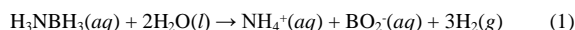


# Enhancing the utilization efficacy of noble metal(0) nanocatalysts in hydrogen generation from the hydrolysis of ammonia borane

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The growing concern on global warming [1] and the increasing worry on the depletion of fossil energy reserves [2] appeal the replacing fossil fuels with the renewable energy sources for a sustainable energy policy in the future [3]. As environmentally benign energy carrier hydrogen will play key role in such a transition on the way towards a sustainable green future [4,5]. Main hindrances in using H<sub>2</sub> as green energy vector are essentially resulting from the difficulties in its safe and efficient storage [6]. New materials have been persistently developed for storing hydrogen safely and efficiently [7,8,9]. One of the promising candidates for storing hydrogen safely and efficiently is ammonia borane (H<sub>3</sub>NBH<sub>3</sub>, AB) [10]. Its hydrolysis is the best way of releasing hydrogen gas (Equation 1) [11].



However, this reaction takes place at appreciable rate under ambient conditions only in the presence of suitable catalysts [12]. Transition metal nanoparticles are known to be efficient catalysts in hydrogen generation from the hydrolysis of AB [13]. The noble metals such as platinum [14], rhodium [15], palladium [16] or ruthenium [17] show much higher catalytic activity than the non-noble metals in this reaction. However, precious metals have very high price which prevents their employment in this dehydrogenation reaction. Furthermore, the principles of green chemistry require the amount of non-reagent metal to be minimized [18]. Therefore, it is mandatory to keep the metal content of catalyst as low as possible to increase the utilization efficacy of the metal catalyst. Using a minimum catalyst to substrate ratio is another target for developing efficient catalyst. Here, an obvious challenge is to

develop nanocatalysts of noble metals which have outstanding catalytic activity, long lifetime and exceptionally high reusability for the complete release of 3 equivalent H<sub>2</sub> per mole of ammonia borane under ambient conditions. The existing literature will be reviewed to find out all the available methods to increase catalytic efficiency of noble metal nanocatalysts in hydrogen generation from the hydrolysis of AB.

Although colloidal nanoparticles of noble metals can provide high catalytic activity, they are unstable against agglomeration. Supporting nanoparticles on the surface of carbonaceous materials with large surface area such as activated carbon, graphene, nitrogen-doped graphene, carbon nanotubes can provide some escalation in catalytic activity [19]. Since the noble metals are not tightly bound to the surface of carbonaceous materials, they undergo leaching during the catalysis and have short life and low reusability. The use of oxide supports for the noble metal(0) nanoparticles escalate their catalytic activity in the hydrolysis of AB. Particularly, the reducible oxides such as titania, ceria, tungsten(VI) oxide, cobalt(II,III) oxide provide high activity and long lifetime for the supported rhodium(0) [20], ruthenium(0) [17], palladium(0) [21] and platinum(0) [22] nanoparticles. Using the magnetic powders as support for noble metal(0) nanoparticles makes them magnetically separable provided that nanoparticles are tightly bound on the surface of magnetic powder. Thus, magnetically isolable ruthenium(0) [23], palladium(0) [24], rhodium(0) [20] and platinum(0) [25] nanocatalysts have outstanding catalytic activity, long lifetime and exceptionally high reusability in hydrogen generation from the from the hydrolysis of AB at room temperature.

- [1] B. Demirel, N. Bıçakcıoğlu et al. *Int. J. Global Warming* 18 (2019) 385.
- [2] P. Nejat, F. Jomehzadeh, et al. *Renewable Sustainable Energy Rev* 2015, 43, 843-862.
- [3] T.R. Anderson, E. Hawkins, P.D. Jones. *Endeavour*, 40 (2016) 178.
- [4] T. Uyar, D. Beşikçi. *Int. J. Hydrogen Energy*, 42 (2017) 2453–2456.
- [5] M. R. Usman. *Renew Sustain Energy Rev.* 167 (2022) 112743.
- [6] D. Zivar, S. Kumar, J. Foroozesh. *Int J Hydrogen Energy* 2021, 46, 23436-23462.
- [7] E. Boateng, A. Chen. *Materials today Adv.* 2020, 6, 100022.
- [8] N. A. Ali, N. A. Sazelee, M. Ismail. *Int. J. Hydrogen Energy* 46 (2021) 31674.
- [9] T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen. *Nat. Rev. Mater.* 1 (2016) 1.
- [10] U. B. Demirci. *Int. J. Hydrogen Energy* 42 (2017) 9978.
- [11] M. Chandra, Q. Xu, J. Power Sources 156 (2006) 190.
- [12] M. Zahmakıran, S. Özkar. *Topics in Catal.*, 56 (2013) 1171.
- [13] S. Akbayrak, S. Özkar, *Int. J. Hydrogen Energy* 43 (2018) 18592.
- [14] S. Özkar. *Int. J. Energy Res.*, 46 (2022) 22089.
- [15] S. Özkar. *Int. J. Hydrogen Energy*, 54 (2024) 54, 327.
- [16] L. Zhang, et al. J. Zhu. *Nano Research* 15 (2022) 3034.
- [17] S. Akbayrak, Y. Tonbul, S. Özkar. *Turk. J. Chem.* 47 (2023) 1224.
- [18] M. Poliakoff, J. M. Fitzpatrick, et al. *Science* 2002, 297, 807-810.
- [19] S. Akbayrak, S. Özkar, *ACS Appl. Mater. Interfaces* 4 (2012) 6302.
- [20] Y. Tonbul, S. Akbayrak, S. Özkar, *ACS Sustainable Chem. Eng.* 8 (2020) 4216.
- [21] S. Akbayrak, S. Özkar, *J. Colloid Interface Sci.* 626 (2022) 752.
- [22] S. Akbayrak, S. Özkar. *ACS Appl. Mater. Interfaces* 13 (2021) 34341.
- [23] S. Akbayrak, G. Çakmak, T. Öztürk, S. Özkar, *Int. J. Hydrogen Energy* 46 (2021) 13548.
- [24] S. Akbayrak, G. Çakmak, T. Öztürk, S. Özkar. *J. Alloys Compounds*, (2024) 175199.
- [25] S. Akbayrak, S. Özkar, *J. Colloid Interface Sci.* 596 (2021) 100.



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