Alternative synthesis of ammonia

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Abstract

Nitrogen atoms are essential for the function of biological molecules and thus are an important component of fertilizers and medicaments. Bonds to nitrogen also find non biological uses in dyes, explosives, and resins. The synthesis of all these materials requires ammonia for natural processes and the chemical industry. Knowledge of the various techniques for the preparation of ammonia is thus of fundamental importance for chemistry. The Haber–Bosch synthesis was the first heterogeneous catalytic system employed in the chemical industry and is still in use today. Understanding the mechanism and developing a renewable energy approach for producing ammonia is a major concern today .

Key Words: Haber- Bosch, Ammonia, Heterogenous, Renewable.

Introduction

How is ammonia synthesized?

A typical modern ammonia-producing plant first converts natural gas (i.e., methane) or LPG (liquefied petroleum gases such as propane and butane) or petroleum naphtha into gaseous hydrogen. The method for producing hydrogen from hydrocarbons is known as steam reforming. The hydrogen is then combined with nitrogen to produce ammonia via the Haber-Bosch process.

Starting with a natural gas feedstock, the processes used in producing the hydrogen are:

The first step in the process is to remove sulfur compounds from the feedstock because sulfur deactivates the catalysts used in subsequent steps. Sulfur removal requires catalytic hydrogenation to convert sulfur compounds in the feedstocks to gaseous hydrogen sulfide:

$$H_2 + RSH \rightarrow RH + H_2S(gas).$$

The gaseous hydrogen sulfide is then adsorbed and removed by passing it through beds of zinc oxide where it is converted to solid zinc sulfide:

$$H_2S + ZnO \rightarrow ZnS + H_2O$$

Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The next step then uses catalytic shift conversion to convert the carbon monoxide to carbon dioxide and more hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.

The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

To produce the desired end-product ammonia, the hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):

$$3H_2 + N_2 \rightarrow 2NH_3$$

Due to the nature of the (typically multi-promoted magnetite) catalyst used in the ammonia synthesis reaction, only very low levels of oxygen-containing (especially CO, CO_2 and H_2O) compounds can be tolerated in the synthesis (hydrogen and nitrogen mixture) gas. Relatively pure nitrogen can be obtained by Air separation, but additional oxygen removal may be required.

Because of relatively low single pass conversion rates (typically less than 20%), a large recycle stream is required. The steam reforming, shift conversion, carbon dioxide removal and methanation steps each operate at absolute pressures of about 25 to 35 bar, and the ammonia synthesis loop operates at absolute pressures ranging from 60 to 180 bar depending upon which proprietary design is used. There are many engineering and construction companies that offer proprietary designs for ammonia synthesis plants. Haldor Topsoe of Denmark, Thyssenkrupp Industrial Solutions GmbH of Germany, Ammonia Casale of Switzerland and Kellogg Brown & Root of the United States are among the most experienced companies in that field.

Sustainable ammonia production

Ammonia production depends on plentiful supplies of energy, predominantly natural gas. Due to ammonia's critical role in intensive agriculture and other processes, sustainable production is desirable. This is possible by using renewable energy **(1)** to generate hydrogen by electrolysis of water. This would be straightforward in a hydrogen economy by diverting some hydrogen production from fuel to feedstock use. For example, in 2002, Iceland produced 2,000 tons of hydrogen gas by electrolysis, using excess electricity production from its hydroelectric plants, primarily for the production of ammonia for fertilizer. The Vemork**(2)** hydroelectric plant in Norway used its surplus electricity output to generate renewable ammonia from 1911 to 1971, requiring 15 MWh/Ton of nitric acid. The same reaction is carried out by lightning, providing a natural source for converting atmospheric nitrogen to soluble nitrates(**3**). In practice, natural gas will remain the major source of hydrogen for ammonia production as long as it is cheapest.

Waste water**(4)** is often high in ammonia. Because discharging ammonia laden water into the environment, even in wastewater treatment plants, can cause problems, nitrification is often necessary to remove the ammonia. This may be a potentially sustainable source of ammonia in the future because of its abundance and the need to remove it from the water anyway. Alternatively, ammonia from waste water is sent into an ammonia electrolyzer (ammonia electrolysis) operating with renewable energy sources (Solar PV and Wind turbine) to produce hydrogen and clean treated water. Ammonia electrolysis may require much less thermodynamic energy than water electrolysis (only 0.06 V in alkaline media).

Another option for recovering ammonia from waste water is to use the mechanics of the ammonia-water thermal absorption cycle. Using this option, ammonia can be recovered either as a liquid or as ammonium hydroxide. The advantage of the former is that it is much easier to handle and transport, whereas the latter also has a commercial value when a concentration of 30 percent ammonium hydroxide in solution is produced.

But despite its importance, the massive use of nitrogen fertilizers involves a great paradox. On the one hand, they are essential for ensuring the large amount of food, but on the other hand, they have a negative impact on the environment.

The reason is that the efficient use of the nitrogen that is employed in the industrial synthesis of fertilizers is very poor, which means that the remaining large amount contributes **to environmental pollution causing the eutrophication of water, loss of biodiversity and negative alteration of the atmospheric balance.**

Researchers developing renewable energy approach for producing ammonia

Researchers at the University of Notre Dame are developing a renewable energy approach for synthesizing ammonia, an essential component of fertilizers that support the world's food production needs. The Haber-Bosch process developed in the early 1900s for producing ammonia relies on non-renewable fossil fuels and has limited applications for only large, centralized chemical plants.

The new process, utilizes a plasma—an ionized gas—in combination with non-noble metal catalysts to generate ammonia at much milder conditions than is possible with Haber-Bosch. The energy in the plasma excites nitrogen molecules, one of the two components that go into making ammonia, allowing them to react more readily on the catalysts. Because the energy for the reaction comes from the plasma rather than high heat and intense pressure, the process can be carried out at small scale. This makes the new process well-suited for use with intermittent renewable energy sources and for distributed ammonia production.

Plasmas have been considered by many as a way to make ammonia that is not dependent on fossil fuels and had the potential to be applied in a less centralized way.The real challenge has been to find the right combination of plasma and catalyst by combining molecular models with results in the laboratory.

The research team led by Schneider; David Go, Rooney Family Associate Professor of Engineering in aerospace and mechanical engineering; and Jason Hicks, associate professor of chemical and biomolecular engineering, discovered that because the nitrogen molecules are activated by the plasma, the requirements on the metal catalysts are less stringent, allowing less expensive materials to be used throughout the process. This approach overcomes fundamental limits on the heat-driven Haber-Bosch process, allowing the reaction to be carried out at Haber-Bosch rates at much milder conditions

Our society is in need of ammonia more than ever. Chemical fertilizers, plastic, fibers, pharmaceuticals, refrigerants in heat pumps, and even explosives all use ammonia as raw material. Moreover, ammonia has been suggested as a hydrogen carrier recently because of its high hydrogen content. In the Haber-Bosch process, which is the main method of ammonia synthesis, nitrogen reacts with hydrogen using a metal catalyst to produce ammonia. However, this industrial process is conducted at 200 atm and high reaction temperatures of nearly 500°C. Additionally, ammonia production requires using much natural gas, so scientists have been looking for alternative methods to sustainably synthesize ammonia at low temperature.

In a recent study, researchers from Waseda University and Nippon Shokubai Co. Ltd.**(5)** achieved a highly efficient ammonia synthesis at low temperature, with the highest yield ever reported. By applying an electric field to the catalyst used in the experiment, they accomplished an efficient, small-scale process for ammonia synthesis under very mild conditions. Using this new method, they can collect highly pure ammonia as compressed liquid and open doors to developing on-demand ammonia production plants that run on renewable energy. It was found that an electric field brings high yield on low temperature catalytic ammonia synthesis over $Cs/Ru/SrZrO_3$ catalyst. The role of the electric field was investigated based on kinetics and isotope effects. Results show that the electric field promotes proton hopping on the catalyst surface, and it brought a change in the reaction mechanism from the conventional one to the N_2H^+ intermediate mechanism. In the electric field, N_2H^+ intermediate plays an important role, enabling low-temperature ammonia synthesis.

Although the Haber-Bosch process, which is highly energy consuming, does not meet current sustainability requirements, there is no replacement alternative, and the balance between human needs and natural resources is still pending.

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