ABSTRACT: The Haber–Bosch process is the main industrial method for producing ammonia from diatomic nitrogen and hydrogen. We use a combination of ab initio thermochemical analysis and reactive molecular dynamics to demonstrate that a significant increase in the ammonia production yield can be achieved using hydroxylated graphene and related species. Exploiting the polarity difference between N2/H2 and NH3, as well as the universal proton acceptor behavior of NH3, we demonstrate a strong shift of the equilibrium of the Haber–Bosch process toward ammonia (ca. 50 kJ mol⁻¹ enthalpy gain and ca. 60–70 kJ mol⁻¹ free energy gain). The modified process is of significant importance to the chemical industry.

The Haber–Bosch process consumes high amounts of energy; therefore, it is economically demanding. Depending on the particular technology, the synthesis takes place at 700–900 K and 200–400 bar. Maintaining both high temperature and high pressure for the ammonia synthesis worldwide consumes 1–2% of all energy generated by humans.8 A fundamental scientific finding or an engineering development that can either improve the reaction yield and the catalyst performance, or adjust the synthesis conditions, will have great global significance.

Despite the extreme simplicity of the chemical reaction, N₂ + 3H₂ ↔ 2NH₃, the process appears highly resistant to technological optimization. On the basis of the purely thermodynamic considerations, ammonia should be spontaneously synthesized at room conditions. In reality, the rate of this reaction is so low that it can be scarcely observed. The primary reason is that the ternary nitrogen–nitrogen bond, 942 kJ mol⁻¹, must be broken prior to binding three hydrogen atoms. This slowest step determines the overall reaction rate. Metal catalysts are employed to create transition complexes with molecular nitrogen fostering its dissociation.9

The Pursuit Continues. Many catalysts for ammonia synthesis have been introduced since the Haber–Bosch process was implemented on an industrial scale. Iron, cobalt, ruthenium, molybdenum, cerium, and carbon containing compounds with admixtures of potassium, calcium, aluminum, and silicon have been proposed at different times.10 Many of these catalysts themselves require high temperatures, ca. 700 K, to act efficiently in relation to N₂. Dinitrogen is expected to undergo dissociative adsorption on the catalyst surface to provide N°. Afterward, each N° reacts with 1.5H₂ to produce NH₃. Ultimately, NH₃ leaves the catalyst surface under the pressure of other nitrogen molecules. The tools employed to cleave the nitrogen–nitrogen triple bond can be divided into three groups: (1) reductive catalysts, which provide electrons to N₂ (this type of activation occurs in the Haber–Bosch process); (2) oxidative catalysts, which take electrons away from N₂ (no such catalysts have been developed to date, because the first ionization energy of N₂ is high); and (3) extreme conditions, such as high voltage, plasma treatment, and photoinduced electron excitation: N₂ → 2N°, N₂ → 2N° + e. The last method consumes excessive amounts of energy, preventing its cost-efficient industrial implementation. Several novel catalysts allow one to adjust somewhat the reaction temperature and pressure, e.g. Ru/C catalysts,11 Ru/C₁₂A₁₂⁻ with the highly electron donating 12CaO-7Al₂O₃ support,12 metal complexes inducing hydrogenation at ambient conditions,13 and the proton-conducting cell reactor,14 photocatalysts,15 etc.

While the main research efforts are concentrated on the development of catalysts able to increase the rate of N₂ cleavage, another fundamental option to adjust ammonia yield has been largely omitted. The N₂ + 3H₂ ↔ 2NH₃ process constitutes a relatively nonabundant type of chemical reaction, in which two nonpolar particles form one strongly

Received: May 30, 2016
Accepted: June 24, 2016
Published: June 24, 2016

© 2016 American Chemical Society
polar particle. Indeed, N₂ and H₂ have no dipole moments, while the dipole moment of NH₃ is 1.4 D. This is much larger than the dipole moment of phosphine, 0.58 D, the phosphorus analog of ammonia. Furthermore, ammonia is a universal proton acceptor. This property is rarely utilized during its numerous reactions with organic compounds. If the newly formed NH₃ molecules are provided an opportunity to interact with a proton-donating group, the reaction thermodynamics can change significantly, strongly affecting the equilibrium constant and enabling higher NH₃ yields.

We use ab initio quantum chemistry and reactive chemical dynamics simulations to demonstrate up to a 9% increase of the ammonia yield in the Haber–Bosch process using hydroxylated graphene quantum dots (GQDs, Figure 1). The reported simulations of the ammonia synthesis reaction from molecular nitrogen and molecular hydrogen were performed by the RMD method. RMD employs quantum chemistry (QC)-based reactive force fields (ReaxFF). The methodology was applied previously with considerable success to address complicated problems in organic chemistry and catalysis. ReaxFF provides a realistic description of reactive potential surfaces for many-component systems. It allows one to reproduce bond formation and breaking without optimizing the corresponding wave functions. Simulations including a few thousands of interaction centers are within reach of RMD. The instantaneous electrostatic point-charge residing on each atom is evaluated from the instantaneous electrostatic field. Interaction between two charged particles is represented as a shielded Coulomb potential. The instantaneous valence force and interaction energy are determined through the instantaneous electrostatic field.

The recent G4 theory offers an effective chemical accuracy of the thermodynamic quantities in the gas phase, such as enthalpy, entropy, Gibbs free energy, heat of formation, heat capacity, etc. G4 is based on a series of energy evaluations, as well as a thorough geometry optimization at the beginning. The G4MP2 method is a variation of G4, wherein MP3 and MP4 levels of theory are avoided to decrease the computational cost, in particular the computer memory requirement. G4MP2 still includes an effect of electron correlation, because electron correlation is important for deriving accurate molecular partition functions. The average absolute deviation from the experimental data, evaluated over a large test set (454 energies) equals 4.3 kJ mol⁻¹. This accuracy is considered good for chemical applications, including the Haber process, exceeding that of the earlier methods. The G4MP2 method is still expensive and can hardly be applied to large (and periodic) systems, such as nanotubes, graphene, quantum dots, and biomolecules. The implementations of G4 and G4MP2 are available in the GAMESS quantum chemistry suite.

The Journal of Physical Chemistry Letters

Figure 1. Molecules participating in the synthesis of ammonia: (a) ammonia, NH₃; (b) diammonia, N₂H₆; (c) hydrazine, N₂H₄; (d) diazene, N₂H₂; (e) GQD; (f) hydroxylated GQD-I; (i) hydroxylated GQD-II; and (j) elementary cell for ammonia synthesis.

Hydroxylated graphene provides the polar environment shifting the equilibrium toward the product, while at the same time remaining intact under the investigated thermodynamic conditions, including 298–1300 K and 1–1000 bar. The achieved thermodynamic advantage remains nearly constant over these temperature and pressure ranges. The closely related alcohols, CₓH₂Oₓ, do not react with NH₃ (K ≪ 1), because the NH₃ leaving group, which is the conjugate base of NH₄⁺, is much stronger than the OH⁻ leaving group, which is the conjugate base of H₂O. Despite a strong interaction, the aminated GQD is not formed, leaving NH₃ intact, as necessary. Nonpolar dinitrogen and dihydrogen remain indifferent to the hydroxylated GQD, and the thermodynamic equilibrium is shifted from the reactants to the product; 50 kJ mol⁻¹ enthalpy and 60–70 kJ mol⁻¹ free energy gains are achieved.

The enhancement of the yield of the ammonia synthesis via the Haber process has been demonstrated by two independent techniques. The thermodynamics of the process have been investigated by the highly accurate ab initio Gaussian-4 (G4) theory. The kinetic details of the chemical reaction have been investigated further using reactive molecular dynamics (RMD).

The recent G4 theory offers an effective chemical accuracy of the thermodynamic quantities in the gas phase, such as enthalpy, entropy, Gibbs free energy, heat of formation, heat capacity, etc. G4 is based on a series of energy evaluations, as well as a thorough geometry optimization at the beginning. The G4MP2 method was used to obtain the thermodynamic quantities by a sequence of the predefined procedures. The equilibrium N(NH₃)−H(OH) distance amounts to 1.87 Å, which significantly exceeds the 1.02 Å N−H bond length in NH₃. The distance of 1.87 Å qualifies for a hydrogen bond.
angles involving the hydrogen bond, H–N–H, are 105°, 115°, and 116°, while the H–N–H angles in the coordinated NH₃ are 107° each. The hydrogen bond brings a significant energy gain favoring the forward reaction, ca. 50 kJ mol⁻¹ of enthalpy and ca. 60–70 kJ mol⁻¹ of free energy.

Generation of NH₃ from H₂ and N₂ is exothermic. According to the Châtelier’s principle, temperature increase is unfavorable because it shifts the equilibrium toward the reactants. At the same time, the reaction is too slow at room temperature; hence, higher temperatures accelerate reaction kinetics and approach to the chemical equilibrium. Formation of NH₃ decreases the number of gas molecules in the reaction mixture, and hence pressure, by a factor of 2. Thus, an increased pressure shifts the equilibrium toward the products and is favorable for the ammonia synthesis. These considerations are confirmed by computational thermodynamics (Figures 2 and 3), both with and without the hydroxylated GQD.

Low temperature and high pressure constitute the ideal thermodynamic conditions for the NH₃ synthesis. Note that generation of high pressure is expensive in many aspects, especially on the industrial scale. Pipes and reaction vessels have to be strengthened. High-quality valves are needed. Running pumps and compressors takes considerable amounts of energy. Working at 200 bar and above requires extra safety precautions. A balance between reaction yield and operation expenses has to be found for the synthesis to be cost efficient. The industry considers a single pass to be efficient if it yields ca. 15% of the product. Multiple cycles are conducted to achieve an acceptable nitrogen conversion degree, above 90%. If the equilibrium in every cycle is shifted to the products, as suggested by the thermodynamics analysis of Figures 2 and 3, the resulting performance gain will be very significant.

To support our thermodynamic predictions with realistic, many-particle systems, we carried out RMD simulations using the force field model provided by van Duin and co-workers. The parametrization of the method is based on reproducing a potential energy surface relevant to the chemical reactions in question using multiple density functional theory calculations. Each simulated system consisted of ca. 1000 atoms, including 100 dinitrogen and 300 dihydrogen molecules (Figure 1j). The N₂ + 3H₂ ↔ 2NH₃ reaction is very slow, and establishing thermodynamic equilibrium takes macroscopic times. Therefore, the RMD simulations were conducted at 1500 K with the reactant mixture density of 710 kg m⁻³. If needed, the results can be extrapolated to the conditions of interest. The equations-of-motion were propagated with a 0.0001 ps time-step, and each system was simulated during 100 ps, achieving a sampling of 1 000 000 molecular configurations.

Nitrogen molecules decompose quickly at the elevated temperature (Figure 4). After 60 ps of the RMD simulation, their content is below 10 mol %, while over 20 mol % of hydrogen molecules are still available. Significant amounts of diazene and hydrazine are generated. The N₂H₂ content reaches maximum at around 20 ps and then slowly decreases. In turn, the content of N₂H₄ versus time exhibits no maximum. In most cases, the difference between the systems with and without the hydroxylated GQD can be seen. Note that the reaction is simulated without the metallic catalyst, for simplicity, because the catalyst does not impact the reaction equilibrium.

Real-time visual examination and statistical analysis, such as that presented in Figure 4, allows us to assign the following mechanism to the simulated reaction. Dihydrogen attaches to dinitrogen forming various chains of low stability (such as ...H–H–N≡N–H–H...). The triple bond in N₂ is hereby substituted by the double bond. These chains quickly break down generating N₂H₂. According to Figure 4, N₂H₂ molecules are formed already during the initial simulation steps. An additional H₂ molecule binds to N₂H₂ shortly after, to generate N₂H₄ which finally consumes a third H₂ molecule and transforms into N₂H₆. Diammonia N₂H₆ is unstable and can be observed only for a few femtoseconds before it cleaves into two NH₃ molecules.

The presence of the hydroxylated GQD is not favorable for the last N₂H₄ + H₂ → N₂H₆ → 2NH₃ transformation, because N₂H₄ is more polar, μ = 1.85 D, than NH₃ and it also interacts with the OH groups. However, this reaction is strongly favorable energetically, ΔG = −291 kJ mol⁻¹, at ambient conditions. The overall NH₃ yield is dependent on the presence of the hydroxylated GQD (Figure 4a). It increases from 33 to 38% when a single hydroxylated GQD (Figure 1f,i) is provided and to 44% when two hydroxylated GQDs are provided. To isolate the impact of the GQD itself, we simulated a pristine
GQD (Figure 1e) and observed the same yield, 33%, as in the case of the bulk mixture. Thus, the reaction equilibrium gets shifted because of the hydroxyl groups, while the GQD acts exclusively as a matrix/support. We also compared GQDs with higher (Figure 1f) and lower (Figure 1e) content of hydroxyl groups. It was observed that both GQDs provide comparable NH₃ yields, ca. 38%. We found that a small distance separating the hydroxyl groups, such as in Figure 1f, favors intramolecular hydrogen bonding, being therefore inefficient. This conclusion is also confirmed by the RMD simulation of the two hydroxylated GQDs. When the distance between the hydroxylated GQDs was fixed at 10 Å, the yield was 44%. In turn, when they were allowed to approach one another, the yield dropped to 35%, which is only modestly higher than that in the bulk mixture.

The theoretical threshold of the reaction yield can be calculated from the thermochemical results via the following formula,  
\[ K = \exp(-\Delta G/RT) \]

where \( K \) is the equilibrium reaction constant and \( R \) is the gas constant; \( T \) is temperature, and \( \Delta G \) is the free energy change. Compare \( \Delta G = +35.7 \) kJ mol\(^{-1}\) at 800 K and 100 bar (similar to the technological conditions) without the hydroxylated GQD and \( \Delta G = -29.1 \) kJ mol\(^{-1}\) with the hydroxylated GQD at the same temperature and pressure. Consequently, the corresponding equilibrium constants differ by more than a factor of 10 000.

The proposed method allows one to adjust reaction conditions appropriately. It does not substitute or compete with the metallic catalysts to cleave N₂. The metallic catalysts do not contain polarized hydrogen atoms, which would interact strongly with NH₃. Additionally, the topology of the metal catalysts is not optimal for hosting multiple hydroxyl groups. Graphene or GQDs can be decorated with multiple hydroxyl groups, which would be evenly distributed not only at the edge positions but also throughout the surface. This material is easily fabricated from graphite oxide. The latter is obtained by acting with potassium permanganate on graphite, which subsequently exfoliates. It is a standard method to oxidize organic compounds. The hydroxylated graphene can be arranged in layers to maximize its working surface area. It is particularly beneficial in practice that the hydroxylated graphene does not chemically modify ammonia.

The industrial advantages of the demonstrated approach depend on other factors, besides the reaction yield. It is important that the demonstrated yield enhancement holds over a broad temperature and pressure range. Other factors include energy, material cost, and manufacturability. While graphene and its derivatives, including hydroxylated graphene, are expensive, graphite oxide and related compounds are very affordable. The demonstrated principle will hold with these cheaper alternatives. All other factors, including the energy expense, catalyst use, multiple conversion cycles, etc. should remain similar as in the current technology.

To recapitulate, we introduced a new method for controlling ammonia synthesis by exploiting differences in the polarities of GQD (Figure 1e) and observed the same yield, 33%, as in the case of the bulk mixture. Thus, the reaction equilibrium gets shifted because of the hydroxyl groups, while the GQD acts exclusively as a matrix/support. We also compared GQDs with higher (Figure 1f) and lower (Figure 1e) content of hydroxyl groups. It was observed that both GQDs provide comparable NH₃ yields, ca. 38%. We found that a small distance separating the hydroxyl groups, such as in Figure 1f, favors intramolecular hydrogen bonding, being therefore inefficient. This conclusion is also confirmed by the RMD simulation of the two hydroxylated GQDs. When the distance between the hydroxylated GQDs was fixed at 10 Å, the yield was 44%. In turn, when they were allowed to approach one another, the yield dropped to 35%, which is only modestly higher than that in the bulk mixture.

The theoretical threshold of the reaction yield can be calculated from the thermochemical results via the following formula, \( K = \exp(-\Delta G/RT) \), where \( K \) is the equilibrium reaction constant and \( R \) is the gas constant; \( T \) is temperature, and \( \Delta G \) is the free energy change. Compare \( \Delta G = +35.7 \) kJ mol\(^{-1}\) at 800 K and 100 bar (similar to the technological conditions) without the hydroxylated GQD and \( \Delta G = -29.1 \) kJ mol\(^{-1}\) with the hydroxylated GQD at the same temperature and pressure. Consequently, the corresponding equilibrium constants differ by more than a factor of 10 000.

The proposed method allows one to adjust reaction conditions appropriately. It does not substitute or compete with the metallic catalysts to cleave N₂. The metallic catalysts do not contain polarized hydrogen atoms, which would interact strongly with NH₃. Additionally, the topology of the metal catalysts is not optimal for hosting multiple hydroxyl groups. Graphene or GQDs can be decorated with multiple hydroxyl groups, which would be evenly distributed not only at the edge positions but also throughout the surface. This material is easily fabricated from graphite oxide. The latter is obtained by acting with potassium permanganate on graphite, which subsequently exfoliates. It is a standard method to oxidize organic compounds. The hydroxylated graphene can be arranged in layers to maximize its working surface area. It is particularly beneficial in practice that the hydroxylated graphene does not chemically modify ammonia.

The industrial advantages of the demonstrated approach depend on other factors, besides the reaction yield. It is important that the demonstrated yield enhancement holds over a broad temperature and pressure range. Other factors include energy, material cost, and manufacturability. While graphene and its derivatives, including hydroxylated graphene, are expensive, graphite oxide and related compounds are very affordable. The demonstrated principle will hold with these cheaper alternatives. All other factors, including the energy expense, catalyst use, multiple conversion cycles, etc. should remain similar as in the current technology.

To recapitulate, we introduced a new method for controlling ammonia synthesis by exploiting differences in the polarities of GQD (Figure 1e) and observed the same yield, 33%, as in the case of the bulk mixture. Thus, the reaction equilibrium gets shifted because of the hydroxyl groups, while the GQD acts exclusively as a matrix/support. We also compared GQDs with higher (Figure 1f) and lower (Figure 1e) content of hydroxyl groups. It was observed that both GQDs provide comparable NH₃ yields, ca. 38%. We found that a small distance separating the hydroxyl groups, such as in Figure 1f, favors intramolecular hydrogen bonding, being therefore inefficient. This conclusion is also confirmed by the RMD simulation of the two hydroxylated GQDs. When the distance between the hydroxylated GQDs was fixed at 10 Å, the yield was 44%. In turn, when they were allowed to approach one another, the yield dropped to 35%, which is only modestly higher than that in the bulk mixture.

The theoretical threshold of the reaction yield can be calculated from the thermochemical results via the following formula, \( K = \exp(-\Delta G/RT) \), where \( K \) is the equilibrium reaction constant and \( R \) is the gas constant; \( T \) is temperature, and \( \Delta G \) is the free energy change. Compare \( \Delta G = +35.7 \) kJ mol\(^{-1}\) at 800 K and 100 bar (similar to the technological conditions) without the hydroxylated GQD and \( \Delta G = -29.1 \) kJ mol\(^{-1}\) with the hydroxylated GQD at the same temperature and pressure. Consequently, the corresponding equilibrium constants differ by more than a factor of 10 000.

The proposed method allows one to adjust reaction conditions appropriately. It does not substitute or compete with the metallic catalysts to cleave N₂. The metallic catalysts do not contain polarized hydrogen atoms, which would interact strongly with NH₃. Additionally, the topology of the metal catalysts is not optimal for hosting multiple hydroxyl groups. Graphene or GQDs can be decorated with multiple hydroxyl groups, which would be evenly distributed not only at the edge positions but also throughout the surface. This material is easily fabricated from graphite oxide. The latter is obtained by acting with potassium permanganate on graphite, which subsequently exfoliates. It is a standard method to oxidize organic compounds. The hydroxylated graphene can be arranged in layers to maximize its working surface area. It is particularly beneficial in practice that the hydroxylated graphene does not chemically modify ammonia.

The industrial advantages of the demonstrated approach depend on other factors, besides the reaction yield. It is important that the demonstrated yield enhancement holds over a broad temperature and pressure range. Other factors include energy, material cost, and manufacturability. While graphene and its derivatives, including hydroxylated graphene, are expensive, graphite oxide and related compounds are very affordable. The demonstrated principle will hold with these cheaper alternatives. All other factors, including the energy expense, catalyst use, multiple conversion cycles, etc. should remain similar as in the current technology.

To recapitulate, we introduced a new method for controlling ammonia synthesis by exploiting differences in the polarities of
the reactants and the product, and the strong proton acceptor ability of NH$_3$. We reported a significant performance increase in the ammonia yield over a broad range of thermodynamic conditions, with temperature ranging from 300 to 1500 K and pressure ranging from 1 to 1000 bar. The differences between the original Haber–Bosch process and the improved process generally depend on external conditions. The proposed method was justified by two independent theoretical approaches, ab initio quantum thermochemistry and reactive molecular dynamics, providing strong theoretical support of the suggested technique. The advance allows one to decrease the number of passes/stages to obtain a desired degree of nitrogen conversion. The method also allows one to decrease the target temperature and pressure. It is particularly interesting to use the proposed method for shifting the thermodynamic equilibrium in conjunction with the novel catalysts,\cite{12} which accelerate the kinetics. The topology of the functionalized GQD and graphene deserve further engineering in order to increase the product yield. The demonstrated principle is general and can be applied with many polar groups functionalizing a substrate with a high surface area, as long as the groups and the substrate are not chemically reactive with H$_2$, N$_2$, and NH$_3$. The achieved advance is expected to have great economic and societal impacts.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: prezhdo@usc.edu.*

*E-mail: vchaban@gmail.com.*

**Notes**

The authors declare no competing financial interest.

**REFERENCES**


