Heterogeneous Metal-Free Hydrogenation over Defect-Laden Hexagonal Boron Nitride

David J. Nash,‡ David T. Restrepo,† Natalia S. Parra,‡ Kyle E. Giesler,‡ Rachel A. Penabade,‡ Maral Aminpour,† Duy Le,‡ Zhanyong Li,∥ Omar K. Farha,⊥ James K. Harper,∥ Talat S. Rahman,‡ and Richard G. Blair†

© 2016 American Chemical Society
DOI: 10.1021/acsomega.6b00315

ABSTRACT: Catalytic hydrogenation is an important process used for the production of everything from foods to fuels. Current heterogeneous implementations of this process utilize metals as the active species. Until recently, catalytic heterogeneous hydrogenation over a metal-free solid was unknown; implementation of such a system would eliminate the health, environmental, and economic concerns associated with metal-based catalysts. Here, we report good hydrogenation rates and yields for a metal-free heterogeneous hydrogenation catalyst as well as its unique hydrogenation mechanism. Catalytic hydrogenation of olefins was achieved over defect-laden h-BN (dh-BN) in a reactor designed to maximize the defects in h-BN sheets. Good yields (>90%) and turnover frequencies (6 × 10^−3−4 × 10^−3) were obtained for the hydrogenation of propene, cyclohexene, 1,1-diphenylethene, (E)- and (Z)-1,2-diphenylethene, octadecene, and benzylideneacetophenone. Temperature-programmed desorption of ethene over processed h-BN indicates the formation of a highly defective structure. Solid-state NMR (SSNMR) measurements of dh-BN with high and low propene surface coverages show four different binding modes. The introduction of defects into h-BN creates regions of electronic deficiency and excess. Density functional theory calculations show that both the alkene and hydrogen-bond order are reduced over four specific defects: boron substitution for nitrogen (B_{N}), vacancies (V_{B} and V_{N}), and Stone–Wales defects. SSNMR and binding-energy calculations show that V_{N} are most likely the catalytically active sites. This work shows that catalytic sites can be introduced into a material previously thought to be catalytically inactive through the production of defects.

INTRODUCTION

Originally discovered in 1897 by Sabatier, who received a Nobel prize for this work in 1912, catalytic hydrogenation is widely used in industry and is heavily utilized in the synthesis of many pharmaceutical and agricultural chemicals. Although the conversion of olefins to alkanes is thermodynamically favored under appropriate conditions, such reactions are so sluggish that a catalyst is required to facilitate hydrogenation. It was first observed that traces of nickel could mediate the addition of H₂ to olefins and later that palladium, platinum, rhodium, and other precious metals exhibited similar catalytic activities, owing to the overlap between the metal d-orbitals and hydrogen molecular orbitals.

Two disadvantages of the use of these metals are their cost and leaching of the metals into the product. Utilizing nickel-based catalysts, particularly in the hydrogenation of fats, has largely circumvented the problem of cost. However, nickel is readily poisoned by sulfur-containing compounds when natural fats or decomposition products introduce sulfides into the catalytic system. In addition, unacceptable levels of nickel can leach into the final product, with nickel levels of 0.1−1.5 ppm known to be present in hydrogenated oils. These and other factors have stimulated research efforts to develop benign, nonmetallic hydrogenation catalysts.

Homogeneous nonmetallic catalysis has been developed for a wide range of reactions. However, metal-free hydrogenations using molecular hydrogen were not realized until 2006, when Stephan and co-workers developed the first non-transition-metal system capable of releasing and absorbing molecular hydrogen. Soon after, the term “frustrated Lewis pair” or FLP was coined to describe these systems. An explosion of research activity followed.10−12 The key feature of an FLP-catalyzed
reaction is the formation of a Lewis acid and base that cannot form a conventional adduct, from either steric or electronic frustration. Early work showed that these FLPs could bind olefins and alkanes. Through their interaction with hydrogen and other molecules, FLPs have been shown to successfully catalyze the hydrogenation of imines, enamines, aldehydes, and alkenes. More recently, carbon dioxide has been reduced over a solid indium oxide-based FLP.

Heterogeneous catalytic hydrogenation, which is preferred for large-scale industrial processes due to the ease of catalyst separation and applicability to continuous flow reactions, has only recently been reported for metal-free systems with low conversion rates. On the basis of our experience with mechanochemical processes and the fact that defects in the substrate can cause the sheet to distort above (SW1) or below the original plane (SW2). SW2 has the most favorable interaction with the substrate. Chemisorption of hydrogen (up to 70% of the adsorbed hydrogen) is favored over these sites. In fact, single sheets and nanotubes of BN can absorb up to 4.6 mass % hydrogen. If h-BN has a high affinity for hydrogen, then it may also have a high affinity for olefins. We omitted silicon-substituted structures and examined the eight remaining defects for affinity for olefin and hydrogen binding (Figures S16 and S17). We found that four of these defects exhibited an affinity for olefins. Binding-energy calculations (Table 1) confirm this assertion, with the binding energies of ethene, propene, and hydrogen being at par with those of metals that possess known hydrogenation activity (Pt, Pd, and Ni). Of these defects, B_N and V_N have binding energies closest to those of metals with known hydrogenation activity. Olefin binding at SW defects is less favored (desorption may reduce the availability of activated species), and hydrogen binding is disfavored. Binding at V_N sites is highly favored for both the olefin and hydrogen, and the reactivity will be limited. Solid-state NMR (SSNMR) experiments on propene-saturated dh-BN showed a low concentration of B_N sites and a much higher concentration of V_N sites. Additionally, there is evidence of V_N formation after ball milling.

### RESULTS AND DISCUSSION

Defects have been shown to be important features of active catalytic solids and are responsible for the increased hydrogenation activity observed in catalysts prepared mechanochemically as well as catalysts under the application of mechanical force. These results suggest that a defect-laden solid with regions of electron deficiency and excess will interact with olefins and molecular hydrogen to reduce their respective bond orders enough to facilitate hydrogenation. Prior work on hydrogen storage examined the role of defects in h-BN. Density functional theory (DFT) calculations show a favorable binding energy for hydrogen on nitrogen vacancies (V_N), boron vacancies (V_B), boron nitrogen swap (B/N), boron substitution for nitrogen (B_N), nitrogen substitution for boron (N_B), carbon substitution (C_D and C_N), silicon substitution (N_Si and B_Si), and Stone–Wales (SW) defects. We assessed two five-membered rings and two seven-membered-ring SW defects. These defects can cause the sheet to distort above (SW1) or below the original plane (SW2). SW2 had the most favorable interaction with the substrate. Chemisorption of hydrogen (up to 70% of the adsorbed hydrogen) is favored over these sites. In fact, single sheets and nanotubes of BN can absorb up to 4.6 mass % hydrogen. If h-BN has a high affinity for hydrogen, then it may also have a high affinity for olefins. We omitted silicon-substituted structures and examined the eight remaining defects for affinity for olefin and hydrogen binding (Figures S16 and S17). We found that four of these defects exhibited an affinity for olefins. Binding-energy calculations (Table 1) confirm this assertion, with the binding energies of ethene, propene, and hydrogen being at par with those of metals that possess known hydrogenation activity (Pt, Pd, and Ni). Of these defects, B_N and V_N have binding energies closest to those of metals with known hydrogenation activity. Olefin binding at SW defects is less favored (desorption may reduce the availability of activated species), and hydrogen binding is disfavored. Binding at V_N sites is highly favored for both the olefin and hydrogen, and the reactivity will be limited. Solid-state NMR (SSNMR) experiments on propene-saturated dh-BN showed a low concentration of B_N sites and a much higher concentration of V_N sites. Additionally, there is evidence of V_N formation after ball milling.

### Table 1. Binding Energies for Ethene and Propene on h-BN, Hydrogen on BN (All Calculated in This Work), Ethene on Platinum Group Metals, Hydrogen on Pt(100), Hydrogen on Pd(100), and Hydrogen on Ni(100)

| Defect    | Ethene binding energy (eV) | Propene binding energy (eV) | Hydrogen binding energy (eV) |
|-----------|----------------------------|-----------------------------|----------------------------|
| BN        | -3.71                      | -3.69                       | -4.95                      |
| V_N       | -1.90                      | -1.76                       | -1.43                      |
| SW2       | -0.23                      | -0.35                       | 0.62                       |
| B_N       | -1.95                      | -2.05                       | -1.77                      |
| Pt 100    | di sigma                   | -2.32                       | -2.88                      |
|           | pi-top                     | -1.55                       |                            |
| Pd 100    | di sigma                   | -0.84                       | -2.92                      |
|           | pi-top                     | -0.33                       |                            |
| Ni 100    | di sigma                   | -1.76                       | -2.81                      |
|           | pi-top                     | -0.82                       |                            |

*No temperature or pressure effects were included in these calculations.*

**Figure 1.** Hydrogenation of (E)-1,2-diphenylethene [6] under excess hydrogen at 170 °C with different catalyst loadings. Five grams (27.7 mmol) of olefin was used. Both 1 g of dh-BN activated for 48 h under hydrogen (a) and nonactivated h-BN-coated milling media (b) effectively hydrogenated the olefin bond.
milling, and \( V_N \) are some of the most stable defects in \( h\)-BN.\(^{28-30}\)

**Producing Defects.** Pristine sheets of \( h\)-BN are exceptionally robust and chemically inert,\(^{25,35,36}\) the application of mechanical force is required to induce delamination and introduce point defects.\(^{37}\) By designing a hydrogenation reactor around a pebble mill, we have been able to study the catalytic activity of defects in \( h\)-BN. The continuous grinding motion within the mill prevents cluster formation, maximizes the number of few-layer sheets, and induces plastic deformation in the catalyst. To verify the presence of these sheets and defects, transmission electron microscopy (TEM) was used to characterize the morphology of the \( dh\)-BN catalyst (Figure S20b,c). Nanosheets are observed by TEM and appear to form tubular structures or nanoscrolls, as seen in Figure S20c. Although point defects could not be imaged directly, the material shows significant disruption of the structure (Figure S20a,b). Powder X-ray diffraction (PXRD) of pristine and defect-laden \( h\)-BN (\( dh\)-BN) (Figures S18 and S19) shows disorder in the \( c\)-direction, consistent with delamination and retention of order in the sheet. Propene uptake experiments (Figure S3) indicate a defect level of 0.46 mol %. Integral breadth analysis using the 001 and h\( 00 \) peaks found that the average crystalline region in the sheet was 6.7 nm, with 0.56% strain, and the average crystallite size in the \( c\)-direction was 18.3 nm (or \( 55\ h\)-BN layers), with 0.23% strain. The higher in-sheet strain is indicative of defects and is confirmed by TEM images.

**Bulk-Scale Experiments.** Nearly complete hydrogenation, of substrates without acidic functional groups, was achieved with reactor temperatures as low as 20 °C. This temperature is much lower than that used for industrial hydroprocessing (300–450 °C).\(^{38}\) No aromatic carbons were hydrogenated, such as that over Raney nickel.\(^{39}\) Benzylideneacetophenone was not reduced to an alcohol, such as that with metal-based catalysts. Additionally, no C–H activation products were observed, as was reported over nanocrystals of \( h\)-BN.\(^{40}\) The hydrogenation product of phenylethene (a known product of the thermal decomposition of (\( E\)-cinnamic acid [7]) was observed in the by-products of the hydrogenation of (\( E\)-cinnamic acid [7]) at 170 °C.\(^{40}\) For all substrates, except the two carboxylic acids, the upper limits for the TOFs were determined from the steepest slope of the hydrogen uptake curve (Figure 2) and from propene adsorption studies (Figure S3). For the carboxylic acids, TOFs were determined from the product yield and total reaction time. Turnover numbers were calculated assuming deactivation after one reaction, although we have been able to recycle the catalyst three times with minimal loss of catalytic efficiency (Figure S21). The results are presented in Table 2, as are those for other catalytic systems. The TOFs over \( dh\)-BN are better than those achieved using FLPs for the same substrate. Although the internal sheet atoms of a single \( h\)-BN layer are relatively inert, the defects and edges are potentially reactive. In the presence of hydrogen, the edges of the \( dh\)-BN sheets possess reactive species, which reductively aminate carboxylic acids. Lower yields of hydrogenation products were realized from reactions with (\( E\)-cinnamic acid [7] (Table S1) and (9Z)-octadec-9-enoic acid [8], as a result of reaction of the carboxylic acid group with these edges. This is evidenced by the production of nitriles from these reagents (Table 2). Nitriles are produced by reaction of the carboxylic acid with the edge nitrogens on the \( dh\)-BN sheet, followed by dehydration. X-ray photoelectron spectroscopy (XPS) analysis of the catalyst after hydrogenation confirmed the presence of carbon on the surface (Figure S14d), and thermogravimetric analysis (TGA) of the catalyst after propene hydrogenation shows that coking is reduced at lower temperatures (Figure S14c).

**Metal-Free Hydrogenation.** Small amounts of metal impurities can lead to the observation of anomalous catalytic activity,\(^{41}\) and hydrogenation over stainless steel has recently been observed.\(^{42}\) Mechanical processing can introduce metals into the material through wear of the media and vessel. The two main components of steel used are iron and nickel. Both of these metals can be active toward hydrogenation. Nickel is a known hydrogenation catalyst, and iron acts as a catalyst when in the nanoparticle form.\(^{43,44}\) In a previous study using graphite, iron was not incorporated into the product even after extended milling times.\(^{35}\) Inductively coupled plasma atomic emission analysis (ICP-AES) of the boron nitride before and after activation indicated that little metal incorporation occurred. The starting material contained no detectable iron or nickel. After activation, the material had 7 ppm of iron and 10 ppm of nickel.

**Mechanically Equivalent Blank.** The effect of a small amount of metal contamination was examined by substituting graphite and graphic \( C_{3}N_{4} \) for boron nitride. Both have mechanical properties similar to those of boron nitride and exhibit wear behavior. Although graphite is a suitable support for iron and nickel catalysts, it lacks the electronic structure needed for hydrogen and alkene binding. Both, graphite and \( C_{3}N_{4} \) were processed in a hydrogen atmosphere in the same manner as was boron nitride and then used in (\( E\)-cinnamic acid [7] hydrogenation reactions at 170 °C and propene [1] hydrogenation reactions at 20 °C. No hydrogen uptake or hydrogenation products were observed.

**Rigorously Metal-Free Implementation.** To further eliminate the possibility of metal-mediated hydrogenation, a metal-free (alumina) reactor was constructed (Figure S2c). Additionally, propene was chosen as a substrate, as it would be free from metal impurities that may be found in liquid or solid substrates. Initially, propene [1] was hydrogenated with 90% efficiency after a much longer induction period.

**Mechanical Factors Affecting Induction Periods and Reaction Rates.** Discrete elemental models of the catalysts used in this study indicated that the compressive forces
achieved in both the steel and alumina reactors were comparable. However, the total amount of compressive force delivered over a 10 s time period was significantly less for the alumina reactor (Figure S15d). Without activation, a significant

Table 2. Hydrogenation Yields, TOFs, and Single-Use TONs of Various Substrates over dh-BN and other Catalytic Systems with a Mill Speed of 66 rpm Unless Otherwise Specified$^ {a,b}$

| Reference Number / Compound | Reactant | Product(s) | Reaction Temperature (°C) | TOF (s$^{-1}$/TON | Yield/Comments |
|----------------------------|----------|------------|---------------------------|-----------------|----------------|
| [1] Propene                |          |            | 20                        | 1.25 x 10$^4$/16.10 | 100%; 114 RPM  |
|                            |          |            | 200                       | 4.15 x 10$^3$/90.69 | 100%           |
| [2] Cyclohexene            |          |            | 20                        | 2.88 x 10$^{-1}$/15.88 | 100%; 114 RPM  |
| [3] octadec-1-ene          |          |            | 150                       | 6.51 x 10$^{-3}$/3.92 | 35% at 150 °C  |
|                            |          |            | 220                       | 1.86 x 10$^{-4}$/11.19 | 100% at 220 °C |
| [4] 1,1-diphenylethane     |          |            | 170                       | 1.17 x 10$^{-3}$/21.07 | 97%            |
| [5] (Z)-1,2-diphenylethane |          |            | 170                       | 1.41 x 10$^{-3}$/14.49 | 100%           |
| [6] (E)-1,2-diphenylethane |          |            | 135                       | 1.09 x 10$^{-3}$/5.00  | 99%            |
|                            |          |            |                            | 1.15 x 10$^{-3}$/13.47 | 99%            |
| [7] (E)-cinnamic acid      |          |            | 170                       | 1.19 x 10$^{-3}$/10.28 | 55.1% hydrogenic acid after catalyst recycle |
| [8] (E)-Octadec-9-enoic acid |      |            | 170                       | 5.79 x 10$^{-3}$/5.00  | 58% oleyl nitrile, 33% stearyl nitrile, 10% oleylamide |
| [9] benzyldieneacetophene  |          |            | 240                       | 1.56 x 10$^{-4}$/13.56 | 90%            |
| [10] eugenol               |          |            | 240                       |                       | 65%            |

1,1-diphenylethane          Room Temp.        5.73 x 10$^{-3}$/4.95 99% 20 mol% [(C$_6$F$_5$)$_3$Br(C$_6$F$_5$)]Ph$_2$ $^p$6
1,1-diphenylethane          Room Temp.        1.21 x 10$^{-3}$/17.4 87% 5 mol% [(C$_6$F$_5$)$_3$Br]pTol$_2$NMe$^p$6
(E)-N-benzyldiene-2-methylpropan-2-amine Room Temp. 2.61 x 10$^{-3}$/470 47% 0.1 mol% [(MeCNCl)C]$_2$C$_8$H$_{15}$ [B(C$_6$F$_5$)$_4$]$^{16}$
1-methyl-1,2-diphenylethane Room Temp. 5.22 x 10$^{-3}$/18.79 Fe-dinitrogen complex$^{27}$
cyclohexene                  20              3.2 x 10$^{-3}$ to 6.6 x 10$^{-3}$ Ni on various supports$^{28}$
benzene                     50-170          4 x 10$^{-3}$ to 1.6 x 10$^{-3}$ Ni on various supports$^{28}$
cyclooctene                  80              6 x 10$^{-3}$/38 graphene$^{29}$

$^a$All information was derived from steel reactor data. Full product chromatograms are reported in Figures S4–S11. $^b$After addition of 5 mass % fumed silica.
induction period (over 16 h; Figure S21) was observed. The initial activation step, which produces dh-BN, was performed with 20 g of the material. At such a high loading, the impacts of the media are dampened. By activating a smaller amount (5 g) of boron nitride, the induction period was eliminated and stoichiometric yields were obtained (Figure 2).

Defects, which are stable up to 900 °C, can be produced during hydrogenation or in a pretreatment step. However, they must be mobile for the bound hydrogen and olefin to interact. Defects are mobile during plastic deformation, which occurs when the yield strength of a material is exceeded. The motion of defects in h-BN nanotubes has been observed under applied load as well as modeled in h-BN sheets and the forces generated during milling can be sufficient to exceed the compressive yield strength of h-BN (41.3 MPa). However, the generation of high forces during milling requires efficient transfer of mechanical force to dh-BN. Therefore, the rheological properties of the reaction mixture during hydrogenation are important factors. There must be media (ball)—media impacts or media—wall impacts for force to be transferred to the reaction. This occurs as frictional forces allow the media to climb up the wall of the rotating reactor. At a certain point, gravity predominates and the media tumble (A video of this process is supplied in the Supporting Information). Liquids, such as octadec-1-ene, lower the impact forces by reducing friction and eliminating tumbling. They are effective lubricants. If tumbling is reduced or eliminated, impact forces are reduced and the amount of plastic deformation experienced by the dh-BN catalyst is limited. Consequently, lower hydrogenation yields were obtained when pure octadec-1-ene was utilized. Discrete element method (DEM) models showed that the lowered coefficients of restitution, static friction, and rolling friction produced by lubrication significantly reduced the number of high-force impacts. By adding 5 mass % fumed silica, the lubricity of the mixture was greatly reduced and hydrogenation proceeded rapidly.

Surface Analyses, Bound Species, and Sites. Two separate samples were prepared, and 13C isotropic spectra were acquired for each. The first sample was exposed to propene under a pressure of 310 kPa for 4 days, whereas the second sample was exposed to small quantities of propene present in our Ar-filled glovebox (partial pressure <100 Pa or 4.5 ppt). Both samples show some uptake of propene, best observed from the presence of methyl signals from 5 to 30 ppm (Figure 3) and from the thermograms (Figure S12). The surface area of the parent BN was 5 m²/g. After activation by milling in a zirconia vial, the surface area increased to 340 m²/g, and it decreased to 270 m²/g upon exposure to propene. This suggests that propene tightly binds to a fraction of the adsorption sites or 0.70 mass % of the catalyst.

The presence of five distinct CH₃ resonances in each sample indicates that multiple environments are available to propene. This is consistent with the presence of at least five structurally unique defect sites. A tentative assignment of each site can be made using prior work establishing that methyl groups at lower frequencies represent those most sterically imposed upon by neighboring sites. A summary of C−H···X steric interactions (X = N or B) for each structural model is given in Table 3. Site 1, represented by the signal near 7 ppm, is only occupied at low surface coverages and, on the basis of the 13C shift, is expected to display the most significant steric interactions with neighboring sites. A summary of C−H···X steric interactions (X = N or B) for each structural model is given in Table 3. Site 1, represented by the signal near 7 ppm, is only occupied at low surface coverages and, on the basis of the 13C shift, is expected to display the most significant steric interactions with neighboring sites. A summary of C−H···X steric interactions (X = N or B) for each structural model is given in Table 3. Site 1, represented by the signal near 7 ppm, is only occupied at low surface coverages and, on the basis of the 13C shift, is expected to display the most significant steric interactions with neighboring sites. A summary of C−H···X steric interactions (X = N or B) for each structural model is given in Table 3. Site 1, represented by the signal near 7 ppm, is only occupied at low surface coverages and, on the basis of the 13C shift, is expected to display the most significant steric interactions with neighboring sites. A summary of C−H···X steric interactions (X = N or B) for each structural model is given in Table 3. Site 1, represented by the signal near 7 ppm, is only occupied at low surface coverages and, on the basis of the 13C shift, is expected to display the most significant steric interactions with neighboring sites.

Figure 3. 13C SSNMR of dh-BN exposed to high and low partial pressures of propene. The peaks around 25 ppm are due to the methyl carbon on propene and show four distinct binding modes. The peaks at 62 and 83 ppm are likely due to partial oxidation of the bound propene molecule. The spectra were obtained using a cross-polarization technique.
occupied regardless of the preparation condition. Site 3 is consistent with \( V_N \), whereas site 4 is tentatively assigned to model SW2, with two \( C-H::X \) contacts <3.0 Å. It is notable that the resonance near 17 ppm is also more strongly represented in the pressurized sample. Site 5 near 30 ppm is the least sterically involved with neighboring sites and is thus assigned to structural model SW1, with one \( C-H::X \) interaction >3.0 Å.

Overall, these \( ^{13}C \) NMR results suggest that there are at least five structurally distinct sites and that some are solely or preferentially occupied at higher pressures. We note that the olefinic carbons are also observed in the spectrum at 107 ppm (tentatively assigned as CH) and at 122–127 ppm (CH₂). These are less useful for analysis due to the low signal-to-noise ratio, but help verify the presence of propene. Curiously, in both samples an additional resonance is observed at 62 and 83 ppm in the high- and low-pressure samples, respectively. This is consistent with the formation of two distinct species containing \( C-H \) and \( C=H \) bonds, perhaps from oxidation of the double bond after protonation. The results do not chemisorb onto pristine h-BN sheets. This was also noted for hydrogen adsorption on h-BN sheets, which is at best weakly favored. Olefin chemisorption occurs at four of the eight defects investigated.

The effect that these defects have on the carbon double bond can be elucidated by focusing on hybridization of the olefinic carbons interacting with the defect. A comparison of the charge density along a vertical plane passing through the two C atoms to that for gas-phase \( C_2H_4 \) and \( C_2H_6 \) illustrates the effect of the substrate (Figure 5). When ethene or propene chemisorbs onto electronic structure of the propene molecule on the boron nitride substrate. Ethene \( (C_2H_4) \), the simplest possible molecule with such a bond, and propene were investigated. First-principles electronic structure calculations of \( C_2H_4 \) and \( C_2H_6 \) molecules on a single \( h \)-BN layer were employed by utilizing the van der Waals density functional (vdW-DF)\(^{61,62}\). It quickly became clear that these olefins do not chemisorb onto pristine \( h \)-BN sheets. This was also noted for hydrogen adsorption on \( h \)-BN sheets, which is at best weakly favored. Olefin chemisorption occurs at four of the eight defects investigated.

Catalytically Active Defects and Reaction Mechanism. Hydrogenation over traditional metal catalysts proceeds through the Horiiuti–Polanyi mechanism, where the olefin adsorbs onto a hydrogenated surface, hydrogen migrates to the \( \beta \) carbon of the olefin, and the free alkane is reductively eliminated from the surface.\(^{58}\) This is significantly different from the mechanism of olefin activation using an FLP. In an FLP system, hydrogenation proceeds via three steps: addition of molecular hydrogen to the FLP, olefin protonation to form a carbocation, and hydride transfer to the carbocation.\(^{59}\) This also differs from hydrogenation observed over acid zeolites where the olefin first reacts with an acidic proton to form a transient carbonium ion.\(^{60}\) To understand this process, it is useful to evaluate the binding energy and

---

Table 3. Close Contacts with CH₃ Hydrogens in the Modeled Structures and Olefin Bond Lengths

| model | close contacts | distance (Å) | olefin bond length (Å) |
|-------|---------------|-------------|------------------------|
| alkene C–C | none | none | 1.54 |
| alkene C≡C | none | none | 1.34 |
| SW1 | C–H₆–B11 | 2.89 | 1.340 |
| BN | C–H₆–N74 | 2.90 | 1.456 |
| | C–H₆–B7 | 2.86 |
| | C–H₆–B37 | 2.91 |
| | C–H₆–B2 | 2.95 |
| SW2 | C–H₆–B35 | 2.86 | 1.537 |
| | C–H₆–B2 | 2.81 |
| VN | C–H₆–B35 | 2.84 | 1.566 |
| | C–H₆–N64 | 2.88 |
| | C–H₆–B35 | 2.77 |
| VB | C–H₆–N69 | 2.72 | 1.568 |
| | C–H₆–B34 | 2.80 |

*Both SW1 and SW2 consist of two five-membered rings and two seven-membered rings. SW1 is distorted away from the substrate and SW2 is distorted toward the substrate. *Numbering refers to the model structures provided in the Supporting Information.*

---

Figure 4. TPD of ethene on \( dh \)-BN. The desorption profile is similar to that from defect-laden surfaces.\(^{56,57}\)

Figure 5. Electronic density cross sections plotted along the vertical plane, passing through the center of the two carbon atoms of gas-phase (A) ethene \( (C_2H_4) \), (B) ethane \( (C_2H_6) \), and (C) \( C_2H_4/dh-BN \) for the defects \( B_N \), SW, \( V_N \), and \( V_B \). Contours are drawn in a linear scale (nine contours from 0 to 0.27 e/bohr\(^3\)). It can be seen that the electronic density of ethene on \( dh \)-BN exhibits a similar structure to that of \( C_2H_4 \), indicating a reduction of the bond order of the C–C bond in the adsorbed ethene.

A B₄ defect, its C atoms partially retain their original sp\(^3\) hybridization (C≡C), but when the molecule adsorbs onto an SW, \( V_N \) or \( V_B \) defect, its C atoms rehybridize to sp\(^3\) (C–C), facilitating hydrogenation and desorption of \( C_2H_4 \). The results also hold for the adsorption of propene onto defect-laden BN. Coupled with the previously calculated binding modes of \( H_2 \) on \( h \)-BN \(^{19}\) defects, the data suggests that the hydrogenation
mechanism is closer to the Horiuti–Polanyi mechanism for olefin hydrogenation over metals than that proposed for FLP-catalyzed hydrogenation or acid-zeolite-catalyzed hydrogenation. The significant difference between hydrogen bound to defects on an h-BN sheet and that bound to a metal surface is that the resultant protons bound to the surface are confined to the region by the defect.

It is difficult to unambiguously identify the active site and hydrogenation mechanism. This is mainly due to the fact that there are many possible defects on the surface and due to the dynamic nature of the milling process. On the binding energies of propene, the calculated C=C bond lengths, and the SSNMR data as well as previous studies on the binding of hydrogen to defects in h-BN, it is most likely that hydrogenation occurs over VSN. The calculated binding energy of H2, with a barrier of 0.52 eV, to form a co-adsorption state (with a barrier of 5 meV), followed by dissociative adsorption (Figure 6). The minimum energy path for such a hydrogenation pathway of propene hydrogenation on this defect is shown in Figure 6. The reaction pathway of propene hydrogenation on this defect is shown in Figure 6. The barrier (in electronvolts) for each elementary reaction step is calculated using the climbing image nudged elastic band method and is shown by the number (eV) between the states. The barrier in the minimum energy pathway of propene hydrogenation over VSN is 1.53 eV (148 kJ/mol). The zero potential energy corresponds to propene and hydrogen in the gas phase without any interaction with h-BN. The thick horizontal bars represent intermediate states. *Adsorbed species. The insets are structures of (a) co-adsorbed propene and hydrogen (C3H6* + 2H*) and (b) intermediate state C3H4*.

starts with the practically barrierless adsorption of propene (with a barrier of 5 meV), followed by dissociative adsorption of H2P with a barrier of 0.52 eV, to form a co-adsorption state (C3H6* + 2H*), with a co-adsorption binding energy of 2.22 eV. C3H6* then picks an atomic hydrogen (H*) to form CH2CH2CH3*. This reaction has a barrier of 0.50 eV. C3H6* will then react with the remaining H* to form propane. This reaction faces a large barrier of 1.53 eV (148 kJ/mol). An alternative pathway for forming the co-adsorption state is also calculated. In this pathway, the dissociative adsorption of H2 occurs first, with a barrier of 1.01 eV, followed by the adsorption of propene with a barrier of 0.37 eV. Hydrogenation over a VN has a much larger barrier of 3.67 eV (Figure S22).

It is worth noting that the calculated barriers are low enough for facile reactions under experimental conditions (room temperature and the application of mechanical force). Reactions with activation energies between 95 and 134 kJ/mol have been driven mechanochemically and our computed maximum barrier is not far outside this range. Our calculated barrier lies between that for propene hydrogenation over zeolites (58–90 kJ/mol) and that for hydrogenation of propene over a silica-supported Zn(II) catalyst (191 kJ/mol).

### EXPERIMENTAL SECTION

**Synthesis of dh-BN.** dh-BN was prepared using three methods. For all of these methods, pristine h-BN (Grade PCTFS; Saint-Gobain Ceramic Materials) was first dried at 180 °C under dynamic vacuum for 12 h and transferred to an argon-filled glovebox.

**Method 1.** Approximately 2 g of h-BN was mixed with 0.200 g of lithium (99.9%, Alfa-Aesar) and reacted via high-energy ball milling in an 8000M and/or 8000D SPEX CertiPrep mixer/mill. Milling vials were constructed from 440C stainless steel, with an approximate volume of 65 mL. Buna-N quad o-rings were used to maintain a seal during milling. Kinetic energy was supplied for 30 min with one 12.7 mm stainless steel ball weighing approximately 8.0 g. After 30 min, two additional 12.7 mm stainless steel balls were added, and the reaction was milled for an additional 7.5 h. The resulting lithiated solid was subsequently hydrolyzed using excess H2O to remove Li2N, producing vacancies in the h-BN sheets. The morphology of this dh-BN was examined via scanning electron microscopy (SEM) performed on a Tescan Vega SBH operating at 30 kV (Figure S1d).

**Method 2.** Dry h-BN (20 g) was loaded into a custom pebble mill in an argon-filled glovebox. The milling container was made of 304 stainless steel. Spherical milling media (440C) were added in the following quantities and sizes: (12) 19.1 mm balls, (27) 12.7 mm balls, and (50) 6.35 mm balls. The mill was run at 60 rpm for 96 h under 929 kPa of ultrahigh purity hydrogen. The milling container was transferred to an argon-filled glovebox, and the prepared catalyst powder was removed and stored until use.

**Method 3.** Dry h-BN (5 g) was loaded into a 65 mL zirconia milling vial. Silicone o-rings and a custom clamping mechanism were used to maintain a seal during milling. Kinetic energy was supplied for 30 min with four 12.7 mm zirconia balls weighing approximately 5.97 g each. The material was removed with plastic tools, and at no point in its preparation was it exposed to metal. The resulting defect-laden solid was used for catalysis without further processing. The morphology of this material is shown in the TEM images in Figure S20. It was found that activation by milling alone was just as effective as using lithium. Higher-energy activation (method 3) resulted in shorter induction periods (Figure 2).

**Hydrogenation.** Hydrogenation was performed in a custom pebble mill with gas-tight milling containers made of 304 stainless steel and high alumina (Figure S2). All hydrogenation data presented in this article are from mechanically activated BN.

**Steel.** Two 2.75 in. Conflat flanges (A&N Corporation CF275 flanges with a 1.5 in. bore, 275–162) were welded onto two 1.5 × 3 in.2 conical reducers (A&N Corporation 300X150-WCR) welded large end to end to produce the reaction vessel in Figure S2. Deublin rotary feedthroughs (1005-020-019, 1005 Series, RH and 1005-020-039, 1005 Series, LH) retrofitted with Kalrez o-rings and Krytox lubricant (GPL 105) were used to
maintain gas-tight conditions during operation. The feed-throughs were sealed to two 2.75 in. Conflat flanges with 10–32 tapped-through holes (A&N Corporation; CF275 blank flanges 275-000). The seal between the feedthrough and the flange was maintained with a copper gasket. Stainless steel frits (6–32 threaded) (applied porous materials) were fitted to the tapped entry and exit feedthroughs to eliminate the accumulation of dust in the sealing surfaces of the feedthroughs. The flange seals were maintained with either two silicone or Kalrez o-rings (ASA-223), depending on the substrate being used at the time. Spherical milling media (440C, \( d = 7.67 \text{ g/cm}^3 \)) was added in the following quantities and sizes: (12) 19.1 mm balls, (53) 12.7 mm balls, and (86) 6.35 mm balls.

**Alumina.** Two alumina reactor designs were implemented. A small ceramic-lined reactor with straight sides was constructed by boring holes in the bottom and lid of a high-alumina crucible (99.8%, Part #65540; CoorsTek). The crucible was used to line a steel reactor with parallel walls and Conflat flanges. A high-temperature room temperature vulcanizing sealant (tin-cured) was used to seal the crucible lid onto the body. The steel frits were replaced with glass filters. Spherical milling media (yttria-stabilized zirconia, \( d = 6 \text{ g/cm}^3 \), Inframat Advanced Materials LLC) was added in the following quantities and sizes: (5) 19.1 mm balls, (15) 12.7 mm balls, and (50) 6.35 mm balls. A duplicate of the steel reactor, with a high alumina content (99.8%) and 6 mm walls, was manufactured by CoorsTek, Inc. Titanium flanges with the same dimensions as those of the steel flanges, except that the Conflat knife edge was replaced by an o-ring groove, were machined. Titanium was chosen to match the coefficient of thermal expansion of the alumina body and reduce the risk associated with incorporation of catalytically active metals. The titanium flanges were anodized to reduce the possibility of hydrogen embrittlement. The flanges were sealed to the alumina body using Cotronics Duralco 4700 two-part epoxy. A 1 mm thick polytetrafluoroethylene (PTFE) shield was placed between the frit body and the flange to eliminate the interaction of the media with the flange material. The steel frit was covered with a piece of tensioned silicone tube (i.d. = 6.35 mm) to prevent the media from interacting with the steel of the frit. Spherical milling media (yttria-stabilized zirconia, \( d = 6 \text{ g/cm}^3 \), Inframat Advanced Materials LLC) were added in the following quantities and sizes: (12) 20 mm balls, (53) 12.7 mm balls, and (86) 6.35 mm balls. Before any hydrogenation, the media and reactor interior were washed with concentrated nitric acid and rinsed three times with ultrapure water.

**Control.** Temperature was controlled with an Omega CN3000 process controller and a K-type thermocouple spring mounted to the inlet flange. A wound NiChrome heating element embedded in a shaped firebrick applied heat. The pressure was monitored with a NOSHOK pressure transducer and controlled with a MicroMod 53MC5000 loop controller. The mill’s rotational speed was controlled with a 1/3 hp variable speed DC motor coupled to the reactor with a steel drive chain.

**Reactions.** Hydrogenations were performed with 5 g of substrate and varying quantities of catalyst (trace to 7.5 g of \( dh\)-BN). Hydrogenations were performed with 5 g of substrate and trace to 7.5 g of \( dh\)-BN. Trace quantities of \( dh\)-BN were introduced into the reactor by suspending 1 g of \( dh\)-BN in 200 mL of dry acetone and pouring it over the milling media. The wet media were then dried at 100 °C. The substrates investigated were as follows: propene \([1]\) (Worthington Industries, 95%), allyl bromide (Fisher Scientific, 99%), allyl butyl ether (Sigma-Aldrich, 90%), phenylmethacrylate (Acros Organics, 99%), cyclohexene \([2]\) (Fisher Scientific), octadec-1-ene \([3]\) (Acros Organics 90%), \( d\)-limonene (Florida Chemical, technical grade), 1,1-diphenylethene \([4]\) (Sigma-Aldrich, 97%), (Z)-1,2-diphenylethene \([5]\) (Alfa-Aesar 97%), (E)-1,2-diphenylethene \([6]\) (Sigma-Aldrich, 96%), (E)-cinnamic acid \([7]\) (Eastman, Practical Grade), (9Z)-Octadec-9-enoic acid \([8]\) (Fisher Scientific, Lab Grade), benzylidenecacetophenone \([9]\) (Acros Organics, 97%), and eugenol \([10]\) (clove bud oil, Nature’s Alchemy, 80–90%).

**Mechanically Similar Blanks.** Dry graphite and dry graphitic carbon nitride (\([C_3N_4]\)) were used as blanks, with mechanical properties similar to those of BN. Graphitic carbon nitride was prepared by heating 10 g of dicynandiamide (Alfa Aesar 99%) for 1 h in air at 500 °C. Two grams of each compound was loaded into the reactor in an argon-filled glovebox. Hydrogenation activity was examined by milling 20 g of (E)-cinnamic acid \([7]\) with 2 g of processed graphite at 170 °C, pressures between 446 and 1135 kPa, and rotary speeds of 66 rpm. Hydrogenation of propene with graphitic carbon nitride was investigated by milling 2 g of \( g\)-\( C_3N_4 \) at 425 kPa of an equimolar mixture of hydrogen and propene at 20 °C.

**Active Sites.** Active sites were measured by loading the steel reactor with 5 g of \( dh\)-BN and pressurizing to 345 kPa with propane, propene, hydrogen, or argon. Surface adsorption produced a measurable pressure loss. No pressure loss was observed for argon, and it was minimal for hydrogen. Both propane (which is expected to physisorb) and propene (which is expected to chemisorb as well as physisorb) showed pressure loss with more loss observed using propene (Figure S3).

**Surface Area.** Brunauer–Emmett–Teller surface area testing was performed with a Micromeritics Tristar II 3020 instrument at 77 K. Before measurement, each sample was evacuated on a Smart Vac Prep for 5 h at 50 °C. The surface areas of pristine, defect-laden, and propene-adsorbed defect-laden BN were measured.

**TPD.** The TPD experiment was carried out with an Altamira AMI-200 instrument, using ethene as an adsorbed gas.

**SSNMR.** All SSNMR spectra were acquired on a 500 MHz Agilent narrow-bore spectrometer operating at 125.68 MHz. A 1.6 mm Agilent T3 probe was employed using a spinning speed of 12.0 kHz. A \(^1\)H pulse width of 1.0 \( \mu \text{s} \) was utilized, followed by a conventional (i.e., constant amplitude) cross-polarization step, with a time of 3 ms. SPINAL \(^1\)H decoupling at a frequency of 499.78 MHz was employed using a 165 \( \mu \text{s} \) pulse of 1.84 \( \mu \text{s} \). Both spectra were acquired using spectral widths of 29.8 kHz, acquisition times of 17.2 ms, and recycle times of 15 s to avoid sample heating. The digital resolution acquired for each spectrum was of 58.1 Hz/pixel.

**Coking.** After use in hydrogenation, the \( dh\)-BN exhibited a color change from white to brown (Figure S14a). The color deepened at elevated reaction temperatures, with little observed color change for propene hydrogenations performed at room temperature. This color change was due to the incorporation of carbon compounds. This coking was highly fluorescent (Figure S14b). TGA was performed on a TA Instruments model, 2050 TGA. The results for coked and pristine materials are shown in Figure S14c.

**Gas Chromatography (GC) with Mass-Sensitive Detection.** GC–MS spectrometry (MS) analysis was performed on an Agilent 6890 GC, with an Agilent 7000B-433E HP-5MS column (5% phenyl methyl siloxane, 30 m × 250 \( \mu \text{m} \)).
× 0.25 μm nom.) coupled with a 5975C VL mass-selective detector. Samples were extracted from the reactor, dissolved in dichloromethane, and filtered through a Whatman 0.2 μm PTFE syringe filter before injection. Quantitation of the (E)-cinnamic acid [7] hydrogenation products was performed using external standard solutions of (E)-cinnamic acid [7] (Eastman, Practical Grade) and hydrocinnamic acid (Acrors Organics, 99%) in dichloromethane.

Gas samples from propene [1] hydrogenation experiments were obtained by venting the reactor into a 50 mL serum vial crimp sealed with a PTFE-lined septum. Gas was introduced via a 22 gauge needle attached to the vent line and an additional 22 gauge exit needle that was properly vented. Quantitation of the propene/propane ratios was performed using external standards consisting of mixtures of propene and propane.

**ICP-AES.** ICP-AES was performed by Saint-Gobain Advanced Ceramics. Samples of boron nitride before and after activation were digested in an oxygen bomb and analyzed for iron and nickel.

**X-ray Photoelectron Spectra (XPS).** XPS were recorded on a Physical Electronics 5400 photoelectron spectrometer with a magnesium source. The spectra of the carbon 1s region is presented in Figure S14d.

**XRD.** PXRD was performed using a Rigaku Multiflex theta–theta powder X-ray diffractometer with a copper source (Cu Kα = 1.5418 Å). Diffractograms were collected from 5 to 80° 2θ using 0.010° steps and a 0.3 s dwell time. Size and strain were analyzed by applying the method of integral breadths70 and constructing a Williamson–Hall plot. Sheet parallel and perpendicular diffraction peaks were analyzed separately to obtain in-sheet size and strain and intersheet ordering.

**TGA and DSC.** Pristine, defect-laden, and propene-adsorbed BN samples were studied with TA Instruments 2950 TGA and 2920 DSC. Propene-adsorbed samples were prepared by loading a 500 mL pressure cell with 2 g of material in an argon-filled glovebox. The pressure cell was then removed and filled with 310.3 kPa of propene. The sample was allowed to equilibrate for 3 days and then removed from the cell and stored in an argon-filled glovebox. TGA samples were stored in argon-filled vials and loaded into the sample pan in air. TGA runs were performed under flowing air. DSC samples were loaded into unsealed aluminum pans under argon and loaded into the DSC cell in air. All defect-laden samples were found to retain their propene even after extended storage at 1 atm.

**Discrete Element Modeling (DEM).** DEMs of the milling process were generated using EDEM (DEM Solutions Ltd.). The geometry and composition of the reaction vessel was investigated using DEM. Three reaction vessels were investigated: steel (Figure S15a, left), one with a high alumina content and sloped sides (Figure S15a, center), and one with a high alumina and straight sides (Figure S15a, right).

**TOF.** TOFs were estimated using the minimum of the derivative of each substrate’s hydrogen uptake curve as the maximum rate of hydrogenation.

**Computational Details.** DFT calculations were performed to evaluate the binding energies and electronic structure of the C3H4 molecule on defective boron nitride single layers employing the formalism of the vdW-DF71–74 as implemented in the VASP code.75 In this formalism, the exchange-correlation energy is calculated as $E_{XC} = E_{XC}^\text{GGA} + E_C^\text{revPBE}$, where $E_{XC}^\text{GGA}$ is a semilocal exchange functional from the revised generalized-gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof functional (revPBE),75 $E_C^\text{revPBE}$ is the local correlation energy described within the local density approximation, and $E_{XC}^\text{GGA}$ is the nonlocal correlation energy, as described by Dion et al.61 The efficient algorithm proposed by Román–Pérez and Soler76 is responsible for making the computation feasible for systems such as ours, which contain a large number of atoms in the calculational super cell. The projector augmented wave scheme77,78 is utilized, with the potentials taken from the potential library provided with VASP. The electronic wave functions were expanded in a plane wave basis set, with a cutoff of 500 eV. Given the size of the super cell, a single k-point (Γ) was deemed adequate to sample the Brillouin zone of a (6 × 6) BN slab with 15 Å vacuum on top of it. The systems were optimized so that all force components acting on each atom are smaller than 0.01 eV/Å. The lattice parameters of h-BN were optimized to be 2.523 Å (in agreement with the experimental value of 2.505 Å79). No temperature or pressure effects were included in our DFT calculations.

**Binding Energies.** The binding energy is calculated using the formula $E_{BE} = E_{\text{system}} - (E_{\text{mol}} + E_{\text{def}})$, where $E_{\text{system}}$, $E_{\text{mol}}$, and $E_{\text{def}}$ are the total energy of the molecule on the substrate, of the molecule alone, and of the defective h-BN substrate, respectively.

# CONCLUSIONS

A new metal-free heterogeneous hydrogenation catalyst has been realized through the introduction of defects into h-BN sheets. Stoichiometric yields were obtained for both simple olefins (propene [1]) and complex olefins (benzylideneacetophenone [9]), with TOFs 1–2 orders of magnitude higher than those for catalytic hydrogenation of the same olefin over metal-free FLPs and graphene catalysts. Superior selectivity was observed, with minimal dehydrogenation and no cracking products produced at low temperatures. Through the application of a metal-free reactor, we confirmed that the observed hydrogenation is due to dh-BN and not due to the introduced metal impurities. DFT calculations show that the olefinic bond in ethene and propene is weakened over four types of defect sites: boron substitution for nitrogen ($\text{B}_n\text{N}$), nitrogen ($\text{V}_\text{N}$) vacancies, boron ($\text{V}_\text{B}$) vacancies, and SW defects. The binding energy for olefins and hydrogen at the $\text{V}_\text{N}$ defect is at par with that of metals currently used for catalytic hydrogenation. It is most likely that the majority of catalytic activity is due to $\text{V}_\text{N}$ defects. The use of metal-free hydrogenation catalysts will reduce the risks associated with the incorporation of metals into hydrogenation products.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00315.

Scanning electron microscope images, propene and propane absorption curves, reactor configuration, discrete element model results, postreaction catalyst characterization, h-BN vacancy description, charge density maps, structure files for propene interacting with defects (PDF)

Crystal data (CIF)

Movie of a simulation of media tumbling in a steel reaction vessel (AVI)
AUTHOR INFORMATION

Corresponding Author
*E-mail: Richard.Blair@ucf.edu.

ORCID
Zhan Yong Li: 0000-0002-3230-5955
Omar K. Farha: 0000-0002-9904-9845
Richard G. Blair: 0000-0002-8208-9787

Author Contributions
The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript. All authors contributed equally.

Funding
D.J.N., D.T.R., N.S.P., K.E.G., R.A.P., and R.G.B. contributed to synthesis and catalytic characterization in this work, which was partially supported by USA AFRL, through grant FA8650-11-C-2127, and the NSF, through CHE-1465105. D.L., M.A., and T.S.R. contributed DFT calculations in this work, which was funded by DOE grant DE-FG02-07ER15842. J.K.H contributed to SSNMR characterization of the catalyst which was partially supported by the NSF through CHE-1455159 and calculations were carried out at UCF's high-performance computational facility STOKES and at the Extreme Science and Engineering Discovery Environment (XSEDE) resources (project DMR13009).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors thank Dr. Masa Ishagami of the University of Central Florida Physics department for assistance with SEM. DEM software was obtained under the DEM Solutions EDEM Academic Partner Program (EAPP). The authors thank Dr. Nina Orlovskaya of the University of Central Florida Physics department for assistance with SEM. The authors thank Dr. Nina Orlovskaya of the University of Central Florida Physics department for assistance with SEM. The authors thank Dr. Nina Orlovskaya of the University of Central Florida Physics department for assistance with SEM. The authors thank Dr. Nina Orlovskaya of the University of Central Florida Physics department for assistance with SEM.

DEDICATION
This work is dedicated to the memory of Cynthia Blair (1947–2013).

REFERENCES
(1) Bullock, M. R. Front Matter. In Catalysis without Precious Metals; Bullock, M. R., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2010; pp I–XVIII.
(2) Stephan, D. W.; Greenberg, S.; Graham, T. W.; Chase, P.; Hastie, J. J.; Geier, S. J.; Farrell, J. M.; Brown, C. C.; Heiden, Z. M.; Welch, G. C.; Ulrich, M. Metal-Free Catalytic Hydrogenation of Polar Substrates by Frustrated Lewis Pairs. Inorg. Chem. 2011, 50, 12338–12348.
(3) Irandoni, S.; Edvardsson, J. Poisoning of nickel-based catalysts in fat hydrogenation. J. Am. Oil Chem. Soc. 1993, 70, 1149–1156.
(4) Anwa, F.; Kazi, T. G.; Salem, R.; Bhangar, M. I. Rapid determination of some trace metals in several oils and fats. Grasas Aceites (Sevilla, Spain) 2004, 55, 160–168.
(5) Cempel, M.; Nielk, G. Nickel: A review of its sources and environmental toxicology. Pol. J. Environ. Stud. 2006, 15, 375–382 http://www.pjoes.com/abstracts/2006/Vol15/No03/02.html.
(6) Select Committee on GRAS Substances (SCOGS) Opinion: Nickel (elemental); SCOGS-Report Number: 97; U.S. Food and Drug Administration: Washington, D.C., 1979. http://www.fda.gov/Food/IngredientsPackagingLabeling/GRAS/SCOGS/ucm260909.htm.
(7) Bertelsen, S.; Jorgensen, K. A. Organocatalysis-after the gold rush. Chem. Soc. Rev. 2009, 38, 2178–2189.
(8) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. Science 2006, 314, 1124–1126.
(9) McCallih, J. S. J.; Welch, G. C.; Stephan, D. W. Reactivity of “frustrated Lewis pairs”: three-component reactions of phosphines, a borane, and olefins. Angew. Chem., Int. Ed. Engl. 2007, 46, 4968–71.
(10) Stephan, D. W. Frustrated Lewis Pairs. J. Am. Chem. Soc. 2015, 137, 10018–32.
(11) Stephan, D. W. Frustrated Lewis Pairs: From Concept to Catalysis. Acc. Chem. Res. 2015, 48, 306–316.
(12) Stephan, D. W.; Erker, G. Frustrated Lewis pair chemistry: development and perspectives. Angew. Chem., Int. Ed. Engl. 2015, 54, 6400–41.
(13) Dureen, M. A.; Stephan, D. W. Terminal alkyn activation by frustrated and classical Lewis acid/phosphine pairs. J. Am. Chem. Soc. 2009, 131, 8396–7.
(14) Stephan, D. W. Frustrated Lewis pairs: a new strategy to small molecule activation and hydrogenation catalysis. Dalton Trans. 2009, 17, 3129–3136.
(15) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. Tuning Lewis acidity using the reactivity of “frustrated Lewis pairs”: facile formation of phosphine-boranes and cationic phosphonium-boranes. Dalton Trans. 2007, 31, 3407–3414.
(16) Greb, L.; Ortiz-Burgos, P.; Schirmer, B.; Grimmke, S.; Stephan, D. W.; Paradies, J. Metal-free Catalytic Olefin Hydrogenation: Low-Temperature H2 Activation by Frustrated Lewis Pairs. Angew. Chem., Int. Ed. Engl. 2012, 51, 10164–10168.
(17) Chemichenko, K.; Madarasz, Á.; Pápai, I.; Nieder, M.; Leskelä, M.; Repo, T. A frustrated-Lewis-pair approach to catalytic reduction of alkynes to cis-alkenes. Nat. Chem. 2013, 5, 718–723.
(18) Ghuman, K. K.; Hoch, L. B.; Szymanski, P.; Loh, J. Y. Y.; Kherani, N. P.; El-Sayed, M. A.; Saleem, R.; Bhanger, M. I. Rapid, selective hydrogenation of acetylene hydrogenation and alkene hydrogenation. Dalton Trans. 2009, 17, 3129–3136.
(19) Stephan, D. W. Frustrated Lewis Pairs: From Concept to Catalysis. Acc. Chem. Res. 2015, 48, 306–316.
(20) Primo, A.; Neatu, F.; Florea, M.; Parvulescu, V.; Garcia, H. Graphenes in the absence of metals as carboxylates for selective acetylene hydrogenation and alkene hydrogenation. Nat. Commun. 2014, 5, No. 5291.
(21) Behrens, M.; Studt, F.; Kasatkin, I.; Kuhl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girsedtes, F.; Kurr, P.; Kniep, B.-L.; Tovar, M.; Fischer, R. W.; Norskov, K. J.; Schiøtt, R. The Active Site of Methanol Synthesis over Cu/ZnO/Al2O3 Industrial Catalysts. Science 2012, 336, 893–897.
(22) Polarz, S.; Strunk, J.; Ischenko, V.; van den Berg, M. W. E.; Hinrichsen, O.; Muhler, M.; Driess, M. On the role of oxygen defects in the catalytic performance of zinc oxide. Angew. Chem., Int. Ed. Engl. 2006, 45, 2965–2969.
(23) Voorhoeve, R. J. H.; Demeijer, R. J. P.; Trimble, L. E. Defect chemistry and catalysis in oxidation and reduction over perovskite-type oxides. Am. N. Y. Acad. Sci. 1976, 272, 3–21.
(24) Ralphy, K.; Hardacre, C.; James, S. L. Application of heterogeneous catalysts prepared by mechanochemical synthesis. Chem. Soc. Rev. 2013, 42, 7701–7718.
(25) Immohr, S.; Felderhoff, M.; Weidenhauer, C.; Schüth, F. An Orders-of-Magnitude Increase in the Rate of the Solid-Catalyzed CO Oxidation by In Situ Ball Milling. Angew. Chem., Int. Ed. Engl. 2013, 52, 12688–12691.
(26) Wu, J. C. S.; Cheng, T.-S.; Lai, C.-L. Boron nitride supported PtFe catalysts for selective hydrogenation of crotonaldehyde. Appl. Catal., A 2006, 314, 233–239.
(69) Schweitzer, N. M.; Hu, B.; Das, U.; Kim, H.; Greeley, J.; Curtiss, L. A.; Stair, P. C.; Miller, J. T.; Hock, A. S. Propylene Hydrogenation and Propane Dehydrogenation by a Single-Site Zn²⁺ on Silica Catalyst. *ACS Catal.* 2014, 4, 1091–1098.

(70) Klug, H. P.; Alexander, L. E. Method of Integral Breadths. In *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; John Wiley & Sons: New York, 1974; pp 661–665.

(71) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6, 15–50.

(72) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1996, 54, 11169–11186.

(73) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1993, 47, 558–561.

(74) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Phys. Rev. B* 1994, 49, 14251–14269.

(75) Zhang, Y.; Yang, W. Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.* 1998, 80, 890.

(76) Román-Pérez, G.; Soler, J. M. Efficient Implementation of a van der Waals Density Functional: Application to Double-Wall Carbon Nanotubes. *Phys. Rev. Lett.* 2009, 103, No. 096102.

(77) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1994, 50, 17953–17979.

(78) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1999, 59, 1758–1775.

(79) Paszkowicz, W.; Pelka, J. B.; Knapp, M.; Szyszko, T.; Podsiadlo, S. Lattice parameters and anisotropic thermal expansion of hexagonal boron nitride in the 10–297.5 K temperature range. *Appl. Phys. A: Mater. Sci. Process.* 2002, 75, 431–435.