

HYDROGEN FOR VEHICLE APPLICATIONS FROM AMMONIA BORANE: HYDROGEN YIELD, THERMAL CHARACTERISTICS, AND AMMONIA FORMATION

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Summary

Ammonia borane (AB) is a promising hydrogen storage material as it contains 19.6 wt% hydrogen. We recently proposed and demonstrated a new method for hydrogen generation involving noncatalytic hydrothermolysis of AB solutions. In this paper, the hydrothermolysis approach is studied over a wide range of AB concentrations at different temperatures, pressures and heating rates. This approach provides the maximum H₂ yield up to 12.6 and 14.3 wt%, at the reactor temperature ~ 85 °C and at pressure 14.7 and 200 psia, respectively. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high H₂ yield values at below PEM fuel cell operating temperatures. Ammonia formation was also observed, and quantified using various methods, for AB hydrothermolysis as well as pure thermolysis (in absence of water).

Keywords

Hydrogen storage, Ammonia Borane, Hydrothermolysis, Ammonia

Introduction

Ammonia borane (AB) is of significant interest as a hydrogen storage material for fuel cells (FC) because of its high hydrogen content (19.6 wt%).¹ Due to limited AB solubility in water, however, catalytic hydrolysis provides low theoretical H₂ yield (~ 5.6 wt%) and it also requires expensive catalysts such as ruthenium. Thermolysis, on the other hand, requires an external heating source to provide relatively high temperature (~ 170 °C) to release two moles of H₂ per mol of AB, while the third H₂ mole requires even higher temperature (~ 500 °C).¹

In this context, we have recently proposed and demonstrated a novel noncatalytic AB hydrothermolysis method, where heating lean AB solutions (~10 wt%) in water at ~135 °C under moderate argon pressure (~10 atm) generates 1 and 2 equivalents of H₂ by thermolysis and hydrolysis, respectively.² In the present work, the hydrothermolysis approach to generate hydrogen is studied over a wide range of AB concentrations at different pressures, temperatures and heating rates.

It is observed in the present work that both hydrothermolysis and pure thermolysis generate significant amounts of ammonia. This ammonia must be removed for use in polymer electrolyte membrane (PEM) FC, as the FC components are poisoned by traces of NH₃. The quantification of NH₃ using various methods was

conducted and an effective method for NH₃ removal is currently being developed in our laboratory.

Experimental

The hydrothermolysis experiments were conducted in a 300 mL stainless steel reactor (Parr Instrument Co.) while a smaller Parr reactor (~ 70 mL) was utilized to better understand the thermal characteristics of the reaction system. The samples (0.5-1.0 g) were prepared by mixing AB with H₂O in varying weight ratios. The mixture was placed in a small glass vial (3 ml) inside the reactor, under argon environment. The reactor pressure was monitored using a transducer. Apart from the reactor temperature (T_{reactor}), the sample temperature (T_{sample}) was also recorded by inserting a thermocouple inside the sample.

The product gas composition was analyzed by mass-spectrometry (Hiden, HPR-20). The NH₃ was quantified by titration technique and the results were confirmed by using Dräger (or Draeger) tubing and mass-spectrometry.

Results and Discussion

Figure 1 shows the overall H₂ yield as a function of AB concentration for different temperature and pressure values. At 85 °C and 200 psia, from 43 to 77 wt% AB, H₂ yield increased from 8.2 to 14.3 wt%. Further increase in AB concentration decreased the H₂ yield. The reason for this decrease is related to the lower heat release from the

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hydrolysis reaction that drives the AB thermolysis. Figure 1 also shows the effect of initial argon pressure on H₂ yield. For AB concentration < 77 wt%, the results show no significant effect of pressure on H₂ yield. For 77 wt% AB, the H₂ yield for 14.7 psia was lower (12.6 wt%, 1.9 H₂ molar eq.) as compared to 200 psia (14.3 wt%, 2.2 H₂ molar eq.). Since the water content in high AB concentration mixtures is small, its evaporation has a strong impact and raises the effective mixture AB concentration beyond 77 wt%. For AB concentrations > 77 wt%, the H₂ yield decreases continuously until ~ 8.3 wt% (1.3 H₂ molar eq.) for pure AB.³

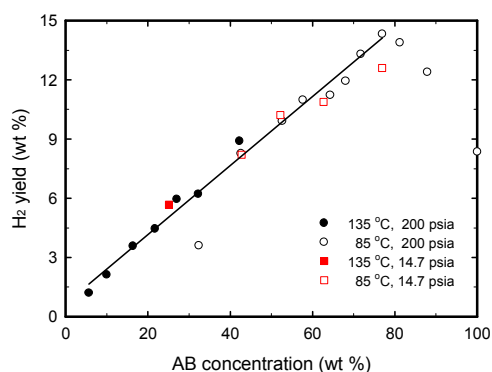


Figure 1 Hydrogen yield as a function of AB concentration, at different operating conditions.

The temperature profiles obtained during AB hydrothermolysis for different heating rates (β , °C/min) are shown in Figure 2. The T_{reactor} was increased at heating rate of 0.2 - 10 °C/min from room temperature to 85 °C set point. For 200 psia, the sharp evolution reactor temperature increases with increasing heating rate. Also, the maximum T_{sample} increases with heating rate. It is likely that for lower heating rates, more hydrolysis prior to sharp evolution occurred at T_{reactor} above 60 °C due to prolonged heating of the sample. More consumption of the sample during this period results in less exothermicity at sharp evolution time. It is known that the release of H₂ from AB via both thermolysis and hydrolysis is exothermic, where the latter is more exothermic than the former.

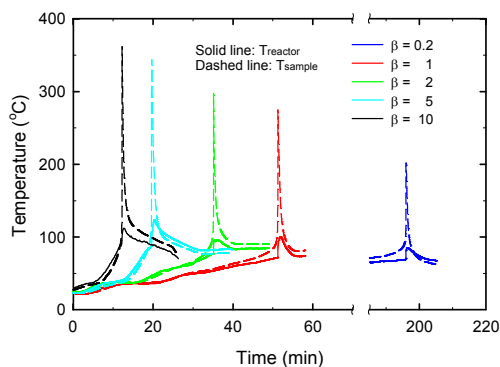


Figure 2 Temperature profiles for different heating rates (60 wt% AB, P = 200 psia)

It was found that AB converted to NH₃ (NH₃/AB) increased with decreasing AB concentration. For 200 psia,

from 69 to 90 wt% AB, AB converted to NH₃ decreased from ~ 25 % to ~ 5 %. Since NH₃ is considered to be a product of hydrolysis, it was expected that NH₃/AB ratio would increase with water content in the AB-water mixture. It is remarkable that nearly the same amount of AB is converted to NH₃ by pure thermolysis (in absence of water), where 2-3 % of AB was converted to NH₃ regardless of the initial pressure. It is noteworthy that there are many published articles on pure thermolysis and hydrolysis of AB but, to our knowledge, formation of ammonia has never been reported for pure thermolysis.

For use in PEM FC, ammonia must be removed from the H₂ stream. In addition to potentially poisoning the anode catalyst site, ammonia can also cause ion exchange with protons in the polymer electrolyte. It has been reported that as low as 13 ppm NH₃ can significantly decrease the FC performance, and that the degradation is irreversible for long-term exposure (15 hr) to 30 ppm NH₃. NH₃ can be removed from gaseous streams by various methods. The most effective method for NH₃ removal is currently being developed in our laboratory and more details will be presented in the full manuscript.

Conclusions

A novel noncatalytic AB hydrothermolysis method to release hydrogen was studied over a wide range of AB concentrations at different pressures, temperatures and heating rates. It was shown that with increasing AB concentration (6-77 wt%), the H₂ yield increased. The H₂ yield up to 12.6 and 14.3 wt%, along with rapid kinetics, at $T_{\text{reactor}} \sim 85$ °C and at pressure 14.7 and 200 psia, respectively was demonstrated. To our knowledge, on a material basis, **the AB hydrothermolysis process is the first one to provide such high H₂ yield values at below PEM FC operating temperatures.** It was also found that both the sharp evolution temperature and the maximum T_{sample} are influenced by heating rate. Ammonia formation was observed for hydrothermolysis and even for pure thermolysis. An effective method for NH₃ removal is currently being developed in our laboratory and more details will be presented in the full manuscript.

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