



Coordination chemistry insights into the role of alkali metal promoters in dinitrogen reduction



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ABSTRACT

The Haber-Bosch process is a major contributor to fixed nitrogen that supports the world's nutritional needs and is one of the largest-scale industrial processes known. It has also served as a testing ground for chemists' understanding of surface chemistry. Thus, it is significant that the most thoroughly developed catalysts for N₂ reduction use potassium as an electronic promoter. In this review, we discuss the literature on alkali metal cations as promoters for N₂ reduction, in the context of the growing knowledge about cooperative interactions between N₂, transition metals, and alkali metals in coordination compounds. Because the structures and properties are easier to characterize in these compounds, they give useful information on alkali metal interactions with N₂. Here, we review a variety of interactions, with emphasis on recent work on iron complexes by the authors. Finally, we draw conclusions about the nature of these interactions and areas for future research.

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1. Introduction

1.1. Perspectives, goals

Many heterogeneous catalysts are promoted by addition of alkali cations, and the study of promoters is important for development of more efficient catalysts [1–4]. The Haber-Bosch (H-B) process for N₂ conversion to NH₃ is one example of a very well-studied heterogeneous process that benefits from alkali cation promoters [5–7]. There has been a resurgence of interest in production of NH₃ from N₂ because of its potential as a carbon-free fuel and because of the energy savings that would accrue from even small improvements in this very large-scale process [7–9]. Despite the fact that N₂ reduction is one of the best-studied surface processes, the atomic-level detail of the interactions between the alkali-metal cation and the substrate are still not clear.

Atomic-level detail is much easier to acquire for soluble molecular compounds, which are amenable to X-ray crystallography to <1 Å resolution as well as a variety of solution methods that elucidate dynamics that would be difficult or impossible to resolve on a surface. Moreover, the ability to isolate pure, structurally-characterized samples of homogeneous species enables mechanistic studies that are simpler to interpret. Though

many interactions are not identical between solution and surface species, advances in the understanding of solution compounds can provide models and analogies that are useful for further development of the potential surface chemistry on heterogeneous catalysts.

With this idea in mind, this article presents a review focusing on the roles of alkali metal cations during the binding and cleavage of N₂ in solution complexes. As will be seen below, interactions between these cations and N₂ can greatly facilitate cleavage of the N–N bond, and current research is making significant strides in elucidating the interactions that are important in solution alkali-metal promoters. It is our hope that these emerging results will lead to new ideas for surface promoters as well.

1.2. Mechanism of the Fe-catalyzed Haber-Bosch process

During the H-B process, a feedstock of H₂ and N₂ gas in a 3:1 ratio is reacted over a promoted Fe catalyst at ~700 K and ~100 bar. The technical catalyst, developed by Mittasch close to a century ago, is a fused-Fe catalyst promoted with alumina and potash (a mixture of water-soluble potassium salts such as KOH and K₂CO₃) [10,11]. The average oxidation state of Fe in the Mittasch catalyst is between 0 and +1 [12]. The direct observation of the technical H-B catalyst under catalytic conditions is difficult, so many studies probing the mechanism and kinetics of the H-B process are done using single-crystal Fe surfaces [13]. Samples where the Fe(111) plane is exposed are the most active single-crystal Fe catalysts for the H-B process [14]. Somorjai attributed this to the fact that the Fe(111)

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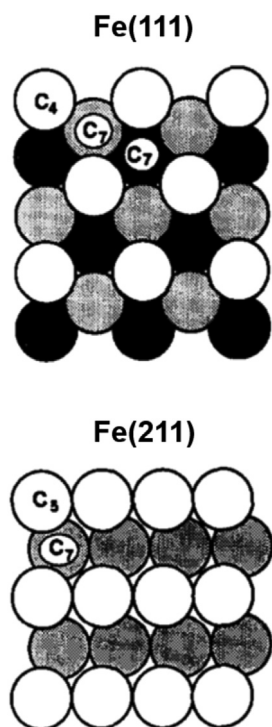


Fig. 1. Examples of Fe planes that expose highly active C_7 sites for ammonia synthesis. Reprinted with permission from [15]. Copyright Elsevier, 1987.

plane has the highest concentration of exposed C_7 sites (where an Fe atom has seven nearest neighboring Fe atoms), at which the high-coordination number facilitates charge-transfer reactions (such as N_2 reduction) via local electronic fluctuations [15,16]. However, the Fe(111) surface reconstructs and incorporates sub-surface nitrides under reaction conditions [17,18]. In addition to the Fe(111) plane, the Fe(211) and Fe(310) planes are quite active towards small molecule activation [19–21]. Fig. 1 illustrates the Fe(111) and Fe(211) planes, each of which exposes C_7 sites [15].

On surfaces, extensive kinetic studies have shown that the mechanism of N_2 reduction to NH_3 involves dissociative H_2 and N_2 adsorption to the Fe surface, followed by hydrogenation of adsorbed N-atoms, and ultimately desorption of NH_3 [5,6]. On single-crystal Fe catalysts, the dissociation of adsorbed N_2 to form two nitrides is the rate-limiting step of catalysis [22–26]. An analogous mechanism occurs using the Mittasch catalyst, with the dissociative adsorption of N_2 generally considered to be the rate-limiting step [27,28].

1.3. Promoters in the Fe-catalyzed Haber-Bosch process

During the development of the technical ammonia synthesis catalyst in the early 20th century, Mittasch discovered that the addition of foreign substances to the magnetite (Fe_3O_4) catalyst had a more pronounced effect on activity than the nature of the magnetite itself [10]. This prompted Mittasch and coworkers to systematically test the effect of thousands of additives on Fe catalysts for ammonia synthesis. Building from these studies, industrial Mittasch catalysts for the H-B process are synthesized through the fusion of Fe_3O_4 with various amounts of Al_2O_3 , CaO, MgO, SiO_2 , and K_2O . The first four are considered structural promoters that increase catalyst surface area, stabilize catalytically active Fe sites on the surface, and prevent sintering of the magnetite [29–32]. The potassium is generally considered to be an “electronic promoter;” its large ionic radius prevents incorporation into the magnetite during synthesis, and therefore it is localized at the surface [32].

Catalytic activity reaches a maximum at a certain amount of added potassium, both on polycrystalline Fe foil [33] and in the technical H-B catalyst [31]. The dropoff at higher surface coverage is explainable since the K^+ resides on the surface and large amounts could block Fe active sites.

The seminal research by Mittasch, as well as many other subsequent studies, notes that other alkali metals also promote the technical catalyst [10,28,34–36]. Ruthenium-based H-B catalysts are also promoted with alkali metals [32]. In general, Ru catalysts exhibit higher activity with larger alkali metals, but recently Li was found to be a competent promoter [6,37–39]. Analogous studies on alkali metal promoters for Fe catalysts do not always agree on the relative changes in activity when changing the alkali metal [28,32,34–36]. Understanding the precise role that these alkali metals play in improving the activity of structurally-promoted catalysts is vital for developing new ammonia synthesis catalysts with higher activity and robustness.

1.3.1. Determining the role of potassium in the Mittasch catalyst

The specific role of potassium in promoting the technical H-B catalyst is a topic of great interest, considering the enhancement of catalytic activity upon addition of potash to the iron oxide precursor [32,34]. Hypothetical explanations include potassium involvement in N_2 chemisorption to the Fe surface, hydrogenation of adsorbed N-atoms, and desorption of NH_3 [40,33,30,31,41,28,42,11]. Auger electron spectroscopy data indicate that the concentration of N_2 adsorbed to an Fe(111) single-crystal surface increases in the presence of co-adsorbed potassium, suggesting that potassium increases the N_2 adsorption energy to the Fe(111) surface [43]. Further investigating this effect, Whitman et al. reported that co-adsorption of potassium to Fe(111) specifically stabilizes N_2 adsorption parallel to the surface, which is the precursor for N_2 dissociation. They hypothesized that the potassium lowers the energy barrier for conversion of terminally bound N_2 to the parallel-bound N_2 dissociation precursor. Interestingly, no shift in the N–N stretching frequency (ν_{NN}) occurs for perpendicular or parallel adsorbed N_2 in the presence of potassium, suggesting the absence of direct potassium- N_2 interactions that weaken the N–N bond [41]. This contrasts with the shift of vibrational frequency of adsorbed CO between bare and cation-promoted surfaces in some cases [44,45].

Potassium may also have electronic effects on the Fe surface that play a role. In studies done on the technical H-B catalyst, Altenburg et al. found that the amount of potassium added to the Fe/Al_2O_3 catalyst affects the reaction order of H_2 in the reduction of NH_3 [40]. Nielsen et al., expanding on Temkin’s original kinetic model for the H-B process, established that the overall rate of NH_3 formation depends on the order of H_2 in the rate law [46,47]. The order of H_2 is in turn dependent on the ratio of N^* , NH^* , and NH_2^* (where the asterisk indicates surface-adsorbed fragments) formed after rate-determining N_2 chemisorption to the Fe catalyst; N^* , NH^* , and NH_2^* react with 1.5, 1, and 0.5 equiv of H_2 to form NH_3^* , respectively. This relationship implies that potassium promotes formation of N^* species over partially hydrogenated species, leading to an increase in order of H_2 and faster NH_3 generation under catalytic conditions.

Altenburg et al. proposed a model in which stabilization of NH^* and NH_2^* by hydrogen bonding with acidic OH groups inhibits the rate [40]. In this model, the presence of K^+ on the surface decreases the coverage of surface Al^{3+} -OH groups that would form stronger hydrogen bonds, and thus K^+ gives a greater dependence of the rate on $[H_2]$ and faster rates at high pressure. This model predicts that the rate should be faster for cations with a smaller charge-to-radius ratio. Direct evidence supporting this theory is limited to kinetic data; however, observations by Au et al. that hydroxyl groups present on Zn(0001) hydrogenate chemisorbed N^* to form NH^* and NH_2^* support the tenets of this theory [48].

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