

Kinetic Investigation of Ammonia Decomposition over Ru/CeO₂ Catalysts Synthesized by Conventional IWI and Novel Mechanochemical Approaches

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Significance and Relevance

Ru is unanimously recognized as catalyst of choice for NH_3 decomposition, but the rate of reaction is strongly limited by the Ru–H^{*} interaction, especially at higher temperatures (required for complete NH_3 conversion). The role of the support is of key importance. CeO₂ offers outstanding performance and minimizes H^{*} poisoning, and both factors are emphasized over the catalyst obtained by milling.

Preferred and 2nd choice for the topic: **Preferred:** H₂ **storage and transportation, green** H₂ **production, hydrogen vectors;** 2nd **choice: Sustainable and clean energy production and transport** Preferred presentation: **Oral preferred or Short Oral**

Introduction and Motivations

Green NH₃ is considered as a promising H₂ carrier because of its high hydrogen density, welldeveloped technologies and infrastructures for synthesis, storage and transportation¹. Catalysts for NH₃ decomposition are actively studied in the literature, which documents the superiority of Ru². Among supports, CeO₂ is attracting attention as an electron donor which could facilitate N–H bond cleavage and associative desorption of N* and H* species³. In this work, Ru/CeO₂ catalysts were prepared by conventional impregnation and novel mechanochemical methodology to investigate the role of the support on the activity and kinetics of NH₃ decomposition. The performance was evaluated by comparison with a reference Ru/Al₂O₃ catalyst.

Materials and Methods

Ru/Al₂O₃-IWI and Ru/CeO₂-IWI catalysts were prepared via incipient wetness impregnation, using Ru(NO)(NO₃)₃ as Ru precursor. Ru/CeO₂-BM was obtained by ball milling a mixture of Ru₃(CO)₁₂ (thus starting from Ru with metal character) and CeO₂ at 15 Hz in a zirconia jar with a single zirconia ball for a total of 20 min. Catalysts were characterized by XRD, Raman, DRIFTS, CO chemisorption and HR-TEM. Prior to tests, the catalyst was reduced in flowing H₂ at 450 °C. NH₃ cracking was tested in micro-fixed bed unit, with diluted feeds (0.3–2.5% NH₃ in He). H₂ cofeeding tests were performed up to 25%, to characterize the kinetics under fully representative conditions. The effect of N₂ was also studied by cofeeding 10% N₂ with NH₃. All the experiments were performed at 20,000 NI/h/kg_{cat}. The modelling analysis was based on 1D pseudo-homogeneous isothermal and isobaric reactor model.

Results and Discussion

The bulk of characterization results suggests a very high dispersion of Ru for all the catalysts. In the CeO₂-catalysts obtained by both IWI and BM, Raman and DRIFTS showed intense signals associated with interfacial Ru–O–Ce sites, supporting the hypothesis of strong metal support interaction facilitated by high dispersion.

Tests were performed to highlight the main kinetic dependences and evaluate the effect of the nature of the support and of the preparation procedure. Figure 1 shows a comparison of the measured NH₃ conversion at the reference condition of 1% NH₃ in He; it is clear that the Ru/CeO₂ catalysts outperformed the reference Ru/Al₂O₃ catalyst. Assuming pseudo-first order kinetics (Arrhenius plots, Figure 2), a slope change is observed for both Ru/CeO₂ catalysts, which suggests a change of the rate



determining from below and above 300°C. Extensive kinetic investigations were performed over all catalysts, consisting of data at varying NH_3 concentration, H_2 -cofeed and N_2 -cofeed and crossed effects. Trends were rationalized by a kinetic modelling. In the case of Ru/Al_2O_3 the kinetic dependences are consistent with the assumption that the rate determining step is the second N–H cleavage and that H* is the most abundant surface intermediate, which results in a first order dependence on NH_3 and a negative order -1.5 on H_2 . The solid lines in Figure 3 show the model fit according to such conclusions.

Instead, in the case of both Ru/CeO₂ catalysts, the low temperature data are best described by assuming that N* associative desorption is rate determining and N* is accordingly the most abundant surface intermediate, while at higher temperature the observed trends suggest that NH₃ activation (first N–H cleavage) and H* poisoning are the controlling factors. The solid lines in Figure 4 show the very satisfactory description obtained by developing a model that interpolates the two limiting kinetic models and describes a change of the reaction order on NH₃ from zero to 1.

 H_2 and NH_3 adsorption/desorption experiments are being performed to investigate the nature, the abundance and adsorption strength of surface intermediates on Ru sites, and the effect of supports; these studies are of fundamental importance to support the mechanistic hypotheses. Dynamic experiments, for instance, show high retention of hydrogen over CeO₂, which suggests that Ru–H* bond is weakened by the H*–support interaction, thus promoting the reaction kinetics.

The ball milled Ru/CeO_2 obtained from the organometallic precursor showed higher activity and further reduced H* poisoning, possibly the result of an intimate metal-support interaction.



effects of NH_3 and H_2 , Ru/Al_2O_3



References

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