POWER LAW KINETIC MODEL FOR SYNTHESIS OF SODIUM AMIDOBORANE (NaNH₂BH₃)

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REFERENCE NO	ABSTRACT
HYPR-03	One of the newly developed solid state hydrogen storage materials is sodium amidoborane ($NaNH_2BH_3$), an ammonia borane (NH_3BH_3) derivative. Sodium amidoborane ($NaNH_2BH_3$) is of interest by virtue of its approximately 7.46 wt % theoretical hydrogen capacity at significantly lower temperatures. Hydrolysis of $NaNH_2BH_3$ is faster than that of ammonia borane at room temperature and stable, In this study, synthesis of sodium amidoborane was conducted by reacting NaH and ammonia borane in Tetrahydrofuran (THF) solution. These experiments were carried out at different temperature ranges between 4-20°C, and different inlet molar ratios (n_{SAB}/n_{NaH}=0.75–1.25). The aim of this study is to determine a power law kinetic model capable of finely estimating the overall $NaNH_2BH_3$ synthesis behaviour. After the parametric experiments were conducted, empirical power law was evaluated for the synthesis reaction. The power-law model was reproduced as $$r_{apparent} = 3.47 e^{-\frac{7700}{RT}} C_{NaH}^{0.2} C_{AB}^{0.8}$$
Keywords: Hydrogen production, Sodium amidoborane, Power law kinetic model, Reaction rate coefficient	

1. INTRODUCTION

Hydrogen has been mostly regarded as energy carrier to satisfy the ever-increasing demand for the efficient, safe and clean energy supply. Hydrogen can be stored in either gaseous, liquid or solid state [1-6]. The most convenient form would be the solid state for safety and space reasons. Therefore, more research efforts mainly focus on materials composed of light elements and with high hydrogen content [4-10].

Ammonia borane (NH_3BH_3, AB) is a white molecular crystal under ambient conditions with a density of 0.74 g cm^{-3} and soluble in water and other relatively polar solvents. It exhibits theoretical hydrogen content 19.4 wt% and according to weight consideration AB is a very attractive for the storage of hydrogen [11, 12].

The hydrogen stored in AB and SAB can be released by thermolysis, catalytic hydrolysis or methanolysis. About 1 mol H_2 (i.e., 6.5 wt % H) per mol AB is released by thermal decomposition of AB under moderate conditions (<100°C). Higher temperature is needed to maximize the use of hydrogen in AB, but it is caused in the release of the side products which are including monomeric aminoborane (BH_2NH_2), borazine (BH_2NH_2), and diborane (B_2H_6) [12-14]. Metal amidoboranes ($M(NH_2BH_3)_n$) have been identified as a new class of hopeful hydrogen storage materials which are the AB derivatives replacing one H^+ by M^+, where the cation M^+ acts as charge balancer in MAB, M^+ $[NH_2BH_3]^-$ [12-14]. $NaNH_2BH_3$ (SAB) occur from the solid-state interaction between NH_3BH_3 and sodium hydride (NaH) [15].

SAB, release to 7.5wt % hydrogen, at significantly lower temperatures with no borazine emission. The low temperature release of a large amount of hydrogen is significant and provides the potential to carry out many of the principal criteria required for an on-board hydrogen store [16-18]

The formation reaction of SAB given in Eq(1) is exothermic at room temperature and one equivalent of H_2 per AB is released and sequent decomposition of SAB which is given in Eq(2) at 90 ˚C.

$$NH_3BH_3 + NaH \rightarrow NaNH_2BH_3 + H_2 \quad (1)$$
$$NaNH_2BH_3 \rightarrow NaNBH + 2H_2 \quad (2)$$

In this study, a wet route using THF as a solvent was synthesized SAB at given temperatures. Synthesis products were analysed by powder XRD and FT-IR. H_2 was generated during the reaction. Data of H_2 production was calculated with volumetric measurements. Then, thanks to this data was determined power law kinetic model of the synthesis of SAB. Although kinetic model studies based on the synthesis of AB in the literature have been encountered [19], there is no research into kinetic study of SAB which was investigated in this study.

2. EXPERIMENTAL

2.1. Synthesis of $NaNH_2BH_3$
NaH (95%) and NH_3BH_3 (97%) were Sigma Aldrich products and used as received. The synthesis of SAB experiments was carried out at different temperature ranges between 4-20°C, and different inlet molar ratios (n_{SAB}/n_{NaH}=0.75 – 1.25). AB was determined to have a great effect in the SAB synthesis reaction. Therefore, the mole ratio of reactants was attempted to be 1, 25. For example; n_{SAB} and n_{NaH} are 0.00961 mole and 0.00767 mole respectively. These reagents were added to 25 ml THF. All solution preparation process was done under an inert atmosphere in a nitrogen filled glove box. Then, the chemical reaction of NH_3BH_3 with NaH in THF was conducted in a commercial stirring tank reactor (STR) at constant temperature. The experiment was repeated at 4°C, 12°C and 20°C respectively.

Data of H_2 production was calculated with volumetric measurements. After, the reaction solution was filtered and washed three times with THF. Then, It was been removal of the volatiles by remaining under vacuum for 16 h. Synthesized SAB samples were analysed by diffuse reflectance Fourier Transform Infrared spectroscopy (Jasco FT-IR 480+) and KBr pellets. Structural identifications of samples were performed on a Bruker Brand D8 Advance Model (XRD) equipped with an *in situ* cell as well. X-ray diffraction data was collected from 10 to 60° in 2θ using Cu $K_α$ radiation (λ = 1.5406 angstrom).

3. RESULTS AND DISCUSSION

3.1. Result of Synthesis

3.1.1. Hydrogen evolution
Fig. 1 shows the hydrogen evolutions obtained at the various temperatures. Both the hydrogen generation rate and the total conversion are increased at the low temperature. In fact two observations stand out from Fig. 1 and Table 1:

Hydrogen gas was evolved vigorously after dropping NH_3BH_3–THF solution into the NaH-THF solution. The hydrogen evolution changes giving a first part, rapid and a second one, much less rapid, being the synthesis of SAB. Synthesis reaction is virtually completed in the first 12 minutes.

Using Eq. 1, the total conversion was calculated by the ratio of the number of moles of H_2 obtained from the reaction to the stoichiometry moles of H_2. The total conversions obtained for the temperature 4°C was 99%, while that obtained for the temperature 12°C and 20°C were 87% and 84% respectively.
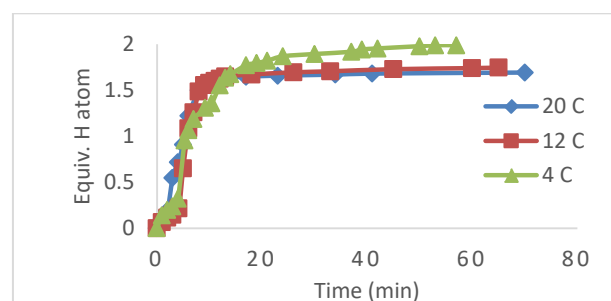

Fig. 1. Time dependence of hydrogen gas evolution from NaH–AB–THF solution at temperatures of 4°C, 12°C and 20°C

Table 1. Data of SAB synthesis reaction

	Theoretical H_2 volume(ml)	Experimental H_2 volume (ml)	Total NaH conversion %
4°C	165	164	99
12°C	174	152	87
20°C	178	151	84

3.1.2. Synthesis Kinetic of Sodium Amidobarane

These synthesis experiments were carried out at different temperature ranges between 4°C, 12 °C and 20°C, and different inlet molar ratios (n_{SAB}/n_{NaH}=0.75–1.25). A power-law model was chosen to describe the reaction rate in terms of concentration of NH_3BH_3 and sodium hydride. It was considered that the reaction rate expression follows a power law (according to Eq. (1):

$$r_{observed} = k\, C_{AB}{}^n\, C_{NaH}{}^m \qquad (3)$$

where n; the reaction order versus the AB concentration
m; the reaction order versus the NaH concentration.
k: the rate constants are predicted by the Arrhenius equation:

$$k = k_o\, e^{(-Ea/RT)} \qquad (4)$$

in which k_0 frequency constant and E_a the apparent activation energy

For constant volume batch reactor, mole balance for NaH (A), is

$$r_A V = \frac{d\,(n_{NaH})}{dt} \qquad (5)$$

$$r = \frac{d\,(C_{NaH})}{dt} = -k\, C_{AB}^n\, C_{NaH}^m \qquad (6)$$

[a (1- m) (1- X_A)$^{(1-n)}$ +2b (1- n) (1,25-$X_A$$^{)(1-m)}$]=[a (1- m) + 2b (1-n) (1,25)$^{(1-m)}$]- k (1-n)(1-m) $C_{A0}$$^{(n+m-1)}$ t   (7)

Common analytic solution approaches derived from Eqs. (5) and (6) were made as shown in Eq (7) and the kinetic parameters are determined by the integral method. Coefficients (a and b) are the solution to the ordinary differential equation integration method of Eq. (6). With these experimental data, Equation (7) can be linearized for estimation of the three parameters: conversion of NaH (X_A), and reaction orders m and n. The parameters were obtained by solver command using Excel program. Adoption of

m = 0.2 and n = 0.8 was made; It was found to be a=1.3 and b=-0.35. Using Eq. 7, a value calculated from the experimental data (γ = [a (1- m) (1- X_A)$^{(1-n)}$ +2b (1- n) (1,25-$X_A$$^{)(1-m)}$]) under the different condition. After, graph of these values against the time was plotted (Fig. 2).
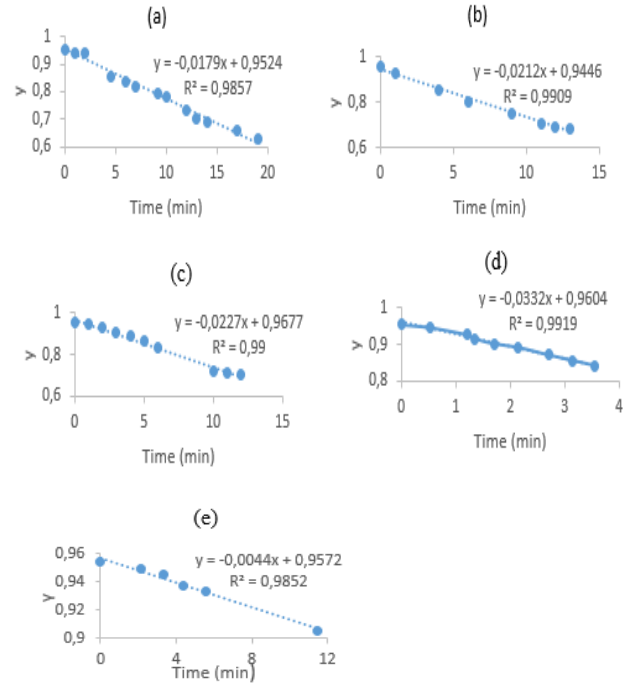

Fig. 2. At (a) 4 °C and n_{AB}/n_{NaH}=1.25, (b) 12 °C and $n_{AB/NaH}$=1,25, (c) 20°C and $n_{AB/NaH}$=1.25 (d) 20°C and n_{AB}/n_{NaH}=0.75, (e) 20°C and n_{AB}/n_{NaH}=1.0 under the conditions of that synthesis experiment and when m=0.2 & n=0.8 is account in the lineer equation and R^2 value

AB was determined to have a great effect in the SAB synthesis reaction. Therefore, power law kinetic model for synthesis of sodium amidoborane is determined for inlet ratio 1.25. The synthesis obeys 1st-order kinetics over the whole temperature range and the mole ratio of reactants. The high R^2 values shows that the acceptance of m=0.2 & n=0.8 is true. The determined kinetic model was also applied to synthesis data of 1 and 0.75 inlet ratios at 20°C and R^2 value was found to be quite high. According to data of SAB synthesis experiments, which are carried out

1.25 inlet ratio, k value is determined for each temperature (Table 2.)

Table 2. Power law kinetic parameters for SAB synthesis, $r = k\,[AB]^n[NaH]^m$

Temperature	k	m	n
4 °C	0.1418 h^{-1}	0.2	0.8
12 °C	0.1325 h^{-1}	0.2	0.8
20 °C	0.118 h^{-1}	0.2	0.8

1 / T is plotted against ln(k) values, Fig. 3 is obtained. The apparent activation energy was determined for 1.25 mole ratio of AB-NaH over the temperature range 4-20 °C. Pay attention of SAB synthesis being exothermic the temperature inside the reactor increases despite the thermostat bath, especially at low temperatures. Hence, the apparent activation energy is calculated over the range of the measured temperatures.
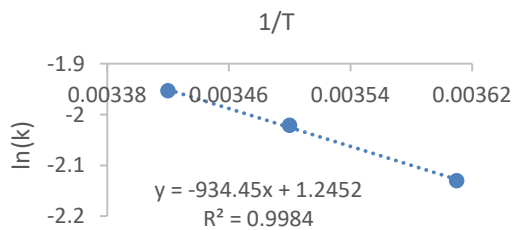

Fig. 3. The graph of ln(k) versus 1/T

According to Fig. 3, E_a and k_o were calculated about 7700 J/mol and 3.47 h^{-1} respectively. The observed reaction rate expression is given Eq.8.
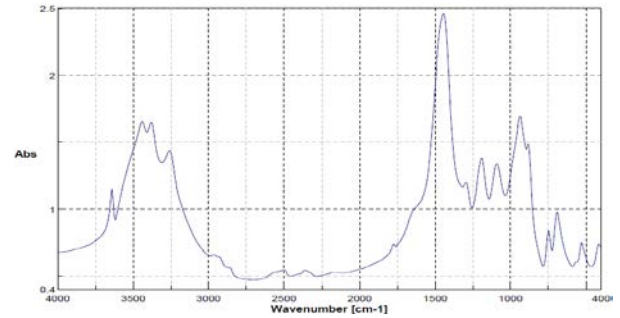
$$r_{apparent} = 3.47 e^{-\frac{7700}{RT}} C_{NaH}^{0.2} C_{AB}^{0.8} \qquad (8)$$

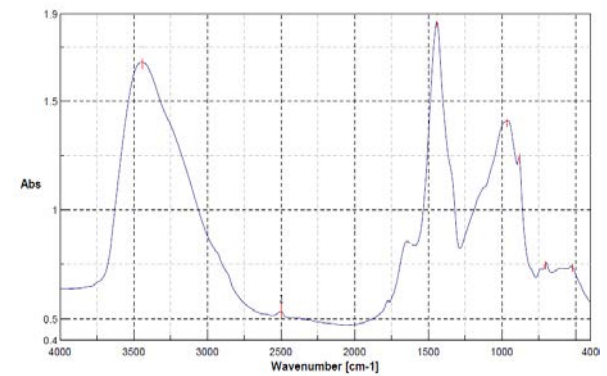**3.2. Structural and spectroscopic characterization of Sodium Amidobarane**

3.2.1. FT-IR
The synthesis of SAB experiments was carried out different temperature ranges 4-20°C and inlet molar ratio n_{AB}/n_{NaH}= 1.25. FTIR analyses of the products of the synthesis experiment conducted at 4 and 12˚C are similar, whereas it conducted at 20˚C is different. as seen in Fig. 4, It was been strong adsor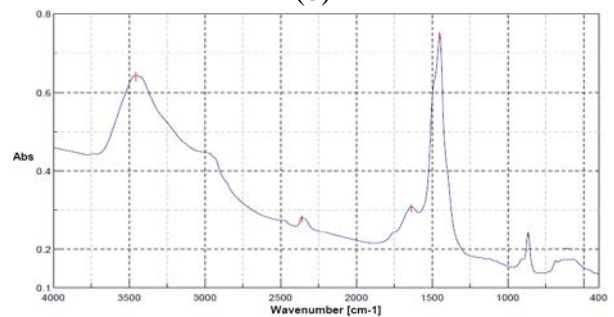ption bands in the NH stretching region (3200-3700 cm^{-1}); less intense bands in the BH stretching region (1850-2550 cm^{-1}); strong adsorption bands in the NH bending region (1380-1700 cm^{-1}); strong adsorption bands in the BH bending region (1000-1300 cm^{-1}); strong adsorption bands in the BN stretching region (1300-1400 cm^{-1}).

(a)

(b)

(c)

Fig. 4. FTIR analysis of n_{AB}/n_{NaH}=1.25 (a) at 4°C (b) At 12 °C and (c) at 20 °C under conditions of SAB synthesis

Both NaNH$_2$ and unreacted NaH are contributed to the bands at around 1400 cm^{-1}. Thus, this band has very strong adsorption band. Moreover, as the temperature increases, the peak intensities of the BH tension decrease. The reason of this is thought that the

gas product, which is a bonded BH bond, is produced at high temperature.

3.2.2. XRD

In the XRD analysis of the SAB samples (n_{AB}/n_{NaH}=1.25 and 4, 12 and 20˚C), the similar results were obtained and surprisingly, it was detected SAB with $NaNH_2$ and unreacted NaH. In the three syntheses of SAB, it was seen that the product structure was crystalline due to the sharp and vertical reflection peaks. The XRD difragtometer degrees of the SAB gave a strong peak at 20°, 24°, 26°, 30° and 32°, the degrees of NaH 36° and 38°, and the degree of $NaNH_2$ had a very intense peak at 17° and the other peaks at 40°, 45° and 50° (Fig. 5)

The synthesis reaction, which is carried out in excess of the stoichiometric proportion of AB, is thought to be as in Eq. 9. Diborane is not seen in XRD analysis, because it is a gas.

$$4NaH + 4NH_3BH_3 \rightarrow 2NaNH_2 +$$

$$2NaNH_2BH_3 + B_2H_6 + 4H_2 \qquad (9)$$
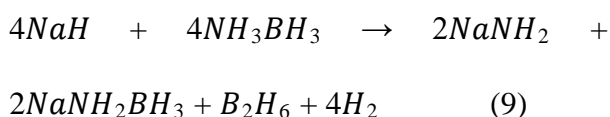
CONCLUSIONS

Sodium amidoborane was synthesized through the reaction of NaH and NH_3BH_3 in THF at 4°C, 12°C and 20°C temperatures. The most efficient synthesis temperature is 4°C. The total conversions obtained for this temperature was 99%, while that obtained for the temperature 12°C and 20°C were 87% and 84% respectively. AB was determined to have a great effect in the SAB synthesis reaction. Therefore, power law kinetic model for synthesis of sodium amidoborane is determined for inlet ratio 1.25. The synthesis obeys 1st-order kinetics over the whole temperature range and the mole ratio of reactants. Power low coefficients and the apparent activation energy were calculated as 0.2 & 0.8 and 7.7 kj/mol respectively. k_o was calculated as 3.47h^{-1}. The synthesis kinetic was determined from the data of hydrogen. NH_3BH_3 have a major effect on the reaction progression and rate.
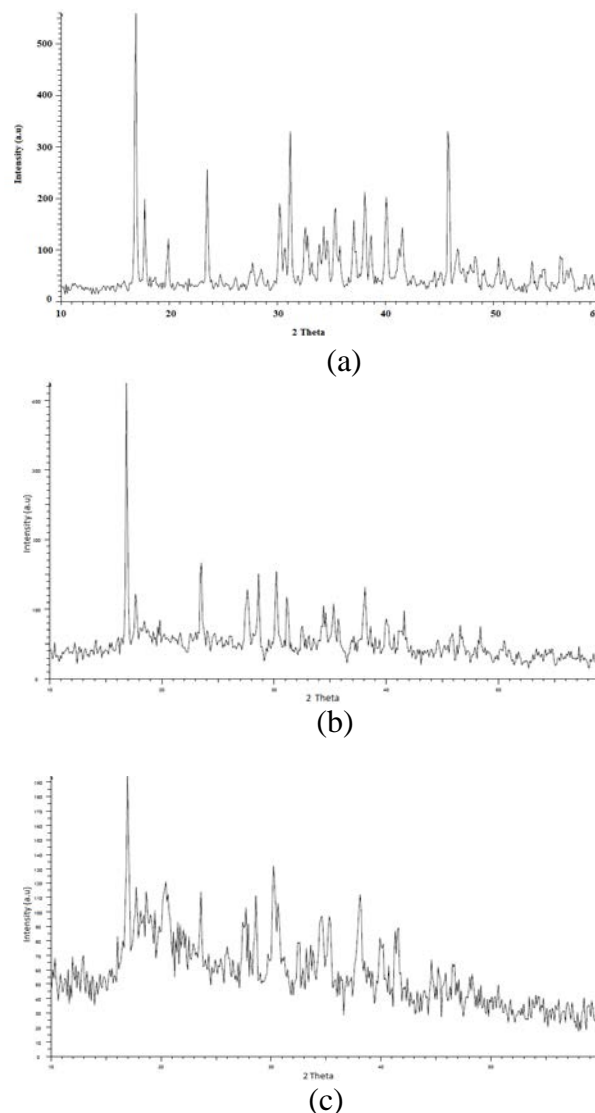

(a)

(b)

(c)

Fig. 5. XRD analysis of n_{AB}/n_{NaH}=1,25 (a) at 4°C (b) At 12°C and (c) at 20 °C under conditions of SAB synthesis

Nomenclature

AB	Ammonia borane
C	Concentration
E_a	The apparent activation energy
k	Frequency constant
m	The reaction order of NaH concentration
n	The reaction order of AB concentration
R	Gas constant
SAB	Sodium amidoborane
T	Temperature

Greek Letters

θ	the incidence angle of the x-ray beam
λ	the wavelength of the incident X-ray beam

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