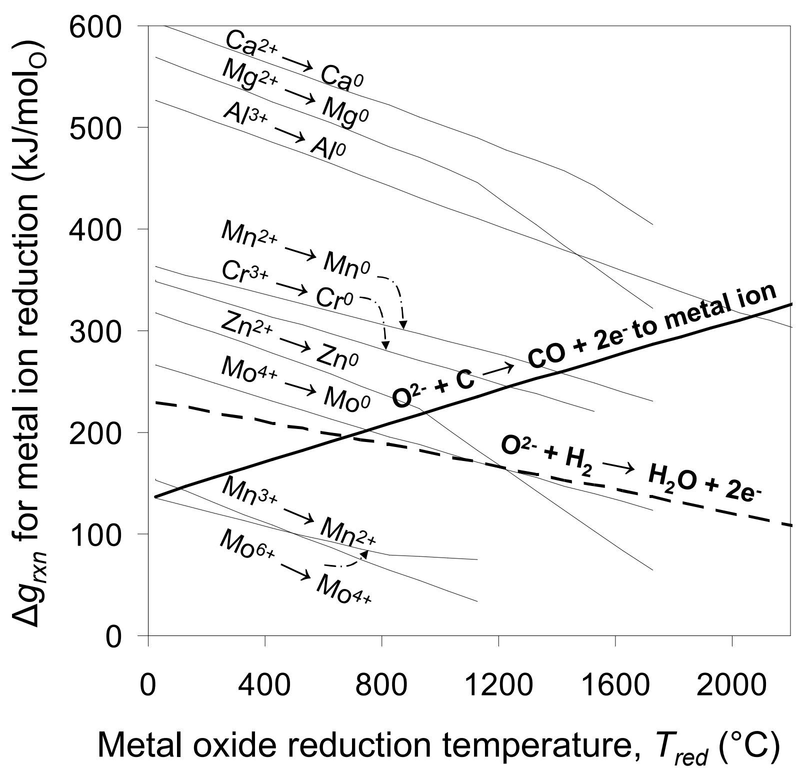
Supporting Information for:

An Ionicity Rationale to Design Solid phase Metal Nitride Reactants for Solar Ammonia Production

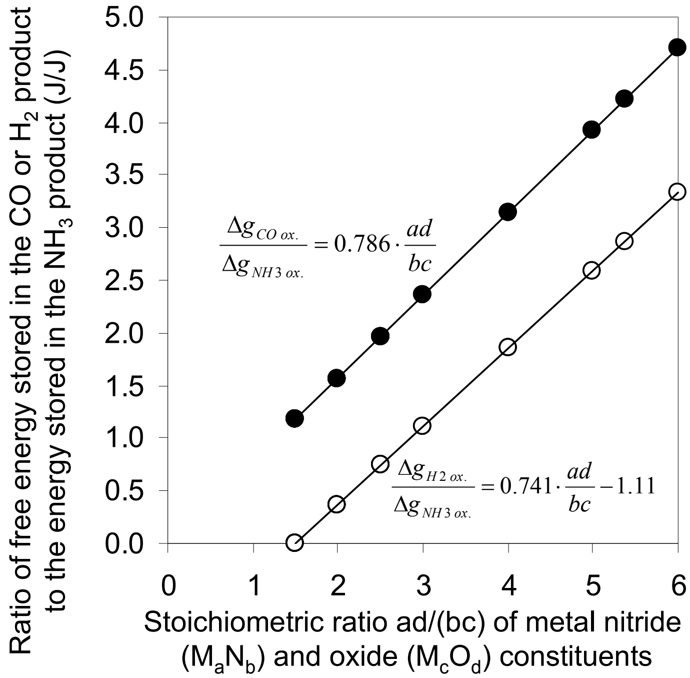
Ronald Michalsky[†,‡,§] and Peter H. Pfromm[‡,*]

[†]NSF IGERT associate in biorefining and [‡]Department of Chemical Engineering, 1005 Durland Hall, Kansas State University, Manhattan, Kansas, 66506, United States

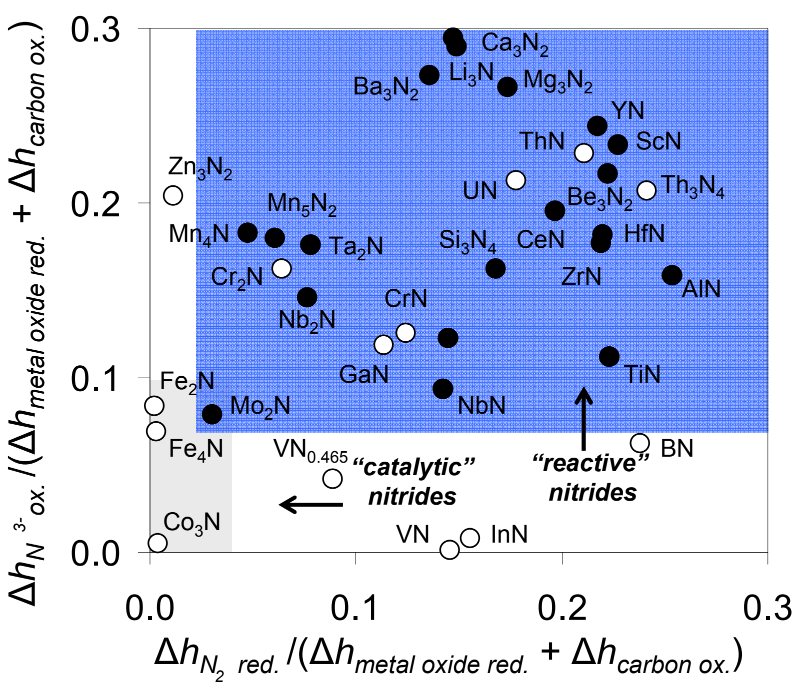
Corresponding Author
[*]E-mail: pfromm@ksu.edu. Telephone: +1 785-532-4312. Fax: +1 785-532-7372.
Present Address
[§]Current address: Brown University, School of Engineering, Box D, 182 Hope Street, Providence, RI 02912, United States



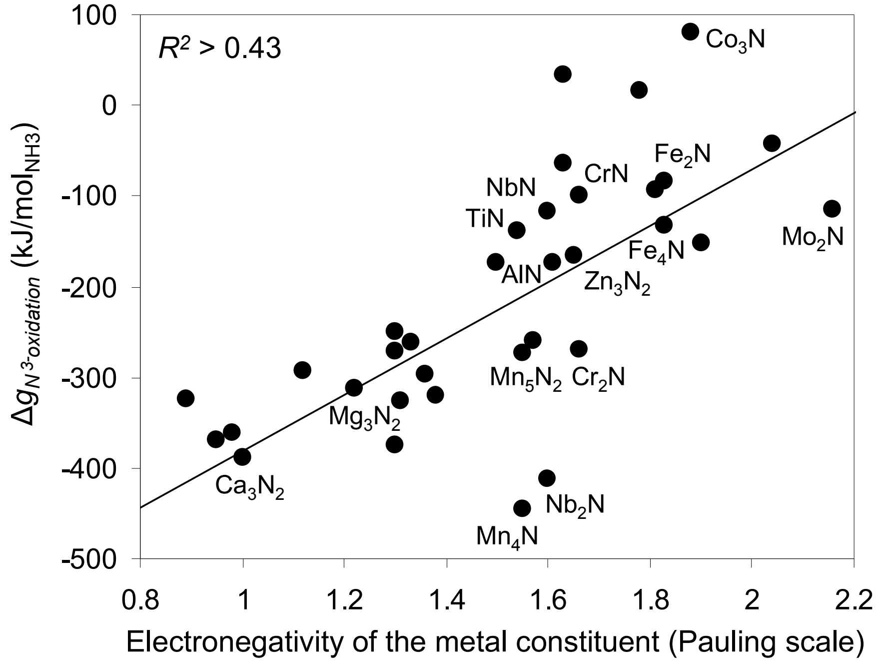
Ellingham diagram to determine required temperatures and necessary reducing agents (solid graphite or gaseous H_2 if the metal ion reduction intersects their oxidation or none if Δg_{rxn} = 0) of the solar thermochemical metal oxide reduction step.



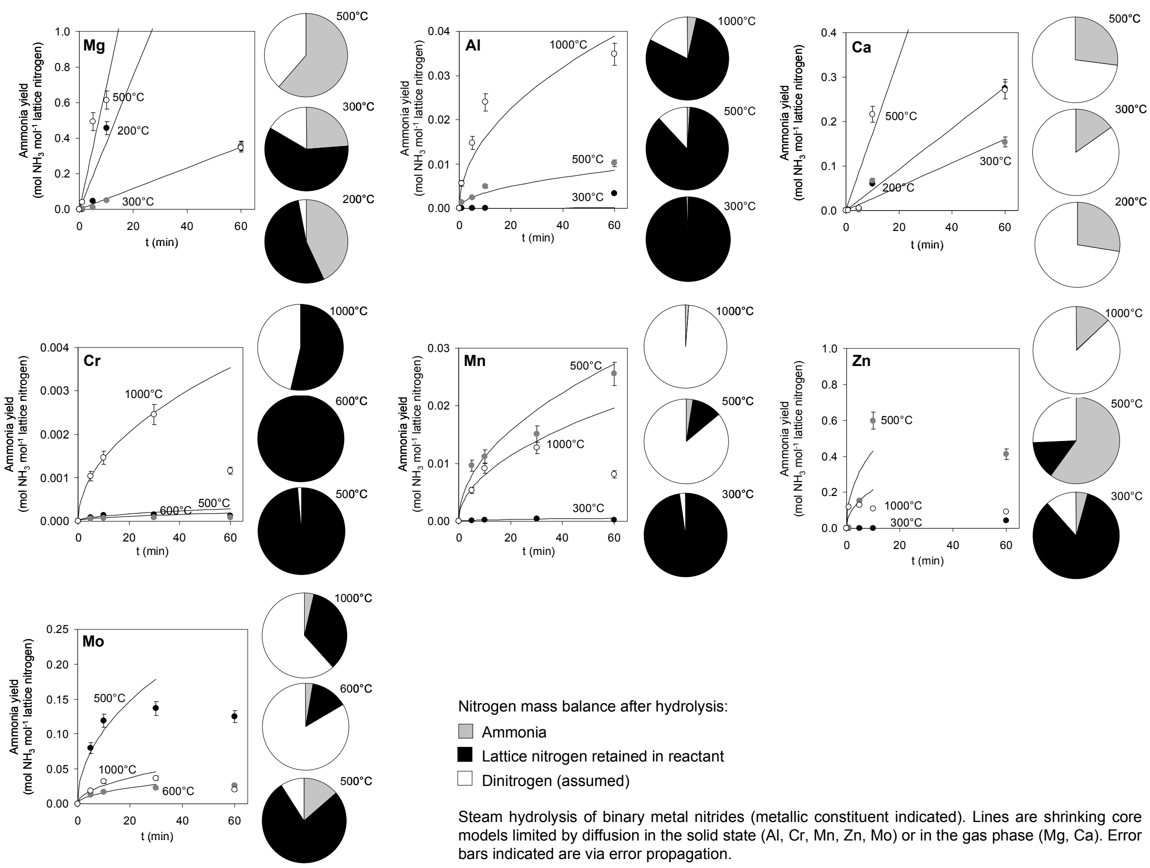
Correlation of the free energy (at 25°C and 0.1 MPa) released by oxidation of the cycle products (NH_3,CO or H_2 with O_2 to N_2, H_2O, or CO_2) and the stoichiometric composition of the nitride/ oxide reactant.



Heat liberated during the N^{3-} oxidation vs. N_2 reduction, both relative to the energy supplied during the carbothermal metal oxide reduction step (all at 25°C and 0.1 MPa). Empty circles mark materials that do not fix 0.1 MPa N_2, do not liberate NH_3 effectively, or are radioactive.



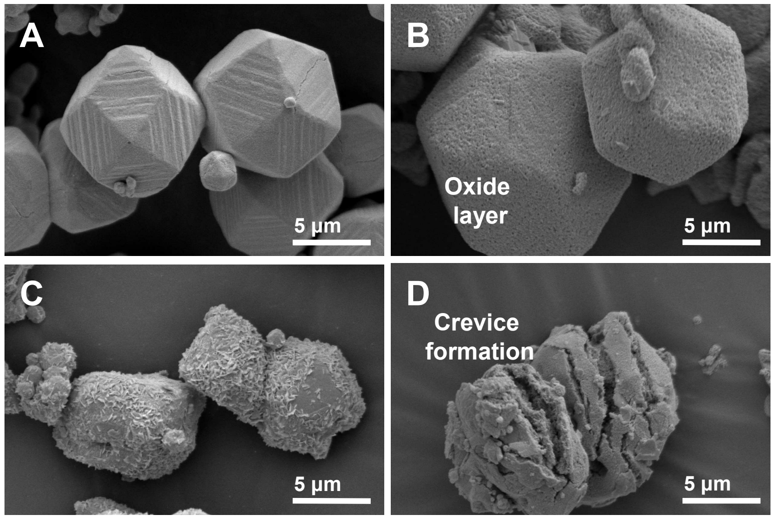
Free energy (at 25°C and 0.1 MPa) of NH_3 formation via H_2O cleavage with metal nitrides versus the electronegativity of the metal constituent of the nitride.



Nitrogen mass balance after hydrolysis:

- Ammonia
- Lattice nitrogen retained in reactant
- Dinitrogen (assumed)

Steam hydrolysis of binary metal nitrides (metallic constituent indicated). Lines are shrinking core models limited by diffusion in the solid state (Al, Cr, Mn, Zn, Mo) or in the gas phase (Mg, Ca). Error bars indicated are via error propagation.



SEM micrographs of Mo_2N (A, B) or Zn_3N_2 (C, D) before (A, C) or after (B, D) hydrolysis for 60 min at 500°C

References (complete author list)

(7) Hellman, A.; Baerends, E. J.; Biczysko, M.; Bligaard, T.; Christensen, C. H.; Clary, D. C.; Dahl, S.; van Harrevelt, R.; Honkala, K.; Jonsson, H.; Kroes, G. J.; Luppi, M.; Manthe, U.; Nørskov, J. K.; Olsen, R. A.; Rossmeisl, J.; Skúlason, E.; Tautermann, C. S.; Varandas, A. J. C.; Vincent, J. K. *J. Phys. Chem. B* **2006**, *110*, 17719-17735.

(9) Churchard, A. J.; Banach, E.; Borgschulte, A.; Caputo, R.; Chen, J.-C.; Clary, D. C.; Fijalkowski, K. J.; Geerlings, H.; Genova, R. V.; Grochala, W.; Jaroń, T.; Juanes-Marcos, J. C.; Kasemo, B.; Kroes, G.-J.; Ljubić, I.; Naujoks, N.; Nørskov, J. K.; Olsen, R. A.; Pendolino, F.; Remhof, A.; Románszki, L.; Tekin, A.; Vegge, T.; Zäch, M.; Züttel, A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16955-16972.

(13) Valov, I.; Luerssen, B.; Mutoro, E.; Gregoratti, L.; De Souza, R. A.; Bredow, T.; Günther, S.; Barinov, A.; Dudin, P.; Martin, M.; Janek, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3394-3410.