Title: Pd/BP2000 Nanocomposites: Efficient Catalyst for Hydrolytic Dehydrogenation of Ammonia-borane

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Pd/BP2000 Nanocomposites: Efficient Catalyst for Hydrolytic Dehydrogenation of Ammonia-borane

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Abstract

In current work, the activity of BP2000 supported Pd nanoparticles (NPs) were researched based on hydrolysis of ammonia borane (AB) reaction. Borane-tert-butylamine used for reduction of palladium (II) acetylacetonate for synthesize procedure of Pd NPs under mild conditions. As prepared Pd NPs were assembled on the BP2000, by liquid-phase self-assembly method. X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively coupled plasma-mass spectroscopy (ICP-MS) -advanced analytical techniques- were performed for detailed characterization. BP2000-supported Pd NPs were exhibited excellent activity and stability for the hydrolysis of AB. Pd/BP2000 nanocatalyst were showed the enhance catalytic activity that calculated turnover frequency (TOF) of 20.4 min^{-1}. The detailed report clarified the kinetics of Pd/BP2000 nanocatalyst parameters on catalyst amount, AB concentration, temperature and reusability. After the hydrolysis of AB with Pd/BP2000 nanocatalyst, activation energy of reaction was calculated to be 41.5 kJ mol^{-1}.

Keywords: Palladium, nanoparticles, BP2000, hydrogen, ammonia-borane.

1. INTRODUCTION

Energy consumption has been really high in these days because of ındustrial companies and human habits. Scientists focus on the new energy sources which contains less harmful poisoning-gas products. Hydrogen is still clean and safe energy source but transferring of hydrogen is still problem in an economic way. At this point, researchers ınterested in some compounds which has high hydrogen capacity. Formic acid [1], dimethlyamine borane [2-5], methlyamine borane [6] and ammonia-borane [7-10] are high hydrogen containing compounds. Ammonia-borane is well-known hydrogen carrier with the capacity of 19.6% hydrogen. When ıt is catalyzed by the convenient catalyst, ıt gives 3 moles of hydrogen [11]. (Eq1) It has unique specialties that non-poisining, high solubility, eco-friendly and good stability at room temperature [12].

$$NH_3BH_3(aq)+2H_2O(1)\rightarrow$$
$$NH_4BO_2(aq)+3H_2(g) \tag{1}$$
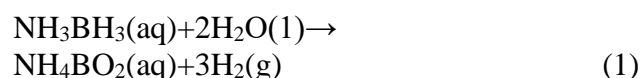
Up to now, many noble-metal catalysts, RuPd [13], Ru [14], Rh [15,16], Pt [17,18], RuRh [19] and Pd [20] nanoparticles were studied for hydrolysis of AB and showed high catalytic activity. Chen et al. [21] synthesized chitosan supported Pd nanocomposites with the range of 4-8 nm and showed good stability of chitosan structure onto the Pd nanoparticles for hydrolysis of AB with TOF value of 24.76 min^{-1}. Deka et al. [22] studied on carboxylic acid functionalized

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mesoporous organosilicas supported Pd nanoparticles or hydrolysis of AB and investigated the effect of carbocyclic acid groups. Pd nanoparticles are also catalyzed many important organic coupling reactions [23-25]. Sun et al. [26] synthesized Pd nanoparticles and supported on graphene oxide nanosheets and they worked on hydrogen generation from p-nitrophenol. The other support material is graphene hydrogel also active for hydrolysis of ammonia-borane. [27] Jia et al. also synthesized magnetic-graphene oxide Pd nanoparticles reusable and active catalyst for this reaction [28].

Inspired by these studies, this work focused on the cheaper and high surface area carbon materials which is called BP2000 commercial carbon. Firstly, Pd nanoparticles were synthesized under mild- conditions and supported onto the BP2000 surface by liquid-phase self-assembly method. Advanced analytical techniques were used for characterization for 3.5nm Pd/BP2000 nanocomposites.

2. EXPERIMENTAL

2.1. Materials and Methods

Oleylamine (OAm) (>70%), 1-octadecene (ODE, 90%), palladium (II) acetylacetonate (Pd(acac)$_2$, 99%), borane-tert-butylamine (BTB, 97%), hexane (99%), ethanol (99%), acetone (97%), were purchased from Sigma-Aldrich® and used as received. BP2000 carbon was received from Cabot.

2.2. Instrumentation

All transmission electron microscope (TEM) images were recorded by transmission electron microscope (TEM, Hitachi HT7700 with EXALENS, 120 kV) working at high-resolution (HR) mode with the magnification range of 10-800k. X-ray diffraction (XRD) patterns were recorded on a PANalytical Empyrean diffractometer with Cu-Kα radiation (40 kV, 15 mA, 1.54051 Å) over a 2θ range from 10º-90º at room temperature. Elemental analysis measurements were carried out by inductively coupled plasma-mass spectroscopy (ICP-MS,

Agilent Technologies 7700) after each sample was completely dissolved in aqua-regia (HCl/HNO$_3$: 3/1 vol. ratio).

2.3. Synthesis of Pd nanoparticles and supported onto the BP2000

Pd nanoparticles were synthesized under mild conditions with minör modifications [29]. In four-neckled reactor, Pd metal salt (100 mg) were disssolved in oleylamine (5 mL) and 1-octadecen (8 mL) in argon atmosphere and the second solution was prepered for the reduction of metal. Borane-tert-butylamine (173 mg) was dissolved in oleylamine (2 mL) and added to the first solution at 80˚C. Reaction mixture was raised up to 100˚C and mixed at this temperature for 1 hour. After reaction to get nanoparticles, reaction mixture was centrifuged with acetone and ethanol at 8500 rpm, 10 min, respectively. The colloidal nanoparticles was dispersed in hexane. 52 mg colloidal nanoparticles were founded after the centrifuge procedure. To support BP2000; 104 mg BP2000 was dissolved in an ethanol and sonicated half an hour. After that Pd nanoparticles was added by dropwise and sonicated 2 hours and then centrifuged at 7500 rpm, 10 min to remove the unsupported nanoparticles.

2.4. Hydrolytic dehydrogenation of Ammonia-borane catalyzed by Pd/BP2000 nanocomposites

For measuring of released hydrogen, there is set-up with water filled buret system for hydrogen production. In a typical set-up 10 mg catalyst is sonicated in 7 mL of water for 10 min. and 1mmol of AB is dissolved in 3 mL of water. The mechanism temperature is set up 25 ± 1˚C. Two necked-jacketed reaction tube set up and stirrer is arranged to 1000 rpm. After that AB solution is injected to the catalyst solution and the reaction is start-up. Hydrogen production is measured. The detailed reaction kinetics are research with the same hydrogen production set-up. Different temperature (293, 298, 303, 308 K), different AB amount (50, 100, 150, 200 mM) and different catalyst amount (2.5, 5, 7.5, 10mg) kinetics are studied keeping to stabile all of other parameters. For the last one, Durability of catalyst was tested.

20 mg catalyst was used for this experiment. After first cycle, the catalyst is centrifuged and washed then ıt is used for the second cycle. This procedure is done for five cycles.

3. RESULTS AND DISCUSSIONS

Monodisperse Pd nanoparticles were synthesized under mild conditions. OAm was used as surfactant, ODE was used as solvent and BTB was used as reducing agent ın this recipe. TEM images of colloidal nanoparticles were showed ın the Fig. 1. The homogenous dispersion and spherical shape of 3.5 nm of Pd nanoparticles can be seen ın the Fig. 1, Pd nanoparticles were also dispersed onto the BP2000 surface with sonication. (Fig 1. b)
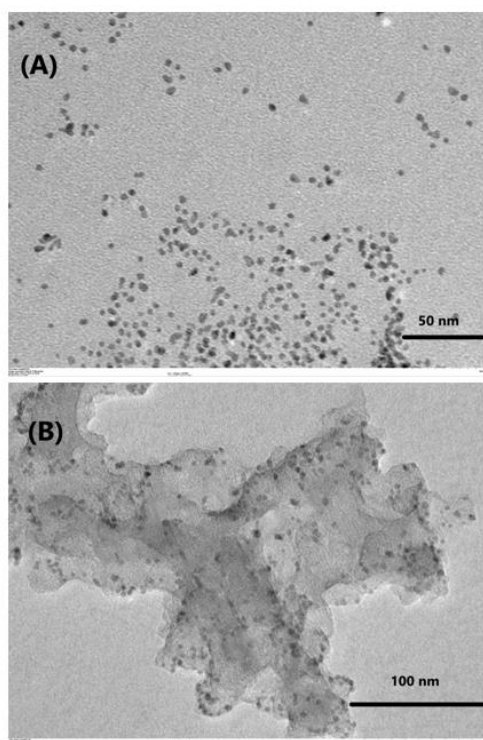

Figure 1 TEM images of a) colloidal Pd nanoparticles b) Pd/BP2000 nanocomposites.

XRD analyses of Pd/BP2000, (Fig. 2) ıt can be seen fcc-Pd(111) peak at 39.2º, the other characteristic peak of Pd 44.8º (200); 66.5 º (220); 80.04 º (311) (JCPDS card no 05-0681) [30] and observed peak at 21.5º corresponds to the BP2000. To find the metal ratio of composite, ICP-MS was performed for the nanocomposite and ıt was found 17.3% Pd.
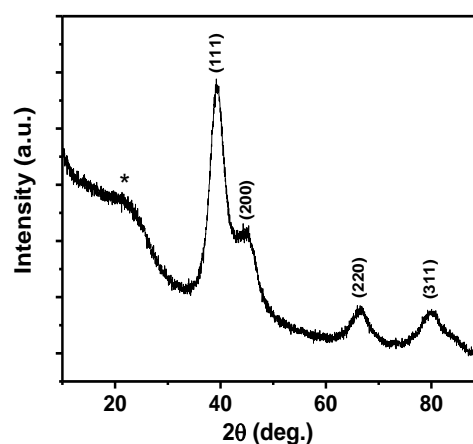

Figure 2 XRD patterns of Pd/BP2000 nanocomposites.

After detailed characterization of Pd/BP2000, the kinetics of hydrolytic dehydrogenation of AB was performed. The detailed report showed the kinetics of Pd/BP2000 nanocatalyst parameters on AB concentration, catalyst amount, temperature and reusability. Figure 3 shows the production of hydrogen versus to time plots during the hydrolysis of AB (100 mM) at different Pd/BP2000 nanocomposite amounts (2.5–10 mg,) at $25 \pm 1\,^\circ$C, 1mmol AB. According to the results, when amount of catalyst was increase, hydrogen production rate was also increased. In Fig. 3, linear curves were used as reference for calculating of reaction rate for each nanocatalyst concentrations. The linear increase is can be seen from Fig. 4 between the reaction rate and Pd/BP2000 concentration. $\ln[\text{rate}] = 0.66634\ln[\text{Pd}] + 3.52148$ equation was calculated. From the linear graph (slope of this line 0.66) the hydrogen releases to the first rate law according to the catalyst concentration.
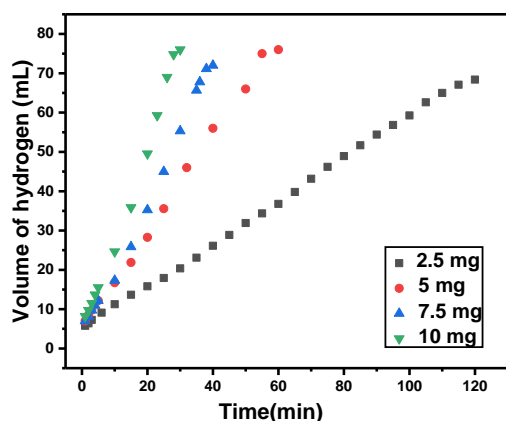
Figure 3 Hydrogen gas generation versus time throughout the hydrolysis of AB by Pd/BP2000 nanocomposites at different amount.
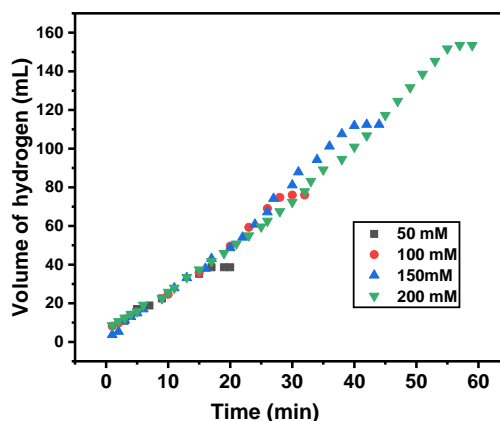

Figure 5 Hydrogen gas generation versus time throughout the hydrolysis of AB by Pd/BP2000 nanocomposites at different amount of AB.
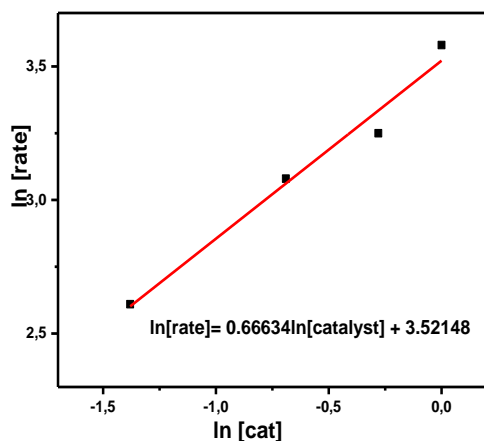

Figure 4 Logarithmic plots of H_2 generation rate versus catalyst concentrations

Figure 6 Logarithmic plots of H_2 generation rate versus AB concentrations.

In the Fig. 5, 10 mg catalyst was performed versus AB concentration was changed between 50-200 mM and hydrogen released at room temperature. The amount of produced hydrogen gas versus to time for each concentration was plotted. The reaction equation was found as ln[rate] = -0.00431ln[AB] + 2.63528. According to this equation, hydrogen was produced zeroth order kinetic rule versus to the concentration of AB in assisting of Pd/BP2000 catalyst.
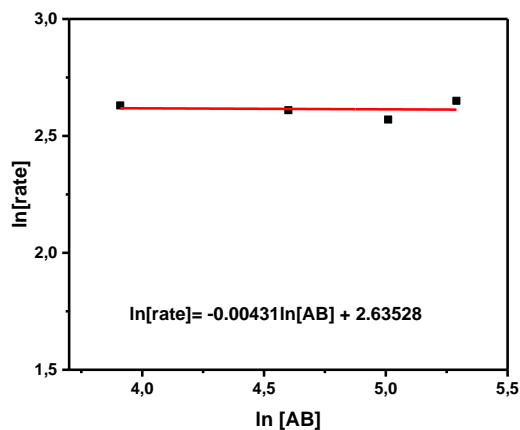
The other kinetic study was performed for different temperature (293-308 K), 1 mmol AB and 10 mg of catalyst. According to the Fig 7, When the temperature is increased, hydrogen releasing rate is increased and ıt is compatible with molecular kinetic energy laws. The resulted values were plotted against 1/T, and the Arrhenius plot y = −5066.87x + 19.8648 given in Figure 8 was plotted. Activation energy of reaction was calculated to be 41.5 kJ mol^{-1}. Arrhenius equation is given below.

$$k = Ae-\frac{Ea}{RT} \qquad (1)$$

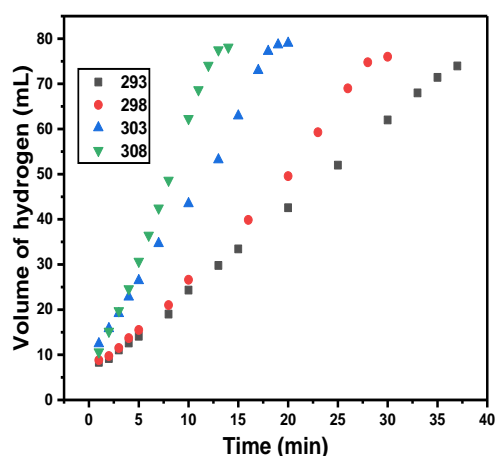$$\ln k = -\frac{Ea}{RT} + \ln A \qquad (2)$$

Figure 7 Hydrogen gas generation versus time throughout the hydrolysis of AB by Pd/BP2000 nanocomposites at different temperutares.
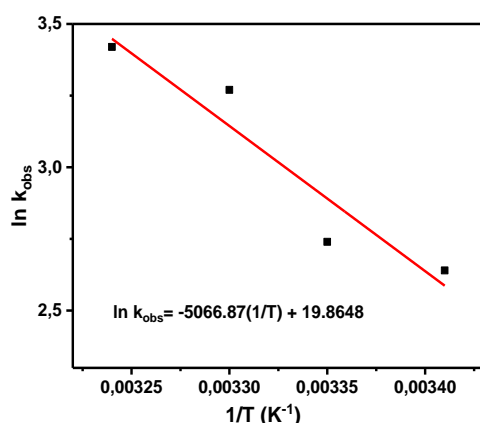

Figure 8 Arrhenius plot of ln k_{obs} versus 1/T.

After the detailed kinetic reactions of catalyst, the stability of catalyst was performed during the five hydrolysis cycle. In the Fig. 9, ıt can be seen that activity of catalyst was not decreased too much with the advantage of using commercial BP2000 carbon. It is still an efficient catalyst for hydrolysis of AB. The morphology and homogeneous dispersion of the catalyst are still the same (Fig 9, inset). It is stable and excellent catalyst for the hydrolysis of AB.
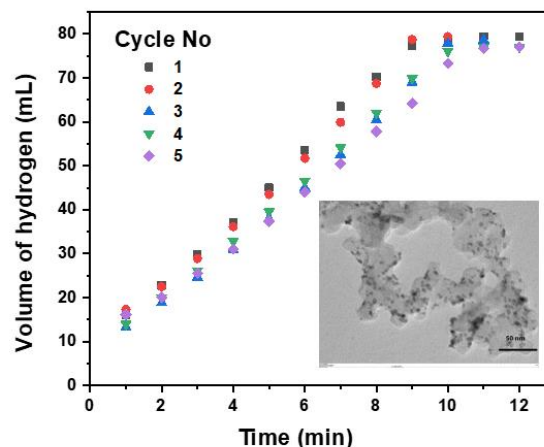

Figure 9 The five cycle hydrolysis of Pd/BP2000 nanocatalyst. inset: TEM image of the catalyst after five cycle.

4.CONCLUSIONS

In summary, monodisperse Pd nanoparticles were synthesized with stabilizers and reducing agent under mild conditions and they were assembled on BP2000 surface. After detailed characterization of Pd/BP2000 nanocatalyst was performed for hydrolytic dehydrogenation of AB. It shows high performance, 20.4 min^{-1} high TOF value and recyclability for the hydrolysis of AB.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

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The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

REFERENCES

[1]   M. Grasemann and G. Laurenczy, "Formic acid as a hydrogen source–recent developments and future trends," Energy & Environmental Science, vol. 5, no. 8, pp. 8171-8181, 2012.

[2]   Y. Chen, J. L. Fulton, J. C. Linehan, and T. Autrey, "In situ XAFS and NMR study of rhodium-catalyzed dehydrogenation of dimethylamine borane," Journal of the American Chemical Society, vol.127, no.10 pp. 3254-3255, 2005.

[3]   Z. Wen, Q. Fu, J. Wu, G. Fan, "Ultrafine Pd Nanoparticles Supported on Soft Nitriding Porous Carbon for Hydrogen Production from Hydrolytic Dehydrogenation of Dimethyl Amine-Borane," Nanomaterials, vol.10, no.8 pp.1612, 2020.

[4]   S. Karaboga, S. Özkar, "Ceria supported ruthenium nanoparticles: Remarkable catalyst for H_2 evolution from dimethylamine borane," International Journal of Hydrogen Energy, vol.44, no.48 pp.26296-26307, 2020.

[5]   L. L. Al-mahamad, "Gold nanoparticles as a catalyst for dehydrogenation reaction of dimethylamine borane at room temperature, "International Journal of Hydrogen Energy, vol.45, no.21, pp.11916-11922, 2020.

[6]   N. Cao, J. Su, W. Luo, and G. Cheng, "Hydrolytic dehydrogenation of ammonia borane and methylamine borane catalyzed by graphene supported Ru@ Ni core–shell nanoparticles," International journal of hydrogen energy, vol. 39, no.1, pp. 426-435, 2014.

[7]   M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, and K. I. Goldberg, "Efficient catalysis of ammonia borane dehydrogenation," Journal of the American Chemical Society, vol. 128, no. 37, pp. 12048-12049, 2006.

[8]   A. Al-Kukhun, H. T. Hwang, and A. Varma, "Mechanistic studies of ammonia borane dehydrogenation," International journal of hydrogen energy, vol. 38, no. 1, pp. 169-179, 2013.

[9]   O. Metin, V. Mazumder, S. Ozkar, and S. Sun, "Monodisperse nickel nanoparticles and their catalysis in hydrolytic dehydrogenation of ammonia borane, "Journal of the American Chemical Society, vol. 132, no. 5, pp. 1468-1469, 2010.

[10]   W. W. Zhan, Q. L. Zhu, and Q. Xu, "Dehydrogenation of ammonia borane by metal nanoparticle catalysts," Acs Catalysis, vol. 6, no. 10, pp. 6892-6905, 2016.

[11]   M. Chandra, and Q. Xu, "A high-performance hydrogen generation system: Transition metal-catalyzed dissociation and hydrolysis of ammonia–borane," Journal of Power Sources, vol. 156, no. 2, pp. 190-194, 2006.

[12]   M. Chandra, and Q. Xu, "Room temperature hydrogen generation from aqueous ammonia-borane using noble metal nano-clusters as highly active catalysts," Journal of Power Sources, vol. 168, no. 1, pp.135-142, 2007.

[13]   Y. T. Li, X. L. Zhang, Z. K. Peng, P. Liu, and X. C. Zheng, "Highly efficient hydrolysis of ammonia borane using ultrafine bimetallic RuPd nanoalloys

encapsulated in porous g-C_3N_4, '' Fuel, vol. 277, no.1 pp. 118243, 2020.

[14] C. Du, Q. Ao, N. Cao, L. Yang, W. Luo, and G. Cheng, "Facile synthesis of monodisperse ruthenium nanoparticles supported on graphene for hydrogen generation from hydrolysis of ammonia borane,'' International Journal of Hydrogen Energy, vol. 40, no. 18, pp. 6180-6187, 2015.

[15] S. Akbayrak, Y. Tonbul, and S. Özkar, "Ceria supported rhodium nanoparticles: superb catalytic activity in hydrogen generation from the hydrolysis of ammonia borane,''Applied Catalysis B: Environmental, vol. 198, pp. 162-170, 2016.

[16] F. Zhong, Q. Wang, C. Xu, Y. Wang, B. Xu, Y. Zhang, and G. Fan, "Catalytically active rhodium nanoparticles stabilized by nitrogen doped carbon for the hydrolysis of ammonia borane,'' International Journal of Hydrogen Energy, vol. 43, no. 49, pp. 22273-22280, 2018.

[17] M. Yuan, Z. Cui, J. Yang, X. Cui, M. Tian, D. Xu, Z. Dong, "Ultrafine platinum nanoparticles modified on cotton derived carbon fibers as a highly efficient catalyst for hydrogen evolution from ammonia borane,'' International Journal of Hydrogen Energy, vol. 42, no.49, pp.29244-29253, 2017.

[18] S. Akbayrak, and S. Özkar, "Cobalt ferrite supported platinum nanoparticles: Superb catalytic activity and outstanding reusability in hydrogen generation from the hydrolysis of ammonia borane,'' Journal of Colloid and Interface Science, vol. 596, pp.100-107, 2021.

[19] M. Rakap, "PVP-stabilized Ru–Rh nanoparticles as highly efficient catalysts for hydrogen generation from hydrolysis of ammonia borane,'' Journal of Alloys and Compounds, vol. 649, pp. 1025-1030, 2015.

[20] N. Tunç, B. Abay, and Rakap, M. "Hydrogen generation from hydrolytic dehydrogenation of hydrazine borane by poly (N-vinyl-2-pyrrolidone)-stabilized palladium nanoparticles,'' Journal of Power Sources, vol. 299, pp. 403-407, 2015.

[21] X. Chen, X. J. Xu, X. C. Zheng, X. X. Guan, and P. Liu, "Chitosan supported palladium nanoparticles: The novel catalysts for hydrogen generation from hydrolysis of ammonia borane,'' Materials Research Bulletin, vol.103, pp. 89-95, 2018.

[22] J. R. Deka, D. Saikia, P. H. Chen, K. T. Chen H. M. Kao, and Y. C. Yang, "Palladium nanoparticles encapsulated in carboxylic acid functionalized periodic mesoporous organosilicas as efficient and reusable heterogeneous catalysts for hydrogen generation from ammonia borane,'' Materials Research Bulletin, vol. 125, pp. 110786, 2020.

[23] A. Balanta, C. Godard, C. Claver, "Pd nanoparticles for C–C coupling reactions,'' Chemical Society Reviews, vol. 40, no.10, pp.4973-4985, 2011.

[24] M. T. Reetz, E. Westermann, "Phosphane-free palladium-catalyzed coupling reactions: the decisive role of Pd nanoparticles,'' Angewandte Chemie International Edition, vol.39, no.1, pp.165-168, 2000.

[25] Z. Zhang, Z. Wang, "Diatomite-supported Pd nanoparticles: an efficient catalyst for Heck and Suzuki reactions,'' The Journal of organic chemistry, vol. 71, no.19, pp.7485-7487, 2006.

[26] W. Sun, X. Lu, Y. Tong, Z. Zhang, J. Lei, G. Nie, and C. Wang, "Fabrication of highly dispersed palladium/graphene oxide nanocomposites and their catalytic properties for efficient hydrogenation of p-nitrophenol and hydrogen generation,'' International journal of hydrogen energy, vol. 39, no. 17, pp. 9080-9086, 2014.

[27] X. K. Tian, C. Yang, Z. X. Zhou, X. W. Liu, and Y. Li, "Active 3D Pd/graphene aerogel catalyst for hydrogen generation from the hydrolysis of ammonia-borane,'' International Journal of Hydrogen Energy, vol. 41, no. 34, pp. 15225-15235, 2016.

[28] H. Jia, Y. Zhu, X. Song, X. Zheng, and P. Liu, "Magnetic graphene oxide-ionic liquid grafted chitosan composites anchored Pd (0) nanoparticles: A robust heterogeneous catalyst with enhanced activity and superior reusability for hydrogen generation from ammonia borane,'' International Journal of Hydrogen Energy, vol. 43, no. 43, pp. 19939-19946, 2018.

[29] V. Mazumder, and S. Sun, "Oleylamine-mediated synthesis of Pd nanoparticles for catalytic formic acid oxidation,'' Journal of the American Chemical Society, vol. 131, no. 13, pp. 4588-4589, 2009.

[30] M. Celebi, K. Karakas, I. E. Ertas, M. Kaya, and M. Zahmakiran, "Palladium nanoparticles decorated graphene oxide: active and reusable nanocatalyst for the catalytic reduction of hexavalent chromium (VI),'' ChemistrySelect, vol. 2, no. 27, pp. 8312-8319, 2017.