Facilitated hydrogen release kinetics from amine borane functionalization on gate-opening metal-organic framework

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ABSTRACT

For the first time, we functionalized the gate-opening metal-organic framework (GO-MOF) of MIL-53(Al) with ammonia borane (AB, NH_3BH_3) via post-synthesis method. In this report, unusual structural breathing and dehydrogenation behaviors of AB doped MOF (MIL-53-AB) were discovered. Surface coating triggered the GO-MOF breathing phenomenon and opened the structure, and gate was closed after dehydrogenation. The dehydrogenation peak temperature was greatly reduced by 30 °C compared to that of pristine AB with suppressed byproduct like ammonia. The MOFs with surface coated AB exhibited remarkably fast hydrogen generation rate and corresponding low apparent activation energy, estimated at < 40 kJ/mol, which is much lower than that of crystalline AB, and even comparable to AB hydrolysis with catalysts. The ammonia borane functionalized MIL-53 has shown greatly improved dehydrogenation from solid phase of AB.

1. Introduction

For the past several decades, people have developed a greater dependence on fossil fuel, a non-renewable energy system that has limited reserves in the world and generates greenhouse gas CO_2, leading to global warming issues. With merits of high gravimetric energy density (142 MJ/kg), abundance in the universe, and clean product of water after utilization, hydrogen has been proposed as one of the most promising renewable energy resources [1]. However, safety concern of hydrogen due to its flammability requires the development of solid phase hydrogen storage [2], utilizing adsorbents like activated carbon [3] and metal-organic frameworks (MOFs) [4, 5], metal hydrides ($LiAlH_4$, $LiBH_4$, etc.) [6], and chemical hydride like ammonia borane (AB) [7, 8].

Compared to other hydrogen storage materials [9], AB has drawn attention for its high gravimetric content of hydrogen (19.6 wt%), moderate dehydrogenation temperature compared to other complex hydrides, and good thermal stability at room temperature [8]. Though the hydrogen capacity of AB exceeds the target of 300-mile driving range for onboard transportation purpose from the United States Department of Energy (DOE) [10], high decomposition temperature and accompanying byproducts impede the utilization of AB in hydrogen economy. Three-step AB solid crystal thermolysis occurs at about 120 °C, 150 °C, and over 500 °C with equivalent 6.5 wt% of generated

hydrogen in each step, with undesirable volatile detrimental byproducts such as ammonia (NH_3), diborane (B_2H_6), and borazine ($B_3H_6N_3$) [8].

The current methods to overcome high dehydrogenation temperatures and byproduct generation can be summarized as catalytic decomposition [11–15] and nanoconfinement. The latter technique is the incorporation of AB physically into microporous materials, including porous carbon [16–20], MOFs [21–31], etc. For example, AB recrystallized in IRMOF-1 from methanol solution releases hydrogen at peak temperature 84 °C, generates less byproducts, and has improved activation energy (E_a) ~70 kJ/mol [30]. It has been reported that the mechanism of reduced AB decomposition temperature is because of the altered thermodynamic properties due to geometrical constraints in pores. One possible theory of enhanced thermolysis is likened to size effect on melting/freezing temperature considering surface tension of nanoparticles [8, 32]. Sepehri et al. [16] demonstrated a linear temperature reduction with the pore size of scaffold. On the other hand, with scrutinized thermodynamic equations on the Gibbs free energy considering surface tension, we have reported that the reduction in dehydrogenation temperature is linearly proportional to the reciprocal of AB size, while MOF catalytic environment has less impact [31].

In addition, the apparent activation energy for AB confined in carbon [17, 20] or MOF [23, 27, 29, 30] with/without supported catalysts can be improved to 70–130 kJ/mol, while crystalline AB has E_a

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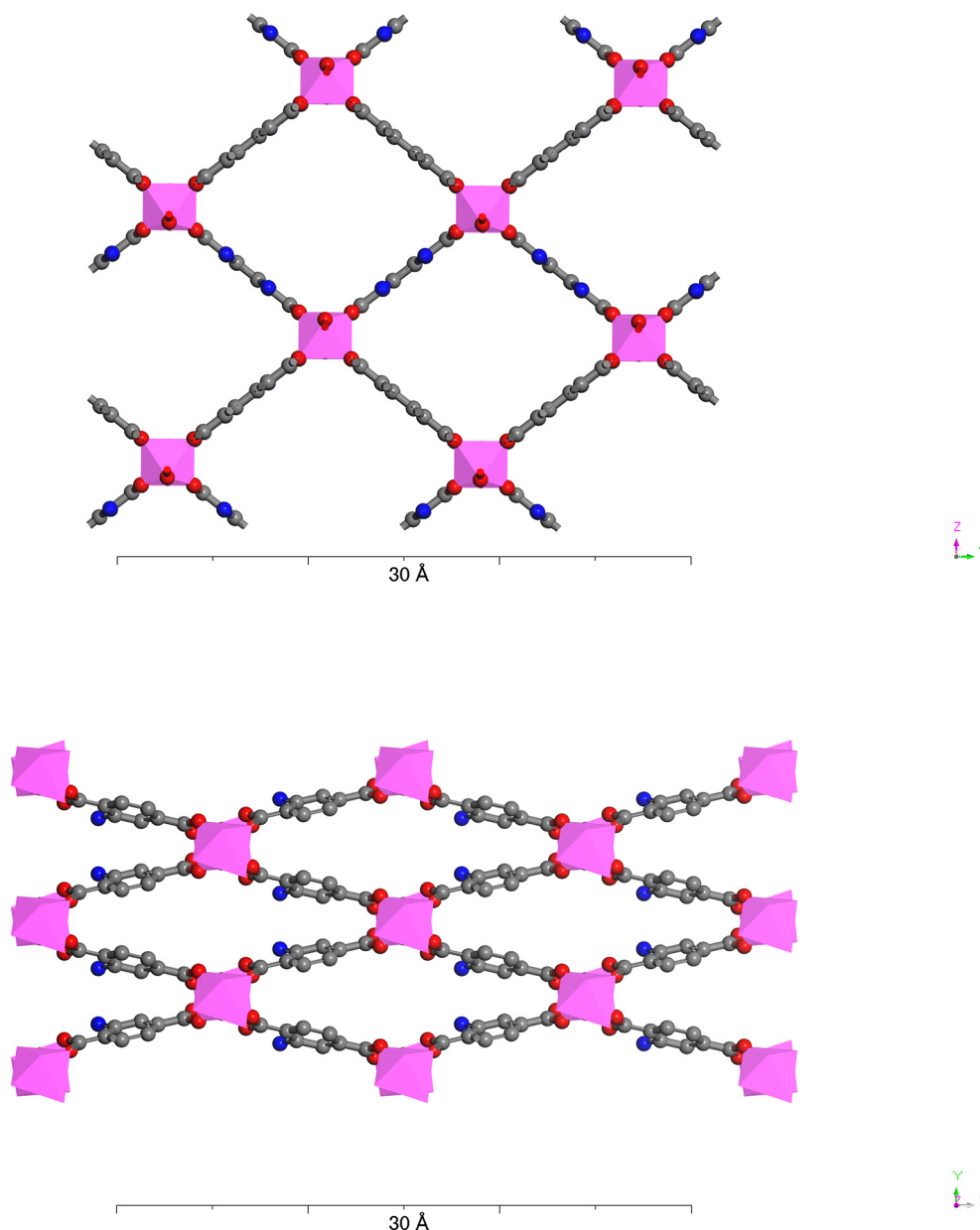
Fig. 1. Structures of MIL-53(Al)-NH$_2$ in (A) large pore (lp) and in (B) narrow pore (np) structure configuration. Color code: Al: pink; C: gray; N: blue, O: red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reported from 130 to 180 kJ/mol [23, 30]. Though the kinetics of hydrogen generation from nanoconfined AB thermolysis are greatly improved, the activation energy is still higher than that of AB hydrolysis with catalysts around 30 to 50 kJ/mol [33–36]. Even when nanoconfinement is effective in reducing AB dehydrogenation temperature, infiltration of AB in microporous materials degrades the porosity, like reducing specific surface area (SSA) completely [20, 23, 30], and could be detrimental to kinetics of evolved hydrogen. In order to avoid possible pore blockage by incorporated AB, gate opening MOF (GO-MOF) could be a possible solution with its breathing effect, which may facilitate gas diffusion when gate is opened [37]. The GO-MOF has amenable porosity transition between large pore (lp, Fig. 1A) and narrow pore (np, Fig. 1B), possibly initiated by the guest molecules [38], pressure [39], applied stress [40], or temperature [41]. For instance, MIL-53(Fe), a GO-MOF with coordinatively saturated Fe corner-sharing clusters connected by organic ligand benzenedicarboxylate (BDC), displayed decreased overall dehydrogenation temperature and activation energy of infiltrated AB [27]. Nonetheless, the E_a of AB@

MIL-53(Fe) still falls in the range of that from nanoconfined AB.

Except for physical loading into microporous materials, substituted derivative of ammonia borane in the form of R-NH$_2$BH$_3$ (functional group of AB on alkyl [42], heterocycle [43, 44], benzene [45], metal cation [46], etc.) is also a means to solve the problems of high hydrogen generation temperature and production of byproducts. Moreover, it has been investigated that chemically modified AB exhibits reduced activation energy. For instance, methyl-AB demonstrated E_a = 115 kJ/mol without catalysts [42], while E_a of hydrazine borane (N$_2$H$_4$BH$_3$) hydrolysis was about 19 to 45 kJ/mol with MOF supported Ni/Pt catalysts [47]. The idea of functionalized AB on porous materials is an alternative route of AB chemical modification to reduce dehydrogenation temperature and activation energy. A similar idea was adopted by Tang et al. [19], who applied oxygen functional groups to anchor NH$_3$-BH$_2$$^+$ on graphene oxide interlayers. They observed lowered dehydrogenation temperature as well as apparent activation energy of 30 kJ/mol. Nevertheless, Li-based catalyst with the same hydroxyl groups to disperse AB atomically on mesoporous carbon CMK-3 had only minor