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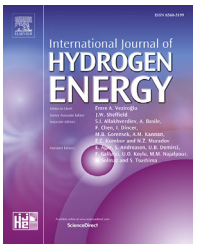

Nanosizing ammonia borane with nickel – An *all-solid* and *all-in-one* approach for H_2 generation by hydrolysis

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ABSTRACT

Ammonia borane NH_3BH_3 (AB) and nickel (Ni) have been considered together as an *all-solid* and *all-in-one* material for H_2 generation by hydrolysis at 20–50 °C. Our novel approach, denoted Ni/AB, consists of AB nanoparticles within a Ni matrix. Upon contact with water, Ni/AB readily hydrolyzes and liberates H_2 with a turnover frequency of 13.8 mol(H_2) mol_{Ni}^{-1} min^{-1} at 43.3 °C. The apparent activation energy, determined over the temperature range 23.5–50.4 °C, is low, with 19.5 ± 4.1 kJ mol^{-1}. These results imply that such a Ni matrix embedding AB acts as an effective catalyst. Beyond the catalytic performance, this is the first report of the successful utilization of an *all-solid* and *all-in-one* approach for the hydrolysis of AB, and the work brings unique perspectives for one-shot catalytic systems.

Introduction

Ammonia borane NH_3BH_3 (AB) has a dual role in the field of chemical hydrogen storage [1]. It is suitable for thermolytic dehydrogenation owing to an equal number of protic ($H^{\delta+}$) and hydridic ($H^{\delta-}$) hydrogens that react above *ca.* 100 °C according to intra-/inter-molecular paths [2–4], merely represented by the following global equation:

$$NH_3BH_3(s) \rightarrow BNH_{2-x}(s) + (2 + x/2)H_2(g) \quad (1)$$

AB is also suitable for hydrolytic dehydrogenation owing to its solubility and good stability in water (for pH > 7) and the facile reaction of its hydridic $H^{\delta-}$ with the protic $H^{\delta+}$ hydrogens of water at ambient conditions [5,6] provided that a metal-based catalyst is used [7–21]:

$$NH_3BH_3(aq) + 3\ H_2O\ (l) \rightarrow NH_3(aq) + B(OH)_3(aq) + 3H_2(g) \quad (2a)$$

$$NH_3BH_3(aq) + 4\ H_2O\ (l) \rightarrow NH_4^+(aq) + B(OH)_4^-(aq) + 3H_2(g) \quad (2b)$$

Both approaches have been widely investigated since the mid-2000s.

In the field of hydrolysis of AB (Eq. 2(a) and (b)), most of the efforts have focused on the development of (highly) active metal-based catalysts [7–9]. The other aspects

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(*e.g.* optimization of the storage capacities, the state of AB, the purity of H_2, the borates evolution) have been, in contrast, overlooked [1,10]. Many active metal-based catalysts have been reported, especially cobalt, nickel, copper, ruthenium, palladium and platinum [7–9]. The catalyst is usually synthesized separately and then mixed with AB before hydrolysis. Catalysts in the form of isolated nanoparticles [11–13], alloys [16,17], core@shell nanostructures [18], borides [19], and deposited on various supports like graphene [14], metal organic frameworks [15], or on foams or thin films [20,21] have been investigated with the aim of achieving high H_2 generation rates. For example, Wang et al. [22] reported one of the best performances by using nickel nanoparticles (2.7 ± 0.3 nm) supported on a zeolitic imidazolate framework ZIF-8. The final catalyst with a specific surface area of 1324.3 $m^2\ g^{-1}$ led to a turnover frequency of 85.7 mol(H_2) $mol_{cat}^{-1}\ min^{-1}$ at 25 °C in an alkaline (0.3 M NaOH) solution of AB (1.215 mmol in 10 mL). This demonstrates the potential of non-noble nickel as an effective catalytic element for the hydrolysis of AB.

Hydrolysis of sodium borohydride $NaBH_4$ (SB) has also been investigated widely, with most of approaches focused on catalysis [10]. Some efforts have been also dedicated to the physical state of SB [10,23], that is, the way of putting SB into contact with the catalyst. The most widespread method to generate H_2 from the hydrolysis of SB is *via* the injection of an aqueous alkaline solution of SB onto a solid-state catalyst [24]. This is also the approach that has been almost exclusively used for AB [7–22]. An alternative approach is based on the use of solid-state SB and a catalyzed/acidified aqueous solution. In this case, an aqueous solution of cobalt chloride $CoCl_2$ (precursor of *in situ*-forming cobalt-based catalyst) [25] or hydrochloric acid (source of protons) can be used [26]. A third approach is *all-solid*; it is based on the use of solid-state catalyzed-SB, which is in fact a mixture of SB and *e.g.* nanoparticles of cobalt [27]. This last approach has shown to have attractive features: it allows maximizing the *effective* gravimetric hydrogen storage capacity of the couple SB-H_2O and it frees the process from the catalyst deactivation (*i.e.* one-shot utilization) [23]. To our knowledge, solid-state catalyzed-AB has never been considered and it is targeted in the present work.

In a previous work, we reported the successful synthesis of intimately-combined nickel and AB nanoparticles (Ni/AB; Fig. 1) [28]. Nanosized AB (white powder) had a particle size ranging from 20 to 160 nm (with crystalline size of 42 ± 2 nm) and the Ni nanoparticles were smaller (1–7 nm). The resulting Ni/AB, a grey solid, was investigated for thermolytic dehydrogenation and partially-reversible hydrogen storage. As mentioned above, nickel is known to have a catalytic effect on AB hydrolysis. Consequently, solid-state Ni/AB is suitable for hydrolytic dehydrogenation. Herein, we report, for the first time, on such a solid-state Ni/AB system, and the use of intimately-combined catalytic Ni nanoparticles and AB nanoparticles (Ni/AB) as an *all-solid* and *all-in-one* material for H_2 generation by hydrolysis.

Experimental

Encapsulation of AB nanoparticles within a Ni matrix was reported previously [28]. The experiments were carried out in an argon-filled glove box (LC Technology Solutions Inc.; O_2 < 1 ppm and H_2O < 1 ppm). In a first step, nanoparticles of AB were synthesized by the anti-precipitation method [29,30]. Typically, an AB (NH_3BH_3 97%; Sigma-Aldrich) solution (515 mg in 2.5 mL of anhydrous tetrahydrofuran of HPLC grade from Fisher Scientific) at 45 °C was added, dropwise, to 5 mL of an anhydrous cyclohexane (HPLC grade; Fisher Scientific) solution of oleic acid (0.025 mL; 99%; Sigma-Aldrich) kept at 15 °C. The mixture was aged at 15 °C under 500 rpm for 2 h. A white precipitate formed. It was recovered by centrifugation, washed with cyclohexane twice and dried under vacuum for 24 h (Fig. 1a). In a second step, nanosized AB was used to be loaded with Ni nanoparticles. Typically, 100 mg of ground AB nanoparticles were mixed with 45 mg of anhydrous nickel chloride ($NiCl_2$; Ajax Finechem) under 250 rpm at room temperature for 3 days. A grey solid, *i.e.* Ni/AB, formed (Fig. 1a).

The H_2 evolution experiments were performed on our set-up based on the inverted burette method. The set-up consists of a Schlenk tube used as reactor placed in a thermostated bath, a trap filled with an aqueous solution of HCl (0.1 M) to trap any evolving ammonia NH_3, and an inverted burette filled with blue-colored water. In an argon-filled glove box (MBraun M200B; O_2 < 1 ppm and H_2O < 1 ppm), 35 mg of Ni/AB were transferred in the reactor. The H_2 evolution was started by injecting 1 mL of water (Millipore milli-Q water; resistivity of

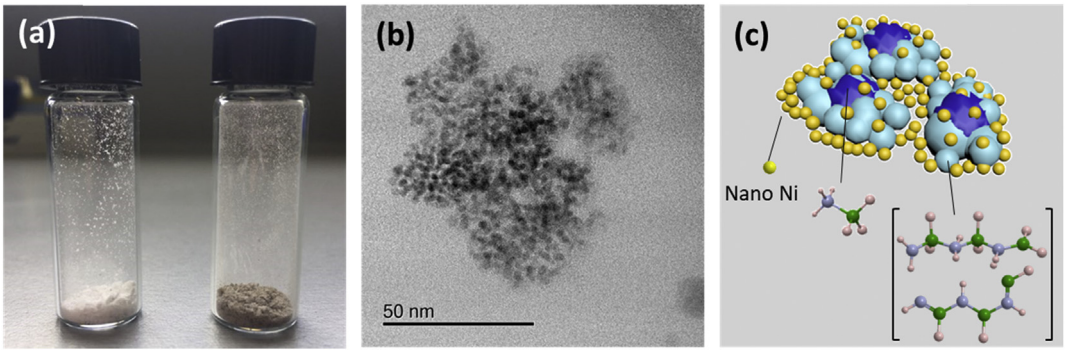

Fig. 1 – (a) Photograph of the AB nanoparticles (white sample at left) and of Ni/AB (grey sample at right). (b) TEM image of Ni/AB. (c) Schematic representation of Ni/AB (crystalline AB nano-domains embedded within a matrix of oligomeric $[BH_xNH_x]_y$ species and isolated metallic Ni nanoparticles).

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