Unprecedented promotion of NH_3 decomposition over Ru via H_2-scavenging: a chemical reaction engineering analysis

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Quantitative comparison between the cases of H_2-inhibited and H_2-scavenged kinetics

It is herein reported that the modelling analysis compares the predicted performance of a conventional packed bed reactor operating at GHSV = 20,000 Nl/kg_{cat}/h for three different cases of feed composition: 1%NH_3 in He, 10%NH_3 in He, pure NH_3. To quantify the promotion in terms of equivalent rate constant, each curve obtained by the H_2-inhibited kinetics was fitted by a pseudo-first order kinetics:

$$r = k_{app}(T) \cdot P_{NH_3} \quad \text{(Eq. S1)}$$

$$k_{app}(T) = k_{app}(600\ K) \cdot exp\left(-\frac{E_{act}}{R}\left(\frac{1}{T} - \frac{1}{600\ K}\right)\right) \quad \text{(Eq. S2)}$$

Table S1 Estimation of k_{app} at 250°C and the ratio of the ideal $k_{no\ inhibition}$ to the k_{app} in real cases

Condition	k_{app} (250 °C) [mol·atm$^{0.5}$/s/g_{cat}/]	$k_{no\ inhibition}$ / k_{app}
No inhibition	3.58 E-4	/
1% NH_3	2.55 E-5	14
10% NH_3	6.28 E-6	57
100% NH_3	5.66 E-7	633

Temperature in catalyst bed vs. setpoint of the furnace in O_2-cofeed experiments

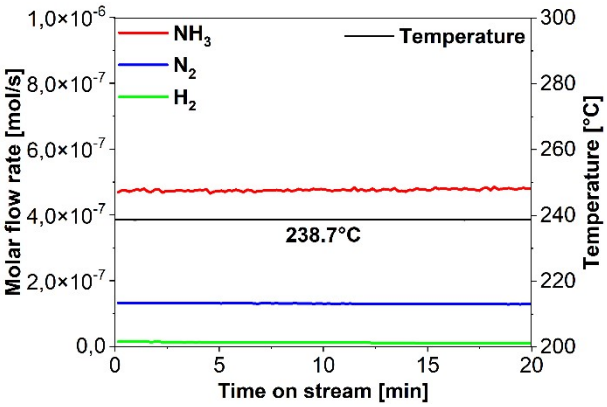

Fig. S1 Molar flow rate of NH_3, H_2, N_2 and temperature along time on stream for 1%NH_3+0.25%O_2 with oven setpoint at 238°C,

Taking 1%NH_3+0.25%O_2 as an example, Fig. S1 illustrates that the temperature increase due to the exothermic H_2 oxidation is negligible in the studied cases.

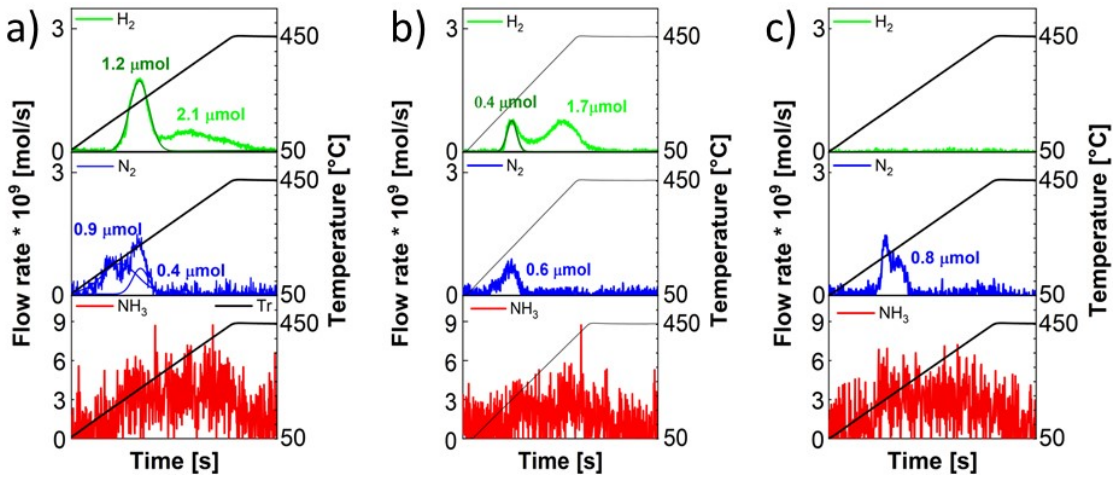

Fig. S2 Molar fractions of NH_3, H_2, N_2 and temperature along time stream during He-TPD for a) 1%NH_3 at 250°C; b) 1%NH_3 at 320°C, c) 1%NH_3+0.25%O_2 at 250°C

Fig. S2a presents the species observed during He-TPD over the catalyst pretreated with 1% NH_3 at 250 °C (corresponding to ~10% NH_3 conversion). The H_2 signal is accompanied by N_2 and residual NH_3. Both the H_2 and N_2 profiles comprise two peaks. After deconvoluting and quantifying them separately, it is found that the first H_2 peak and the second N_2 peak emerge at the same temperature and exhibit an H_2/N_2 ratio of 3, consistent with the stoichiometric requirements of NH_3 decomposition; these features are therefore assigned to NH_3 that undergoes decomposition during the temperature ramp. In contrast, the first N_2 peak and the trailing segment of the H_2 profile are attributed to desorption of surface-bound species. These observations indicate the presence of N*, H*, and NH_3* species on the catalyst surface at 250 °C. It is further noteworthy that hydrogen is strongly retained on the surface, as evidenced by its continuous desorption signal up to 450 °C.

Fig. S2b reports the desorption profiles obtained after 1% NH_3 adsorption at 320 °C (~ 60% NH_3 conversion). The hydrogen signal again comprises two contributions; however, the low-temperature nitrogen shoulder observed at 250 °C is nearly absent. Only a single N_2 peak remains, appearing at the same temperature as the first H_2 peak. Because the measured H_2/N_2 ratio is lower than the stoichiometric value of 3 expected for complete NH_3 decomposition, this feature is more plausibly assigned to the release of NH_x surface intermediates rather than full NH_3 dissociation during the temperature ramp. Under these conditions, the catalyst surface is therefore predominantly populated by H* and NH_3* species.

Fig. S2c shows the desorbing species after adsorption of 1% NH_3 + 0.25% O_2 at 250 °C (~ 70% NH_3 conversion). In this case, hydrogen is not detected, while small amounts of nitrogen and ammonia are still present. And the nitrogen profile consists of two contributions: the first can be attributed to surface nitrogen species, and the second to reacted NH_3. Thus, the surface species here are essentially the same as in the case without O_2 cofeeding at 250°C but with H* effectively removed by O_2.