

Ammonia Synthesis Promoted by Iron Catalysts
Literature Report

Sandra Bencic
Department of Chemistry
Michigan State University
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1. Introduction to Promoted Synthesis of Ammonia

Synthesis of ammonia is the most important industrial process for isolation of nitrogen as well as further production of nitrogen compounds of vital importance (urea, nitric acid and fertilizers). This process is nearly a hundred years old, discovered in the beginning of the 20th century by Fritz Haber and developed for industrial production by Carl Bosch. [1] The reaction between gaseous N₂ and H₂ ($N_2 + 3H_2 \rightarrow 2NH_3$) is exothermic, carried out at high pressures and temperatures and occurs with large yields when iron catalysts are present. The iron catalyst consists of reduced magnetite ore (Fe₃O₄) which is enriched (“promoted”) most frequently with Al- and K- (or Ca, Mg, Si)-oxides while its optimal performance requires reaction temperatures around 400°C and pressures from 150-300 atmospheres. [2, 3] Being a transition metal with partially occupied d-bands iron represents a surface suitable for adsorption and dissociation of N₂ molecules.

Because of extremely high importance of this catalytic process, surfaces of iron catalysts are objects of extended surface studies through various techniques. Chemical, structural and kinetic information can be obtained using Auger Electron Spectroscopy (AES), [4, 5, 6, 7, 8, 9, 10] Low-Energy Electron Diffraction (LEED), [11] Temperature-Programmed Desorption (TPD), [6, 11] X-ray Photoelectron Spectroscopy (XPS), [8] Extended X-ray Absorption Fine Structure (EXAFS), [12] Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDX), [12] Secondary Ion Mass Spectrometry (SIMS) [8] and others. Theoretical models of catalyst surfaces provide different explanations of the process that is still not entirely understood. [13] Studies of catalytic processes are difficult mainly because of pressure and temperature differences between synthesis and study conditions, since synthesis occurs at high temperatures and pressures, while characterization of surfaces needs an UHV environment.

Studies of ammonia synthesis on iron catalysts require specially designed chambers and often inspection of surfaces of industrial catalysts occurs. Nevertheless, conditions at which catalytic surfaces are studied are still far from the industrial ones. [4] Following examples yield basic and recent information on surface structures as well as reaction mechanism and kinetics on pure and promoted catalysts.

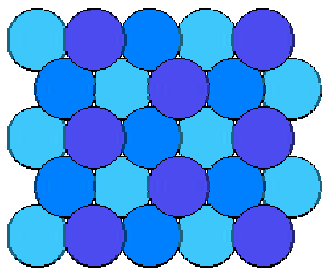
2. Iron Catalyst Surface Properties

2.1. Effect of Surface Orientation on Activity of Iron Catalysts

Catalysis for ammonia synthesis was studied on various surface planes of iron crystals with body centered cubic (bcc) conformation and the reaction rate was found to be dependent on orientation of crystals. [2] Spencer *et al.* intensively studied iron catalysts and found the ratio of reaction rates for ammonia formation at 798 K and 20 atm to be 418:25:1 on Fe(111), Fe(100) and Fe(110) surfaces, respectively. Ammonia formed at a rate of 4.6×10^{-8} moles $\text{cm}^{-2} \text{s}^{-1}$ on Fe(111) face, with activation energy for nitrogen adsorption of 19.4 kcal mole^{-1} . [5] Studies showed that the most active planes on iron catalysts are (111) and (211), while over (100), (110) and (210) planes, the kinetic rates for ammonia synthesis are lower (Fig. 1) [14]. The catalysis experiment was done in a high-pressure cell where synthesis occurred. The generation of ammonia was monitored with a Photoionization Detector (PID), surfaces were analyzed with LEED for structure information, and AES before and after the process, by connecting a UHV chamber to the system.

Figure 1: Rates of ammonia formation over iron crystal surfaces with orientations (111), (211), (100), (210) and (110) [14]

The reason for variation in catalytic activities at different surfaces was first believed to be the surface roughness and openness. Iron surfaces with the lowest roughness (as shown in Figure 2) and high work functions, Fe(110) and Fe(100), experimentally and theoretically represent surfaces with low catalytic activity. [14] Fe(111) face and Fe(210) face exhibit the highest roughness, associated to high surface free energy and low work function. Fe(111) crystal plane is indeed considered to be the most active clean surface for ammonia catalysis.



Fe bcc(111) face

Fe bcc(100) face

Fe bcc(110) face

Fe bcc(211) face

Fe bcc(210) face

Figure 2: Schemes of iron crystal surfaces with different orientations, showing surface roughness and C_7 sites; *adapted from* [14]

Nevertheless, Somorjai [14] proved that rather than roughness, high coordination of sites might be the characteristic that denotes the strength of nitrogen adsorption and kinetics of dissociation, determining the rate of ammonia synthesis. In fact, Fe(211) surfaces are as active as Fe(111) surfaces, but not as rough and open. Both Fe(211) and Fe(111) faces

have in common the presence of highly coordinated C_7 sites, most likely related to larger electronic fluctuations within the solid and therefore ideal sites for adsorption of nitrogen. On the other hand, Fe(210) surfaces are open, exposing third layer atoms, and they are rough and could be as active as Fe(111) surfaces, but do not contain C_7 sites, as seen in Fig. 2. It is experimentally demonstrated that Fe(210) surfaces are not as active as Fe(111) and Fe(211) surfaces. The increased catalytic activity is therefore mostly due to the presence of C_7 sites, the most highly coordinated sites in iron crystal. Therefore, they are the ones that provide the strongest adsorption and fastest dissociation of nitrogen on the catalyst surface.

2.2 Dissociative Nitrogen Adsorption as Rate-Determining Step

The mechanism for iron-catalyzed ammonia synthesis is stated below in three dominant reaction steps [15]:



It is believed that the overall reaction rate of ammonia synthesis is determined by dissociation of nitrogen adsorbed on catalyst surface in reaction (1). Most of the studies confirm this fact, although there is evidence of experiments performed at higher pressures, suggesting the step (2) to be the rate-determining one. [15] AES analysis of nitrogen residues on surface at high atmospheric pressures confirms high coverage of $N(\text{ads})$ on the surface, which implies that the dissociation of $N_2(\text{ads})$ might not be the rate-determining step (in this case, we would expect a higher coverage of $N_2(\text{ads})$ during synthesis). TPD data indicated that two forms of nitrogen were present on the surface during synthesis, as observed in two nitrogen desorption peaks that correspond to $N_2(\text{ads})$ at 120 K and $N(\text{ads})$ at 800-820 K. [16] Inspection of surfaces of working catalyst also showed that nitrogen is mostly present in its dissociated form, $N(\text{ads})$. [2]

Ertl [6] reported a possible explanation for binding of molecular nitrogen on iron, defining it as M-N-N “end-on” configuration. Here, the stabilization of N_2 on iron is due

to σ -donor coupling to the metal and π -backbonding of iron d-electrons with the 2 * lowest empty orbital in N_2 .

The extent of $N_2(ads)$ coverage on Fe surfaces can be followed at elevated temperatures using AES. [2] Slopes of curves representing variation in surface concentration with N_2 exposure can be used for obtaining sticking coefficients for dissociative chemisorption of nitrogen. Sticking coefficients are calculated from the Arrhenius equation, $s = A \exp(-E^*/RT)$, where s , A , E^* and T represent the sticking coefficient, preexponential factor, activation energy (for the process $N_2 \rightarrow 2N$) and temperature, respectively. The sticking coefficients for atomic nitrogen on different Fe catalyst faces increase in order $Fe(110) < Fe(100) < Fe(111)$, demonstrating that Fe(111) surfaces are the ones to assure the highest adsorption energy for N_2 , and the smallest activation energy for dissociation of $N_2(ads)$ to $N(ads)$ (Fig. 3).

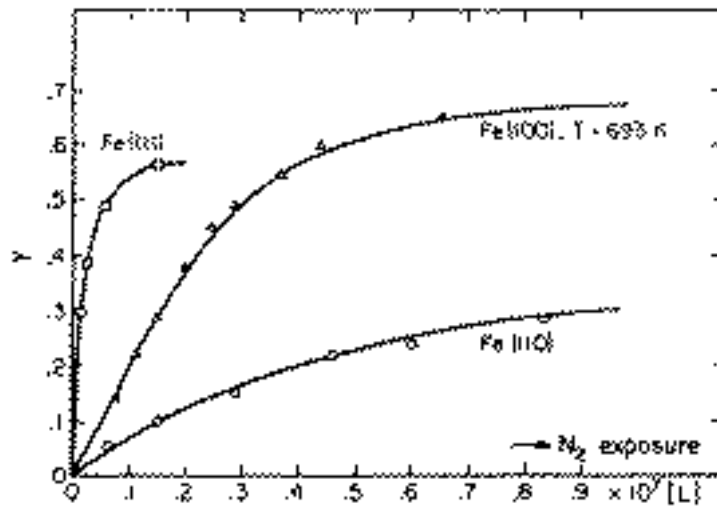


Figure 3: Dependence of relative surface concentration of adsorbed nitrogen on N_2 exposure, measured on Fe(111), Fe(100) and Fe(110) surfaces. [2]

2.3. Effect of Iron Promoters

Although pure Fe(111) and (211) surfaces assure the most suitable conditions for N_2 adsorption and dissociation and thus the highest rate for ammonia synthesis, the performance of most other surface planes is not satisfactory. Increased catalytic activity of these surfaces can be achieved with addition of promoter elements. They can be *electron donors* as potassium, which increases the reaction rate by altering the steady-state concentration of intermediates. Another type of promoters added to iron catalysts are Al-oxide or Ca-oxide, *texture promoters*, known to stabilize the particle size and increase the surface area of the catalyst. [3]

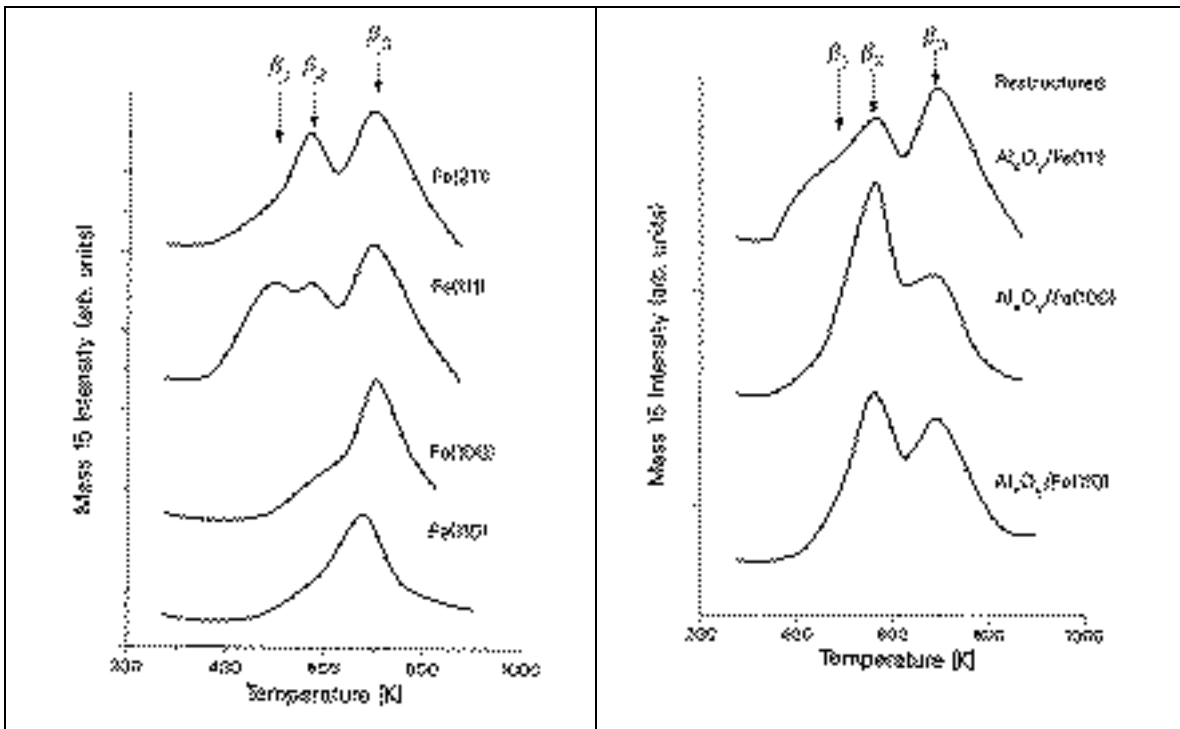


Figure 4: TPD spectra of ammonia desorption from (a) pure iron catalyst surfaces and (b) surfaces promoted with Al_xO_y /vapor [11]

Fe(111) surface barely changes in catalytic performance after addition of Al_xO_y followed by water vapor pretreatment. [11] Fe(100) and Fe(110) surfaces, rather inactive in pure form, drastically improve in activity when exposed to the same treatment. The

explanation for this phenomena is once again formation of C_7 sites on Fe(100) and Fe(110) planes due to surface restructuring that occurs during Al_xO_y /vapor pretreatment. TPD results confirm the fact that restructuring occurs on Fe(100) and Fe(110) surfaces. When monitoring desorption of ammonia from pure single crystal surfaces, Strongin et al. [14] observed three peaks. ν_1 , ν_2 and ν_3 ammonia desorption peaks with maxima at 495 K, 568 K and 676 K were found on Fe(111) pure surface. Only ν_3 desorption peak was seen on Fe(100) and Fe(110) surfaces. Once the surfaces were promoted with Al_xO_y , the ν_1 and ν_2 peaks showed also in desorption from both restructured planes, Fe(100) and Fe(110) (Fig. 5), which now contained active C_7 sites.

Figure 5: Thermal desorption spectra for N_2 from Fe(111) covered with (a) 0.55×10^{14} , (b) 1.5×10^{14} and (c) 3.5×10^{14} K atoms cm^{-2} . [6]

Ertl [6] compared rates for ammonia synthesis on K-promoted Fe(111) and Fe(100) surfaces, using TPD. He discovered that because of the presence of potassium, an increase in electron density of the substrate induces a local increase in adsorption energy for N_2 and a decrease in activation energy needed for its dissociation. In Ertl's experiment, catalyst surfaces were saturated with N_2 at 120 K and TPD spectra were recorded during programmed temperature increase. A peak attributed to $N_2(ads)$ thermal desorption was observed at 160 K (ν_1), while an additional peak in TPD spectra was found from the desorption process of $N(ads)$ (ν_2) at 210 K. The intensity of ν_2 peak increased with an increase in K concentration on the surface, and at the same time, the ν_1 peak intensity decreased, as shown in Fig. 5. Similarly, the intensity increase for ν_2 and a decrease for ν_1 were observed upon addition of K on Fe(100) surface.

Silverman and Boudart [7] inspected promoted catalyst surfaces with quantitative AES. Using a calculation for obtaining concentrations of iron promoters from Auger current, they obtained a complete composition of surface fractions. They also monitored CO chemisorption on iron surface. CO is isoelectric with N_2 and adsorbs on Fe and K_2O but it

does not adsorb on Al_2O_3 , where only N_2 physisorption occurs. Using this approach one can obtain the composition of different surface fragments. The authors deduced that in a fused iron catalyst, the surface is covered with K_2O and CaO promoter oxides. Pure Fe islands were present, surrounded by Al_2O_3 which was found to be lying below the K_2O .

3. Microstructure, Morphology Information and Models of Iron Catalysts

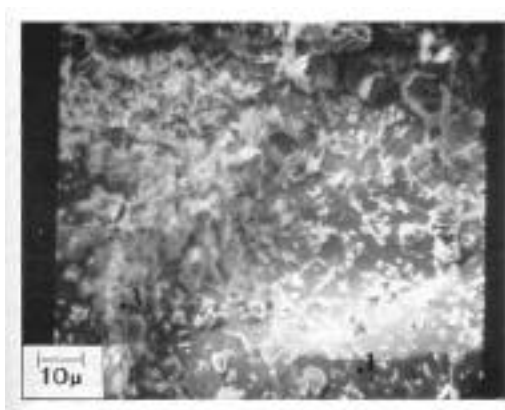
From the beginning of the 80's until recently, several studies tried to correlate the composition of iron catalyst surfaces with the morphology on a micron scale. [7, 8, 9, 12] The latest publications try to combine all the surface information gathered and model promoted iron catalyst surfaces for a thorough explanation of the catalytic process. [13]

Ertl and Prigge [8] imaged iron surfaces with SEM and AES Secondary Electron Distribution (SED) Mapping for determining composition and topography of industrial synthesis catalyst before and after its reduction (activation of the surface). SEM images of a specific area were taken and compared with elemental composition maps. As shown in Table 1, the unreduced catalyst surface consisted of mostly K and O while iron was nearly absent, since covered by the oxide layer. There were only small quantities of Al and Ca found on the surface. Compared to the bulk, iron catalyst surface was enriched with K that was not dissolved in the magnetite crystals, but segregated on grain boundaries. After reduction treatment with $\text{H}_2 + \text{N}_2$ (3:1) mixture at 500 Torr and 720 K, magnetite (Fe_2O_3) was completely reduced to elemental iron. The total surface area was increased due to the presence of segregated Al_2O_3 that had been dissolved in the magnetite lattice before reduction. Additionally, the surface exhibited smaller uniform pores resulting in an increase in porosity and internal surface area caused by Al_2O_3 . The gain in the free Fe surface was thus assigned as a cause for increased catalyst activity. On the other hand, potassium, responsible for the increase in the rate of nitrogen dissociation, was uniformly distributed on about 30% of the surface. The most plausible explanation for potassium activity was that $\text{K} + \text{O}$ form a monoatomic layer on top of the Fe substrate.

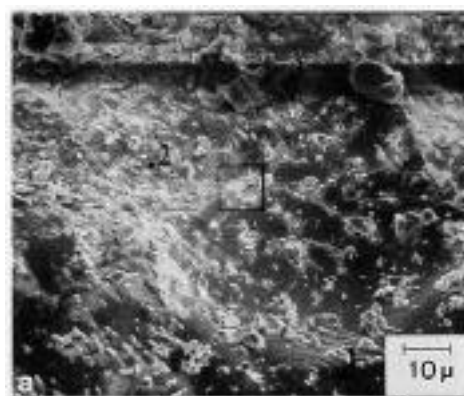
Table 1: Elemental composition of unreduced and reduced catalyst measured with XPS and AES (on various spots on the surface). [8]

Fig. 6 shows Auger maps (b, c, d, e, f) of reduced catalyst surface analyzed and showed in a secondary electron image (a). The K coverage is rather uniformly distributed on Fe and this surface exhibits a low Al content. The rest of the surface is quite evenly covered with Al, which is believed to be insoluble in the bulk because of the reduction of magnetite to pure Fe.

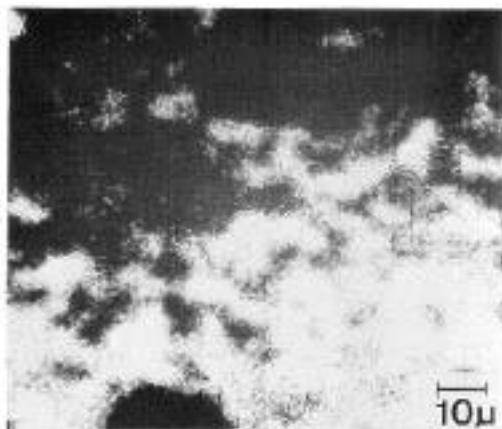
Similar chemical and morphological trend was observed in SEM/EDS study of real catalyst surfaces done by Weinberg et al. [12]



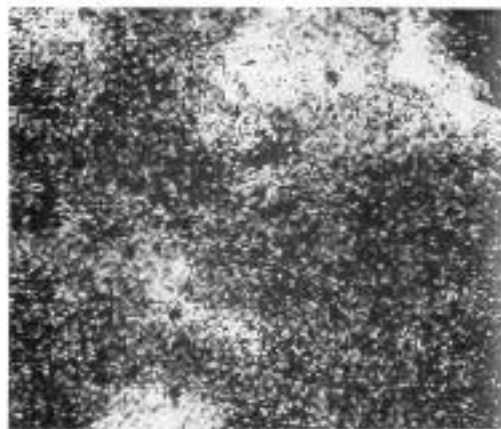
(a) unreduced catalyst



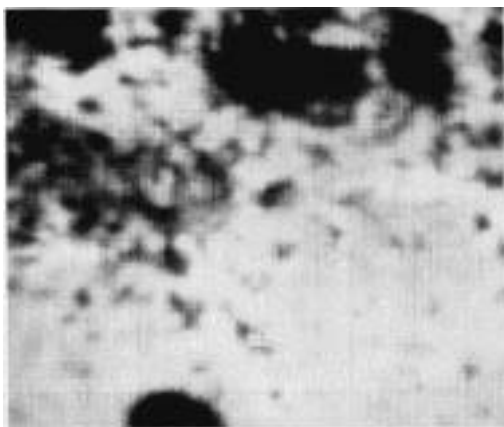
(b) reduced catalyst



(c) Fe



(d) Al



(e) K



(f) Ca

Figure 6: Secondary electron distribution (SED) image of the unreduced (a) and the reduced catalyst (b) with Auger maps for Fe (c), Al (d), K (e) and Ca (f) compositions.

[8]

Recently, a new model for the promoted iron catalyst surface was presented and explained in detail by Arabczyk [13], taking in account most of the studies and discoveries about iron catalysts discussed in the past. He proposed a double-layer model of promoter oxides on the surface of iron catalyst. The first layer consists of oxygen atoms and adsorption sites for nitrogen dissociation. Since oxygen covers the pure iron surface, the formation of Fe-O bonds increases its surface free energy and the surface roughness. When the surface is covered by oxygen, there are less active sites available. Arabczyk claims that oxygen atoms are necessary for stabilization of promoter atoms

(alkali and earth alkali metals) on surface, [10] where K, Ca and Al are compensated and stabilized with 1, 2 or 3 oxygen atoms, respectively. Since the number of oxygen atoms on surface denotes the amount of surface area, the presence of Ca and Al atoms that need more oxygen for compensation implies the presence of a larger surface area, thus a larger roughness. Model calculations for structures of promoter atoms on the iron surface (that took in account the above assumptions) suggest that 50-60% of the sites are occupied by oxygen and 40-50% of the sites can be free for nitrogen adsorption and ammonia synthesis. On the other hand, the presence of aluminum on the surface is crucial for compensation of oxygen and increase of surface energy and surface area. It is also believed that after activation (reduction) of the catalyst, FeAl_2O_4 forms on the surface that allows growth of an adlayer of the most active Fe(111) surface. On the other hand, the addition of potassium causes a decrease in surface area, but at the same time an increase in the number of free adsorption sites. Equilibrium is maintained between the surface, bulk and the spacers located between iron crystallites. A scheme of the model surface described above clearly shows the presence of the double layer of oxygen and promoter atoms (Fig.7a) and the presence of adsorption sites on the iron catalyst (Fig. 7b).

(a)

(b)

Figure 7: Schematic of a promoted iron catalyst surface: (a) side view and (b) top view showing free adsorption sites. [13]

4. Summary

Although promoted iron catalysis for ammonia synthesis is still not entirely understood, there is strong evidence about structure and possible functioning mechanisms. The rate-determining step for ammonia synthesis is most likely the adsorption and dissociation of nitrogen on the catalyst surface. Pure iron catalyst form is active only in the Fe(111) and Fe(211) conformations because of the presence of highly coordinated C_7 sites that provide the strongest adsorption for nitrogen. The addition of Al, K and Ca promoter atoms drastically increases the activity of other Fe planes. It is believed that potassium acts as an electron donor that increases the electron density and thus provides a higher number of active sites on the surface. The presence of aluminum influences the morphology of the catalyst, increasing its porosity and free surface area. Since iron aluminate ($FeAl_2O_4$) is formed during the activation of the surface and allows growth of a Fe(111) adlayer, the catalytic activity increases additionally. A model of promoted iron catalyst takes all of the research efforts in account. It introduces a double layer structure on iron surface, active because of increase in surface free area due to oxygen compensated with aluminum atoms in the first layer, together with the increase of free adsorption sites because of potassium presence in the overlayer.

In despite of the intense and thorough studies performed since the discovery of ammonia catalyzed formation, the function of promoted iron surfaces is still not completely understood. Future experiments will most likely focus on studies of real catalyst crystals with catalytic history and efforts will be made for exploitation of these processes in a high vacuum and high temperature system, representing actual experimental conditions.

5. Literature

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