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Review

Ammonia synthesis catalyst 100 years: Practice, enlightenment and challenge

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ABSTRACT

Ammonia synthesis catalyst found by Haber-Bosch achieves its history of 100 years. The current understanding and enlightenment from foundation and development of ammonia synthesis catalyst are reviewed, and its future and facing new challenge remained today are expected. Catalytic ammonia synthesis technology has played a central role in the development of the chemical industry during the 20th century. During 100 years, ammonia synthesis catalyst has come through diversified seedtime such as Fe_3O_4 -based iron catalysts, Fe_{1-x}O -based iron catalysts, ruthenium-based catalysts, and discovery of a Co-Mo-N system. Often new techniques, methods, and theories of catalysis have initially been developed and applied in connection with studies of this system. Similarly, new discoveries in the field of ammonia synthesis have been extended to other fields of catalysis. There is no other practically relevant reaction that leads to such a close interconnection between theory, model catalysis, and experiment as the high-pressure synthesis of ammonia. Catalytic synthesis ammonia reaction is yet a perfect model system for academic research in the field of heterogeneous catalysis. Understanding the mechanism and the translation of the knowledge into technical perfection has become a fundamental criterion for scientific development in catalysis research. The never-ending story has not ended yet. In addition to questions about the elementary steps of the reaction and the importance of the real structure and subnitrides for the catalyst efficiency, as well as the wide-open question about new catalyst materials, there are also different challenges thrown down by theory for the experimentalist in the prediction of a biomimetic ammonia-synthesis path at room temperature and atmospheric pressure including electrocatalysis, photocatalysis and biomimetic nitrogen fixation.

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1. The invention and enlightenment of ammonia synthesis catalyst

The ammonia synthesis industry has developed rapidly since the first ammonia synthesis device over the world started to produce ammonia in September 9th, 1913. To early 2000s, the ammonia synthesis devices with daily production capability of 1000 or 2200 t are worldwide. Ammonia synthesis has been a pillar of chemical industry and a milestone in the history of conquest of nature made by human beings.

In the process of this great invention, unprecedented difficulties have been encountered [1]. In 1787, C. L. Berthollet proposed that ammonia consisted of elemental nitrogen and hydrogen. Many distinguished chemists at that time, including W. H. Nernst, W. Ostward, F. Haber, etc., immediately contributed great efforts into research about ammonia synthesis by elemental nitrogen and hydrogen. However, the first obstacle they faced was chemical equilibrium. The law of mass action and the law of chemical equilibrium did not be found at that time, so that concentration of ammonia in the equilibrium was

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unclear. At atmospheric pressure, ammonia was only generated at very low temperature, but it decomposed at high temperature. Therefore, many scientists even believed that the generation of ammonia by the elemental hydrogen and nitrogen was an insurmountable obstacle.

At that critical moment, Haber first proposed to use high pressure reaction technique. However, it was still hard to realize industrial scale production due to low conversion-per-pass of ammonia. So Haber abandoned the popular static view and adopts a dynamic method by introducing an important concept, the reaction rate, which using space-time yield to replace reaction yield. Based on this important principle, he developed closed process flow and loop operation technology. These three technologies and concept of reaction rate were a great invention that provided the basis for the construction of experimental apparatus to produce ammonia and achieved the first pressurized catalytic process in industrial history. This was a milestone in the development history of the catalytic process that represented the beginning of a new era of industrial catalysis. Only a few years later, methanol synthesis, Fischer-Tropsch synthesis and high-pressure reaction technology in the presence of heterogeneous catalysts that appeared subsequently have become essential practices in the field of organic chemistry, and promoted the entire chemical and material industries. Haber's unprecedented creations established the basis for the entire chemical engineering science.

In February 1908, Haber signed an agreement with Baden Aniline and Soda Company (BASF). BASF assigned the task of industrial development to Carl Bosch. Bosch immediately was aware enough of the fact that he had to address three major challenges: designing methods to produce low-cost hydrogen and nitrogen; exploring an efficient and stable catalyst; developing equipment and materials for high-pressure ammonia synthesis.

Haber and other scientists energetically explored catalysts. Haber discovered that osmium and uranium-uranium carbide catalysts displayed excellent performance on ammonia synthesis. BASF Corporation acquired purchase rights for osmium in stock all over the world, a total of about 100 kg. Although it sounds incredible today, it did fully reflect the passion of scientists and entrepreneurs at that time. However, Haber was appointed the director of the Institute of Physical Chemistry and

Electrochemistry Kaiser Wilhelm Institute in 1912, which also marked the end of Haber's research activities in the field of ammonia synthesis.

Bosch assigned the task on finding efficient and stable catalysts to his assistant Alwin Mittasch. Mittasch first conducted extensive studies on metal nitrides in an attempt to fix the nitrogen in air by the indirect route. Although that technique was unsuccessful for the ammonia synthesis, it provided valuable information on the catalytic properties of almost all the metal elements in periodic table. He recognized that many of metals itself presented only little or no catalytic effect, but an additive could improve their catalytic activity. Based on these findings, in February 1909 he made an unproven hypothesis: "the winning catalyst should be a multi-components system" and it needed a very large number of tests to determine. For this reason, BASF produced a variety of model reactors for catalyst tests. From 1909 to 1911, in about a year and a half, 2500 of different catalysts were tested at 6500 times. That amazing catalyst selection trial, continued until 1922 before it was over, with a total of 20000 times of testing for over 5000 different catalyst systems.

Iron has been known as an effective catalyst for ammonia synthesis since the year of 1905. However, it was proved to be disappointing in BASF's initial experiments. Someday Mittasch's assistant Wolf inadvertently used Swedish-produced Gallivare iron ore samples which had been placed on the shelf of the laboratory a few years to test the synthesis of ammonia, and received unexpected results. He found that if a few percent of alumina, a small amount of calcium oxide and potassium alkali were fused into pure iron, a suitable catalyst for the synthesis of ammonia was obtained. The best catalyst was proved to be a multi-component mixture, which comprised the similar composition of Gallivare magnetite. That is the magnetite-based fused iron catalyst with a small amount of promoter which is still used today. The mixed catalyst is proved to be so effective that even now all ammonia catalysts in the world are still manufactured based on this principle.

Haber, Bosch, Mittasch, and Ertl these four great scientists have made a great contribution on the creation and development of ammonia synthetic industry, among whom Haber, Bosch, and Ertl were awarded the Nobel Prize in Chemistry.

The successful development of synthetic ammonia industry

Fritz Haber (1868–1934)
Laid the theoretical basis on synthesis of ammonia, awarded the 1919 Nobel Prize in Chemistry.

Carl Bosch (1874–1940)
Realized the industrial synthesis of ammonia, awarded the 1931 Nobel Prize in Chemistry.

Alwin Mittasch (1869–1953)
The major developer for fused iron catalyst, who proposed the concept of mixed catalyst.

Gerhard Ertl (1936–)
Great contribution on iron catalyst surface chemistry research, awarded the 2007 Nobel Prize in Chemistry.

is not only a great technical achievement but also a masterpiece of the organization work, which become a precedent in early stage for today's prevalent collaborative innovation (team work). In the creation process, Haber, Bosch and Mittasch's the great creation, brilliant scientific ideas and innovative spirit, the passion and spirit of cooperation from scientists and entrepreneurs, as well as the team spirit of cooperation and collaborative innovation among chemists, engineers, physicists, materials scientists and a variety of artisans group, are worthy of our admiration and learning.

Great success on ammonia industry has changed the history of world food production. According to the statistics from UN Food and Agriculture Organization (FAO), fertilizer contributes more than 40% to food production. Thus, the catalytic ammonia synthesis technology invented by Haber and Bosch is considered to be one of the greatest contributions to human beings. From the technological invention to the present, the Earth's population has grown by 4.2 times from 1.7 billion at the beginning of the 20th century, while food production has increased by 7.8 times. Humans can still produce ample food and clothing under the limited land resources, mainly rely on such technology created by Haber and Bosch. Now, 50% of nitrogen in our body is from ammonia synthesis [2], which mean, if without such invention, 50% of people in the Earth cannot survive. China is also unlikely to feed 20 percent of the world's population by only 7% of arable land all over the world.

After a century of development, catalytic synthesis of ammonia has made tremendous progress. The production capacity of single set equipment has been improved from the original 5 t of daily ammonia production to the current 2200 t. The reaction pressure has dropped to 10–15 MPa from the original 100 MPa. The energy consumption has decreased to 27.2 GJ from the original 78 GJ, which is close to the theoretical energy consumption of 20.1 GJ. But as the second largest chemicals, the ammonia production still consumes 2% of total energy supply in the world and releases more than 400 Mt of CO₂, which accounts for 1.6% of total global CO₂ emissions.

2. The development and enlightenment of ammonia synthesis catalysts

The invention of fused iron catalyst creates a catalytic ammonia synthesis industry. Iron catalysts for ammonia synthesis become one of the most successful and studied thorough catalysts in the world. With the development of petrochemical, coal chemical, bio-chemical, polymer, materials, energy and environment, the relative position of research on ammonia synthesis catalyst in the catalytic domain gradually declines, and it is no longer the main aspects of catalysis research, but the rigid demand for food decides the irreplaceable traditional ammonia industry can only rely on technological progress to constantly evolve. The catalyst of any progress can improve thermodynamic efficiency and lower product prices. Therefore, advances of ammonia industry and its catalyst technology will not stop. Initially, the suitable Fe catalyst was only found by F. Haber from about 5000 tried catalysts; currently, in order to further improve the process and reduce energy consumption, further

improving the catalyst is still the only hope.

2.1. Development of ammonia synthesis catalyst

Currently fused iron catalysts still occupy the absolute position in industry with tens of catalyst product types, of which more than ten kinds are developed by Chinese. Nanjing Chemical Industry Company developed the A102 ammonia synthesis catalyst in 1951, which was the first Chinese self-developed ammonia synthesis catalyst, and followed by successful development of type A106 and A109 ammonia synthesis catalysts. In 1979, Zhejiang University of Technology successfully developed type A110-2 low temperature ammonia synthesis catalyst [3]. After that the Nanjing Chemical Industry Research Institute, Fuzhou University, Lin Qu Catalyst Plant, Zhengzhou University, Hubei Institute of Chemistry, etc. successfully developed type A110-1, A110-3, A110-4, A110-5Q (spherical) and A110-6 catalysts, which formed a widely applied A110 catalysts family since 1980s [4].

Co-containing catalyst is an important development for the traditional Fe₃O₄-based fused iron catalyst. The British company ICI applied patents on cobalt-containing catalyst in 1978, and successfully developed 74-1 type cobalt-containing catalyst in 1979. In 1985, Fuzhou University successfully developed A201 type cobalt catalyst [5], then the amount of cobalt in A201 was further reduced and CeO₂ was added, which was called as the type A202 cobalt-containing catalyst in 1995 [6]. In addition, South China University of Technology, Nanjing Chemical Company, Zhengzhou University, also developed their cobalt-containing catalysts [4,7].

Since ruthenium-based catalyst for ammonia synthesis is invented in the 1990s, most of scientists have shifted their main research directions and attention to the study of ruthenium-based catalyst, and thus fused iron catalyst research has become less popular. Only a few of universities and research institutions around the world are still studying fused iron catalysts, such as Szczecin University of Technology in Poland [8–10], Fuzhou University [11] and Zhejiang University of Technology [12]. Others such as the Fritz Haber Institute Max-Planck-Society in Germany [13] occasionally published research papers on iron catalysts for ammonia synthesis.

To 1970s, the fused iron catalyst was considered well consolidated and no special improvement was still expected. The industrial iron catalyst presently used is not basically different from that developed 100 years ago [14]. It has become more difficult to achieve significant progress. This will encourage people to seek a major technological breakthrough—one kind of jumping or discontinuous technological progress. Nearly 30 years, the discoveries of Fe_{1-x}O-based catalyst system, ruthenium-based catalyst and cobalt and molybdenum bimetallic nitride catalyst are expressing the idea of seeking technical breakthroughs (Table 1).

2.1.1. The discovery of Fe_{1-x}O-based ammonia synthesis catalyst

In the past century, scholars always believed that when the precursor of fused iron catalysts was Fe₃O₄, catalysts showed the highest activity. Therefore, people confined their thinking

Table 1

Development of ammonia synthesis catalysts.

Development stage	Year	Inventor	Catalyst type	Chemical composition
(1) Fe ₃ O ₄ -based catalyst	1913	BASF, Germany	S6-10, KM	Fe ₃ O ₄ +Al ₂ O ₃ +K ₂ O+CaO+...
(2) Fe _{1-x} O-based catalyst	1986	Zhejiang Univ. of Technol., China	A301, ZA-5	Fe _{1-x} O+Al ₂ O ₃ +K ₂ O+CaO+...
(3) Ru-based catalyst	1992	UK-BP, Japan	KAAP	Ru-Ba-K/AC

on Fe₃O₄ catalyst in the past fused iron catalyst research and development, and improved the catalyst activity and life just by changing the type and number of promoter, while ignoring the impact of catalyst precursor phase. Although research and improvement had been doing by scientists in countries, magnetite was still of the dominance [15]. In 1986 Zhejiang University of Technology [16–21] invented Fe_{1-x}O-based catalyst with Wustite structure, which broke the shackle of the traditional conclusion "the fused iron catalyst with Fe₃O₄ as precursor shows the highest activity", and found a breakthrough in improving the performance of fused iron catalyst-Wustite catalyst system. It marked 80 years of research on fused iron catalysts had been made a substantial progress which kept the development of fused iron catalyst alive. Fe_{1-x}O-based ammonia synthesis catalyst is most active fused iron catalyst in the world. This discovery causes widespread concern and interest in domestic and foreign scholars [13,14,22,23], and has been widely used in industry.

The author [24] has the opportunity to witness the construction and development of China's ammonia industry from the 1960s, and devotes his life to the development of catalytic ammonia technology. He contributes his effort on the various research stages of the catalyst which start from Fe₃O₄-based, cobalt-containing Fe₃O₄-based, Fe_{1-x}O-based to ruthenium-based catalysts. He created the Fe_{1-x}O-based catalyst and its theory system based on the monophasic principle of iron oxides, and collaborated with his colleagues to successfully develop new industrial catalysts of type A110-2, A301, ZA-5, etc., which have become one of major industrial ammonia synthesis catalysts in nearly 30 years.

2.1.2. The discovery of ruthenium-based catalysts for ammonia synthesis

The Fe₃O₄-based iron catalyst was considered well consolidated and no special improvement was still expected. Scientists abroad started to look for non-ferrous noble metal catalysts. 40 years ago, Ozaki et al. [25] in a review article proposed that chemical adsorption of nitrogen and catalytic efficiency of elements in ammonia synthesis and decomposition could be associated, and thus could obtain a volcano-shaped curve to quantitatively describe the catalytic efficiency of metal elements in ammonia synthesis. In this graph, ruthenium, osmium, and iron are at the top of the volcano-shaped curve. Under industrial conditions, the use of Ru and Os catalysts has been close to the optimum point. Both theoretical and practical studies in nearly a hundred years have shown that Ru, Os and Fe are the best pure metal catalysts.

The development of ruthenium catalyst has a long history [26]. The first report about the application of ruthenium catalyst in synthesis of ammonia was published in 1917, in which

Mittasch, etc. believed that catalytic activity of ruthenium catalysts in the ammonia process is not as good as that of iron catalyst. Then ruthenium catalyst had not been reported in a long time period. In 1969, Tamaru [27] proposed a transition metal electron donor-acceptor type (EDA) of ammonia synthesis catalyst system. In this catalyst system, they chose the alkali metal potassium or sodium as electron donors, transition metals such as iron, ruthenium, osmium, cobalt, etc. as electron acceptors and staff with electrons transport capability such as phthalocyanine, polyphenylene quinone, graphite or graphitized carbon as carriers, and it showed high catalytic activity in ammonia synthesis under mild conditions. In 1972, Ozaki et al. [28] found that when ruthenium as an active component, potassium as a metal promoter, carbon as a catalyst carrier, the catalyst system showed high activity for ammonia synthesis. That discovery once again sparked scientists' interest in studying ruthenium catalysts. After that, researchers in Japan, Russia, UK, USA, Italy and other countries, as well as Zhejiang University of Technology, Fuzhou University, Xiamen University, Dalian Institute of Chemical Physics (DICP) and other units in our country [29–32] put a large amount of energy into the development of ruthenium catalysts in order to replace traditional iron-based catalysts. British Petroleum (BP) was responsible for loading ruthenium carbonyl compounds on graphite carbon carriers to be a new Ru/C catalyst. Kellogg was responsible for developing the ammonia synthesis process by using that Ru/C catalyst. With 10 years of joint efforts, they successfully developed in 1992 a new ammonia synthesis process KAAP (Kellogg Advanced Ammonia Process) which was applicable to Ru/C catalyst, and achieved its industrial applications [33–35].

Although ruthenium catalysts are highly active, their strong inhibition of H₂ and the methanation of carbon material of the carriers in Ru catalyst under conditions of ammonia synthesis which results in loss of active carbon carrier and shortening the life of catalyst, are weaknesses of the ruthenium catalysts. Meanwhile, the Ru and Os are very expensive, which is lack of commercial appealing compared to the third-best Fe catalyst [36]. Os and U are abandoned by Haber in the early 20th century. Ru / C catalyst is not much advantage in energy efficiency (Table 2). From 1992 to 2010, only 16 ammonia plants used ruthenium catalysts. Therefore, it can be said that theoretical meaning of ruthenium catalysts is larger than its practical meaning. The industry is still necessary to find more efficient and cheaper catalysts than ruthenium catalysts.

2.1.3. The discovery of Co-Mo nitride catalyst for ammonia synthesis

Nörskov et al. [36] proposed an alloy catalyst is designed by interpolation in the periodic table. This catalyst development strategy was obtained by simple physical principles, so its basic

Table 2

Comparison of iron catalysts and ruthenium catalysts.

Catalyst type	Resource	Manufacturing cost (10 ³ * Yuan/m ³)	Conditions			Energy consumption (GJ/t)
			T/°C	P/MPa	H ₂ /N ₂	
Fe	abundant	30	350–525 (wide)	10–30	2–3	~ 27
Ru/AC	scarce	1600	325–450 (narrow)	≤ 10	≤ 2	~ 27

principle could be widely applied. According to this principle, a reasonable assumption was that the elements which reacted with nitrogen very actively and very inactive in A. Ozaki volcano-shaped curve together form alloy to construct a new active surface in order to achieve the most optimal performance. The result showed that the activity of cobalt-molybdenum nitride catalyst was higher than that of Ru and Os catalysts; was also better than the activity of either single component for ammonia synthesis; was even better than Fe and Ru at low NH₃ concentration [37–41]. The discovery of cobalt-molybdenum nitride catalyst is considered to be the latest vertex so far in the study of ammonia synthesis catalyst according to theoretical predictions [42,43].

The experiments of Ertl [44] and Somorjai [45] can improve understanding on ammonia synthesis and allow quantitative theoretical description and prediction on the reaction. First, on the basis of basic knowledge on reaction pathways and transition state theory, the quantitative description of catalytic efficiency of the elements in the ammonia synthesis can be obtained. It thus can predict the catalytic efficiency of alloy systems [36,46]. Research results on the Co-Mo-N system [36,47] confirm that the both theory and experience in the choice of catalyst are equally useful. This impressive success stories show that according to the target reaction process, a new catalyst system can be designed base on pure theory [36,48]. Thus, the discovery of non-ferrous and alloy catalysts will once again promote the development of heterogeneous catalysis science.

Herein, that we need to concern is what the research methods of discovery and development of catalyst for ammonia synthesis can give inspiration to us. During the invention of ammonia synthesis catalyst, Mittasch, etc. used test screening method which relied on a large number of experiments and was a completely novel approach at that time. That method is so effective that people are still following it. The discovery of cobalt molybdenum nitride catalyst provide us with another new research method, which means that catalyst can be designed by pure theory, including the interpolation in the periodic table to design catalysts. With understanding the theoretical knowledge and regularities of catalytic science in depth, as well as accumulation of a lot of information and experience, especially with the development of computer technology, design of catalyst based on the theory and in the "molecular" level changes to be possible. In recent years, a variety of expert systems to assist the design of catalysts have developed [49–52].

2.2. Peculiarity of fused Fe catalyst and inspirations from its theory and practice

The catalytic chemistry in ammonia synthesis has special charm. so that attracts the attention and interest from many

chemists., Many famous physical chemist and catalytic scientists at the present age, such as W.H. Nernst, W. Ostward, F. Haber, C. Bosch, M.I. Temkin, G. Ertl, P. Emmett, A. Nielsen, H. Topsøe, G.A. Somorjai, J.A. Dumesic, J.K. Norskov, M. Boudart, etc. have been attended or involved in research of catalytic ammonia synthesis [53–58], and published a number of monographs [24,59–62]. This is because the fused iron catalysts have some special properties.

(1) In the development of the chemical industry in the 20th century, the catalytic ammonia technology played a critical role [63]. The importance of this industry associated with that people's strong interest on understanding of important scientific value and technological progress on the ammonia synthesis catalyst. Typically, the development of new technologies, new methods and new theory which were relative to catalysis usually started from this reaction system, or were first applied to this reaction system. Similarly, new discoveries in the field of catalytic synthesis of ammonia were often extended to other catalytic fields. The development of fine characterization techniques, dynamic analysis and new theoretical models have greatly promoted to the in-depth understanding of the foundation of ammonia synthesis catalysts.

Even being constantly improved for centuries, the nature of fused iron catalyst still unchanged. To date, all studies on the synthesis of ammonia have been based on this catalyst. For example, the completion of well-known BET adsorption theory on the iron catalyst; method for determining the active component of the catalyst surface by selective chemical adsorption invented by P. Emmett; the work based on nitrogen selective adsorption on Fe(111) crystal face laid the foundation of metal cluster catalysis theory which gradually formed in the 1980s; the important assumption of "crystal surface with the largest ligand number shows the greatest catalytic activity" and the concept of structure-sensitive reactions proposed by G. A. Somorjai; the concept of stoichiometric number was proposed by J. Horiuti to verify the kinetics mechanism of ammonia synthesis reaction; M.I. Temkin theory and his famous ammonia synthesis kinetic equation, was the first successfully employed and is now still being used in design of industrial reactors, and also laid the foundation for heterogeneous catalytic reaction kinetics. These theories and concepts, led the development of a series of basic theory, laid the foundation for heterogeneous catalysis science. History of ammonia synthesis reaction and the catalyst is a microcosm of the history of heterogeneous catalysis.

Temkin's theory of catalytic reaction kinetics on non-uniform surface not only has been proven by data of overall reaction kinetics on ammonia synthesis using iron catalyst, but also more importantly, perhaps, can induce some very useful and universal results. For example, firstly, Temkin equation is re-

duced based on a two-step mechanism or those can be simplified as a two-step mechanism, and non-uniformity of the catalyst surface can usually be treated as a uniform surface in the kinetics of catalysis. Therefore it can be applied to any type of catalytic reactions. Secondly, as for multiple sites adsorption, the large difference on catalytic activity from different catalysts is driven from the multiple reasoning to active site, which is extremely important to the discussion of the structural sensitivity of heterogeneous catalytic reactions. Thirdly, the concept of distribution function on active site is introduced in the derivation of the Temkin theory, which can induce many well-known adsorption isotherms such as Freundlich, Frumkin-Temkin expressions and their formulas, and other laws of adsorption rate such as Elovich equation. It can deduce that optimum active site or best active catalyst should have moderate affinity value, which means energy distribution is in the center of active sites of the surface. These results can be considered as the Sabatier principle which best catalyst can be easily formed sufficiently stable but not too stable intermediates [64].

These theories provide valuable information for catalysis study that, the affinity value must be changed in order to get the best catalyst. For example, the following three methods can be used for the metal catalysts: First, changing the exposed crystal surface or the particle size to alter the surface structure, which includes the changes of the relative distribution ratio of atoms on the surface with different coordination numbers; Second, forming an alloy (e.g., copper is added into nickel) or adding surface impurities (e.g., sulfur, carbon, oxygen or nitrogen) to the modified metal catalysts [9]; Third, according periodic table to changes metal components in the catalyst in order to select the best catalyst, such as the discovery of cobalt-molybdenum nitride catalyst. To make this approach meaningful, it must assume that reaction mechanism does not change. However, when the activity of a catalyst increases to a certain level, the further increase of them becomes very difficult. To break through this level, it has to find a different reaction mechanism.

Practice shows that there is no other reaction like ammonia synthesis reaction, which can link the theories, models and experiments together. The results obtained in the low-pressure experiments can be confirmed by high-pressure experiments; dynamics resulting obtained under the ultra-high vacuum condition can be extrapolated to the industrial conditions; studies on a single crystal can be described by the theory [44,65]. This situation can not only be applied to the iron catalyst, but also to the ruthenium catalyst and $\text{Co}_3\text{Mo}_3\text{N}$ catalyst. Moreover, the required time to understand these catalysts is getting shorter, even though the structure and chemical composition of catalysts become more complex [13]. Therefore, the catalytic ammonia synthesis reaction is still an ideal model system for studying theories of heterogeneous catalysis.

(2) The ammonia synthesis reaction is one of the simplest chemical reactions which doesn't generate a by-product and is a green chemical reaction with 100% of atomic utilization. The cogeneration of ammonia synthesis with CO_2 for urea or ammonium bicarbonate is a clean production process without any

emission, which is a rare and matured industrial technology of combining the CO_2 capture, storage and use [66]; In industry, achieving the ammonia synthesis reaction is one of the most complex and typical chemical process; In theory, the reaction is able to be completed at room temperature and atmospheric pressure but it practically is very difficult to be achieved unless at high temperature and high pressure conditions. Therefore, understanding the mechanism of the catalytic ammonia synthesis reaction and converting it into a perfect technology has been the primary standard on development of catalytic domain.

(3) The modern industrial iron catalysts are a nanostructured metastable substance, which is formed during the surprisingly complex synthesis of the oxide precursor [67,68]. Its metastability is also the reason on sensitivity of overheat stress generated during the activation and oxidative activation of materials. The pathway to prepare nanostructures can be selected, such as, $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_{1-x}\text{O}$ [69–72], and a seemingly very simple structure of the iron catalyst is actually very complicated. A startling example is that just using different catalyst precursors causes a tremendous change in the nanostructures of metal surface. Wustite-based catalyst has been demonstrated to be more active than the magnetite-based catalyst [23]. Quantitative analysis [73] reveals that, only less than 1% of the iron surface of the iron catalyst is involved in the activation of nitrogen, and the remaining 99% of the iron only plays the role of a support. If there can be more exposed surface on iron, the activity of the catalyst will be greatly enhanced. For instance, scientists used the iron catalyst as carrier, coated its surface with nano-iron to prepare coated nano-iron catalyst.

(4) Ammonia synthesis catalyst is the most stable catalyst in all industrial catalysts. The structure of such metastable materials with nanostructure is almost unchanged even being used under the harsh reaction conditions for more than 15 years. A lot of researches and characterizations regarding this property have been conducted, and many models have been proposed to explain the stability of the active surface and mechanism of its formation [10,55,74–79].

(5) The catalytic synthesis of ammonia which tightly associated with industry is still a key reaction for creating new life and a prototype model reaction that helps in gaining a fundamental understanding of catalysis in general and therefore of considerable scientific and cultural importance. It is mainly this reason that drives the research in ammonia synthesis forward, especially since evidence for a knowledge-based improvement of a catalyst would have a strong signaling effect on other fields of catalysis research [80].

For example, during ammonia synthesis process, from the gasification, purification to the synthesis, the major chemical reactions are heterogeneous catalytic process, so the catalyst plays a very important role. Nine catalysts are used in the steam conversion ammonia synthesis by using natural gas or naphtha as raw materials, which include hydrocarbon hydrogenation catalyst, steam reforming catalyst in first stage and second stage, high and low temperature shift catalyst, methanation catalyst, ammonia synthesis catalyst, CO selective oxidation catalyst, etc.; the partial oxidation process using residue as raw material and coal pressured gasification process

also use sulphur-resistant CO shift catalysts, Claus sulfur recovery catalyst, CO₂ dehydrogenation catalysts, various detoxification catalyst and molecular sieve drying agents [81]. Whichever the ammonia synthesis process, shift catalyst and ammonia synthesis catalyst are indispensable and are the core catalyst in ammonia industry.

This dozen of catalyst, most of them are basic catalysts in other chemical processes, such as coal chemical, petrochemical, natural gas chemical, bio-chemical, energy chemical, oil refining industry as well as environmental protection and other chemical process. In addition, ammonia synthesis industry also contains a series of high-tech and common key technologies need to be solved in emerging industries of strategic importance. The catalytic ammonia synthesis process itself also contains a huge potential for energy saving. People will continue to improve these catalysts. Therefore, the development of synthetic ammonia catalysts will promote the development of other catalysts. Understanding ammonia synthesis catalysts and process has a strong inspiration and reference on a series of common, key technologies in the modern chemical industry, energy, materials and environmental protection fields, especially for energy saving of traditional industries, modern coal chemical industry, hydrogen production and clean energy and other emerging industries of strategic importance [82].

3. The challenges of the ammonia synthesis catalyst

In the 21st century, ammonia synthesis was called as "sun-set industry". Some scientists also lament all quiet at the nitrogen front and the low visibility of research in nitrogen fixation in general [83]. In this regard, the German scientist R. Schlögl [13] published a report entitled "Catalytic Synthesis of Ammonia—A Never-Ending Story?", pointed out the story of catalytic ammonia synthesis is never over.

(1) The nitrogen cycling is one of most important cycling in nature to sustain life on Earth. Ammonia is also an essential raw material for the operation of modern society, which gives the ammonia industry exuberant vitality. The synthesis of these materials requires ammonia as the activated state nitrogen. Catalytic ammonia synthesis is an important part of the nitrogen cycling in nature, also an important complement needed by organisms (including humans), and currently the only way to obtain activated state nitrogen in industrial-scale. Currently generating activated state nitrogen through other methods is still only the subject of scientific research. The production of ammonia requires the use of a variety of carbon-containing fuels to obtain H₂ gas, however, no matter how scarce energy supplies and how strict the environmental controls will be, the rigid demand for food determines the ammonia industry must rely on scientific and technological progress to face this grim situation and continue its development and promote the continuous improvement and innovation on ammonia synthesis catalyst to meet the needs of human's existence and social development.

Therefore, ammonia industry is an irreplaceable traditional industry with vitality.

(2) Ammonia production of raw materials and fuels both are

energy. Current global focuses on energy issues are closely relative to the ammonia industry. The emission of CO₂ will also be severely restrict, saving energy and reducing emission have always been the major issues to the ammonia industry. The comprehensive energy consumption of advanced ammonia plant by using natural gas as a raw material has reached around 27.5 GJ/t, with the process total thermal efficiency of more than 70% [84]. Commercial iron catalyst and ruthenium catalyst both can achieve the above benefits [85,86]. Any advancement in the catalyst can improve the thermodynamic efficiency and reduce the price of the product [87]. It should be emphasized that, superficially, the energy loss mainly comes from the transformation process and essentially should be from synthesis of ammonia. The power consumption which accounts the total energy consumption for about 30% is mainly for the service of synthesis [88]. The high pressure in ammonia synthesis is used to overcome the activation barrier of reaction, which depends on the catalyst activity. To overcome this reaction energy barrier we pay a how high price! Therefore, the development of new catalyst for low-pressure ammonia synthesis is meaningful.

(3) Haber-Bosch nitrogen fixation process does not involve the use of other forms of energy in catalytic reactions, such as electric energy, light energy, etc., neither the role of catalyst in different energy transformation. In reality production practice, the transformation of other forms of energy, such as the chemical energy, solar, wind, hydro and nuclear energy transferring into electric energy; or electric energy, light energy transferring into chemical energy; etc. is so extraordinarily interesting.

In the Haber-Bosch nitrogen fixation process which uses heat energy from fossil fuel as the sole driving force, even in the ammonia plant with the most advanced waste heat recovery and cascade utilization of energy (total energy efficiency is up to 74%), there is not only more than 20% of the energy-saving potential, but also consumption of fossil fuels for at least 27.5 GJ/t of energy. Even in the limit state (the total energy efficiency is 100%), it still has to consume fossil fuels for 20.13 GJ/t of energy.

Therefore, the introduction of electric energy, solar energy, and radiation energy into ammonia synthesis to assist the activation of nitrogen molecule or change the reaction pathways, and the study of the role of a catalyst in the transformation between different forms of energy, are in the practical and theoretical significance.

(4) As everyone knows, focus and difficulties of catalytic chemistry research is the activation of the most stable of several small molecules in nature (CO₂, H₂O, CO, CH₄, H₂, N₂, O₂). Nitrogen molecule is one of hardest activated elemental substances and chemical bond. The dissociation energy of N $\equiv$ N triple bond is the 942 kJ/mol, and its break requires high energy. How to activate nitrogen molecule is a key theoretical issues to nitrogen fixation. Nitrogen molecule has also become one of the prototype molecules in chemistry and catalysis research with a typical representative significance.

(5) The standard equilibrium constant of ammonia synthesis reaction at 25 °C is as high as 6.8×10^5 . Therefore, the ammonia synthesis at room temperature and under atmospheric

pressure is theoretically possible, but the reaction rate is almost impossible to be detected. This is a new challenge. Since nitrogen fixation is important for human survival and development, achieving ammonia synthesis at normal temperature and pressure has been the goal with relentless pursuit by human beings.

In summary, reducing energy consumption of the existing ammonia technology, looking for new ways and means of ammonia synthesis, exploring the possibility of ammonia synthesis at normal temperature and pressure, etc., are the new challenges faced by the catalytic ammonia technology.

The key to achieve ammonia synthesis at normal temperature and pressure is the activation of nitrogen molecule and forms and ways to provide energy.

3.1. Activation of nitrogen molecule

The process of converting the free state of nitrogen in air into nitrogen compounds is known as nitrogen fixation, including chemical and biological nitrogen fixation. There are mainly three ways to chemically activate nitrogen molecule:

(1) Reduction method, by using a reducing agent to give N_2 electrons. Catalytic ammonia synthesis belongs to reduction method.

(2) Oxidation method, by using an oxidizing agent to take the electrons away from nitrogen molecule. Since the first ionization energy of N_2 is high, such a strong oxidant has not been found to form a suitable catalytic cycle.

(3) physical-chemical method (activation method), by using strong conditions such as high Volt with discharge, plasma and other physical means to excite the N_2 molecule from the ground state to the high energy state, or even take it apart to make it become a nitrogen atom or a nitrogen ion in order to react with other substances. For example: arc method and calcium cyanamide method at early stage. Enormous energy consumption greatly limits the industrial application of these two methods. In recent years, ammonia synthesis by the plasma [89–92], the magnetic induction method [93] and other studies are also active, but they are still in the exploratory stage.

Thus, the catalytic reduction method occupies undisputed dominance, which is also currently the only industrial-scale of chemical nitrogen fixation method. After a long time research and exploration, under the catalysis of ruthenium- and $Fe_{1-x}O$ -based catalysts, the initial active temperature of the catalysts can be reduced to about 200 °C [94]. For example, in the industrial process of high-purity ammonia, by using ZA-5 catalyst, under the conditions of 8 MPa of pressure and the reaction temperature at the inlet and exit of reactor is 215 °C and 363 °C respectively, the net value of ammonia is the more than 10%, which has met the economic requirement for net value of ammonia in industry, the key is the development of the corresponding low pressures process. But it is expectedly difficult to further develop higher activity catalyst under lower temperatures.

The research on catalytic ammonia synthesis, which lasts for a century, is the study of the activation of N_2 and its nature. Many kinds of modern physical-chemical instruments have

Fig. 1. Mechanism and potential energy diagram of ammonia synthesis on iron [98]. The energy is in kJ/mol.

been used to study the mechanism of activation of N_2 . However, so far, it still is controversial about the activation of nitrogen on iron catalysts, which is ever belonging to dissociative adsorption or molecular adsorption. The most of experiments support the dissociative adsorption [70,95–97]. For example, to Fe catalysts, G. Ertl [98] proposed a mechanism of catalytic ammonia synthesis reaction and potential energy diagram of its thermodynamics and kinetics based on N_2 dissociative adsorption (Fig. 1). This is one of representative achievements when G. Ertl won the Nobel Prize in Chemistry in 2007 [99].

M. Boudart [80] considered that Figure 1 gave a lot of guidance. To really understand the mechanism of catalytic reaction, it should be able to provide a kind of thermal chemical kinetic profiles as clear as that of ammonia catalytic reaction shown Fig. 1. Theorists are trying to calculate a lot of missing energy value of the elementary steps in the catalytic cycle [100].

There are also many experiments to support the N_2 molecular adsorption [65,101–106]. For example, Liao et al. [107,108] studied both mechanisms of ammonia synthesis, the associative and the dissociative, on iron catalysts surface by using the molecule design system for heterogeneous catalysis based on reactive energetics, the Bond Order Conservation-Morse Potential (BOC-MP) approach and anti-deuterium isotope effect [109]. The calculations showed that the activation energy barrier of rate-determining step (rds) on associative mechanism was below to that of rds on dissociative mechanism, but the activation energy barrier of reaction was significantly lower than that of rds on dissociative mechanism. It could be inferred that there are two competing reaction pathways on the surface of the iron catalyst.

In the ammonia synthesis by using iron catalyst, the stoichiometric number σ_{rds} of overall reaction and rate-determining step which are detected from transfer of the chemical tracers can be equal to 1 or 2 (Fig. 2). Both values have been reported in the experimental work. Horiuti et al. [110,111] found that $\sigma_{rds} = 2$ near equilibrium. Tanaka [112] found that σ_{rds} of synthesis reaction equals to 2 away from the equilibrium, but the σ_{rds} of decomposition reaction equals to 1. $\sigma_{rds} = 2$ is good for the rate-determining step in step 2 of Fig. 2(a), but many evidences indicates that the nitrogen adsorption is rate-determining step, where σ_{rds} equals to 1. However it cannot determine whether the adsorption is dissociation or not when $\sigma_{rds} =$

Fig. 2. The mechanisms of N_2 dissociative adsorption (a) and molecular adsorption (b) and their stoichiometric number.

1. It is conceivable that the reaction sequence shown in Fig. 2(b) exists, wherein the first two steps are considered to be the pathway through which the nitrogenase realizes nitrogen fixation. If so, σ_{rds} still equals to 1. However, the evidence on the dissociative adsorption of nitrogen on iron catalyst is now overwhelming. The dissociation on iron catalysts and non-dissociation on the nitrogenase respectively just characterize industrial catalysis at high temperature and enzyme catalysis at low temperature. Therefore, in order to improve the activity of the iron catalyst on ammonia synthesis, it may need to essentially change the nature of each step in the iron-catalyzed reaction sequence [10].

Thus, the problems, such as the activated forms of N_2 shown in Figs. 1 and 2, the basic steps of ammonia synthesis reaction and the real structure etc., still contain many science implies. The new and efficient method on activation of nitrogen molecule is still being explored [57]. The activation of nitrogen molecule is still a challenge in chemistry and catalysis science, and still has theoretical and practical significance.

3.2. New challenges in theory of catalytic ammonia

Although the heat value and the effective energy (exergy) of ammonia is 21.29 and 20.13 GJ/t, respectively, the actual energy consumption is much higher. So no matter what materials and process are used to synthesize ammonia, the provided effective energy cannot be less than 20.13 GJ/t. In the Haber-Bosch process of nitrogen fixation, because the effective energy value of the raw material is more than effective energy value of the product, ideal work of the process is positive. Each production of 1 ton of saturated liquid ammonia, theoretically, is external work process (Table 3). For example, the ammonia synthesis process by using pure H_2 and N_2 as raw materials can provide 0.63 GJ/t of external work, but directly using the water and air as raw materials for the nitrogen fixation process must

consume external work of 20.31 GJ/t at least. The comparison shows that the main energy loss of the process derives from extractions of nitrogen in air and the hydrogen in water. Therefore, if other forms of energy, such as electric-, light-energy, etc., can be introduced into nitrogen fixation process to take the hydrogen out of water, then the reaction pathway can be changed. Although at least 20.31 GJ of electric work needs to be consumed, electric energy can be derived from renewable energy sources, such as solar, wind, hydro or nuclear energy. If nitrogen fixation process do not have to use fossil fuels, that will be a completely revolution to ammonia industry!

Therefore, introducing the electric energy, solar energy, etc. into nitrogen fixation process, changing the reaction pathway or biomimetic synthesis is one of the major challenges thrown down to catalytic scientists and has great theoretical and practical significance.

3.2.1. The studies of electrocatalysis catalysts

Electrocatalysis can promote the thermodynamic non-spontaneous reaction $N_2 + 3H_2O = 2NH_3 + 1.5O_2$ ($K_{298} = 10^{-120}$) to occur by electric energy, thus expands the ammonia synthesis research field; It also allows the ammonia synthesis reaction which is limited by the equilibrium is not or less affected by the thermodynamic equilibrium. Therefore, the introduction of the electric energy into ammonia synthesis process to activate activation of nitrogen molecule or change the reaction pathway has been one of the concerned research areas. Electrochemical synthesis method has similar efficiency with that of existing methods and is a desirable method to synthesize ammonia under normal temperature and pressure [114]. For example, for the electrochemical process of ammonia synthesis at a high temperature (570 °C) and atmospheric pressure, the conversion of hydrogen is close to 100%. Thus, in recent years, studies of electrochemical method for ammonia synthesis at normal temperature and pressure ammonia are also very active

Table 3

Theoretical energy consumption of ammonia synthesis [113].

Raw material	Total reaction equation of process	$\Delta H = \Delta H_v$	Theoretical energy consumption of process (GJ/t)	Theoretical energy consumption of product (GJ/t)
Water, air	$H_2O + N_2 \rightarrow NH_3 + O_2$	21.26	20.31	20.13
Water, air, coal	$C + H_2O + (N_2 + O_2) \rightarrow NH_3 + CO_2$	0.80	-0.19	20.13
Water, air, nature gas	$CH_4 + H_2O + (N_2 + O_2) \rightarrow NH_3 + CO_2$	-1.85	-0.94	20.13
Water, air, light oil	$C_9H_2O + H_2O + (N_2 + O_2) \rightarrow NH_3 + CO_2$	-1.41	-1.65	20.13
Pure H_2 and N_2	$H_2 + N_2 \rightarrow NH_3$	-3.95	-0.63	20.13

[115–118].

The main electro-catalysts which have been studied include iron phthalocyanine catalyst-loaded gas diffusion electrodes, the ceramic solid electrolyte and the molten salts (LiCl/KCl/CsCl) and so on. Using solid electrolytes with high proton conductivity at room temperature to improve the current efficiency and the stability of electrodes is an important direction for future research on electrochemical ammonia synthesis [87,119,120].

Low current efficiency is the key to influence the efficiency and product costs of electrochemical ammonia synthesis. With the in-depth study of the electrochemical ammonia synthesis, if current efficiency and conversion rates can be significantly improved so that the cost of the electrochemical ammonia synthesis can be focused on consumption of electric energy, the electrochemical ammonia synthesis in the remote districts of sufficient in electric energy, or effectively converting solar energy, wind and water energy into electricity is expected to have its place. Especially when the energy crisis in the future leads to prices of oil, nature gas and coal etc. raise sharply which results in costs of Haber-Bosch ammonia synthesis growing exponentially, the electrochemical ammonia synthesis will be regarded as a useful alternative. Therefore, the study of electrochemical ammonia synthesis still has potential application [115].

3.2.2. Research on photocatalytic ammonia synthesis catalysts

The most familiar photocatalytic reaction is natural photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$. Green plants absorb sunlight by chlorophyll (photosensitizer), convert CO_2 and H_2O by plant enzymes to carbohydrate and release O_2 . Photosynthesis is the most important way to convert solar energy into chemical energy. The most critical step in complex process of photosynthesis is the substances in photosynthetic reaction center absorb photo energy to release electrons which are transferred into cells to cause chemical synthesis reaction so that solar energy is stored up [121].

At room temperature and atmospheric pressure using water as a hydrogen source and solar energy as energy, a photocatalytic way to directly transform the nitrogen in air into ammonia: $\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 1.5\text{O}_2$, need to resolve the solar energy input and photocatalysts of problems.

These two reactions are both thermodynamically non-spontaneous reactions, and N_2 is activated the harder than CO_2 , but their photocatalysis are both theoretically achievable. Whichever the natural CO_2 reduction reaction or artificial water reduction (producing H_2) and oxidation (producing O_2) reaction, is a very complex catalytic process that usually occurs through multiple electrons pathway, and combinations of elementary reactions. Michel and Deisenhofer who co-winners of the Nobel Prize in Chemistry in 1988 [122,123] used theoretical calculations to conclude that the common effect of asymmetric nuclear Frank-Condon factors and the electronic coupling is likely the main reason for unidirectional electron transfer. The study results of mechanism of photosynthesis and its center structure will provide inspiration for photocatalytic ammonia synthesis.

The research on photocatalysis has more than 50 years of

history [124]. Most of the photocatalyst used as the material having semiconductor characteristics, such as different series of metal-doped TiO_2 and WO_3 series [125], and CdS/GaP-Pt , $\alpha\text{-Fe}_2\text{O}_3\text{-Nd}_2\text{O}_3$ catalyst and so on [126–132]. Currently people are constantly developing more effective catalyst and the new methods for ammonia synthesis at normal temperature and pressure [133–135]. This shows that people are exploring to this long-term goal.

3.2.3. Studies on chemical simulation of nitrogenase ammonia synthesis

In nature, there is a microorganism, which comprises a catalyst with a special ability—nitrogenase, that can directly reduce the nitrogen in air to ammonia at normal temperature and pressure conditions. Its nitrogen fixation capacity is thousand-fold of Haber-Bosch chemical nitrogen fixation process. It is estimated that today the biological fixation of nitrogen reached 200 million tons, covering about 48% of the combined nitrogen in earth surface (the remaining 52% is provided by catalytic ammonia synthesis). Biological nitrogen fixation, both its required conditions and nitrogen fixation capability, is much higher than chemical nitrogen fixation. Biological nitrogen fixation can be divided into biological and biomimetic chemistry nitrogen fixation.

Biomimetic chemistry nitrogen fixation uses chemical methods to simulate the function of nitrogenase in vivo to prepare fine chemical catalyst in order to achieve ammonia synthesis at normal temperature and pressure. This is a challenge facing catalysis scientists. It is both theoretically and practically significance on studies about mechanism of biological nitrogen fixation. It can provide an important basis for the chemical simulation of biological nitrogen fixation. To achieve nitrogen fixation by nitrogen fixation microbes, there are three basic conditions [136]: (1) nitrogenase; (2) Mg-ATP^{2-} ; (3) electron donors, such as reduced ferredoxin, reduced flavodoxin, or artificial $\text{Na}_2\text{S}_2\text{O}_4$ to provide electrons for N_2 reduction. The 1970s–1980s, a group of Chinese scientists led by famous scientists Aoqing Tang, Jiayi Lu and Qirui Cai in-depthly studied the nitrogenase and its chemical simulation [137], and proposed a model of the active center of the nitrogenase [138]. After continuous efforts of scientists around the world, the chemical simulation of nitrogenase has been developed, and nitrogen fixation molecular genetics has been created, which have made biological nitrogen fixation research significant progress. Since the American scholar Rees et al [139–143] clarified the three-dimensional structure of nitrogenase active central atom clusters and polypeptides around, the studies about chemical simulation of biological nitrogen fixation are once again on the rise [144–151]. Meanwhile, the development of selective enzymes will be a rich source of catalysts for organic chemistry and biotechnology [152]. Although no satisfactory practical result has been achieved so far, the research and exploration for biological nitrogen fixation and biomimetic ammonia synthesis will not be stopped.

In addition, in the biological azotobacter nitrogen fixation method, mainly non-leguminous crops are inoculated by rhizobium using bio-engineering technology to introduce the nitro-

genase genes and other related genes so that it can achieve self-provided nitrogen [153]. With the development of breeding transgenic technology to achieve non-leguminous crops with inoculation of rhizobium for self-provided nitrogen and a large number of planting leguminous and other oil plants (nitrogen-containing 7%–8%), and reducing the amount of chemical nitrogen fertilizer is one way to solve negative effects of a lot of fertilizer application in the agricultural production [154].

4. Conclusions

Ammonia synthesis in catalytic chemistry is charismatic. Fused iron catalysts have some special properties which are beyond compare to a number of other catalysts. The ammonia synthesis reaction of high industrial relevance is also a key reaction for creating new life and a prototypical model reaction that helps in gaining a fundamental understanding of catalysis in general and therefore of considerable science and culture importance. Understanding of the mechanism of catalytic ammonia synthesis and converting it into the perfect technology has been a basic standard in the catalytic domain, especially since evidence for a knowledge based improvement of a catalyst would have a strong signaling effect on other fields of catalysis research. Therefore, it is still an ideal model system for heterogeneous catalysis research.

Catalytic ammonia technology plays a central role in the development of the chemical industry in the 20th century. Humans need food, and food needs nitrogen, so the story of catalytic ammonia synthesis is never end. Ammonia is also an essential raw material for the operation of modern society, which gives exuberant vitality to ammonia industry, and will continue to promote the improvement and innovation on catalyst for

ammonia synthesis. In the 21st century, catalytic ammonia technology will face new challenges in theory and practice and in new application of ammonia. Reducing the energy consumption of existing catalytic ammonia synthesis technology, introducing electric energy, light energy into ammonia synthesis process, looking for new ways of ammonia synthesis, exploring electrocatalysis, photocatalysis and chemical simulation biological nitrogen fixation on ammonia synthesis at normal temperature and pressure are concerned research field.

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Graphical Abstract

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Ammonia synthesis catalyst 100 years: Practice, enlightenment and challenge

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The achievement and progress of the ammonia synthesis catalysts in theory and practice during about 100 years, and a new challenge in face of a biomimetic ammonia-synthesis path at room temperature and atmospheric pressure, including electrocatalysis, photocatalysis and biocatalysis, are presented. Understanding the mechanism and the translation of the knowledge into technical perfection has become a fundamental criterion for scientific development in catalysis research.

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氨合成催化剂100年：实践、启迪和挑战

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摘要: Haber-Bosch发明的氨合成催化剂创立已经100周年. 介绍了氨合成催化剂在理论和实践方面的发展、成就及其启迪, 展望了氨合成催化剂的未来和面临的新挑战. 催化合成氨技术在20世纪化学工业的发展中起着核心的作用. 一个世纪以来, 氨合成催化剂经历了 Fe_3O_4 基熔铁催化剂、 Fe_{1-x}O 基熔铁催化剂、Ru基催化剂等发展阶段, 以及钴钼双金属氮化物催化剂的发现. 实践表明, 氨合成催化剂是多相催化领域中许多基础研究的起点和试金石, 没有别的反应象氨合成反应一样, 能够把理论、模型催化剂和实验连接起来. 催化合成氨反应仍然是多相催化理论研究的一个理想的模型体系. 理解该反应机理并转换成完美技术成为催化研究领域发展的基本标准. 这个永不结束的故事仍然没有结束. 除了关于反应的基本步骤、真实结构、亚氮化物这些问题之外, 催化合成氨在理论上一个新的挑战是关于在室温和常压下氨合成的预测, 包括电催化合成氨、光催化合成氨和化学模拟生物固氮以及包括氮分子在内的催化化学研究中几种最稳定的小分子的活化方法等.

关键词: 氨合成催化剂; 发明; 发展; 挑战; 实践; 启迪

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1. 氨合成催化剂的发明与启示

硅1913年9月9日, 世界上第一座合成氨装置投产. 之后, 合成氨工业迅速发展, 到21世纪初, 日产合成氨1000和2200 t的装置遍布全球. 合成氨成为一个庞大的支柱化学工业. 这是人类征服自然的一个划时代的丰碑.

在这项伟大的发明过程中, 曾遭遇了前所未有的困难^[1]. 1787年, C. L. Berthollet提出氨是由氮和氢元素组成的. 当时杰出化学家, 包括W. H. Nernst, W. Ostward和F. Haber等, 立即以极大的努力专心致力于通过元素氮和氢合成氨的研究, 然而却首先遭遇了化学平衡的障碍和争议. 因为当时质量作用定律和化学平衡的规律尚未发现, 在平衡时氨的浓度究竟有多大不清楚. 在常压下只有在相当低的温度时才生成氨, 而在高温下氨分子会发生分解. 因此, 当时许多科学家甚至认为由元素生成氨存在着不可逾越的障碍.

在这个关键时刻, Haber第一个提出了高压反应技术. 但是, 氨的单程合成率太低仍不能实现工业规模生产; 于是他抛弃了当时化学科学上流行的静止观点而采用考虑动力学的动态方法, 引入了反应速率即时-空产率(space-time yield)的概念, 替代了反应产率概念. 根据这个重要原理, 提出了封闭流程和循环操作工艺技术. 这三项技术和反应速率的概念是一个伟大的创造, 正是以此为基础, 实现了工业史上第一个加压催化过程. 这是催化工艺发展史上的一个里程碑, 它标志着工业催化新纪元的开端. 仅在几年之后, 相继出现的甲醇合成、费

托合成油和在多相催化剂存在下的高压反应技术就成为有机化学领域中的基本实践, 推动了整个化学工业和材料工业的发展. Haber的这一系列史无前例的创造奠定了整个化学工程科学的基础!

1908年2月, Haber与德国巴登苯胺纯碱公司(Badische Anilin und Soda Fabrik, 简称巴斯夫BASF)签订了协议. BASF把工业开发的任务交给化学家Carl Bosch. Bosch立即认识到他必须着手解决3个主要难题: 设计出生产廉价氢和氮的方法; 寻找一种高效且稳定的催化剂; 开发适用于高压临氢合成氨反应的设备和材料.

Haber等精力充沛地进行了催化剂的探索. Haber发现了钨和铀-碳化铀催化剂对合成氨反应显示出优异性能. BASF公司获得了全世界所有Os存货的购买权, 总计大约100 kg. 这在现在听起来是不可思议的, 充分反映了当时科学家和企业家的激情. 但是, 1912年Haber被任命为Kaiser Wilhelm研究所的物理化学与电化学研究所所长, 这也标志了Haber在氨合成领域中研究活动的结束.

Bosch把寻找高效且稳定的催化剂的任务交给助手Alwin Mittasch. Mittasch首先在金属氮化物上进行了广泛研究, 试图通过这种间接途径来固定空气中的氮. 虽然这对于氨合成技术是不成功的, 但提供了关于周期表中几乎所有金属元素催化性质的有价值信息. 他认识到许多金属本身只呈现较少的或者没有催化效应, 然而某种添加剂能提高它们的催化活性. 在这些发现的基础上, 1909年2月他提出一个未经证明的假设: “获胜的催

化剂是多组分体系”, 并需要进行极大量的系列试验. 为此, BASF公司为催化剂试验制作了各种模型反应器, 到1911年, 在约一年半时间内, 对2500个不同催化剂进行了6500次试验. 这一针对催化剂选择的惊人的试验, 一直进行到1922年才告结束, 前后共试验了20000多次, 研究了5000多个不同催化剂体系.

铁是合成氨反应有效的催化剂, 在1905年就为人所知. 但在BASF公司初期的实验中, 被证明是令人失望的. 这时Mittasch的助手Wolf无意中用数年前就放在实验室搁板上的瑞典产的Gallivare铁矿石样品做试验, 得到了意外的结果. 当纯铁与百分之几的氧化铝, 少量钾碱和氧化钙共熔时, 就得到了一个适用于合成氨的催化剂. 最好的催化剂被证明是一个多组分混合物, 其组成与Gallivare的磁铁矿相近. 这就是沿用至今的少量助催化剂促进的磁铁矿基熔铁催化剂. 这个混合催化剂被证明是如此有效, 乃至现在全世界所有的氨催化剂还仍然依据这个原理制造.

Haber, Bosch, Mittasch和Ertl这4位伟大的科学家为合成氨工业的创立和发展作出了巨大的贡献, 其中Haber, Bosch和Ertl分别获得诺贝尔化学奖.

合成氨工业的开发成功, 既是技术上的成就, 也是组织工作上的一项杰作, 它成为当今较为通用的协同创新(team work)的早期先例. 在创立过程中, Haber, Bosch和Mittasch伟大的创造性、光辉的科学思想和创新精神, 科学家和企业家的激情和合作精神, 以及化学家、工程师、物理学家、材料学家与各种工匠群体合作、协同创新的团队精神等, 都是值得我们敬佩和学习的.

合成氨工业的巨大成功, 改变了世界粮食生产的历史. 据联合国粮农组织(FAO)的统计, 化肥对粮食生产的贡献率占40%以上. 因此, Haber-Bosch发明的催化合成氨技术被认为是催化技术对人类最伟大的贡献之一. 从20世纪初该技术发明到现在, 地球上的人口从17亿增长了4.2倍, 而粮食的产量却增长了7.8倍, 人类至今可以在有限的土地资源上丰衣足食, 其主要贡献者就是发明该技术的Haber和Bosch. 现在我们人体中50%的氮来自于合成氨^[2], 也就是说, 如果没有这项发明, 地球上将有50%的人不能生存. 我国也不可能以占世界7%的耕地养活占世界20%的人口.

经过百年的发展, 催化合成氨技术取得了巨大的进步. 单套生产装置的规模已由当初的日产合成氨5 t发展到目前的2200 t, 反应压力已由当初的100 MPa降到了10–15 MPa, 能耗已从当初的78 GJ降到27.2 GJ, 已接近

理论能耗20.1 GJ. 但作为第二个最大化学品的合成氨的生产过程中, 仍然要消耗占全球能源供应总量的2%, 排放CO₂超过(400 Mt), 占全球CO₂排放总量的1.6%.

2. 氨合成催化剂的发展与实践的启示

熔铁催化剂的发明, 开创了催化合成氨工业. 合成氨铁催化剂成为世界上研究得最成功、最透彻的催化剂之一. 虽然随着石油化工、新型煤化工、生物化工、高分子、材料、能源、环境等催化领域的崛起, 合成氨催化剂的研究在催化领域的相对地位逐渐下降, 目前已不再是催化研究的主要方面, 但粮食的刚性需求决定了不可替代的传统合成氨工业只能依靠科技进步不断发展. 而催化剂的任何一个进步都能够提高热力学效率和降低产品的价格. 因此, 合成氨工业及其催化剂技术进步不会停止. 当初, Haber从试验过的约5000个催化剂中才找出适合于生产的Fe催化剂, 今天为了进一步完善这个工艺和降低能耗, 依然只有寄希望于催化剂的进一步改进上.

2.1. 氨合成催化剂的发展

目前, 工业上熔铁催化剂仍占绝对地位, 催化剂产品型号不少于数十种, 仅我国就有十余种. 我国南京化学工业公司于1951年研制了A102型氨合成催化剂. 这是我国自行研制的第一个氨合成催化剂, 此后又研制成功A106型和A109型氨合成催化剂. 1979年, 浙江工业大学研制成功A110-2型低温氨合成催化剂^[3], 此后南京化工研究院、福州大学、临朐催化剂厂、郑州大学和湖北化学研究所等相继研制成功A110-1, A110-3, A110-4, A110-5Q(球形)和A110-6型, 形成了我国20世纪80年代以来广为应用的A110系列催化剂^[4].

含钴催化剂的开发是传统Fe₃O₄基熔铁催化剂的一个重要发展. 1978年, 英国ICI公司申请了有关含钴催化剂的专利, 1979年开发成功74-1型含钴催化剂. 1985年, 福州大学研制成功A201型含钴催化剂^[5], 此后进一步降低了A201型催化剂中钴的含量并添加CeO₂改进其性能, 并于1995年推出了A202型含钴催化剂^[6]. 此外, 华南理工大学、南化公司研究院、郑州大学等也相继开发了含钴催化剂^[4,7].

自20世纪90年代钨基氨合成催化剂发明以来, 国内外在本领域的主要研究方向和注意力都转移到钨催化剂的研究上, 熔铁催化剂的研究反而成了冷门. 目前, 全世界只有少数大学及研究所仍在研究熔铁催化剂, 其中主要是波兰Szczecin理工大学^[8–10]、福州大学^[11]和浙江

工业大学^[12]，其它如德国马普学会的Fritz Haber研究所等^[13]偶有有关氨合成铁催化剂的研究论文发表。

熔铁催化剂到20世纪60–70年代已基本定型，工业上使用的铁催化剂与100年前BASF开发的没有根本不同^[14]。技术已经发展到成熟阶段，要想取得显著的进步将会变得更为困难。这将促使人们寻求重大的技术突破——一种跳跃式或非连续性的技术进步。近30多年来， Fe_{1-x}O 基催化剂体系、钌基催化剂以及钴钼双金属氮化物催化剂的发现，正是这种寻求技术突破的思想体现(表1)。

2.1.1. Fe_{1-x}O 基氨合成催化剂的发现

近百年来，国内外学者一直认为熔铁催化剂的母体为 Fe_3O_4 时催化剂具有最高的活性。在过去的熔铁催化剂研究开发中，人们局限于 Fe_3O_4 催化剂的思维，仅通过改变助催化剂的种类和数量来改善催化剂的活性和寿命，而忽视了催化剂母体相的影响。虽然各国一直在不停地研究和改进，但一直是磁铁矿一统天下^[15]。1986年，浙江工业大学^[16–21]发明的具有维氏体(Wustite)结构的 Fe_{1-x}O 基催化剂，突破了“以 Fe_3O_4 为母体的熔铁催化剂具有最高活性”传统定论的束缚，找到了提高熔铁催化剂性能的突破口——维氏体催化剂体系。它标志着80多年来熔铁催化剂的研究取得了实质性的进展，为熔铁催化剂的发展注入了一线生机。 Fe_{1-x}O 基氨合成催化剂是目前世界上活性最高的熔融铁催化剂。这一发现引起了国内外同行学者的广泛关注和兴趣^[13,14,22,23]，并已在工业上得到广泛应用。

作者^[24]有幸从20世纪60年代开始目睹了我国合成氨工业的建设和发展，毕生致力于催化合成氨技术的研究，参加了从 Fe_3O_4 基、含钴 Fe_3O_4 基、 Fe_{1-x}O 基到钌基催化剂等各阶段催化剂的研究，并努力做出贡献。创立了其中的 Fe_{1-x}O 基催化剂，与同事们一起开发成功A110-2、A301、ZA-5等系列新型工业催化剂，成为我国近30年合成氨工业主干催化剂之一。

2.1.2. 钌基氨合成催化剂的发现

国外对固定不变的 Fe_3O_4 基催化剂已不期待有很大的提高，开始寻找替代铁催化剂的非铁贵金属催化剂。40多年前，Ozaki等^[25]在一篇综述文章中提出了氨合成和分解中元素的催化效率与氮的化学吸附能相关联，得到一条能够定量描述金属元素在氨合成中的催化效率的火山形曲线。在这条曲线中，钌、钨和铁在火山形的顶端。在工业条件下，使用Ru和Os催化剂已经接近最佳点。近百年的理论和实践研究结果都表明，Ru、Os和Fe在纯

金属中是最好的催化剂。

钌催化剂已有着较长的发展历史^[26]。第一个有关钌用于氨合成催化反应的研究报道是在1917年，Mittasch等认为在合成氨过程中钌催化剂的活性不如铁催化剂。之后，很长一段时间未见文献报道。1969年，Tamaru等^[27]提出过渡金属电子授受型(EDA, electron donor-acceptor)氨合成催化体系，碱金属钾或钠为电子授予体，过渡金属铁、钌、钨、钴等为电子接受体，选择具有电子传输能力的酞菁、聚苯醌、石墨或石墨化活性炭为载体，在温和条件下具有较高的氨合成催化活性。1972年，Ozaki课题组等^[28]发现，钌为活性组分、金属钾为促进剂、活性炭为载体的催化剂对氨合成有很高的活性。这一发现再次激发了人们研究钌催化剂的兴趣。之后，日本、苏联、英国、美国、意大利等国的学者，以及我国浙江工业大学、福州大学、厦门大学、大连化物所等单位^[29–32]将大量的精力投入到研制钌催化剂以期取代传统的铁基催化剂上。由英国石油公司(BP)负责开发以钌的羰基化合物负载于含石墨炭载体上的Ru/C催化剂，以Kellogg负责开发与其配套的氨合成工艺，经过10年的共同努力，于1992年开发成功适用Ru/C催化剂的KAAP(Kellogg Advanced Ammonia Process)新型氨合成工艺流程，并实现了工业应用^[33–35]。

钌催化剂虽然活性很高，但存在 H_2 的强烈抑制作用，而且以炭材料为载体的Ru催化剂在合成氨的条件下，载体碳在钌的作用下会发生甲烷化反应，致使活性炭载体的流失而影响催化剂的寿命。这是钌催化剂的一个弱点。同时，由于Ru和Os非常昂贵，相对第三好的Fe催化剂而言缺乏商业吸引力^[36]。Os和U在20世纪初就被Haber的早期研究所淘汰。Ru/C催化剂在节能方面也没有太大的优越性(表2)。从1992年至2010年，仅有16家合成氨装置采用钌催化剂。因此，可以说钌催化剂的理论意义大于实用意义，工业上仍有必要寻找比钌更廉价的高效催化剂。

2.1.3. 钴钼氮化物氨合成催化剂的发现

Nørskov课题组等^[36]提出了一种周期表内插入法预测合金催化剂的原理。这种催化剂开发策略是通过简单的物理原理得出，其基本原理可以广泛应用。根据这个原理，一个合理的设想是，在A.Ozaki等得到的火山形曲线中，把这条曲线上与氮反应很活泼的与很不活泼的元素形成合金来构造一个活性表面，以达到最优化的性能。结果发现，钴钼氮化物催化剂的活性比Ru和Os更接近曲线的顶点；比各自组分有更好的氨合成活性，在低 NH_3

浓度下比Fe和Ru还要好^[37–41]。非钌的钴钼氮化物催化剂的发现被认为是到目前为止在氨合成催化剂的研究中根据理论预测而合理发展的最新顶点^[42,43]。

G. Ertl^[44]和Somorjai课题组^[45]的实验可以提高对氨合成的认识,并且允许对这个反应进行定量的理论描述和预测。首先在反应途径的基本知识和过渡态理论的基础上,能够得到元素在氨合成中催化效率的火山型曲线的定量描述。由此可以预测合金体系的催化效率^[36,46]。在Co-Mo-N体系上得到的研究结果^[36,47],证实了理论和经验在催化剂的选择上是同等有用的。这一令人瞩目的成功例子表明:根据目标反应过程,在纯理论上可以设计一个催化剂体系^[36,48]。因此,非铁类和合金类催化剂的发现将再次推动多相催化科学的发展。

这里值得关注的是,氨合成催化剂的发现和发展在催化剂的研究方法上给我们提供的启发。在发明氨合成催化剂时,Mittasch等采用的是大量试验的研究方法,在当时是一种完全新颖的方法。这种方法如此有效,以致迄今基本上仍然沿用这种方法。而钴钼氮化物催化剂的发现给我们提供了另一种全新的研究方法,即可以在纯的理论基础上来设计催化剂,包括周期表内插入法设计催化剂。随着催化科学理论知识和规律性认识的深入,大量丰富的资料和经验的积累,特别是随着计算机技术的发展,为从理论上并在“分子”水平上来设计催化剂,提供了可能。近年来人们纷纷开发各种专家系统等来辅助催化剂的设计^[49–52]。

2.2. 熔铁催化剂的特征及其理论与实践的启示

合成氨中的催化化学极具魅力,吸引了众多化学家的注意力和兴趣。许多当代著名的物理化学家和催化科学家,如W. H. Nernst, W. Ostward, F. Haber, C. Bosch, M. I. Temkin, G. Ertl, P. Emmett, A. Nielsen, H. Topsøe, G. A. Somorjai, J. A. Dumesic, J. K. Norskov, M. Boudart等都曾参与或涉及合成氨催化剂的研究^[53–58],出版了不少专论^[24,59–62]。这是因为熔铁催化剂具有某些特殊的性能。

(1) 在20世纪化学工业的发展中,催化合成氨技术起着核心的作用^[63]。这个工业的重要性与人们对氨合成催化剂的重要科学价值和技术进步的理解具有浓厚兴趣相关联。通常,与催化作用相关的新技术、新方法和新理论的发展往往是从这个反应系统的研究开始,或者首先被应用于这个反应体系。同样地,在氨合成催化领域得到的新发现往往被延伸到其它催化领域。而精细的表征技术、动力学分析、新理论模型的发展也极大地促

进了人们对氨合成催化剂基础的深入理解。

百年来,虽然历经不断地改进,但熔铁催化剂的本质未变。迄今为止,所有对氨合成反应理论的研究都是以这种催化剂为基础的。例如,在铁催化剂上完成的著名的BET吸附理论;P. Emmett用选择性化学吸附测定催化剂表面活性组分的方法;建立在以氮对Fe(111)晶面有选择性吸附现象为基础的工作,奠定了20世纪80年代逐步形成的金属簇催化理论;G. A. Somorjai的“具有最大配位体的晶面具有最高催化活性”的重要假定以及结构敏感反应概念;J. Horiuti的化学计量数的概念首先是为了验证合成氨反应动力学机理而提出的,M. I. Temkin理论及其著名的合成氨反应动力学方程,第一次成功地而且至今仍然应用于工业反应器设计,并奠定了多相催化反应动力学基础。这些理论和概念,带动了一系列基础理论的发展,奠定了多相催化科学的基础。氨合成反应及其催化剂的发展史是多相催化学科发展史的缩影。

Temkin的非均匀表面的催化反应动力学理论不仅得到了铁催化剂上合成氨总包反应动力学数据的证实,而且更重要的或许还是由这个理论导出一些非常有用的普遍性结果。例如,Temkin方程是在两步机理或者能简化为两步机理的基础上推导得到的,并且在催化动力学研究中,通常可以忽略催化剂表面的非均匀性,把它当作均匀表面来处理,因此适用于任何一类催化反应。其次,对于多位吸附,不同的催化剂活性具有巨大差别源自于活性位的多重性的推理,对于非均相催化反应的结构敏感性的讨论是极其重要的。第三,在Temkin理论的推导中引入了活性位分布函数的概念,由此可导出许多众所周知的吸附等温线,如Freundlich, Frumkin-Temkin表达式及其它公式以及Elovich方程式等吸附速率定律。由此推导得出最佳活性位或最佳催化剂应该具有适中的亲和势数值,即表面能量分布处于中央的活性位。这些结果可以看成是Sabatie最佳催化剂能够容易形成足够稳定但又不太稳定的中间化合物原理的体现并得到解释^[64]。

这些理论为催化研究提供了有价值的信息,即为了得到最佳催化剂,必须改变亲和势的数值。例如,对于金属催化剂可用如下3种方法:首先,通过改变暴露的晶面或改变粒子的大小来改变表面结构,在这两种情况下,都包括改变具有不同配位数的原子在表面的相对分布比例;第二,可通过形成合金(例如将铜加入到镍中)或添加表面杂质(例如硫、碳、氧、氮)来改性金属催化剂^[9];

第三, 根据周期表改变催化剂中金属成分筛选最佳催化剂, 例如钴钼氮化物催化剂的发现. 为了使这种方法比较有意义, 必须假定反应机理不发生变化. 但是, 通常在引进一种新催化剂并经过一些时间后, 其活性可提高到一定水平, 进一步提高将变得十分困难. 要突破这一水平, 似乎必须发现不同的化学反应步骤序列, 即要发现另一种不同的反应机理.

实践表明, 没有别的反应象氨合成反应一样, 能够把理论、模型催化剂和实验连接起来. 在低压得到的研究结果能够被高压实验证实; 从超高真空得到的动力学可以外推到工业条件; 在单晶上的研究结果可以应用理论来描述^[44,65]. 这个状态不但对铁催化剂适用, 对钨催化剂和 $\text{Co}_3\text{Mo}_3\text{N}$ 催化剂都适用. 而且, 了解这些催化剂知识所需的时间越来越短, 尽管催化剂在结构和化学组成上变得更加复杂^[13]. 因此, 催化合成氨反应仍然是多相催化理论研究的一个理想的模型体系.

(2) 氨合成反应是最简单的化学反应之一, 是一个没有副产物、没有选择性的原子利用率为100%的绿色化学反应, 特别是通常产品氨与排放的 CO_2 联产尿素或碳酸氢铵时, 更是一个没有排放的清洁生产工艺, 是至今工业上少有的 CO_2 捕集、封存和利用的成熟技术之一^[66]. 在工业上, 实现该反应的合成氨过程却是化学工业中最复杂、最典型的化工过程之一; 在理论上, 该反应是一个在常温常压下能够实现而在实践上却是一个非常困难、必须在高温高压下实现的反应. 因此, 理解氨合成催化反应机理并转换成完美技术成为催化领域发展的基本标准.

(3) 现代工业铁催化剂是一种纳米结构的亚稳态物质, 它是以氧化物为前驱体在非常复杂的过程中合成的^[67,68]. 这个亚稳态也是在活化和氧化活化材料时产生过热应力的敏感性的原因. 制备纳米结构的路线是可以选择的, 例如 $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_{1-x}\text{O}$ ^[69–72], 并且看起来似乎非常简单的铁催化剂的结构却是非常复杂的. 一个令人吃惊的例子是仅仅使用不同的催化剂前驱体能引起金属表面纳米结构的巨大改变. 新发明的维氏体基催化剂已经被证实比磁铁矿基催化剂具有更高的活性^[23]. 定量分析研究表明, 在铁催化剂中, 只有不到1%铁表面参与了氮的活化, 其余99%的铁只是起着一种载体的作用^[73]. 如果能够有更多的铁暴露在表面, 将可以大大提高催化剂的活性. 有人则以铁催化剂为载体, 在其表面涂附上纳米铁, 制备出涂附纳米铁的铁催化剂.

(4) 氨合成催化剂是所有工业催化剂中最稳定的.

上述这种纳米结构的亚稳态物质在多孔和苛刻的反应条件下使用15年以上, 其结构几乎不变. 对此, 曾进行了大量的研究和表征, 提出了许多模型来解释这种稳定的活性表面结构及其形成机理^[10,55,74–79].

(5) 高度与工业关联的催化氨合成反应仍然是一个制造新生命的关键反应, 一个有助于催化剂的基本理解, 在科学和文化上有着相当重要性的原型反应^[80]. 尤其是基础知识的进步对其它领域的催化剂研究有较大的影响.

例如, 在合成氨的生产过程中, 从制气、净化到合成, 主要的化学反应都是通过多相催化过程完成的, 催化剂起着极为重要的作用. 其中以天然气或石脑油为原料的蒸气转化法制氨过程中使用了9种催化剂, 包括烃类加氢转化催化剂、一段/二段蒸气转化催化剂、高温/低温变换催化剂、甲烷化催化剂、氨合成催化剂、 CO 选择性氧化催化剂等; 以渣油为原料的部分氧化法和煤加压气化制氨工艺还使用耐硫变换催化剂、 Claus 硫回收催化剂、 CO_2 脱氢催化剂、各种脱毒催化剂、分子筛干燥剂以及工艺过程制氮催化剂等^[81]. 无论何种制氨工艺, 变换催化剂和氨合成催化剂都是不可缺少的, 它们是合成氨工业的核心催化剂.

这十几种催化剂, 大多数是其它化工过程, 例如煤化工、石油化工、天然气化工、生物化工、能源化工、炼油工业以及环境保护等领域的基本催化剂, 例如加氢转化脱硫催化剂、变换催化剂等是这些工业不可或缺的催化剂. 此外, 合成氨工业还蕴含着一系列高新技术和战略性新兴产业中需要解决的系列共性-关键技术. 而催化合成氨过程本身还蕴含着巨大的节能潜力, 人们还将继续不断地改进上述各种催化剂. 因此, 合成氨催化剂的发展必将带动一系列其它催化剂的发展. 了解和熟悉氨合成催化剂及合成氨工艺流程及其成熟技术和实践经验, 对于了解现代化工、能源、材料、环保领域一系列共性、关键技术, 尤其是对于传统工业的节能减排、新型煤化工、制氢和清洁能源等战略性新兴产业, 具有强烈的启迪和借鉴作用^[82].

3. 氨合成催化剂面临的挑战

进入21世纪, 有人把合成氨称之为是“夕阳工业”. 国外也有人哀叹: 固氮化学的前景黯淡^[83]. 对此, 德国Schlögl^[13]发表了题为“Catalytic Synthesis of Ammonia—A Never-Ending Story?”的短评, 指出催化合成氨的故事永远不会结束.

(1) 氮的循环是自然界中维持地球上生命的最重要的循环之一, 氮也是现代社会运转必不可少的原料, 它赋予合成氨工业旺盛的生命力. 这些材料的合成都需要合成氨作为活化态的氮. 催化合成氨是自然界中氮循环的重要一环, 是生物(包括人类)所需要的活化态氮的重要补充, 而且是目前唯一具有工业规模的获取活化态氮的方法. 目前除了催化合成氨以外, 期望通过其他途径获得活化态氮都还只能是科学研究的课题. 虽然生产合成氨需要使用各种含碳燃料获得 H_2 气, 然而无论能源供应将会如何紧缺, 环境控制如何日益严格, 粮食的刚性需求决定了合成氨工业必须依靠科技进步来面对这一严峻形势而继续发展, 并推动着氨合成催化剂的不断改进与创新, 以满足人类生存和社会发展的需要. 因此, 合成氨工业是一个具有旺盛生命力的不可替代的传统工业.

(2) 合成氨生产的原料和燃料都是能源. 当今全球关注的能源问题又摆在合成氨工业的面前, CO_2 的排放也将受到严格限制, 节能减排始终是合成氨工业面临的重大课题. 现代以天然气为原料的先进氨厂的综合能耗已达到27.5GJ/t左右, 过程的总热效率达到70%以上^[84]. 商业铁催化剂和钨催化剂能够达到上述效益^[85,86]. 催化剂中的任何一个进步都能够提高热力学效益和降低产物的价格^[87]. 应该强调的是, 从表面上看, 能量损耗主要在于转化工序, 而实质上应在于合成工序. 因为占能耗30%左右的动力消耗主要为合成服务^[88]. 合成氨的高压主要是为了跨越合成氨反应的活化能势垒, 而活化能势垒高低决定于催化剂的活性. 为了跨越这一反应障碍, 消耗了占吨氨总能耗约30%的能量, 付出了多么高昂的代价! 因此, 开发新型低压合成氨催化剂意义非同小可.

(3) Haber-Bosch固氮过程中没有涉及在催化反应中使用别种形式的能量, 如电能、光能等, 以及催化剂在不同形式的能量相互转化中的作用. 在现实生产实践中, 别种形式的能量转化, 如由化学能、太阳能、风能、水能和核能转化为电能; 电能、光能转化成化学能等都格外引人注目.

在以矿石燃料的热能作为唯一驱动力的Haber-Bosch固氮过程中, 即使余热回收及梯级利用最先进的氨厂(总能效高达74%以上), 不仅还有20%以上的节能潜力, 而且至少消耗27.5 GJ/t以上热能的燃料. 即使在极限状态(总能效100%)下, 也必须消耗20.13 GJ/t以上热能的矿石燃料.

因此, 将电能、光能、辐射能引入合成氨过程辅助氮分子的活化或改变反应途径, 并研究催化剂在不同形式的能量相互转化中的作用具有现实和理论意义.

(4) 众所周知, 催化化学研究的重点和难点是自然界中最稳定的几种小分子(CO_2 , H_2O , CO , CH_4 , H_2 , N_2 , O_2). 氮分子是最难活化的单质, $N\equiv N$ 三键离解能高达942 kJ/mol, 断裂该键需要极高的能量. 如何活化氮分子是固氮所面临的关键理论问题. 氮分子的活化也成为化学和催化领域研究的原型分子之一, 具有典型的代表性意义.

(5) 氨合成反应在25 °C的标准平衡常数高达 6.8×10^5 , 理论上预测在室温和常压下氨合成是可能的, 但反应速率几乎无法察觉. 因此, 这是一个新的挑战. 由于固氮对人类的生存和发展具有重要意义, 因此实现常温常压合成氨一直是人类不懈追求的目标.

综上所述, 降低现有合成氨技术的能耗, 寻找新的合成氨的方法和途径, 探索常温常压合成氨的可能性等, 是催化合成氨技术面临的新挑战.

实现常温常压合成氨的关键是氮分子的活化和能量的提供形式与途径.

3.1. 氮分子的活化

将空气中游离态的氮气转化为含氮化合物的过程称为固氮, 主要包括化学固氮和生物固氮. 用化学方法活化氮分子主要有3条途径.

(1) 还原法, 用还原剂给予 N_2 电子. 催化合成氨属于还原法. (2) 氧化法, 用氧化剂夺走氮分子中的电子. 由于 N_2 的第一电离能很高, 目前尚未找到这样强的合适的可形成催化循环的氧化剂. (3) 物理-化学法(激活法), 用强烈的条件如高压放电、等离子体等物理手段, 把 N_2 从基态激发到高能状态, 甚至把它拆开, 使之成为氮原子或氮离子, 然后与别的物质起反应. 例如: 早期的电弧法和氰胺化钙法. 巨大的能量消耗大大限制了这两种方法的工业应用. 近年来, 关于等离子体合成氨^[89–92], 磁诱导法合成氨^[93]等的研究方面也较活跃, 但目前仍处于探索阶段.

因此, 催化还原法占据无可争议的主导地位, 也是目前唯一具有工业规模的化学固氮方法. 由于人们对此过程进行了长期的研究和探索, 目前在钨和 $Fe_{1-x}O$ 基铁催化剂作用下, 起始活性温度已可以降低到200 °C左右^[94]. 例如, ZA-5在某企业合成高纯氨制备工艺中, 进口温度215 °C, 出口温度363 °C, 压力8 MPa, 氨净值高于10%, 已经可以满足工程上经济性对氨净值的要求, 关

键在于相应低压工艺技术的开发。但可以预见, 进一步开发更低温度和压力下高活性催化剂仍有相当的难度。

历时长达一个世纪的催化合成氨的研究, 可以说就是 N_2 的活化方式及其本质的研究历程。各种现代精密物理-化学仪器都曾用于 N_2 的活化及其机理的研究。然而, 迄今在铁催化剂上氮的活化究竟属于解离吸附还是分子吸附仍时有争议。绝大多实验事实是支持 N_2 解离吸附的^[70,95–97]。例如对于在Fe催化剂上, G. Ertl^[98]提出了一个基于 N_2 解离吸附的合成氨催化反应机理及其热化学动力学位能图(图1)。这是2007年G. Ertl获诺贝尔化学奖的代表性成就之一^[99]。M. Boudart^[80]认为图1具有很大的指导意义, 要真正清楚地了解催化反应机理, 就要象合成氨催化反应那样, 能够提供如图1那样的热化学动力学剖面图。理论工作者正在设法去计算催化循环中基元步骤所缺少的许多能量值^[100]。

也有许多实验事实是支持 N_2 分子吸附的^[65,101–106]。例如, 廖代伟等^[107,108]用反应能量学的多相催化反应分子设计和键级守恒莫尔势函数法(BOC-MP)以及氘反同位素效应^[109]研究了铁和钨催化剂表面氨合成反应的缔合式和解离式两种机理, 计算表明缔合式机理速控步骤的活化能垒低于解离式速控步骤的活化能垒, 但反应的活化能垒又明显低于缔合式途径速控步骤的活化能垒。由此可推断, 在铁催化剂表面存在着两种氨合成竞争反应途径。

在铁催化剂上合成氨中, 从示踪物的转移测得的总包反应和速率决定步骤的化学计算数 σ_{rds} 可以等于1或2, 如图2所示。这两种数值在实验工作中都已有报道。Horiuti等^[110,111]发现在接近平衡时, $\sigma_{rds} = 2$; 而Tanaka^[112]发现在远离平衡时, 合成反应的 $\sigma_{rds} = 2$, 而分解反应的 $\sigma_{rds} = 1$ 。 $\sigma_{rds} = 2$ 适合于图2(a)步骤2为速率决定步骤, 但是很多证据指出氮的吸附是速率决定步骤, 这时 $\sigma_{rds} = 1$, 但 $\sigma_{rds} = 1$ 却不能确定吸附是解离的还是不解离的。可以想象的是存在如图2(b)所示的反应序列, 其中最先的两步被认为是固氮酶通过它们实现固氮。倘若如此, σ_{rds} 仍等于1。然而, 在铁上氮的解离化学吸附的证据现在是占压倒优势的。在铁上解离和在固氮酶上不解离这两种反应序列正好是高温下工业催化作用和低温下酶催化作用各自的特征。因此, 为了从本质上改善当前合成氨铁催化剂的活性, 可能必须根本改变在铁催化剂上反应序列中各步的性质^[10]。

因此, 图1和图2所示关于 N_2 的活化形式、氨合成反应的基本步骤、真实结构, 这些问题还蕴涵着丰富的科

学暗示, 新的高效的氮分子活化方法还有待探索^[57]。氮分子活化在化学和催化科学研究中依然是一个挑战, 依然具有重要的理论和现实意义。

3.2. 催化合成氨在理论上的新挑战

液氨的热值为21.29 GJ/t, 有效能(exergy)为20.13 GJ/t, 而实际能耗要高得多。因此无论用什么原料和工艺合成氨, 需要提供的有效能不可能少于20.13 GJ/t。以水和空气为原料、矿石燃料的热能为驱动力的Haber-Bosch固氮过程, 由于原料提供的有效能值多于产品的有效能值, 因而该过程的理想功为正, 每生产1t 25 °C的饱和液氨, 理论上都是可以对外做功的过程(表3)。例如以纯 H_2 和纯 N_2 为原料的制氨过程可以对外提供0.63 GJ/t的外功, 但直接以水和空气为原料的固氮过程, 必须消耗外功, 其过程理论能耗达20.31 GJ/t。由两者的比较可知, 固氮过程中能量主要损耗在把空气中的氮和水中的氢取出来的过程。因此, 如果能通过其它形式的能量如电能、光能等, 把水中的氢取出来, 就可以改变反应途径。虽然仍然至少要消耗20.31 GJ/t以上的电功, 但电能可以采用可再生能源, 如太阳能、风能、水能或核能等转化而来。由此固氮过程就可以不使用矿石燃料, 那将是合成氨工业的彻底革命!

因此, 将电能、光能等引入固氮过程, 改变反应途径或仿生合成氨是催化科学工作者面临的重大挑战之一, 具有重大的理论和现实意义。

3.2.1. 电催化合成氨催化剂研究

电催化合成氨可使热力学非自发反应 $N_2 + 3H_2O = 2NH_3 + 1.5O_2$ ($K_{298} = 10^{-120}$) 在电能的推动下发生, 从而拓展氨合成方式的研究领域; 也可使受平衡限制的合成氨反应不受或少受热力学平衡的限制。因此, 将电能引入合成氨过程辅助氮分子的活化或改变反应途径一直是备受关注的研究领域之一。电化学方法与现有合成方法的效率相似, 是一种可取的常温常压合成氨方法^[114]。例如, 在高温(570 °C)常压下进行的电化学方法合成氨, 氢气的转化率可接近100%。因此, 近年来电化学常温常压合成氨的研究也相当活跃^[115–118]。

曾研究过的主要电催化剂包括负载铁酞菁催化剂的气体扩散电极, 陶瓷固体电解质以及熔盐(LiCl/KCl/CsCl)等。采用室温下具有高质子导电性的固体电解质, 提高电流效率和电极稳定性是电化学合成氨未来研究的重要方向^[87,119,120]。

电流效率过低是影响电化学合成氨效率和产品成本的关键。随着电化学合成氨的深入研究, 如果能够大

幅度提高电流效率和转化率,使得电化学生成氨的成本主要集中到单纯的电能消耗上,则电化学生成氨在电能充足、或可能有效地将太阳能、风能和热能转化为电能的偏远地区有望占有一席之地。特别是在未来当由于能源危机导致石油、天然气、煤炭等合成氨原料价格大幅度上扬致使合成氨成本成倍增长时,电化学生成氨将不失为一种有益的选择。因此,电化学生成氨研究依然具有潜在的应用前景^[115]。

3.2.2. 光催化合成氨催化剂的研究

人们最为熟悉的光催化反应是自然界的光合作用: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$ 。绿色植物通过叶绿素(光敏剂)吸收阳光,通过植物体中的酶,由 CO_2 和 H_2O 光合成碳水化合物,放出 O_2 。光合作用是将光能转化为化学能的最重要途径。复杂的光合作用进程中最关键的一步是光合作用反应中心里的物质接受光能释放出电荷,并将电子转送到细胞中引起化学合成反应,从而将光能储存起来^[121]。

在常温常压下以水为氢源,以太阳能为能源,用光催化的办法使空气中的氮直接转化为氨的反应: $\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 1.5\text{O}_2$,则需要解决太阳能的输入方式和采用光催化剂。

这两个反应相似,都是热力学非自发反应,且 N_2 比 CO_2 更难活化,但在光催化理论上是是可以实现的。无论是自然界中的 CO_2 还原反应还是人工的水还原(产 H_2)和氧化(产 O_2)反应,都是一个相当复杂的催化过程,通常是通过多电子途径发生、由若干个基元反应组合而成的。1988年诺贝尔化学奖共同获得者Deisenhofer等^[122]和Michel等^[123]通过理论计算,认为非对称核因素(nuclear Frank-condon factors)与电子耦合的共同效应极可能是单向电子传递的主要原因。光合作用反应机理及其中心结构的研究结果将为光催化合成氨提供启示。

光催化研究已有50多年历史^[124]。所使用的光催化剂大多为具有半导体特性的材料,例如不同金属掺杂的 TiO_2 系列和 WO_3 系列^[125],以及 CdS/GaP-Pt , $\alpha\text{-Fe}_2\text{O}_3\text{-Nd}_2\text{O}_3$ 等催化剂^[126–132]。目前人们正在不断地研制更有效的催化剂^[133–135],提出常温常压合成氨的新方法。这说明人们正在向这个长期的奋斗目标探索。

3.2.3. 化学模拟固氮酶仿生合成氨的研究

在自然界,有一种固氮微生物,它们体内含有一种具有特殊本领的催化剂—固氮酶,它能在常温常压条件下将空气中的氮直接还原为氨。其固氮能力比Haber-Bosch化学固氮过程高出成千倍。据估计,当今由

生物固定的氮已达0.2 Gt,占地表化合态氮的48%左右(其余52%由合成氨提供)。生物固氮,无论从它所需的条件,还是固氮能力,都大大超过了化学固氮。生物固氮可分为生物固氮菌固氮法和仿生化学固氮法。

仿生化学固氮是用化学的方法,模拟生物体内固氮酶的功能,制备优良的化学催化剂,实现常温常压合成氨。这是催化科学工作者面临的一项挑战。研究生物固氮机理,无论是生产上还是理论上都有重大的意义。它可以为化学模拟生物固氮提供重要的依据。固氮微生物要实现固氮,必须具备三个基本条件^[136]: (1) 固氮酶; (2) Mg-ATP^{2-} ; (3) 电子供体,如还原型铁氧还蛋白,还原型黄素氧还蛋白,或人为的 $\text{Na}_2\text{S}_2\text{O}_4$,为 N_2 还原提供电子。20世纪70–80年代,我国著名科学家唐熬庆、卢嘉锡、蔡启瑞为首的一批科技工作者深入开展了生物固氮酶及其化学模拟研究工作^[137],并提出了固氮酶活性中心模型^[138]。经过世界各国科学家不断努力,发展了化学模拟固氮酶,并创立了固氮分子遗传学方法,使生物固氮研究取得了重大进展,特别是自美国学者Rees等^[139–143]阐明了固氮酶的活性中心原子簇及其周围多肽分子的三维结构后,化学模拟生物固氮的研究再次掀起热潮^[144–151]。同时,选择性酶的发展将是有机化学和生物技术丰富的催化剂来源^[152]。虽然,迄今未能取得令人满意的实用性成果,但是人们对于生物固氮及其仿生氮合成的研究和探索不会停止。

此外,生物固氮菌固氮法中,主要是通过生物工程,在非豆科作物接种根瘤菌,将固氮基因和其它相关基因或固氮生物引入非豆科作物,实行自我供氮^[153]。随着转基因育种技术的发展,实现非豆科作物接种根瘤菌自我供氮,并大量种植豆科等油料作物(含氮7%–8%),充分发挥油料作物根瘤菌共生固氮作用,减少化学氮肥用量是解决农业生产中大量施用化肥的负面影响的途径之一^[137]。

4. 结束语

合成氨中的催化化学极具魅力,熔铁催化剂所具有的某些特殊性能是其它许多催化剂难以比拟的。高度与工业关联的催化氨合成反应仍然是一个制造新生命的关键反应,一个有助于催化剂的基本理解,在科学和文化上有着相当重要性的原型反应,理解氨合成催化反应机理并转换成完美技术成为催化领域发展的基本标准,尤其是基础知识的进步对其它领域的催化剂研究有较大的影响,它仍然是多相催化理论研究的一个理想的模

型体系.

催化合成氨技术在20世纪化学工业的发展中,起着核心的作用. 人类需要食物, 食物需要氮素, 催化合成氨的故事永远不会结束. 氨也是现代社会运转必不可少的原料, 它赋予合成氨工业旺盛的生命力, 并将继续推动着氨合成催化剂的不断改进与创新. 在21世纪, 催化合

成氨技术将面临新的理论和实践的挑战. 降低现有催化合成氨技术的能耗, 将电能、光能引入合成氨过程及化学模拟固氮酶辅助氮分子的活化或改变反应途径, 寻找新的合成氨的方法和途径, 探索常温常压电化学催化、光催化合成氨、化学模拟生物固氮的研究, 是备受关注的研究领域.