



## A review of the existing and alternative methods for greener nitrogen fixation



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### ABSTRACT

The conversion of atmospheric nitrogen into valuable substances such as fertilisers and fine chemicals is essential for agriculture and many other processes that sustain life on the planet. Although the Haber–Bosch process is the most important method of nitrogen fixation, the process is associated with major environmental concerns because it is very energy intensive and requires non-renewable feedstock to generate hydrogen. Hence, alternative ways of nitrogen fixation are being studied, from plasma synthesis and biological processes to metallocomplex catalysis, while existing methods are being improved using novel catalysts. This review covers all of the major areas of nitrogen fixation, discusses the industrial feasibility of each process, the reaction mechanisms, and provides a comparative evaluation of the various nitrogen fixation processes in terms of energy efficiency. Considering energy efficiency, the Haber–Bosch process and non-thermal plasma nitrogen fixation are promising methods for green industrial nitrogen fixation. Although metallocomplex nitrogen fixation takes place at ambient pressures, energy estimations show that this method does not provide higher energy efficiency than biological nitrogen fixation or the Haber–Bosch process. Biological nitrogen fixation on the other hand, has energy efficiency comparable to that of the Haber–Bosch process.

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### 1. Introduction

Nitrogen is an essential constituent of all living organisms and can be found in amino acids, proteins and nucleic acids. Animals, including humans, consume nitrogen in the form of organic compounds, requiring eight to ten particular amino acids for their nutrition. The human body requires 1–2 g of protein per kg of body

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mass per day to survive [1–3]. Plants and bacteria, on the other hand, are less demanding because they can synthesise the much-needed amino acids from various organic and inorganic nitrogen compounds. However, the most abundant nitrogen source, the atmosphere, is not available to the majority of organisms because of the inertness of molecular nitrogen due to the high strength of its triple bond and very stable electron configuration which make almost any first reaction step unusually energy demanding. As a result, the most challenging stage of nitrogen fixation (NF) is the conversion of dinitrogen molecules into simple nitrogen compounds such as ammonia or nitric oxide which can be further used as precursors for the synthesis or biosynthesis of more complex molecules. This problem is being addressed by active research into various methods of NF including the Haber–Bosch (H–B) process, plasma synthesis, biological NF, and metalcomplex NF.

The production of nitrogen fertilisers from atmospheric nitrogen has been a major problem at the beginning of 20th century [4]. In 1913, the H–B process of the high-pressure binding of nitrogen with hydrogen was introduced providing much needed fertilisers. From then on, NF has progressed in much the same manner as the growth in human population, and nowadays, about 40% of world population depend on nitrogen fixed by the H–B process [3,5]. Recently, the amount of synthetic nitrogen obtained by human activities has exceeded natural biological fixation [6]. This intensification has led to more than doubling of the number of humans supported by a hectare of arable land [2,4].

Extensive use of NF, however, comes at a price as the H–B process consumes more than 1% of the world's total energy production, emits more than 300 million metric tons of carbon dioxide and utilizes about 2% of the world's natural gas output, which is converted to hydrogen by steam reforming process [7–9]. Therefore, there is room for efficiency optimisation in NF because even minor benefits multiplied by world-scale production will give rise to huge economic savings.

To address the environmental and other concerns associated with the H–B process, research is conducted in many areas aiming to (a) improve the catalysts for the H–B process while decreasing the reaction temperature and pressure, (b) investigate plasma methods, (c) explore the mechanism of biological NF, and (d) investigate ways of NF with metalcomplex homogeneous catalysts under ambient pressure. These methods fall into two groups. The first group uses carefully optimised catalysts to perform NF under mild conditions by a slow, stepwise process of adding one electron after another while the second group uses extreme conditions of temperature and pressure to weaken the strong dinitrogen bonds. Both methods have been demonstrated in biological metalcomplex systems and in industry, respectively. This review also discusses and evaluates the various NF methods in the light of current research and compares the methods in terms of energy efficiency, environmental impact and sustainability.

## 2. The Haber–Bosch process

The Haber–Bosch process represents a major success of industry. It is now the most important source of nitrogen compounds and, although ammonia synthesis is one of the most studied reactions, modern iron catalysts are essentially the same as they were a century ago [10]. The iron catalysts are promoted with oxides of aluminium and potassium. Aluminium acts mainly as a structural promoter, preventing the sintering of iron particles and has no direct effect on the reaction rate [10–12]. Potassium increases the rate of ammonia formation by more than two orders of magnitude due to a combination of electron donation leading to a weakening of the dinitrogen bond and facilitating ammonia desorption from the catalyst surface [13–16]. Iron catalysts require high temperatures (650–750 K) for their operation in order to

increase reaction rates and high pressure of about 100 bars to compensate for the shift in ammonia equilibrium concentration. These conditions mean high energy consumption, high equipment and gas compressions costs [9].

In the 1990s, novel carbon-supported Ru catalysts were applied industrially, capable of operating at a lower reaction pressure [9,17–19]. They are usually promoted with Cs and Ba [20,21] which, similar to alkali promoters of Fe catalysts, increase electron density on Ru nanoparticles [22,23]. An important area of continuing research is how to enhance the thermal stability of the support which can be achieved by graphitisation of carbon support by thermal annealing [24] or by using alternative non-carbon supports such as MgAl<sub>2</sub>O<sub>4</sub> [25], boron nitride [26] or electron-trapping mixed calcium-aluminium oxide [27]. The activity of ruthenium-based catalysts is higher than that of iron catalysts, which suggests that the reaction temperature and pressure may be reduced, or Ru catalysts may be used in combination with iron-based catalysts to increase ammonia production in a smaller reaction volume. On the other hand, Ru-based catalysts are prone to deactivation by chlorine or sulphur [28–32], and are also significantly more expensive. Recently, a novel class of catalysts was proposed – ternary nitrides including Co<sub>3</sub>Mo<sub>3</sub>N or Fe<sub>3</sub>Mo<sub>3</sub>N [33] obtained by ammonolysis from the corresponding molybdate precursors [34]. The most active Cs-promoted Co<sub>3</sub>Mo<sub>3</sub>N catalyst was twice as active as commercial iron-based catalyst under industrial conditions, and was resistant to deactivation for at least many weeks [33,35–38].

Ammonia synthesis is a structure sensitive reaction. On Fe catalysts, active sites are surface atoms with coordination number 7, while on Ru active sites, called B<sub>5</sub> step sites, are ensembles of 5 Ru atoms [25,39,40]. Ammonia synthesis using industrial catalysis is described by a dissociative mechanism involving the adsorption of dinitrogen and dihydrogen molecules on the surface of the catalyst while hydrogen molecules quickly dissociate at a temperature above 473 K, forming highly mobile adsorbed hydrogen species on the catalyst surface, Fig. 1a. Molecular nitrogen, in contrast, is weakly adsorbed and may dissociate with low probability producing atomic nitrogen species which are bound strongly to the catalyst surface, Fig. 1b. Adsorbed hydrogen species react with adsorbed nitrogen to form ammonia, followed by desorption from the catalyst surface, Fig. 1c [11,41,42]. The rate-limiting step is dissociation of dinitrogen under all industrial conditions.

The H–B process has progressed in terms of energy consumption, decreasing by almost three times to 0.48 MJ per mole of ammonia produced. This improvement has been brought about by the change of feedstock, from coal to natural gas, and improvements in the technical aspects of the process enabling all available heat to be utilised [9].

Another important issue of the modern H–B process is the requirement of the non-renewable natural gas to generate hydrogen. Considering sustainable H–B process that uses hydrogen generated by the electrolysis of water (it requires 360–480 kJ/mol [43]), the energy consumption of renewable production of ammonia by the H–B will be almost 3 times higher – 1.5 MJ/mol, which is more than the energy consumption of many other alternative methods (see Section 6).

## 3. Plasma-induced nitrogen fixation

Nitrogen fixation in plasma is one of the pioneering ways of industrial nitrogen fixation and may be subdivided into two broad areas – thermal plasma and non-thermal plasma. The equipment required, reaction mechanisms and the energy efficiency of these processes are very different; so, these methods are discussed separately, in Sections 3.1 and 3.2, respectively.

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