Kinetic Analysis of Ammonia Cracking over Ru-based Catalysts for COx-free Hydrogen Production

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Highlights
- The following scale of intrinsic activity is found: $Ru/MgAl_2O_4 > Ru/MgO > Ru/Al_2O_3$.
- Independently from the nature of the support, H_2 adsorption inhibits NH_3 cracking.
- The kinetic dependences support that H^* extraction from NH_2^* is the RDS.

1. Introduction

To achieve net-zero CO_2 emission in the coming decades, hydrogen is considered as one of the most promising energy carriers for the future energy systems [1]. To overcome the challenges for the storage and transportation of H_2, liquid H_2-vectors are promising candidates [2]. Among them, ammonia has attracted increasing attention, due to well established production and distribution infrastructure, zero carbon emissions during dehydrogenation and no side reactions [3]. The development of efficient catalysts with outstanding performances at relatively low temperatures is thus of utmost interest. According to the state of the art, Ru is the most active metal for NH_3 decomposition [4]. Although widely studied, the mechanism and kinetics of NH_3 decomposition over Ru-based catalysts are still under discussion. In this work, a kinetic investigation of NH_3 decomposition was performed over Ru-based catalysts, with a systematic experimental and modelling work.

2. Methods

$Ru/\gamma-Al_2O_3$, Ru/MgO and $Ru/MgAl_2O_4$ catalysts were prepared via an incipient wetness impregnation by using $Ru(NO)(NO_3)_3$ as precursor. Catalysts were characterized by BET, ICP-MS, H_2-chemisorption, SEM, TEM and NH_3-TPD. Catalytic tests were carried out in a continuous fixed-bed flow reactor, after reduction in flowing H_2 at 450 °C. NH_3 decomposition was tested in a micro fixed bed reactor with diluted NH_3-feeds, in order to guarantee isothermal conditions. Tests were thus simulated by a an isothermal 1D pseudo-homogeneous reactor model. Experiments were performed at varying ammonia concentration, and with H_2 and N_2 co-feed. Gas composition was analyzed by an on-line MS.

3. Results and discussion

Characterization results are reported in Table 1; they show that the morphological properties were favorable for $Ru/\gamma-Al_2O_3$ and $Ru/MgAl_2O_4$, but extremely poor in the case of Ru/MgO. As a consequence, Ru dispersion was especially low for Ru/MgO. However, the catalytic tests (Figure 1) showed the activity order: $Ru/MgAl_2O_4 > Ru/MgO > Ru/\gamma-Al_2O_3$ thus the process was clearly enhanced by the basicity of MgO and $MgAl_2O_4$ and by the high Ru dispersion offered by the latter support. The kinetic investigation showed an apparent negative order with respect to NH_3 (Figure 2), but H_2 cofeed tests (Figure 3) revealed that the reaction is strongly inhibited by H_2, such that first order dependence on NH_3 is recovered at large H_2 feed content. NH_3 conversion was instead insensitive to N_2 cofeed (Figure 4).

$$r = k(T) * \frac{P_{NH_3}}{P_{H_2}^{1.5}} \quad (Eq. 1)$$

A simple power-law expression (Eq.1) (order 1 with respect to NH_3 and order -1.5 with respect to H_2) could well explain the data, suggesting that the rate-determining step is within the NH_3 dehydrogenation pathway. The same dependencies were found over all the catalysts despite the different activity. The basicity of MgO and $MgAl_2O_4$ might favor the reaction by weakening the Ru-H bond, which suggests a

direction for catalyst optimization (e.g. through proper design of the support). Besides, multifunctional reactors with H_2-selective removal appear a promising strategy to overcome the kinetic barrier.

Table 1. Textural properties of catalysts

Sample	S_{BET} / $m^2.g^{-1}$ [a]	V_p / $mL.g^{-1}$ [a]	$d_p/\text{Å}$ [a]	$D_{Ru}/\%$ [b]
Ru/γ-Al$_2$O$_3$	139	0,44	94	15,6
Ru/MgO	13	0,09	253	8,2
Ru/MgAl$_2$O$_4$	113	0,39	94	29,6

[a] via BET
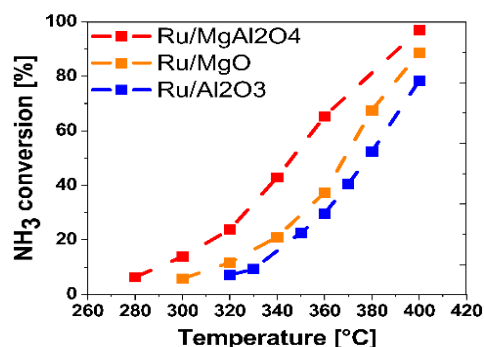[b] via H_2 chemisorption performed at 40°C

Figure 1. Effect of supports, 2.55% NH_3 in He. GHSV=20000 Nl/h/Kg$_{cat}$.
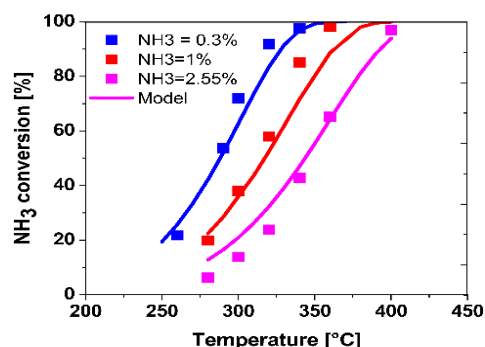

Figure 2. Effect of NH_3-inlet concentration over catalyst Ru/MgAl$_2$O$_4$. GHSV=20000 Nl/h/Kg$_{cat}$.
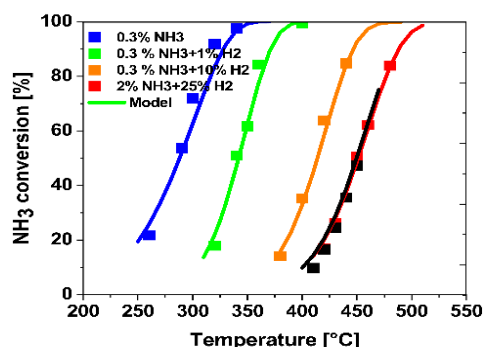
Figure 3. effect of H_2 co-feed, GHSV=20000 Nl/h/Kg$_{cat}$.
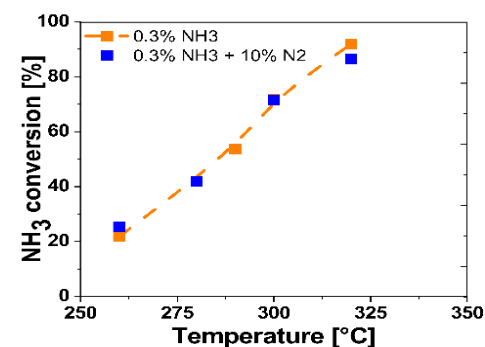
Figure 4. effect of N_2 cofeed on Ru/MgAl$_2$O$_4$, GHSV=20000 Nl/h/Kg$_{cat}$.

4. Conclusions

Ru/γ-Al$_2$O$_3$, Ru/MgO and Ru/MgAl$_2$O$_4$ catalysts were prepared and tested to investigate the kinetics of NH_3 cracking. Results showed the favorable impact of the support basicity. Another important finding is that the kinetics of ammonia cracking on Ru are strongly limited by H_2-inhibition. Recognizing this crucial factor can lead to optimized catalysts formulations (basicity) and reactor designs (integrated H_2 separation).

References

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Keywords