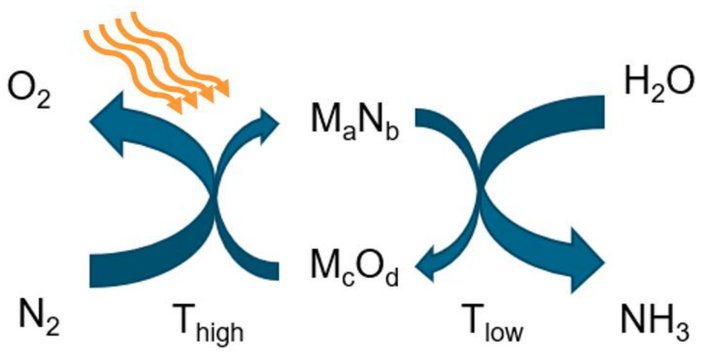
Theoretical Modeling of Metal Nitride/Oxide Pairs for Sustainable Ammonia Production Using Thermochemical Cycles

C. M. Brandenburg, E. Dashjav, D. Koch, P. U. Biedermann, L. Klaas, M. Pein, M. Roeb
German Aerospace Center (DLR), Institute of Future Fuels, Cologne

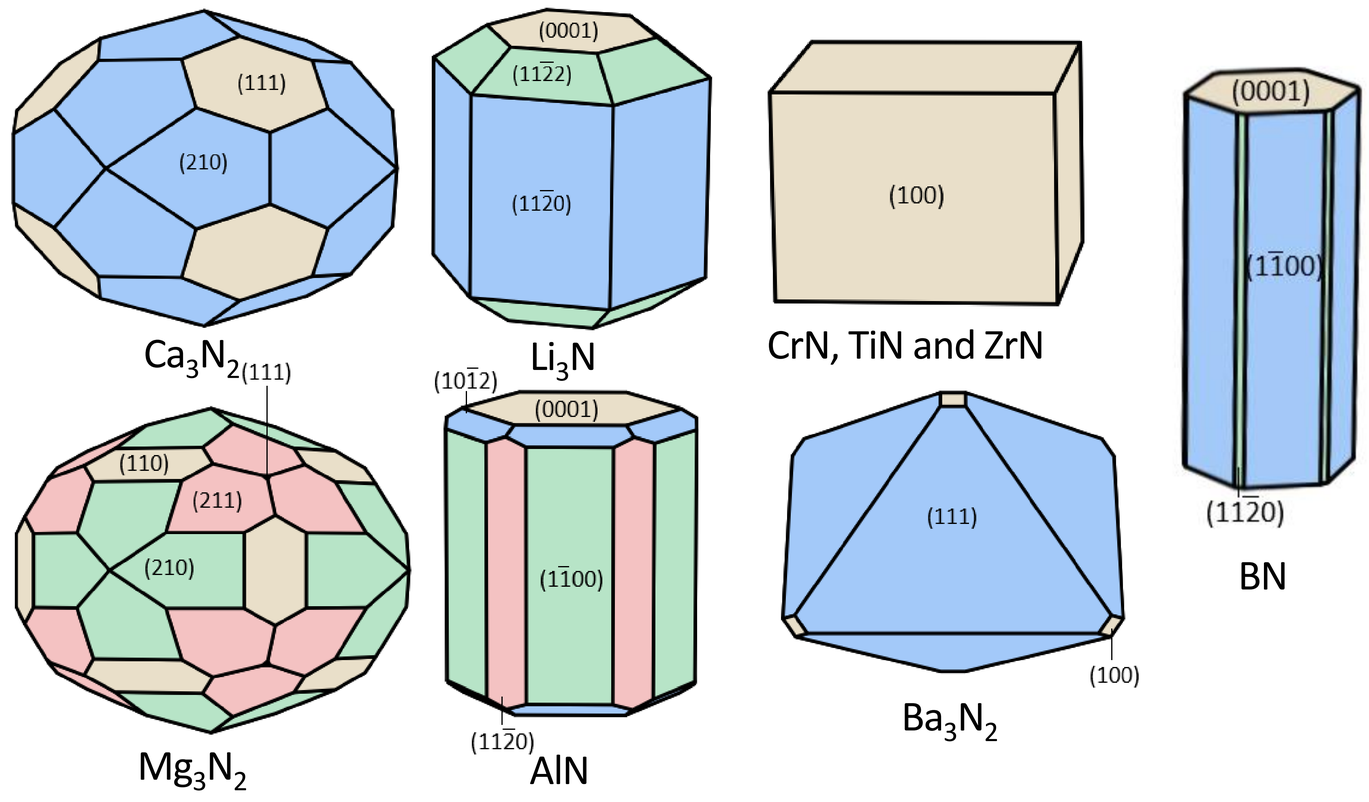
Summary: Hydrolysis reactions of several metal nitride surfaces were studied from first principles. Reaction energies for NH_3 formation on the most exposed nitride surfaces were calculated and compared. Significant differences in reaction thermochemistry and hydrolysis mechanisms were found. The results can enable a targeted search for suitable nitride materials for solar thermochemical ammonia production in the future.

Ammonia Production Using Two-Step Thermochemical Cycles



Step 1: Hydrolysis of nitrogen carrier ($\mathbf{M_aN_b}$) at low temperature.
Step 2: Regeneration of nitrogen carrier with $\mathbf{N_2}$ at high temperatures (with reducing agent). Heating through concentrated solar radiation.

Wulff Construction of the Chosen Nitrogen Carriers



Only 1 – 4 different surfaces occur in the Wulff construction depending on the material.
Same space groups exhibit similar surfaces (AlN and BN; Ba_3N_2, Ca_3N_2 and Mg_3N_2).
CrN, TiN and ZrN all show the same construction consisting of only the (100) surface.

Workflow and Methodology

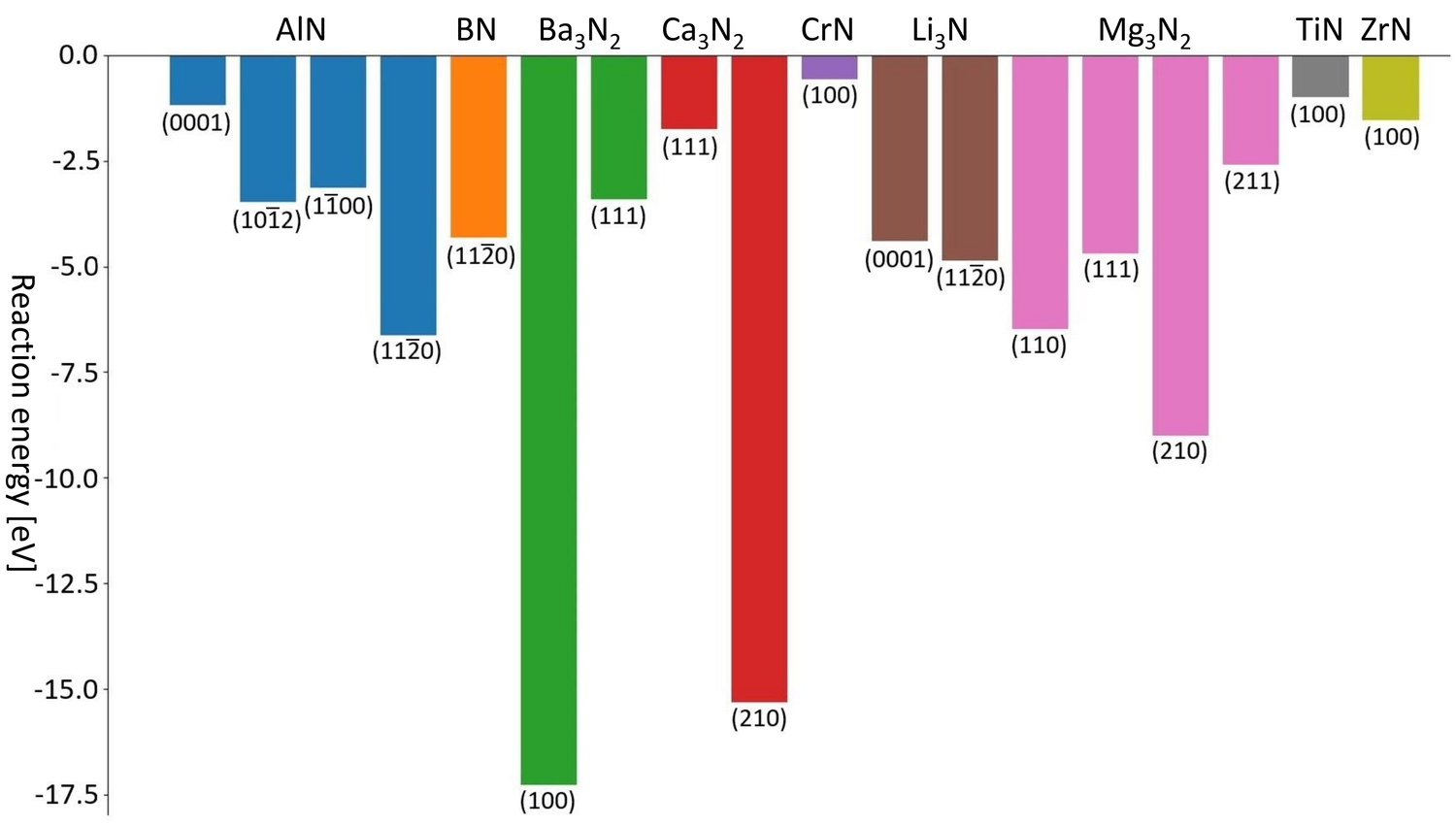
DFT calculations with PBE as implemented in SIESTA
Choice of binary nitrogen carrier ($\mathbf{M_aN_b}$)
- Have already been experimentally tested
- Different reactivities towards H_2O

Wulff constructions
- Calculation of low index surface energies of all materials

Determine surface reaction energies $\Delta E = \Delta E^{(1)} + \Delta E^{(2)} + \Delta E^{(3)}$

1. $\mathbf{M_aN_b + H_2O \rightarrow M_aN_b\text{-}OH_{2(surf)} + \Delta E^{(1)}}$
2. $\mathbf{M_aN_b\text{-}OH_{2(surf)} + H_2O \rightarrow M_aN_b\text{-}(OH_{2(surf)})_2 + \Delta E^{(2)}}$
3. $\mathbf{M_aN_b\text{-}(OH_{2(surf)})_2 \rightarrow M_aON_{b\text{-}1}\text{-}OH_{(surf)} + NH_{3(g)} + \Delta E^{(3)}}$

Reaction Energies for the Production of a NH_3 Molecule



Reactions on all surfaces proceed with a negative reaction energy. Similar surfaces across the nitrides result in similar reaction energies. The reaction energies follow the trend that lower electronegativities of the metal centers (more ionic M-N bonds) result in more negative reaction energies.

Why do BN and CrN not work?

Both BN and CrN show a negative surface hydrolysis reaction energy. However, the materials only yield little ammonia in experimental investigations. A reason could lie in the dissociation of adsorbed water molecules. For CrN, the adsorption energy is low (-0.37 eV) and the dissociation energy is -0.72 eV. For BN, dissociated hydrogen moves to boron instead of nitrogen, inhibiting the formation of NH_3.

The authors gratefully acknowledge the computational and data resources provided through the joint high-performance data analytics (HPDA) project "terrabyte" of the German Aerospace Center (DLR) and the Leibniz Supercomputing Center (LRZ).