

Pushing the boundaries of ammonia synthesis – An approach to evaluate the potential of *in situ* product removal towards full single-pass conversion

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Highlights

- Equilibrium and kinetic models for sorption-enhanced ammonia synthesis are developed and validated
- Near-full hydrogen conversion is achieved in the sorption-enhanced ammonia synthesis equilibrium
- Reactor simulations confirm the reachability of near-full conversion at industrially relevant conditions
- Full single-pass conversion renders reactant recycling unnecessary and minimizes purging losses

1. Introduction

The synthesis of ammonia is strongly limited by chemical equilibrium, which requires high pressures in conventional industrial-scale processes [1]. However, H₂ and N₂ conversions of > 20 % are usually not achieved under industrial conditions [2]. Thus, ammonia is separated from the product stream either by condensation or absorption and the unconverted reactants are recycled [1]. This requires compression of the recycle stream, which can significantly downgrade the process efficiency [1, 3]. Even more importantly, substantial purging is required due to impurities in the feed [1], which causes significant loss of the reactants H₂ and N₂. Hence, full single-pass conversion would be highly desirable to drastically improve the atom and energy efficiency of ammonia synthesis.

A promising process intensification strategy to increase the single-pass conversion in equilibrium-limited reactions is *in situ* sorptive product removal, i.e. sorption-enhancement [1, 3]. For the case of ammonia, mainly metal chlorides like MgCl₂ and zeolites are discussed for ab- or adsorption at conditions relevant for synthesis [2, 4]. In this study, we determine the thermodynamic potential of sorption-enhanced ammonia synthesis by equilibrium modeling. Moreover, we demonstrate the reachability of this potential at relevant process conditions by kinetic modeling of sorption-enhanced ammonia synthesis reactors as well as experimental investigations.

2. Methods

To evaluate the thermodynamic potential of sorption-enhanced ammonia synthesis, an equilibrium model based on Gibbs energy minimization is developed which calculates the equilibrium composition based on temperature, pressure and inlet composition. The model includes ammonia synthesis as well as absorption using metal chlorides. To be able to include the latter, Gibbs energies of formation of loaded metal chlorides were obtained by parameter fitting to measured sorption equilibria.

Kinetic simulations are performed using a steady-state 1D1D heterogeneous continuous gas-flowing solids-fixed-bed reactor (GFSBR) [3]. Kinetics for ammonia synthesis on Fe- and Ru-based catalysts from own measurements [5] are implemented as well as kinetics for ammonia absorption using MgCl₂. The applicability of different sorbent materials is tested in ammonia sorption experiments. Furthermore, sorption-enhanced ammonia synthesis experiments are performed in a lab-scale reactor using a physical mixture of ammonia synthesis catalyst and ammonia sorbent material.

3. Results and discussion

Figure 1 shows results of both the equilibrium and the reactor simulations. Regarding the equilibrium, we can observe that the addition of a sorbent into the ammonia synthesis reactor ($\lambda = 1$) significantly increases the equilibrium conversion of nitrogen over the entire temperature range. At the conditions

applied here, near-full conversion is thermodynamically possible at 300 °C, and the equilibrium conversion only marginally decreases with increasing temperature. In contrast, the conventional ammonia synthesis ($\lambda = 0$) suffers from limited conversion at 300 °C, which strongly decreases at higher temperatures. Hence, the thermodynamic analysis highlights the great potential for process intensification by enabling virtually full conversion with the sorption-enhancement concept.

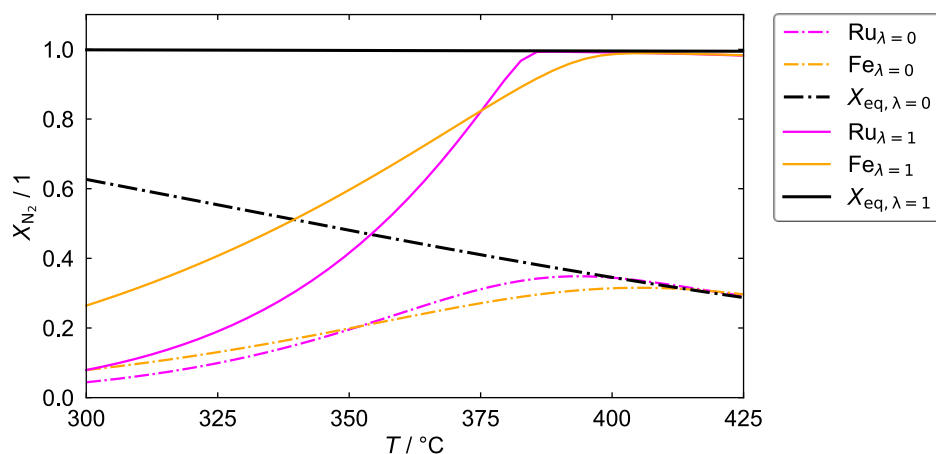


Figure 1. Nitrogen conversion over temperature as calculated with equilibrium model (black), and reactor model using Ru-based kinetics (magenta) and Fe-based kinetics (orange) at 80 bar, $H_2/N_2 = 3$, 2.5 % inert dilution, without ($\lambda = 0$) and with $MgCl_2$ sorbent ($\lambda = 1$), $\lambda = \frac{n_{0,MgCl_2}}{n_{NH_3, X_{N_2}=1}}$.

The kinetic simulations show two major features: 1. In the low temperature region, there is a significant increase in nitrogen conversion under sorption-enhanced conditions, particularly for the Fe-based catalyst. This indicates a kinetic benefit of the ammonia removal in addition to the increased driving force, which was also observed by Movick et al. for Ru-based catalysts [4]. 2. In the high temperature region, the nitrogen conversion in the sorption-enhanced case surpasses the conventional ($\lambda = 0$) equilibrium for both catalysts and reaches the sorption-enhanced ($\lambda = 1$) equilibrium at 380 °C and 400 °C for the Ru-based and the Fe-based catalyst, respectively. Hence, near-full conversion in single-pass operation becomes feasible from kinetic perspective, as well.

The suitability of different sorbent materials, e.g. zeolites or metal halides, for use in sorption-enhanced ammonia synthesis is evaluated and ammonia sorption kinetics are investigated experimentally. Subsequently, ammonia synthesis and *in situ* absorption will be combined in sorption-enhanced ammonia synthesis experiments.

4. Conclusions

In our study, we are able to show that process intensification by sorption-enhancement is a realistic perspective for ammonia synthesis. The addition of a solid sorbent to an ammonia synthesis reactor has the potential to shift the chemical equilibrium to virtually full conversion even at mild pressures and temperatures still high enough for sufficient reaction rates. Kinetic modeling of sorption-enhanced ammonia synthesis on both Ru- and Fe-based catalysts confirms that the shifted equilibrium is within reach at relevant process conditions. This way, high single-pass conversion becomes possible, which significantly reduces the need for recycling and purging and thus enhances the atom efficiency of ammonia synthesis.

References

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Keywords

ammonia synthesis, sorption-enhancement, equilibrium modeling, kinetic modeling