



# Experimental and modeling study of ammonia borane-based hydrogen storage systems



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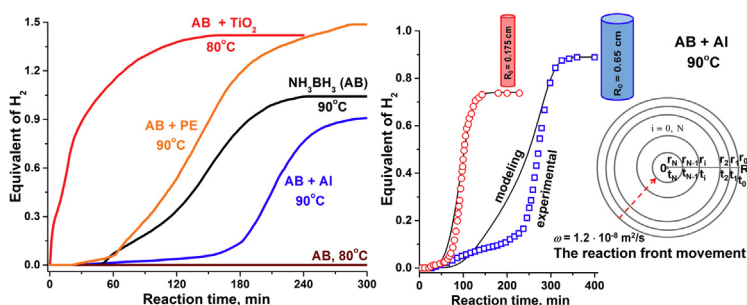
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## HIGHLIGHTS

- Low-temperature H<sub>2</sub> evolution from NH<sub>3</sub>BH<sub>3</sub> (AB) mixed with different solids is studied.
- The radius of tubular reactor is a key factor influencing the H<sub>2</sub> kinetics from solid bed.
- The reaction front propagation from the heated reactor wall to its axis is modelled.
- AB-solids chemical interaction and bed heat conductivity influence the reaction rate.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Available online 4 May 2017

### Keywords:

Hydrogen storage  
Ammonia borane  
Modifiers  
Mathematical model  
Mass and heat transfer  
Radius of tubular reactor

## ABSTRACT

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) is considered to be a promising hydrogen storage material owing to its very high content of hydrogen (19.6 wt%), high stability in air at ambient temperatures and the low temperature of the dehydrogenation process. In this work solid-state decomposition of NH<sub>3</sub>BH<sub>3</sub> in contact with a series of solid materials has been investigated. It was shown that the reactivity of the studied AB-based hydrogen-generating systems was changing under the action of both the chemical nature and thermal conducting properties of the studied modifiers. It is important that, according to ATR-FTIR spectroscopy, the contact of AB with oxygen-containing supports (TiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, HY zeolite) destabilizes the AB structure to evolve hydrogen already at 80 °C, independently of their chemical nature. On the other hand, it was shown that in a heat insulator reaction medium the temperature in the reaction zone increases leading to an increased yield of hydrogen. In addition to this, the reaction properties of AB have for the first time been studied depending on the radius of the tubular reactor during the low-temperature dehydrogenation (90 °C) under conditions preventing appearance of local thermal spikes. A mathematical model has been developed which describes the obtained experimental results taking into account the propagation of the reagent-product interface from the heated reactor wall towards its axis.

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## 1. Introduction

The development of environmentally friendly hydrogen-based technologies for power production and their practical applications are not possible without safe and efficient systems for the storage

of hydrogen. Solid hydrides, such as NaBH<sub>4</sub>, LiBH<sub>4</sub>, NaAlH<sub>4</sub>, LiH, MgH<sub>2</sub>, NH<sub>3</sub>BH<sub>3</sub> etc., as potential sources of hydrogen and the development of optimal ways for the release of hydrogen is a rapidly growing field of research towards this aim [1,2]. Thermolysis of solid-state hydride-based systems seems to be the most promising process because of the high gravimetric hydrogen densities of the hydrides, exceeding 5.5 wt%. In this series of hydrides, reversible systems are of particular interest [3] and among them NaAlH<sub>4</sub> is

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## Nomenclature

$AB$	ammonia borane, $NH_3BH_3$	$-\Delta H$	enthalpy of reaction, J/mol
$PAB$	polyaminoborane, $[NH_2BH_2]_n$	$W(r)$	reaction rate, $kg/(m^3 \cdot s)$
$H_2$	hydrogen	$T, T_w$	temperature inside the reactor and external heating, K
$D_r^e$	effective radial diffusion coefficient of $H_2$ , $m^2/s$	$\alpha_w$	heat exchange coefficient between the wall of the reactor and the bed, $J/(m^2 \cdot s \cdot K)$
$D_g$	molecular diffusion coefficient, $m^2/s$	$r$	radial coordinate of the reactor, m
$F$	tortuosity coefficient	$R_0$	radius of the reactor, m
$\varepsilon$	porosity of the bed	$T$	time, s
$M_{AB}$	molar weight of AB, g/mol	$d_e$	equivalent diameter of pores between particles, $4 \cdot \varepsilon \cdot D_p / (6 \cdot (1 - \varepsilon))$ , m
$m_{AB}, m_{PAB}$	concentration of AB and PAB, $kg/m^3$	$D_p$	diameter of the particles
$Nu_{we}$	equivalent Nusselt number, $2 \cdot \lambda_r^e / (3 \cdot \lambda_g)$	$\delta$	amount of the unreacted AB
$C_{H_2}$	concentration of $H_2$ , $mol/m^3$	$\omega$	rate of reaction front propagation, $m^2/s$
$\lambda_r^e$	effective radial thermal conductivity of the bed, $J/(m \cdot s \cdot K)$	<i>Index: 0</i>	initial values
$\lambda_s$	heat conductivity of solid phase, $J/(m \cdot s \cdot K)$		
$\lambda_g$	heat conductivity of gas phase, $J/(m \cdot s \cdot K)$		
$C_s$	heat capacity of the bed, $J/(m^3 \cdot K)$		

an outstanding representative. Reversibility of this compound was first reported by Bogdanović et al. when using a titan-doped catalyst [4]. At present, reversible systems consisting of simple hydride and amide of alkali/alkali earth metals (for example,  $Mg(NH_2)_2 \cdot 2LiH$  [1,2]), including doped ones [5] are also actively investigated. Such reversible hydrides allow an on-board regeneration of the dehydrogenation products within the same unit. On the other hand, it was believed [1,6–8], that, in spite of the absence of reversibility, hydrides with a low thermolysis temperature and a high content of hydrogen ( $AlH_3$ ,  $NH_3BH_3$ ) also deserve attention. Such systems require an off-board regeneration [6] so that for a successful practical application of  $NH_3BH_3$  as a hydrogen storage system a breakthrough in commercial regeneration technologies will be necessary.

Ammonia borane ( $NH_3BH_3$ , AB) is of particular interest because of its very high content of hydrogen (19.6 wt%) and high stability in air at ambient temperatures. As compared with other hydrides, this compound releases  $H_2$  at comparatively low temperatures of the external heating. Dehydrogenation of AB is known [9] to proceed in steps: evolution of the first equivalent of  $H_2$  to produce the polymeric product of  $[NH_2BH_2]_n$  – polyaminoborane (PAB) takes place at temperatures around 100 °C; the release of the second equivalent of  $H_2$  to form  $[NHBH]_n$  takes place at a higher temperature around 150 °C and the evolution of the third equivalent of  $H_2$  requires very high temperatures (>500 °C) [10] and therefore the last stage is beyond the interest of researches in the field of hydrogen economy. At temperatures above 120 °C there appear complications in the hydrogen generation because of the formation of volatile by-products (ammonia, diborane, borazine and others) [11]. Therefore, decreasing the AB dehydrogenation temperature (to <90 °C) and increasing purity of the hydrogen product are among the important tasks to be solved when developing AB-based hydrogen storage systems.

These challenges gave rise to different directions in the research to find ways for a low-temperature release of hydrogen using different AB based materials. Creation of hydrogen-generating materials on the basis of ammonia borane and different oxygen-containing compounds to achieve high values of hydrogen gravimetric capacity at  $\leq 85$  °C is a rapidly developing field of research. A notable contribution towards this aim was the synthesis of nanoscaffold AB-based materials [12], where used as porous matrices were MOFs, silica gels, zeolites, carbon materials and others. The AB incorporation into the porous space was performed using solution procedures [13,14] and less frequently by mechanical

activation [14,15] and melt infiltration [12,14]. Materials on the basis of different polymer supports were also prepared using solutions of AB [16] and by electrospinning [17]. According to the authors, it is very difficult to differentiate between the activation by the porous structure of the material from that by its functional groups. Various mechanisms of destabilization of the AB structure by different functional groups have been discussed in the literature: silanol groups [18], carbonyl groups of poly(methyl acrylate) [16], carboxyl groups of activated carbon [14], the etheral oxygen of polyethylene oxide [17] and others. But at the moment the results are poorly systematized and none of the published works gives an analysis of the effect of surface functional groups with different acidities on the process of the AB thermolysis. On the other hand, an acid-base route of AB dehydrogenation by surface carboxyl groups of activated carbon has already been proposed in [14].

Therefore, in the first part of this work we describe the results of experiments where AB was brought in contact with the surface of known inorganic solids with different acid-base properties ( $TiO_2$ ,  $\gamma-Al_2O_3$ ,  $SiO_2$ ,  $MgO$ , HY zeolite,  $CaF_2$ ) by simple mechanical mixing where the porous structure of the solids was not involved in the interaction with the hydride (*Series A*). Novel results on the low-temperature stability of AB have been obtained which may be of importance both in designing hydrogen storage and generation systems and from the point of the materials science and for ensuring safety in handling this hydride.

The dehydrogenation of ammonia borane is known to proceed with evolution of heat (the standard values of the enthalpy upon evolution of 1 and 2 equivalents of  $H_2$  are 22 and 15 kJ/mol, respectively [19,20]). It can be suggested that the transport of this heat through the reaction bed will have an effect on the rate of hydrogen generation from AB. Unfortunately the literature gives practically no information on this problem [21]. Therefore in the experimental *Series B* thermolysis of AB has been studied using modifiers with different heat-conducting properties: Cu powder, Al powder, polyethylene, quartz sand.

In the second part of the article the kinetics parameters of a low-temperature (90 °C) release of hydrogen from composites of AB with heat-conducting material have been calculated and a mathematical model of the solid-state decomposition of AB in a tubular reactor has been developed which took into account the reaction front propagated from the heated reactor wall towards its axis. Modeling of the processes in fixed-bed tubular reactors has been widely discussed for the cases where the reagents and

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