

Ammonia as Hydrogen Carrier: Catalysis for Synthesis and Decomposition

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Ammonia is an attractive transport and storage molecule for hydrogen produced from renewable energy [1]. It can be liquefied as already 8 bar and, as a major base chemical, the logistics for long-distance transport of ammonia are well established. Most importantly, the release of hydrogen from ammonia is a carbon-free reaction. In the context of hydrogen storage in ammonia, catalysis of the ammonia decomposition reaction has become a research focus recently, but also further optimization of the ammonia synthesis catalyst gets renewed interest, as the thermal catalytic conversion still promises the highest yields compared to other approaches.

Regarding the expected scale of hydrogen storage, one goal of such research activities is to find abundant and cheap catalysts that are highly active and stable. Base metals such as iron, cobalt and nickel are therefore attractive for catalyst development. We have recently shown that Fe,Co alloy particles supported on MgO are interesting catalysts for ammonia decomposition. Their high activity can be explained by the preparation of highly-loaded catalysts via the co-precipitation and decomposition of crystalline precursors with up to 74 wt.% metal loading and by the moderation of the too strong binding energy of iron by alloying with cobalt. Furthermore, the formation of the alloy hinders the transformation of the catalyst into metal nitrides, which show a too weak N-binding [2]. Also the effect of alkali promoters on these catalysts in ammonia decomposition and synthesis will be covered in our contribution and first results will be presented.

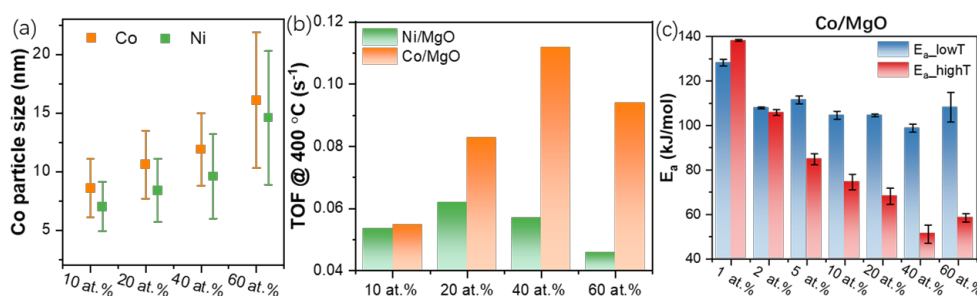


Figure 1: (a) Average nanoparticle size after reduction based on TEM analysis and (b) TOF@400 °C as a function of metal loading for both Ni and Co catalysts, (c) apparent activation energy E_a in both low and high temperature regions as a function of metal loading for Co/MgO.

We have furthermore looked into the particle size and support effects of supported cobalt and nickel catalysts. Comparative investigation of a series of differently loaded catalysts revealed a correlation between loading and particle

size (Fig. 1a). An optimal TOF was found for 20% (Ni) and 40% (Co) loading corresponding to a particle size around 8 and 12 nm, respectively (Fig. 1b). Interestingly, small and larger particles showed different behavior with increasing reaction temperature, which can be interpreted as a change in the rate-determining step from desorptive N recombination towards ammonia dehydrogenation for larger particles at higher temperatures [3], which is reflected in a lower activation energy (Fig. 1c).

In our contribution, our recent findings will be summarized, compared to the state-of-the-art and to other recent catalyst developments, and an outlook on the challenges of catalyst development will be presented.

[1] Ristig et al., *Chem. Ing. Technol.* **2022**, 94, 1413. [2] S. Chen et al., *Nat. Commun.* **2024**, 15, 871. [3] Jihao Wang, *Dissertation* **2024**, Kiel University.