RAISING THE STANDARDS:
ENHANCED CATALYTIC PERFORMANCE
FOR GLOBAL AMMONIA PRODUCTION

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Overview

A multi-billion dollar global industry, catalysts are essential to the world’s industrial production. As much as 90% of all chemical processes utilize catalysts (petroleum refining, pollution abatement, and production of fuels and chemicals) and 60% of all consumer and industrial products (including fertilizers, plastics, pharmaceuticals, and batteries) are made using catalysts. Catalysts are now seen as a preferred way to improve process efficiency, lower costs, increase output, use less energy, and meet both performance and environmental standards. This places a strong emphasis on the development of new catalysts with higher activity, increased longevity, and reduced environmental impact.

With a global annual production capacity of over 195 million metric tonnes, and a market that is expected to exceed US$100 billion within the next five years, ammonia is the second most produced chemical on the planet. The most recent analyst consensus estimates that the market will grow at an annual rate of 3.1% from 2014-2019. China holds the largest market share, followed by India, Russia and the United States.

Global ammonia production consumes 1-2% of the world’s energy supply annually. Over 80% of ammonia output is used as agricultural fertilizer for both food crops (supplying 50% of all human protein consumed), and non-food crops including biofuel feedstocks.

The most common feedstock for ammonia production is natural gas, except for China and India which use coal. It has been estimated that the amount of greenhouse gases generated by ammonia plants globally exceeds 400 million metric tonnes annually, 1.6% of the total CO₂ emissions. Recent clean air mandates have focused on reducing plant emissions. These mandates, while posing a threat to the ammonia industry, are also a driver for innovation. For example, in the United States the Environmental Protection Agency seeks to cut carbon emissions 30% by 2030.

Ammonia is synthesized industrially from its precursors, molecular nitrogen and hydrogen, utilizing a century-old process at high temperatures and pressures. The chemical conversion rate is extremely slow and only happens at a reasonable speed in the presence of an iron-based catalyst, which is essentially the same process as used in the initial commercial setting over 100 years ago. The catalyst market is clearly in strong need of advanced higher performance catalysts that can operate in more moderate conditions with increased efficiency.

QuantumSphere, Inc. (QSI) catalysts have the potential to benefit numerous multi-billion dollar process applications in the refining, petrochemical, chemical, pharmaceutical, and agricultural industries.

Currently QSI’s lead application and commercialization focus the FeNIX™ nano iron catalyst for ammonia synthesis, a highly critical and energy-intensive process. By lowering the reaction temperature and pressure and increasing overall conversion efficiency, QSI’s turbo-charged nanoscale iron catalysts have demonstrated an increase in ammonia output of 10-15% in a production-scale ammonia plant. QSI believes a 20% increase in output is possible with further plant optimization. A 5% increase in production can translate into millions of dollars annually for a typical-sized plant. Widely deployed, this breakthrough promises not only significant energy and infrastructure savings to the 100-year-old Haber-Bosch process, but also compelling improvements in the net output of both food and fuel production.

QSI’s high surface area FeNIX™ nano iron catalysts have the potential to increase ammonia production by “turbo charging” existing commercial catalysts, achieving greater output in more energy efficient conditions.
COMPANY SPOTLIGHT

Founded in 2002, QuantumSphere, Inc. (OTCBB: QSIM) has the potential to access the $100 billion global ammonia market, and to generate $100+ million dollars in annual revenue within the industrial gases and chemicals industries over the next five years. In addition to nanoscale iron catalysts for enhanced ammonia synthesis, QSI is also developing advanced high surface area catalysts designed to increase the production efficiency of methanol and Gas-to-Olefins. The company anticipates formally undertaking external lab testing for these additional materials and target applications with one or more commercial partners in Europe and Asia to validate iron-, copper-, nickel-, and cobalt-based nano catalysts. Upon achievement of successful lab validation results, commercial validation testing will likely commence in production-scale chemical plants.

HISTORY OF AMMONIA CATALYST AT QSI

The utilization of nano iron for improving ammonia production efficiency was first proposed by QSI co-founder, Dr. Douglas Carpenter, in May 2007. Originally, it was suggested as a way to produce small amounts of ammonia onboard an automobile or larger vehicle to remove NOx from engine exhaust. Combining NOx and ammonia in a small selective catalyst reduction (SCR) converter produces water and nitrogen. This process works on both gasoline and diesel engines.

Ammonia production utilizing QSI’s nanoscale iron particles was reduced to practice on September 12, 2007 with pure unsupported nano iron at 400 °C and atmospheric pressure. Only a small amount of ammonia was produced, which was captured in water.

Further experiments using pure nano iron at 600 °C noted deactivation of the catalyst due to sintering in only three hours of operation. To reduce the sintering, the nanoscale iron particles needed to be dispersed onto a larger substrate. The use of standard ammonia catalysts as a support (utilizing BASF SG9801R ammonia catalyst) was first undertaken in January of 2009.

Testing QSI’s nanoscale iron particles in conjunction with many different commercial iron catalyst supports led to the realization that metal oxide promoters on the surface of those larger commercial catalysts were critical to the high activity and long life of the nano iron coating. The activity of the nanoscale iron was found to involve C7 sites and interaction with metal oxide promoters. QSI’s 30 nanometer-sized iron particles contain approximately 10,000 times as many C7 sites as the 2-3 millimeter-sized commercial iron particles, per gram.

Later in 2009, QSI’s ammonia synthesis system was improved through the addition of mass flow controllers, a back flow regulator, internal thermocouples and a new reactor oven. The foregoing permitted system operation up to 1000 psi, control of the space velocity in the reactors, and determination of the temperature profile in the catalyst bed. In November 2013, a 3000 psi ammonia synthesis system was built, tested and demonstrated at the lab facilities of a large Chinese ammonia plant operator using a mixture of hydrogen and nitrogen gases flowing directly from a commercial ammonia reactor. The system included titration equipment which provided the Chinese entity with the ability to continue testing different ammonia catalysts enhanced with QSI’s nano iron coating (Product Name: FeNIX™), flow rates, and pressures using mixed ammonia converter input gas. A new 6000 psi system was completed, calibrated and implemented in July 2014 at QSI.

A production-scale commercial validation commenced in China in Q-1 of 2015. The commercial validation resulted in an increase in ammonia production of 10-15% while decreasing the required operating energy.
Nitrogen is an essential element for life on Earth and a crucial nutrient to sustain plant life; it is present in the atmosphere in the form of the diatomic molecule $N_2$ ($N=\equiv N$). The triple bond is remarkably strong and its dissociation requires a large amount of energy (945 Kcal/mol). Thus, even though it is abundantly available in the air at ~78% by volume, it is hard to use. Bacteria and plants can convert nitrogen gas into ammonia in a process called biological nitrogen fixation. In the form of ammonia, nitrogen can undergo further processing in the nitrogen cycle of the biosphere and is used to create other compounds that are vital for humans both directly (amino-acid, DNA and RNA) and indirectly (chlorophyll). Humans learned how to convert nitrogen into ammonia synthetically over 100 years ago in a process discovered by Fritz Haber. The technology was purchased by BASF and the German chemist Carl Bosch scaled it up to industrial level. Both scientists were awarded the Nobel Prize for their critical research and the synthesis of ammonia is now known as the Haber-Bosch process, which takes place from the reaction between nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \text{(step 1)}$$

The conversion typically occurs at temperatures between 300-550 °C (572-1,022 °F), and under extremely high pressure between 150-250 bar. Thermodynamically, the formation of ammonia is favored at low temperatures and high pressure. However, because the reaction rate is very low, both high temperature and pressure are used in the presence of an iron-based catalyst to lower the activation energy of the reaction, which is, in the case of ammonia, the energy required to dissociate molecular nitrogen (Figure 1). The nitrogen atoms are then absorbed (ads) onto the catalyst and proceed to further reaction as detailed below:

$$N_2(\text{ads}) \rightarrow 2N(\text{ads}) \quad \text{(step 2)}$$
$$H_2(\text{ads}) \rightarrow 2H(\text{ads}) \quad \text{(step 3)}$$
$$N(\text{ads}) + 3H \rightarrow NH_3(\text{ads}) \quad \text{(step 4)}$$
$$NH_3(\text{ads}) \rightarrow NH_3(g) \quad \text{(step 5)}$$

Several points of evidence lead to the conclusion that step #2 is the slowest step. Above 750 bar, the conversion to ammonia can reach 100%. However, the amount of energy required to maintain this exceedingly high pressure is not practical and presents unreasonable safety concerns. Because of this, 150-250 bar is typically used. For example, at a temperature of 475 °C and 200 bar, the yield of ammonia generally ranges from 10-20%, which is low, but the costs of running the plants are also contained.

1.1 THE CATALYST

The function of the catalyst is to increase the reaction rate. In the absence of a catalyst, the reaction is so slow that it almost does not happen at all. The catalyst guarantees that the reaction proceeds at a reasonable speed during the short time that the gases are actually in the reactor so that they can combine to form ammonia. For the past 100 years the ammonia production process has been essentially unchanged and only a few major improvements on the catalyst have been made during that time.

For the past 100 years the Haber-Bosch process has remained largely unchanged.
2. GLOBAL AMMONIA MARKET

On a global scale, approximately 82% of ammonia is used for the production of fertilizers and nearly half of this is used for the synthesis of Urea (Chart 1). Ammonium nitrate, diammonium phosphate (DAP) and monoammonium phosphate (MAP) are other common fertilizers that are manufactured from ammonia. Only 18% is employed for uses other than agriculture.

Over 80% of the global ammonia production is used to synthesize fertilizers, which are responsible for sustaining over 30% of the Earth’s population.

This fraction is used as the precursor for the synthesis of important nitrogen-containing compounds like acrylonitrile, amino acids, hydrogen cyanide, hydrazine, hydroxylamine and many more. In the United States, because agriculture practices are highly developed, over 40% of ammonia is used directly for agricultural applications.

Chart 1. Ammonia is predominantly used for fertilizer production (82% in 2013). The remaining fraction is used as the precursor of many important chemicals. Source: Fertecon.
2.1 GROWTH IN THE GLOBAL AMMONIA MARKET

The global market of ammonia is highly fragmented (Chart 2). In 2013, China was the world’s largest producer of ammonia with a market share of more than 30%, producing nearly 70 million metric tonnes. India followed with 7.1% market share, Russia with 6.1% and the United States with 6.0%. In the United States, 36.5% of ammonia is imported, predominantly from Trinidad and Tobago (62%). The United States currently has approximately 28 plants owned by 13 companies, and in the next five years annual production capacity is anticipated to increase by approximately 7 million metric tonnes as additional ammonia plants go into production.

Historically, the production of ammonia has steadily increased over the past 100 years at a 2% growth rate. However, due to a strong increase in fertilizer demand, the ammonia market is expected to grow at an unprecedented 3.1% compound annual growth rate (CAGR) in the next five years (Chart 3A) and reach global revenues of over $100 billion in 2019. The consumption of ammonia for industrial purposes, other than agriculture, is slowly recovering from the economic recession of the past few years.

AMMONIA PRODUCTION CAPACITY BY REGION
2013 MARKET SHARE

Chart 2. Globally, ammonia production is a highly segmented market with China as the world’s largest manufacturer. Source: USGS.
Natural gas is the typical feedstock used for ammonia production in all countries, except for India and China. Therefore, it is a decentralized industry that relies on contingent factors. Additionally, the price of ammonia is highly dependent on the price of natural gas (Charts 3B and 3D). In 2013, the price of natural gas averaged $3.70 per million BTU, and has been stable for a long period, thus allowing companies to upgrade their plants. In 2014, the price of natural gas is forecast to average $3.84 per million BTU with prices continuing to increase over the next five years.

Several companies recently announced that they would build new ammonia plants, which together will add over 30 million tons of annual production capacity globally. Because of the low price of natural gas in North America, approximately 7 million tons of increased capacity are expected in the U.S. alone. New plants are under construction in Azerbaijan, Bolivia, Indonesia, Nigeria, Russia, China, and Saudi Arabia.

2.2 A NOTE ON CHINA

China is the largest producer of ammonia in the world with over 460 industrial plants and just below 70 million metric tonnes per year of production capacity. The industry is highly diversified and decentralized: ammonia plants vary greatly in size from 40,000 to 500,000 tonnes per year. More than 80% of ammonia in China is used to produce fertilizers. China’s typical feedstock is coal, so ammonia plants typically use atmospheric pressure fixed-bed batch process or oxygen-rich continuous coal gasification process.

Coal accounts for 80% of the total feedstock used in ammonia production in China. The remaining 20% comes from natural gas, for which imported processes have historically been used. However, China recently signed a 30-year agreement worth $400 billion to buy natural gas from Russia, so this ratio may change significantly over the next few years.

China is building several new plants and it is forecast that in 2015, the annual production capacity will reach 73 million tonnes per year. However, since its annual consumption will not increase as fast, it is likely that exports will grow.

2.3 CATALYSTS FOR AMMONIA: A GROWING MARKET DEMANDING INNOVATION

Nearly 90% of all global industrial chemical processes rely on the use of catalysts. The current global market of catalysts, including refinery, polymers and chemicals, is valued at $16.3 billion. World demand for catalysts is forecast to increase at 4.8% per year to $20.6 billion in 2018. The fastest growing regions in the catalyst market are Asia and the Middle East, while Brazil will be the leading country in Central and South America. The need for cleaner fuel and for energy efficient processes are strong drivers for this market. Driven by an ever-increasing agricultural demand for fertilizer, the market of catalysts for ammonia production is forecast to increase at a CAGR of 3.9% in the period 2014-2019.

The original catalyst used in the Haber-Bosch process was osmium, a rare transition metal found as a trace element in some ores. For economic reasons, it was soon replaced by less expensive iron-based catalysts promoted with metal oxides (like potassium, aluminum and calcium). Even though transition metal catalysts are available and can operate at milder conditions, the high cost of rare-elements is not competitive with inexpensive iron oxides. During the process, the iron oxide catalysts are reduced to metallic iron by exposure to heat and hydrogen gas. Even after reduction, the catalyst maintains a porous structure, which guarantees high surface area for nitrogen absorption. However, the pores tend to close up over time, reducing catalytic activity. 100 years since the discovery of the ammonia synthesis process, relatively few major improvements have occurred. As a result, there are major opportunities to make significant improvements.

Figure 2. The amount of greenhouse gases generated by ammonia plants exceeds 400 million metric tonnes annually. A more efficient catalyst may reduce not only energy costs, but also greenhouse gases emissions.
**Chart 3**

**A.**

**Global Ammonia Production Capacity Since 1960**

CAGR 2014-2019 +3.1%

Source: USGS

**B.**

**Ammonia Unit Value in $/Ton Since 1960**

Source: USGS

**C.**

**World Ammonia Capacity Addition in Million Tonnes (Excluding China)**

Source: Fertecon

**D.**

**Ammonia Production Cost**

Source: Fertecon
3. INTERNATIONAL MARKET TRENDS

Some of the most important global issues, such as the increasing world population and the need to decrease greenhouse gas emissions, are related, either directly or indirectly to the use of catalysts. Because ammonia production has such a great impact on population growth and on the global energy consumption, the use of a more efficient catalyst has the potential to dramatically offset these international trends. The schematic below delineates how all of these issues are interconnected.

![Scheme 1. Global trends lead to the same conclusion: the market's need for new catalysts.](image)

![Figure 3. QSI's FeNIX™ nanocatalyst (left image) can be applied to commercially available ammonia catalyst substrate (center image) to produce a thin layer (1.5% by weight) coating (right image), improving catalytic activity by up to 20%.](image)

4. QSI-NANO FeNIX™ CATALYSTS: COMPETITIVE ADVANTAGE

QuantumSphere’s proprietary technology consisting of iron nano catalysts used in ammonia production addresses the needs of a rapidly growing market that demands (i) more efficient catalysts; (ii) reduced greenhouse emissions; and (iii) decreased energy consumption.

Through commercial validation testing in industrial plants, precisely controlled testing in QSI and third-party laboratories, and complex academic modeling - compared to other existing commercial catalysts, QSI-Nano FeNIX™ catalysts have outperformed, displaying:

- Higher activity
- Improved durability
- Less degradation
- Faster light-off
We are committed to working closely with our partners to ensure that maximum performance of the catalyst is realized and cost savings is transferred to our customers.

Increased catalytic activity can result in:
- Less energy use
- Greater efficiency
- Reduced greenhouse emissions

4.1 INTELLECTUAL PROPERTY

QuantumSphere’s patented gas phase condensation (GPS) process (Patent No. 7,282,167 issued on October 16, 2007) produces advanced nanoscale catalysts. An additional patent application has been filed for the use of QSI’s FeNIX™ nano catalysts for more efficient ammonia production. QSI’s high surface area nanoscale iron particles can be applied to commercial catalysts and have demonstrated a significant improvement in activity, at lower temperatures and pressures in laboratories as well as full-scale production facilities. This enables improved per-pass conversion of the nitrogen and hydrogen gases in the ammonia loop that can translate into a decrease in energy consumption or an increase in capacity throughput, or a combination of both.

4.2 COMPETING TECHNOLOGIES

Synthetic or man-made nanoscale materials were first created in the 1970’s using the gas phase condensation method. Today, there are a dozen processes available for producing nanoscale materials worldwide. These processes include chemical vapor deposition, physical vapor deposition, reactive sputtering, laser pyrolysis, plasma gun spray conversion, mechanical alloying, grinding and sol gel, among others. Most of these manufacturing processes are extremely expensive and require sophisticated and complex equipment and labor-intensive maintenance. In addition, these methods may result in products with inconsistent particle size, distribution, morphology, shape and impurities, with little ability to scale up to commercial quantities at reasonable prices. Most importantly, catalyst material from these competing processes has not demonstrated increased efficacy in commercial chemical processes.

4.3 QUANTUMSPHERE’S PROCESS

QSI’s proprietary technology realized significant improvements in the fabrication of nanomaterials, specifically for narrowing particle size distribution, which can be obtained by reducing turbulence in the flow of vaporized material and cooling gas. The patented process is safe, environmentally friendly (closed loop), automated and requires low supervision and minimal down time for reactor maintenance. Unlike competitive processes, QuantumSphere has removed the potential for human error and much of the expensive labor from the manufacturing equation.
QuantumSphere’s increased production rates combined with lower labor and conversion costs have enabled commercial application of these advanced materials by industry-leading companies commercializing multiple consumer and industrial products. With the ability to deliver high quality nanoscale catalysts in commercial quantities at reasonable prices, QuantumSphere and its partners are opening the door to allow for mass-market penetration and accelerated commercialization of these new advanced materials. As every ammonia plant is unique, QSI is committed to working closely with its commercial partners to ensure that maximum performance of the catalyst is realized and cost savings is transferred directly to the ammonia plant operators.

FeNIX™ NANOcATALYSTS CAN BE USED WITH EXISTING COMMERCIAL CATALYSTS

Different from other technologies that may require a significant and costly re-design of the plant, QSI’s FeNIX™ catalysts can be seamlessly integrated and placed directly onto existing commercial catalysts, with minimal reconfiguration. Using existing equipment, with negligible upstreaming revamping, an older refurbed plant could gain up to 20% increased capacity. The highly increased activity of FeNIX™ (Chart 4) allows for lower operating pressures and temperatures.

FeNIX™ DISPLAYS IMPROVED AMMONIA CONVERSION OVER A WIDE TEMPERATURE RANGE

The performance of QSI’s FeNIX™ catalysts has been confirmed over a range of different space velocities and exhibits less sintering and deactivation than bare commercial catalysts. FeNIX™ enhanced catalysts deactivate over time at substantially lower rates than the commercial bare catalyst. This has been demonstrated using a number of commercial catalysts in high temperature side-by-side deactivation tests. FeNIX™ enhanced catalysts do not rely on the interior pore structure of the bare catalyst and are less prone to the deactivation that occurs in commercial ammonia catalysts due to pore shrinkage over time.

FeNIX™ EXHIBITS FASTER LIGHT-OFF ACTIVITY THAN COMMERCIAL CATALYSTS

FeNIX™ nanocatalysts begin producing ammonia (faster light off) at a much lower temperature than commercial catalysts (typically 100 degrees lower). As a result, FeNIX™ can be used in the entry catalyst bed to accelerate reduction of the remaining catalyst charge. Using FeNIX™, the entire converter can be activated in as little as 48 hours (Chart 5).
5. CONCLUSIONS

QuantumSphere is a leader in the production of advanced high surface area nano catalysts. Currently, the Company’s main application focuses on nanoscale iron-based catalysts designed to improve ammonia synthesis efficiency, a highly critical and demanding process from both energy and cost perspective. QSI’s leading product is FeNIX™ nano catalyst. FeNIX™ coated catalysts have been compared to many other bare commercial catalysts, and have displayed both higher catalytic activity as well as lower deactivation rate over time. A number of deactivation tests have confirmed these findings independently.

Many ammonia plants currently operate at maximum capacity and struggle to increase capacity further. By operating at lower temperature and lower pressure, QSI’s enhanced FeNIX™ catalysts address the need for greater energy savings and higher throughput, making them among the best ‘turbo charged’ catalysts for ammonia production currently available on the market.

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