



# Hydrogen Production from Ammonia Decomposition over Zirconium Oxynitride



H. Soerijanto<sup>1,2</sup>, C. Rödel<sup>2</sup>, U. Wild<sup>1</sup>, M. Lerch<sup>2</sup>, R. Schomäcker<sup>2</sup>, R. Schlögl<sup>1</sup>, R. Jentoft<sup>1</sup>, G. Weinberg<sup>1</sup>, D. Wang<sup>1</sup>, T. Ressler<sup>2</sup>

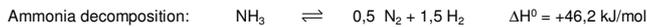
<sup>1</sup>Fritz-Haber-Institut der MPG, Abt. Anorg. Chemie, Faradayweg 4-6, 14195 Berlin

<sup>2</sup>Institut für Chemie, TU Berlin, Straße des 17. Juni 135, 10623 Berlin

## Introduction

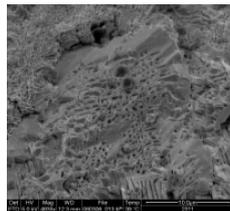
While the hydrogen production from hydrocarbon has a disadvantage due to its CO impurities which poisons the Pt-electrode of fuel cells, the production of hydrogen from ammonia is absolutely CO-free. One of the fuel cell types: AFC (Alkaline Fuel Cell) can be operated at temperatures between 60°C and 200°C. This low operating temperature and its possibility to miniaturization [1] opens a broad application for small portable systems.

On the other hand it is still interesting for chemical industry to find a new catalyst generation which works under milder reaction conditions than energy intensive conditions of Haber Bosch Process (Fe<sub>3</sub>O<sub>4</sub>, 500°C, 200 bar). Driven by these two goals some zirconia oxynitride was prepared, characterized, and tested for ammonia decomposition.



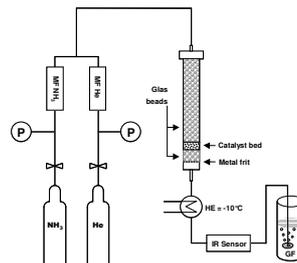
## Catalyst preparation

Zirconium oxynitride (ZrON) pellets were prepared from isostatically pressed commercial zirconia powder nitrided at 1900°C in nitrogen atmosphere for 2 h (graphite heated resistance furnace), resulting in a mixture of nitrogen-free monoclinic ZrO<sub>2</sub> and the β'-type of zirconium oxynitride phases (~Zr<sub>7</sub>O<sub>9,5</sub>N<sub>5</sub>) [2]. Subsequently, the material was quenched from a vertical tube furnace from 1300°C (nitrogen atmosphere) in water. An image of a quenched sample is displayed.



X-ray analysis after quenching shows a reduced amount of monoclinic zirconia and the metastable β'-phase of zirconium oxynitride (~Zr<sub>7</sub>O<sub>11</sub>N<sub>2</sub>) [3]. For the catalyst testing described here a sample consisting of 51 wt-% ZrO<sub>2</sub> and 49 % β' phase was used. Hot gas extraction of the as-prepared material yielded a total amount of nitrogen of 1.63 wt-% (theoretical 1.62 wt-%). After three month time on stream during ammonia decomposition the material exhibited only a minor decrease in the amount of nitrogen (-0.30 wt-%).

## Catalytic investigation



Scheme of catalysis testing device

Catalytic measurements were carried out in a fixed bed reactor at atmosphere pressure at various temperatures and various feed concentrations by applying a mixture of ammonia and helium. Effluent gases were analyzed by ammonia sensor (Binos IR detector, Rosemount) and afterwards washed by sulfuric acid in the gas flask. The experimental results were fitted to the reaction material balance to determine the activation energy.

A blank reactor with just glass beads and another one with 1 g magnetite as catalyst were also measured for control and comparison.

## Experimental results

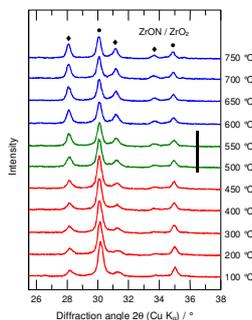


Figure 1: Evolution of XRD patterns measured during thermal treatment of a mixture of ZrON (●) and ZrO<sub>2</sub> (▲) in the temperature range from 100°C to 750°C. The phase change from the β' phase to the β'' phase of ZrON is indicated (bar).

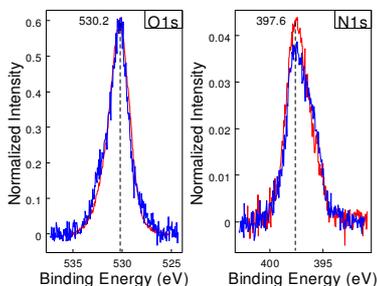


Figure 2: XPS O1s & N1s at 200°C (blue curves) and at 600°C (red curves) of β' sample, charging corrected with BE of ZrO<sub>2</sub> Zr 3d<sub>5/2</sub> at 182,2 eV as standard.

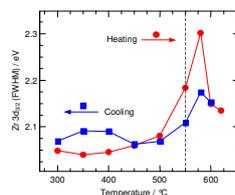
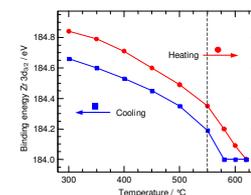


Figure 3: Evolution of width (left) and position (right) of XPS Zr 3d<sub>5/2</sub> peak of β' ZrON during heating and subsequent cooling. The dashed line indicates the onset of the phase change from β' ZrON to β'' ZrON and catalytic activity.



### Summary:

1. Zirconium oxynitride is a promising material for the new generation of ammonia catalysts. It showed an ignition activation due the phase transition.
2. The dramatic change in activity is also correlated to a rapid change in the electronic structure of the surface that accompanies the formation of the more active β'' ZrON phase.
3. The results presented show for the first time a direct correlation between the onset of ion conductivity as a bulk property, a modified electronic structure of the surface, and the catalytic performance of a heterogeneous catalyst.
4. The activation energy of 95 kJ/mol coincides well with the activation energy of ion conductivity in zirconia based materials.
5. While the XRD analysis showed a minor decrease of nitrogen content, the XPS data revealed an increase amount of nitrogen on the surface after heating to 600°C (~8%).
6. The ZrON is also an excellent candidate for ammonia cracker in AFC. A test with 4-(dimethylamino)-benzaldehyde showed no detectable hydrazine even after five weeks of time on stream.

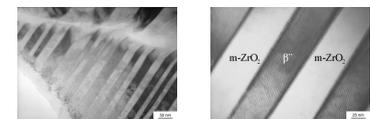


Figure 4: Bright-field TEM images show the coexistence of the monoclinic ZrO<sub>2</sub> phase and the modulated β' phase.

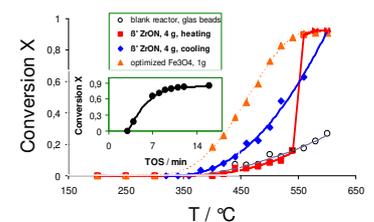


Figure 5: Evolution of NH<sub>3</sub> conversion as a function of temperature during NH<sub>3</sub> decomposition (feed 50 ml/min He with 4100 ppm NH<sub>3</sub>) on Fe<sub>3</sub>O<sub>4</sub>, ZrON (heating and cooling), and blank reactor. The activity at the conversion jump appeared 4 minutes after switching from 540°C to 560°C

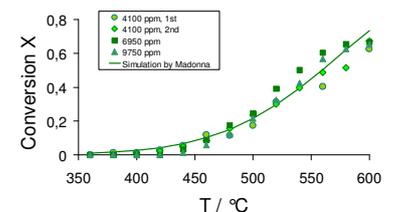


Figure 6: Conversion of NH<sub>3</sub> on 4 g ZrON measured at various feed concentrations. The solid line represents a refinement of a first order reaction in a PFTR

## Literature

- [1] R.Z. Sorensen, J.E. Nielsen, S. Jensen, O. Hansen, T. Johannessen, U. Quaade, C.H. Christensen, *Cat. Comm.* 6 (2005) 229-232
- [2] M. Lerch, *J. Am. Ceram. Soc.*, 79 (10), (1996), 2641-2644
- [3] M. Lerch, O. Rahäuser, *J. Mat. Sci.* 32 (1997), 1357-1363

## Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft, DFG (LE 781/9-1, SCHL 332/6-1), is gratefully acknowledged.