

Dehydrogenation of ammonia on free-standing and epitaxial hexagonal boron nitride

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Supplementary Material

<p>Figure S1. Adsorption of ammonia over a VBN defect of a hBN monolayer with an E_{Ads} of -0.25 eV. The nitrogen atom is closer to the surface than the hydrogens (with the three N-H bonds point upwards) at a height of 2.76 Å. Slight tilting of the ammonia molecule allows the lone pair on the nitrogen to interact with the electron-deficient B-B bond, forming a weak intermolecular bond. The ammonia adsorbs almost directly above the vacant nitrogen position of VBN. This geometry is the first step of the deportation reaction which mechanism is illustrated in Figure 6 of the main text.</p>	3
<p>Concentration of NH₃ as a function of time</p>	4
<p>Figure S2. Concentration of $\text{NH}_3(\text{gas}) + \text{hBN}(\text{surf})$ (R), $\text{NH}_3(\text{ads}) + \text{hBN}(\text{surf})$ (I) and, $\text{NH}_2(\text{ads}) + \text{H}(\text{ads}) + \text{hBN}(\text{surf})$ (P) as a function of time at 600 K, 800 K, 1000 K and 1200 K. I remains at a very low steady-state concentration throughout the reaction. The intersection of the red and black lines gives the time it takes for approximately half of R to be changed into P. The equilibrium was reached roughly at 400 s, 12 s, 3.5 s and 0.54 s, at 600 K, 800 K, 1000 K and 1200 K, respectively. At 600 K the reaction is expected to take 400 s (6.6 minutes) and only 0.4 s at 1200K. Therefore, NH₃ is expected to dissociate into NH₂ and H in a reasonable amount of time.</p>	5
<p>Figure S3. Surface hydrogen geometries following dissociation of ammonia with a VBN. (a) Ground state configuration of a hydrated VB with H-H distances of 1.88 Å. (b) Transition state to re-arrange two adjacent hydrogens with a minimal activation energy barrier of 0.07 eV. (c) Arrangement of surface hydrogens with a pair within 1.45 Å. The ΔE between (a) and (c) is 0.06 eV. Here the B-H bonds shift to bring two hydrogen atoms within 1.45 Å of each other an event that would easily happen even at moderate surface temperatures.</p>	6

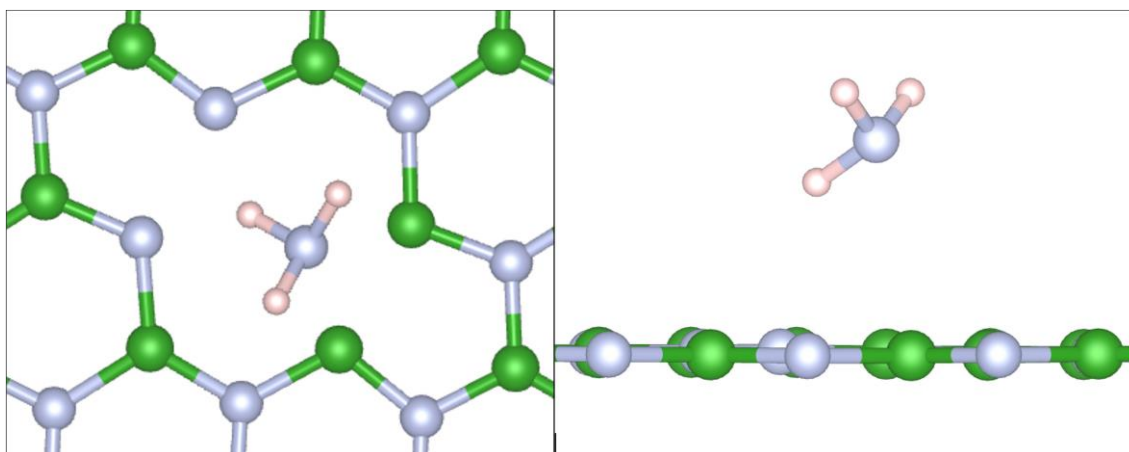


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Concentration of NH₃ as a function of time

As the barriers to NH₃ desorption and dissociation are 0.25 eV and 0.52 eV respectively both processes are competitive. Therefore, the kinetics of the reactions we considered to suggest the formation rate of the NH₂ and H species on the surface. The Γ -point phonons for each of the 5 stationary points (isolated NH₃, VB, NH₃ adsorbed on the divacancy, TS1 and NH₂ + H chemisorbed on VBN) was calculated. Due to the absence of the adsorption barrier, a Morse potential was adopted for the movement of NH₃ alongside a perpendicular coordinate between NH₃ and VBN. The respective imaginary frequency of the transition state for the NH₃ dissociation was obtained at a value of 454.11 cm⁻¹. Rate coefficients were obtained by means of the Transition State Theory, at the temperatures of 600 K, 800 K, 1000 K and 1200 K which were possible operation temperature values of catalytic H₂ production. In this regard, the Variational Transition State Theory was adopted for the adsorption/desorption and the Conventional Transition State Theory was considered for the NH₃ dissociation on the divacancy. Internal modes of the hBN surface, NH₃ in gas-phase and the adsorbed NH₃, were considered for the adsorption/desorption and internal modes respective to the adsorbed system and transition state were assumed for the NH₃ dissociation. The lattice-gas thermodynamic model was adopted in all calculations. Concentration of the NH_{3(gas)} + hBN_(surf) (R), NH_{3(ads)} + hBN_(surf) (I) and NH_{2(ads)} + H_(ads) + hBN_(surf) (P), as a function of time, were obtained and reported in Figure S2.

It was possible to suggest that, at 600 K, the complete convergence of the adsorbed NH₃ into NH₂ and H, was obtained, at roughly 400 seconds (6.6 minutes), whereas, complete convergence was achieved in 0.4 seconds at 1200 K. Therefore, although the equilibrium was dislocated towards NH₃ desorption, the step determinant reaction (NH_{3(ads)} → NH_{3(ads)} + H_(ads)) was able to proceed, being kinetically viable at the studied temperatures and NH₃ is expected to dissociate into NH₂ and H in a reasonable amount of time.

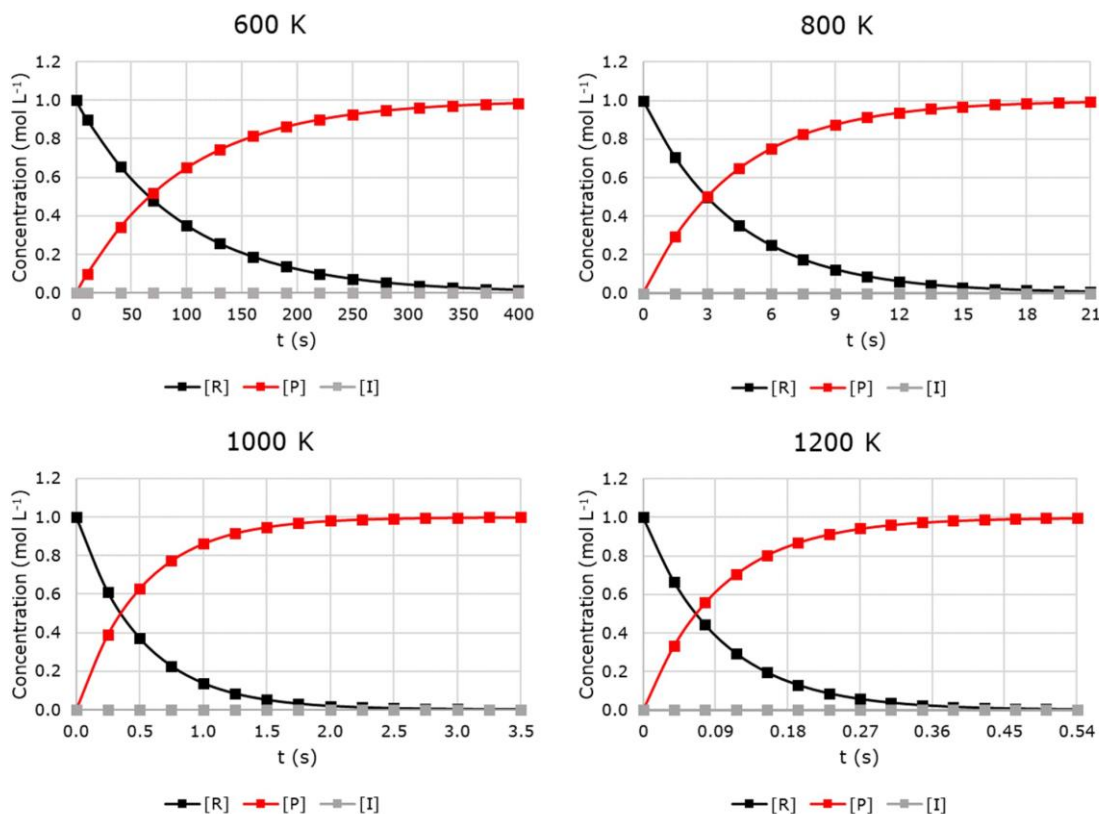


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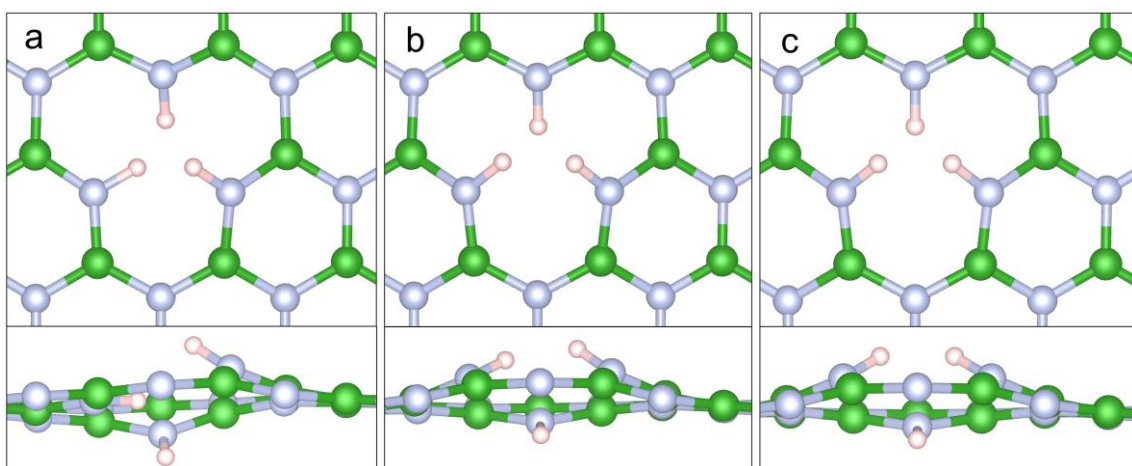


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