Chinese Journal of Catalysis 35 (2014) 1619–1640

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Review

Ammonia synthesis catalyst 100 years: Practice, enlightenment and challenge

Huazhang Liu *

Institute of Industrial Catalysis of Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China

A R T I C L E I N F O

Article history:
Received 19 March 2014
Accepted 23 April 2014
Published 20 October 2014

Keywords:
Ammonia synthesis catalyst
Discovery
Development
Challenge
Practice
Enlightenment

A B S T R A C T

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.

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

* Corresponding author. Tel: +86-571-88320063; Fax: +86-571-88320259; E-mail: cuihua@zjut.edu.cn
DOI: 10.1016/S1872-2067(14)60118-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 10, October 2014

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.

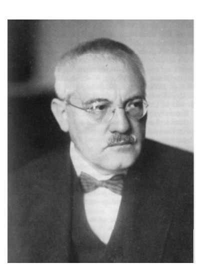
Bosch assigned the task on finding efficient and stable catalysts to his assistant Alwin Mittasch. Mittasch first conducted extensive studies on metal nitrides in an attempt to fix the nitrogen in air by the indirect route. Although that technique was unsuccessful for the ammonia synthesis, it provided 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.