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Nitrogen-containing carbon nanostructures: A promising carrier for catalysis of ammonia borane dehydrogenation

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ABSTRACT

The first-principles calculations demonstrate that nitrogen-containing carbon nanostructures (NCCN), such as nitrogen-doped graphene, nitrogen-doped carbon nanotubes, and covalent triazine-based framework (CTF) are promising metal-free catalysts for the first step dehydrogenation of ammonia borane (AB). It reveals that nitrogen lone pairs in NCCN function as hydrogen acceptors to allow metal-free hydrogen transfer from AB to NCCN, resulting in facile release of pure H_2 from AB. The dehydrogenation of AB–NCCN combined systems involves two key steps: First, there is a net transfer of hydrogen atoms from AB to NCCN that results in simultaneous dehydrogenation of AB and hydrogenation of the NCCN, and then, the hydrogenated NCCN further react with AB to release H_2 with relatively low reaction barriers. The experimental results further confirm that the CTF can act as effective catalysts for AB dehydrogenation at relatively low temperature. Our study leads to a promising scheme that can be readily tailored for application to many nitrogen-containing nanostructure systems that may favorably catalyze the dehydrogenation of ammonia borane and other related boron–nitrogen species.

1. Introduction

Ammonia borane (NH_3BH_3, AB) has been regarded as one of the most promising media for a chemical hydride-based hydrogen storage system because of its satisfactory air stability and remarkably high energy-storage density [1–4]. In particular, breakthrough research has recently demonstrated the successful conversion of polyborazylene (PB), one of the spent fuels of AB, to AB via reaction with hydrazine in liquid ammonia [5]. The direct use of pristine AB as a hydrogen energy carrier in on-board applications, however, is impeded by its sluggish dehydrogenation kinetics below 100 °C and by the concurrent release of a large amount of detrimental volatile by-products (i.e., ammonia, borazine, and diborane) [1,2,6], which not only poison the catalyst in a proton membrane fuel cell, but also causes irrecoverable component loss of B and N elements during decomposition, thus making efficient regeneration of this reaction unlikely.

In recent years, infiltration of AB into various nanoscaffolds, e.g., metal–organic frameworks (MOFs) [7–10], mesoporous silica [11,12], or carbon aerogel [13], has been demonstrated to be an effective route to improve the dehydrogenation properties of AB in terms of reduced dehydrogenation temperature and depressed emission of impurities, which is attributed to a combination of the nanosize effect and the AB–scaffold interaction. For instance, nanoconfined AB within MOFs

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showed improved kinetics and/or reduced impurity via a synergistic effect of the nanoconfinement and the metal catalyst centers in the MOFs [7–9]. The loading ratio of AB in these systems is relatively low, however, due to the heavy metal element content or/and low available space for holding guests in most of the common nanoscaffolds (e.g., ~8 wt.% for an MOF–AB system) [9]. Additionally, tremendous efforts, including the use of catalysts [14–17], ionic liquids [18,19], additives [20], and base-metal substitutions [21,22], have been adopted to promote the efficient release of pure H_2 from AB, although many of these methods rely on the usage of metal cations that function as the catalyst in dehydrogenating AB, in which the presence of residual metal catalyst in the final spent-fuel would complicate the AB regeneration process [5]. Therefore, an alternative approach to improving the catalyst system towards facile regeneration is to seek new nanocatalysts that employ only metal-free elements in place of the metal-containing catalysts.

It is well known that chemical doping with foreign atoms is an effective approach to enrich the physical properties of materials, increase the reactivity of carbon nanostructures, and render the final product potentially useful for various applications [23–26]. In this regard, doping carbon nanostructures with appropriate elements appears to hold considerable promise as effective AB dehydrogenation catalysts. Our recent report has demonstrated that mesoporous graphitic carbon nitride (MGCN) can serve as strong Lewis base sites that effectively catalyze the dehydrogenation of AB and produce PB as the single spent-fuel component, which significantly improve the dehydrogenation and regeneration of AB [27]. This suggests that incorporation of electron-accepting nitrogen atoms into various carbon nanostructures may serve as high-active carriers in destabilizing the N–H bonds in AB due to the strong electron affinity of the nitrogen atoms in the nanostructures, thus catalyzing pure H_2 release from AB at relatively low temperatures. In this paper, a series of first-principles calculations based on density functional theory (DFT) were performed to understand the interaction between AB and the nitrogen-containing carbon nanostructures, and then the kinetics and dynamics of hydrogen release from the AB-nanostructure combined systems were described in terms of the reaction energies and barriers. The experimental data further confirm that the CTF can effectively catalyze the first step dehydrogenation of AB at relatively low temperature. Our results suggest that nitrogen-containing carbon nanostructure, e.g., graphene, nanotube and CTF, can serve as excellent metal-free catalysts for facilitating the hydrogen release of AB with relatively low energy barriers. These findings establish a promising approach via utilizing NCCN as metal-free catalysts for the dehydrogenation of ammonia borane and other related boron–nitrogen species.

2. Methods

2.1. Computational details

Total energy calculations were carried out by using DFT implemented in the Vienna ab initio simulation package (VASP) [28], using the generalized gradient approximation of Perdew–Burke–Ernzerhof [29,30]. The electron–ion interactions were described by the projector-augmented wave approach [31]. The energy cut-off for the plane wave expansion was set to 400 eV to ensure sufficient convergence (less than 1 meV/cell). The Brillouin zones were sampled by Monkhorst–Pack k-point meshes [32] for all compounds, with meshes chosen to give a roughly constant density of k points (20 $Å^3$) for all compounds. Tests showed that our choice of k points yielded energies that converged within 0.01 eV/(f.u.). The geometric optimization was performed using fixed lattice constants, while atomic positions in the supercell were allowed to fully relax until the residual forces were less than 0.03 eV $Å^{-1}$. To investigate the dehydrogenation dynamics for NH_3BH_3 adsorption on the surface of carbon nanostructures, we calculated the corresponding energy barriers by using the CI-NEB method [33].

Pristine graphene sheet was modeled using a supercell containing 64 carbon atoms, and infinite (6,6) carbon nanotube was modeled by a periodic tube with an axial length of ~9.83 Å. Owing to the fact that the CTF composite is a predominantly amorphous structure, which has, at most, short-range ordering, we employed a planar sheet which contained several pyridine and bipyridyl structures as the prototype for the experimental large-size amorphous structure of CTF [34]. In our calculations, a vacuum of 15 Å was employed to eliminate the van der Waals interaction between two neighboring nanostructures. The binding energies and equilibrium structures for AB molecules attached to the surfaces of nanostructures were calculated by adding the AB molecules to the system and relaxing the positions of all atoms within the previously optimized supercells under the condition of a fixed supercell volume.

The adsorption energy (E_{ads}) is defined by:

$$E_{ads} = E_{tot} - E_{AB} - E_{nanostructure}$$

where E_{tot} is the total energy of the nanostructure-AB combined system; E_{AB} is the energy of isolated AB; $E_{nanostructure}$ is the total energy of the nanostructure. Positive adsorption energy for any AB content indicates that AB molecules do not adsorb on the nanostructure, which renders it unsuitable for functionalization.

2.2. Reagents and synthesis

Ammonia borane (NH_3BH_3, AB) (purity 95%) was purchased from Sigma–Aldrich Corp. and used without further purification. The covalent triazine-based framework (CTF) was synthesized by utilizing 2,6-dicyanopyridine as the monomer and following a procedure in the literature [47]. The CTF–AB sample was prepared by solvent infiltration of a tetahydrofuran (THF) solution into the carbon materials. In a typical experiment, AB (350 mg) was dissolved in THF (4 ml, distilled before use) at room temperature, and the saturated solution of AB in THF was added to a sample of CTF (700 mg) using a syringe. The THF solution appeared to fill the internal channels of the nanoporous scaffold immediately through immersion. The mixture of NH_3BH_3 solution and carbon material was further sonicated for about 4 h at 0 °C to obtain homogeneous, finely dispersed CTF–AB sample. Finally, the samples were exposed to vacuum at room temperature for 4 h to remove the THF, leading to the formation of CTF–AB sample with mass ratio of 1:2.