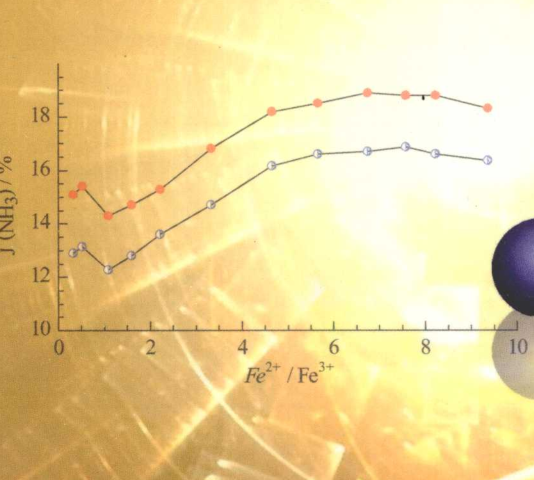
Ammonia Synthesis Catalysts

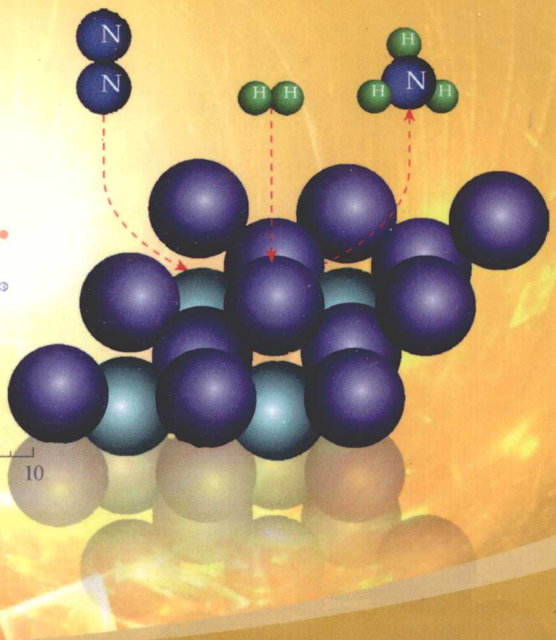
Innovation and Practice

氨合成催化剂

——创新与实践

刘化章（Huazhang Liu） 著





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合成氨是极其重要的化工产品，氨合成催化剂的重要性不言而喻。催化合成氨基础知识的进步对其它领域的催化剂研究有较大的影响。本书从理论与实践相结合的视角，全面系统地论述了氨合成催化剂研究、开发和工业应用的基本理论和方法，阐述了氨合成催化剂制备的理论、方法、实验技术及相关的催化反应机理、催化反应器、反应工程与工艺及其应用。

作者刘化章教授从事氨合成及其催化剂的开发研究数十年。本书以作者获国家发明二等奖的 $Fe_{1-x}O$ 催化剂为主线，结合其多年研究成果，全面、系统地论述有关氨合成催化剂（包括钌催化剂）的理论和相关技术问题。本书尤其注重理论与实践密切结合，既具有一定的理论深度，又与催化剂研发、工业应用和工程技术相结合。既有作者的实践基础，又汲取国内外的研究成果，并涉及基本原理和科学基础。本书同时阐述了根据催化剂性能选择工业应用条件及其对催化过程经济效益的影响，并介绍了近年来氨合成催化剂研究的新探索、新技术，包括光催化、电催化、生物催化以及氨的新用途等方面的新成果、新进展。

本书可供广大从事催化剂研究、开发和有关工业的科研人员、高校师生和工程技术人员参考。

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Liu Huazhang

Professor, Director of Institute of Industrial Catalysis, Zhejiang University of Technology (ZJUT); Syndic and Vice Director of Chemical Fertilizer Committee of Chemical Industry and Engineering Society of China and Member of the Catalysis Committee of Chinese Chemistry Society.

Liu was born in Zhejiang in 1940. He received his bachelor degree in Chemical Engineering at the ZJUT in 1964 and has been working in ZJUT since then. As a visiting scholar, he was engaged in catalytic reaction engineering in National University of Yokohama of Japan in 1982 and in catalytic chemistry in Hokkaido University of Japan in 1996.

Since 1964, he has been engaged in the study of ammonia synthesis catalyst and Fischer–Tropsch synthesis catalyst and chemical engineering, including iron based- and ruthenium based-catalysts. He invented the first $Fe_{1-x}O$-based ammonia synthesis catalysts and their theoretic system in the world in 1986, and developed successfully the A110-2, A301, ZA-5 series industrial ammonia synthesis catalysts. He has over 270 scientific papers, 21 patents and books to his credit. As a first contributor, he has received many important national awards of science and technology, including the second and third prize of National Invention Award, the second prize of National Scientific & Technological Progress Award, and seven times for the first prize of Scientific & Technological Progress Award from Zhejiang province and the Ministry of Chemical Industry.

Professor Liu has won a series of prestigious honors, such as the National Outstanding Specialized Technical Talent, the National Young Experts in Science & Technology with Prominent Contribution, the National Overseas Returnees with Prominent Contribution, the National WUYI Labor Medal, the Achievement Award of HOU Debang Chemical Industry Science & Technology Award and the Honor Teacher and the Superfine Professor of Zhejiang province and so on.

Preface

The first high-pressure ammonia synthesis reactor in the world designed by C. Bosch in 1911 is still standing in a small garden in front of the building of BASF ammonia synthesis institute. It is a milestone in the history of catalytic ammonia synthesis process. On 9 September 1913, the first catalytic ammonia synthesis setup started its commission which could produce five tons of ammonia per day in the world. After that, the industry of ammonia synthesis has been developed rapidly. The catalytic ammonia synthesis technology has played a central role in the development of the chemical industry during the 20th century. Till the beginning of the 21st century, the ammonia synthesis plants with a capacity of 1,000 or 2,000 tons per day spread all over the world. This is an epoch-making achievement which proved that the ability of human could conquer the nature.

The tremendous success of synthetic ammonia industry not only meets the growing need for food due to the growth of population, but also leads the development of a series of basic theories. Ammonia synthesis industry itself contains a great number of creative scientific thoughts. All of the following theories promoted the development of the entire chemical industry and materials industries, including the application of chemical equilibrium and the law of mass action forward; high-pressure reaction technology realized by Haber, operating in a closed flow path, the concept of dynamic reaction rate and the concept of multi-promoters complex catalysts put forward by Mittasch etc. It is a precedent of the success that leads to the close cooperation of chemists, physicists, engineers, material scientists and various artisans. The tremendous success of ammonia synthesis industry and its catalytic process established a foundation for heterogeneous catalysis. Often new techniques, methods and theories of catalysis have initially been developed and applied in connection with studies of this system.

The fused iron catalyst is one of the most successful and most fully studied catalysts in the world. But the discussion on the inbeing of the ammonia synthesis reaction has not ended. There are a lot of questions still needing to be answered on the structure of the catalysts and the formation mechanism of ammonia molecules. Although the relative importance of research on catalytic ammonia synthesis has decreased and now it is not the focus of research on catalysis due to the development of the fields on petrochemistry, biochemistry, macromolecule and environmental catalysis etc, the development of ammonia synthesis industry and the progress of the catalytic technology will never stop.

The modern industrial iron catalyst is a nanostructured metastable substance, which is formed during the surprisingly complex synthesis of the oxide precursor.

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Its metastability is the reason for its sensitivity towards thermal overstress during activation and oxidation of the activated material. The formation of the nanostructured system is related to alternative preparation routes i.e., the oxide precursor. It was commonly considered for about 100 years that the fused iron catalysts with Fe_3O_4 as precursor were the most active. Therefore the research for fused iron catalysts was limited to Fe_3O_4 and the effect of the oxide precursor on the performances of catalyst was neglected. The iron catalysts used in industry almost have no fundamental differences compared with the one that BASF Company developed 100 years ago. On the whole, this catalyst with Fe_3O_4 as precursor was considered well consolidated and no special improvement was expected. It will prompt people to seek a new technical breakthrough — a kind of discontinuously and leapfrog technical progress. The discovery of $Fe_{1-x}O$-based and ruthenium-based catalysts and Co–Mo bimetallic nitride catalyst is a proof of the idea.

The discovery of the $Fe_{1-x}O$ based catalyst with wüstite structure was a breakthrough of the classical theory on the oxide precursor and the activity is higher than the best magnetite-based catalysts in the world. This invention indicates an essential improvement on the research for ammonia synthesis catalysts since 1913. It is a chance for further progress of iron catalyst and aroused much attention of the scientists in the field. At present, the $Fe_{1-x}O$ based catalyst has been widely used in industry.

Ruthenium and Co–Mo bimetallic nitrides stand out in the group of the non-iron catalysts. Among single metal, ruthenium, osmium and iron are the most active catalysts for ammonia synthesis. Ruthenium-based catalysts have a much longer history of development and are applied successfully. However, these metals are very expensive and thus less commercially attractive compared to the third-best catalyst, Fe, and there is no significant advantage in terms of energy-saving. Therefore, in industry, it is still necessary to find a catalyst which is cheaper and more efficient than ruthenium catalysts.

Norskov proposed a more scientific and effective theory, i.e., interpolation in the periodic table, for designing bimetallic catalysts. According to this theory, a reasonable assumption is to combine the most active and less active elements for activation of nitrogen together to construct an active surface to achieve the best performance. The idea was proved by an efficient non-ruthenium catalyst on the basis of cobalt–molybdenum nitride, which can be regarded as the current climax of a systematically but empirically justified development based on the theoretical prediction of the ammonia synthesis catalyst research up to now.

At present, the whole world has paid more and more attention to the energy problems and the strict limit of CO_2 emission. This makes the ammonia synthesis industry face a great new challenge.

The new challenge on the theory is about the prediction of biomimetic ammonia-synthesis path at room temperature and atmospheric pressure. There are some reports on the study of photocatalytic, bio-catalytic and electrochemical ammonia synthesis catalysts. The latter should be achieved preferably by electrochemical processes with efficiency similar to the synthesis strategies that are available today.

There are also new challenges for new applications. In the 21st century, nitrogenous fertilizer is not only an agrochemical but also an industrial product which is responsible both for the increase of agricultural production and the bio-energy. Ammonia would make a convenient storage molecule for hydrogen for operation in fuel cells. Synthesis and decomposition of ammonia can be well controlled and it is one of the preferred work-medium for effective solar energy conversion, transmission and storage. Ammonia synthesis plant is actually an energy conversion device; if a practical and safe transfer of the industrial logistic into an end-consumer field were to be obtained, then a powerful alternative for the generation of hydrogen could be at our disposal.

Nitrogen atoms are essential for the function of biological molecules and thus are important component of fertilizers and medicaments. Ammonia is also used in non-biological field, such as printing and dyeing, explosives and resins. Synthesis of these materials requires ammonia as an activated nitrogen building block. The nitrogen cycle is one of the most important cycles in nature that maintains life in the world. The catalytic ammonia synthesis is one of the key elements in the nitrogen cycle in nature, which is very important complementarity for activated nitrogen. At present, catalytic ammonia synthesis is still the only way to obtain activated nitrogen in industry.

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. As well as being of high industrial relevance, the catalytic synthesis of ammonia 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 scientific and cultural importance. It is mainly this reason that drives the ongoing research in ammonia synthesis, especially since evidence for a knowledge based improvement of a catalyst would have a strong signaling effect on other fields of catalysis research.

Fortunately, since 1960s, the author has discerned the development of ammonia synthesis industry in China, and has joined in the research of Fe_3O_4-based, Fe_3O_4-cobalt-based, $Fe_{1-x}O$-based and ruthenium-based catalysts. The author and his co-workers have first invented a novel generation of $Fe_{1-x}O$-based catalysts which is more active than the best magnetite-based catalysts in the world, and have developed successfully a series of new catalysts such as A110-2, A301 and ZA-5 etc that are widely used in industry.

These are outlines of the development of ammonia synthesis catalyst and also our experience of the research on catalyst for the past 46 years. This book is based on the new generation of $Fe_{1-x}O$-based catalysts, and focuses on the innovation, development and application of catalyst and is mainly based on our own practice. At the same time, this book draws a lot of achievements of research in the field, which makes this book unique with depth to explain basic concepts and the scientific basis, and combines catalyst with engineering, so it can help readers understand more about ammonia synthesis.

This book comprises 10 chapters which can be classified into four parts. The first part deals with the catalyst itself, including the development (Chapter 1), chemical components and physical structure (Chapter 3); preparation and reduction (Chapters 4 & 5) and the performance evaluation of the catalysts (Chapter 7). Those of ruthenium catalysts are solely put in Chapter 6. The second part is about the reaction mechanism and kinetics of ammonia synthesis (Chapter 2). The third part is a combination of the above two, namely, is centered on the relationship between the performance of catalysts and reaction, which includes reaction condition, reactor, process and application condition and its impact on the economic benefit of catalytic process (Chapters 8 & 9). In the final part of this book, new exploration for catalyst and new technologies for ammonia synthesis including Co–Mo nitride catalyst, photo-catalysis, electrochemical catalysis, and biocatalysis, and new use of ammonia are introduced.

Here, I would like to thank all of my co-workers for their contribution and support during my over 46 years of catalytic study. I wish to extend my appreciation to all my friends and scholars, e.g., Prof. Chen Songying (Zhejiang University), Liang Changhai (Daliang University of Technology), Polock Yue (Hong Kong University of Science and Technology), Kong Yuhua (Hubei Research Academy of Chemistry), and Hu Weixiao, Chang Hai, Xiao Lihua, Wang Jianguo, Huo Cao, Shi Hongxian, Yao Nan, Li Ying, Hu Xiaojun, Zhou Chunhui, Han Wenfeng, Liu Zhongjian (Zhejiang University of Technology) *et al.*, and N. Pernicone (Universities of Milan and Venice in Italy) for their support, and also for the support from Chemical Industry Press in China, World Scientific Publishing Co. Ptc. Ltd. in Singapore and Zhejiang University of Technology. I thank Dr. Cen Yaqing for her assistance with preparation of this manuscript.

LIU Huazhang
18 December 2010

Foreword

Human beings live on grains and grain production is inseparable from fertilizers. In the past, human beings used to add animal excrements and rotten plants to soil as fertilizers. The use of chemical fertilizers has changed the history of grain production. According to Food and Agriculture Organization (FAO), the contribution of chemical fertilizers in grain production is about 40%. Without chemical fertilizers, more people would be under the threat of hunger and poverty. It would be impossible for China to feed the world's 22% population with only 7% arable land.

There are mainly three kinds of chemical fertilizers, i.e., nitrogen, phosphorus and potassium fertilizers. In order to increase the production and quality of grain, different kinds of chemical fertilizers should be used according to the nature of the soil and the crops. Among the three fertilizers, nitrogen fertilizer based on synthetic ammonia is the most widely used.

China is the largest producer of synthetic ammonia in the world. Ammonia production in 2007 reached 53 million tons in China, which greatly contributed to grain production. Producing synthetic ammonia is highly energy-consuming. The annual energy consumption for ammonia production is about 100 million tons of standard coal according to current energy consumption level, which is responsible for 3.4% of China's total energy consumption. Thus, reducing energy consumption in ammonia production is a great challenge for the industry. Practices show that reduction in energy consumption in chemical production mainly comes from technology advance in catalysts and process innovation. The catalytic ammonia synthesis process has been developed to a mature stage in the past century; therefore lower energy consumption will depend mainly on the technique development of catalysts and process improvement based on the new catalysts. Fortunately, the new generation of ammonia synthesis catalysts has been industrialized, which is expected to bring revolution to the ammonia synthesis industry. With the application of new catalysts, the syn-loop operating pressure will be further reduced. Through the use of $Fe_{1-x}O$-based fused iron catalysts and ruthenium catalysts, it is possible to realize the isotonic pressure ammonia synthesis for the process using partial oxidation of heavy oil at 8.7 MPa. If the pressure can be decreased to below 5 MPa, the isotonic pressure ammonia synthesis for the process using natural gas reforming can also be realized in the near future. With the innovation of new catalysts and related development of low pressure process, it is possible to skip out of the scope of high-pressure industry for ammonia synthesis, significantly saving energy. More than half of the output of ammonia in China is by small to medium scale equipments. Their energy consumption is 50% higher than that at the advanced level, thus with high potential in energy-saving. The application of new energy-saving catalysts and the technology based on low-pressure process are effective in saving energy.

Ammonia synthesis catalyst is well known as a textbook catalyst, which is mentioned in most of the textbooks and publications on catalysis. However, the information and knowledge about ammonia synthesis is not complete and only mentioned in some chapters of those books. In this sense, this book is a rare one, presenting relatively thorough and systematic description of ammonia synthesis catalysts and their industrial application.

The author, Professor Huazhang Liu, has been working in catalysts and related engineering techniques of ammonia synthesis for more than 40 years. He contributed a lot to the research of the Fe_3O_4-based, $Fe_{1-x}O$-based, and ruthenium-based ammonia synthesis catalysts. He invented the novel $Fe_{1-x}O$-based ammonia synthesis catalysts. His research also covers the theory and methodology on catalysts preparation, reaction mechanism, catalytic reactor, chemical engineering and related fields.

This book puts more attention on the development and applications of the catalysts with a combination of the author's experience and updated research results. This book is useful due to a combination of practices and theory, including the research, development, application and reaction engineering of catalysts. It has practical value as well as theoretical depth. These features make the book more comprehensive, novel and practical.

This book is of important reference value to researchers, engineers and graduate students who undertake catalysis research and industrial applications. It is believed that the publication of this book will promote the development and industrial applications of ammonia synthesis catalysts and is beneficial for energy saving of the ammonia synthesis industry.

Academician of the Chinese Academy of Engineering
CAO Xianghong
16 December 2010

Cao Xianghong

Professoriate senior engineer, Vice President and Chief Engineer of Sinopec Group, Board Director and Senior Vice President of Sinopec Corp., President of Chemical Industry and Engineering Society of China, Vice President of Chinese Petroleum Society, Vice President of China Energy Research Society, Director of Refined Products and Lubricant Technical Committee of Chinese Standardization Administration, Member of National Energy Expert Committee, and Member and Director of Chemical, Metallurgical and Materials Engineering Division of CAE (Chinese Academy of Engineering). Since 2008, he is Senior Advisor of the Sinopec.

Mr. Cao was born in Jiangsu in 1945. Since 1970, he had been working in Yanshan Petrochemical for 30 years and in Sinopec since 2000, responsible for the company's development and management of technology and production. He has contributed enormously to the improvement of Sinopec's core competitiveness and the development of China's refining and petrochemical industry. He has received many important national awards of science and technology, including five National Science & Technology Advancement Awards (one special prize, one first prize, one second prize and two third prizes), and nine Provincial/Ministry-level Science & Technology Advancement Awards.

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