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Monodisperse palladium nanocatalysts for dehydrocoupling of dimethylamineborane

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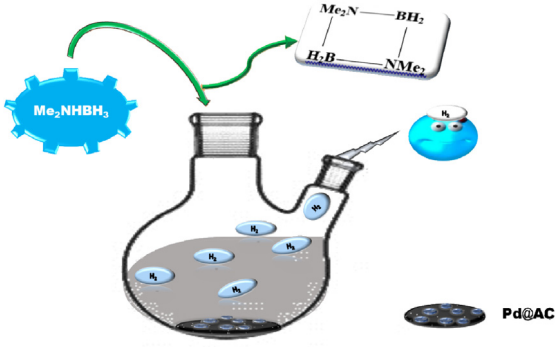
HIGHLIGHTS

- The discovery of an efficient nanocatalyst for hydrogen generation reaction.
- The synthesis of monodisperse octylamine stabilized Pd@AC nanocatalyst
- The one of the best TOF value of Pd@AC NPs for dehydrogenation reaction.
- Higher efficiency and durability due to the small sizes, monodispersity and high metallic ratio of prepared catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

Over the last several decades, dimethylamine borane, which is one of the ammonia borane derivatives, has been attracting attention as one of the most effective solid hydrogen storage materials. Herein, the preparation and characterization of activated carbon supported palladium nanoparticles was reported as a highly efficient catalyst for dehydrogenation of dimethylamine borane under ambient conditions. The characterization of prepared nanomaterials was made by using some analytical methods such as XRD, XPS, TEM, HR-TEM. The prepared nanomaterials were observed in the range of 3.46–4.36 nm with an approximate mean diameter of 4 nm. The results of these analyses showed that the new palladium nanoparticles were colloidally stable and crystalline. The catalytic activity and durability of prepared nanomaterials were investigated for the dehydrogenation of dimethylamine borane. The one of the best TOF ($100.3\ h^{-1}$) value was obtained for the dehydrogenation of dimethylamine borane. The investigations showed that the palladium nanoparticles have very high catalytic activity and stability at room conditions.

1. Introduction

Considering the decrease in fossil fuel reserves and environmental damage caused by fossil fuels, the importance of hydrogen technology is steadily increasing. Hydrogen stands out as a clean energy material that can overcome the top of the global energy problem arising from limited reserves of fossil fuels and reduce environmental pollution resulting from the use of fossil fuels [1–3]. For this purpose, amine-boranes are the materials that can be preferred for the hydrogen production due to their high hydrogen content and low weight. Recently the catalytic hydrogen generation from dimethylamine-borane, which is one of the important amine borane derivatives, has taken so many attentions. The last studies [4–10] have shown that a potential H_2 release of 3.5% by the reaction of dehydrogenation of dimethylamine - borane (DMAB) was carried out with the suitable catalyst (Scheme 1). For this aim, various catalysts have been tried for hydrogen generation

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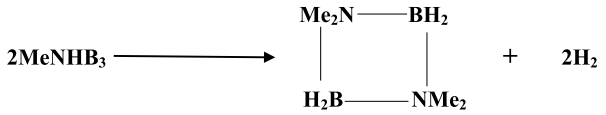

Scheme 1. The generation of hydrogen from dimethylamine borane-containing palladium (0) nanoparticles.

reaction [11–23]. However, among the prepared catalysts systems, metal nanoparticle catalysts have much more advantages according to homogeneous catalysts. These advantages are reusability, catalyst recovery, simple product isolation, etc. Therefore, this paper is focused on the new type of catalyst for the dehydrocoupling of DMAB. In this context, this paper presents the synthesis and characterization of monodisperse activated carbon supported Pd (0) nanoclusters, which is called Pd@AC. Pd@AC were prepared by ultrasonic double solvent reduction method with the help of $PdCl_2$ at room temperature. Pd nanoparticles were characterized by using TEM, HRTEM, XRD and XPS spectroscopic techniques [24–27]. The characterization analysis demonstrated that the palladium (0) nanoparticles were formed as the highly stable crystalline structure and their diameters are in the 3.46–4.36 nm range. The catalytic activity, reusability and lifetime of palladium nanoparticles were examined for the dehydrogenation reaction of DMAB at ambient conditions, and it showed high catalytic activity with a good reusability performance.

2. Experimental

2.1. Preparation of active carbon stabilized palladium nanoparticles (Pd@AC)

For the preparation of active carbon supported palladium nanoparticles, ultrasonic double solvent reduction method was performed. According to this method, 0.25 mmol of $PdCl_2$ and octylamine solution was reduced using lithium triethyl borohydride solution and ethanol in ultrasonic conditions. The formation of octylamine stabilized palladium nanoclusters can be seen by the brown color observed in the solution. The excess surfactants and contaminants present in the catalyst were removed by using ethanol, and then the catalyst was dried under vacuum. After the preparation of Pd nanoparticles, activated carbon was added to the Pd nanoparticles (in 1:1 ratio) in a small amount of ethanol.

3. Results and discussion

3.1. Characterization and analyzing of activated carbon supported palladium nanoparticles

Monodisperse Pd@AC was produced from $PdCl_2$ by the ultrasonic double solvent reduction method at room temperature. The initially formed Pd nanoparticles are rapidly collected and precipitated in the tetrahydrofuran solution when $PdCl_2$ reduction was performed in the presence of stabilizing ligands such as octylamine and activated carbon. Palladium nanoparticles formed by the reduction process in the presence of the octylamine and activated carbon ligand have been found to be stable against agglomeration for a very long time. Accordingly, it can be said that activated carbon and octylamine are a well-stabilizing material for palladium nanoparticles. To remove the excesses onto the palladium nanoparticle, the catalyst was washed with ethanol and then dried under vacuum to evaporate the solvent. XPS, XRD, TEM and HRTEM analyses were made for the pre-characterization of the palladium nanoparticles [28–31].

Powder X-ray diffraction (P-XRD) patterns of monodisperse Pd@AC are given in Fig. 1. The crystal structure of the XRD pattern

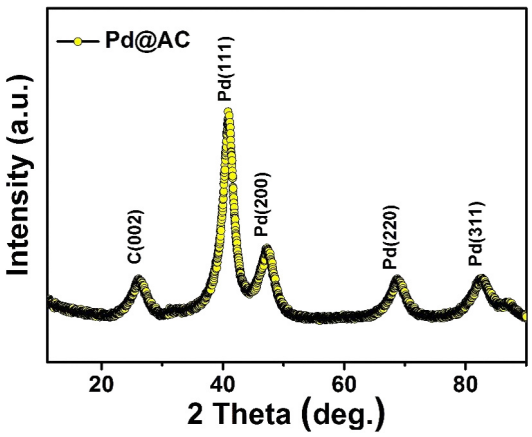

Fig. 1. A P-XRD pattern of activated carbon stabilized Pd nanoclusters in the 2θ range of 10–90°.

showed that the peak near 24.6° corresponds to the activated carbon (002) plane. Moreover, the prepared nanomaterial can be attributed to the crystal planes of the palladium (111), (200), (220) and (311) of the face-centered cubic (fcc) structures as shown in Fig. 1 [32–34]. The lattice parameter of palladium was calculated with the help of Pd (220) X-ray diffraction peak. The cage constants of uniformly distributed Pd@AC nanoparticles were calculated to be 3.887 Å using Eq. (1), which is good agreement with 3.910 Å for pure Palladium [32–34].

$$\sin\phi = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\alpha} \tag{1}$$

The average crystallized particle size of well-dispersed activated carbon stabilized palladium was found to be 3.59 ± 0.41 nm by the help of Scherrer formula [32–39].

Moreover, the crystallinity, morphology, and size of activated carbon palladium nanoparticles were investigated by high-resolution electron microscopy (HRTEM) and transmission electron microscopy (TEM) analysis. These analyses are given in Fig. 2 (a, b). According to Fig. 2, the presence of monodisperse Pd@AC was observed in the range of 3.46–4.36 nm with a mean diameter of 3.91 ± 0.45 nm. These results are consistent with the results of XRD. Pd@AC nanoparticles show a homogeneous distribution on activated carbon. Moreover, it can be seen in HR-TEM results that the particles have a spherical structure and that there is no aggregation in the prepared catalysts. Fig. 2 also reveals that these palladium nanoparticles have been well dispersed with a crystalline spacing of 0.22 nm, and this value is excellent consistency for nominal palladium nanoparticles [32–34,40,41].

X-ray photoelectron spectroscopy (XPS) was used to examining the oxidation state of the metal in the monodisperse Pd@AC catalyst. X-ray photoelectron spectroscopy results (Fig. 3) proved that the peak at 335.5 eV indicates the reduction of Pd (II) to Pd (0). Besides, as shown in Fig. 3, the Palladium (II) peak is observed at 338.6 eV. This peak is due to the chemical absorption of the O_2 during surface preparation or surface oxidation [32–34].

3.2. Catalytic activation of activated carbon palladium nanoparticles

A series of experiments were done for determining catalytic activation of Pd@AC s at room temperature. During the dehydrocoupling of dimethylamine borane, the hydrogen gas was released. The catalytic activity of the palladium nanoparticles was determined by using a measure of the gas volume evolved, and NMR spectroscopy was used for investigation of the gas released. DMAB has added to the THF solution of monodisperse Pd@AC and