Ammonia Synthesis Enhanced by Magnesium Chloride Absorption

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DOI 10.1002/aic.14733

Conversion to ammonia with Haber–Bosch catalysts can be increased above 95% by selective absorption of ammonia by $MgCl_2$. The maximum conversion depends on reaction and absorption equilibria. At very short times, the measured conversion rate is the same with and without absorption by the $MgCl_2$ salt; the overall rate constants are comparable to those in the literature. At larger times, conversion to ammonia can be over seven times greater with $MgCl_2$ than without. However, the overall rate constants can be over 10 times slower because they are controlled by ammonia diffusion in the solid salt. An approximate, pseudosteady state theory consistent with these results provides a strategy for improving the overall rate while keeping the conversion over 90%. For example, the absorption rates might be increased using smaller particles of absorbent on a porous inert absorbent support. The results provide part of the basis for designing small scale ammonia plants. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 1364–1371, 2015
Keywords: mass transfer, ammonia, absorption, conversion kinetics, separation techniques

Introduction

Ammonia is one of the most important chemicals in our society.[1,2] It is basic to chemical fertilizer and a key to feeding a large percentage of the world's population. Ammonia is usually made by burning coal or natural gas in air to produce a mixture of nitrogen, hydrogen, water, and carbon dioxide. After the carbon dioxide and water are carefully removed, the nitrogen and hydrogen are reacted at high pressure and temperature over an iron catalyst to make ammonia. Because the reaction is not complete, the resulting gas mixture must be separated. The ammonia product is harvested, and the unreacted nitrogen and hydrogen are recycled. Part of this recycle must be purged to prevent build-up of argon which is present in the original air.

This process works well, the result of a century of careful optimization.[3,4] It is a centerpiece of our modern industrial society. At the same time, it requires a major capital investment and a fossil fuel feedstock, and so may be hard to sustain in the centuries to come. Accordingly, dreamers in scattered agricultural stations have imagined making ammonia locally from air, water, and wind.[5–7] The air is separated to make nitrogen; the water is split by electrolysis to make hydrogen, using wind-generated electricity. However, when the nitrogen and hydrogen are combined over the catalyst at high pressure and temperature, the reaction is still incomplete: the unreacted gases must still be separated and recycled. While such a process will work, the need for the recycle means that the process is just a scaled down version of the current one. Because the economies of scale of the large plants are lost, the locally made ammonia will be more expensive.

This article explores the potential of a small-scale ammonia process which uses solid magnesium chloride as an ammonia-selective absorbent.[8] This absorbent has been carefully studied as a possible means of storing ammonia as a fuel for automobiles.[9–13] It absorbs and releases ammonia at temperatures and pressures like those used in conventional ammonia synthesis.[14–16] Moreover, as is shown in Figure 1, the combination of reaction and absorption can allow nearly complete conversion of the nitrogen and hydrogen. In this figure, the circles and diamonds are the conversions vs. time with and without the absorbent, respectively. To be sure, the times in Figure 1 are longer than the 1 min used in commercial practice. However, as we show below, these times reflect the amounts of catalyst and absorbent used and can be reduced.

To explore these ideas in more detail, we first review the kinetics of reaction and absorption.[17,18] We then describe our experiments and the results that they yield. Finally, we discuss the potential of this process for small-scale ammonia production.

Theory

The equipment used in these experiments, shown schematically in Figure 2, consists of two chambers and a pump. One chamber contains catalyst at a temperature around 400°C; the second contains magnesium chloride absorbent, sometimes at a lower temperature. The pump moves the gases between the chambers. After the system is charged with a 1:3 ratio of N_2 and H_2, the catalyst produces ammonia, which can be absorbed by the $MgCl_2$. Because the reaction reduces the number of moles in the system, that is

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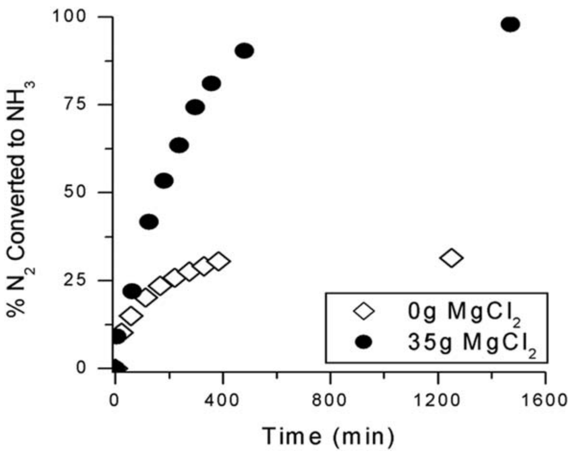

Figure 1. Conversion with MgCl$_2$ is increased.

While the eventual conversion is much higher when the absorbent is present, the initial rates are comparable.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{1}$$

there is a change in total pressure, which is measured vs. time.

The system involves three rates: that of reaction, that of absorption, and that of convection, that is, that due to the pump. The rates of reaction and absorption are both highly nonlinear. Most obviously, the reaction is exothermic, and the reaction's rate constants show a sharp Arrhenius temperature dependence. The forward reaction rate for consuming nitrogen is linear in nitrogen but nonlinear in hydrogen and varies inversely with ammonia. The reverse reaction rate varies about linearly with ammonia but inversely with hydrogen. The absorption rate does vary linearly with the ammonia concentration minus the concentration at equilibrium, but that equilibrium concentration is a sharp nonlinear function of temperature: one mole of MgCl$_2$ can pick up one, two, or six moles of ammonia. Because the absorption is diffusion controlled, it is nonlinear in time.

The modeling of the preliminary experiments reported here will be approximate, always seeking a linear form. The reaction making ammonia is, under conditions used here, controlled by nitrogen absorption on the catalyst. Under many important conditions, the rate r_{N_2} of nitrogen consumption per volume catalyst V_R is given by the Temkin–Pyzhev equation[19–22]

$$r_{N_2} = -k_R\, p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}}\right)^{\alpha} + k'_R \left(\frac{p_{NH_3}^2}{(p_{H_2})^3}\right)^{1-\alpha} \tag{2}$$

where p_i is the partial pressure of component "i," k_R, and k'_R are forward and reverse reaction rate constants, respectively, and α is a parameter close to one half. While this equation often successfully correlates experimental data, it is less successful at low partial pressures of ammonia. That is the case studied here. In this limit, an alternative expression is[22]

$$r_{N_2} \doteq \frac{-k_R}{RT}\left(p_{N_2} - p_{NH_3}/K\right) \tag{3}$$

where k_R and K are different constants. We will assume that in our experiments, absorption keeps the ammonia pressure low, so we have the simple linear kinetics of Eq. 3. Note this implies that when the ammonia product accumulates, the reverse reaction is linear in ammonia.

Earlier experiments have shown that the absorption rate per absorbent volume r_{NH_3} of pure low pressure ammonia by magnesium chloride is explained at small times by the penetration theory of mass transfer[23,24]

$$r_{NH_3} = \left(\sqrt{\frac{D}{\pi t}}\,\frac{Ha}{RT}\right) p_{NH_3} \tag{4}$$

where D is the diffusion coefficient of ammonia in solid MgCl$_2$, t is the time, a is the absorbent area per bed volume, and H is a partition coefficient between solid and gas. In our case, because we are absorbing ammonia from a high pressure mixed gas, ammonia concentration gradients may exist both in the solid and in the mixed gas. Thus we postulate that

$$r_{NH_3} = \frac{k_A}{RT}\, a\left(p_{NH_3} - p^*_{NH_3}\right) \tag{5}$$

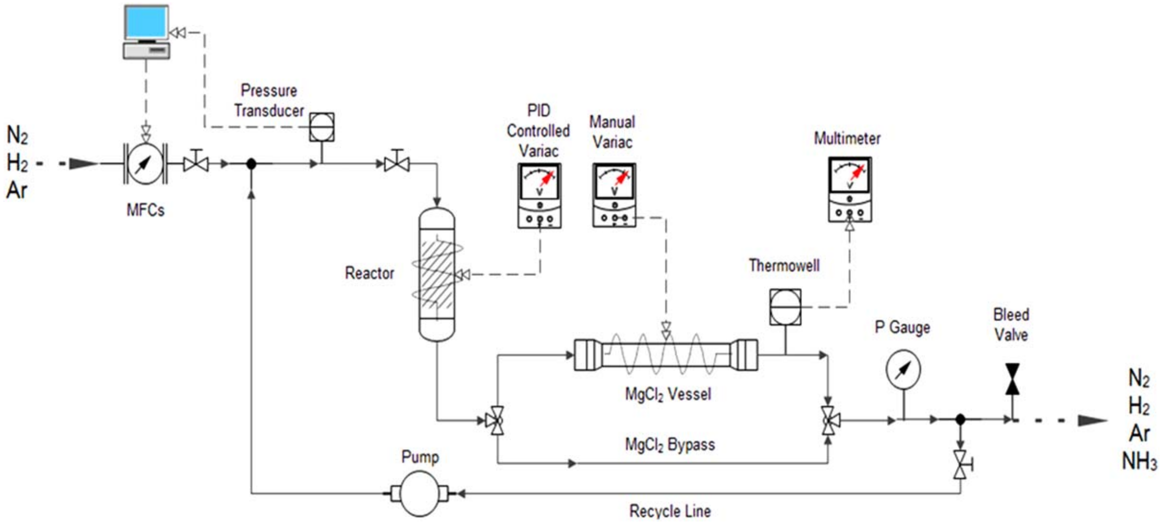

Figure 2. Apparatus used in this work.

This equipment is used for the kinetic and transport studies described in this article. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where k_A is an overall mass-transfer coefficient for absorption and a is the absorbent area per absorbent volume. The effective equilibrium partial pressure may be high if the amount of absorbent is so limited that it is saturated.

Next, we combine these rate processes and the flow through the pump in Figure 2 to find the overall rate of the process. Because we are interested in correlating the preliminary data obtained in this article, we give this description in terms of the average "lumped" concentrations in reactor and absorber. Moreover, in our experiments, the gas flow rates are typically 2 L/min, and the entire equipment volume is about 0.3 L, so the cycle times is under 10 s, much shorter than the total time of these experiments. Thus a single cycle is near steady state, even though the total experiments are unsteady.

We begin with a mass balance on the ammonia in the reactor, which we approximate for this small reactor as well-mixed

$$0=Q\ \left(p_{NH_3}-p'_{NH_3}\right)+2\ k_R\ V_R\ \left(p'_{N_2}-p'_{NH_3}/K\right) \tag{6}$$

where p_i amd p'_i are the inlet and outlet partial pressures of species "i," respectively; Q is the flow rate; and V_R is the reactor volume. We also make a similar balance on the absorber, which we also approximate as well-mixed

$$0=Q\ \left(p'_{NH_3}-p_{NH_3}\right)-k_A a V_A\left(p_{NH_3}-p^*_{NH_3}\right) \tag{7}$$

where p_i and p'_i are now the outlet and inlet pressures, respectively; V_A is the solid absorbent volume; and $p^*_{NH_3}$ is the ammonia pressure which would be in equilibrium with the solid. We also have the stoichiometric constraint

$$2\left(p_{N_2}-p'_{N_2}\right)=p'_{NH_3}-p_{NH_3} \tag{8}$$

By combining Eqs. 6–8, we make a pseudosteady-state approximation on ammonia gas—that ammonia produced equals ammonia absorbed—and so can eliminate p_{N_2} and p_{NH_3} to find

$$p_{N_2} = \frac{p_{NH_3}}{K}+\left[\frac{k_A a V_A}{Q}\left(\frac{1}{K}+\frac{1}{2}\right)+\frac{k_A a V_A}{2k_R V_R}\right]\left(p_{NH_3}-p^*_{NH_3}\right) \tag{9}$$

At the longer times and many cycles used for our experiments, we make an unsteady state balance on nitrogen in the full system volume, that is, both the reactor and the absorber. The overall nitrogen atom gas balance, continuing the pseudosteady-state assumption on ammonia gas occurring after the short transient buildup of ammonia, says that twice the moles of nitrogen gas converted to ammonia gas equals the moles of ammonia absorbed by the solid

$$2V\frac{dp_{N_2}}{dt}=-k_A a V_A\left(p_{NH_3}-p^*_{NH_3}\right) \tag{10}$$

where V is the total volume of gas. Combining Eqs. 9 and 10, we find

$$2V\frac{dp_{N_2}}{dt}=-\frac{p_{N_2}-p^*_{NH_3}/K}{\left[\frac{1}{2k_R V_R}+\frac{1}{Kk_A a V_A}+\left(\frac{1}{K}+\frac{1}{2}\right)\frac{1}{Q}\right]} \tag{11}$$

Notice that this rate increases with absorption rate k_A and absorber capacity V_A, and that it also increases with flow rate Q. Both trends reflect improved removal of product ammonia from the reactor, thereby suppressing the reverse reaction. When absorption and pumping are fast enough, and the absorbent permits a low ammonia partial pressure, Eq. 11 suggests that we can experience the best case, where the rate observed approaches the forward reaction rate.

The total pressure also varies with the nitrogen gas partial pressure

$$\frac{dp}{dt}=2\frac{dp_{N_2}}{dt} \tag{12}$$

Neglecting the transient as the ammonia partial pressure builds up to the pseudosteady-state value, we approximate

$$p=p_0-2\left(p_{N_{2,0}}-p_{N_2}\right) \tag{13}$$

Thus the reactor loop transient in terms of the total pressure p is approximately

$$\frac{dp}{dt}=-\frac{p-p^*}{\left\{V\left[\frac{1}{k_R V_R}+\frac{2}{Kk_A a V_A}+\left(\frac{1}{K}+\frac{1}{2}\right)\frac{2}{Q}\right]\right\}}=-k(p-p^*) \tag{14}$$

where p^* is the final equilibrium pressure, and k is an overall rate constant for these experiments, equal to the reciprocal of the quantity in braces.

Equation 14, which will be used to analyze the data presented in this article, merits some discussion now. First, the final value of p includes both the effects of reaction equilibrium (as K) and absorption equilibrium (as $p^*_{NH_3}$). Second, the three rate processes involved are harmonically averaged in k as resistances in series. The resistance of the reaction kinetics is $[V/V_R k_R]$. The resistance of absorption is $[V/Kk_A a V_A]$; note this varies with reaction reversibility (as K) and with the amount of absorbent (as V_A). This resistance also depends on the size of the absorbent particles, for a equals $(6/d)$ where d is the adsorbent particle size, the diameter for spheres or the side for cubes. The resistance of the pump, that is, the delay in moving the ammonia from the reactor to the absorber, is represented by the term containing the flow Q. We will use these approximate expectations as a basis for discussing our experiments, described next.

Experimental

Materials

Reagent grade anhydrous magnesium chloride ($MgCl_2$), purchased from Sigma Aldrich, was used without further purification. The catalysts for ammonia production vary, largely because of variations if ruthenium and alumina[25–28]; that chosen for this work was AmoMax-10, a prereduced magnetite (Fe_3O_4) catalyst from Süd-Chemie. The reactor contained 1.5 g of catalyst in each experiment. Both the $MgCl_2$ and catalyst were stored in an inert nitrogen environment. The gases N_2, H_2, Ar, and He (ultrahigh purity; 99.9995%) were purchased from Matheson Trigas. Brooks 0–5 VDC mass flow controllers were used to control gas supply from the pressurized cylinders. Liquid nitrogen was purchased from Matheson Trigas in 160 L dewars.

Apparatus

The lab-scale apparatus, shown schematically in Figure 2, was built using Swagelok 316 stainless steel tubing. The reactor and absorbent vessels were of 1 inch diameter tubing. The catalytic reactor, 4 inches long and containing the magnetite catalyst, was positioned upstream from an absorbent vessel containing the $MgCl_2$ crystals. One of two absorbent vessels was used: the smaller was 2 inches long, and the larger was 5.5 inches long. Both the catalyst and $MgCl_2$ were supported on quartz wool. Heating tapes connected to Variacs were used to control the temperatures in the reactor and the absorbent vessel, which were measured by Omega KMTIN-032U-12 thermocouples within the vessels. A Micromega CN77000 programmable proportional-intergral-derivative controller was used to maintain the temperature within the catalyst bed in the reactor. A WIKIA pressure transducer (Model # 8392476), mounted directly before the reactor, and a US Gauge 0–2000 psig analog pressure gauge, placed after the absorbent bed, were used to measure system pressure. The system was operated as a circulating batch system with a variable speed piston pump (Model PW2070N, PumpWorks, Minneapolis, MN) powering the flow of gases through the system. National Instruments Labview software was used to control and record data from the mass flow controllers, actuator, and pressure transducer. A Swagelok SS-4BMW bleeder valve installed downstream of the absorbent vessel was used to obtain 1 mL gaseous samples which were injected into an Agilent 6890 gas chromatograph with a Hewlett-Packard Plot Q 30 m × 0.32 mm 20 μm capillary column—HP 19091P-Q04. Helium was used as an inert carrier at constant makeup rate and a trace amount of argon was added to the reaction system for use as an inert. The column was held at $-60°$C for 3 min during which time H_2, N_2, and Ar exited the column. The column was then heated at a rate 20°C per minute for 12 min to elute the ammonia. Thus 14 min were required to elute all four gases. The system took roughly 4 min to cool for the next injection. As the amount of argon in the system remained constant, this amount was used to determine the response factor *RF* of the other gases

$$RF=\frac{F_{\text{gas}}}{A_{\text{gas}}}\div\frac{F_{\text{inert}}}{A_{\text{inert}}}=\frac{F_{\text{gas}}}{F_{\text{inert}}}\left(\frac{A_{\text{inert}}}{A_{\text{gas}}}\right) \tag{15}$$

where *F* is the flow of the gas of interest, and *A* is the area under the peak. Once the response factors for N_2, H_2, and NH_3 based on Ar were known, they were used to determine the amount of the gas of interest. System conversion was then calculated based on N_2 and H_2 measurements. The average of these two values was reported as percent system conversion

$$\%\text{Conv}_{N_2}=2*100*\left(\frac{N_2-N_2^{\text{initial}}}{N_2^{\text{initial}}}\right) \tag{16}$$

$$\%\text{Conv}_{H_2}=\frac{2}{3}*100*\left(\frac{H_2-H_2^{\text{initial}}}{H_2^{\text{initial}}}\right) \tag{17}$$

Agilent ChemStation software was used to control and record data from the gas chromatograph.

Procedure

Catalyst was pretreated before any ammonia experiments were begun. New catalyst was added to the reactor and the reactor sealed. Stoichiometric nitrogen and hydrogen were flowed through the reactor vessel while slowly heating the reactor to 400°C over 16 h. The reactor was then held at 400°C for 24 h while flowing nitrogen and hydrogen to ensure the protective coating was burned off and the catalyst fully reduced. During the entire reduction, the system pressure was held at 8 MPa using a CPU-controlled actuator at the system exit.

For each experiment, the reactor vessel was preheated to 400°C over 2 h and held at that temperature for 1 h before the experiments began. If the absorbent vessel was used during the experiment, it was preheated to 200°C over 2 h and held at that temperature for 1 h. Before the first experiment, the system was flushed with N_2 at 1 SLPM for 30 min. A similar flushing was performed for 15 min following each experiment. All system contents were flared to exhaust during the N_2 flushing and when emptying the system after each experiment.

To pressurize the system, the system exit valve was closed. Most experiments used either the reactor alone or the reactor and the absorbent vessel. Mass flow controllers were used to feed N_2 and H_2 into the system at a molar ratio of 1:3, along with the trace of Ar. The recirculating pump, turned on at the beginning of pressurization, gave a recirculation rate of 0.5–6 L(STP)/min. Once the system reached the operating pressure of 80 bar, the feed valve to the system was closed and the mass flow controllers turned off. The system was allowed to react for at least 45 min. Small gas samples were pulled from the system using the bleeder valve every ~20 min for analysis. Once the experiment was complete, the system exit valve was opened, the system contents completely emptied and flared to exhaust, and nitrogen flushed through the system for 15 min. Measurements without catalyst but with magnesium chloride showed a constant pressure, suggesting little nonselective absorption of hydrogen or nitrogen.

Experiments focusing on strictly the absorption of NH_3 by $MgCl_2$ were operated in a slightly different manner. First, the system consisting of the reactor and recycle line only was reacted to equilibrium, which took roughly 3 h. This resulted in a NH_3 gas-phase mole fraction of 15.6 ± 0.3. The gases produced then flowed through three-way valves into the empty, preheated absorbent vessel. The pressure in the absorbent vessel monitored vs. time allowed the absorption kinetics of compressed ammonia to be studied at higher total pressures than possible using pressurized ammonia cylinders.

Results

This work uses absorption to increase conversion of nitrogen and hydrogen into ammonia at temperatures similar to those used in the Haber–Bosch process. The conversion rate is a function both of catalyst activity in gases and of diffusion into solid magnesium chloride. The rates and the mechanism for this conversion are the focus of the experiments reported here.

Data illustrating the reproducibility of these experiments are shown in Figure 3. Normally, the key measurement is of the system's total pressure as a function of time. The system is initially charged with stoichiometric amounts of nitrogen and hydrogen to an initial temperature of 400°C. Two groups of such experiments, shown in the figure, used 1.5 g catalyst with either 15 or 35 g $MgCl_2$. The system's pressure *p*, normalized with its initial pressure of 80 bar, decays with time as shown. The reproducability of ±3% is typical of all our measurements.

The better conversion effected by the presence of the absorbent $MgCl_2$ is illustrated in Figure 4. Each of these groups of experiments used 1.5 g catalyst; all but one also used magnesium chloride in the amounts shown. The conversion at a given time is dramatically improved by adding absorbent. One and a half grams of absorbent increases conversion by 12 times. Fifteen and 35 grams $MgCl_2$ increase conversion 13 and 18 times, respectively.

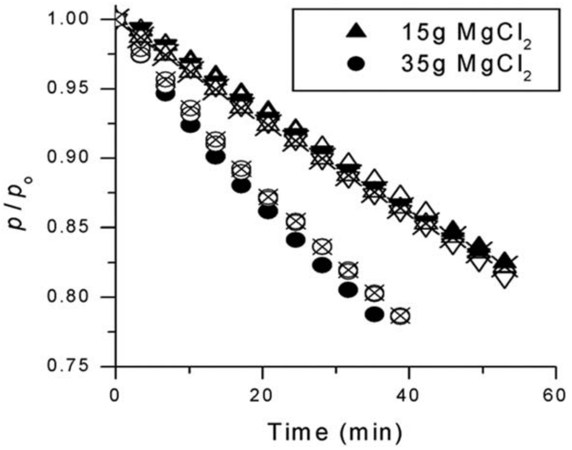

Figure 3. Repeated measurements of ammonia synthesis and absorption.

In each experiment, the reactor and absorber temperatures were 400°C and 200°C, respectively.

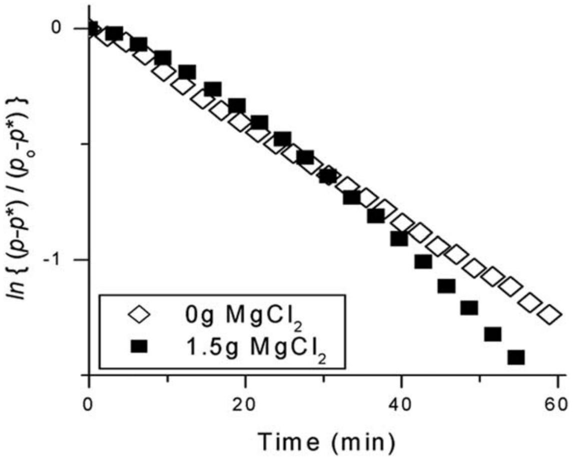

Figure 5. Reaction with minimal absorption.

The initial slope corresponds to a catalyst activity of 0.38 kg NH_3/hr kg catalyst, consistent with the literature. The p^* values are 68 bar with no $MgCl_2$, and 63 bar with 1.5 g $MgCl_2$. A small amount of absorption shifts the equilibrium limit with no noticeable change in the apparent rate constant.

The reasons for these increases in conversion vary, as suggested by the theory summarized by Eqs. 11 and 14 above. If we integrate Eq. 14 for small conversion, we get

$$\frac{p-p^*}{p_0-p^*}=e^{-kt} \tag{18}$$

Thus a plot of the logarithm of the left hand side of this equation should be linear in time. It is, as shown in Figure 5. We see that the initial slopes of the data for 0.0 and 1.5 g absorbent are the same, even though the degree of conversion shown in Figure 4 is different. The reaction rate when ammonia is absent is too fast for us to measure, as implied by the initially infinite rate suggest by Eq. 2. Nonetheless, we expected the initial slope with $MgCl_2$ present would be greater than that without $MgCl_2$. It is about the same—suggesting that under these conditions, the kinetics are unaffected by the equilibrium.

From the slopes in Figure 5, we infer that the catalyst activity is about 0.38 kg NH_3 /h kg catalyst. This agrees with values in the literature, which range for 0.3–0.4 and average 0.35 in the same units.[22] The difference between the data for 1.5 g $MgCl_2$ in Figures 4 and 5 largely reflects the altered p^*, even while the apparent initial rate is almost the same. Without $MgCl_2$, p^* is larger, and the pressure quickly approaches equilibrium; with $MgCl_2$, p^* is smaller and the reaction runs longer. Under these conditions, the overall rate constant k is almost independent of the amount of $MgCl_2$.

The resistances of chemical kinetics and of flow do both matter, as shown by the experiments without any magnesium chloride absorbent in Figure 6. Here, the conversion is plotted vs. the reciprocal of flow rate: the line showing nitrogen conversion equals (16.8–6.1 (pumping rate)$^{-1}$). Low flows result in low conversion because the reaction is slowed by the reverse reaction as the ammonia produced is allowed to stay longer and reach higher concentration in the reactor, and the empty absorber is not helping, except by diluting the product.

The kinetics for larger amounts of absorbent also fit the first order kinetics of Eq. 18, as shown in Figure 7. Now, however, the rates, which include the effect of equilibria lowered by ammonia absorption, show a clear effect of the

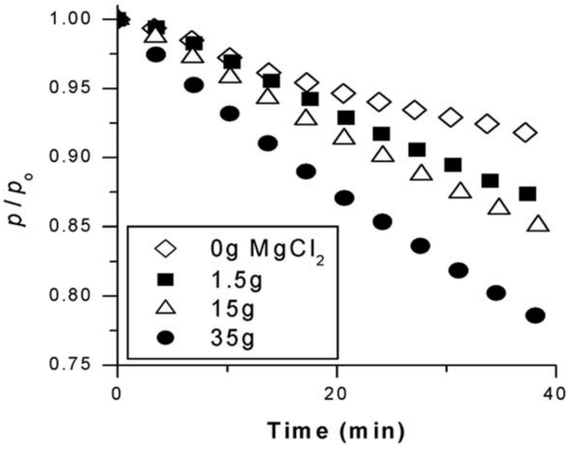

Figure 4. Reactor Pressure vs. amount of absorbent.

More absorbent gives greater conversion, though the mechanism responsible is complicated.

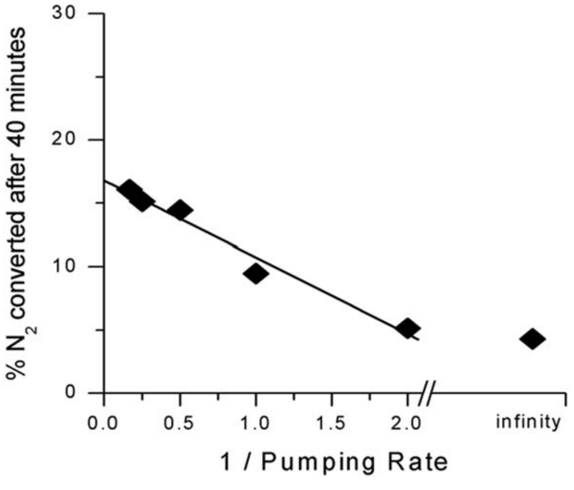

Figure 6. Reaction without absorption vs. flow.

The kinetics at infinite flow reflects only chemistry; the flow offers no resistance.

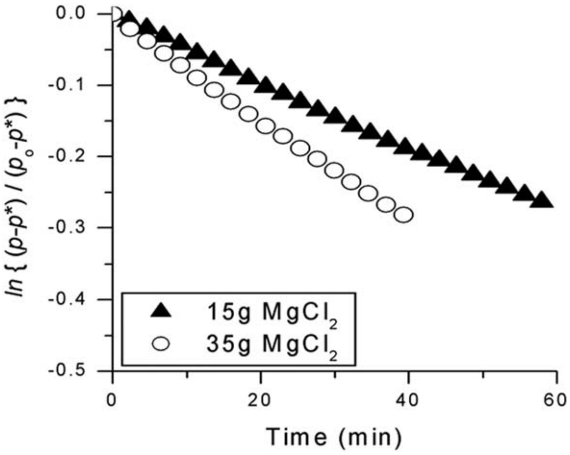

Figure 7. Reaction with absorption vs. time.

A substantial amount of absorbent both shifts equilibrium and significantly affects the apparent rate constant. The ordinate values differ from Figure 5 differ because the equilibrium *p is so shifted (*p** values: 9 bar with 15 g $MgCl_2$, and 2 bar with 35 g $MgCl_2$).**

absorbent amount—more absorbent raises the apparent rate constant. This is consistent with Eq. 11, which suggests that in the limit of high absorption rate and flow rate, one could approach a forward reaction rate dominated by chemical kinetics. Published studies of ammonia syntheses kinetics[18–22] imply that if ammonia were very rapidly absorbed, this overall rate would be very fast.

A difficulty remaining in our analysis is revealed by somewhat different experiments. In these, the system is started and run until some ammonia has been made. Then the absorber is isolated from the reactor by closing inlet and outlet valves, and the absorber pressure is measured as a function of time. The results do not show the variation suggested by Eq. 18, which is log linear in time. Instead, the logarithm of pressure varies with the square root of time, as shown by the results in Figure 8. Such behavior is a common characteristic of a diffusion-controlled process; in particular, the data are consistent with the penetration theory of mass transfer.[23] This is true both when absorption occurs from the N_2—H_2—NH_3 mixtures used here and from pure ammonia studied earlier.[24] However, the details of the rate-limiting step in these studies is not completely clear. The ratio of the slopes of the lines shown in Figure 8 is 5.3:1. If mass transfer were the only concern, the ratio of the slopes should be the ratio of the absorbent surface areas, which is $(35/1.5)^{2/3}$, or 8.2:1. The reason for this discrepancy is not clear but probably reflects altered absorbent geometry.[24] In addition, the partition coefficient measured here at 200°C was 0.0367 g NH_3/ atm cm^3 $MgCl_2$. The average earlier value in the literature between 172 and 235°C was similar but smaller, 0.012 in the same units.[15,16,24]

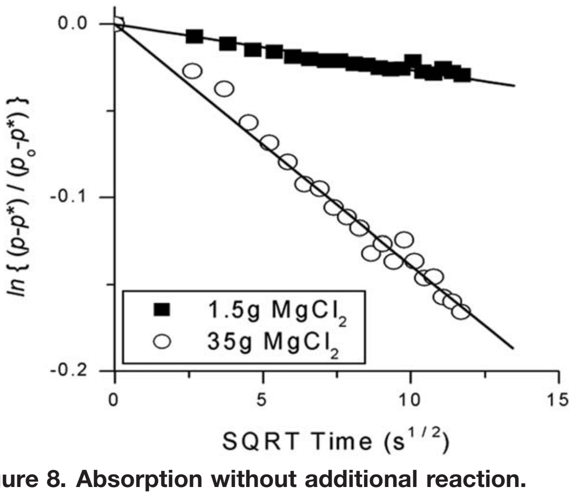

Figure 8. Absorption without additional reaction.

The variation with the square root of time, and not with time, is a characteristic of a diffusion-controlled process. In these experiments, *p was 36 bar with 1.5 g $MgCl_2$ and 31 bar with 35 g $MgCl_2$.**

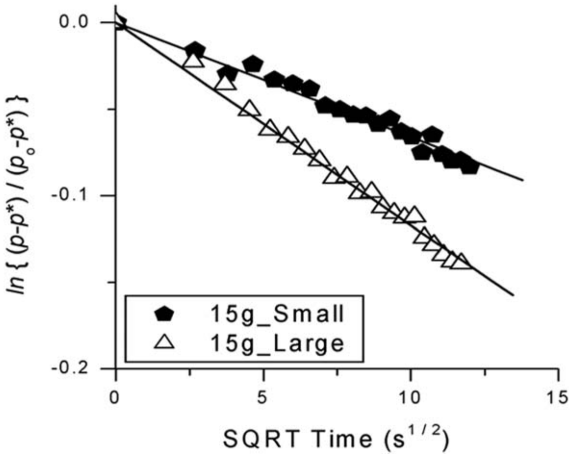

Figure 9. Absorption in different beds.

While both beds contain the same amount of $MgCl_2$, the absorbent in the larger bed is diluted with the same volume of glass beads. In these experiments, *p was 33 bar.**

While the results in Figure 8 imply that absorption is controlled by diffusion only in the solid, we are not sure whether this is always completely true. In one attempted redesign of the absorber, we diluted 15 g $MgCl_2$ with a roughly equal volume of glass beads. As shown in Figure 9, absorption rates in this diluted bed are 1.8 times faster than those in the undiluted bed. In particular, the data in the small bed—the pentagons—have a slope of 0.0066; but the results for the diluted bed—the triangles—have a slope is 0.0117, or a ratio of 1.77. This may suggest that the mass-transfer coefficients are larger when the bed is diluted, indicating a mass-transfer resistance in the gas phase as well as in the solid. We will explore other implications of all these results in the discussion section which follows.

Discussion

The theory and experiments above show how the conversion rate of nitrogen and hydrogen into ammonia can be increased with a solid ammonia selective absorbent. Ammonia synthesis is exothermic, and so occurs spontaneously at ambient temperature and pressure. However, the rate is very slow, so slow that practical amounts of ammonia are not produced. To overcome this, Haber famously used a catalytic reaction at high pressure and temperature.[1,2] The high pressure enhanced ammonia conversion because the number of moles in the reaction decreases. The high temperature increased the reaction rate, but at the expense of reducing the equilibrium conversion. Commercial reactors are currently run at high pressure and temperature with only perhaps twenty percent conversion, which necessitates cooling the product gases, separating the ammonia, and recycling the unreacted hydrogen and nitrogen.

This research suggests one way of potentially removing the need for nitrogen and hydrogen separation and recycle. It shows that the ammonia-selective absorbent, magnesium chloride, can dramatically increase the conversion. In the simplest case studied here, shown in Figure 1, the conversion is increased from around twenty percent to over 95%. If we use still more of the absorbent, we may get still higher conversion.

However, this conclusion can be clouded by the interaction of kinetics and equilibria. The kinetics includes those of chemistry, of flow, and of absorption, as summarized by Eqs. 11, 14, and 18. The equilibria involve those of both reaction and absorption. These can complicate the interpretation of the data.

To illustrate this, we consider the kinetics shown in Figure 4. This figure shows the changes in total pressure as a function of time. The pressure changes for catalyst without absorbent may at first appear to be less than those caused by catalyst plus absorbent, at least at larger times. But Eqs. 11 and 14 show that this can not be true at very small times. Specifically, when we add additional kinetic resistances from flow or from absorption, we see that the rates can not be faster than that expected for the reaction alone. To be sure, the rate of absorption shown in Figure 5 is initially extremely fast, but even this would just make the initial overall rates of the two processes have the same, chemical kinetically-limited speed. However, in our current equipment, we can not reliably make experiments at such small times that no sort of equilibrium affects the measurements. When we look at data like those in Figure 4, we must remember that we are looking at conversion affected by both kinetics and equilibria.

This complexity influences our strategies about how we can reduce the time required for high conversion, which Figure 1 shows is much higher but takes much longer when absorbent is present. In particular, for the conditions shown, the conversion with absorbent takes about 40 times longer than that with catalyst alone. We can increase the absorbent kinetics in three ways: by increasing the absorbent volume, by decreasing the absorbent particle size, or by frequently regenerating the absorbent. Each merits discussion.

To increase the absorbent kinetics forty times, we can simply increase the volume of the 200 μm absorbent particles by forty times. This will reduce the resistance to solid diffusion by forty times by changing the term ($Kk_A\ aV_A$) in Eq. 11. We should stress that this will work for the conditions in Figure 1, but that further increases in absorbent volume will have less effect because the rate of ammonia production will now be more nearly controlled by chemical kinetics. Because we already know that we have enough capacity for ammonia from the results in Figure 1, we will have considerable excess capacity in our new larger absorber. Still, the absorbent is cheap.

Alternatively, we might use smaller absorbent particles to provide a larger surface area and get similar results. For example, if we used a four times greater volume of 20 μm particles, we would have the same change in the term ($Kk_A\ aV_A$). Such smaller particles are often used in separation processes to get faster mass-transfer rates, though these particles will risk higher pressure drops through any packed bed in the redesigned absorber. To get both fast kinetics and low pressure drop, we could try absorbent particles 20 μm or smaller supported on 200 μm glass beads. However, while these strategies are well established, we did have trouble using them in other preliminary experiments.[24] Very small particles of magnesium chloride showed an area which decreased slightly over the first few cycles of absorption and desorption. While we are not sure why, we suspect that this was due to softening and fusing of the smaller particles.

A third method of accelerating the absorption step is to regenerate the absorbent frequently. The gain in doing this depends on the fact that the chemical kinetics is first order in time, but that the absorption varies with the square root of time (cf. Figures 5 and 8). Thus absorption is fastest at small times, always faster than kinetics. We can get better conversion if we frequently regenerate the absorbent particles. We considered a variety of cycle times for doing so, recognizing the strong parallels with pressure swing adsorption[29]; but we have not studied the process sufficiently to provide a basis for intelligent choice between these alternatives. We do want to emphasize, however, that this is still another way to accelerate absorption.

In carrying this work forward, we have also considered whether the catalyst and the absorbent would function better in a separate reactor and absorber, or whether they will work better in one combined piece of equipment. In most chemical syntheses, the reaction and separation are better carried out in two separate pieces of equipment because we can optimize each process via the specific conditions used.[30] In this case, we have done some of this, running the reactor at 400°C and the absorber at 200°C. The higher reactor temperature gives faster kinetics; and the lower absorber temperature gives more favorable absorber equilibrium. In addition, separate equipment allows us to easily separate and regenerate a loaded absorber without changing the conditions in the reactor. Thus the reactor can continue to operate at what is basically a steady state, even while different absorbers are cycled in and out of the system. Such conditions do challenge the recirculation pump: we did occasionally get anomalous results at high recirculation rates, which were probably due to uneven temperatures.

The idea of a separate reactor and absorber also offers the chance of effective heat integration in any larger scale apparatus. The reaction is exothermic. While the absorption is also exothermic, the desorption needed for $MgCl_2$ salt regeneration is endothermic. The obvious process improvement is to use reactor heat to regenerate the salt. We note this opportunity, but we have not done anything to realize it at this time.

At the same time, we remain intrigued by the prospect of putting catalyst and absorbent particles in the same piece of equipment, because this would simplify the process. There is then no recirculation pump or any extra heat exchange, so that we can imagine a very simple ammonia synthesis process suited for distributed manufacture. In such manufacture, a single farm could potentially make its own fertilizer. However, in preliminary experiments, we found that mixing catalyst and absorbent gave poor results. We are not sure why; we suspect that the $MgCl_2$ as received may contain small amounts of water, especially as this salt does form a variety of stable hydrates. The water in these hydrates would be expected to poison the Haber process catalyst.[8,22] While we could fuse the absorbent and then grind it under dry conditions to insure that no water is present, we decided that the idea of combined reaction and absorption had enough obvious disadvantages to not merit major effort now.

Conclusion

Ammonia is synthesized by the reaction of nitrogen and hydrogen at high pressure and temperature. The conversion of these gases at these conditions is compromised by equilibrium under the conditions normally used in commercial manufacture. This conversion can be made nearly complete by complementing the reaction with selective absorption using the common salt magnesium chloride. However, while the salt increases the conversion possible at equilibrium, the conversion rate is slower because it is controlled by ammonia diffusion in the solid. By analyzing how the reaction and absorption are coupled, we identify conditions under which both can occur at similar speeds, and thus how the conversion in this important process can be enhanced.

Acknowledgments

This work was partly supported by the Initiative for Renewable Energy & the Environment (IREE), and by the MNDrive inititive, which seeks to foster transdisiplinary research valuable to the State of Minnesota.

Notation

a = absorbent area per absorbent volume, cm^{-1}
D = diffusion coefficient of ammonia in solid $MgCl_2$, cm^2 s^{-1}
H = partition coefficient between solid and gas
k = overall rate constant, s^{-1}
K = apparent equilibrium constant for the ammonia synthesis reaction
k_R = forward reaction rate constant, s^{-1}
k'_R = reverse reaction rate constant, s^{-1}
RF = HPLC response factor for gas of interest
p = total gas pressure, bar
p_i = partial pressure of component "i," bar
$p^*_{NH_3}$ = ammonia pressure in equilibrium with solid absorbent, bar
Q = flow rate/RT, cm^3 s^{-1}
R = gas constant, cm^3 bar mol^{-1} K^{-1}
r_{N_2} = reaction rate consuming nitrogen per volume catalyst, mol cm^{-3} s^{-1}
r_{NH_3} = absorption rate per absorbent volume, mol cm^{-3} s^{-1}
t = time, s
T = temperature, K
V = total gas volume, cm^3
V_A = solid absorbent volume, cm^3
V_R = catalyst volume, cm^3
α = empirical kinetic constant, about 0.5

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Manuscript received Aug. 6, 2014, and revision received Dec. 22, 2014.