

Ruthenium based Catalysts for Ammonia Synthesis

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Abstract

The development of alternate catalyst systems with required conversion levels under milder experimental conditions in terms of pressure and temperature as compared to those employed for ammonia synthesis on iron-based catalysts is one of the prime objectives of research today. In this connection, ruthenium-based catalysts with suitable support and promoter have been examined extensively. The status of the development and perspectives are examined in this presentation.

Introduction

The reaction that has contributed to sustainability of living beings on earth, as well as for most of the developments in science including catalytic science, is ammonia synthesis, introduced in the initial years of the last century, even though this process was known earlier. Catalytic ammonia synthesis technology has been playing a crucial role in the development of the chemical industry in the last 110 years. Ammonia is used mainly as nitrogenous fertilizer and as a raw material for the production of many of inorganic compounds like nitric acid, ammonium salts, cyanide and organic compounds, such as amines, sulfanilamide and many others in addition to being an excellent refrigerant^[1]. Ammonia has an important position in any economy since nearly 1 percent of total energy demand of the universe is utilized in this synthesis.

Historically, in the 19th century, ammonia was obtained from natural saltpeter or recovered from coal. In order to meet the increasing demand for nitrogenous fertilizers, a variety of methods were tried to fix nitrogen from air. From 1902 to 1913, three nitrogen-fixing processes were created, i.e., the electric arc process, calcium cyanamide process and catalytic ammonia syn-

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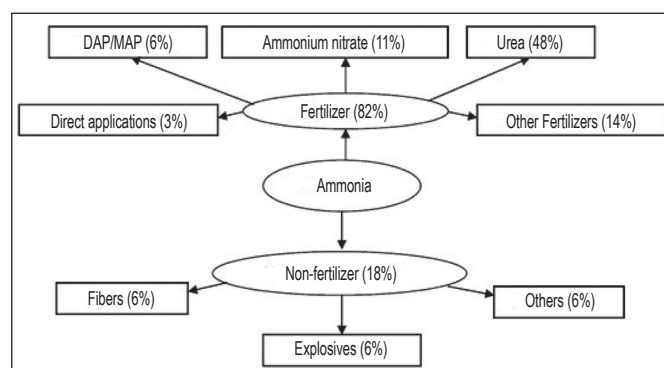


Fig 1. A flow chart on the possible uses (with percentages) of ammonia.

thesis technology.

Catalytic ammonia synthesis from dinitrogen and hydrogen molecule was developed by Fritz Haber, and then Carl Bosch applied this process to industrial production of ammonia successfully in the early years of 20th century. The first ammonia plant was built for the production of 30 tons of ammonia per day in 1913 at Oppau, Germany. Up to 1934, this catalytic process became the dominant route for nitrogen fixation. Because of the extensive use of nitrogenous fertilizers, catalytic ammonia synthesis plays an important role in agriculture and other industries.

There are various aspects of ammonia synthesis like economically generating the synthesis gas and their purification and also other engineering aspects of the process^[2]. In this presentation we will focus only on the development of Ru based catalysts for the ammonia synthesis reaction though other catalytic processes are involved in synthesis reaction.

Catalysts for ammonia synthesis

The development of catalyst systems for ammonia synthesis has seen many stages and tracing the history is now nearly impossible except for the observation that mostly iron based systems (especially magnetite Fe_3O_4) have been found to be active for industrial production of ammonia. However, as stated above, the energy requirement for this process especially for the production of synthesis gas is high and the ammonia synthesis step itself requires about 14 percent of this total energy consumed in this reaction. However, efforts have been on to reduce the temperature (instead of the usual range 400-500°C) and the pressure (150-300 bar) employed in the synthesis using magnetite catalyst.

Systematic study of the catalytic activities of various metal surfaces for ammonia synthesis was first made by Haber, including on easily and not so easily reducible metals. Platinum was also tested, but its activity is poor. Among these elements, some metals, such as Mo, V, and U are transformed into nitrides during the reaction.

Ru based catalyst

Around 1970s, British Petroleum and M.W. Kellogg companies developed a new type of catalyst, ruthenium over carbon support (Ru/C). The Kellogg advanced ammonia process (KAAP), now licensed by Kellogg/Brown & Root, Inc., uses a new Ru-based catalyst supported on graphite-containing carbon and co-promoted with Cs (Rb) and Ba. These promoters are supposed to be electronic ones, thus enriching the charge density around the metal centres. This process is capable of producing ammonia with a higher yield 40-50 percent

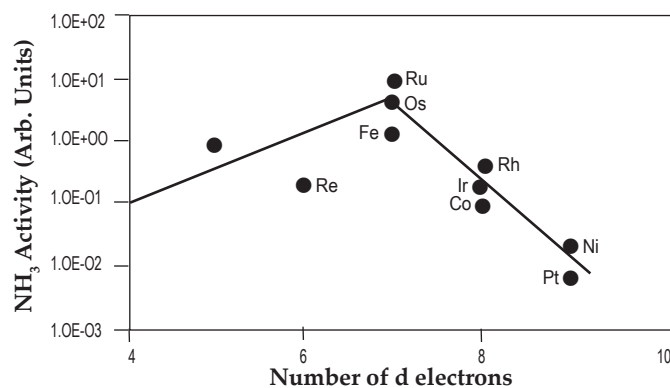


Fig.2. Typical volcano plot for activity correlation – between the d-electron configuration of the metals and activity for ammonia synthesis [reproduced from ref.3.]

➤ A new approach is to employ nano sized materials in catalyst formulation method to achieve more active ammonia synthesis catalysts. Reducing the size to nanometer range will greatly increase the surface area and possibly the active sites, which in turn increases the level of catalytic activity.

at lower pressures 50-100 atm and lower temperatures (370-400°C) conditions than those employed for a conventional Fe-based catalyst.

When ammonia synthesis activity is plotted against the number of electrons in d orbital for Group VIII metals, a volcano type plot is obtained. A typical plot is shown in Fig. 2. It is interesting to note that

the three most active metals (Fe, Ru and Os) have the same number of d-electrons namely 7 in their d orbital. Among these metals, the most commonly used catalyst is still magnetite (Fe based) because of its cost and availability issues, in comparison to ruthenium and osmium. It has been reported that ruthenium catalyst displayed five times higher activity under same temperature and at half the pressure.

Ruthenium is a rather rare element, comprising only about 10–8 percent of the earth's crust. It is one of the precious metals and its resources are scarce and expensive; the high content required in the catalyst's composition results in high cost and this impedes its commercial application. In fact, the major disadvantage of this catalyst system is its extremely high cost. Therefore, the development of active catalysts with lower Ru content is important for the economic use of Ru-based catalysts for ammonia synthesis.

Supported Ru-M (M = Fe, Co, Ni, Mo) bimetallic active center catalysts with a potassium electronic promoter for ammonia synthesis have been extensively studied. The activity of the Ru-Co catalyst was the highest, and the activity of the Ru-Mo catalyst was the lowest. Ruthenium is markedly promoted by addition of alkali (metallic or oxide mainly as electronic promoter) for the activation of dinitrogen, although it has the drawback of suffering from inhibition by hydrogen. The high activity thus attained makes it possible to reduce the reaction temperature so that the total pressure may be lowered to attain a desired conversion level. Another advantage of Ru is that it has lower susceptibility to poisons such as water and carbon monoxide than iron when promoted with basic oxides instead of alkali metals and their salts. Thus, the direct synthesis of ammonia from dinitrogen, is possible even if the feed contains carbon monoxide, and water as possible impurities on ruthenium-based catalysts.

Effect of Particle Size on Catalysis

A new approach is to employ nano sized materials in catalyst formulation method to achieve more active ammonia synthesis catalysts. Reducing the size to

nanometer range will greatly increase the surface area and possibly the active sites, which in turn increases the level of catalytic activity.

The importance of particle size effects in catalysis is of great interest. One goal in the development of nanocatalysts is to understand how decreasing the size of catalytic particles alters the intrinsic catalytic performance beyond simply expanding surface area. Nanosized effects in catalysis by metals have been known for a long time, since Professor Boudart's classification^[4] of structure-sensitive and structure-insensitive reactions. For both supported and unsupported particles various examples are known where the catalytic performance was proven to be dependent on particle size and shape. With decreasing particle size in the nanometer range, bulk properties are lost as the continuum of electronic states breaks down (i.e., quantum size effects) and as the fraction of surface atoms becomes large. Due to the different effects in terms of volume, quantum size, surface, and macroscopic quantum tunnel, nanometer-sized particles are expected to possess many improved properties over those of bulk and micrometer-sized particles. These reasons account for the versatility and effectiveness of nanocatalysts in controlling the activity, selectivity, and lifetime of catalysts. However, the drawbacks of these systems is due to factors related to thermal-stability and difficulties in separation of the catalyst particles after the reaction is completed.

Structure Sensitivity

The structure sensitivity of ammonia synthesis has been established from the observation that (111) Miller-index planes exposed iron surfaces are nearly 600 times as active as that of (100) or (110) planes of iron surfaces. It is possible that the particular process adopted in the production of iron-based catalysts with suitable support and promoter may be conducive to generation of these planes preferentially and thus could have accounted for the observed high activity.

The structure sensitivity of ammonia synthesis on ruthenium is ascribed to the presence of the so-called B₅ sites, which are believed to be extremely active and thus to dominate the reaction rate. B₅ type sites may exist on the surfaces of various metals, such as platinum, palladium, nickel, and ruthenium, and they were recognized early on to be responsible for strong physical adsorption of nitrogen. This aspect will be taken up in the next section. The fraction of B₅ sites in the supported Ru catalysts depends on both the crystal morphology and its size; the morphology is determined by the kind of support material. Promoters, like barium, do

not influence the number of active sites. They electrostatically modify the potential around the B₅ sites (electronic promotion), making them significantly more active for N₂ dissociation.

It may be worthwhile to compare the performance of Ru based catalysts with that of conventional industrial catalysts. In Table 1 the data on the rate of ammonia synthesis in the units of mmol per gram per hour are given at five different temperatures. These are only representative data and more extensive data are available in literature

Table 1. Ammonia synthesis rate in mmol. g⁻¹ h⁻¹ for Ru-based and commercial catalysts. [Data reproduced from *Chinese Journal of Chemical Engg.*, 19,273-277 (2011).

Temperature in K/ Catalyst	578	623	648	673	698
Ru based catalyst	38.4	70.8	101.2	108.9	97.5
A 302 catalyst	14.1	18.8	20.1	22.3	23.1

The data given in Table 1 possibly shows the higher performance level of Ru based catalysts for ammonia synthesis. However, the conversion levels will be far below the equilibrium levels only in both the catalysts.

Mechanistic aspects of ammonia synthesis

The reaction of nitrogen and hydrogen to yield ammonia is an exothermic reaction as shown in equation (1)



There is considerable energy barrier for the dissociative adsorption of nitrogen on metallic surfaces, but there is mostly none for hydrogen sorption. In this sense one can even consider that hydrogen can block the sites for the chemisorption of nitrogen. As stated previously, the active sites have been identified by Density Functional Theory (DFT) that an ensemble of five atoms (the so called B₅ sites) are appropriate for the activation of nitrogen. Typical models of B₅ sites in Ru (001) and small crystals sizes of 1.8 -2.5 nm of Ru metal are shown in Fig.3. In this configuration (namely B₅ sites) the Ru atoms expose a three-fold hollow site and a bridge site and part of the atoms have low coordination, which favours the activation of nitrogen. This configuration favours nitrogen activation though one of the atoms of the diatomic molecule. The formation of this type of sites may be favoured by the support and promoter species incorporated in the catalyst. The promoters not only contribute to the electronic density around the active sites but also may favour to segregate Ru atoms in this geometrical arrangement. The support depending on the extent of load-

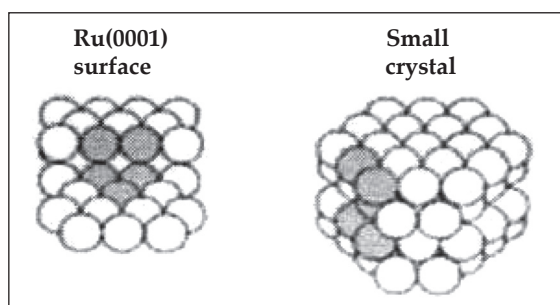


Fig 3. Models for B5 sites and small crystal of Ru metallic particle

ing of Ru atoms can give rise to different morphologies like round or flat surface (at high concentrations ~10 at %) and thus account for the differences in exhibited reactivities. It must be remarked that the nature of the support (heat sink and dispersion) and promoter (electronic or geometric) may have additional roles to play in ammonia synthesis reaction^[5].

Even though the activation of dinitrogen is an important and possibly also rate controlling in the synthesis of ammonia, it must be remarked that many metals form thermodynamically feasible nitrides and hence these metallic systems may not be suitable as catalyst for this reaction. The parameter of interest in this connection is the exothermic heat of chemisorption of nitrogen and the values for both supported and promoted ruthenium surfaces are in the range of 55-100 kJ/mol. Typical potential energy diagram is shown in fig 4. It can be deduced that nitrogen chemisorption is the rate controlling step and all other subsequent hy-

drogenation steps are facile process.

Preparation of Ru-based catalysts

The performance of ruthenium catalysts in ammonia synthesis depends on the loading and distribution of ruthenium particle sizes and shapes, which in turn depends on preparation methods and experimental conditions employed for the synthesis reaction. Different preparation methods mainly employing RuCl_3 as precursor have been used for synthesis of conventional ruthenium catalysts including melting, sublimation, ion exchange, precipitation, impregnation, and sol-gel methods, as well as microwave-assisted and ultrasound-assisted synthesis. The preparation methods of ruthenium nano-catalysts can be classified as impregnation, precipitation, in situ reduction, using the top-down or bottom-up approaches in order to control the particle sizes and shapes. The precursors commonly employed for loading Ru metal are the carbonyl complexes or acetylacetonate or chloride (including ruthenium ammonium chloride) or nitrate salts. The reduction conditions employed to generate the active catalysts depend on the precursor, temperature (depending on the supports used) and in turn control the size and shape of the Ru particle loaded on the support; (usually carbon supports give rise to smaller (~2 nm) particle sizes) and the pH used to precipitate the components.

Alkali, alkaline earth and rare earth metals are commonly employed as promoters for Ru based ammonia synthesis catalysts. Conventionally, the promoters are considered as contributing to the changes in electron density around the active site. However, it is necessary that one should elucidate the role of these promoters in dispersion (by altering the surface tension or surface forces) of the metal particle sizes and their shape. In addition, the exact role of these promoters in altering the poisoning effect by chloride ions (normally contributed by the precursor used) as well as the agglomeration or anchoring the active metallic particles (mostly dependent on the nature of the support employed) has to be established.

Epilogue

Answers to some of the challenges listed below will give better understanding on this industrially important reaction:

1. In spite of extensive theoretical and experimental studies on the effect of sup-

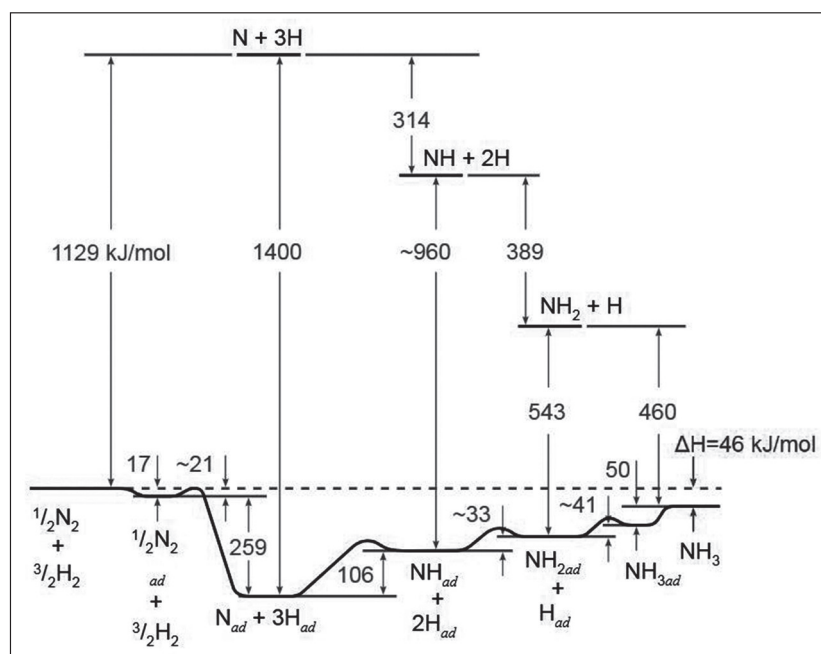


Fig 4. Potential energy diagram for ammonia synthesis [reproduced from literature]

- ports (the conventional supports employed for Ru based ammonia synthesis catalyst are various types of carbon, (possibly also participating in the side methanation reaction) meso-porous solids including zeolites, alumina, magnesia, ceria and so on and that of promoters (like Cs>Ba>K>Na on the basis of inverse trend of electronegativity values), their exact role in the observed turn over numbers of the ruthenium based catalysts has not been unequivocally established.
- There are various sizes (in the range 2 to 10 nm) of Ru metal particles are considered to be active and the methods employed for the determination of this parameter (TEM, CO or Hydrogen adsorption and XRD (not suitable for Ru particles) do not yield consistent results. It is necessary to establish an acceptable procedure.
 - Conventionally the role of supports and promoters are rationalized in terms of electronic or geometric factors. Their role in formulating, increasing and sustaining particular types of sites like terrace sites, step atoms and other geometry of the active sites is yet to be established. Though B₅ sites are considered the active sites for ammonia synthesis, there are reports, which claim other geometries to be also active for ammonia synthesis. This is one aspect which should be resolved for this reaction.
 - As stated above, the ammonia synthesis based on iron catalysts (a mature technology) is energy intensive. It is necessary that alternative technology with lesser energy consumption so as to satisfy the increasing demand for ammonia, based on alternate catalyst has to be formulated.
 - Though Ru-based catalysts have shown promise in ammonia synthesis, the performance of the catalyst is dependent on the nature of the promoter and support and this aspect has to be clearly discerned. In spite of extensive theoretical and experimental studies reported on this catalyst system, it is necessary that the exact role of support and promoter in the performance of the active catalyst system has to be elucidated.
 - It may be necessary now that more in situ studies are carried out on the active nano catalysts so as to understand and discern the exact nature of the active sites on this catalyst system.
 - More extensive theoretical studies are required to decipher the active sites, transition state, the active component-support and -promoter interactions at least on some of the real catalytic systems.
 - Novel combinations of supports and promoters should be predicted and tested for making this process to become industrially feasible.
 - Poisoning effect of hydrogen on the catalyst system proposed should be understood and it should be reduced.
 - Though the ammonia synthesis reaction consumes 14 percent of the total energy requirement for this process, it may still be possible to focus attention on the reduction of this energy requirement.
 - It may become essential to apply technically sophisticated analytical techniques, which can identify and evaluate molecular level active sites generated on the fabricated catalyst system. This will enable to design and fabricate new active catalyst compositions.
 - The role of the nature of the precursors (typical ones for Ru are RuCl₃, Ru(acac)₃, Ru₃(CO)₁₂, Ru(NO)(NO₃)₃, Ru(NH₃)₅Cl₃ and so on and similarly for the support and promoter), solvents (typically water, acetone, THF) and the reduction methodology (polyol, laser irradiation, and other reduction procedures using reducing agents like ammonia-Borane, hydrazine and others) and other conditions (precipitation, impregnation and other conventional preparation procedures must be properly identified more precisely.
- It may be noted that only a few aspects of ruthenium-based ammonia synthesis catalyst systems are outlined and there is scope for many other technological aspects of this reaction, which need careful consideration. The listing of the perspectives is only indicative and there is scope for improvement on this aspect. It is hoped that in the near future, the technology of ammonia synthesis will continue to keep maturing and more cost-effective production may become possible.

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