Green synthesis of Pd nanoparticles supported on LDHs and its application in the Suzuki coupling reaction

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Abstract. Palladium nanoparticle supported on layered double hydroxides (PdNPs/LDHs) were prepared via a green route employing Pine needle extract (PNE) as a reducing and capping agent. The prepared PdNPs/LDHs were characterized by XRD, TEM, EDS, N₂-adsorption analysis. The PdNPs with an average size of 1.75 nm are uniformly dispersed on the LDHs surface. It exhibits high catalytic activity toward the Suzuki coupling reaction with only 0.05 mol% of the catalyst. And the catalyst could be reused for 8 times without an obvious loss of activity.

1. Introduction
Pd catalyzed C-C coupling reactions have been well-known for many years. In these reactions, heterogeneous Pd catalysts are preferred over homogeneous catalysts due to their facile separation from the reaction mixture and the possibility of recycling [1-5].

The catalytic process is a surface phenomenon, a sufficiently high dispersion of metal nanoparticles on the surface of support is crucial for the enhancement of catalytic activity. Layered double hydroxides (LDHs) have attracted interest as a novel support for the dispersal and stabilization of nanoparticles in nanocomposites preparation [6-7], due to its specific interparticle mesoporosity, the ability to exchange anions, and the structure memory effect.

In the recent years, the utilization of biological systems has been became a new method for the synthesis of metal NPs, because it is suitable to develop a low-cost, reliable and eco-friendly route for preparation nano materials [8-10].

In this work, we present a ‘green’ method for the synthesis of supported Pd NPs using Pine needle extract as the reducing agent and the LDHs as the carrier. As expected and shown here, the as-prepared Pd/LDHs complexes could serve as a heterogeneous catalyst, which exhibited excellent catalytic activity for the Suzuki coupling reactions.

2. Experimental

2.1. Preparation of PNE
The sundried Pine needles were milled. Then, 2 g of the milled powder was added into 100 ml deionized water and heated at 60 °C for 1 h. The PNE obtained was centrifuged at 4000 rpm and filtered through Whatman No.1 filter paper. The filtrate was collected in an Erlenmeyer flask and
stored at 4 °C for further use. The main FT-IR absorption bands of PNE appear at 3415, 2923, 1627, 1515, 1405, 1262 and 1074 cm⁻¹. The broad peak at 3415 cm⁻¹ is attributed to the O - H (phenolic) stretch used as a reducing agent and the peaks at 1627, 1515, 1405, 1262 and 1074 cm⁻¹ are assigned to the stretching vibrations of (NH)-C=O (protein), C=C (aromatic), C-O-C (esters, ethers) and C-OH/C-H (polyols) which can serve as a stabilizing agent for protecting the Pd NPs.

2.2. Preparation of Pd/LDHs catalyst
To synthesize PdNPs/LDHs(magnesium-aluminum hydrotalcite) with 3 wt% Pd (Pd₀.03/LDHs-PNE), LDHs (0.5 g) was dispersed in the Na₂PdCl₄ solution (15 ml, 0.01 M) and impregnated for 12h at room temperature. Subsequently, 22.5 ml of the PNE was added into this precursor mixture with stirring at 60 °C for 3 h.

2.3. Catalytic Suzuki Coupling Reaction
Under air atmosphere, 4-bromotoluene (1 mmol), K₂CO₃ (2 mmol) and the catalyst (0.05 mol%) were added into a mixed solvent of 15 ml of EtOH:H₂O (1:1) with constant stirring at room temperature for 10 min to obtain an evenly disperse system. Then, phenylboronic acid (1.5 mmol) was added into the mixture. After completion of the reaction, the obtained products were determined by HPLC analysis.

3. Result and discussion
Figure 1 shows the XRD patterns of the Mg₃Al₂-CO₃-LDHs and Pd₀.03/LDHs-PNE. The LDHs sample exhibits the characteristic reflections of typical and well-ordered layered double hydroxides with a basal spacing (003) of 0.76 nm, indicating that only CO₃²⁻ ions occupy the gallery region. However, no diffraction peak of Pd species was observed in Figure 1b because of the lower Pd loading amount and small Pd particle size.

![XRD patterns](image)

**Figure 1.** XRD patterns of (a) LDHs, (b) Pd₀.03/LDHs-PNE

The N₂ adsorption-desorption isotherms for LDHs and Pd₀.03/LDHs-PNE are shown in figure 2. All of the characteristic isotherms correspond to a type IV isotherm with a type H3 hysteresis loop.
As shown in table 1, the BET surfaces decreases from 175.24 m$^2$/g to 118.23 m$^2$/g and the pore volume also decreases from 20.49 nm to 16.97 nm. The decrease suggests that Pd at least partially located inside the channels of the carrier.

Table 1. Textural properties of the LDHs and Pd$_{0.03}$/LDHs-PNE

| Sample                  | BET surface area/m$^2$/g | Pore volume/cm$^3$/g | Pore size/nm |
|-------------------------|--------------------------|----------------------|--------------|
| LDHs                    | 175.24                   | 0.76                 | 20.49        |
| Pd$_{0.03}$/LDHs-PNE    | 118.23                   | 0.53                 | 16.97        |

The image offigure 3a shows the nano-laminated structure of LDHs. Figure 3c clearly demonstrates that in Pd$_{0.03}$/LDHs-PNE nanocomposite, PdNPs were highly dispersed on the LDHs surface. The size of PdNPs ranges from 1.24 nm to 3.11 nm (an average diameter of about 1.75 nm from Figure 3d). EDS was used to identify the elemental composition of Mg$_3$Al$_2$CO$_3$-LDHs and the EDS spectrum indicated...
the presence of C, O, Mg, Al and a small amount of Cl (figure 3b). The Mg/Al atomic ratio of the sample was 25.2:15.4, which is approximately equal to the theoretical Mg/Al ratio (3:2).

Figure 3. TEM images of LDHs (a), EDS pattern (b), Pd$_{0.03}$/LDHs-PNE (c) and corresponding size distributions (d).

Figure 4a shows the yields at different intervals with the catalyst. The conversion of 4-bromotoluene reached to 99% at 30 min with 0.05 mol% catalyst. This catalyst could be recycled simply by centrifugation. In addition, the yield decreased to 95% (figure 4b) in the eighth cycle, but it decreased to 81% (figure 4b) in the tenth cycle.

Figure 4. (a) The effect of time in the Suzuki reaction and (b) the reusability of the Pd$_{0.03}$/LDHs-PNE catalyst.

4. Conclusions
In summary, an effective and reusable Pd/LDHs catalyst was designed and successfully prepared by a low-cost and green method using Pine needle extract as the reducing agent and the LDHs as the carrier. The PdNPs with an average particle size of 1.75 nm. The conversion of 4-bromotoluene catalyzed by Pd$_{0.03}$/LDHs-PNE reached 99% with 0.05 mol% catalyst under mild reaction conditions. In addition,
the yield of Pd$_{0.03}$/LDHs-PNE nanocomposite was 95% after recycling eight times. This method provides a simple and eco-friendly route for synthesis supported PdNPs, which may find potential application in other nano metal materials.

**Acknowledgements**
This work was supported by the National Natural Science Foundation of China (No. 21676074), Heilongjiang Provincial Science and Technology Projects (ZY17A06) and Science Foundation of Heilongjiang Academy of Sciences (YY2017SH01& ZNBZ2018SH01).

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