Re-thinking the catalyst validation for ammonia synthesis in green conditions

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Highlights

- The catalytic activity under green ammonia conditions is studied
- The catalytic activity is not affected by dynamic operating conditions under clean feed
- Oxygen concentration affects the activity of the catalyst
- At 450°C the catalytic activity is completely restored after poisoning deactivation.

1. Introduction

Ammonia is a fundamental feedstock for the agriculture and energy sectors [1]. Conventional ammonia production plants are source of carbon emission, in particular due to the use of grey H_2. Hence, the research of sustainable production of ammonia, replacing fossil fuels with green or zero-carbon, is fundamental for academia, industries and governments. Green ammonia (gNH_3) production involves the use of green hydrogen in the Haber-Bosh process using renewable energy [2]. Since the flow of renewable energy sources is intrinsically dynamic, it is crucial to investigate ammonia converters under dynamic operating conditions [3]. In particular, the performance of ammonia synthesis catalyst must be studied: the scientific literature lacks studies of such catalyst under non-stationary conditions. In this view, the goal of this work is the assessment of the catalyst activity under accelerated green NH_3 conditions, characterized by frequent oscillations of the main operating variables including catalyst bed temperature, pressure, space velocity, as well as changes in the inlet gas feed composition with the addition of oxygenates. This allows to achieve a deep understanding of the current ammonia synthesis catalyst in green NH_3 process, allowing also to better understand the operating conditions and the operative costs of green NH_3 converters.

2. Methods

A packed bed reactor, placed in an electric furnace was used. The axial temperature profile of the catalytic bed was measured by means of a multipoint thermocouple. Bottles of pure N_2 and H_2 (Purity Grade 4.5) were used as feedstock. Moreover, certified bottles of O_2 in N_2 mixtures were used for poisoning tests. N_2 and H_2 were further purified from oxygen and water traces. Mass flow controllers were used to dose the gases to the inlet of the reactor. An internally developed LabVIEW program was used to log and program the experimental conditions. Online micro-GC measurements were performed to detect and quantify ammonia concentration at the outlet of the reactor as a function of time.

The investigated operating conditions are aligned to the possible industrial operating conditions of green NH_3 (g-NH_3) converters. Accelerated dynamic g-NH_3 conditions tests were performed. In particular, multiple sequences of ramp up and ramp down cycles of the operating variables were performed. Oscillations of i) the catalyst bed temperature, ii) pressure, iii) GHSV (between 10 and 100% of max load capacity) and iv) inlet gas feed compositions (with clean syngas, poisoning agent, and syngas + NH_3), have been performed with spans of 90, 60 and 30 min.

3. Results and discussion

Experiments were performed by varying the selected parameters as temperature, pressure and GHSV in cyclic alterations. Moreover, the effect of these conditions was also evaluated in both clean and poisoned feed.

Preliminary results of fast cycles of temperature in clean conditions reveal that the catalyst is stable (Figure 1). Thus, the catalytic activity is not affected by the dynamic operating conditions with a feed cleaned from oxygenates.

When oxygen is fed to the reactor, initially, ammonia concentration at the outlet of the reactor decreases over time. This is due to the partial deactivation of the catalyst by oxygen. Then, ammonia concentration stabilizes, indicating the absence of further catalyst deactivation. The loss in catalyst activity due to oxygenating compounds is proportional to the oxygen concentration in the feed: the higher the concentration of oxygen in the feed, the higher the catalyst deactivation.

After the poisoning deactivation, the feed of pure syngas (i.e., without oxygen in the feed) at 450°C restores the original catalytic activity. The time length of the restore process to obtain the original catalytic activity depends on the oxygen concentration during the catalyst deactivation: the higher the oxygen concentration, the higher the time required for the restore of the original catalytic activity. Thus, alterations of the temperature combined with different oxygen concentrations in the syngas mixture do not cause a permanent and irreversible deactivation of the catalyst.

Based on the results obtained it is possible to define the conditions and instrumentation to be used in the design of green NH_3 plant. Moreover, experimental results can be used to develop operating procedures that may support troubleshooting, heating/cooling policies and catalyst activity recovery in industrial green NH_3 process operations.

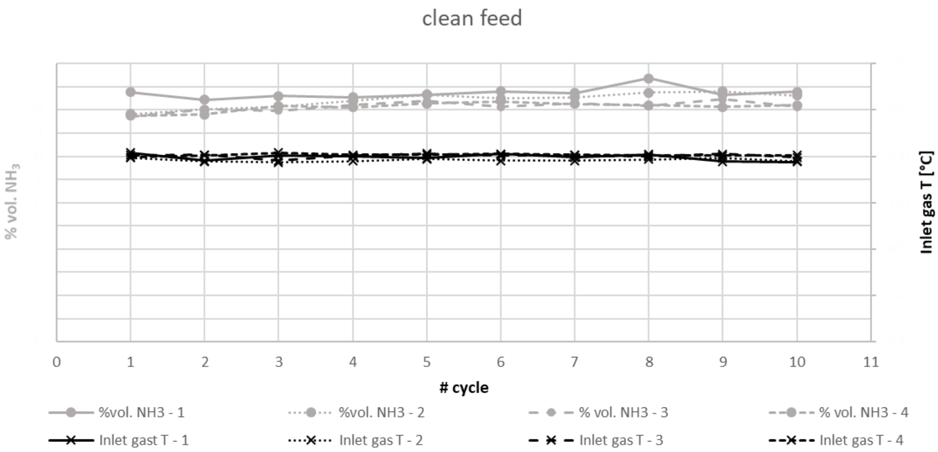

Figure 1. Figure 1 % NH3 out (grey) and Temperature at gas inlet (black) during each sequence (1, 2, 3, and 4) composed of 10 fast temperature cycle in clean conditions.

4. Conclusions

This study provided new insights in the behavior of ammonia synthesis catalyst under dynamic operating conditions aligned with green NH_3 converters. The results obtained will support the improvement of the industrial operating conditions, allowing to identify problems in real plant and helping to act in a due time to preserve the catalyst and the production of ammonia. This work paves the way towards the design and optimization of industrial scale reactors and plants for green NH_3 production.

References

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Keywords
Ammonia; Green Ammonia; Dynamic tests; Poisoning