Unprecedented promotion of ammonia cracking over Ru via surface H-scavenging, demonstrated by O_2-cofeed

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Highlights
- The kinetics of NH_3 cracking on Ru-catalysts suffers from H* surface saturation.
- The promoting effect of H_2 removal was experimentally proven by simple O_2-cofeed.
- Modelling shows the huge potential of H_2-scavenging on NH_3 conversion on Ru.

1. Introduction

Ammonia is a potential green-hydrogen carrier; several favorable features (C-less nature, well developed production technology and existing distribution infrastructure) make it an ideal candidate for the chemical storage and distribution of renewable energy [1]. As a result, NH_3 cracking (the reaction needed to obtain H_2) is presently an open field of research regarding both catalysts and reactors. Ru is unanimously recognized as superior active metal and a variety of formulations have been studied in the literature [2]. Based on the literature and our background knowledge, it is herein recognized that the main kinetic bottleneck of the reaction is the surface saturation by H* species [3]. In this work, we analyze the implications of such fundamental kinetic finding and explore by modelling and experiments the potential behind the concept of H-scavenging.

2. Methods

Among several Ru-supported catalysts, 1% $Ru/MgAl_2O_4$ was selected as reference; it was prepared via an incipient wetness impregnation, using $Ru(NO)(NO_3)_3$ as precursor, and reduced in flowing H_2 at 450 °C. NH_3 decomposition was tested in micro-fixed bed unit, with diluted feeds (0.3–2.5% NH_3 in He). H_2-cofeed tests were performed up to 25%, to characterize the kinetics under fully representative conditions. O_2-cofeed tests were also performed (0.1–0.5% O_2, 1% NH_3 in He) to demonstrate the positive effect of H_2-subtraction. All the experiments were performed at 20,000 $Nl/h/kg_{cat}$. The modelling analysis was based on 1D pseudo-homogeneous isothermal and isobaric reactor model.

3. Results and discussion

A broad kinetic investigation was performed over the $Ru/MgAl_2O_4$ catalyst. In line with the literature, an apparent negative order with respect to NH_3 was revealed by experiments at increasing NH_3 feed concentration (Figure 1). However, as shown in Figure 2, the results of experiments where NH_3 concentration was kept constant and H_2 was added to the feed showed the strong inhibiting effect of H_2. As a matter of fact, the kinetic analysis of the entire bulk of data showed that these and other effects can be fully reconciled with a simple power-law model of the form: $r \propto P_{NH3}/P_{H2}^{1.5}$, that is consistent with the hypothesis that the rate determining step of NH_3 cracking is the second extraction of H*, as proposed by [4], being H* the most abundant surface intermediate.

Aim of this work is to explore the potential benefit of removing the condition of surface saturation by the H* species. This was first investigated by modelling; at this scope the rate law was re-written in the form:
$$r = k(T)\frac{P_{NH3}}{(1+k_{H2}P_{H2})^{1.5}} \quad \text{(Eq. 1)}$$

that has no direct mechanistic derivation but reflects the correct kinetic dependences and is numerically more robust than the power-law model. Eq.1 was adapted to the data. Figures 1 and 2 show the model simulations of the measured effect of NH_3 feed concentration and H_2-cofeed as solid lines, together with the parameters estimates; besides, Figure 1 extrapolates the simulation up to the condition of pure

NH$_3$ feed. The kinetic effect produced by H$_2$-inhibition is dramatic since the NH$_3$ conversion curves shift by several hundred degrees when passing from highly diluted feed (0.3% to 2.5%, experiments and model) to the pure NH$_3$ feed. In the latter case, given the large extrapolation from the experimental campaign on the Ru/MgAl$_2$O$_4$ catalyst, we have also reported as a qualitative comparison the performance of a commercial Heraeus catalyst with similar composition, tested in an independent study [5].

The modelling exercise of predicting the performance of the catalyst under the ideal condition of H*-coverage = 0 was done by assuming K$_{H2}$=0 in rate eq. (1). The prediction is reported in Figure 3 (blue line), where (given the pure first order dependence of the new rate law) the calculated conversion curve is concentration independent; a condition dramatically different from the H$_2$-inhibited response of the catalyst (black lines). The simulations show that the potential advantage of full H-scavenging is enormous: at 250°C, the benefit on the turnover frequency amounts to a factor of 14 at 1% NH$_3$ feed, but this factor grows to over 50 at 10% NH$_3$ and over 600 for pure NH$_3$ feed.

To demonstrate experimentally the concept, we performed simple O$_2$-cofeeding experiments, where H$_2$ could be fully swept from the surface by consecutive oxidation. Figure 3 shows the results of experiments where the diluted NH$_3$ feed (1% in He) was enriched with small amounts of O$_2$ (0.1, 0.25, 0.5%). Experiments were performed at varying temperatures; Figure 3 reports the measured conversion of NH$_3$ at the very temperature level where O$_2$ conversion was complete and no H$_2$ was produced (thus the condition where the consumption of H$_2$ by oxidation perfectly matched the production by NH$_3$ cracking). The measured NH$_3$ conversions were much higher than those measured in the reference 1% NH$_3$ feed test and very nicely approached the predicted ideal conversion at zero H-coverage (blue line).
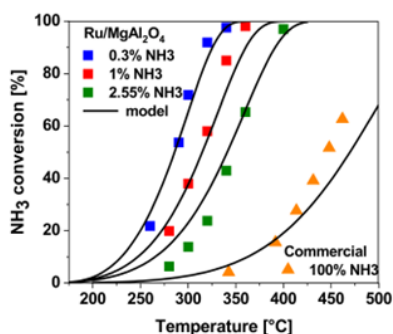

Fig. 1. Exp. and modelled effect of NH$_3$ concentration. Parameters eq. (1): k(600K) = 3.64e-2 (mol/s/g$_{cat}$/atm); E$_{act}$ = 37.5 kcal/mol; K$_{H2}$ = 5e3 (atm^{-1}).
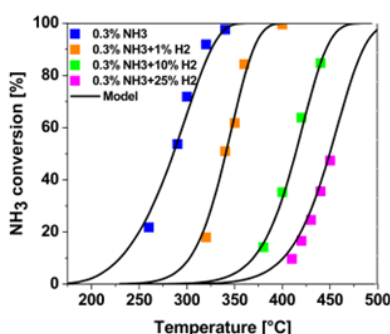
Fig. 2. Experimental and modelled effect of H$_2$-cofeed.

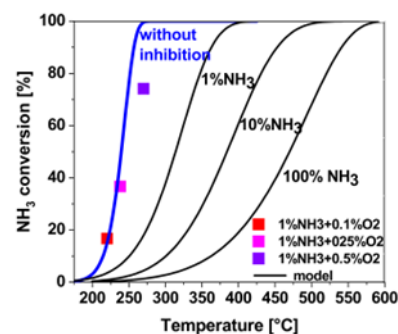Model parameters as in Fig 1.

Fig. 3. Predicted performance at zero H*-coverage (blue line, model in eq.(1) with K$_{H2}$ =0) and O$_2$-cofeed tests at 1% NH$_3$ feed.

4. Conclusions

We demonstrate that a huge margin of improvement of NH$_3$-cracking kinetics lies in the elimination of the H*-saturation. This concept (here demonstrated by simple O$_2$-cofeed tests) opens to the design of multifunctional reactors where H$_2$ is removed from the Ru sites by separation (membrane reactors), H-storage (H-sorbents), chemical consumption (coupling of NH$_3$ cracking with H$_2$-consuming reactions), H$^+$ removal (PEM-fuel cell): a boundless playground for chemical reaction engineering.

References

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