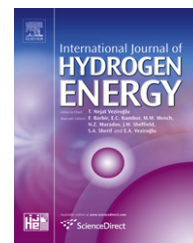


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Zn-MOF assisted dehydrogenation of ammonia borane: Enhanced kinetics and clean hydrogen generation

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ABSTRACT

We report controllable and enhanced hydrogen release kinetics at reduced temperatures in ammonia borane (AB) catalyzed by Zn-MOF-74. AB is loaded into the unsaturated Zn-metal coordinated one-dimensional hexagonal open nanopores of MOF-74 (ABMOF) via solution infiltration. The ABMOF system provides clean hydrogen by suppressing the release of detrimental volatile byproducts such as ammonia, borazine and diborane. These byproducts prevent the direct use of AB as a hydrogen source for polymer electrolyte membrane fuel cell applications. The H₂ release temperature, kinetics, and byproduct generation are dependent on the amount of AB loading. We show that nanoconfinement of AB and its interaction with the active Zn-metal centers in MOF are important in promoting efficient and clean hydrogen generation.

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1. Introduction

In an effort to solve the hydrogen production and storage problems of hydrogen-powered fuel cell vehicles, hydrogen storage in the solid-state appears to have the greatest potential to fulfill the requirements [1–7]. Complex hydrides, such as metal-borohydrides, are considered as an efficient on-board hydrogen storage medium [2–9]. The satisfactory air stability and light-weight ammonia borane (AB, NH₃BH₃), for example, has high amounts of hydrogen content by both weight (up to 19.6 wt.%), and volume (up to 140 g/L) with a moderate decomposition temperature. These attributes are necessary to attain the desired system-level hydrogen storage

targets [7]. Unfortunately, the direct use of AB in practical applications so far is prevented due to its very slow H₂ release kinetics below 100 °C and the release of detrimental byproducts, such as ammonia, borazine and diborane [6–9]. The dehydrogenation rate can be increased with additives, metallic catalysts, or by impregnating AB into porous solid supports [6,10]. Despite the improved kinetics, many systems suffer from uncontrollable desorption or not effectively prevent the generation of the byproducts [6,9,10]. Therefore, new approaches are needed. Very recently, AB confined metal-organic frameworks (MOFs) have been used to produce clean hydrogen [11–13]. The porous MOF with active and unsaturated metal-centers enable nanoconfinement and

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catalytic dehydrogenation of AB [14–16]. MOF pore sizes can be rationally designed through choice of metal and linker. Tailored porosity and active metal-centers have made MOFs promising multifunctional materials for catalysis [11–13,16] shape-selectivity [14–20], templating [11–13,21] and gas purification [14–20].

In this paper, we demonstrate the promising hydrogen storage capabilities of ammonia borane confined in the Zn-metal coordinated nanopores of Zn-MOF-74 ($\text{Zn}_2(\text{C}_8\text{H}_2\text{O}_6)$) [14,18–20]. ABMOF system exhibits controllable and enhanced kinetics at reduced temperatures. The system also prevents the generation of all the volatile byproducts such as ammonia, borazine and diborane. The importance of nanoconfinement and interaction between AB and active metal-centers in MOF to promote efficient hydrogen release is demonstrated.

2. Experimental

2.1. Synthesis of Zn-MOF-74 ($\text{Zn}_2(\text{C}_8\text{H}_2\text{O}_6)$)

Zn-MOF-74 was synthesized according to the reported procedure [18]. 2,5-dihydroxybenzene-1,4-dicarboxylic acid (3.0 g) and zinc nitrate tetrahydrate (12.0 g) were dissolved in 600 mL of *N,N*-dimethylformamide (DMF) and 30 mL of deionized water. The solution was transferred into a Teflon lined autoclave and placed in an oven at 100 °C for 24 h. The powder product was obtained by filtering and washing with methanol. To remove occluded DMF, the MOF product was exchanged several times with methanol for 4 days. Finally, the MOF was activated at 200 °C under dynamic vacuum for 24 h to remove any residue from the MOF pores.

2.2. Synthesis of ABMOFs

ABMOFs were synthesized through a simple solution-blending process. AB (Sigma Aldrich, 97% [22]) was dissolved in anhydrous methanol (0.5 M) at room temperature in a glove bag. The required amount of activated Zn-MOF was then added to the solution and the mixture was stirred for 30 min at room temperature. The homogeneous solution was then dried at room temperature for 24 h to remove methanol solvent. Two samples with AB:Zn loadings of 1:1 and 2:1 mol ratio were prepared, and named as 1ABMOF and 2ABMOF, respectively. The samples were stored and handled in a helium filled glove box before further characterization.

2.3. Characterization

Powder X-ray diffraction (XRD) was carried out on samples sealed in a glass capillary with Cu K α radiation. Fourier-Transform Infrared (FTIR) spectra were collected at room temperature from sample/KBr pellets. The N_2 and H_2 physisorption measurements were performed at 77 K in a Sievert apparatus [23]. The simultaneous thermogravimetry, differential scanning calorimetry and mass spectrometry (TG/DSC/MS) measurements were carried out between room temperature and 200 °C at a heating rate of 2 °C per minute under N_2 atmosphere. The volumetric thermal desorption of hydrogen at 2 °C per minute and isothermal dehydrogenation kinetics at

various temperatures were performed using a carefully calibrated Sievert apparatus [23] by maintaining base pressure of <10 mbar.

3. Results and discussion

Fig. 1a represents the framework structure of as-synthesized Zn-MOF-74 with terminal water molecules. The framework consists of one-dimensional (1D) hexagonal channels with a nominal diameter of 11 Å running parallel to the DOBDC ligands [14,18–20]. The edges of the pore channels are coordinated with Zn-metal centers. The activated MOF exhibits an open and rigid framework structure with unsaturated Zn-metal centers (Fig. 1b). Thus the unsaturated Zn-metal centers in the activated MOF play a vital role in catalytic dehydrogenation for nanoconfined AB within the pores. For the given pore structure of Zn-MOF-74, an AB:Zn in 1:1 mol ratio is easily obtained (Fig. 1c). This corresponds to 19 wt.% of AB loading in the MOF.

Successful AB loading and nanoconfinement within the MOF pores was investigated using powder XRD (Fig. 2a), FTIR (Fig. 2b), and N_2 and H_2 physisorption (Fig. 2c and d). The disappearance of bulk crystalline AB peaks in the XRD pattern of 1ABMOF indicates the nanophase of the confined AB within the pores. In addition, the clear evidence for AB confinement is seen from the complete loss of N_2 and H_2 physisorption capacity at 77 K. Before AB loading, the MOF exhibits high H_2 and N_2 uptake, attributed to its high BET surface area of about 1000 m²/g. Furthermore, the confined AB exhibits narrowed IR absorbance for the H–B vibration around 2400 cm^{−1} compared to pristine AB [24].

The improvements in desorption temperature, desorbed amount and rate of desorption ABMOFs are summarized in Fig. 3. All plots are based on volumetric measurements. It should be noted that the desorbed wt.% of H_2 in the ABMOF system is solely based on the confined AB. As evidenced from TPD plots in Figure 3a, 1ABMOF shows a considerably lowered onset desorption temperature, 60 °C compared to 110 °C in pristine AB. In addition, 1ABMOF releases about 10 wt.% H_2 at 100 °C. Pristine AB is still solid at this point, and the same amount of H_2 is not released until 150 °C. The dehydrogenation temperature of 2ABMOF increases but it is still less than pristine AB. The controllability over rate and desorbed amount of H_2 from ABMOFs was further studied with isothermal kinetics (Fig. 3b–d) over a range of temperatures. The results demonstrate highly enhanced kinetics below 100 °C compared to pristine AB. For instance, pristine AB exhibits a prolonged induction time at temperatures below 100 °C and releases maximum of 6 wt.% H_2 over many hours. However, our 1ABMOF delivers about 10 wt.% H_2 over a few minutes at temperatures below 100 °C without any induction time. As shown in Fig. 3d, about 9 wt.% H_2 is generated from 1ABMOF at temperatures between 85 °C and 75 °C within 2 h compared to only 5 wt.% H_2 at 85 °C after 6 h from pristine AB. More importantly, 1ABMOF release about 8 wt.% H_2 at temperature as low as 65 °C. However, the kinetics of 2ABMOF (Fig. 3c) exhibits clear decrease in rate and amount of dehydrogenation below 100 °C, in good agreement with the TPD data given in Fig. 3a. This behavior can be explained by the overfilling of

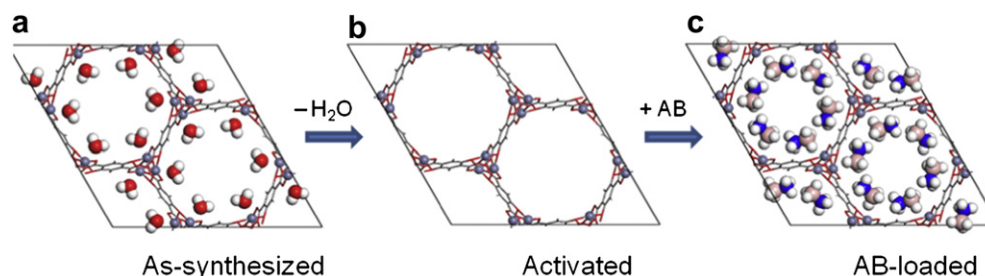


Fig. 1 – The framework structure of Zn-MOF-74: a) as-synthesized, b) activated, and c) AB-infiltrated; gray C, red O, white H, purple Zn, blue B, and orange N. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the MOF. Excess AB deposits outside the pores with increased loading. Thus, the mere mixture of AB and MOF does not lead to enhanced dehydrogenation; AB has to be within the pore and access to the active Zn-metal centers.

We further studied the desorption properties of ABMOF system with simultaneous TGA/DSC/MS (Fig. 4). The desorption temperature and TGA weight loss is in good agreement with volumetric results (Fig. 3). Importantly, the complete suppression of ammonia, borazine and diborane generation is seen in 1ABMOF. The endothermic melting process that precedes AB decomposition was completely suppressed, and no foaming was observed. 2ABMOF shows trace amounts of

byproducts in MS and a prominent exothermic peak in DSC, demonstrating that a small amount of bulk AB exists outside the MOF pores.

Even though, byproducts are not produced from 1ABMOF, the trapping of B–N complexes within the MOF pores are evidenced from the N_2 and H_2 physisorption capacity after thermal desorption (Fig. 2c and d). This is attributed to the interaction of electropositive B in $-BH_3$ group and electronegative N in $-NH_3$ group with the carboxylate ligands and the metal-centers in the MOF [6,9–11]. This also leads to a weakened N–B and B–H bonds and reduction in dehydrogenation temperature. In addition, the considerably increased surface

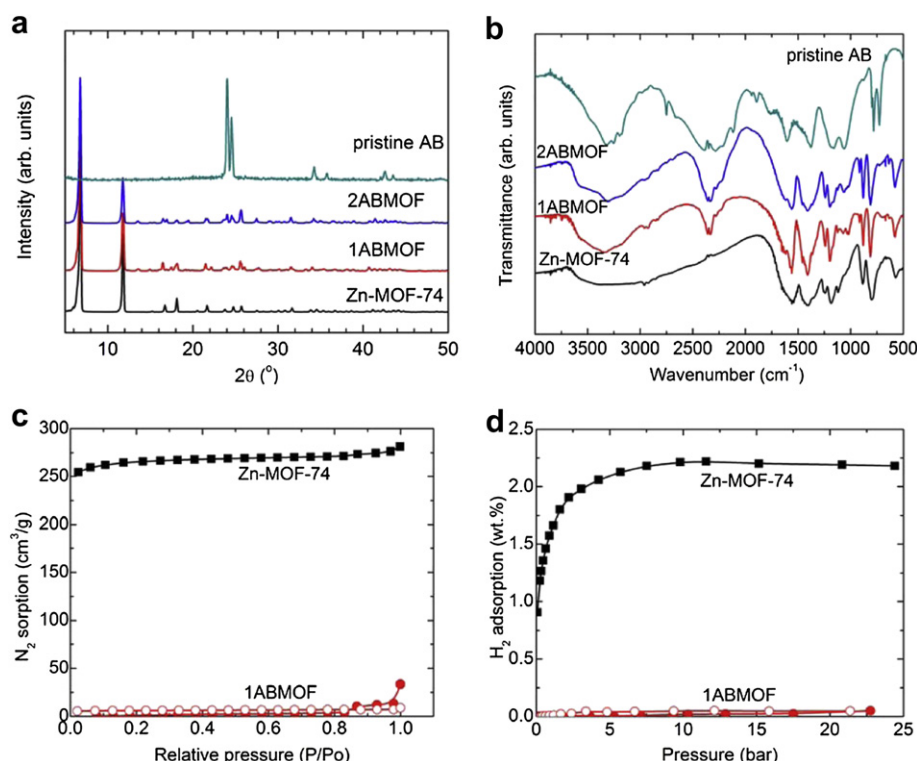


Fig. 2 – a) XRD patterns, b) FTIR spectra, c) N_2 physisorption isotherms, and d) H_2 physisorption isotherms of host Zn-MOF-74, and ABMOFs. The XRD pattern and FTIR spectrum of pristine AB is also shown. In c) and d) the solid and open data points represent adsorption isotherms of ABMOF before and after thermal desorption respectively. All gas physisorption isotherms were measured at 77 K. In pristine AB FTIR, the broad IR modes between 3200 cm^{-1} and 3500 cm^{-1} , and 2200 cm^{-1} and 2500 cm^{-1} correspond to the H–N and H–B stretching bonds, respectively. In addition, H–N scissor modes at 1602 cm^{-1} and 1376 cm^{-1} , H–B scissor mode at 1160 cm^{-1} , and H-wagging modes at 1065 cm^{-1} and 727 cm^{-1} are observed. The mode at 781 cm^{-1} is assigned to B–N stretching [24].

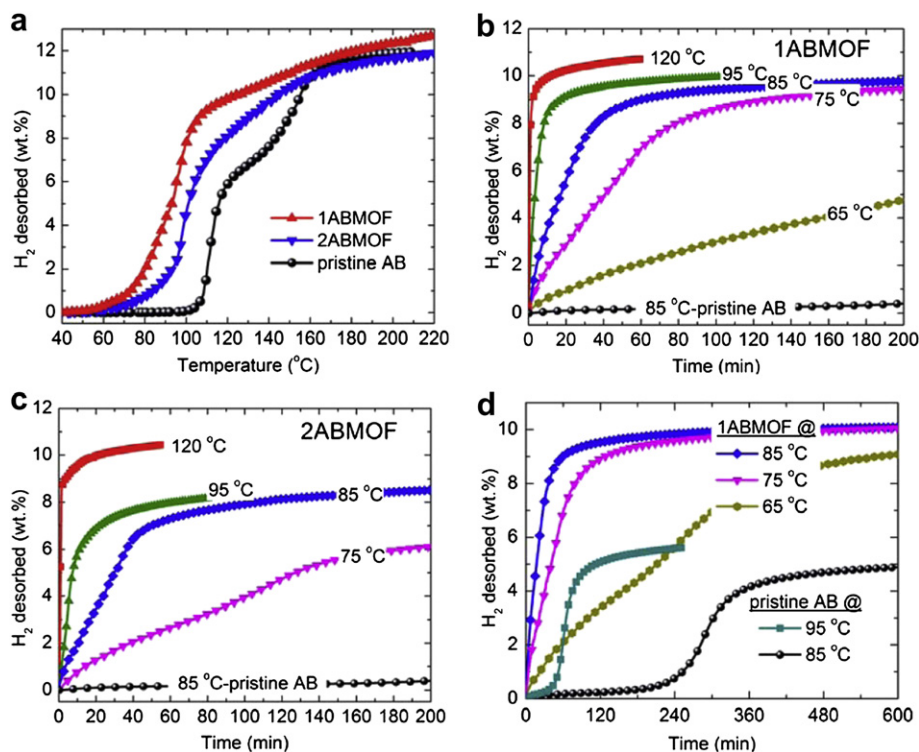


Fig. 3 – a) Volumetric TPD of AB and ABMOFs, and isothermal kinetics of b) 1ABMOF and c) 2ABMOF. d) Comparison of the extended time kinetic plots of pristine AB and 1ABMOF below 100 °C.

area for the infiltrated AB due to limited nanoconfinement within the pore channels also have prominent effect on the dehydrogenation temperature as well as kinetics. Furthermore, early hydrogen release from weakened B–H bonding and subsequent B–O bond formation is clearly evident in the FTIR spectra (Fig. 5) of dehydrogenated 1ABMOFs at various temperatures [24–27]. In agreement with the volumetric thermal dehydrogenation properties in Fig. 3, the FTIR spectra

show clear differences in dehydrogenation mechanism between 1ABMOF, 2ABMOF, and pristine AB. For instance, when dehydrogenated below 100 °C, pristine AB shows clear B–H (–BH₂) IR modes that are not present in the 1ABMOF sample. It should be noted that samples dehydrogenated at temperatures between 65 °C and 95 °C exhibit similar IR spectra with strong B coordinated O modes at $\approx 1024\text{ cm}^{-1}$, $\approx 709\text{ cm}^{-1}$ and $\approx 650\text{ cm}^{-1}$ and depleted B–H modes $\approx 2400\text{ cm}^{-1}$ [24–27].

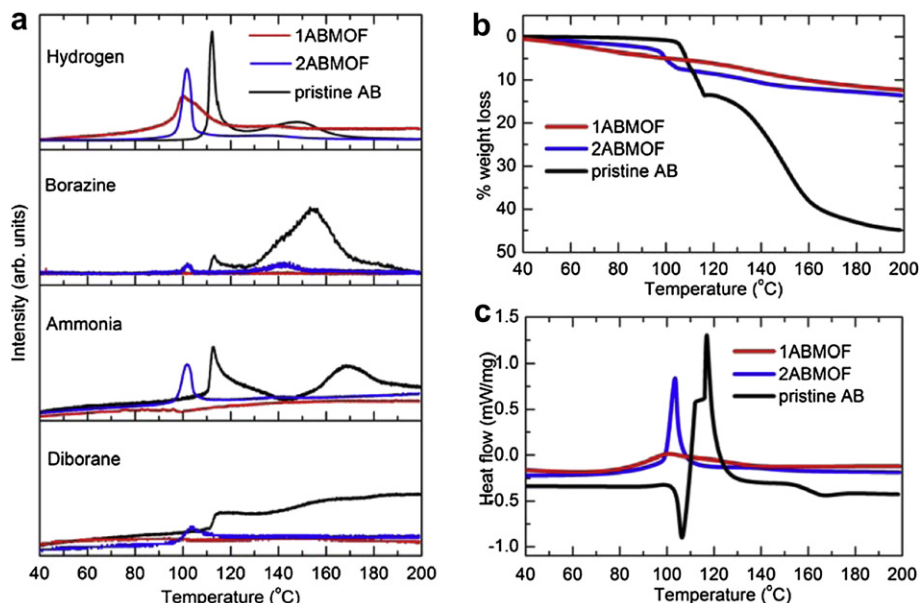


Fig. 4 – a) MS, b) TG, and c) DSC plots of pristine AB and ABMOFs.

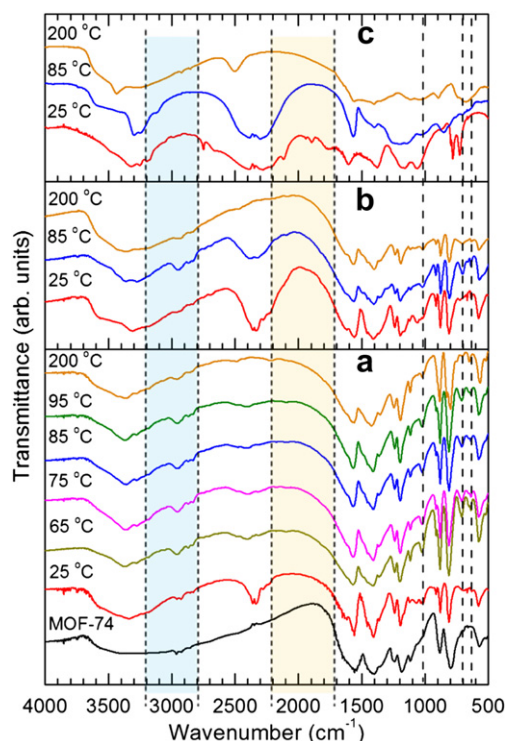


Fig. 5 – FTIR spectra of AB and ABMOFs dehydrogenated at different temperatures: (a) 1ABMOF, (b) 2ABMOF, and (c) pristine AB. Considerable differences in the H–N and H–B bonds between 3200 cm^{-1} and 3500 cm^{-1} , and 2200 cm^{-1} and 2500 cm^{-1} are seen with respect to the desorption temperature as well as to AB confined or bulk phase. Clear evidence of low temperature depleted H–B bonds is seen in considerable reduction in intensity of broad band at around 2200 cm^{-1} and 2500 cm^{-1} . The new prominent IR modes at $\approx 1024\text{ cm}^{-1}$, $\approx 709\text{ cm}^{-1}$ and $\approx 650\text{ cm}^{-1}$ (vertical dotted line) associated with a B coordinated O [24–27].

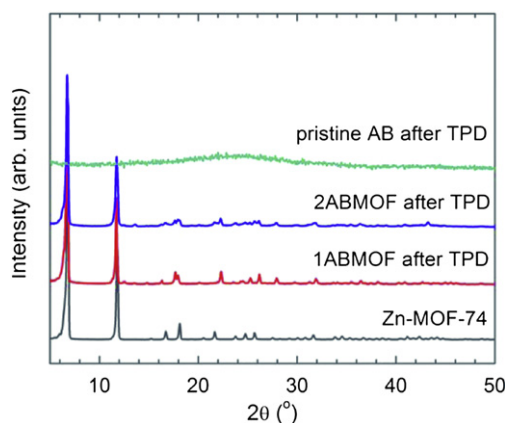


Fig. 6 – XRD patterns of the samples after the volumetric TPD measurements were performed. The XRD from clean (i.e. activated) MOF-74 is also shown for comparison.

This suggests weakened B–H bonds that lose hydrogen at low temperatures. The FTIR spectra and XRD patterns in Figs. 1, 5 and 6 indicate that the MOF skeleton structure is unaffected by thermal desorption.

4. Conclusion

In summary, we demonstrated improved solid-state thermal dehydrogenation properties, enhanced kinetics at reduced temperatures, and complete suppression of ammonia, borazine and diborane from the ABMOF system. Zn-MOF-74 with its specific one-dimensional hexagonal pore structure facilitates $\approx 20\text{ wt.}\%$ AB loading, completely confining AB within its pores. Our results also reveal the importance of interactions between Zn and confined AB for clean hydrogen generation. Given the flexibility in MOF design to tune chemistry and geometry, we believe it is possible to make further improvements in AB loading and efficient hydrogen release.

Acknowledgments

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