

Low Temperature and Pressure Single-Vessel Integrated Ammonia Synthesis and Separation using Commercial KATALCO Catalysts

Green ammonia synthesis using renewable energy

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In recent years, the potential for 'green' ammonia produced from renewable energy has renewed the pursuit of a low-pressure, low-temperature ammonia synthesis process using novel catalysts capable of operating under these conditions. In past decades, the trend of decreasing the pressure in the existing Haber-Bosch process to the *de facto* limit of condensation at 80 bar has been achieved through catalysts such as Johnson Matthey's (formally ICI, UK) iron-based KATALCO™ 74-1. By replacing the separation of ammonia *via* condensation by absorption, the process loop can be integrated into a single vessel at constant temperature, and the operating region drastically shifts to lower pressures (<30 bar) and temperatures (<380°C) unknown to commercial catalysts. Herein, the low-temperature and low-pressure activity of KATALCO 74-1 and KATALCO

35-8A catalysts is studied and compared to a ruthenium and caesium on ceria catalyst known to have low-temperature activity through resistance to hydrogen inhibition. Due to its low temperature and high conversion activity, KATALCO 74-1 can be deployed in an integrated reaction and absorptive-separation using $\text{MnCl}_2/\text{SiO}_2$ as absorbent. Although further catalyst development is needed to increase compatibility with the absorbent in a feasible reactor design, this study clearly demonstrates the need to re-evaluate the viability of commercial ammonia synthesis catalysts, especially iron-based ones, for their deployment on novel green ammonia synthesis processes driven exclusively by renewable energy.

Introduction

Since the early 20th century, the Haber-Bosch process for ammonia synthesis has been at the core of the chemical industry due to its role sustaining population growth through synthetic fertiliser (1). Conventionally, the overall process is split into two highly integrated steps: (a) hydrogen production; and (b) ammonia loop. First, hydrogen is produced through the reforming of fossil fuels (such as methane), generating excess energy stored in the form of steam. The hydrogen is then fed with nitrogen to the ammonia loop, as shown in **Figure 1(a)**, to catalytically synthesise ammonia at high temperatures and pressures. Due to the low single pass

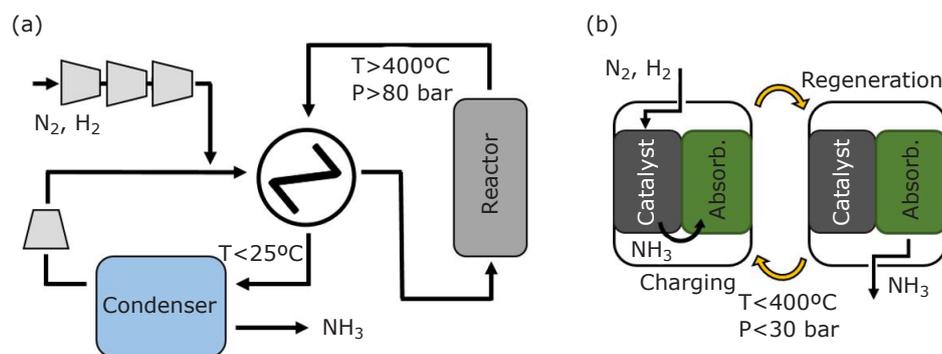


Fig. 1. Schematic of conventional Haber-Bosch and novel single-vessel process: (a) conventional Haber-Bosch process operating at high temperatures and pressure with a temperature swing to remove ammonia by condensation; (b) novel single-vessel process operating at moderate temperatures and pressure without a recycle or heat exchange

conversion ($\sim 15\text{--}25\%$), ammonia is separated at low temperatures using condensation such that unreacted gases can be recycled. The predominant energy consumption for the ammonia synthesis loop is associated to the feed compression, which has led to a thorough optimisation for integrating excess energy from methane reforming to drive feed compressors, in addition to recycle and refrigeration compressors (2).

When shifting ammonia production away from fossil fuels using exclusively renewable electricity (i.e. green ammonia), a new optimisation is required (3). Hydrogen produced using electrolysis is less efficient, more expensive and does not generate excess energy to be used to drive the compressors for the high-pressure ammonia loop. Renewable electricity sourced from solar and wind energy is also inherently distributed and intermittent, thus the economic feasibility of green ammonia requires a process that is low capital cost and agile to replace the capital intensive and continuously operated Haber-Bosch process. The current high operating pressures of the Haber-Bosch reactor not only increase the capital requirements but are also unsuitable to dynamic operation. Adjusting the production to follow the renewable energy production pattern can potentially overheat the reactor due to the exothermicity of the reaction (under steady state operation, the heat of reaction is partially transferred to the reactor inlet stream). Additionally, the heat exchange required for the drastic swing in temperature from the reactor to condenser requires additional capital and is not conducive to operating in a non-steady state.

The concept of electrically driven ammonia synthesis has been previously considered, particularly from hydroelectricity early in the 20th

century, but it never gained widespread adoption over coal- or methane-fed processes due to the lack of competitiveness of renewable energy and the advent of abundant and cheap natural gas. Now, stimulated by the current environmental, social and political pressures, and enabled by the steady drop in the cost of solar and wind electricity, green ammonia is being reconsidered for commercial feasibility. As a result, there is renewed impetus to design an ammonia synthesis process driven exclusively by renewable energy and thus, able to operate at low pressures with minimal gas compression, fast production response and reduced heat integration in the process loop.

Ammonia synthesis catalysts (conventionally iron-based) facilitate fast kinetics to break the nitrogen triple bond at $400\text{--}500^\circ\text{C}$, but high pressures ($150\text{--}250 \text{ bar}$) are necessary to increase the conversion through increased equilibrium. Improved catalysts (both iron- and ruthenium-based) can decrease the operating reactor pressure to $\sim 80 \text{ bar}$, but further reduction causes the process to become separation limited. While operating at 80 bar offers benefits through decreased capital and increased agility, it is generally accepted that it is a 'flat' optimum with respect to energy consumption because the decrease in feed compression is balanced by an increase in refrigeration compression to drive ammonia condensation (4). As total reactor pressure decreases, the reaction equilibrium pressure of ammonia decreases and achieving the same level of separation in the condenser requires the vapour pressure of ammonia to be decreased through colder temperatures. Indeed, at very low pressures, separation by condensation becomes impossible as the ammonia equilibrium pressure drops below the limit of practical vapour pressures (1.2 bar at -30°C) (5).

In response, the replacement of ammonia condensation by absorption has been developed to remove ammonia at lower partial pressures and ambient temperatures, facilitating a lower pressure process (6). Absorption of ammonia by a metal halide is a chemical reaction in the crystal lattice rather than adsorption onto the surface of a sorbent, thereby displaying a strong interaction for near complete ammonia removal (<0.01 bar equilibrium pressure), but also requiring substantial heat (60–80 kJ mol⁻¹) for desorption of ammonia at increased temperatures or decreased pressures before final liquefaction (7, 8). By utilising high-temperature absorption and low-temperature catalysis, we have further advanced this process by integrating the absorption separation and catalytic synthesis in a single vessel to remove the need for recycle and heat integration of gas flows between synthesis and separation, as shown schematically in **Figure 1(b)**. The integrated process is rooted in aligning the operating conditions of catalysis, which favours high temperatures and low ammonia pressures, with absorption, which favours low temperatures and high ammonia pressures. A proof-of-concept has been achieved using MnCl₂/SiO₂ absorbent and a ruthenium and caesium on ceria catalyst to exceed single pass equilibrium conversion (9).

In order to achieve low-temperature and low-pressure ammonia synthesis, catalytic research has focused over recent decades on the development of ruthenium-based catalysts which have superior activity compared to conventional iron catalysts. In particular, ruthenium has been proven to have low-pressure and high-conversion activity (10), and we have recently demonstrated the activity of ruthenium on ceria at low temperature by removing hydrogen inhibition (9). In 1980, bp and Kellogg Corporation developed the Kellogg advanced ammonia process (KAAP) operating at 90 bar using a ruthenium catalyst downstream of the primary iron catalyst to achieve higher single-pass conversions unattainable with ammonia inhibited iron catalysts (11, 12). In parallel during the 1980s, ICI (now Johnson Matthey) developed the KATALCO 74-1 iron catalyst promoted with cobalt for deployment in the ICI AMV and leading concept ammonia (LCA) processes operating at similarly low pressures (~80 bar) without the high cost and fragility of a ruthenium catalyst (4, 13). This catalyst has been proven to have a favourable combination of low-temperature reduction (to avoid sintering), high conversion activity and exceptional stability (14–16). While recent

research has focused on developing increasingly complex ruthenium hydride (17) and electride (18) catalysts, it is crucial to re-examine conventional and commercially available catalysts for suitability in unconventional low pressures and temperatures that arise from novel process designs such as the abovementioned single-vessel system. As a result, we herein describe the low-temperature (300°C) and low-pressure (20 bar) activity of the KATALCO 74-1 and KATALCO 35-8A catalysts and their application in an integrated process using absorption separation.

Methodology

The catalysts used in this study were ruthenium impregnated onto ceria nanorods and promoted with caesium (5%Ru/10%Cs/CeO₂), as described previously (9) and commercial KATALCO 74-1 and KATALCO 35-8A provided by Johnson Matthey crushed to a powder. Catalyst beds utilised inert SiC to generate even flow in the packed bed and keep the total volume constant. The absorbent used for the integrated system was manganese chloride impregnated onto silica gel (MnCl₂/SiO₂). We have recently demonstrated that MnCl₂ resists decomposition at high temperatures after exposure to air. In addition, supported MnCl₂ remain stable over several cycles compared to bulk MnCl₂ (9).

The experimental rig and procedure used for analysis has been described in detail previously (9). Briefly, nitrogen and hydrogen at 20 barg were fed to primary and secondary reaction vessels (**Figure 2**) whose configuration depended on the operating mode of the system, before exiting the system through a mass flow meter. During catalytic tests, the activity of a catalyst in the primary reaction vessel was analysed by the change in flow after completely removing ammonia using MnCl₂/SiO₂ as absorbent in the second vessel at ambient temperature. For some tests, the second reaction vessel was bypassed in order to measure the concentration of ammonia directly using gas chromatography. During the analysis of the integrated reaction and separation system, the secondary reaction vessel was packed with a specified amount of absorbent (~1.5 g) and an additional catalyst bed (~1.5 g) pre-reduced in the primary reaction vessel and transferred in a glovebox. Both vessels were operated under the same temperature. To evaluate the effect of the presence of the absorbent, the system was initially pressurised with hydrogen before switching to a stoichiometric reaction mixture at the beginning

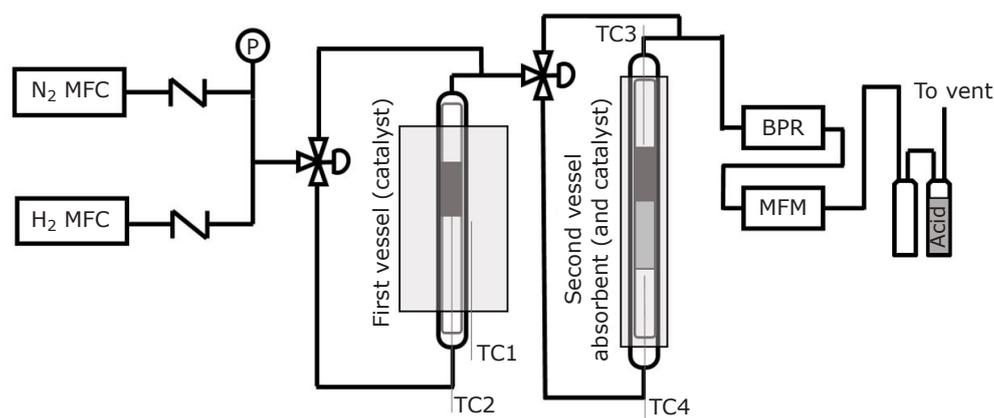


Fig. 2. Schematic of the reactor system. Nitrogen and hydrogen enter the system at a controlled rate with mass flow controllers (MFCs). The gases pass through the first vessel containing catalyst only, and a second vessel containing either excess absorbent or controlled absorbent and catalyst for a catalyst or integrated system test, respectively. The system is pressurised using a back pressure regulator (BPR) and a mass flow meter (MFM) measures the change of flow through the system

of the reaction. Conversion in the primary reaction vessel was measured through the molar flowrate change of ammonia synthesis, while bypassing the secondary reaction vessel. Once the primary reaction bed reached steady state, its outlet flow was switched to pass through the secondary reaction vessel. The flow at the outlet of the secondary vessel was measured to quantify the combined effect of the absorbent and secondary catalyst bed, with conversion being approximated by isolating the absorption component through kinetic models. After several hours when the data was no longer transient, the system was reset by regenerating the absorbent at $\sim 380^\circ\text{C}$ and ambient pressure under nitrogen flow for at least 1 h.

Results and Discussion

The ideal properties of a catalyst for the integrated reaction and absorption separation system are: (a) low-temperature activity; and (b) high conversion activity because absorption is more favourable at lower temperatures and higher pressures of ammonia. Thus, KATALCO 74-1 and KATALCO 35-8A catalysts were tested for ammonia synthesis at 20 barg, at temperatures between 220°C and 400°C (using stoichiometric ratios of hydrogen to nitrogen). Prior to catalytic testing, the catalysts were reduced under a high flow rate ($40\text{ cm}^3\text{ min}^{-1}$) of hydrogen. In order to keep water vapour levels low during reduction to avoid sintering (14), the catalyst was crushed to decrease internal mass transfer. In addition, the temperature was gradually increased to 500°C

over 18 h, then held for increments of 3 h with activity tested in between. The activity increased with time during reduction at 500°C until ~ 12 h, after which it remained constant (Figure S1 in the Supplementary Information), indicating the importance of completely reducing the catalyst in order to properly assess the low-temperature and low-pressure activity. To examine the effect of cobalt promotion on low-temperature and low-pressure activity, KATALCO 35-8A was also treated with the same reduction procedure.

As shown in **Figure 3(a)**, both KATALCO 74-1 and KATALCO 35-8A exhibit low-temperature activity at 20 barg comparable to 5%Ru/10%Cs/CeO₂, but do not approach equilibrium as quickly as the ruthenium catalyst due to increased ammonia inhibition for an iron-based catalyst. However, cobalt promotion causes KATALCO 74-1 to be less inhibited by ammonia, facilitating higher conversions, as has been indicated in previous studies under industrial conditions (4, 15). While KATALCO 35-8A is not significantly less active within experimental error compared to KATALCO 74-1 at low conversion ($<350^\circ\text{C}$, 200 mg catalyst), there is greater differentiation in activity at high conversion (1.5 g catalyst) due to a more precipitous drop in activity with increased ammonia pressure for KATALCO 35-8A, until both catalysts begin to converge toward equilibrium (400°C). Since cobalt in solid solution in the magnetite phase is believed to restructure iron crystallites rather than forming new active sites (14), promotion with cobalt does not decrease the temperature at which activity starts. Still, while both catalysts are stable at

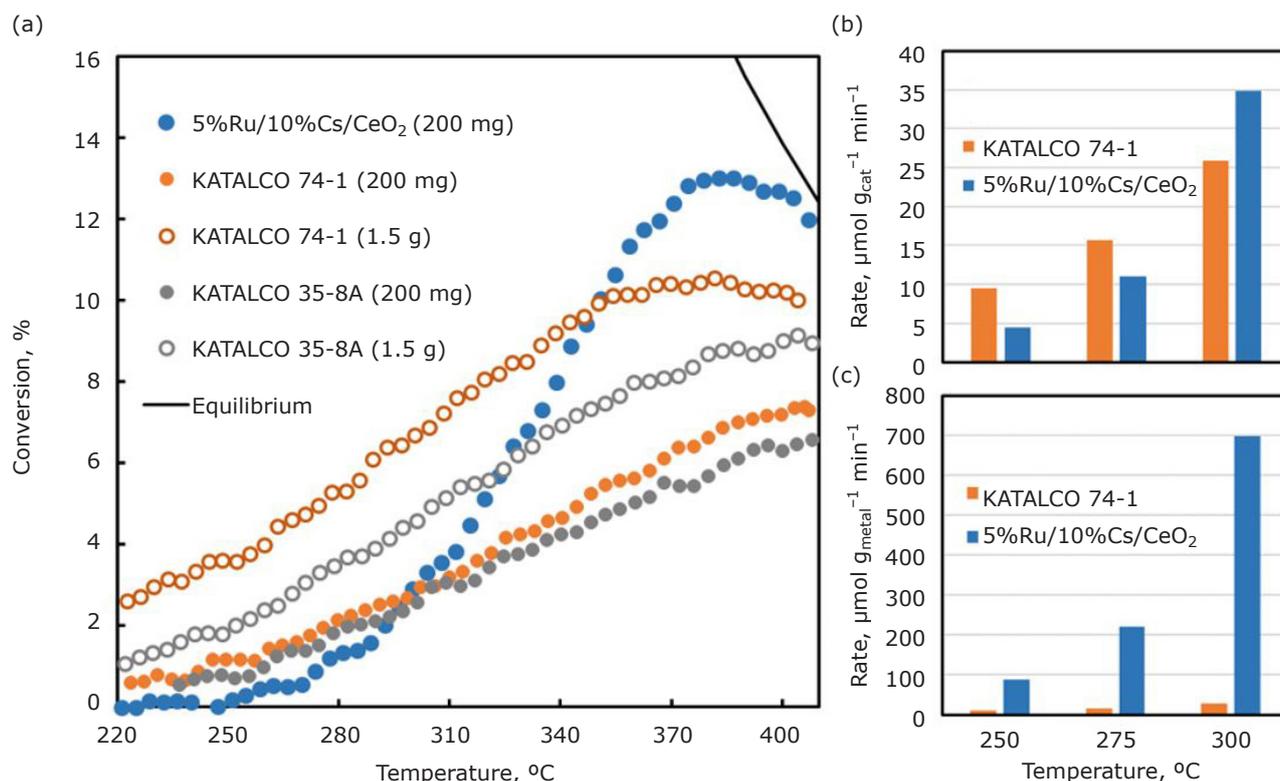


Fig. 3. Catalytic activity of KATALCO 74-1 and ruthenium and caesium on ceria at 20 barg and 1:3 nitrogen-to-hydrogen ratio: (a) activity as a function of temperature and mass of catalyst; (b) selected low-temperature activities as measured by gas chromatograph under reduced space velocity and normalised by the total catalyst mass; (c) selected low-temperature activities normalised by mass of active metal approximating KATALCO 74-1 >92% iron and cobalt

300 °C and 350 °C for several hours, it is possible that cobalt promotion will also make the catalyst resilient to degradation over months or years (4). The low-temperature activity was confirmed with gas chromatograph measurements, as shown in **Figure 3(b)**, which indicate superior activity of the KATALCO 74-1 catalyst <300 °C with respect to ruthenium and caesium on ceria when compared on a mass basis. Still, when compared on the basis of active metal (**Figure 3(c)**), the ruthenium catalyst is more active because it contains a much smaller amount of active metal, as would be expected from conventional wisdom regarding the relative activity of ruthenium compared to iron.

Nevertheless, the intrinsic activity of a catalyst is significantly less important for overall process design than catalyst cost and reactor volume. It is well known that ruthenium-based catalysts are hampered by high costs compounded by faster degradation (especially if carbon is used as support) which shift the paradigm of catalyst typically constituting <1% of total process cost (11). Further, supported ruthenium catalysts are often of lower bulk density than conventional iron-based catalysts, leading to overall

larger reactor sizing. This is particularly critical when designing small modular processes for distributed ammonia synthesis using renewable electricity. Consequently, a larger mass of KATALCO 74-1 (1.5 g) was tested to compare activity in terms of volume with ruthenium and caesium on ceria. As shown in **Figure 3(a)**, similar volumes of both catalysts show comparable activities at high temperatures. Even more interesting is the higher activity of the commercial iron-based catalyst KATALCO 74-1 at low temperatures (<340 °C). While conversion does not increase proportionally to the mass of catalyst, likely due to ammonia inhibition inducing decreased returns, it indicates the potential to achieve conversions at low temperatures competitive with ruthenium for a given volume, with cost likely to be lower even with far more catalyst mass.

Given the low temperature, high conversion activity of KATALCO 74-1, the commercial catalyst was then tested in an integrated system where catalyst and absorbent are in the same vessel operating at the same conditions. This system was analysed using a layered configuration in two

reaction vessels in which the primary reaction vessel contains the first layer of catalyst (1.5 g KATALCO 74-1) and the second reaction vessel contains a layer of absorbent (1.5 g $\text{MnCl}_2/\text{SiO}_2$) followed by another layer of catalyst (1.5 g KATALCO 74-1). The conversion from the first vessel is approximately the highest reasonably possible even though it is short of equilibrium due to the diminished returns for added catalyst as a result of ammonia inhibition at higher conversions, as shown in **Figure 3(a)**. When the steady-state effluent of the first reaction vessel is passed through the second reaction vessel, the flow decreases as a result of both ammonia absorption and additional conversion of nitrogen and hydrogen to ammonia. Therefore, decoupling these effects requires a model to predict the absorption component, which has been developed previously using kinetic data of ammonia absorption in $\text{MgCl}_2/\text{SiO}_2$ (9). Any decrease in flow beyond that predicted for the absorption component can be ascribed to additional ammonia production from the second catalyst bed. It should be noted that this experimental framework of layered catalyst and absorbent serves as a proof-of-concept to show overlap in activity between catalyst and absorbent and is not intended to be the targeted process design, which requires further optimisation.

As shown in **Figure 4** for three different combinations of reaction vessel temperatures, there is a notable change in flow when passing through the second reaction vessel, and once the absorption component is isolated (represented by the dash black line in the figure), the additional conversion from the second catalyst bed ranges

from approximately 3.5–5% at its maximum. Over time, as the absorbent layer gets saturated, it causes the flow to decrease. The lower than expected measurement at long times in **Figure 4(c)** is likely due to the absorbent not being fully regenerated before the test. Although it may be expected that the second catalyst bed should increase conversion at steady-state if the first catalyst bed is below equilibrium, increased catalyst mass has severely diminished returns at high conversion due to ammonia inhibition, as indicated in **Figure 2(a)**. Therefore, a return of flow to approximately the original value at long times is reasonable, and any transient increase in conversion must be due to partial removal of ammonia.

The integrated system analysis clearly demonstrates that the absorbent and catalyst are operating under the same conditions. However, several factors should be considered for further optimisation and development when deploying commercial KATALCO 74-1 catalyst (or similar) in an integrated ammonia synthesis and separation system. First, as the high reduction temperatures of KATALCO 74-1 will likely sinter and decompose the absorbent, the second catalyst bed was reduced separately before being transferred into the second reaction vessel in a glovebox. In this process, there is the possibility of partially deactivating the catalyst either from slight air exposure, potential contamination within the glovebox or extended time at low temperatures. Second, it is possible that the absorbent decomposes and releases chlorides which poison the catalyst, but this possibility was mitigated by: (a) using MnCl_2 absorbent, which is

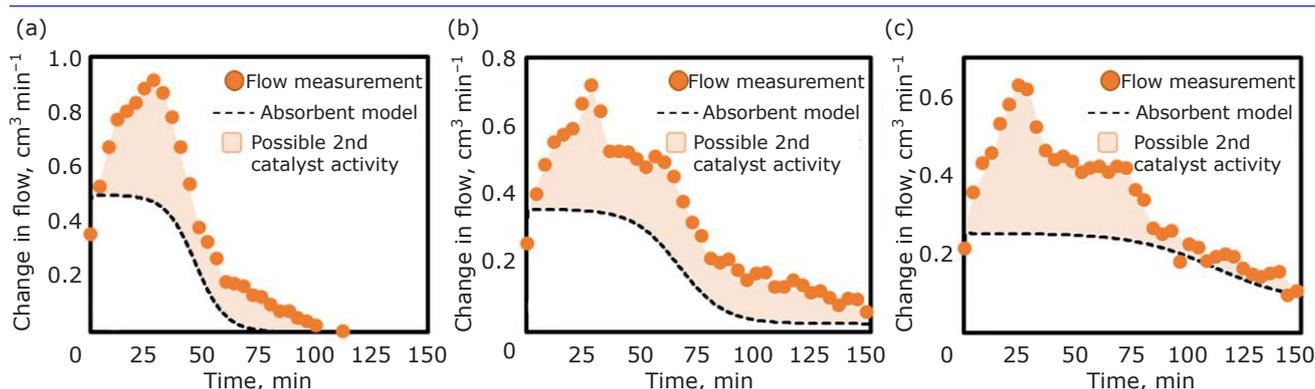


Fig. 4. Transient performance of integrated system at 20 barg with KATALCO 74-1 and $\text{MnCl}_2/\text{SiO}_2$: (a) first reaction vessel at 370°C, second reaction vessel at 360°C; (b) first reaction vessel at 320°C, second reaction vessel at 330°C; (c) first reaction vessel at 310°C, second reaction vessel at 310°C. At time zero, the steady-state effluent from the first reaction vessel containing ~1.5 g KATALCO 74-1 is switched from bypassing to flow through the second reaction vessel with ~1.5 $\text{MnCl}_2/\text{SiO}_2$ and ~1.5 g KATALCO 74-1 in series. The temperatures were varied to investigate the behaviour of the system within the approximate range where catalyst and absorbent overlap

resistant to decomposition (9); and (b) preheating the absorbent to allow any potential decomposition to occur before combining with catalyst. It should also be noted that for complete process implementation, ammonia must be desorbed from the absorbent at higher temperatures and lower pressures with the input of heat. The re-decomposition of ammonia over the catalyst during regeneration is anticipated to affect overall process feasibility, thereby requiring novel reactor design. Still, it is also expected that conventional iron-based catalysts will re-decompose less ammonia than a ruthenium-based catalyst (19).

Conclusions

As interest grows in producing ammonia from renewable electricity as both green fertiliser and carbon-free renewable energy vector, a redefinition of the Haber-Bosch process is needed to enhance its ability to follow the energy profile of solar and wind. Integration of ammonia synthesis and its separation *via* absorption in a single vessel will provide the agility required using low pressures (~20 barg) and no recycle. Such single-vessel ammonia production requires a catalyst with low temperature and high conversion activity such that reaction occurs under the same conditions as absorption separation. In developing this process, this paper demonstrates the importance of re-examining existing commercial catalysts at low temperature (<350°C) to determine their applicability for this integrated and future processes to learn from their beneficial aspects in developing the next generation of commercial iron-based catalysts. Consequently, the KATALCO 74-1 and KATALCO 35-8A commercial catalysts have herein been shown to have low temperature (300°C) and pressure (20 barg) activity competitive with recently developed ruthenium and caesium on ceria catalyst on a total mass and volume basis, with KATALCO 74-1 attaining higher conversions compared to KATALCO 35-8A due to cobalt promotion reducing ammonia inhibition. When utilised for the integrated reaction and absorption separation with $\text{MnCl}_2/\text{SiO}_2$, KATALCO 74-1 indicates overlap in activity with the absorbent operating under the same conditions. While further analyses with respect to reduction temperature and structure sensitivity are necessary for future development, initial results indicate positive prospects. Using available commercial catalysts rather than novel catalysts for integrated ammonia production can potentially reduce the cost and accelerate the deployment of green ammonia

production using the novel integrated, low-cost and agile single-vessel process.

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KATALCO is a trademark of the Johnson Matthey group of companies.

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