Inorganic Chemistry

Communication

pubs.acs.org/IC

Improved Hydrogen Release from Ammonia–Borane with ZIF-8

Rui-Qin Zhong,[†] Ru-Qiang Zou,[‡] Tessui Nakagawa,[†] Michael Janicke,[§] Troy A. Semelsberger,[†] Anthony K. Burrell,*[,¶] and Rico E. Del Sesto*[,†]

[†]Materials Chemistry, Los Alamos National Laboratory, Mail Stop J514, Los Alamos, New Mexico 87545, United States

[‡]College of Engineering, Peking University, Beijing 100871, China

[§]Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, United States

[¶]Chemical Sciences and Engineering, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439, United States

S *Supporting Information*

ABSTRACT: The promotion for hydrogen release from ammonia–borane (AB) was observed in the presence of ZIF-8. Even at concentrations of ZIF-8 as low as 0.25 mol %, a reduction of the onset temperature for dehydrogenation accompanies an increase in both the rate and amount of hydrogen released from AB.

One of the critical issues in the increasing worldwide demand for clean energy sources is the development of new hydrogen-storage materials that can be used in automotive applications.[1] U.S. Department of Energy (DOE) 2015 targets for onboard hydrogen-storage systems are 90 g kg^{-1} gravimetric density and 81 g L^{-1} volumetric density of deliverable hydrogen.[2] In particular, hydrogen should be released at sufficient rates near 85 °C, as defined by current polymer electrolyte membrane fuel operating conditions. Ammonia–borane (AB; NH_3BH_3) is a promising potential candidate owing to its high stoichiometric hydrogen content[3] moderate dehydrogenation temperature, and stability at room temperature.[4] However, currently there are limits to the practical fuel-cell application of AB including slow kinetics, irreversible hydrogen loss, and formation of volatile impurities.[5] Great efforts have been devoted to addressi these roadblocks including the use of catalysts,[4b,6] ionic liquids,[7] additives,[8] base-metal substitutions,[9] and Lewis and Brønsted acid catalysts.[10]

In 2005, Autrey et al. reported an enhanced hydrogen release of AB at the surface of mesoporous silica.[11] This report provided a new approach by using nanoscaffolds to improve the dehydrogenation of AB.[12] Since then, metal–organic frameworks (MOFs), a family of nanoporous crystalline material constructed of metal centers and organic ligands,[13] were explored for the nanoconfinement of AB and showed improved kinetics or impurity reduction of AB dehydrogenation.[14] The MOF-confined AB composites were prepared via complex methods either in organic solvents or by a vapor-phase-infiltration method. They addressed the function of "nanoconfinement" or MOF-confined AB as the catalytic seeds and suggested that the synergistic effect of nanoconfinement and metal catalyst centers of MOFs contributes to the enhanced AB dehydrogenation kinetics. However, there is still a lack of evidence to confirm the hypothesis that "nanoconfinement" is the key contributing factor. In addition, previous reports focused on experimental methods and qualitative investigation rather than the issues of low overall gravimetric storage capacity.[11−14] However, solving these issues is important to further developing MOFs as candidates and improving its performance for AB dehydrogenation for practical applications.

ZIF-8 [Zn(2-methylimidazolate)$_2$], a sodalite zeolite-type structure with nanopore structural features reflected by a large surface area (1947 m^2 g^{-1}), large cavities (11.6 Å), and small pore apertures (3.4 Å),[15] is one of the most popular MOFs because it is chemically robust, thermally stable (over 500 °C), and commercially available. Thanks to these properties, ZIF-8 has been extensively investigated in many areas including gas-storage materials,[15] catalysts for the transesterification,[16] and supports for preparing nanoparticulate gold catalysts.[17] Recently, ZIF-8 was reported to catalyze the dehydrocoupling of $H_3B{\cdot}NMe_2H$ to yield $(H_2B{\cdot}NMe_2)_2$.[18] The crucial factors were thought to be size-confinement effects and the polar and Lewis acid/base properties of the porous matrix.

Herein we employ ZIF-8 to catalyze the dehydrogenation of AB through solid-state mixing and compare the results to those obtained from the nanoconfined composite analogue prepared using solvent-based impregnation techniques.

A homogeneous physical mixture of AB and ZIF-8 was prepared by hand milling in a mortar and pestle in a glovebox at room temperature for 2−3 min. Solid-state ^{11}B NMR spectra of the milled mixtures show only BH_3 (Figure S1 in the Supporting Information), thus indicating that no chemical reaction has occurred between ZIF-8 and AB during the milling process. The powder X-ray diffraction (PXRD) patterns (Figure S2 in the Supporting Information) show an intact framework of ZIF-8 and crystalline AB, which is identified by the strong diffraction peaks at $2\theta = 24°$ and 34°.

Differential scanning calorimetry (DSC) was measured from 25 to 200 °C heating at 1 °C min^{-1} (Figure 1). Neat AB has an exothermic peak centered at 111 °C, following an endothermic melting peak centered at 109 °C, and a second broad exothermic peak centered at approximately 160 °C. In contrast to neat AB, AB/ZIF-8 samples decomposed in several steps within a temperature range of 60−160 °C. As the concentration of AB in a mixture of AB/ZIF-8 increased from 6 to 75 wt %, no significant peak position changes were observed in the DSC

Received: November 28, 2011
Published: February 17, 2012

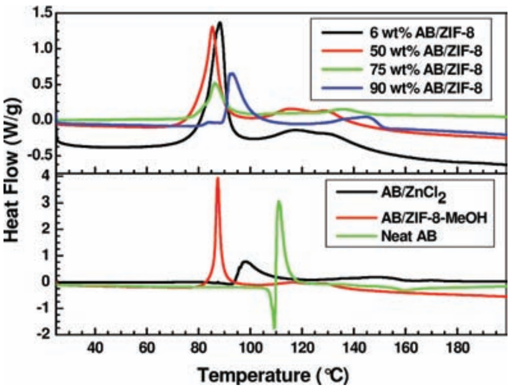

Figure 1. DSC curves: (above) AB/ZIF-8 samples; (below) $AB/ZnCl_2$ and AB/ZIF-MeOH samples and neat AB.

traces. In general, the first strong exothermic peak, corresponding to hydrogen release, occurred at 85−88 °C and two other minor exothermic peaks were observed above 114 °C. The broad peaks in the ZIF-8 samples, compared to the nanoconfined sample, are due to the latter having more homogeneous AB domains relative to the coarsely hand-milled AB/ZIF-8 materials, leading to more rapid dehydrogenation kinetics.

It was not until the concentration of AB was increased to 90 wt % (0.25 mol %) that the first exothermic peak was shifted to higher temperatures (92 °C), but it is still much lower than that of neat AB. The absence of the endothermic melting peak is due to solid-state interaction between AB and ZIF-8, which results in lower dehydrogenation temperatures than the melting temperature of neat AB.[14a] We expected that zinc was acting as a catalyst, so we prepared a mixture of AB and zinc chloride. The milled mixture of $AB/ZnCl_2$, which contains the same zinc concentration (1.5 mol % Zn) as that in 90 wt % AB/ZIF-8, was used for DSC measurements. The DSC curve of $AB/ZnCl_2$ shows one endothermic melt transition at 92 °C and two exothermic peaks with maxima at 98 and 149 °C. It is deduced that Zn ions can promote hydrogen release from AB.

The main point of looking at ZIF-8 was to determine if nanoconfinement was useful in enhancing the hydrogen release kinetics of AB. A 40 wt % AB/ZIF-8-MeOH sample was prepared by immersing the mixture of ZIF-8 and AB in an anhydrous methanol solvent and stirring for 3 h in a glovebox at room temperature and then removing the solvent by high vacuum for 24 h. Brunauer−Emmett−Teller (BET) measurements show that the ZIF-8 surface area was reduced from 1253 $m^2\ g^{-1}$ before loading to <66 $m^2\ g^{-1}$ after loading, which indicates that the pores of ZIF-8 have been impregnated with AB. This sharply reduced surface area measured by BET was also previously reported as evidence of AB confinement.[11,14c] For comparison, the hand-mixed 50 wt % AB/ZIF-8 exhibited a surface area of 1148 $m^2\ g^{-1}$ for ZIF-8, showing that AB not migrate into the pores of ZIF-8. The DSC curve of the AB/ZIF-8-MeOH showed exothermic peaks centered at 87 °C and two minor exothermic peaks at 116 and 129 °C, similar to that of the milled AB/ZIF-8 samples. It is therefore unlikely that nanoconfinement is a key factor in this case.

Hydrogen release from the 75 and 90 wt % AB/ZIF-8 samples was quantified using a pressure−composition−temperature (PCT) instrument and Sieverts' method from 25 to 195 °C heating at 1 °C min^{-1} (Figure 2). It was observed that 75 wt % AB/ZIF-8 released 0.05 equiv of hydrogen as low as 71 °C, and two maximum rates were observed at 82 and 133 °C. Up to 195 °C, 2.66 equiv of hydrogen was released. Compared with 75 wt % AB/ZIF-8, 90 wt % AB/ZIF-8 released 0.05 equiv of hydrogen at a higher temperature of 80 °C and reached two maximum rates at 89 and 140 °C. A total of 2.57 equiv of hydrogen was released up to 195 °C. Compared with neat AB, which begins dehydrogenation above 100 °C and releases 2.35 equiv of hydrogen up to 195 °C, the performance of 90 wt % AB/ZIF-8 is still improved over neat AB.

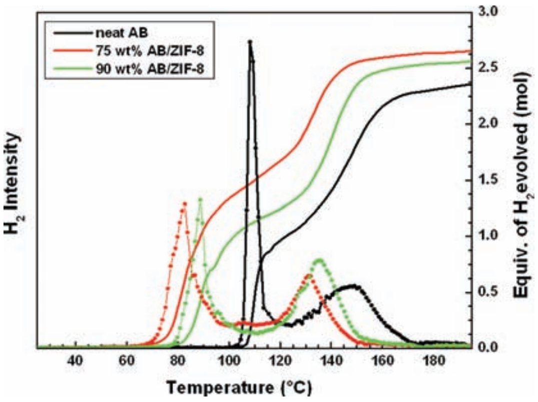

Figure 2. Equivalents of hydrogen and intensities of evolved hydrogen from (left) 75 wt % AB/ZIF-8 and (right) 90 wt % AB/ZIF-8.

Isothermal kinetics of AB/ZIF-8, $AB/ZnCl_2$, and AB/ZIF-8-MeOH were evaluated by volumetric gas buret measurement at 90 °C. For comparison, $AB/ZnCl_2$, AB/ZIF-8-MeOH, and neat AB have also been measured under the same conditions. All four composites have better results on both the rate and volume of hydrogen released compared to neat AB. In the first 10 min, approximately 0.91 and 0.65 equiv of hydrogen were released from the 75 and 90 wt % AB/ZIF-8 samples, respectively (Figure 33). After 2 h of hydrogen generation, 1.18 and 1 equiv of hydrogen were evolved, respectively. The rate of hydrogen release from AB/ZIF-8-MeOH is similar to that from 75 and 90 wt % AB/ZIF-8 samples, but the amount of hydrogen released is much less than that of those two samples. It is likely that, during the preparation of AB/ZIF-8-MeOH, some hydrogen has been released because upon careful examination bubbles can be observed. This is consistent with previous catalyst solution studies.[19] Although the amount of hydrogen released from $AB/ZnCl_2$ is a little less than 90 wt % AB/ZIF-8, the rate is much lower. The induction period typically required for neat AB, which is related to the disruption

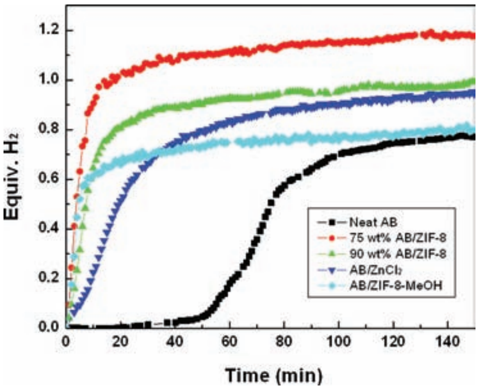

Figure 3. Hydrogen evolved over time at 90 °C.

of dihydrogen-bonding networks, has been bypassed by the AB/ZIF-8 samples.[20] PXRD patterns of AB/ZIF-8 after this measurement show no major changes in the ZIF-8 framework, indicating that ZIF-8 is stable during dehydrogenation and potentially reusable as a catalyst.

While $ZnCl_2$ acts as a catalyst for AB dehydrogenation, it is clear that the catalytic activity of ZIF-8 is greater. Considering the crystalline porous nature of ZIF-8, we speculate that the advantage of ZIF-8 is due to the Zn ions being homogeneously disperse on the surface of ZIF-8. In addition, it is possible that the hydrogen bonding formed between organic ligands of ZIF-8 and AB disturbs the dihydrogen-bonding network among AB.

One further advantage of the ZIF-8 catalyst is that the impurities (borazine, diborane, and ammonia) released from AB/ZIF-8 have been dramatically reduced (Figure S3 in the Supporting Information).

In summary, our research provides a simple but highly efficient method to promote the dehydrogenation of AB by employing MOF as a catalyst. Notably, though the concentration of ZIF-8 is as low as 0.25 mol %, the onset temperature for hydrogen evolution is remarkably reduced, and both the rate and amount of hydrogen released from AB are promoted. Moreover, the data indicate that nanoconfinement may not be a key factor for the promotion of AB dehydrogenation in this case.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, ^{11}B NMR spectra, PXRD patterns, and mass profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Burrell@anl.gov (A.K.B.), Ricod@lanl.gov (R.E.D.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge support of the U.S. DOE, Office of Energy Efficiency and Renewable Energy, for funding. Thanks go to Dr. Benjamin L. Davis for helpful suggestions.

■ REFERENCES

(1) (a) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283–1315. (b) Schlapbach, L.; Zuttel, A. *Nature* **2001**, *414*, 353–358.

(2) http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/hydrogen_storage_roadmap.pdf.

(3) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845.

(4) (a) Karkamkar, A.; Aardahl, C.; Autrey, T. *Mater. Matters* **2007**, *2*, 6–9. (b) Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079–4124. (c) Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2010**, 509–521. (d) Peng, B.; Chen, J. *Energy Environ. Sci.* **2008**, *1*, 479–483. (e) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613–2626. (f) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279–293.

(5) Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7493–7496.

(6) (a) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049. (b) Zimmerman, P. M.; Paul, A.; Zhang, Z.; Musgrave, C. B. *Angew. Chem, Int. Ed.* **2009**, *48*, 2201–2205. (c) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, 962–963; *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434. (d) Blaquiere, N.; Diallo-Garcia, S.; Gorelsky, S. I.; Black, D. A.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 14034–14035. (e) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, 4023–4078. (f) He, T.; Xiong, Z.; Wu, G.; Chu, H.; Wu, C.; Zhang, T.; Chen, P. *Chem. Mater.* **2009**, *21*, 2315–2318. (g) He, T.; Wang, J.; Wu, G.; Kim, H.; Proffen, T.; Wu, A.; Li, W.; Liu, T.; Xiong, Z.; Wu, C.; Chu, H.; Guo, J.; Autrey, T.; Zhang, T.; Chen, P. *Chem.—Eur. J.* **2010**, *16*, 12814–12817.

(7) (a) Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748–7749. (b) Himmelberger, D. W.; Yoon, C. W.; Bluhm, M. E.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2009**, *131*, 14101–14110.

(8) (a) Kang, X. D.; Fang, Z. Z.; Kong, L. Y.; Cheng, H. M.; Yao, X. D.; Lu, G. Q.; Wang, P. *Adv. Mater.* **2008**, *20*, 2756–2759. (b) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290–6295.

(9) (a) Diyabalanage, H. V. K.; Shrestha, R. P.; Semelsberger, T. A.; Scott, B. L.; Bowden, M. E.; Davis, B. L.; Burrell, A. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 8995–8997. (b) Diyabalanage, H. V. K.; Nakagawa, T.; Shrestha, R. P.; Semelsberger, T. A.; Davis, B. L.; Scott, B. L.; Burrell, A. K.; David, W. I. F.; Ryan, K. R.; Jones, M. O.; Edwards, P. P. *J. Am. Chem. Soc.* **2010**, *132*, 11836–11837. (c) Xiong, Z. T.; Yong, C. K.; Wu, G. T.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nat. Mater.* **2008**, *7*, 138–141. (d) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290–6295. (e) Kang, X. D.; Fang, Z. Z.; Kong, L. Y.; Cheng, H. M.; Yao, X. D.; Lu, G. Q.; Wang, P. *Adv. Mater.* **2008**, *20*, 2756–2759.

(10) (a) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746–749. (b) Miller, A. J. M.; Bercaw, J. E. *Chem. Commun.* **2010**, *46*, 1709–1711.

(11) Gutowska, A.; Li, L.; Shin, Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3578–3582.

(12) (a) Zhao, J.; Shi, J.; Zhang, X.; Cheng, F.; Liang, J.; Tao, Z.; Chen, J. *Adv. Mater.* **2010**, *22*, 394–397. (b) Feaver, A.; Sepehri, S.; Shamberger, P.; Stowe, A.; Autrey, T.; Cao, G. *J. Phys. Chem. B* **2007**, *111*, 7469–7472. (c) Li, L.; Yao, X.; Sun, C.; Du, A.; Cheng, L.; Zhu, Z.; Yu, C.; Zou, J.; Smith, S. C.; Wang, P.; Cheng, H.; Frost, R. L.; Lu, G. Q. *Adv. Funct. Mater.* **2009**, *19*, 265–271.

(13) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (b) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *305*, 2040–2042.

(14) (a) Li, Y.; Song, P.; Zheng, J.; Li, X. *Chem.—Eur. J.* **2010**, *16*, 10887–10892. (b) Li, Y.; Xie, L.; Li, Y.; Zheng, J.; Li, X. *Chem.—Eur. J.* **2009**, *15*, 8951–8954. (c) Li, Z.; Zhu, G.; Lu, G.; Qiu, S.; Yao, X. *J. Am. Chem. Soc.* **2010**, *132*, 1490–1491. (d) Si, X.; Sun, L.; Xu, F.; Jiao, C.; Li, F.; Liu, S.; Zhang, J.; Song, L.; Jiang, C.; Wang, S.; Liu, Y.; Sawada, Y. *Int. J. Hydrogen Energy* **2011**, *36*, 6698–6704. (e) Ingleson, M. J.; Barrio, J. P.; Bacsa, J.; Steiner, A.; Darling, G. R.; Jones, J. T. A.; Khimyak, Y. Z.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2012–2016.

(15) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186–10191.

(16) Chizallet, C.; Lazare, S.; Bazer-Bachi, D.; Bonnier, F.; Lecocq, V.; Soyer, E.; Quoineaud, A.; Bats, N. *J. Am. Chem. Soc.* **2010**, *132*, 12365–12377.

(17) Jiang, H.; Liu, B.; Akita, T.; Haruta, M.; Sakurai, H.; Xu, Q. *J. Am. Chem. Soc.* **2009**, *131*, 11302–11303.

(18) Kalidindi, S. B.; Esken, D.; Fischer, R. A. *Chem.—Eur. J.* **2011**, *17*, 6594–6597.

(19) Shrestha, R. P.; Diyabalanage, H. V. K.; Semelsberger, T. A.; Ott, K. C.; Burrell, A. K. *Int. J. Hydrogen Energy* **2009**, *34*, 2616–2621.

(20) Stowe, A. C.; Shaw, W. J.; Linehan, J. C.; Schmid, B.; Autrey, T. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831–1836.