play important roles in immobilizing stable NPs by controlling the interaction of catalysts and reagents, heterogenizing and then enabling recyclability of the catalysts. Therefore, optimized support materials improve catalytic performance. Various materials, such as mesoporous carbon, carbon nanotubes, polymers, dendrimers, functionalized magnetic nanoparticles and metal–organic frameworks (MOF) have all been used to support or embed Pd-NPs to heterogenize the Pd-NP-based catalytic system and improve recyclability with sustained activity [12–18,28–32]. In general, TEM images [32] indicate that Pd-NPs embedded in MOFs are in the size range 1–6 nm (typically around 3 nm).

As indicated above, most catalysts in organic transformations are currently derived from palladium. Compared with those in existing systems, these nanocatalysts display a high level of activity, selectivity and enhanced stability. Some supported Pd NPs have also demonstrated good recyclability. However, due to foreseeable strict environmental and economical requirements to be applied in the chemical and pharmaceutical industries, low-cost and environmentally friendly catalysts are increasingly attracting public attention, and the development of less toxic and non-noble metal-based catalysts is increasingly desirable. The application of a bimetallic or multi-metallic nanocatalysts such as Pd/M (where M = Ni, Ag, Cu, Au, etc.) is an obvious approach to developing a less costly catalyst than the mono-Pd-NP catalysts currently used [12–16,19,32–34]. Thathagar and co-workers reported the preparation of bi- and multi-metallic NPs and investigated their activity in cross-coupling reactions in colloids [19]. For mono-metallic NPs, the activity follows a sequence of Pd > Cu > Ru > Pt (not active); bi-metallic NPs follow the activity sequence of Cu/Pd–Ru/Pd > Pd/Pt > Cu/Ru–Cu/Pt (not active); multi-metallic NPs show activity in the order Cu/Pd/Ru > Cu/Pd/Pt > Ru/Pd/Pt > Cu/Ru/Pt/Pd. These results suggest that combination of copper with palladium produces activity comparable to that of mono-Pd-based catalysts [17]. Therefore, the application of an inexpensive, less toxic and Cu-mixed Pd-NPs-catalyzed coupling reactions is attractive from both the economical and environmental points of view. Carbon-supported NPs were studied by Kim et al., who demonstrated a catalytic activity sequence Pd/Cu > Pd > Pd/Ag > Pd/Ni under similar reaction conditions [32]. However, when ZnO nano-powder was used as a support, Pd-NP-based catalysts showed an activity order of Ag/Pd > Cu/Pd > Ni/Pd > Pd for Suzuki reactions [33]. These results suggest that the performance of a catalyst depends both on the active metal center and its support. In other work, Fe- [14,22], Ni- [14,22,35–37], Rh- [38] and Au-NPs [39,40] have also been investigated for use as catalysts in Suzuki coupling reactions. However, it was observed that Ni-NPs in a colloidal system could be oxidized during the reaction, making the recyclability of the catalyst questionable [37]. Colloid-stabilized Rh-NPs with polyvinylpyrrolidone were prepared by reducing RhCl<sub>3</sub>·3H<sub>2</sub>O with various aliphatic alcohols (from methanol to pentanol) [38]. Rh-NPs obtained from ethanol showed good activity and recyclability for Suzuki coupling reactions [38]. Following initial success with Au<sup>III</sup>- and Au<sup>I</sup>-based complexes as catalysts in Suzuki reactions [39,40] it was shown that Au-NPs also possess a good catalytic performance in colloidal systems, and promising recyclability [39].

In addition to aryl halides, aryl diazonium salts were also shown to undergo cross-coupling reactions with arylboronic acids

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