

# Direct Joule heating of NH<sub>3</sub> catalytic cracking in packed POCS: kinetic study and reactor design

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## Highlights

- Thermally conductive internals grant controlled T-profiles in kinetic investigations.
- NH<sub>3</sub> cracking kinetics has been derived over a commercial Ru-based catalyst.
- Direct joule heating allows for high H<sub>2</sub> productivity with high energy efficiency.

## 1. Introduction

Continuous emission of greenhouse gases has resulted in a severe disruption of the climate, mandating for a rapid introduction of more sustainable alternatives. In this view, the use of hydrogen as an alternative energy carrier provoked significant worldwide interest [1]. In this context, several options are under development to overcome the challenges of large-scale hydrogen storage and transportation, of which, one of the most promising is the use of NH<sub>3</sub> as a hydrogen carrier. With an annual production of more than 150 Mton [2], ammonia is a commodity with a highly optimized production and handling infrastructure. For its use as a hydrogen carrier, however, a substantial development of the ammonia decomposition process is needed.

NH<sub>3</sub> decomposition is a significantly endothermic reaction ( $\text{NH}_3 \rightarrow 3/2 \text{H}_2 + 1/2 \text{N}_2$ ,  $\Delta H^\circ_r = 45.9$  kJ/mol<sub>NH<sub>3</sub></sub>) and efficient heat management in the catalytic reactor is of key importance to optimize catalyst usage and overall system performances. At the industrial scale, high temperature heat of reaction for highly endothermic processes (such as Steam Methane Reforming, MSR) is provided through furnaces, with associated CO<sub>2</sub> emissions. While this solution is a proved and widely used technology, it is only optimal for large scale operations and not suitable for compact, distributed systems; a promising solution to this problem can be the use of cellular SiSiC internals as ohmic heating elements to supply the required reaction heat [3], resulting in increased productivity and energy efficiency of the catalytic system while minimizing the overall volume and, also, the system response time.

## 2. Methods

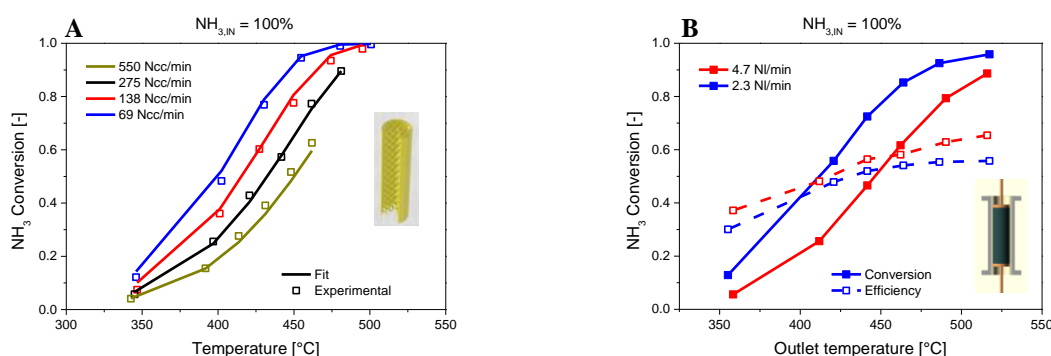
A commercial Ru-based catalyst (Heraeus, 2% Ru/Al<sub>2</sub>O<sub>3</sub>) in the form of 1mm eggshell spheres was selected as the active phase, and a rate expression able to faithfully describe its activity was developed. To ensure a flat temperature profile in the reactor, the catalyst particles were packed in an aluminum POCS [4] (Periodic Open Cell Structure) with diamond unit cell ( $d_{\text{cell}} = 3$  mm, porosity = 0.9) and a sliding thermocouple running along the centerline was inserted in a stainless-steel tubular reactor ( $d_t = 11$  mm) and tested in an electrically heated oven. Pure anhydrous ammonia was fed to the system at various flowrates and at temperatures between 350 and 510°C while monitoring the steady state ammonia conversion as well as the axial and radial thermal gradients. Moreover, the effects of pressure, and products cofeed (H<sub>2</sub> and N<sub>2</sub>) on the reaction kinetics were evaluated.

To test the effectiveness of direct Joule heating for the catalytic NH<sub>3</sub> cracking process, a silicon infiltrated silicon carbide (SiSiC) open cell foam (32 mm diameter, porosity = 0.88) was inserted in a thermally and electrically insulated reactor and electrical power was provided through a variable low voltage DC power supply. The same catalyst for which a kinetic expression was developed was packed in the SiSiC structure and pure anhydrous ammonia was fed to the system at flowrate between 1.2 and 9.3 NL/min. Outlet gas composition was monitored by a mass spectrometer and the ammonia conversion as well as the temperature at different locations of the reactor were recorded at various power settings.

### 3. Results and discussion

Figure 1A, reports the effect of feed flowrate as well as the results of the numerical fit of the kinetic tests performed with the catalyst packed in the thermally conductive POCS. With the use of a LHHW type kinetic expression the effects of GHSV, temperature, pressure and product cofeed (66 independent data points) were fitted with a MAPE of 6% over a  $\text{NH}_3$  conversion range of 0 to 100%.

Figure 1B, shows the  $\text{NH}_3$  conversion as function of temperature and the corresponding energy efficiency for the tests in the electrified SiSiC reactor. Tests at a flowrate of 2.3 NI/min and 4.7 NI/min resulted in conversions of 95% and 90% respectively with an outlet temperature of 515°C; moreover, energy efficiencies of 55% and 65% were calculated as the ratio between the change in enthalpy of the gas stream and the electric power supplied to the system. Such a system can be further optimized e.g. by changing the reactor geometry and reducing external heat dissipations.



**Figure 1.** A) Kinetic tests and numerical fit, effect of flowrate. B) Electrified SiSiC reactor,  $\text{NH}_3$  conversion and energy efficiency vs outlet temperature.

### 4. Conclusions

With the adoption of the packed POCS reactor configuration with a thermally conductive Al structure, it was possible to develop a faithful kinetic model which, thanks to the removal of T-gradients, was able to describe the catalyst activity at process-relevant conditions over a very wide range of temperatures and conversions.

Moreover, by providing the reaction heat needed for the catalytic  $\text{NH}_3$  cracking reaction in-situ via Joule heating, high conversions and energy efficiencies were achieved in a compact catalytic reactor without the need for external heating systems, while allowing for fast heat up of the catalyst bed and a better control of the  $\text{H}_2$  productivity.

A 2D numerical model able to faithfully predict conversion and outlet temperature of the system at a given  $\text{NH}_3$  feed rate and supplied electrical power is under development. This tool will be used to achieve better insight in the temperature and concentration distributions in an effort to optimize the Joule heated reactor configuration.

### References

The authors acknowledge the European Research Council for PoC Grant 101123385 (INCANT).

### References

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### Keywords

$\text{NH}_3$  cracking; Electrification; POCS; Joule Heating.