Research Update: The nitride route to ammonia fertilizers: decoupling food and fossil fuel

By Peter Pfromm, P.h.D., Professor, Department of Chemical Engineering, Kansas State University

A new three-year project at Kansas State University, sponsored by the U.S. Department of Energy, Basic Energy Sciences (U.S. DOE Office of Science, Award No. DE-SC0016453, "Step Catalysis to Synthesize Fossil-Free Ammonia at Atmospheric Pressure"), with $598,866 pursues ammonia for fertilizers produced from renewable resources with a new simple and rugged process. The team of Principal Investigator Dr. Peter Pfromm (Chemical Engineering), and co-Principal Investigators Dr.'s Bin Liu (Chemical Engineering) and Viktor Chikan (Chemistry) and their graduate students are investigating forming metal nitrides from metal alloy nanoparticles to activate nitrogen from air, and then synthesizing ammonia in a second step, all at atmospheric pressure and moderate temperatures. The recent precipitous decline in the cost of renewable electricity[1] allows the needed hydrogen to be made by electrolysis of water so that the entire process is essentially fossil fuel free, economically competitive with fossil fuel based ammonia, and proceeds under conditions that will allow down-scaling and operation on stranded or intermittent renewable electricity.

By the year 2000, nitrogen from synthetic ammonia for fertilizers was responsible for feeding about 44% of the world's population[2]. This makes affordable synthetic ammonia made on a very large scale (currently about 140 million metric tons per year world-wide) the most important achievement of chemistry and chemical engineering. It has been said that synthetic ammonia is the most significant achievement of science and technology overall due to the exceptional impact on life on earth and the size of the human population in particular.

Affordable synthetic ammonia fertilizers became available early in the 20th century through the Haber-Bosch process. Roughly two in five humans on earth owe their existence to the towering achievements of Noble Prize winners Fritz Haber and Carl Bosch, and Alwin Mittasch, at Badische Anilin- und Sodafabriken (BASF) in the 1920's. Today, the Haber-Bosch process is still the only large scale ammonia synthesis process. Coal or natural gas is used to produce ammonia. In a sense, much of our food is fossil fuel derived since about 40% of agricultural yield is due to fossil fuel based ammonia fertilizers.

Before concentrating on the catalytic Haber-Bosch process to synthesize ammonia, several other avenues were pursued at BASF. Among them was the approach of absorbing nitrogen (N_2) from air into a metal to break the formidable nitrogen triple bond, and produce a metal/nitrogen compound called a nitride[3]. In a second step gaseous hydrogen (H_2) would be contacted with the metal nitride to liberate ammonia (NH_3). The demonstrated success of the Haber-Bosch process, however, terminated work on nitrides.

Aluminum nitride was more recently proposed at ETH, Zurich[4] to synthesize ammonia, but the required temperatures as high as 2000°C made it difficult to envision a technical process. Today, the nitride approach is being investigated again by Pfromm, Liu, and Chikan since it proceeds at atmospheric pressure instead of 200-300 atmospheres for the Haber-Bosch process, and since it is more rugged due to bulk metal as the working material instead of the sensitive catalytic surfaces used in the Haber-Bosch process. The team at Kansas State University is building on extensive previous work by Pfromm and co-workers[5,6,7,8].

The new project at K-State will explore manganese-based metal alloys in form of nanoparticles. The early work at BASF will be extended in that advantageous properties not accessible with a single metal may be exploited by alloys. The unusual properties of materials at the nano-scale are expected to advance the nitride approach to ammonia synthesis further towards a viable technical process.

The ultimate goal of the new project by Pfromm, Liu, and Chikan is to advance towards decoupling our food from fossil fuel by synthesizing ammonia in a simple and rugged process from renewable energy. This may enable ammonia synthesis at the regional or local level in areas of the world where agricultural yield increases are sorely needed, and where farmers use little ammonia now due to economic barriers.

---

[1] Revolution…Now The Future Arrives for Five Clean Energy Technologies – 2015 Update, Report, U.S. Department of Energy, November 2015, http://energy.gov/sites/prod/files/2015/11/f27/Revolution-Now-11132015.pdf

[2] Erisman, J.-W.; Sutton, M. A.; Galloway, J. K., Klimont, Z., Winiwarter, W., How a century of ammonia synthesis changed the world, Nature Geoscience, 1(10), 636-639, 2008

[3] A. Mittasch, "Geschichte der Ammoniak-Synthese", Verlag Chemie, Weinheim, 1957

[4] Galvez, M.E., Halmann, M., Steinfeld, A., Ammonia production via a two-step Al2O3/AlN thermochemical cycle. 1. Thermodynamic, environmental, and economic analyses. Industrial & Engineering Chemistry Research 46, 2042–2046, 2007

[5] Michalsky, R., Pfromm, P. H., Steinfeld, A., Rational design of metal nitride redox materials for solar-driven ammonia synthesis, Interface Focus, 5(3), article No. 20140084, 2015

[6] Michalsky, R., Pfromm, P. H., An Ionicity Rationale to Design Solid Phase Metal Nitride Reactants for Solar Ammonia Production, J. Phys. Chem. C, 116(44), 23243-2325, 2012

[7] Michalsky, R., Parman, B. J., Amanor-Boadu, V., Pfromm, P. H., Solar thermochemical production of ammonia from water, air and sunlight: thermodynamic and economic analyses, Energy, 42(1), 251-260, 2012

[8] Thermochemical ammonia and hydrocarbons, U.S. Patent Application 20150315032, Inventors Michalsky, R., Pfromm, P. H., Applicant Kansas State University