Reactive sorption of ammonia to enable low pressure synthesis

Luc Liedtke, Collin Smith, Laura Torrente-Murciano

Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, UK

Highlights
- Integration of ammonia synthesis and separation (sorption) reactions
- Initial kinetic data for the sorption reaction over several cycles
- Insights into manipulating reaction rates through support addition

1. Introduction

The objective of this study is to develop a novel system capable of studying sorption kinetics in flow under isothermal and isobaric conditions to advance our fundamental understanding of the mechanisms and rates of the ammonia sorption reaction in metal halide absorbents. As the role of ammonia expands to encompass those of a carbon-free energy vector, the inevitable development of new ammonia markets will create a surge in ammonia demand with projections indicating a threefold increase by 2050.[1] However, due to its reliance on fossil fuel derived hydrogen, conventional ammonia synthesis via the Haber-Bosch process is one of the most emissions-intensive industrial processes with a contribution to anthropogenic CO2 emissions of >1%.[2] As a result, satisfying growing ammonia demand in a sustainable way requires the development of novel, small-scale ammonia synthesis processes which integrate more effectively with distributed and intermittent renewable energy sources. In this context, our group have demonstrated the possibility of low-pressure ammonia synthesis by integrating the ammonia synthesis and separation reactions in a single vessel (Figure 1).[3] Separation is achieved using solid metal halide absorbents which selectively and reversibly react with ammonia to isolate it from the reaction mixture, thereby suppressing equilibrium restrictions.
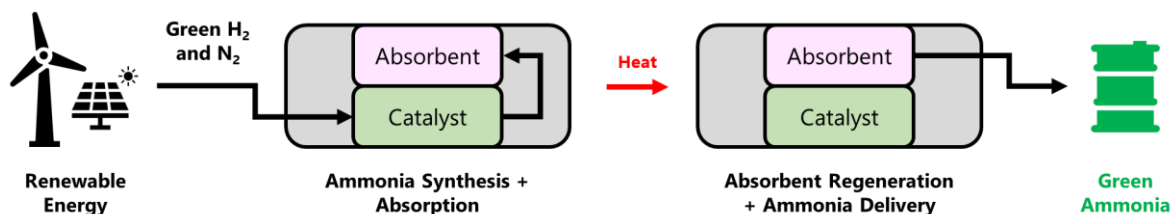

Figure 1. Integrated ammonia synthesis and separation process to enable the production of ammonia from renewable energy at low pressures.

2. Methods

The two absorbents studied were $MnCl_2 \cdot 2H_2O$ obtained after drying $MnCl_2 \cdot 4H_2O$ (99%, Alfa Aesar) and $MnCl_2 \cdot 2H_2O$ supported on SiO_2 (0.062 – 0.105mm, Alfa Aesar) via incipient wetness impregnation with ethanol. Isothermal and isobaric sorption kinetic measurements were performed using a bespoke experimental system capable of controlling inlet flows, composition, pressure and temperature. Both absorbents were subjected to multiple sorption cycles at a temperature of 340°C and an ammonia partial pressure of 1.8 bar and 0 bar for absorption and desorption respectively. The equilibrium ammonia partial pressure at this temperature is 1.02 bar.

3. Results and discussion

Ammonia sorption in metal halide absorbents like $MnCl_2$ are described by a reversible, heterogeneous coordination reactions with accompanying changes in solid density. The absorption reaction, in which ammonia coordinates to the absorbent to form an ammine, experiences an expansion in crystal volume whilst the reverse, desorption reaction undergoes crystal volume contraction. A proposed mechanism for the cyclical process based on the shrinking core model is shown in Figure 2.
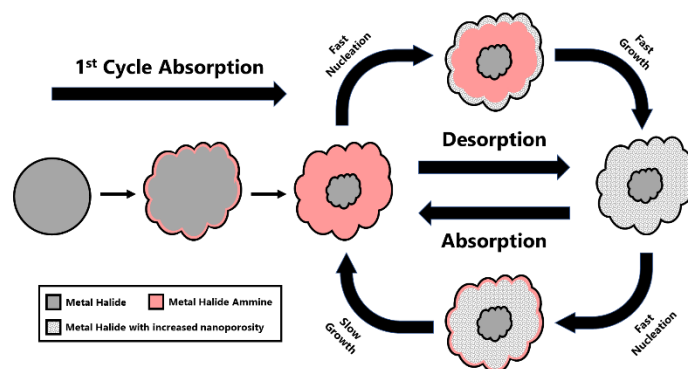
Figure 2. Schematic illustrating the proposed mechanism for cyclical sorption.

Both sorption reactions comprise of two critical reaction stages, namely product nucleation and growth. This is clearly indicated by the sigmoidal shape of their conversion plots (Figure 3) which describe nucleation at early times (<10 mins) and growth at later times (>20 mins). The absorption reaction is characterised by a rapid nucleation step followed by slow product growth as the denser product shell imposes greater internal mass limitations on the ammonia reactant diffusing towards the absorbent core. Conversely, whilst desorption also commences with a fast nucleation step, the nanoporosity created by the contracting product shell enables relatively unrestricted ammonia product diffusion away from the reaction front. As such, product growth for desorption is fast. These conclusions are supported by the reaction conversion plots for unsupported $MnCl_2$ (Figure 3A) which illustrate a slower approach to full conversion for the absorption reaction. Subsequent cycles have no significant implications on the rate of reaction because although particle surface area may change slightly, this has no effect on the rate-limiting product growth step which is restricted by ammonia diffusion through the dense ammine product. When an absorbent is supported on an inert material such as SiO_2, the resulting smaller absorbent particles produce faster absorption kinetics due to reduced internal mass transfer resistance (Figure 3B). This is because for a given overall conversion, the reactant penetration depth will be shorter for smaller particles than larger ones. The desorption rate remains unchanged because mass transfer effects are already relatively negligible in the unsupported absorbent.
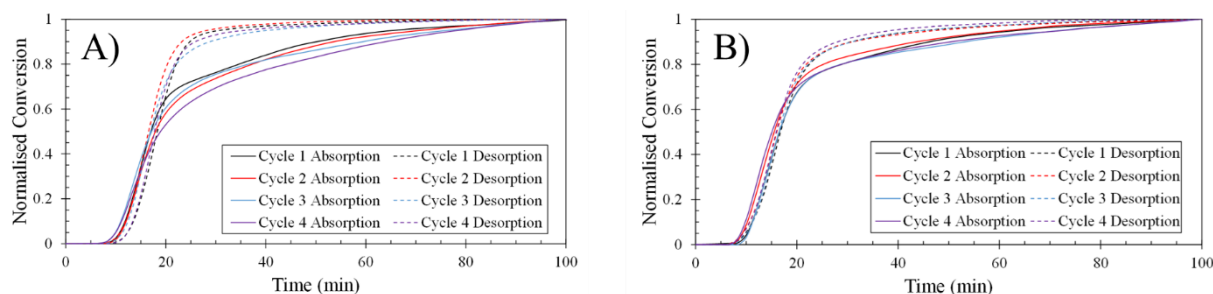
Figure 3. Normalised conversion for A) unsupported $MnCl_2$ and B) $MnCl_2$ supported on SiO_2 over four cycles.

4. Conclusions

The designed experimental system can measure the kinetics of ammonia sorption in flow under isothermal and isobaric conditions. Results collected for sorption in unsupported and supported $MnCl_2$ demonstrate that the kinetics of absorption is more significantly hindered by internal mass transfer effects than for desorption. Depositing the absorbent on a support improves the rate of absorption by mitigating these mass transfer limitations and diminishes the degree of absorbent agglomeration decomposition, enabling greater cyclical stability.

References

[1] IRENA, Innovation Outlook: Renewable Ammonia, 2022
[2] IEA, The Future of Hydrogen, 2019
[3] C. Smith, L. Torrente-Murciano, Adv. Energy Mater. 11 (2021) 2003845