

# New revelations in ammonia synthesis

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Scientists at the University of Cambridge are working on ways to improve the efficiency of the ammonia synthesis process. With between 3-5% of the world's natural gas used to create artificial fertilizers, the new research could have major implications for both the agricultural and energy sectors.

Ammonia ( $\text{NH}_3$ ) is one of the most important chemicals in the modern world, due mainly to its use in the manufacture of artificial fertilisers. [Ammonia](#) synthesis (via the "Haber" or "Haber-Bosch" process) is vital to the production of 100 million tons of fertiliser per year, responsible for sustaining one-third of the Earth's population.

In the natural world, ammonia is generated by plants (predominantly the legumes) and certain bacteria, which extract [nitrogen](#) from the atmosphere in a process known as [nitrogen fixation](#). Natural nitrogen fixation occurs at ambient temperatures and pressures, but artificial nitrogen fixation via the Haber-Bosch process requires high pressures (150-250 atmospheres) and high temperatures (300-550 degrees Celsius) to produce the vast quantities of ammonia necessary to satisfy global demand. The 3-5% of the world's natural gas production referred to earlier is consumed in the Haber-Bosch process, amounting to around 1-2% of the world's man-made energy supply.

Dr Steve Jenkins, of the Department of Chemistry at the University of Cambridge, one of the co-authors of the paper reporting the research, said: "The Haber-Bosch process was developed in the early twentieth century but has changed little since that time. Clearly, given the massive

scale of worldwide ammonia production, even a tiny improvement in the efficiency of the ammonia synthesis process can have massive implications, not only for the economics of fertiliser production, but also for global energy demand."

The key to the Haber-Bosch process is an iron catalyst which encourages the dissociation of  $N_2$  molecules, and provides a platform on which the resulting N atoms can be successively hydrogenated to yield NH,  $NH_2$  and finally  $NH_3$ . (A catalyst is defined as a substance that improves the speed or selectivity of a chemical reaction, whilst not being consumed or produced in the reaction itself.)

Great efforts have been expended over many decades on the problems of understanding how the iron catalyst does its job, why the addition of certain elements such as potassium can improve the catalysts, and whether any of the lessons learnt thus far can help us predict a better catalyst that is economically viable.

The Cambridge group's findings, reported in the journal *Proceedings of the National Academy of Sciences*, address some of these problems and pave the way for a more efficient way to produce fertilisers.

Jenkins continued: "The surface science approach uses single-crystal iron samples of high purity, and typically involves experiments carried out under uhv (ultra high vacuum) conditions (i.e. pressures less than one millionth of a millionth of an atmosphere).

"We have conducted experiments that combine some of the attractive features of single-crystal uhv surface science with those of higher pressure techniques."

The scientists begin by exposing their iron sample to nitrogen ions, in order to readily build up a coverage of nitrogen atoms on the surface (to

a density of just over one nitrogen atom per two top-layer iron atoms at the surface). Under uhv conditions, they can utilise Auger Electron Spectroscopy (AES) to quantify the amount of nitrogen on the surface. Then, they expose the sample to 0.6 mbar H<sub>2</sub> gas for a period of several minutes. This pressure is still very low compared with industrial conditions, but it allows the reaction to proceed sufficiently rapidly for them to take meaningful measurements over a timescale of minutes. If they used only uhv pressures of H<sub>2</sub>, the reaction would be so slow that it would take hours, during which time contamination would build up on the surface and ruin the experiment.

The drawback of using non-uhv pressure is that it prevents them from using AES during the exposure, but they can get around this problem by working episodically. After an exposure of several minutes, they rapidly evacuate the experimental chamber to return to uhv conditions and use AES to evaluate how much nitrogen is left on the surface, then expose to H<sub>2</sub> again and repeat. By doing this several times, they can measure the drop in surface nitrogen (corresponding to production of ammonia) as a function of time and temperature.

Because their hydrogenation experiments start with nitrogen pre-deposited on the surface, and they can also calculate that they never produce enough ammonia to cover more than a small fraction of the surface at the temperatures and pressures involved in their work, they know that their results must correspond to a situation where it is the previously unregarded hydrogenation steps that determine the overall rate.

Professor Sir David King, of the Department of Chemistry at the University of Cambridge said: "Interestingly, we find that the speed-up in reaction achieved when we add a little potassium to the surface - roughly 20% - is similar to that observed by Gabor Somorjai in conditions of minimal ammonia production and hitherto attributed to

enhanced  $N_2$  dissociation. Our results suggest, however, that under certain conditions - namely when the ammonia pressure is kept low - the hydrogenation steps (from N to NH to  $NH_2$  to  $NH_3$ ) may actually be the most important.

"We should be clear that this does not contradict the previous work, but does indicate that we need to be careful in assuming that what is found to be true under one set of conditions must necessarily apply in others."

Dr Jenkins concluded: "Another important aspect of the current work that is worth emphasising is the very great difficulty in working with iron. Compared to other reactive metals used in catalysis generally (e.g. platinum, copper, nickel) iron is extremely prone to containing high levels of impurities, which can hamper reproducibility and mask the properties of the parent material.

"Months of effort by an earlier student were required to clean the current sample, by a combination of hydrogen-treatment, argon ion sputtering, annealing, and oxygen-treatment. Furthermore, previous work on iron single-crystal samples under uhv conditions (i.e Gerhardt Ertl's work) involved deliberately saturating the near-surface region of the material with nitrogen, to prevent unquantified nitrogen diffusion into the bulk. By working with higher-pressure of hydrogen, we can operate at lower temperatures, preventing this from being a problem. Thus, our results are obtained from a properly clean iron sample without sub-surface nitrogen saturation."

**More information:** The paper 'Hydrogenation of N over Fe' was published in the 08 November 2010 edition of the *Proceedings of the National Academy of Sciences*.

Provided by University of Cambridge

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