Boron nitride-palladium nanostructured catalyst: efficient reduction of nitrobenzene derivatives in water

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1. Introduction

Transition metal catalyzed organic reactions have contributed remarkably to the chemical processes and industries [1–4]. In particular, palladium (Pd) has shown promising catalytic activity in the form of complexes, heterogeneous catalysts, and nanoparticles (NPs) [5–9]. Pd NPs possess a large number of merits, among which distinctive quantum properties as well as adjustable size are of the most conspicuous ones. From the application viewpoint, nanostructures containing Pd NPs are known as a practical class of the effective heterogeneous catalysts that are widely used for a variety of organic transformations due to the high surface-to-volume ratio [10–14]. For example, Pd NPs have been extensively employed in many common catalytic reactions such as hydrogenations, cross-coupling reactions, oxidations, etc [15–17]. However, active surface atoms often lead to Pd NPs aggregation, causing a rapid catalyst deactivation [18–22]. In addition, these precious nanocatalysts may encounter various challenges derived by their precipitation and instability as well as low recoverability, limiting their practical applications [23–26]. These drawbacks, however, can be resolved using the heterogeneous systems containing insoluble solid supports and Pd nanocatalysts [27–29]. In other words, the aforementioned limitations could be resolved by using supporting materials which have high surface area, appropriate physiochemical stability, etc. Although Pd NPs individually presents appealing catalytic behavior, their stabilization on solid supports generally present improved catalytic activity (e.g., high durability, stability, and reusability) compared with unsupported ones [30–32]. While several materials including bentonite,
hydroxyapatite, carbon, polymers, and ceramics have been used as the supports for Pd NPs, 2-dimensional nanostructures seem to be promising candidates due to their favorable characteristics, e.g., physicochemical and mechanical stability [33–38]. Accordingly, several inspiring efforts have been dedicated to using graphite flakes as the supporting materials for Pd NPs, resulted in excellent yields for chemical transformations. However, some applications may evoke high strength of the applied supports, particularly when the catalyst is used in highly erosive and/or oxidizing environments [39]. Therefore, other 2-dimentional nanostructured materials such as hexagonal boron nitride (BN) can be considered as potential supports of Pd NPs. The material is recently attended by researchers with various backgrounds, as it presents magnific physical and chemical properties such as low density (2.1 g cm⁻³), preeminent chemical stability, oxidation resistance, high surface area and biocompatibility [40–42]. Some types of BN have highly polar B–N bonds are remarkably stronger than the nonpolar C–C bonds in the graphite structure, which exposes them as very appropriate material with high hardness and chemical stability under oxidative and reductive conditions [43]. Consequently, efforts are already focused on using h-BN in a wide range of applications including organic pollutant adsorption, water purification, energy storage, and catalyst supports [44–46]. However, the application of BN as metal nanocatalysts support is relatively new and essentially limited to the recent research works [47–49]. Sajiki et al has reported a successful application of BN supported Pd NPs for the semi-hydrogenation of alkynes [50, 51]. In addition, BN supported Pd catalyst has also been utilized for the oxidation of lactose and alcohols [52]. BN is also capable of removing contaminants in wastewater treatment, particularly aromatic pollutants which should be removed through degradation reactions [53].

Nitroaromatics basically consist of one or two nitro groups. Having released in the environment, these chemical compounds can give rise to severe environmental pollution [54]. For example, it has been indicated that some nitroaromatics such as nitrobenzene, can negatively affect both animals and humans. Traces of the compound have been detected in malignancies, digestive system disorders, and other metabolic dysfunctions [55–57]. This chemical seems to be highly environmentally destructive, as it is widely used in several industries such as dye, petrochemical, drug, and herbicides, which relatively produce the large volumes of wastewater [58–62]. The United States Environmental Agency has listed nitrobenzene as one of the most hazardous pollutant. It has been estimated that roughly 10,000 tons of nitrobenzene compounds are released in the ecosystem, annually [63]. Hence, it is among the researchers’ high priority to deal with the aforementioned environmental side effects of nitrobenzene derivatives, particularly from the wastewater treatment approach.

There are several methods to refine the ecosystem off the contaminated wastewater, including physicochemical treatments to degrade the toxic compounds. Adsorption, advanced oxidation processes (introducing highly oxidant reagents), chemical oxidation of the pollutants (ozonation), and the reduction of nitroaromatics can be considered as the most common related wastewater treatment methods [64, 65]. The latter process, the reduction of nitroaromatics, is known as an important chemical process to remove the organic amines derived by agrochemical, pharmaceutical, polymer and pigment industries. In addition, this method purifies contaminated water safely, as fewer amounts of hazardous chemical oxidants enters into the environment [66–70].

In this study, we synthesized BN supported Pd NPs (BN-Pd) nanostructured catalyst using a facile and green method for the nitrobenzene reduction process. The catalytic activity of the prepared nanostructured catalyst and its reusability was also investigated.

2. Experimental

2.1. Synthesis of BN-Pd nanostructured catalyst
All chemicals were purchased from Aldrich, Merck, and Fluka companies and were applied without any additional purification. BN-Pd nanostructured catalyst was synthesized through a simple and green mixing process using a mild reductant. At the first step, the BN flakes (2 g) were dispersed in water/ethanol (10:1) medium and ultrasonicated for 30 min. Then, Pluronic F-127 (200 mg) was added in the solution followed by K₂PdCl₄ (200 mg). The mixture was stirred at room temperature for 7 h. Finally, the obtained BN-Pd nanostructured catalyst was filtered and washed with distilled water and ethanol repeatedly, and dried in a vacuum oven.

2.2. Characterizations
The structural properties of the BN-Pd nanostructured catalyst was characterized using a transmission electron microscope (TEM: JEOL JEM 3000 F), and a scanning transmission electron microscope (STEM: JEOL, JEM F200) equipped with an energy-dispersive x-ray spectroscopy detector (EDS). The composition of the BN-Pd nanostructured catalyst was investigated using an x-ray photoelectron spectroscopy (XPS, Sigma probe, VG
The loading amount of Pd NPs on BN support was analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7500 Japan).

2.3. Catalytic reductions

The process in which nitrobenzene is reduced to aminobenzene was catalyzed via a BN-Pd nanostructured catalyst at room temperature in the present of NaBH4. The hydrogenation process took place in 15 min. In a typical experiment, catalyst (1 mol%) was added to 20 ml of distillated water. Afterwards, 1 mmol of nitrobenzene accompanied by 1.5 mmol of NaBH4 added to the mixture in the glass flask. Then, the BN-Pd nanostructured catalyst was separated from the solution after the complete progression of the reduction reaction. The yield of the products and potential intermediate reactions were monitored using a gas chromatography mass spectrometry (GC-MS: Agilent Technologies 7693 Autosampler).

3. Results and discussion

TEM images of the produced BN-Pd nanostructured catalyst is presented in figure 1. While figure 1(a) shows the smooth surface of the commercially available BN flakes, other nanographs of figure 1 clarify the uniform distribution and nanostructure of Pd NPs dispersed on BN support. As can be seen, the Pd NPs have been homogenously dispersed and adorned on BN support, which leads to efficient catalytic performance. The Fast Fourier transform (FFT) of a Pd NP presented in figure 1(e) also confirms the crystallinity of the dispersed NPs, and shows a good adjustment to the previously published reports. The average size of the Pd particles contributed in the BN–Pd nanostructured catalyst can also be measured as ~3 nm, using the high resolution TEM (HRTEM) nanographs presented in figure 1(c). The presence of the Pd NPs in the BN–Pd nanostructured catalyst can also be confirmed, in the EDS elemental map of the material (figure 2). The elemental map also reveals the homogenous distribution of Pd element through the bed consisted of boron and nitrogen atoms. XPS analysis of the synthesized BN–Pd nanostructured catalyst is presented in figure 3, which confirms the aforementioned discussions of Pd NPs distribution and composition of the materials. In addition, the Pd NPs loading on BN support can be simply controlled by particular amount of BN and tuning the ratio of Pd precursor and F127 as mild reducing agent, measured by ICP-AES, was found to be ~2.1 wt%.

The potential and efficiency of the BN–Pd nanostructured catalyst as an active and stable catalyst were investigated in the reduction of nitrobenzene derivatives in water. First, various control experiments were performed to find the most appropriate reaction conditions for the heterogeneous reduction of nitrobenzene.
Figure 2. (a) STEM image of the Pd-BN catalyst, and (b) related EDS elemental spectrum and maps.

Figure 3. XPS analysis of BN-Pd nanostructured catalyst including (a) survey scan, and deconvoluted analyses of (b) B, (c) N, and (d) Pd elements.
Table 1. Optimization of reaction conditions for reduction of nitrobenzene using BN-Pd nanostructured catalyst.\textsuperscript{a}

| Entry | BN-Pd nanostructured catalyst (mol\%) | Time (min) | NaBH\(_4\) (equiv.) | Yield (%)\textsuperscript{b} |
|-------|--------------------------------------|------------|---------------------|-----------------------------|
| 1     | 0.5                                  | 15         | 2                   | 58                          |
| 2     | 0.75                                 | 15         | 2                   | 77                          |
| 3     | 1                                    | 15         | 1                   | 80                          |
| 4     | 1                                    | 10         | 1.5                 | 89                          |
| 5     | 1                                    | 5          | 2                   | 55                          |
| 6     | 1                                    | 10         | 2                   | 84                          |
| 7     | 1                                    | 15         | 1.5                 | 98                          |

\textsuperscript{a} Nitrobenzene (1 mmol), H\(_2\)O (20 ml), r.t.

\textsuperscript{b} The yields were determined by GC-MS.
After finding the optimized conditions, to extend the application of the BN-Pd nanostructured catalyst, under the optimized reaction conditions (1 mol% Pd, 1 nitrobenzene derivatives, 1.5 equiv. NaBH₄, 15 min, H₂O), the reduction of several structurally diverse nitrobenzene derivatives was investigated. As shown in table 2, the Pd nanocatalysts showed high catalytic activity for reduction of various nitroaromatics under mild reaction conditions to afford the corresponding amines in high yields. The nitro group of nitroarenes with different functional groups was selectively reduced to the amino moiety. The halogen groups remained intact.

| Entry | Nitroaromatic | Product | Yield (%) |
|-------|--------------|---------|-----------|
| 1     |              |         | 98        |
| 2     |              |         | 93        |
| 3     |              |         | 92        |
| 4     |              |         | 92        |
| 5     |              |         | 89        |
| 6     |              |         | 87        |
| 7     |              |         | 82        |
| 8     |              |         | 80        |
| 9     |              |         | 85        |

*Table 2. Heterogeneous reduction of nitrobenzene derivatives.*

(a) Substituted nitrobenzene (1 mmol), NaBH₄ (1.5 equiv.), Pd nanocatalyst (1 mol%), H₂O (20 ml), r.t., 15 min.

(b) The yields were determined by GC-MS.

(c) 3 equiv. of NaBH₄ was used.
under the reaction conditions (table 2, entries 2–4). An arene with more than one nitro group could be reduced with good efficiency (table 2, entry 7).

We also compared the catalytic activity of BN-Pd nanostructured catalyst prepared by F127 with other supported Pd NPs, which were synthesized conventionally by using NaBH₄, the result of which is depicted in table 3. Various supported Pd NPs were characterized by TEM analysis (figure 4). The solid catalysts were prepared using NaBH₄ on different supports, namely Pd NPs supported on carbon, mesoporous carbon, hydroxyapatite, SiO₂ NPs, zirconia, and SBA-15 mesoporous silica. Indeed, the agglomeration of Pd NPs prepared under harsh reduction conditions is inevitable. The result shows that the catalytic performances of these catalysts were poor to moderate in the reduction process. It is noteworthy mentioning that BN supported Pd NPs prepared by NaBH₄ also presented agglomerated and polydispersed Pd NPs. On the other hand, BN-Pd nanostructured catalyst prepared under mild reduction of F127 presented monodispersed and uniform Pd NPs providing more efficiently catalytic reduction. Furthermore, the BN-Pd nanostructured catalyst provided higher catalytic activity than the commercially available charcoal supported Pd NPs under identical reaction conditions. It is worth noting that the eminent attributes exhibited by the BN-Pd nanostructured catalyst provided superior activity for the nitroaromatics reduction in shorter reaction time and under milder conditions and in comparison with those summarized for some of the previously reported heterogeneous catalysts (table 4).

Table 3. The reduction of nitrobenzene catalyzed by different supported Pd NP catalysts.

| Entry | Catalyst | Yield (%) |
|-------|----------|-----------|
| 1     | BN-Pd nanostructured catalyst prepared by F127 | 98 |
| 2     | BN supported Pd NPs prepared by NaBH₄ | 82 |
| 3     | Alumina supported Pd NPs prepared by NaBH₄ | 80 |
| 4     | Carbon supported Pd NPs prepared by NaBH₄ | 75 |
| 5     | Commercial charcoal supported Pd NPs | 77 |
| 6     | Hydroxyapatite supported Pd NPs prepared by NaBH₄ | 81 |
| 7     | SBA supported Pd NPs prepared by NaBH₄ | 85 |
| 8     | SiO₂ supported Pd NPs prepared by NaBH₄ | 79 |
| 9     | Zirconia supported Pd NPs prepared by NaBH₄ | 81 |

a Nitrobenzene (1 mmol), NaBH₄ (1.5 equiv.), Pd catalyst (1 mol %), H₂O (20 ml), r.t., 15 min.
b The yields were determined by GC-MS.
The durability and reusability of the BN-Pd nanostructured catalyst are important criteria for the practical industrial applications. To verify these issues, we investigated the recycling of the synthesized BN-Pd nanostructured catalyst in the reduction of nitrobenzene under the optimal conditions. The BN-Pd nanostructured catalyst was successfully recycled and reused for six consecutive cycles (Figure 5). There was a small decrease in catalytic activity of the BN-Pd nanostructured catalyst after five runs. ICP-AES analysis of the reaction solution after the six cycles of reaction and recycle of the BN-Pd nanostructured catalyst showed that 1.2% of Pd species remained in the solution. The catalytic activity decline seems to result from the loss of the BN-Pd nanostructured catalyst during the steps of washing and separation in the consecutive reuses.

### 4. Conclusions

We have developed a new recyclable and efficient heterogeneous catalyst, containing boron nitride and palladium nanoparticles in water. This catalyst presents efficient catalytic activity in the reduction of nitrobenzene derivatives under mild reaction conditions. Furthermore, the introduced heterogeneous catalyst allows an applicable catalyst reuse in the reduction of nitrobenzene for several runs. The simplicity of this novel approach introduces an attractive and practical heterogeneous catalyst class for other chemical processes. The present environmentally friendly method has potential applications for the use in laboratories and industrial scale reactions.

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Conflicts of interest

The authors declare no competing interest.

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