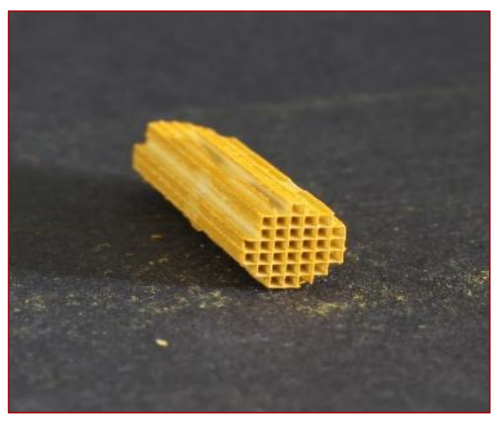
Using honeycomb monoliths as catalyst support for a scalable ammonia synthesis

S. Hoffgaard, U. Kragl, A. F. Rösel

Rostock University, Institute of Chemistry, Albert-Einstein-Str. 3a, 18059 Rostock, Germany.

Introduction

Ammonia is lately discussed as a possible green fuel with the advantage of no release of CO_2.[1] In combination with renewable energy as well as an environmentally friendly source of hydrogen, a nearly complete emission-free production on a medium scale is conceivable in the near future. To gain a delocalized production on a small to medium scale, lowering the high pressure and temperature is necessary. This can be achieved by exchanging the frequently used iron-based catalyst to ruthenium on varying supports.[2]



Most catalytic systems have not yet been tested for their ability to a suitable upscaling for a decentralized ammonia production. Herein we report a self-build reactor setup for ammonia synthesis from the elements on a microscale. Key feature is a robust flow-reactor. For a simple scale-up, cordierite honey comb monoliths are used as support as they are already used in large scale productions, but not within microflowreactors.

Results

Preparing the monoliths as support

For the preparation of the monoliths, the co-support is coated via conventional dip-coating. The Ru-precursor is added with a self developed stepwise dip-coating process. In this procedure, a monolith is repeatedly dipped into a saturated solution of the precursor. Co-Support and Ru-Precursor are each thermally decomposed with an adjusted temperature program.
If a promoter is involved, the precursor is added after the last step with the same coating process. The reduction follows *in situ* under syn-gas at 623 K.

$$Al_aMg_bSi_cO_x\ (Mon) \xrightarrow[\Delta T]{\text{co-support precursor / } H_2O} Mon(co\text{-}supp) \xrightarrow[\Delta T]{Ru_3(CO)_{12}\text{ / THF}} Mon(co\text{-}supp)\text{-}Ru$$

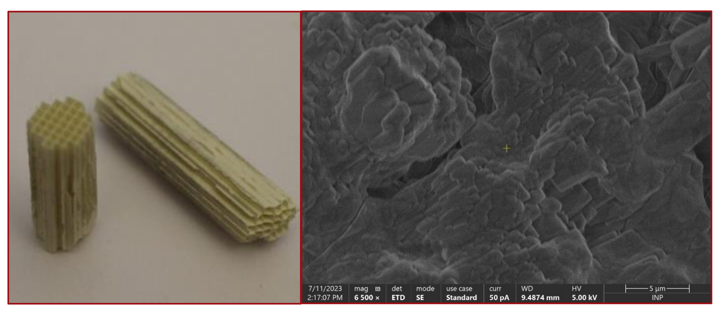


Figure 1: picture of the blanked monolith with HR-SEM

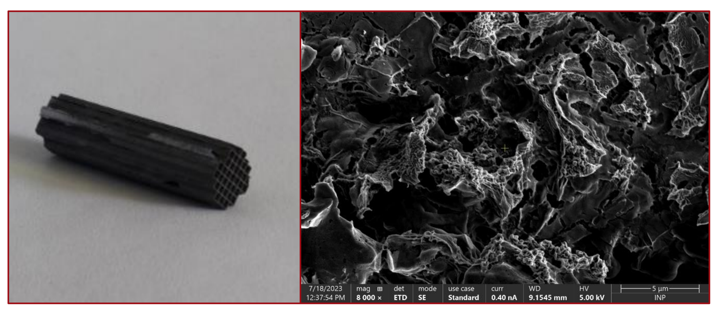


Figure 2: picture of a monolith with MgO as Co-Support with HR-SEM

Lanthanoidoxide powder as support

$$3\ L(NO_3)_3 + 3\ OH^- \longrightarrow L(OH)_3 + 3\ NO_3^-$$

$$2\ L(OH)_3 \xrightarrow{\Delta T} L_2O_3 + 3\ H_2O$$

$$L_2O_3 \xrightarrow[\Delta T]{Ru_3(CO)_{12}\text{ / THF}} L_2O_3\text{-}Ru$$

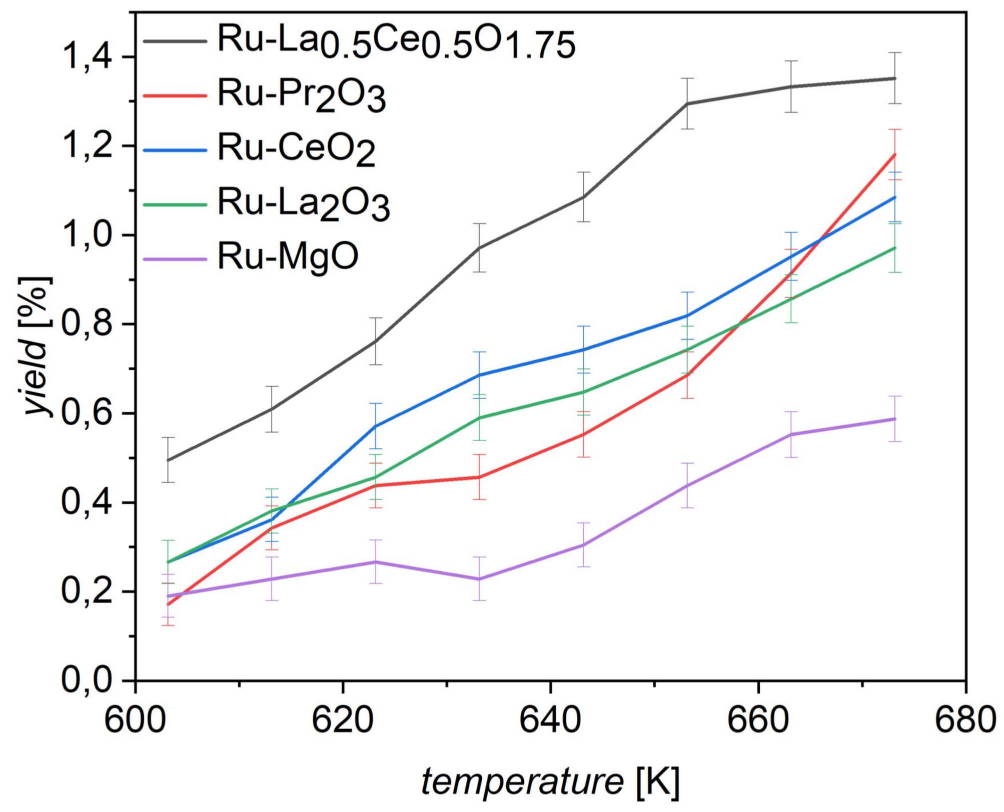


Figure 3: Top: Synthesis route for the lanthanoid based catalysts (L means Lanthanoid in general). **Bottom:** Isobars with lanthanoidoxides as support, Ru-loading 1,1 w%, p= 5 bar, 40 mL/min, H_2/N_2 = 3, 200 mg of cat

Performance of the monoliths

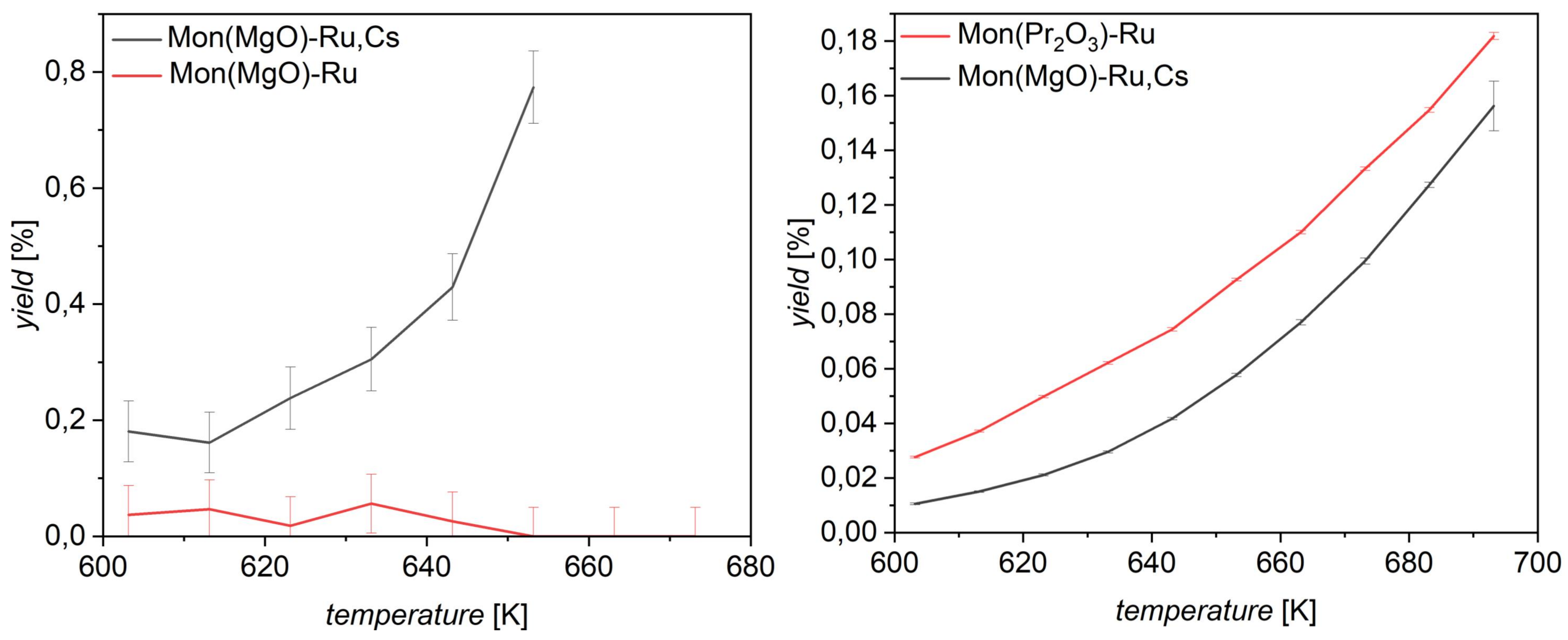


Figure 4 left: Influence of the promoter, Ru-loading; 1,1 w%, p= 5 bar, 40 mL/min, H_2/N_2 = 3; **right:** Influence of the Co-Support; Ru-loading 1,9 w%, p= 5 bar, 40 mL/min, H_2/N_2 = 3;

Influence of the Rutheniumloading

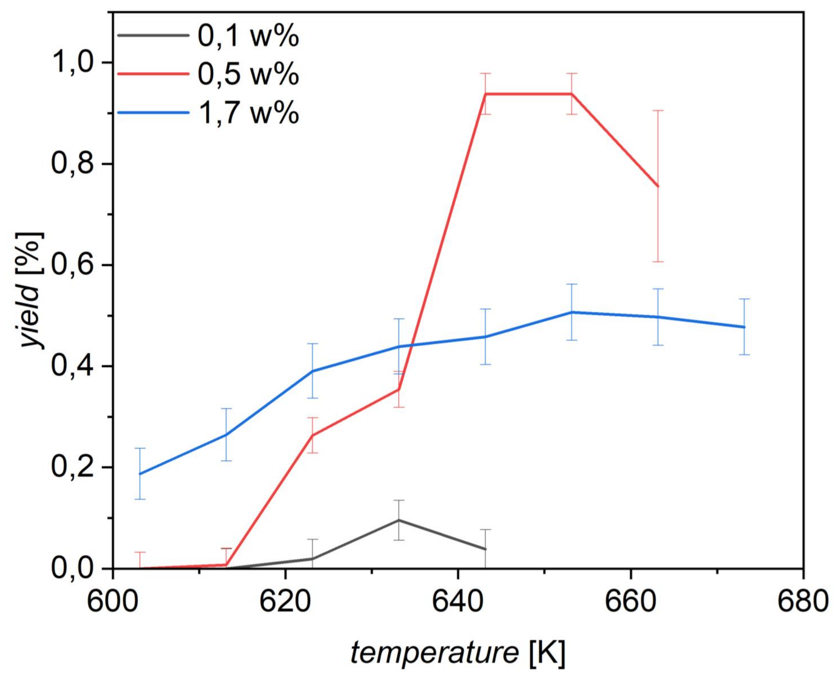


Figure 5 left: Isobars of monolith with different Ru-loadings, p = 1 bar, 40 mL/min, H_2/N_2 = 3

Summary and Outlook

- ✓ Set-up of an easily modifiable reactor
- ✓ Application of the monoliths in a micro reactor
- ✓ Determined bottlenecks when using monoliths in a micro reactor

- ➢ Optimize the coating conditions for the monoliths
- ➢ Testing further lanthanoids as co-support on monoliths

References:

[1] O. Elishav, B. M. Lis, E. M. Miller, D. J. Arent, A. Valera-Medina, A. Grinberg Dana, G. E. Shter, G. S. Grader, *Chem. Rev.* **2020**, *120*, 5352.

[2] K. Aika, *Catal. Today* **2017**, *286*, 14.

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