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## Synthesis of Aminoclay protected Palladium Nanoparticles and Study Its Catalytic Activity in Organic synthesis

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**Abstract:** Aminoclay is one of the important classes of phyllosilicate which can be synthesized by adding 1:2 molar ratio of  $Mg(NO_3)_2$  and 3-aminopropyltrimethoxysilane (APTMS) in ethanol medium. The resulting aminoclay was used as stabilizing agent for the synthesis of water soluble aminoclay protected palladium nanoparticles. Aminoclay-Pd nanoparticles can be used as catalyst in organic synthesis. The catalytic behavior of aminoclay-PdNP was investigated under various experimental conditions. The reaction product was characterized with UV, XRD, IR and NMR studies. The aminoclay catalyst is recoverable and reusable and all reactions were carried out under aqueous medium in both aerobic and anaerobic conditions. The progress of the catalytic reaction was monitored by using NMR study confirmed that the reaction completed within 7 hrs as mentioned in the previous reported method. The present method is considered as one of the greener approach for the synthesis of various organic intermediates using PdNP catalyst. The schematic diagram of the reaction is shown below:



Keywords: Aminoclay, Palladium Nanoparticles, Catalytic Activity, Organic synthesis.

#### 1. Introduction

Organic synthesis is routinely performed in non-aqueous solvents for both academic research and industrial applications. Lack of solubility of generally lipophilic organic or organometallic compounds in water compelled chemists to employ non-aqueous solvents. In contrast, nature, in its unique way, utilizes water for enzymatic transformations of all organic substrates. The use of water, the most abundant and non-toxic solvent is reclaiming its importance due to pressing environmental, economical, and safety concerns<sup>1</sup>. Nanoparticle catalysis in water carrying out efficient reactions under environmentally benign conditions associated with green chemistry and also facilitates separation of products<sup>2</sup> from Pd colloids dispersed in water. Since catalysis takes place on metal surface, nanoparticles are much more reactive than the particulate metal counterpart due to their high surface to volume ratio<sup>3</sup>. In the present work, we report a use of water as solvent with Pd nanoparticles as catalyst which are otherwise insoluble in water<sup>4</sup> for a variety of coupling reactions where predominantly lipophilic organic reactants provide high yield of products in aqueous medium. The palladiumcatalyzed Suzuki–Miyaura coupling reaction, which involves the cross-coupling reaction of aryl halides with aryl boronic acids, is one of the most powerful and convenient synthetic methods for the preparation of biaryl and alkene derivatives that are structural components of natural products, agrochemicals, pharmaceuticals, and polymers and organic electroluminescence (EL) materials<sup>3</sup>. Suzuki–Miyaura coupling reaction has many advantages: tolerance of a wide range of functional groups, low toxicity, and easy handling of reagents and byproducts. Suzuki-Miyaura coupling reactions generally employ homogeneous palladium catalysts in the presence of phosphine ligands<sup>6</sup>. Homogeneous palladium catalysts are usually not reusable and the products are frequently contaminated by residual palladium and ligands, which are difficult to separate from the end product. To overcome these difficulties, the application of a reusable heterogeneous palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has been developed<sup>7</sup>. Because of its availability, easy handling, and reusability, and many applications of Suzuki–Miyaura coupling reactions have been reported<sup>8</sup>. In recent years, there is a growing interest in developing eco-friendly supports for dispersing metal nanoparticles. Specifically, amine functionalized Mg pyllo(organo)silicate is an emerging class of layered material which has shown its remarkable capping action towards metal nanoparticles<sup>9-10</sup> One important feature of aminoclay is its exfoliation in water by the protonation of amine groups which can be restacked by the addition of ethanol or less polar solvent. Also metal nanoparticles can be synthesized by *in-situ* approach to obtain metal nanoparticle-clay hybrids. The Pd-aminoclay for catalytic hydrogenation is a useful method for the reduction of various functional groups in particular carbon–carbon multiple bonds in both academia and industry. In particular, the chemo- selective hydrogenation of unsaturated carbonyl compounds is of prime importance because of its innumerable applications in the synthesis of drugs and fine chemicals<sup>11</sup>. The development of simple, convenient and efficient method using environmentally benign catalysts<sup>12</sup> would expand the scope of catalytic hydrogenation. Many biological and catalytic applications it is necessary to use highly water dispersible clay based nanocatalyst which would interact with desired molecules or substrates. Here we report to study the catalytic activity of Pd-aminoclay for carbon-carbon bond formation by Suzuki coupling under aqueous medium. Though Pd nanoparticles prepared in aminoclay are used for Suzuki reaction<sup>13</sup> the scope of the basic support (aminoclay) has not been fully explored. We have accomplished the Suzuki coupling reaction without using any external base exploiting the basic nature of the Pd-aminoclay nanocomposite. The Pd-aminoclay catalyst can be recovered and reused in multiple applications. This approach therefore addresses several key requirements from a green chemistry perspective. These results demonstrate the successful application of aminoclay to prepare active Pd nano catalyst with tunable catalytic activities for Suzuki cross-coupling reactions.

#### 2. Experimental Details

#### 2.1 Materials required

All the reagents and solvents are used as purchased, without any further purification. Compounds were purified on axially compressed columns, packed with silica, and eluting with *n*-hexane/ethyl acetate mixtures.  $H^1$  NMR and  $C^{13}$  NMR were recorded on Brüker Advance 300 MHz, in CDCl<sub>3</sub> using TMS as the internal standard, chemical shifts were reported in parts per million (ppm) downfield from the tetramethylsilane. UV-Visible absorption spectra were recorded between 200–900 nm with Shimadzu 1800 model spectrophotometer, Japan.

To a solution of magnesium nitrate (4.2 gm) in ethanol (100 ml), APTMS (aminopropyltrimethoxy silane) (3.8 ml) was added drop wise addition and stirred at room temperature for 4 - 5 hrs and then centrifuged using ethanol for 2 to 3 times. A white precipitate was obtained and stored in dark.

#### 2.3. Preparation of Pd-aminoclay

20 mg of aminoclay mixed with of Millipore water (2 ml) was sonicated for two minutes followed by the addition of  $1 \text{mM} \text{PdCl}_2$  (2 ml) and 2 ml of 0.1M sodium borohydride yield aminoclay protected PdNP as a brown colored solution and was used for all catalytic reactions.

#### 2.4 Suzuki coupling reaction with pd-aminoclay

Aryl halide (1 mmol), boronic acid (1.1 mmol), and  $K_2CO_3$  (2 mmol), were added to water (3 ml) containing PdNP-aminoclay nanocomposite. The reaction mixture was then stirred at 90<sup>o</sup> C for 7 h and then cooled to room temperature. The reaction mixture was extracted twice with ethyl acetate (10.0 mL) and washed with water (10 mL). Finally the organic phase was purified and recrystallized by using ethanol as a solvent. The Scheme I depict the PdNP-aminoclay catalyzed Suzuki coupling reaction.



#### 3. Results And Discussion

The aminoclay protected PdNP nanocomposite was prepared by using our previous method <sup>14</sup>. The PdNP-aminoclay nanocomposite is water dispersible and shows a dark brown in color. Figure.1 (a) shows band in the wavelength region of 280-300 nm for aminoclay (b) shows band in the wavelength region of 225-237 nm for PdNP. The absence of absorption band for the precursor  $PdCl_4^{2-}$  at 280 nm confirms the complete reduction of Pd ions and the formation of PdNP-aminoclay nanoparticles.



We employed the water dispersible Pd-aminoclay in the cross coupling reaction of Iodobenzene with 3,4,5methoxyphenylboronic acid (1 mmol of each). The reaction was performed in water at 90  $^{0}$ C for 7 hrs using 10 mg of the catalyst in the presence of K<sub>2</sub>CO<sub>3</sub>. The corresponding product was obtained in good yield (85 %). The reactions are clean, high yielding and no side products were obtained. Moreover, the catalyst is air stable.



This product was confirmed by NMR spectrum.

In <sup>1</sup>H NMR: (300MHz, CDCl<sub>3</sub>):  $\delta$ H 3.90(s, 3H); 3.93(s, 6H); 6.78(s, 2H); 7.34-7.46(m, 3H);

7.56(d, 2H, J=4.5Hz).



In<sup>13</sup>C NMR: (75MHz, CDCl<sub>3</sub>): & 56.2, 61.1, 104.5, 127.1, 127.3, 129.0, 137.2, 141.4, 153.5.



The <sup>1</sup>H NMR spectrum of 3,4,5 methoxybiaryl compound showed singlet at  $\delta$  3.90 and 3.93 for methoxy protons and 6.78(s), 7.34-7.46(m), 7,56 (d) for aromatic protons. The <sup>13</sup>C NMR spectrum of compound showed methoxy carbons at  $\delta$  56.2 and 61.1, in addition to aromatic carbons.

#### Conclusions

We have shown that aminoclay protected palladium nanoparticles are active catalysts for Suzuki-Miyaura cross coupling reaction of aryl halides with aryl boronic acids in water and air. The catalyst exhibits high catalytic activity for Suzuki reaction in aqueous medium in both aerobic and anaerobic conditions. The catalyst can be recycled for more than three times with minimum loss of activity in Suzuki reactions. This product is tested for antioxidant and anticancer drug activity.

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#### **References:**

- 1. (a) Li .C.J, Organic Reactions in Aqueous Media with a Focus on Carbon-Carbon Bond Formations: A Decade Update Chem. Rev., 2005, 105, 3095; (b) Li .C. J, In Organic Synthesis in Water; Lindstrom, U. M., Ed.; Blackwell: New York, NY, 2007, 5, 68.
- 2. Astruc .D, Lu .F, Aranzaes .J. R, Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis, Angew. Chem., Int. Ed., 2005, 44, 7852.
- 3. (a) Schmid .G, Nanoparticles: From Theory to Application; Ed.; Wiley, Weinheim, Germany, 2004;
  (b) Richard .R, Surface and Nanomolecular Catalysis; Ed.; Taylor & Francis: London, 2006.
- (a) Nemamcha .A, Rehspringer .J.L, Khatmi .D, Synthesis of Palladium Nanoparticles by Sonochemical Reduction of Palladium(II) Nitrate in Aqueous Solution, J. Phys. Chem. B, 2006, 110, 383; (b) Kim .S. W, Kim .S, Tracy .J. B, Jasanoff .A, Bawendi .M. G, Phosphine Oxide Polymer for Water-Soluble Nanoparticles, J. Am. Chem. Soc., 2005, 127, 4556.
- (a) Nicolaou .K. C, Bulger .P. G, Sarlah .D, Palladium-Catalyzed Cross-Coupling Reactions in Total Synthesis, Angew. Chem., Int. Ed., 2005, 44, 4442–4489. (b) Suzuki .A, Organoborane coupling reactions (Suzuki Coupling) Proc. Jpn Acad. Ser. B, 2004, 80, 359–371; (c) Hassan .J, SRvignon .M, Gozzi .C, Schulz .E, Lemaire .M, Aryl-Aryl Bond Formation One Century after the Discovery of the Ullmann Reaction, Chem. Rev., 2002, 102, 1359–1469.
- (a) Phan .N. T. S, Sluys .M. V. D, Jones .C. W, On the nature of the Active Species in Palladium Catalyzed Mizoroki-Heck and Suzuki-Miyaura coupling-Homogeneous or Heterogeneous catalysis, A critical Review, Adv. Synth. Catal., 2006, 348, 609–679; (b) Suzuki .A, Carbon-Carbon bonding made easy, Chem. Commun., 2005, 4759–4763; d) Miyaura .N, in Metal-Catalyzed Cross-Coupling

Reactions, 2nd ed (Eds.: A. deMeijere, F. E. Diederich), Wiley-VCH, Weinheim, 2004, chap. 2; (c) Suzuki .A, Single and double Suzuki-Miyaura Coupling with symmetric dihalobenzenes, Organomet. J. Chem., 2002, 653, 83–90.

- (a) Hagio .H, Sugiura .M, Kobayashi .S, A water-compatible highly active and reusable PEG-coated mesoporous silica-supported palladium complex and its application in Suzuki coupling reactions, Org. Lett., 2006, 8, 375–378; (b) Kim .J.W, Kim .J.H, Lee .D.H, Lee .Y.S, Amphiphilic polymer supported N-heterocyclic carbine palladium complex for Suzuki cross-coupling reaction in water, Tetrahedron Lett., 2006, 47, 4745–4748; (c) Knepper .K, Vanderheiden .S, Braese .S, Nitrogen Functionalities in Palladium-Catalyzed reaction on solid supports: A case Study: Eur. J. Org. Chem., 2006, 1886–1898
- 8. Felpin .F. X, Ayad .T, Mitra .S, For a review of the Pd/C catalyzed Suzuki–Miyaura coupling reaction, Eur. J. Org. Chem., 2006, 2679–2690.
- 9. Datta .K.K.R, Eswaramoorthy .M and Rao .C.N.R, Water-solubilized aminoclay-metal nanoparticle composites and their novel properties, J. Mater. Chem., 2007, 17, 613.
- 10. Datta .K.K.R, Kulkarni .C and Eswaramoorthy .M, Aminoclay: a permselective matrix to stabilize copper nanoparticles, Chem. Commun, 2010, 46, 616.
- 11. Nishimura .S, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley-Interscience, New York 2001.
- 12. Ariga .K, Li .M, Richards .G. J and Hill .J.P, Nanoarchitectonics: A Conceptual paradigm for design and Synthesis of Dimensions- Controlled Functional Nanomaterials, J. Nanosci. Nanotechnol., 2011, 11, 1.
- 13. Firouzabadi .H, Iranpoor .N, Ghaderi .A, Ghavami .M and Hoseini .S.J, Palladium Nanoparticles Supported on aminopropyl functionalized clay as an efficient catalyst for Mizoroki-Heck and Suzuki-Miyaura reaction, Bull. Chem. Soc. Jpn., 2011, 84,100.
- 14. Patil .A. J, Muthusamy. E and Mann. S, Synthesis and Self-Assembly of Organoclay-Wrapped Biomolecules, Angew. Chem., Int. Ed., 2004, 43, 4928.

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