Project 1 Report

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1 Introduction

The Haber-Bosch process is one of chemistry's crowning achievements; its invention drastically increased fertilizer availability, raising global food production alongside it. Central to the Haber-Bosch process is the catalytic conversion of nitrogen and hydrogen to ammonia, a reaction that is highly dependent on reaction conditions. One of the key factors influencing the efficiency of this process is the competitive adsorption of hydrogen and nitrogen on the catalyst surface. Understanding the adsorption behavior of these gases is essential for optimizing the reaction conditions, as the rate of ammonia formation depends not only on the availability of surface sites but also on the interactions between the adsorbed species.

This study aims to simulate and analyze the competitive adsorption of nitrogen and hydrogen on a 2D catalyst surface using a Grand Canonical Monte Carlo simulation. By varying the chemical potential of hydrogen while keeping the chemical potential of nitrogen constant, we can model the adsorption of these gases under various conditions.

The simulation explores several sets of parameters, including ideal, repulsive, attractive, immiscible, and like dissolves unlike interactions. For each set of parameters, phase diagrams that display the coverage of nitrogen and hydrogen on the surface as well as selected lattice configurations are analyzed. By exploring these results for the aforementioned interaction parameters, ideal reaction conditions can be determined.

2 Methodology

The competitive adsorption simulation on a surface is performed using a lattice-based model within the framework of the grand canonical ensemble. The simulation is run using the Grand Canonical Monte Carlo method, which implements moves for particle addition and removal. Either move is chosen at random with equal probability.

2.1 Particle Addition

For particle addition, a random empty site is first selected. Then, a choice is made between adsorbate H or N based on random selection. The system's energy change, ΔE, resulting from the addition of the particle is computed by taking the difference in energy before and after particle addition using the following equation for energy:

$$E = \sum_i \left(n_i^H \epsilon_H n_i^N \epsilon_N\right) + \frac{1}{2} \sum_{\langle i,j \rangle} \left(n_i^H n_j^H \epsilon_{HH} + n_i^N n_j^N \epsilon_{NN} + n_i^H n_j^N \epsilon_{HN} + n_i^N n_j^H \epsilon_{HN}\right) \tag{1}$$

where n_i^H and n_i^N represent the occupancy of adsorbates H and N at lattice site i, respectively. For an empty site, both $n_i^H = 0$ and $n_i^N = 0$. Else, if the site is occupied, either $n_i^H = 1$ or $n_i^N = 1$ depending on whether H or N occupies the site, and the other value n_i^{HorN} remains zero. ϵ_H and ϵ_N represent the adsorption energies ϵ_{HH}, ϵ_{NN}, and ϵ_{HN} represent the interaction energies between two particles.

The acceptance probability for the move is adjusted by including the ratio of the proposal

probabilities. The move is accepted according to the probability

$$acc = min[1, \frac{N_a - N_b}{N_s + 1} e^{-\beta[\Delta E - \mu_s]}] \tag{2}$$

for N_a empty sites, N_s sites occupied by particle s. μ_s refers to the chemical potential of particle s, and $\beta = \frac{1}{k_B T}$. A random number ($\in [0, 1]$) is compared to acc to determine if particle addition is performed.

2.2 Particle Removal

For particle removal, a random occupied site is first selected. The system's energy change, ΔE, resulting from the removal of the particle is computed similarly as done for addition.

The acceptance probability for the move is adjusted by including the ratio of the proposal probabilities. The move is accepted according to the probability

$$acc = min[1, \frac{N_s}{N_a - N_s + 1} e^{-\beta[\Delta E + \mu_s]}] \tag{3}$$

Again, a random number ($\in [0, 1]$) is compared to acc to determine if particle addition is performed.

These steps are repeated in the algorithm until the system reaches equilibrium if enough steps are used to get there.

The simulation was run for five different sets of parameters which represent an ideal mixture of nitrogen and hydrogen, a system with purely repulsive interactions, a system with purely attractive interactions, an immiscible mixture of nitrogen and hydrogen, and a "like dissolves unlike" system where nitrogen and hydrogen are attracted to each other but repulsed by other nitrogen and hydrogen molecules respectively. These conditions are simulated by setting specific adsorption and interaction energies that represent each system. Temperatures and μ_H were varied with $\mu_N = -0.1eV$for each system to construct phase diagrams shown in 1.

3 Discussion

The ideal conditions for the Haber-Bosch process occur when the catalyst is fully occupied, nitrogen and hydrogen are preferentially next to each other, and the ratio of hydrogen to nitrogen is 3:1 as is most efficient for the synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

3.1 An Ideal Mixture of Nitrogen and Hydrogen

Using an ideal gas approximation for hydrogen and nitrogen, there is no interaction energy between pairs of particles. Since the energy of adsorption for hydrogen and nitrogen were set to be equal, varying the chemical potential of hydrogen has the greatest effect on the ratio of sites occupied by hydrogen to sites occupied by nitrogen. 1 a) shows the phase diagrams and lattice configurations generated from the simulation. Lower μ_H results in the vast majority of occupied sites being occupied by nitrogen, but as μ_H approaches and eventually equals μ_N, the lattice is almost always equally occupied by nitrogen and hydrogen. Once μ_H surpasses μ_N and reaches its maximum value, $\mu_H = 0eV$, hydrogen fully occupies the lattice, leaving no room for nitrogen occupation.

As temperature is increased, the total occupation of the lattice increases due to the increased probability of interaction. Notably, in the higher temperature range, nitrogen still has a chance of adsorption when $\mu_H > \mu_N$.

3.2 Repulsive Interactions between Nitrogen and Hydrogen

Using a purely repulsive regime for hydrogen and nitrogen, all particles, like or unlike, repel each other. 1 b) shows similar behavior as the ideal system with the same behavior observed for varying temperature and μ_H. However, because of the repulsive interactions between par-

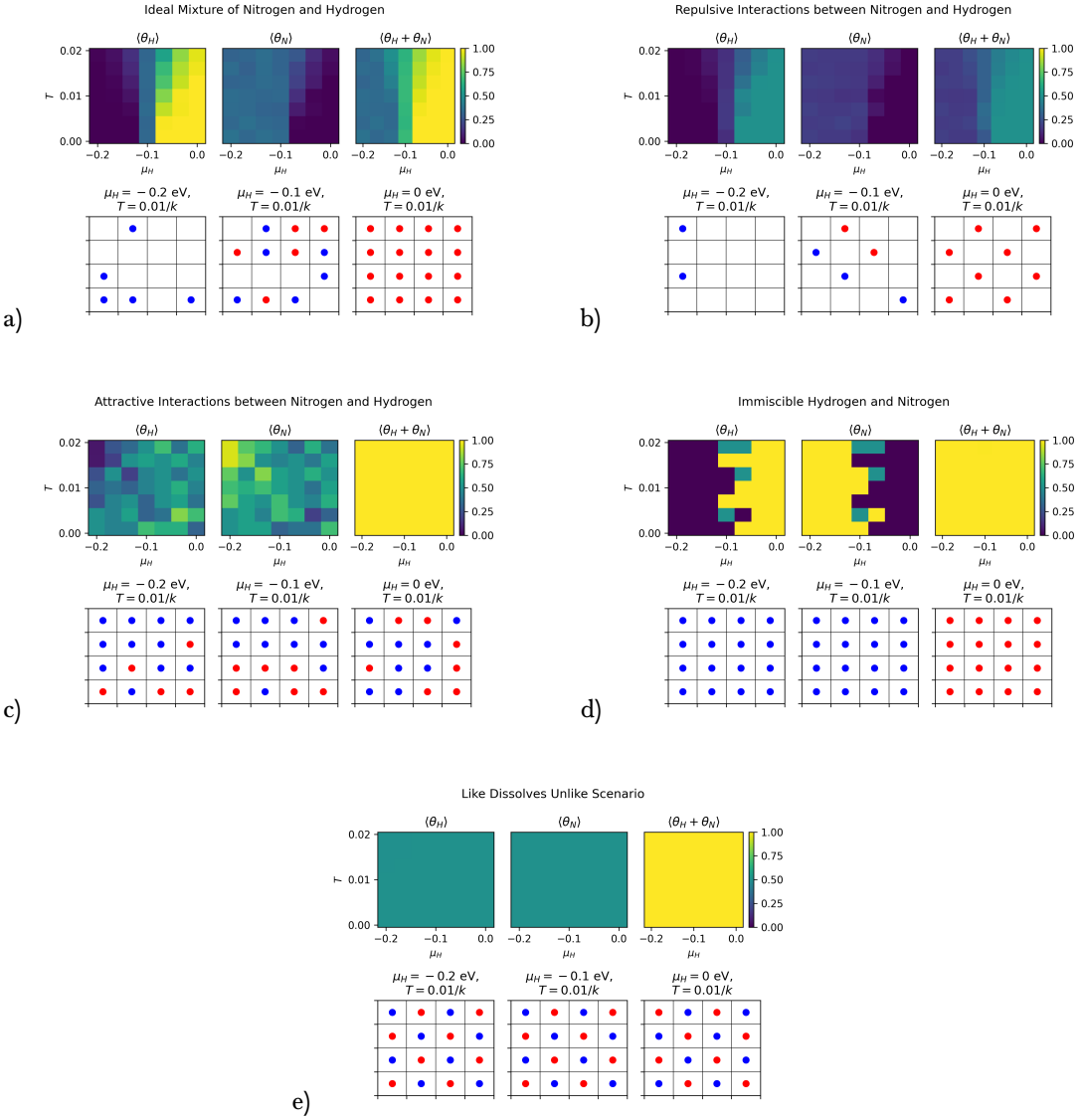


Figure 1: Phase diagrams and selected lattice configurations for various interactions on the catalyst surface: a) Ideal interaction, b) Repulsive interaction, c) Attractive interaction, d) Immiscible interaction, e) Like dissolves unlike interaction. Hydrogen is represented by a red dot and nitrogen is represented by a blue dot in each of the lattice configurations. Temperatures are given in units of k.

ticles, every other site is occupied leaving unoccupied gaps between occupied sites.

3.3 Attractive Interactions between Nitrogen and Hydrogen

A purely attractive scheme (1 c)) behaves similarly than the prior two. Since all particles are equally attracted to one another, there is still no preference for which sites are occupied by hydrogen or nitrogen, and the same trends are followed for varying temperature and μ_H. The main difference for this attractive scenarios is the total occupation of the lattice for every condition.

3.4 Immiscible Nitrogen and Hydrogen

For repulsive interactions between nitrogen and hydrogen and attractive interactions between like pairs (1 d)), the lattice is again entirely occupied, leaving no empty sites. Unlike the last scheme, the repulsive nature of hydrogen-nitrogen interactions leaves the lattice fully occupied with either hydrogen or nitrogen. When $\mu_H < \mu_N$, the lattice is fully occupied by nitrogen, and when $\mu_H > \mu_N$, the lattice is fully occupied by hydrogen. When $\mu_H \approx \mu_N$, the lattice can be occupied equally by hydrogen and nitrogen. High temperatures make that exception more favorable, but otherwise, temperature has little effect. The driving factor of whether the lattice is occupied by hydrogen or nitrogen is μ_H.

3.5 "Like Dissolves Unlike" Scenario

For repulsive interactions between like pairs of particles and attractive interactions between unlike pairs (1 e)), the lattice is again entirely occupied, leaving no empty sites. For every temperature and μ_H sampled, there is equal occupancy of nitrogen and hydrogen on the lattice, and thus, relative occupancy is independent of temperature and μ_H. Sites alternate hydrogen and nitrogen across the lattice creating a checkerboard pattern.

4 Conclusion

The ideal mixture represents an idealized condition where the ratio of hydrogen to nitrogen can be achieved alongside optimal adsorption. Although this aligns with the requirements for ammonia production, the cost of creating near ideal conditions would be low temperature, pressure, and concentrations of each gas, which would make adsorption highly unfavorable.

In the repulsive interaction regime, the overall occupation of the lattice is highly limited, making such conditions unfavorable for the Haber-Bosch process.

In the attractive interaction case, where both hydrogen and nitrogen are equally attracted to each other, the lattice becomes fully occupied across all conditions. However, there is no preference for the segregation of hydrogen and nitrogen; both gases are adsorbed randomly, meaning that the system does not achieve the ideal state where hydrogen and nitrogen are preferentially next to each other in a 3:1 ratio. This scenario, though fully occupied, does not align with the desired selective adsorption and phase behavior needed for ammonia production.

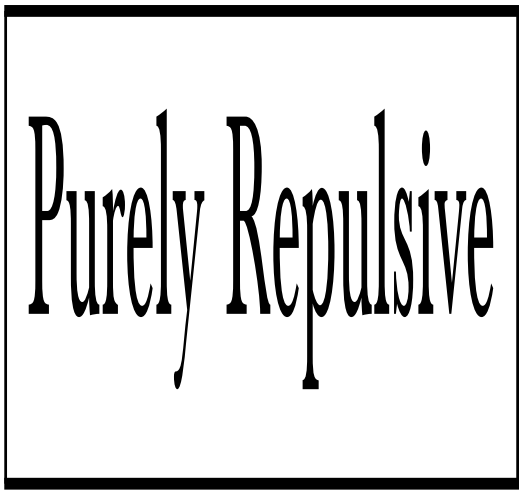
In the immiscible nitrogen and hydrogen scenario, where nitrogen and hydrogen experience repulsive interactions with each other and attractive interactions with like particles, the lattice is fully occupied, but the occupation is either completely nitrogen or completely hydrogen. Clearly this system does not allow for the formation of a 3:1 hydrogen-to-nitrogen ratio, as the occupation is more binary, either fully hydrogen or fully nitrogen, based on the relative chemical potentials.

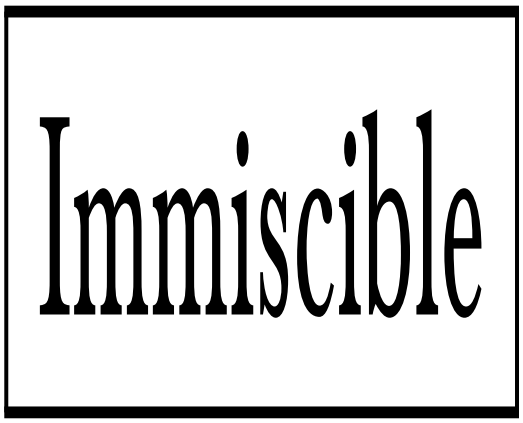
The like dissolves unlike case, where like particles repel each other and unlike particles attract, is the only scenario that achieves the ideal conditions. The lattice is fully occupied, and hydrogen and nitrogen alternate across the

lattice. While this doesn't achieve a perfect 3:1 ratio of hydrogen to nitrogen, since each site on the lattice has four neighbors, this ratio would be impossible to achieve while maintaining three hydrogens around each nitrogen. These conditions best reflect the desired mixture of gases and adsorption behavior needed for the Haber-Bosch process, where the selective interaction between hydrogen and nitrogen ensures efficient ammonia synthesis.

Thus, while most interaction regimes fail to achieve the ideal conditions, the like dissolves scenario successfully creates the desired selective adsorption of hydrogen and nitrogen, fully occupying the lattice with a balanced mixture. Additionally, reaction conditions to achieve such a system–using a specialized catalyst with alternating preference for hydrogen or nitrogen between sites, for one–should be compatible with the high temperature and pressure environments needed for effiecient adsorption.

5 Appendix[1]





[1]Animations can only be viewed through a select few pdf viewers, including adobe acrobat.

"Like dissolves unlike"