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Single Pt Atoms Supported on Oxidized Graphene as a Promising Catalyst for Hydrolysis of Ammonia Borane

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Based on density functional theory calculations, the full hydrolysis of per NH_3BH_3 molecule to produce three hydrogen molecules on single Pt atoms supported on oxidized graphene ($\text{Pt}_1/\text{Gr-O}$) is investigated. It is suggested that the first hydrogen molecule is produced by the combination of two hydrogen atoms from two successive B–H bonds breaking. Then one H_2O molecule attacks the left $^*\text{BHNH}_3$ group (* represents adsorbed state) to form $^*\text{BH}(\text{H}_2\text{O})\text{NH}_3$ and the elongated O–H bond is easily broken to produce $^*\text{BH}(\text{OH})\text{NH}_3$. The second H_2O molecule attacks $^*\text{BH}(\text{OH})\text{NH}_3$ to form $^*\text{BH}(\text{OH})(\text{H}_2\text{O})\text{NH}_3$ and the breaking of O–H bond pointing to the plane of $\text{Pt}_1/\text{Gr-O}$ results in the desorption of $\text{BH}(\text{OH})_2\text{NH}_3$. The second hydrogen molecule is produced from two hydrogen atoms coming from two H_2O molecules and $\text{Pt}_1/\text{Gr-O}$ is recovered after the releasing of hydrogen molecule. The third hydrogen molecule is generated by the further hydrolysis of $\text{BH}(\text{OH})_2\text{NH}_3$ in water solution. The rate-limiting step of the whole process is the combination of one H_2O molecule and $^*\text{BHNH}_3$ with an energy barrier of 16.1 kcal/mol. Thus, $\text{Pt}_1/\text{Gr-O}$ is suggested to be a promising catalyst for hydrolysis of NH_3BH_3 at room temperature.

Key words: Density functional theory, Single atom catalysis, Platinum, Oxidized graphene, Ammonia borane hydrolysis

I. INTRODUCTION

Hydrogen is considered as one of the most potential clean and renewable energy carriers in future. Safe storage and transport of hydrogen is important for its real application [1]. It is expected that hydrogen is stored in types of stable materials under mild condition and can be released steadily by the trigger of catalysts [1–5]. Ammonia borane (NH_3BH_3) is regarded as a promising candidate molecule for hydrogen storage due to its nontoxicity, high hydrogen content (19.6wt% H), and high thermal stability even in water solvent at ambient temperature [6–9]. The best scenario is that per NH_3BH_3 molecule can completely release three hydrogen molecules and can be recovered easily [3, 5–8]. Respect to direct dissociation of NH_3BH_3 at high temperature, hydrolysis of NH_3BH_3 on catalysts is more promising for room temperature hydrogen generation.

Pt-based catalysts, such as small Pt nanoparticles supported on SiO_2 [10], $\gamma\text{-Al}_2\text{O}_3$ [10], porous chromium terephthalate (MIL-101) [11], carbon nanotubes (CNT) [12, 13], and reduced graphene oxide [14], exhibit superior catalytic activity for hydrolysis of NH_3BH_3 . Transition non-noble metals such as Co [15–18], Ni [19–22], and Cu [23–25] are also widely studied to explore the possibility to replace noble metals for their low price. Both experimental and theoretical work were performed to better understand the hydrolysis mechanism of NH_3BH_3 and get clues for catalysts improvement. In early stage, it was proposed that the hydrolysis starts from the B–N bond breaking by the attacking of water molecule [10] or the dissociation of H_2O in the hydroxylation process of the adsorbed NH_3BH_x from B–H breaking [26]. Recently, the O–H bond cleavage of water is experimentally suggested as the rate-limiting step of NH_3BH_3 hydrolysis on the Pt/CNT [27], PtRu/CNT [28], Co/CTF [17], Ni/ZIF-8 [21], and atomically dispersed Pt on the surface of Ni particle [29], *etc.* by kinetic isotope effect (KIE) method. Theoretically, it is suggested that the rate-limiting step could be water assisted B–N bond breaking [19], attacking of

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surfaced adsorbed OH group to break B–N bond [30], and even the dissociation of an O–H bond in H₂O [29] for the production of the first hydrogen molecule. Moreover, the whole picture of the full hydrolysis of NH₃BH₃ with catalysts has not been provided yet.

Till now, the lack of abundance of Pt limits its practical use as catalysts and the catalytic performance of non-noble transition metals is relatively lower than that of Pt [31]. Searching for new types of catalysts is still demanding. An alternative way is to maximize the utilization of noble metal by downsizing the size of nanoparticles even to single atoms on designed substrates [32–34]. Reduced graphene oxide is a good candidate for substrates to anchor single metal atoms [35] for its large surface area, rich and controllable surface structures. Recently, the isolated Pt and Pd atoms supported on reduced graphene oxide have been successfully prepared and exhibited excellent catalytic activity for methanol oxidation [36] and selective hydrogenation of 1,3-butadiene at mild reaction conditions [37], respectively. Also, the isolated Pt anchored by two interfacial oxygen at the edge of reduced graphene oxide was active for the partial hydrolysis of NH₃BH₃ with about one hydrogen molecule released by per NH₃BH₃ molecule [38]. Considering the rich structure configurations on reduced graphene oxide, it is anticipated to design a configuration of single Pt atoms supported on reduced graphene oxide with high catalytic activity for the full hydrolysis of NH₃BH₃.

Herein, in this work we design a single Pt atom supported on trivacancy structure terminated by an oxygen adatom to form an ether group in graphene nanosheet (Pt₁/Gr-O). Pt₁/Gr-O catalyzed full hydrolysis process of NH₃BH₃ is studied, and it is found the rate limiting step is the hydration of *BHNH₃ with an energy barrier of 16.1 kcal/mol. The low activation energy indicates that on Pt₁/Gr-O the full hydrolysis of NH₃BH₃ can proceed at room temperature. Thus Pt₁/Gr-O may be a promising catalyst for NH₃BH₃ hydrolysis.

II. COMPUTATIONAL DETAILS

All the calculations were performed by using spin-polarized density functional theory (DFT) method. The DFT semi-core pseudopotentials method (DSPP) [39] with a single effective potential replacing core electrons and the double numerical basis set together with polarization functions (DNP) were adopted to form the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) [40], implemented in DMol³ package [41, 42]. A smearing of 0.005 Ha (1 Ha=27.21 eV) to the orbital occupation was applied to achieve electronic convergence in geometric optimization and transition state search program. The real-space global cut-off radius was set to be 4.5 Å. A hexagonal supercell containing (6×6) unit cells of graphene monolayer

with 20 Å vacuum layer was used as a support for a single Pt atom. The convergence tolerances of energy, force, and displacement for the geometry optimization were 1×10^{−5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively. In self-consistent-field (SCF) procedures a convergence criterion of 1×10^{−6} Ha and fermi occupation were adopted. 3×3×1 *k*-points grid was used to describe the Brillouin zone for geometric optimization and self-consistent calculations. The transition state for each elementary step was determined by LST/QST method and confirmed via frequency calculations. The H₂O solvent environment was simulated by using a conductor-like screening model (COSMO) [43] in all calculations. The dielectric constant was set to 78.54 for H₂O. To verify the accuracy of our calculation method, we calculated the B–N bond breakage of NH₃BH₃ attacked by one H₂O molecule in aqueous phase. The calculated energy barrier of 38.0 kcal/mol is close to that of 32.9 kcal/mol calculated at CCSD(T)//M06-2X/6-311+G(d,p) level [44]. The adsorption energies of surface species are defined as:

$$E_{\text{ads}} = E_{\text{X/catalyst}} - (E_{\text{catalyst}} + E_{\text{X}})$$

where $E_{\text{X/catalyst}}$, E_{catalyst} , and E_{X} represent the energies of adsorbed systems, catalyst itself, and surface species, respectively. This hydrogen bond (H-bond) energy is calculated by the following formula:

$$E_{\text{H-bond}} = E_{*X\cdots H_2O} - (E_{*X} + E_{H_2O(l)})$$

where $E_{*X\cdots H_2O}$, E_{*X} , and $E_{H_2O(l)}$ represent the energies of the total systems, the adsorbed X species on Pt₁/Gr-O, and a liquid phase H₂O molecule (H₂O(l)), respectively. *X denotes the adsorbed intermediates in the process of NH₃BH₃ hydrolysis. The total energy of Pt₁/Gr-O with one NH₃BH₃ and three H₂O molecules in water solvent is set as zero point for the relative energy for NH₃BH₃ hydrolysis.

III. RESULTS AND DISCUSSION

A. Adsorption on the Pt₁/Gr-O Surface

A trivacancy with an edge ether on graphene basal plane (Gr-O) is designed to anchor a single Pt atom (denoted as Pt₁/Gr-O). In the most stable configuration of Pt₁/Gr-O as shown in FIG. 1(a), the three Pt–C bond lengths are 1.92, 1.95, and 2.00 Å, respectively, which are shorter than the Pt–O bond length of 2.14 Å. The binding energy of a single Pt atom respecting to Pt bulk is calculated as −46.7 kcal/mol, which can effectively prevent the aggregation of single Pt atoms.

In the most stable adsorption configuration of NH₃BH₃ on Pt₁/Gr-O, a NH₃BH₃ molecule binds with Pt atom through two hydrogen atoms of BH₃ group as shown in FIG. 1(b). The adsorption energy of NH₃BH₃ on Pt₁/Gr-O is calculated as −9.8 kcal/mol. The bond

FIG. 1 Top and side views of the most stable configuration of a single Pt atom adsorbed on the Gr-O sheet (a), the optimized structures of NH_3BH_3 (b), H_2O (c), and H_2 (d) adsorbed on the $\text{Pt}_1/\text{Gr-O}$ surface, respectively. The black, red, celadon, pink, blue, and white spheres represent C, O, Pt, B, N, and H atoms, respectively. Critical bond lengths are labeled (in unit of Å).

distances between Pt and two hydrogen atoms are 1.96 and 1.97 Å, respectively. For the interaction between Pt and H, the two B–H bonds are elongated to 1.26 and 1.27 Å from 1.21 Å in isolated solvated NH_3BH_3 . Meanwhile, the B–N bond is shortened by 0.03 Å. The changes in the B–H and B–N bond lengths agree with the results of NH_3BH_3 adsorbed on Pd_2/MgO and Pd_4/MgO [45].

The adsorption energy of one H_2O molecule on $\text{Pt}_1/\text{Gr-O}$ is calculated as 0.2 kcal/mol, which is much lower than that of NH_3BH_3 . The distance between the oxygen atom in the H_2O molecule and Pt atom is 2.37 Å, as shown in FIG. 1(c), which also suggests a weak interaction between water and $\text{Pt}_1/\text{Gr-O}$. The adsorption of one hydrogen molecule is also investigated. With molecularly adsorbed configuration as shown in FIG. 1(d), the adsorption energy is calculated as 2.8 kcal/mol, which indicates the molecularly adsorbed hydrogen is ready to desorb from the catalyst. The bond length of H–H is elongated to 0.81 Å and two Pt–H bond lengths are 1.94 and 1.97 Å, respectively.

B. The elementary reactions of NH_3BH_3 hydrolysis on the $\text{Pt}_1/\text{Gr-O}$ surface

1. The B–H bond activation pathways

Two possible mechanisms have been proposed to initiate the hydrolysis of NH_3BH_3 . One is the bond breakage of B–N bonds attacked by H_2O molecules [10] and the other is the dehydrogenation of BH_3 group [26]. On $\text{Pt}_1/\text{Gr-O}$, the energy barrier of B–N bond breakage with the help of one water molecule is calculated as high as 37.7 kcal/mol (FIG. S1(a) in supplementary materials), which is similar to the result over Ni_2P nanoparticles (38.1 kcal/mol) [19]. While the energy barrier of B–H bond breaking is only 11.3 kcal/mol,

which indicates the adsorbed NH_3BH_3 molecule prefers B–H bond breaking rather than B–N bond breaking. At transition state TS1, a Pt–H–B three-membered ring configuration is formed, and the Pt–H, B–H, and Pt–B distances are 1.64, 1.84, and 2.41 Å as shown in FIG. 2, respectively. After the breaking of B–H bond, the hydrogen atom locates at the bridge site of Pt–C and the $^*\text{BH}_2\text{NH}_3$ group binds to Pt site with the Pt–B bond length of 2.21 Å (I2). The carbon atom near the Pt atom is also active for trapping hydrogen atom, which resembles the Fe–C bridge site for NH_3BH_3 dehydrogenation on prototype iron pincer catalyst [46].

For the next step, four possible reaction pathways (*i.e.*, N–H bond breaking to form BH_2NH_2 , directly producing a gas phase hydrogen molecule, hydrolysis of $^*\text{BH}_2\text{NH}_3$, and the second B–H bond breaking to form a molecularly adsorbed hydrogen) are investigated as shown in FIG. S1 (b)–(d) in supplementary materials and FIG. 2. The energy barriers of these four possible elementary steps are calculated as 33.9, 21.4, 21.4, and 10.0 kcal/mol, respectively. The formation of a molecularly adsorbed hydrogen via bond breaking of the second B–H bond has the lowest energy barrier. At transition state (TS2), the C–H and Pt–B bond lengths elongate by 0.76 and 0.12 Å, respectively. The formed molecular hydrogen weakly adsorbs on $\text{Pt}_1/\text{Gr-O}$ and easily desorbs from catalyst with an energy barrier of 0.9 kcal/mol via transition state (TS3). The production of the first hydrogen releases 1.8 kcal/mol relative to the adsorbed NH_3BH_3 system.

2. Hydroxylation pathways of B atom in NH_3BH_3

After desorption of the first hydrogen molecule, the left $^*\text{BHNH}_3$ adsorbs at bridge site of Pt–C. Four possible ways of the evolution of $^*\text{BHNH}_3$ including the breaking of B–H bond, the breaking of N–H bond

FIG. 2 The relative energy profiles of the releasing of the first hydrogen molecule from NH_3BH_3 catalyzed by $\text{Pt}_1/\text{Gr-O}$. Critical bond lengths are labeled (in unit of Å).

FIG. 3 The relative energy profiles of the hydrolysis of NH_3BH_3 by the first and second H_2O molecules on $\text{Pt}_1/\text{Gr-O}$. Critical bond lengths are labeled (in unit of Å).

and also the attachment of water molecule to form Pt (or C) bound $^*\text{BH}(\text{H}_2\text{O})\text{NH}_3$ are considered as shown in FIG. S2 (a)–(c) in supplementary materials and FIG. 3. The energy barriers are calculated as 42.7, 32.1, 23.0, and 16.1 kcal/mol for the four possible reaction ways, respectively. The combination of a H_2O molecule with $^*\text{BHNH}_3$ to form $\text{C-BH}(\text{H}_2\text{O})\text{NH}_3$ is the most kinetically favorable way. At initial state, a H_2O molecule interacts with the $^*\text{BHNH}_3$ group through the weak $\text{O}\cdots\text{H-N}$ hydrogen bond with bond energy of -6.0 kcal/mol as the intermediate I5 and the geometric parameters are shown in FIG. 3. At transition state (TS4) the distance between O and B is shortened to 2.19 Å from 3.32 Å in I5. The formed $^*\text{BH}(\text{H}_2\text{O})\text{NH}_3$

group locates on the C atom neighboring to Pt atom (I6). The O–H bond pointing to Pt atom is 0.04 Å longer than the other one. The elongated O–H bond easily breaks with an energy barrier of 8.9 kcal/mol, the released reaction energy is 11.7 kcal/mol. At transition state (TS5), the O–H bond length is 1.98 Å. The detached hydrogen atom adsorbs on the Pt–C bridge site and the $^*\text{BH}(\text{OH})\text{NH}_3$ group binds to Pt atom (I7).

Then for the evolution of I7, the most favorable way is the attachment of the second H_2O molecule to $^*\text{BH}(\text{OH})\text{NH}_3$, which is shown in FIG. 3 as the formation of I9 from I8 via TS6. The formation of $^*\text{BH}(\text{OH})(\text{H}_2\text{O})\text{NH}_3$ by combination of a H_2O molecule and $^*\text{BH}(\text{OH})\text{NH}_3$ is an exothermic step (7.1 kcal/mol)

FIG. 4 The relative energy (with I11'' included) profiles of the recovery of Pt₁/Gr-O catalyst. Critical bond lengths are labeled (in unit of Å).

with a relatively low energy barrier of 7.3 kcal/mol. At transition state (TS6), *BH(OH)NH₃ leaves from the Pt atom with the Pt–B distance of 4.12 Å and the bond distance of O–B is 2.91 Å. At I9, *BH(OH)(H₂O)NH₃ adsorbs on the catalyst through one hydrogen atom in (H₂O) fragment and the O–H bond length is elongated to 1.04 Å. The breaking of the elongated O–H bond needs to conquer an energy barrier of 9.7 kcal/mol and it is an endothermic process with a reaction energy of 4.8 kcal/mol. The formed BH(OH)₂NH₃ physically adsorbs on the Pt₁/Gr-O surface and the second isolated H atom adsorbs on the C atom (I10). The adsorption energy of BH(OH)₂NH₃ is only 0.3 kcal/mol and it is supposed that the formed BH(OH)₂NH₃ can easily dissolve in water solution.

3. Recovery of Pt₁/Gr-O catalyst

After the releasing of BH(OH)₂NH₃, two hydrogen atoms present on Pt₁/Gr-O (I11'). By removing hydrogen atoms, the Pt₁/Gr-O catalyst can be recovered. The release of molecular hydrogen can be separated as the transfer of C bonded atomic hydrogen, the formation of chemically adsorbed molecular hydrogen and the desorption of hydrogen molecule. H transfers from I11' to I12 via TS8 with an energy barrier of 11.6 kcal/mol. The distance between two hydrogen atoms are 3.71, 2.51, and 2.04 Å in I11', TS8, and I12, respectively. Then the two hydrogen atoms combine with each other to form chemically adsorbed dihydrogen with an energy barrier of 8.8 kcal/mol. At transition state (TS9), the H–H bond length is 1.17 Å. The adsorption energy of chemically adsorbed hydrogen molecule is 2.8 kcal/mol,

which indicates that the formed dihydrogen is ready to desorb from the catalyst. After the releasing of gas phase hydrogen molecule, the Pt₁/Gr-O catalyst recovers. The recovery of catalyst is an endothermic process with energy of 8.3 kcal/mol, which is easy to be conquered at room temperature if the entropy increasing is considered for the releasing of gas phase hydrogen molecule.

4. The release of the third hydrogen

Now, only two hydrogen molecules are released from one BH₃NH₃ molecule. The third molecular hydrogen comes from further hydrolysis of formed solvated BH(OH)₂NH₃. In solvated BH(OH)₂NH₃, the B–N bond length is 1.67 Å, which is 0.05 Å longer than that of the solvated isolated BH₃NH₃. The B–N bond is easy to be broken with the attack of one water molecule with an energy barrier of 10.6 kcal/mol, which is close to the reported B–N bond dissociation energy of 10.0 kcal/mol in NH₃BH₂OH [47] and much lower than that of the B–N bond breaking in BH₃NH₃ (38.0 kcal/mol). After the cleavage of B–N bond, the resulted BH(OH)₂, H₂O and NH₃ molecules form a cluster (I15) by HO···HO–H and NH···OH₂ hydrogen bonds. Then a complex BH(OH)₃···NH₄ (I16) is formed by the dissociation of water with an energy barrier of 2.8 kcal/mol. The hydrogen bond length in I16 is 1.49 Å and the distance between the left H(–B) and the nearest H(–N) is 3.22 Å. The combination of the two hydrogen atoms conquers an energy barrier of 11.6 kcal/mol and releases energy of 8.6 kcal/mol. At transition state (TS13), the bond lengths of B–H and

FIG. 5 The relative energy (with I11' included) profiles of hydrolysis of the resulted $\text{BH}(\text{OH})_2\text{NH}_3$ group in water solution. Critical bond lengths are labeled (in unit of Å).

N–H are elongated to 1.52 and 1.39 Å, respectively, while the H–H distance is shortened to 0.95 Å. The generated products also include NH_3 and $\text{B}(\text{OH})_3$. The species of products have not been definitely determined yet. Banu *et al.* used $\text{B}(\text{OH})_3$, H_2 and NH_3 as the products for hydrolysis of NH_3BH_3 without catalysts in gas phase and aqueous phase [44]. Chen *et al.* proposed that a $\text{NH}_4\text{B}(\text{OH})_4\text{--B}(\text{OH})_3$ mixture rather than NH_4BO_2 is the main B-containing byproducts after hydrolysis of BH_3NH_3 catalyzed by a Pt/CNT catalyst [27]. But this may be the evolution of hydrolysis species, which are not critical for the production of hydrogen.

The hydrolysis of the resulted $\text{BH}(\text{OH})_2$ group in I15 over $\text{Pt}_1/\text{Gr-O}$ surface is also considered. It is found a $\text{BH}(\text{OH})_2$ molecule adsorbs weakly on $\text{Pt}_1/\text{Gr-O}$ catalyst with the adsorption energy of -0.04 kcal/mol, which is much lower than that of NH_3BH_3 (-9.8 kcal/mol). The hydrolysis of $\text{BH}(\text{OH})_2$ groups can also proceed on $\text{Pt}_1/\text{Gr-O}$ (as shown in FIG. S3 in supplementary materials) without the pre-cover with NH_3BH_3 or atomic hydrogen. The energy barrier of $\text{BH}(\text{OH})_2$ hydrolysis on $\text{Pt}_1/\text{Gr-O}$ is significantly reduced to 4.8 kcal/mol compared to that (39.5 kcal/mol) of $\text{BH}(\text{OH})_2$ hydrolysis without catalysts reported by Banu *et al.* [44].

Based on the aforementioned reaction pathways, the optimal reaction processes of NH_3BH_3 hydrolysis on $\text{Pt}_1/\text{Gr-O}$ are depicted in FIG. 6 as: (i) the preferential adsorption of one NH_3BH_3 molecule on $\text{Pt}_1/\text{Gr-O}$ and the activation of B–H bonds, (ii) the first B–H bond breaking, (iii) the formation of molecularly adsorbed dihydrogen from the second B–H bond breaking, (iv) the desorption of the first gas phase hydrogen molecule; (v) the attacking of the first water molecule, (vi) the attack-

FIG. 6 Proposed mechanism for NH_3BH_3 hydrolysis over $\text{Pt}_1/\text{Gr-O}$ surface.

ing of the second water molecule, (vii) the desorption of $\text{BH}(\text{OH})_2\text{NH}_3$, (viii) the desorption of the second gas phase hydrogen molecule and the recovery of catalyst, (ix) the attacking of the third water molecule, (x) the releasing of the third hydrogen molecule and the formation of final products.

Through the whole reaction pathways for NH_3BH_3 hydrolysis, it is found that the attacking of first H_2O molecule to $^*\text{BHNH}_3$ ($^*\text{BHNH}_3 + \text{H}_2\text{O} \rightarrow ^*\text{B}(\text{H}_2\text{O})\text{HNNH}_3$) is the rate-limiting step on $\text{Pt}_1/\text{Gr-O}$ with an energy barrier of 16.1 kcal/mol. To gain more insight into the origin of the reaction activity of H_2O molecules reacting with the $^*\text{BNH}_3$ group, the local density of states (LDOS) projected onto B atom and

FIG. 7 Left panels are structures of I5, TS4, and I6 in FIG. 3, right panel is the local density of states (LDOS) projected onto B atom and H₂O molecule in the I5, TS4, and I6 over Pt₁/Gr-O surface. E_f denotes the Fermi level. The dot dashed line shows the density states (energy levels) of isolated water molecule with solvent effect included. The energy levels are shifted according to the O 1s orbitals of water molecule in I5 and H₂O(l).

H₂O molecule in the I5, TS4, and I6 over Pt₁/Gr-O has been split as shown in FIG. 7. The highest occupied molecular orbital (HOMO) of water, 1b₁ state, is contributed by the lone pair electrons of oxygen atom. B atom has empty orbitals which can accept electrons from donation atom. At TS4, the density states of 1b₁ expanded and slightly overlapped with the orbitals of B atom. For the interaction between water and *BHNH₃ group, the empty orbitals shift towards low energy direction. At I6, the orbitals of water molecule effectively overlap with that of B atom, which indicates the chemical bonding between water molecule and B atom. For the donation of lone pair electrons, the density of states of water molecule decreases and that of B atom increases below Fermi level. The orbitals above Fermi level shift towards low energy direction for the formation of chemical bond, which makes the hydrolysis of *BHNH₃ group proceed.

IV. CONCLUSION

In conclusion, the NH₃BH₃ hydrolysis mechanisms on single Pt atom anchored to the plane of graphene with a defective carbon atom replaced by an oxygen atom were examined by using first-principles calculations. The Pt₁/Gr-O catalyst prefers to activate the B–H bonds, and first hydrogen molecule is released by two detached H atoms from B–H bonds. The left *BHNH₃ combines with two H₂O molecules to proceed the hydrolysis process. The combination of left *BHNH₃ with the first H₂O molecule is the rate-limiting step with an energy barrier of 16.1 kcal/mol. Both attached water molecules detach one hydrogen atom to form NH₃BH(OH)₂, which can be easily hydrolyzed in

water solvent to release one hydrogen molecule without catalyst. By combination and releasing of the two surface left hydrogen atoms, Pt₁/Gr-O can be recovered. A whole mechanism of NH₃BH₃ hydrolysis over solid catalysts is presented for the first time. Based on the calculated results the Pt₁/Gr-O catalyst exhibits high catalytic activity for NH₃BH₃ hydrolysis at room temperature. Thus Pt single atoms anchored at a designed configuration on graphene nanosheet can perform high activity for hydrolysis of NH₃BH₃ at room temperature.

Supplementary materials: The bond breakage of B–N bond in NH₃BH₃ attacked by one H₂O molecule; the three possible reaction pathways of the *BH₂NH₃ including N–H bond breaking to form BH₂NH₂, direct production of a gas phase hydrogen molecule, and hydrolysis of *BH₂NH₃; the three possible reaction pathways of the *BHNH₃ including the B–H bond breaking, the N–H bond breaking, and the attachment of one water molecule to form Pt bound BH(H₂O)NH₃; and the hydroxylation pathways of BH(OH)₂ on Pt₁/Gr-O are shown in FIG. S1–S3.

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