

Short communication

Hydrolytic cleavage of ammonia-borane complex for hydrogen production

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Received 3 October 2006; received in revised form 15 February 2007; accepted 19 February 2007

Available online 1 March 2007

Abstract

A new process for generating hydrogen via near room temperature hydrolysis of AB complex using small amounts of platinum group metal catalyst has been studied. Using in situ ^{11}B NMR spectroscopy, the overall rate of $\text{K}_2\text{Cl}_6\text{Pt}$ catalyzed hydrolysis of AB complex was calculated to be third-order. The pre-exponential factor (A) and the activation energy (E_a) of Arrhenius equation, $\ln k = \ln A - E_a/RT$, were determined to be: $A = 1.6 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ and $E_a = 86.6 \text{ kJ mol}^{-1}$ for temperature range of (25–35 °C). X-ray photoelectron spectroscopy of the residue suggested that the platinum salt was reduced from Pt^{4+} to Pt^0 within the course of the reaction and X-ray diffraction analysis pattern for the residue showed crystallized single-phase boric acid.

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Keywords: Ammonia-borane; Hydrogen storage; Chemical hydride; Hydrolysis; Catalyst

1. Introduction

Compounds represented by the empirical formula $\text{B}_x\text{N}_x\text{H}_y$ have been known and used as high capacity hydrogen (H_2) carriers. Hydrogen generators based on such carriers can be employed for hydrogen on-demand applications. However, the hydrogen is often too impure for the proton exchange membrane fuel cell (PEMFC) applications, yield is low at low temperatures, and generation requires environmentally harmful materials in the process [1].

Ammonia-borane (AB) complex has the highest material hydrogen content (about 19.6 wt%) with a system-level H_2 energy storage density of about 2.74 kWh L^{-1} (versus 2.36 kWh L^{-1} for a liquid hydrogen Dewar). At near room temperatures and atmospheric pressure, AB is a white crystalline solid, and is stable in both water and ambient air.

Thermolysis has been used as a method of choice to generate hydrogen from AB complex. There are several drawbacks to this technique for generating hydrogen. First, the ammonia-borane pyrolysis begins at temperatures below 140 °C. However, to release substantial amount of the hydrogen contained in AB complex, temperatures above 500 °C are needed. The overall process is exothermic, but requires heat to be added to activate

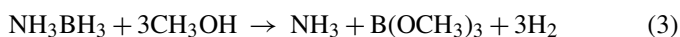
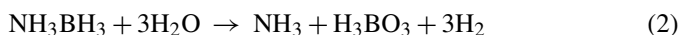
the material. The overall reaction can be written as follows:



Complete pyrolysis of ammonia-borane complex provides 3 mol of hydrogen per mole of AB decomposed. Second, thermolysis of AB involves competing reactions. The FTIR analysis of the evolved gases from AB thermolysis has shown that monomeric aminoborane (BH_2NH_2), borazine, and diborane are produced. The aminoborane comprises poly-(aminoborane) (BH_2NH_2) $_n$.

Poly-(aminoborane), the inorganic analog of polyethylene, is a non-volatile white solid. These compounds are undesirable impurities that make hydrogen from direct thermolysis of AB complex unfit for PEMFC applications. Furthermore, formation of these species lowers H_2 yield from direct AB thermolysis.

An alternative to thermolysis is provided by hydrolysis or methanolysis of AB complex. Hydrolytic or methanolic cleavage of AB provides 3 mol of hydrogen per mole of AB reacted [2–5]. Although this process has been used in the field of modern synthetic organic chemistry and for pharmaceutical applications, only recently has it been applied as a way of utilizing AB complex for the storage of hydrogen. Corresponding reactions are given below:



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As noted above, AB complex is a stable adduct. Therefore, to date, the hydrogen generating reactions (2) and (3) have involved harsh acidic condition, such as refluxing in aqueous HCl or the use of heterogeneous catalysts based on palladium or nickel. In this paper, we describe a method for catalytic hydrolysis of AB for production of high purity hydrogen at low temperatures.

2. Experimental

2.1. General

AB complex (NH_3BH_3) and catalysts used in this work were obtained from Aldrich Chemicals and used without further treatment.

2.2. Characterization and analysis

The X-ray photoelectron spectroscopy (XPS) analysis was done using a Physical Electronic 5400 spectrometer and a Mg anode, at 300 W power, high resolution scans from 1100 to 0 eV step size 0.1 eV, dwell time 50 ms. The X-ray diffraction analysis was done using a Rigaku D-MaxB instrument with a Cu X-ray 40 kV at 30 mA, sample slit 4° , detector slit 1° and scan range $10\text{--}80^\circ$, scan rate 1°min^{-1} . In situ ^{11}B NMR measurements were conducted using a Varian VXR300.

2.3. Hydrolytic dehydrogenation experiments

In a typical reaction, the catalyst was dissolved in water and then added to as received AB. The amount of hydrogen was measured volumetrically.

2.4. Kinetic studies using *in situ* ^{11}B NMR

0.01 g of AB complex was added to 7 mL of 5, 10, and 30 mM K_2PtCl_6 solution in D_2O at 25, 30, and 35°C . The NMR tube cap was modified to allow hydrogen release.

3. Results and discussion

At near room temperatures, AB readily undergoes hydrolytic cleavage in the presence of various platinum group metal (PGM) salts, such as K_2PtCl_6 . Fig. 1 depicts the volume of hydrogen generated versus time for K_2PtCl_6 salt.

The rate of hydrolysis can be affected by varying the rate at which the catalyst solution is introduced onto the AB powder.

Fig. 2 depicts ^{11}B NMR of AB hydrolysis reaction in progress. NH_3BH_3 exhibits a quadruplet centered at $\delta = -23.5$ ppm with $^1J_{\text{B-H}} = 94$ Hz (Fig. 2a). The chemical shift at $\delta = 13.2$ ppm is associated with H_3BO_3 and it changes to $\delta = 10.1$ ppm as the reaction proceeds to completion (Fig. 2b). The ^{11}B NMR chemical shift for an aqueous boric acid solution (pH 5.5) is $\delta = 19.0$ ppm and it has been shown to be pH dependant due to an equilibrium process between H_3BO_3 , BO_2^- and other borate species [6]. The XRD pattern for the residue of AB hydrolysis showed crystallized single-phase boric acid (Fig. 3).

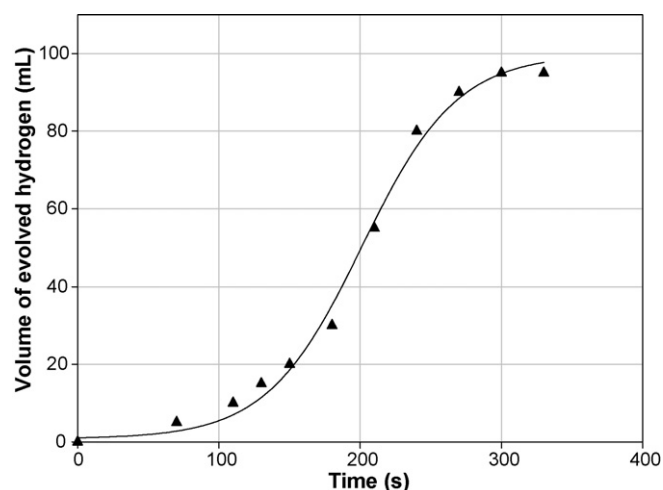


Fig. 1. Hydrogen evolution vs. time for the hydrolytic dehydrogenation of AB complex (0.05 g) in the presence of 0.1 mL of 19 mM solution of K_2PtCl_6 catalyst at room temperature.

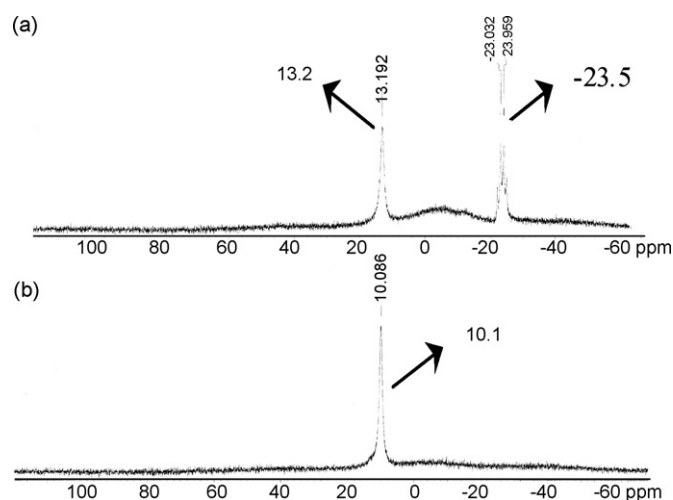


Fig. 2. ^{11}B NMR spectra of AB hydrolysis using K_2PtCl_6 catalyst—(a) reaction in progress, (b) end of reaction.

The kinetic studies were also conducted using *in situ* ^{11}B NMR. In aqueous solutions of K_2PtCl_6 , hydrolysis of the AB complex is first-order with respect to AB concentration $[\text{AB}]$. The apparent first-order rate constant varies with the catalyst concentration as shown in Fig. 4. Fig. 5 depicts the rate of

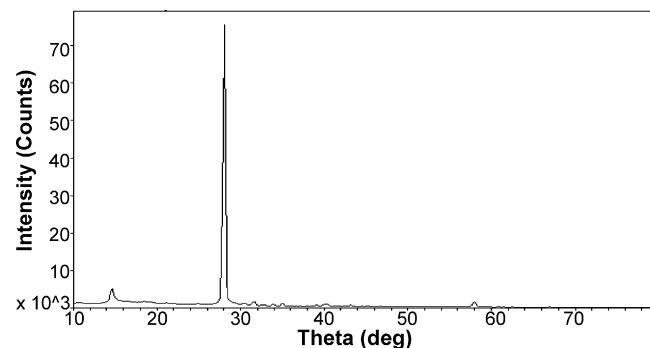


Fig. 3. XRD pattern of the residue from AB hydrolysis.

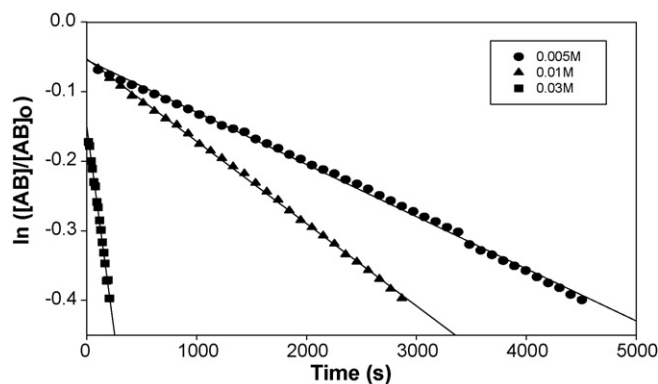


Fig. 4. Rate of hydrolysis for AB complex as a function of time and K_2PtCl_6 concentration. The rate is first-order with respect to AB concentration $[NH_3BH_3]$.

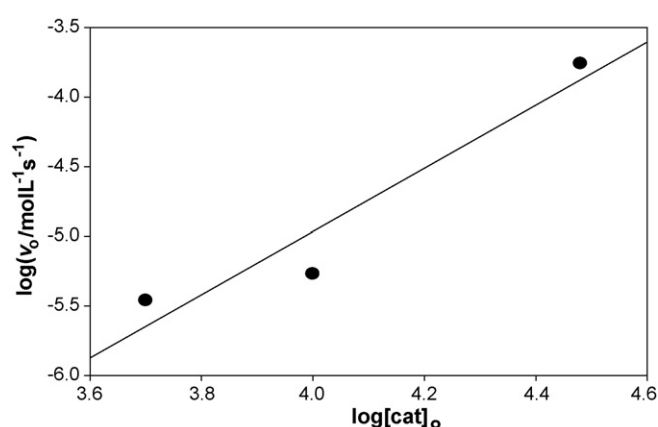


Fig. 5. Rate of NH_3BH_3 hydrolysis in D_2O at $25^\circ C$ for 0.005–0.03 M K_2PtCl_6 catalyst concentration, slope = 2.27 (correlation coefficient = 0.92), $v_0 = k'[AB]$.

the AB hydrolysis versus time for $[K_2PtCl_6]$ in the range of 0.005–0.03 M. The data indicate that hydrolysis of AB is second order with respect to concentration of the catalyst. Therefore, the overall rate of K_2PtCl_6 catalyzed hydrolysis of AB complex is third-order and can be expressed as (it is assumed that the concentration of water remains constant throughout the reaction, thus, $k' = k[H_2O]$):

$$-\frac{d[AB]}{dt} = k'[AB][K_2PtCl_6]^2$$

Fig. 6 depicts the temperature dependency (in the range of 25–35 °C) of the AB hydrolysis reaction rates. The first-order rate constants increase as the temperature increased from 25 to 35 °C (see Table 1). Based on the information given in Table 1, the pre-exponential factor (A) and the activation energy (E_a) were determined from Fig. 7 using the Arrhenius equation,

Table 1
Rate constants and correlation coefficients for the AB hydrolysis at $T=25, 30,$ and $35^\circ C$.

T ($^\circ C$)	k ($L mol^{-1} s^{-1}$)	R^2
25	1.18×10^{-4}	0.999
30	1.42×10^{-4}	0.999
35	3.69×10^{-4}	0.987

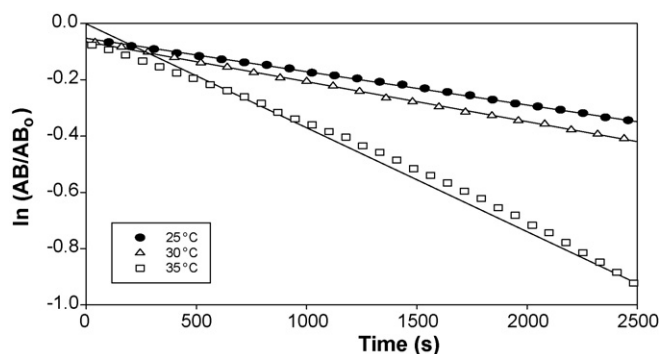


Fig. 6. Rate constant of NH_3BH_3 hydrolysis at 25, 30, and $35^\circ C$ for a first-order reaction with respect to $[NH_3BH_3]$ for 0.01 M K_2PtCl_6 solutions.

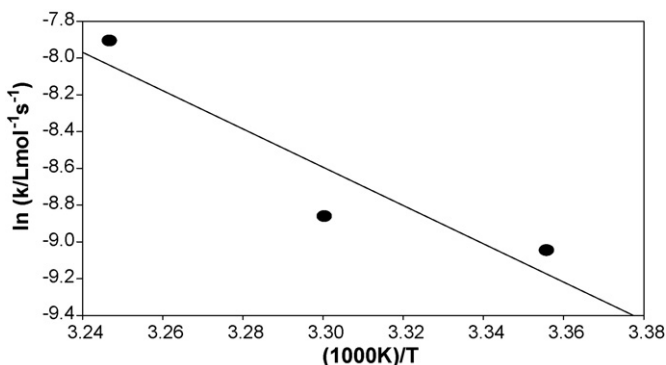


Fig. 7. The Arrhenius plot for the hydrolysis of AB complex using K_2Cl_6Pt as the catalyst, correlation coefficient = 0.86.

tion, $\ln k = \ln A - E_a/RT$, to be: $A = 1.6 \times 10^{11} L mol^{-1} s^{-1}$ and $E_a = 86.6 kJ mol^{-1}$.

X-ray photoelectron spectroscopy (XPS) was used to determine the state of Pt in the spent catalyst. The two binding energy peaks at 71.3 and 74.6 in the spectra are in good agreement with Pt^0 metal [7]. Results suggest that the platinum salt was reduced from Pt^{4+} to Pt^0 within the course of the reaction. We note that the metallic state of the PGM catalysts did not show significant catalytic activity toward hydrolysis of AB complex (Fig. 8).

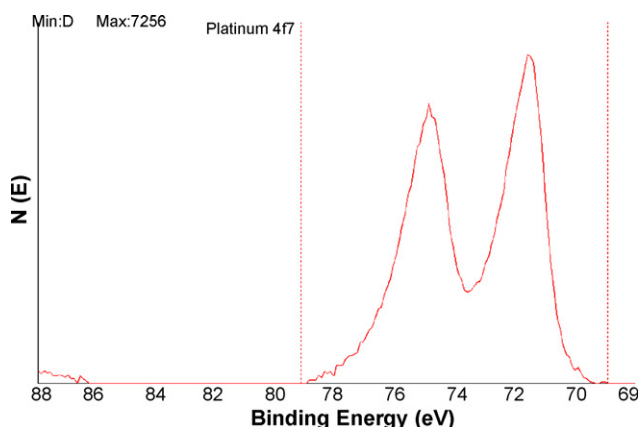


Fig. 8. Pt 4f XPS analysis of spent catalyst during hydrolysis of AB complex with K_2Cl_6Pt .

4. Conclusions

Near room temperature hydrolysis of AB complex has been carried out using small amounts of K_2PtCl_6 salt. The AB hydrolytic reaction is exothermic and can be extremely fast, kinetically. The kinetics of the AB hydrolysis in the presence of K_2PtCl_6 catalyst was studied using in situ ^{11}B NMR spectroscopy. The overall reaction-order was estimated to be three with an apparent activation energy $E_a = 86.6 \text{ kJ mol}^{-1}$.

XPS analysis of the spent material showed that the Pt in the catalyst is reduced to metallic state during the reaction and as such Pt did not display any catalytic activity.

The XRD pattern for the residue of AB hydrolysis showed crystallized single-phase boric acid as the final product.

Acknowledgment

The authors acknowledge the support provided by the National Aeronautics and Space Administration (NASA)

through Glenn Research Center (GRC) under contract no. NAG3-2751. The authors also acknowledge the assistance of Dr. Ion Ghiviriga at University of Florida with the ^{11}B NMR spectroscopy and Mr. Kurk Scammon at the Materials Characterization Facility (MCF) of the University of Central Florida with the XPS and XRD analysis.

References

- [1] A. T-Raissi, A Proceeding of the U.S. DOE Hydrogen Program Annual Review, Golden, CO, May 7, 2002, p. 537.
- [2] M. Couturier, J. Tucker, B.M. Anderson, P. Dubé, J.T. Negri, *Org. Lett.* 3 (2001) 465.
- [3] H.C. Kelly, V.B. Marriott, *Inorg. Chem.* 18 (1979) 2875.
- [4] G.E. Ryschkewitsch, *J. Am. Chem. Soc.* 82 (1960) 3290.
- [5] J.C. Linechan, T. Autrey, J.L. Fulton, Y. Chen, M. Balasubramanian, *Prep. Pap. Am. Chem. Soc., Div. Fuel Chem.* 50 (2) (2005) 540.
- [6] M. Chandra, Q. Xu, *J. Power Sources* 156 (2006) 190.
- [7] G.M. Bancroft, I. Adams, L. Coatsworth, C.D. Bennewitz, J.D. Brown, W.D. Westwood, *Anal. Chem.* 47 (1975) 585.