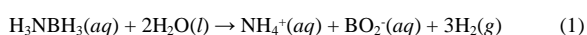


How to increase the catalytic efficacy of platinum-based nanocatalysts for hydrogen generation from the hydrolysis of ammonia borane

Saim Özkar

Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey.

Hydrolysis is the best way of releasing H₂ from ammonia borane (AB) in the presence of catalysts (Equation 1).¹



Significant achievements have been obtained in increasing the rate of releasing H₂ from AB by employing transition metal nanoparticles (NPs) as catalysts.^{2,3,4} Pt is one of the most active transition metals providing high turnover frequency (TOF) for hydrogen generation from the hydrolysis of AB. However, the high price of this precious metal hampers its large-scale applications in catalyzing the hydrolysis of AB. Achieving high catalytic performance with the smallest amount of metal is critical for any catalytic applications of noble metals. While continuous efforts have been devoted to improve the catalytic activity of non-noble metals, an immense challenge in the field is the enhancement of utilization efficiency and catalytic performance, and thus ultimately lowering the cost of noble metal catalysts. For example, reducing the particle size of Pt catalysts to nanoregime increases their surface area and thus, the number of active sites for catalysis.⁵ However, colloidal metal NPs are unstable and tend to aggregate to larger particles, which greatly hampers their recyclability and catalytic performance.⁶ A proper way of overcoming this problem is the immobilization of Pt NPs on a support with large surface area, such as oxides, carbonaceous materials, metal-organic frameworks. The catalytic activity and stability of supported Pt NPs depend on the particle size and size distribution, surface area of support, and strength of metal-support interaction. Selecting suitable supports is of paramount importance in obtaining NPs which are stable and still catalytically active. Using the supporting materials with large surface area certainly helps to increase the catalytic activity of Pt NPs. The strength of platinum-support interaction turns to be crucial for catalytic activity and stability of NPs on the support surface. Although no mathematical correlation between the catalytic activity and the strength of metal-support interaction could be obtained yet, almost all the highly active Pt catalysts have high Pt 4f binding energy as determined by XPS analysis. Increasing the lifetime and reusability of nanocatalysts can certainly help to improve the atom efficiency of Pt catalysts. Lifetime is used as a measure of stability which correlates well to the strength of metal-support interaction relative to metal-metal bond while reusability is mainly determined by the isolability of nanocatalysts for subsequent runs. At this point it would help to differentiate the recyclability and reusability of

nanocatalysts in the present case of hydrolysis. A recyclability test is performed by adding a new batch of AB to the reactor, when the hydrolysis is complete, for the subsequent cycle of hydrolysis without isolating the catalyst or removing the reaction solution from the reactor. Actually, it would not make any difference whether the whole amount of AB is added at once in the commencement or portion wise in the successive cycles. It is noteworthy that the recyclability test can serve to measure the lifetime of catalyst when performed by adding sufficient amount of AB until the cease of H₂ generation.⁷ Thus, recyclability measures the durability of catalysts. On the contrary, reusability test is performed by isolating the catalyst from reaction solution after completion of hydrolysis in the first run and re-dispersing in a new batch of AB for the subsequent run, whereby the retaining activity of catalyst is measured.⁸ In other words, reusability test serves in measuring the stability of catalysts, which is an important parameter to be considered in large scale industrial application. Low reusability is largely caused by material loss during the isolation of catalyst from solution and re-dispersing in a new reaction solution for the succeeding run of catalytic reaction.⁹

A short prelude on the mechanism of catalytic hydrolysis of AB will give insight to understand and appreciate the reported achievements in enhancing the catalytic performance of Pt based catalysts in hydrolysis of AB: The activation of AB molecule on the surface of metal NPs proceeds in the form of dissociative adsorption through interaction between the metal and hydridic hydrogens of borane moiety and the resultant -BH₂ species promotes the dissociation of H₂O which has been suggested to be the rate-determining step in the transition metal catalyzed hydrolysis of AB.^{10,11,12} This is followed by the formation and desorption of H₂ molecule from the nanoparticle surface and the -BH₂(OH) species continues with further hydrolysis.

The progresses in developing highly efficient platinum(0) nanocatalysts which have been reported to be active catalysts in H₂ generation from the hydrolysis of AB will be discussed along with the available parameters including temperature, particle size, surface area of the catalyst or support, the catalyst to substrate ratio used in the catalysis, Arrhenius activation energy obtained for the catalytic hydrolysis, TOF, and the XPS determined Pt 4f binding energy.

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