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Exploring the limits: A low-pressure, low-temperature Haber–Bosch process

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ABSTRACT

The Haber–Bosch process for ammonia synthesis has been suggested to be the most important invention of the 20th century, and called the ‘Bellwether reaction in heterogeneous catalysis’. We examine the catalyst requirements for a new low-pressure, low-temperature synthesis process. We show that the absence of such a process for conventional transition metal catalysts can be understood as a consequence of a scaling relation between the activation energy for N₂ dissociation and N adsorption energy found at the surface of these materials. A better catalyst cannot obey this scaling relation. We define the ideal scaling relation characterizing the most active catalyst possible, and show that it is theoretically possible to have a low pressure, low-temperature Haber–Bosch process. The challenge is to find new classes of catalyst materials with properties approaching the ideal, and we discuss the possibility that transition metal compounds have such properties.

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1. Main text

The Haber–Bosch process, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, requires a solid catalyst and even with the best known catalysts it is only feasible at high temperatures (650–750 K) and pressures (50–200 bar) [1–5]. The process, which has been suggested to be the most important invention of the 20th century [6] and named the ‘Bellwether reaction in heterogeneous catalysis’ [7], just had its 100 year anniversary [8]. While the process engineering has been optimized considerably since then, the industrial catalyst is surprisingly similar to the original [9]. Given that the ammonia synthesis reaction is exergonic at ambient conditions, one can wonder why there is not a catalyst enabling this process at more benign conditions. In nature, the enzyme nitrogenase can catalyze the reduction of N₂ to ammonia at ambient conditions, but this biological process is quite inefficient since it requires 16 ATP per reduced N₂, corresponding to an energy expense of almost 5 eV per turnover of one N₂ molecule (~500 kJ/mol of N₂) [10]. In the present paper we explore the limits of how low temperature and pressure are possible for the thermal Haber–Bosch process to proceed. We show that the theoretical limit for catalyst performance for this reaction is characterized by a certain ideal relationship

between the activation energy for N₂ dissociation and the N binding energy. Our analysis suggests that a low-pressure process is, in principle, possible. At a temperature of 373 K, a 1 bar process with a rate in excess of 1 turnover per active site per second is achievable with an ideal catalyst. The conventional Haber–Bosch metal catalysts are quite far from this, and we discuss how other classes of materials may be needed to get properties approaching the ideal.

As a basis for our discussion, we start by reviewing why high temperature and pressure are needed for the metal-catalyzed Haber–Bosch process. Our discussion builds on calculated free energy diagrams for the ammonia synthesis over a stepped Ru surface as shown in Figure 1 (for calculational details, see Supporting information). It is known that alkali promoted Ru is the best elemental metal catalyst for this process [11–14] (the Fe based catalysts that are slightly less active [13,15] are used industrially because of their significantly lower price) [16]. Stepped surfaces are known to be the most active in N₂ activation over metals, which leads to a significant structure sensitivity of the reaction [17–20]. A potential energy diagram, like that of Figure 1, forms the basis for a good description of the kinetics when compared to experiments on a supported Ru catalyst under industrial conditions [21].

At 300 K and 1 bar the total process is exergonic but it is evident from Figure 1a that the intermediates (adsorbed N, NH and NH₂) bind too strongly to the surface to leave any free sites for the reaction to take place. Increasing the temperature to 700 K alleviates

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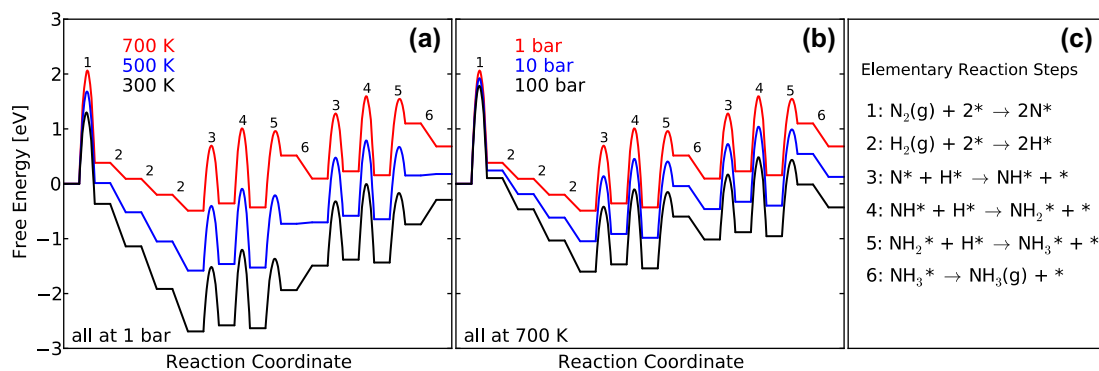


Figure 1. Calculated free energy diagrams for the ammonia synthesis over a stepped Ru surface (a) at different temperatures for a fixed reactant pressure of 1 bar, and (b) at different reactant pressures at a fixed temperature of 700 K. The numbers in (a) and (b) refer to the elementary reaction steps shown in (c). $H_2:N_2$ ratio is fixed at 3, and NH_3 pressure is fixed at 1 bar. Free energies are calculated using ideal gas and harmonic vibrational approximations.

this problem but now the total process becomes uphill in free energy. A substantial increase in pressure is needed in order to change the total reaction back to being exergonic, see Figure 1b. This is the reason for the harsh conditions needed in the Haber–Bosch process even for the best catalysts known today.

From the point of view of the thermodynamics of the gas phase reaction, it is not in principle a problem to have an ammonia synthesis process at ambient conditions. Figure 1 shows that a low temperature process would be feasible if we could find a material that binds NH_x ($x = 0, 1$ and 2) considerably more weakly than Ru and at the same time does not have a higher barrier for N_2 dissociation. The main reason such a catalyst has not been found can be understood from the results shown in Figure 2a. For the most active sites (steps) on metals there is a linear energy scaling (or Brønsted–Evans–Polanyi) relation between the transition-state energy (E_{N-N}), which is equivalent to the apparent activation barrier (ΔE_a) and the N binding energy to the surface, E_N [22–24]. It is therefore impossible for this class of catalysts to vary E_{N-N} and E_N independently. The best catalyst is the one with the optimum balance between the two, given the relationship $E_{N-N}^{step} \propto E_N$ [12,24,25].

Figure 3 shows the result of a simple kinetic model (outlined in the Supplementary information) using the relationship $E_{N-N}^{step} \propto E_N$

between the N_2 transition-state energy and the nitrogen adsorption energy given in Figure 2a. The model exploits the fact that, except for very low temperatures, the N_2 dissociation is the rate-determining step (has the highest free energy barrier in Figure 1). In addition, the model takes advantage of the general finding that the energy of adsorbed NH_x scales with the adsorption energy of N (see Figure 2b) [26], and that the hydrogen adsorption can be considered quasi-equilibrated (see Supplementary information). The existence of the scaling relations means that the rate at a given set of conditions can be plotted as a function of a single descriptor of catalytic activity, E_N . The model describes experimentally observed trends in ammonia synthesis rates well, and correctly gives that Ru and Fe are the elemental metals closest to optimal for the stepped metal active sites.

The scaling relation is specific to the structure of the active site; close-packed metal surfaces, for instance, have a higher lying relationship (i.e. for a given E_N the barrier for N_2 dissociation is higher) [24]. This leads to poorer catalytic activity of the close-packed surfaces as compared to the stepped surfaces. A good, low temperature catalyst would require a catalyst with a value of (E_N, E_{N-N}) which is significantly below the scaling relation for the stepped metal surfaces. In ammonia synthesis this is to a certain extent achieved by promotion of the catalyst by alkali metals [12,19,27–30]. It has been

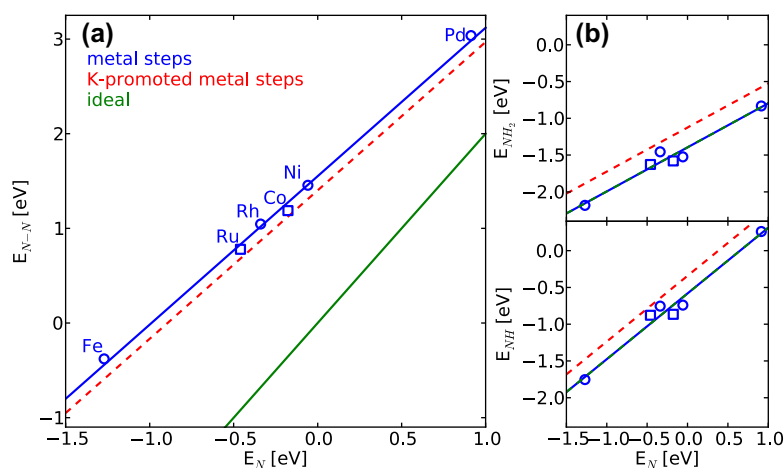


Figure 2. (a) Calculated transition state energies (E_{N-N}) for N_2 dissociation as a function of the nitrogen adsorption energy (E_N) over step sites on hcp (square) and fcc (circle) surfaces of transition metals which are active for ammonia synthesis. The solid blue line represents a least-squared interpolation between the points, the red line depicts the addition of alkali (potassium) promotion (see Supplementary information), and the green line represents the lowest possible transition state energy given by the reaction energy for dissociation. (b) Adsorption energy scaling relations for NH and NH_2 adsorbed intermediates. The blue/green line represents a least-squared interpolation through the points, and is used in the ‘metal steps’ and ‘ideal’ kinetic models. The red line illustrates the effect of alkali promotion, and is used in the ‘K-promoted metal steps’ kinetic model.

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