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Process Intensification in Ammonia Synthesis Using Novel Co-assembled Supported Micro-porous Catalysts Promoted by Nonthermal Plasma

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Abstract:

Integrated Process Intensification approach is used for the synthesis of ammonia using novel coassembled microporous silica supported nickel catalysts and low temperature plasma reactors operating at ca. 140 ± 10 °C and ambient pressure. The conversion levels of nitrogen and hydrogen to ammonia is similar to that is achieved by the current industrial best practice which is however carried out at 100-250 bar and temperatures 350-550 °C. In order to achieve continuous plasma generation, a novel catalysts, which have a surface area of ca. 200 m²/g in the form of lamellae with ca. 2 nm thick plates of nickel catalyst sandwiched between the silica support plates, has been used in the presence of plasma catalysis promoters in the form of spheres made from high permittivity material. In addition to process variables (flow rate, feed composition and plasma power input) the effect of the electrode configuration on conversion was investigated. It is shown that there the catalyst activity remained constant over a continuous period of 72 hours when the reaction was terminated.

Keywords: Ammonia synthesis; Co-assembled catalysts; Dielectric barrier discharge; Plasma, Process intensification.

1. Introduction

Ammonia is the largest volume chemical in the world, consuming some 87% of industrial energy. Although it is a precursor for the manufacture of several pharmaceuticals and cleaning products, its main use (85%) is in agriculture as a fertilizer. Ammonia is synthesized by the Haber-Bosch process developed by Fritz Haber and Carl Bosch a century ago. However, currently, manufacture of this commodity chemical is carried out over several unit processes using fossil fuels as feedstock (mainly natural gas) and at pressures ranging from 100-250 bar and temperatures of 350-550°C. These primary processing conditions are dictated by the reaction kinetics and thermodynamics. Because ammonia synthesis from nitrogen and hydrogen is exothermic, thermodynamic equilibrium calculation indicates the benefit of its synthesis at lower reaction temperatures. Thermodynamic equilibrium theory also demonstrates that higher reaction pressure favors the formation of ammonia in the process. Due to low conversion rates (typically 15%), the unreacted hydrogen and nitrogen have to be separated from ammonia and recycled, hence periodic heating/cooling and pressurization/depressurization, as well as several separation stages, are required in industrial scale processes. A full account of ammonia technology is available.¹

Recently, a new integrated approach has been taken for ammonia synthesis in which the process was intensified and integrated with the end-use (in agriculture) of ammonia as fertilizers in order to intensify the biological plant growth and crop yield.² Fertilizers are introduced to soil either in liquid or solid form, including as slow release particles. However, the uptake of ammonia by plant is not simultaneous and due to washing by water and relatively low levels of interfacial area for mass transfer between plant roots and soil (Rhizosphere), only 30-50% of the fertilizer is used by the plant³. The rhizosphere area per unit volume of the plant⁴ in soil which can be considered as mass Transfer Area Density (TAD) is approximately $6 \text{ k m}^2/\text{m}^3$. In order to enhance TAD and to create a synthetic rhizosphere, SRS (or synthetic root system), micro-porous water absorbent polymers (known as sulphonated PolyHIPE Polymers) or their bioactive form have recently been used in particulate form as soil additive.^{3,4} These so called SRS-polymers are used as solid acids to react with ammonia produced in a process². Therefore a fertilizer-in-SRS-polymer is produced during ammonia synthesis in which relatively low levels of ammonia (10%) in the product stream is removed through acid-base reaction so that the unreacted hydrogen and nitrogen can be recycled. The resulting SRS-polymer filled with ammonium salt can be used directly as fertilizer and achieve

AgroProcess Intensification which occurs when the plant roots grow into the SRS-polymer.^{3,4} The crop or plant growth enhancement achieved by these SRS-polymers can range from 50-300%, especially under water and nutrient stress.^{3,4}

However, the in-situ reactive removal of ammonia from the reaction medium can only be cost-effective if the process is carried out at ambient pressures and temperatures at which the polymer is stable. In this study, we provide an alternative method of ammonia synthesis in which the reaction takes place at atmospheric pressure and low temperatures to achieve direct production of SRSpolymers containing fertilizer. However, the development of such a process requires a new approach to process design in which we adopt integrated process intensification approach.² In this approach, we not only design a new intensified plasma reactor system but also new catalyst system which is compatible with the operation of the plasma reactor.

Catalysts for ammonia synthesis include Fe, Co, Ru, Pt, Ni.⁵⁻⁸ Catalyst supports include graphitised carbon, boron nitride, magnesium oxide and alumina while catalyst promoters include barium.^{8,9} However, apart from Fe catalyst, only Ru/C catalyst has been adopted by industry.⁸

Non-thermal plasma is a promising technique to assist ammonia synthesis from nitrogen and hydrogen at low temperatures and under reduced pressure (<1.5 kPa).¹⁰⁻¹⁹ It has been reported that the electrode material, the catalyst in the plasma, the metals placed in the plasma region or the metallic walls of the reactor chamber can enhance the ammonia production, indicating the catalytic effect of the metals in the plasma.¹⁴⁻¹⁹

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Dielectric-Barrier Discharge (DBD) is one commonly used method for producing a non-equilibrium plasma at atmospheric pressure, which is an effective tool to generate energetic electrons. A great advantage of DBDs over other discharges is that the average energy of electrons can be influenced by changing either the gas pressure (or gas density) or discharge gap width. Thus, in a simple way, the chemical process under investigation can be optimized.²⁰⁻²² For the practical applications of plasma technology in ammonia synthesis from nitrogen and hydrogen at low temperatures, it is important to carry out the reaction under atmospheric pressure. To our knowledge, the ammonia

synthesis over porous catalysts promoted by non-thermal plasma at low temperatures and ambient pressure, has not been studied in detail in literature.^{6, 23-25} Bai et al²³⁻²⁵ studied the plasma synthesis of ammonia from nitrogen and hydrogen in a microgap dielectric barrier discharge at ambient pressure and temperature and shown that the ammonia concentration reaches just over 1 mol %. The microgap DBD could ionize and dissociate N₂ and H₂ molecules for ammonia production. When MgO powder was used as a catalyst in plasma, the ammonia concentration increased by a factor of 1.54-1.75, and reached 0.5% (v/v). Mizushima et al⁶ demonstrated that when an alumina membrane like catalyst is introduced into the nitrogen and hydrogen plasma, the ammonia yield is enhanced, and the further improvement can be achieved by loading the alumina film with Ru, Pt, Ni, and Fe.^{6,24} Metal catalyst loading in DBD-plasma reactors must be limited since it increases the conductivity of the catalyst particles leading to the extinction of plasma. Enhancement of electrical conductivity is particularly acute when for example carbon is used as catalyst support (i.e., Ru/C catalysts adopted industrially).

As summarized above, catalysts used in the Haber-Bosh process need to be adopted for DBD plasma applications in order to sustain the plasma for nitrogen dissociation. In this study, we use novel silica catalysts, some of which are coated to enhance plasma activity on the coat surface and to prevent plasma extinction. The reaction between the activated species takes place within the core of the catalysts. In order to prevent diffusional resistance, the catalyst itself is highly porous with a bimodal pore size in micron and nanometer scale. In some of the research published on the catalytic nonthermal plasma synthesis of ammonia, the catalyst activity decays rapidly thus rendering the process unacceptable. Therefore, the long term continuous testing of the catalyst activity should also be an important part of any study.

Finally, for industrial applications, it is necessary to consider the scale-up criteria of the process. In this study we adopt the process intensification philosophy of process design in which the production capacity enhancement is based on the numbering-up of the single reactor rather than physical enlargement. Integrated intensified processes are especially useful for production at small scale as they do not carry the burden of economies of scale.²⁶ When such processes are integrated on a global scale, they can deliver a sustainable production platform.^{26,27}

The objective of this study is to introduce an integrated-intensified ammonia production method which is fundamentally different then the Haber-Bosh process with particular emphasis on catalyst and its performance under plasma conditions.

2. Experimental

2.1 Materials

Gases: Hydrogen and nitrogen gases were supplied by BOC Industrial Gases, UK.

Glass spheres: Borosilicate glass spheres (3 mm in diameter) were purchased from Sigma-Aldrich Ltd, and used in the reaction without further treatment.

Barium titanate spheres: Barium titanate (BaTiO_3) beads with diameter of 1 or 3 mm, were obtained from Catal Ltd., and used without further treatment. The density of the BaTiO_3 spheres was 3.3g/cm^3 and the permittivity of these beads was about 1000.

Catalyst precursor: Catalyst precursor used in this study was analytical grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ supplied by Sigma Aldrich.

Silica dispersion: Epoxy silane (γ -Glycidoxypolytrimethoxysilane) coated silica dispersion was supplied by AkzoNobel in the form of a 30 wt% dispersion under the trade name of Bindzil 30 CC. The size of the silica particles was 7 nm. Despite its very large silica loading, its viscosity is low, thus enabling its processing using standard laboratory equipment.

Mass Flow Controllers (MFCs) and Gas Pre-mixing: MFCs (for accurate dosing of gases) and gas pre-mixing unit were supplied by Bronkhorst (UK) Ltd, UK.

Plasma electrode material: Stainless steel mesh (grade 316 Stainless steel) was purchased from F. H. Brundle. The mesh size was 3.175mm (LW), and 1.81 mm (SW). The strand width was 0.254mm, and its thickness was 0.152 mm. The open area of the mesh was 60%.

2.2. Analytical

BET Surface Area Analysis: A Beckman-Coulter SA 3100 analyzer was for the measurement of the specific surface area of the catalyst at various stages of its production and use using gas sorption technique.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Analysis: The scanning electron microscope used in the present work was an Environmental Scanning Electron Microscopy (XL30 ESEM-FEG) fitted with a Rontec Quantax system for Energy Dispersive X-Ray

(EDX) analysis to obtain local atomic concentration of various elements in metallic samples after heat treatment. Since the metallic samples were conductive, they were not coated. However, at high magnifications (i.e., 110k), the samples were gold coated.

Transmission Electron Microscopy (TEM): The fine structure of the catalyst samples were analyzed with a Philips CM100 Transmission Electron Microscope (TEM), and the images were collected using an AMT CCD camera.

X-Ray Diffraction (XRD): The X-Ray Diffraction (XRD) equipment was a PANalytical X'Pert Pro diffractometer, fitted with an X'Celerator. The X'Celerator is a relatively new attachment to the X'Pert and has the effect of giving a good quality pattern in a fraction of the time of the traditional diffractometer. XRD was not only used to identify the phase structures of the catalysts but also to estimate the crystal size using the Scherrer equation.^{28,29}

2.3. Catalytic Plasma Reactor

A general purpose gas-to-liquid plasma reactor system shown in Fig. 1 was established³⁰⁻³² and used both catalyst reduction and Fischer-Tropsch reactions.³² Fig 1a shows the overall flow diagram while Fig. 1b is the detail of the plasma reactor. We have used 3 different electrode configuration in order to enhance conversion and optimize reactor design. The electrode configuration are shown in Fig 2 which also shows how the Plasma Catalysis Promoters (PCPs) and the catalyst particles are located in the plasma discharge space (reaction zone).

(a)

(b)

Fig. 1 Flow diagram and diagram of the plasma reactor of the ammonia synthesis using low temperature plasma. (a) Flow diagram; (b) Diagram of the reactor. Adopted from².

2.3.1. Flow diagram

In the reactor system, hydrogen and nitrogen feed gases were supplied through the gas cylinders (No=202-n) in which the flow rates could be increased accurately by using more than one gas cylinder. In the case of any spectroscopic measurements, a separate reference gas supply was used (No=213). Flow rates are controlled through Mass Flow Controllers (MFCs) associated with each gas supply cylinder (No= 203-n). Feed gases (H_2 and N_3) were mixed (No= 204) before being fed into the plasma reactor. The reaction mixture emerging from the plasma reactor is cooled (No=212) and fed into an off-line analysis of the gases. The emerging gases from the reactor or from the offline analysis could be further analyzed using gas-chromatography/mass-spectroscopy facility before being discharged into the atmosphere.

2.3.2. Catalytic plasma reactor

A schematic diagram of the reactor is depicted in Fig. 1b. A Dielectric-barrier discharge (DBD) reactor was designed and constructed to incorporate High Voltage (HV) electrodes for plasma generation. It consists of two glass tubes one inside the other. The wall thickness of the glass tubes

is 1.5 mm. The outer glass tube had 32mm inner diameter and 300mm length. The inner tube had 17mm outer diameter. Hence the gap between the two tubes is 7.5 mm.

In Fig. 1b, both electrodes are outside the reactor and are not in contact with the catalyst or the reaction mixture. A stainless steel mesh was wrapped around the outer surface of the external glass tube and the other mesh was inserted inside the inner glass tube. A high-voltage power supply could feed between 0 and 150 W into the discharge reactor by adjusting the amplitude of the applied voltage. An alternating sinusoidal high voltage of up to 20 kV amplitude (peak-to-peak) and about 20 kHz frequency was applied to the stainless steel mesh electrodes. The discharge was maintained in an annular discharge gap of 7.5 mm radial width and 175 mm length, giving a discharge volume of about 100 ml.

The wall power consumed by the plasma system was measured by a plug-in power meter. The plasma power dissipated in the discharge was calculated by integrating the product of voltage and current. Voltage-charge Lissajous diagrams were recorded by using a TPS 2014 Four Channel Digital Storage Oscilloscope.

The plasma discharge volume of the reactor was filled with 100mL of glass spheres of 3mm in diameter, or 100mL of BaTiO₃ spheres of 3mm in diameter, or 100 mL of the porous Ni based catalyst (20 g) with the particle size of 2-3mm, or the mixture of above dielectric materials with porous catalysts. Prior to the plasma reaction, the catalyst was reduced at 550 °C in a hydrogen flow of 50 ml/min for 12 hours. After catalyst reduction, the furnace was switched off and the reactor was allowed to cool down to room temperature in the hydrogen flow of 50 mL/min.

The feed gases, N₂ and H₂, were introduced into the reactor from high-pressure bottles purchased from BOC via mass flow controllers (MFCs), admitting a total gas flow of 20 to 100 mL/min at room temperature (20°C). A back pressure valve at the inlet of the DBD reactor was used to regulate the pressure in the reactor up to a maximum pressure of 5 bar. The preselected temperature of the reactor could be maintained by a tubular furnace.

The concentration of ammonia in the effluent was measured by bubbling the reaction mixture from the reactor into a 10ml of 0.05M H₂SO₄ solution, using a methyl orange indicator to monitor the pH change of the solution at room temperature. When the color of the solution changes from pink to yellow, the H₂SO₄ in the solution is neutralized by ammonia from the effluent. The concentration of ammonia in the effluent is defined as,

$$\text{NH}_3 \% = 100 * \frac{24.04}{(V_{H_2} * t + V_{N_2} * t - 24.04)}$$

Where V_{H_2} is the input volume of hydrogen, and V_{N_2} is the input volume of nitrogen at 20°C; t is the time used to neutralize 10.0ml 0.05 M of H_2SO_4 by NH_3 produced by plasma; 24.04 is the molar volume of gas at 20°C).

The conversion of N_2 is defined as

$$N_2 \text{ Conversion (mole \%)} = 100 * \frac{N_2(\text{mole input}) - N_2(\text{mole output})}{N_2(\text{mole input})}$$

2.3.3. Electrode configurations

Fig. 2 illustrates the electrode configurations in the plasma reactor. Here, the cross-section of the reactor is shown with the high permittivity spheres (glass or barium titanate) mixed with catalyst particles. The outer electrode (No=206) or the inner electrode (No=207) are placed either outside the glass reactor (Fig. 2a) or inside the reactor (Fig. 2b,c). In order to reduce power consumption, it is preferable to use a solid stainless steel rod as the inner electrode when it is in the annular gap as in Fig. 2 a,c. Therefore, the following electrode configurations are available: (i) Both electrodes are outside the reaction space (Fig 2.a); (ii) Both electrodes are in contact with the reactants and catalysts (Fig.2b) and (iii) Outer electrode is in contact with the reactants/catalyst (Fig 2c).

Fig. 2 *Electrode configurations in plasma reactor. Adopted from².*

2.4. Silica supported nickel catalyst preparation through co-assembly of catalyst and support

The novel generic supported catalyst series used in this study was based on the co-assembly of the catalyst and support precursor in liquid induced by combined and radiation.³³ Using the notation in the description of these catalysts³³, this catalyst is coded as Ni/Si=1/4 Mw-ABC. The molar ratio of catalyst (Ni) to support (SiO_2) was $[Ni]/[Si]=1/4$. At this catalyst/support molar ratio of 1/4, the

corresponding weight fraction of NiO in the SiO₂ support is 0.24. Sufficient amount of catalyst precursor salt, Ni(NO₃)₂ · 6H₂O was dissolved in the catalyst support precursor fluid (Bindzil CC30) to obtain the desired molar ratio. The pH of this fluid was 5.5. 10 ml of this fluid was placed in a 19 cm diameter watch glass and subjected to microwave radiation at 1 kW power for a period of 4 minutes at room temperature. Microwave radiation was carried out on a turn-table to ensure uniformity of irradiation. As a result of this treatment, an expanded, highly porous silica supported nickel oxide solid mass was obtained. This material (coded as Ni/Si=1/4 Mw-A) was then heat treated at 600 °C in order to burn off the silane coating. Starting from room temperature, the furnace was heated at a rate of 10 °C/min. After reaching 600 °C, the temperature was kept at this temperature for another hour before turning off the heat. The catalyst was allowed to cool down over a period of 24 hours. This material was coded Ni/Si=1/4 Mw-AB. After reducing the size of the heat treated supported catalyst, it was placed into a tubular reactor with a stream of hydrogen at a rate of 50 ml/min (STP) and reduced for 24 hours at 550 °C. The resulting supported catalyst (in reduced form) was coded as Ni/Si=1/4 Mw-ABC. The reduced catalyst was then used in the ammonia synthesis and the resulting spent catalyst was coded as Ni/Si=1/4 Mw-ABCD.

The size of the supported catalyst particles was ca. 2-3 mm. 20g of the reduced catalyst pellets were introduced into the dielectric discharge gap (100 mL) of the plasma reactor thus giving a bulk density of 0.2 g/cm³.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD and BET surface area

XRD pattern of the catalysts at various stages (including that of the spent catalyst after 24 hours of operation) are shown in Fig. 3. These stages include: (A) Microwave irradiation of the catalystsupport precursor solution; (B) Heat treatment at 600 °C; (C) Reduction; and (D) Use in ammonia synthesis. In this figure, bands at $2\theta = 36.9^\circ$ and 43.2° (dominant peak); 62.7° are associated with NiO and the bands at $2\theta = 44.5^\circ$ (dominant peak); 51.9° and 76.4° are associated with Ni. The broad peak at $2\theta = 21.9^\circ$ is SiO₂. The ‘apparent’ catalyst sizes are calculated using the Sherrer equation^{28,29} and are based on the dominant peaks at $2\theta = 43.2^\circ$ (for NiO) and $2\theta = 44.5^\circ$ (for Ni). The summary of the XRD catalyst size is given in Table 1 where BET surface area data are also summarized. As seen in Fig.3, the peaks associated with NiO and Ni for the spent catalyst

(Ni/Si=1/4 Mw-ABCD) are very weak and broad indicating that this catalyst is almost amorphous. Hence the catalyst size is referred to as being $< 1\text{nm}$. However, the amorphous silica support with a broad peak at $2\theta = 21.9^\circ$ appears to develop crystalline structure as apparent from the sharp peaks appearing at $2\theta = 20.1^\circ$ and $2\theta = 22.1^\circ$

The catalyst surface area reduces with heat treatment. However, the surface area appears to increase slightly after being used in ammonia synthesis.

Fig. 3 XRD pattern of the micro-porous nickel catalyst at various stages of processing (A,B,C) and after being continuously used for 72 h in ammonia synthesis. Nickel catalyst is supported on SiO_2 at a molar ratio of Ni/Si=1/4. a) Microwave synthesis from the catalyst and supported precursor fluid (Ni/Si=1/4 Mw-A); b) Heat treatment of sample from stage-A at 600°C (Ni/Si=1/4 Mw-AB); c) Reduction of sample from stage-B at 550°C in hydrogen for 24 hours (Ni/Si=1/4 Mw-ABC); d) After continuous synthesis of ammonia for 72 h (Ni/Si=1/4 Mw-ABCD). XRD-based crystallite sizes at the dominant peaks are summarized in Table 1.

Table 1 Summary of the XRD-based catalyst size and BET surface area for the catalyst at various stages of processing and use.

(Stage): Sample Code	NiO size $2\theta = 43.2^\circ$	Ni size $2\theta = 44.5^\circ$	Surface Area (m^2/g)
(A): Ni/Si=1/4 Mw-A	3.50	-	208
(B): Ni/Si=1/4Mw-AB	4.49	-	196
(C): Ni/Si=1/4 Mw-ABC	3.08	2.76	181
(D): Ni/Si=1/4 Mw-ABCD	< 1	< 1	187

3.1.2. Catalyst imaging by SEM

Scanning electron microscopy (SEM) imaging in Fig.4 provided here is only useful in the assessment of the overall micro-structure, showing the hierarchic pore structure at micrometer and sub-micrometer levels. These images show that the catalyst system is highly porous, thus providing mass transfer with diffusion path length at micrometer-to- sub-micrometer level.

Fig. 4 Scanning Electron Microscopy images of the silica supported catalyst obtained after stage-A (Sample Ni/Si=1/4 Mw-A) showing the hierarchy of the pores in the bulk (a,b) and within the walls of the catalyst (c,d) at different magnifications. (a) Scale bar= 10 μm ; (b) Scale bar= 5 μm ; (c) Scale bar= 1 μm ; (d) Scale bar= 500 nm.

Fig.5 represents the SEM image (Fig. 5a) of the sample Ni/Si=1/4 Mw-AB and distribution of the catalyst (Ni/NiO) (Fig 5b) and support (SiO_2) (Fig 5c) on the surface and within the core of a catalyst oxide particle before being reduced in hydrogen atmosphere and ammonia synthesis. It can be seen from Fig. 5b,c that the porous skin of the catalyst is dominantly Ni/NiO while the walls of the catalyst contains less nickel. In order to quantify the relative values of $[\text{Ni}]/[\text{Si}]$ on the skin and the within the walls of the catalyst, the Energy Dispersive X-ray (EDX) spectra at two locations are taken as indicated on Fig.5a. These locations correspond to the skin and within the core of the catalyst. The molar ratio of nickel and silicon at these two locations are $\{[\text{Ni}]/[\text{Si}]\}_{\text{skin}} = 0.746$ and $\{[\text{Ni}]/[\text{Si}]\}_{\text{core}} = 0.251$ respectively. We note that the skin/core structure is repeated within a catalyst particle because of the mechanism of the catalyst generation. Hence, all of the porous walls have a skin layer where the catalyst/support concentration ratio is higher compared with the walls of the catalyst particles. As a result, although overall catalyst/support ratio is $[\text{Ni}]/[\text{Si}] = 0.25$ in the catalyst sample, the distribution of $[\text{Ni}]/[\text{Si}]$ is not uniform and is dependent on whether or not skin or the walls are dominant in the location where the EDX-spectrum is taken.

The conductivity of the catalyst is therefore high which can result in local electrical discharge and temperature rise. This is prevented by using two isolated electrodes (Reactor-1). In the case of one

isolated or no-isolated electrode, it is possible to coat the surface of the catalyst with a porous layer using a high permittivity material, such as barium titanate.²

Electron Image 3

(a)

Si Kα1

Ni Kα1

(b)

(c)

Fig. 5 Electron image of the catalyst Ni/Si=1/4 Mw-AB before being reduced and subsequently used in ammonia synthesis. (a) SEM image; (b) Si distribution; (c) Ni distribution.

3.1.3. Catalyst imaging by TEM

TEM imaging of the catalyst at two magnifications (100k and 450k) are shown in Fig.6. These images show that the catalyst and support form a lamellar structure which appear as ribbons with printed bar-codes. Here, the catalyst is in the form of sheets, ca. 0.6 -2 nm thick and ca. 10 nm wide. These ribbons can extend over several hundred nanometers. The XRD-based catalyst size is therefore an average size. In this respect, the current catalyst system is fundamentally different from the classical supported catalysts which appear as near spherical particles on the support. The current technique, not only results in small overall structure, but also allows very high catalyst loading. Due to the formation of lamellar structure, where the catalyst domains are prevented from coalescence because of the presence of silica layers, catalyst size does not change significantly during heat treatment.

NiSi14A 2.tif
NiSi14 A
Cal: 0.128584 nm/pix
12:28:22 10/09/13

20 nm
Direct Mag: 450000x
EM Research Services

NiSi14AB 2.tif
NiSi14 AB
Cal: 0.128584 nm/pix
13:10:22 10/09/13

20 nm
Direct Mag: 450000x
EM Research Services

(a)

(b)

(c)

(d)

Fig. 6 Transmission Electron Microscopy of the nickel catalyst at various stages of processing (A,B,C) and after being continuously used for 72 h in ammonia synthesis. Nickel catalyst is supported on SiO₂ at a molar ratio of Ni/Si=1/4. (a) Microwave synthesis from the catalyst and supported precursor fluid (Ni/Si=1/4 Mw-A); (b) Heat treatment of sample from stage-A at 600 °C (Ni/Si=1/4 Mw-AB); (c) Reduction of sample from stage-B at 550 °C in hydrogen for 24 hours (Ni/Si=1/4 Mw-ABC); (d) After continuous synthesis of ammonia for 72 h (Ni/Si=1/4 Mw-ABCD). Scale Bar=20 nm in all figures.

3.2. Ammonia synthesis using catalytic plasma reactors

Catalytic plasma reactors were used previously for ammonia synthesis at low temperatures and atmospheric pressure.¹⁰⁻¹⁹ However, both ammonia yield was very low and the catalyst activity decayed very rapidly. In these experiments plasma was generated across the discharge gap which was very small in order to sustain plasma activity. Here we use a relatively large discharge zone but maintain the plasma activity through spherical high permittivity materials such as barium titanate. We refer to these high permittivity spheres as ‘Plasma Catalysis Promoters’ (PCPs). The voids generated through the random filling of PCPs (ca. 36%) is then partially filled by the catalyst particles. As illustrated previously (Section 3.1.2), catalyst particles are not good conductors and

their conductivity is even more reduced at the surface by virtue of silica rich skin. This process ensures that the plasma is maintained across the gap and over the PCPs and catalyst particles. Therefore, the diffusion path length of the reactive species generated by plasma is reduced as these reactive species react with the reactants adsorbed on the catalyst surface.

We therefore initially investigate the contribution made by PCPs in ammonia synthesis. In this investigation we also study the effect of H_2/N_2 molar ratio on conversion. Subsequently, we evaluate the effects of catalyst, electrode configuration and plasma power input on ammonia generation.

3.2.1. Effect of plasma catalysis promoter (PCP) and H_2/N_2 molar ratio on ammonia synthesis

To get a better understanding of the reaction under plasma conditions, we carried out the experiment by applying non-porous glass and $BaTiO_3$ spheres in the plasma discharge zone. In these experiments we used Electrode Configuration-1 in which both electrodes were outside the reactor (Fig 2a) in which the volume of the discharge zone (filled with PCP) was 100 ml. Total input flow rate of the gases was 25 ml/min. The external wall temperature was kept at 150°C. The H_2/N_2 molar ratio range was 0.5 – 4. Following the determination of NH_3 concentration in the effluent stream, N_2 conversion was calculated and tabulated in Table 2. The plasma power input (wall power) remained constant during the continuous process. The tabulated NH_3 concentration and N_2 conversion values quoted in Table 2 are obtained after 24 hours of continuous reaction.

Table 2 Plasma ammonia synthesis over 3 mm diameter Plasma Catalysis Promotor (PCPs) using glass spheres and $BaTiO_3$ spheres

Type of PCP	H_2/N_2 (Molar Ratio) $\Rightarrow$	0.5	1	2	3	4	Wall Power
Glass Spheres	NH_3 concentration (%)	2.8	3.0	2.9	3.1	3.0	115 W
	N_2 Conversion (%)	2.0	2.9	4.2	6.0	7.2	
$BaTiO_3$ Spheres	NH_3 concentration (%)	3.0	3.6	3.7	3.8	3.2	93 W
	N_2 Conversion (%)	2.2	3.4	5.3	7.3	7.8	

$BaTiO_3$ spheres in the plasma zone resulted in higher ammonia concentration and nitrogen conversion at all H_2/N_2 molar ratios while operating at a lower power input compared with the glass spheres.

Varying the molar ratio of H_2/N_2 had only small influence on the ammonia concentration in the effluent when the molar ratio is higher than one using glass balls as barrier material in the discharge gap. The highest ammonia concentration over glass balls reached 3.1% when the wall power was at 115W and the molar ratio of hydrogen to nitrogen was 3. For $BaTiO_3$ balls, the concentration of ammonia in the effluent increased with increasing H_2/N_2 molar ratio, reaching a maximum value of 3.8% when the H_2/N_2 ratio was 3. In contrast, at molar ratios above 3, the concentration of ammonia decreases further with an increase in the molar ratio. It is important to note that the conversion of N_2 increases with an increase of the molar ratio over both glass balls and $BaTiO_3$ balls in the discharge zone. The maximum N_2 conversion reached 7.8% over $BaTiO_3$ balls when the molar ratio is 4/1 at the discharge power of 78W.

As mentioned by Eliasson and Kogelchatz²², one important property of DBD is that the average energy of the electrons produced in the discharge can be influenced by varying the product of discharge gap (d) and the gas density (n) which is proportional to gas pressure. The parameter between $n \times d$ and the electron energy (ϵ) is the reduced breakdown field. If there is no barrier material in the discharge gap, the gap width is 7.5mm which is large compared to the normal gap width of 1mm or less in DBD experiment. The large discharge gap width will result in the formation of a spark-like discharge and lower average electron energy. When the dielectric barrier materials, glass balls or $BaTiO_3$ balls, are filled into the discharge gap, the effective discharge gap is reduced. Therefore, homogenous plasma can be formed between the balls due to the significantly increased breakdown field in the DBD reactor. A higher fraction of the electrons in the discharge can get sufficient energy to activate the nitrogen and hydrogen molecules for the formation of ammonia.

Permittivity, which characterizes the tendency of the atomic charge in an insulating material to distort in the presence of an electric field, is an important factor affecting ammonia synthesis from N_2 and H_2 under plasma conditions. The larger the tendency for charge distortion (also called electric polarization), the larger the value of the permittivity of a material will be. Generally, substances with high permittivity break down more easily than materials with low dielectric constant in intense electric fields. The permittivity of glass is 4-6, and that of $BaTiO_3$ is about 1000 which can improve the dielectric barrier discharge performance in the process. It is clear that the higher permittivity material such as $BaTiO_3$ balls favors the ammonia synthesis from N_2 and H_2 in the plasma by generating more activated species at lower energy consumption. Therefore, in the subsequent experiments, we only used $BaTiO_3$ as PCP in the discharge zone and H_2/N_2 molar ratio of 3 (stoichiometric value).

3.2.2. Effect of catalyst

The incorporation of catalyst into the reactor can be carried out in different ways. Here we mixed the catalyst with the PCP (BaTiO_3) so that the catalyst separated the PCPs, thus minimising the distance between the plasma zone for the generation of reactive species and catalyst zone for the promotion of the reaction. In these experiments, we used Reactor-1 where the electrodes were outside the reactor. In all cases, the plasma and mixed PCP and catalyst zone was 100 ml. The weight percent of catalyst in the PCP+Catalyst mixture could be changed by using different sized catalyst particles, since the catalyst had hierarchic pore structure.

The processing conditions were: $\text{H}_2/\text{N}_2 = 3/1$; total gas flow rate was 25 ml/min; the wall temperature of the reactor was 150 °C. The wall power was changeable for each set of experiments due to the fact that the generation and maintenance of plasma required increasing power input with increasing catalyst concentration. The results, obtained after 24 hours of continuous run, are shown in Table 3.

Table 3 The effect of catalyst concentration ($\text{Ni/Si}=1/4$ Mw-ABC) on the ammonia synthesis in a DBD reactor with 3 mm diameter BaTiO_3 spheres as PCP

Catalyst		NH ₃ conc. (%)	N ₂ Conversion (%)	Wall power (W)	Specific Energy MJ/mol
Wt %	Vol %				
0 ^a	0	3.8	7.3	93	143
4.5 ^b	50	6.4	12	115	107
10.8 ^c	60	5.7	10.7	125	132
100 ^d	100	5.9	11.2	140	140

$\text{H}_2/\text{N}_2 = 3/1$, Total flow rate: 25ml/min; External wall temperature of reactor :150°C. ^a

330 g (100 ml) BaTiO_3 spheres were used in the plasma zone; ^b 8 g (50 ml) catalyst

($\text{Ni/Si}=1/4$ Mw-ABC) mixed with 165 g (50 ml) BaTiO_3 spheres ; ^c 16 g (60 ml)

catalyst ($\text{Ni/Si}=1/4$ Mw-ABC) mixed with 132 g (40 ml) BaTiO_3 spheres; ^d 20 g (100

ml) catalyst ($\text{Ni/Si}=1/4$ Mw-ABC).

In the plasma assisted ammonia synthesis over catalysts, we consider at least 2 factors affecting the reaction. The first factor is to generate plasma activated species, and the second is to let the activated species react on the surface of a catalyst to form more ammonia. Our experiment reveals that BaTiO₃ (or glass) spheres in the plasma can promote the formation of plasma. At the same time, the plasma activated species between BaTiO₃ (or glass) spheres can form ammonia either on the surface of BaTiO₃ (or glass) spheres or in the gas phase when there is no catalyst in the discharge. The results from Bai et al²⁵ in which the discharge zone did not have any PCP, indicates that the conversion in the gas phase was very low (ca. 1%). Therefore, we can conclude that BaTiO₃ and glass surfaces do have a catalytic effect on ammonia formation.

In order to achieve a better synergy effect on ammonia synthesis, we studied the effect of the combination of dielectric material (BaTiO₃ spheres) with the amount of catalyst in the reaction. The results are summarized in Table 3. If we keep the total volume of the mixture of catalyst and BaTiO₃ spheres as constant, and vary the volume ratio of catalyst and BaTiO₃ spheres, it is clear that the amount of catalyst influences not only the ammonia concentration and nitrogen conversion, but also the energy consumption in the plasma. When the amount of the catalyst in the mixture of a catalyst plus BaTiO₃ spheres is increased from 0 to 100% in the plasma zone, the energy consumption increases from 93W to 140W while the nitrogen conversion increases from 7.3% to 11.2%.

In the reaction, using 100% of BaTiO₃ spheres in the plasma zone gives only 3.8% of ammonia, and using 100% of the catalyst gives 5.9% of it in the effluent. The specific energy consumption is nearly the same (1.43×10^8 J/mol and 1.39×10^8 J/mol respectively). A proper amount of the catalyst with BaTiO₃ spheres in the plasma improves the reaction significantly with apparently improved specific energy consumption (1.07×10^8 J/mol). The concentration of ammonia in the effluent reached the maximum (6.4%) with the nitrogen conversion of 12% when the volume ratio of catalyst to BaTiO₃ spheres was 1/1 (4.5% w/w). Although the ammonia concentration and nitrogen conversion decreases with an increase in the catalyst amount in the mixture, they are still higher than that with 100% BaTiO₃ balls only in the plasma zone, indicating that the catalyst in the mixture can promote the reaction. The optimization of the composition of the catalyst and dielectric material for the highest synergy effect is important in plasma catalysis.

The increase in plasma power with increasing catalyst can be explained by considering the conductivity of the silica supported catalyst particles. It is likely that the conductivity of the catalyst can be reduced by surface coating of the catalyst particles using high permittivity materials such as BaTiO₃ in which plasma is generated within ca. 10 µm (thickness of the coating) rather than several millimeter away on the surface of the PCPs.

3.2.3. Effect of plasma reactor configuration

For a better understanding of the influence of the reactor configuration on the reaction under plasma conditions, we expose one of the two electrodes to the catalyst and the mixture of nitrogen and hydrogen by moving the external stainless steel mesh electrode from the external surface to the internal surface of the external glass tube of the reactor (Reactor 2, Fig. 2b). The results are summarized in Table 4.

Table 4 *The Influence of reactor configuration on the reaction*

Reactor Type	Catalyst		NH ₃ conc. (%)	N ₂ Conversion (%)	Wall power (W)	Specific Energy MJ/mol	Reactor Wall Temperature (°C)
	Wt%	Vol%					
Reactor-1	0 ^a	0	3.8	7.3	93	143	150
Reactor-2	0 ^a	0	3.8	7.3	77	112	130
Reactor-1	4.5 ^b	50	6.4	12	115	132	150
Reactor-2	4.5 ^b	50	6.4	12	87	81	130

H₂/N₂ =3, Total flow rate: 25ml/min; Catalyst: Ni/Si=1/4 Mw-ABC^a

BaTiO₃ Spheres: 330 g (100 ml); Without catalyst;

^b A mixture of 8 g (50 ml) catalyst + 165 g (50 ml) BaTiO₃ spheres;

When the discharge gap of the reactor was filled with a mixture of catalyst and BaTiO₃ spheres, compared with the reactor with 2 electrodes insulated by quartz tubes (Reactor-1), the plasma energy consumption was reduced by 32% (from 115W to 87W) for the same amount of ammonia production (6.4%) and the same level of nitrogen conversion (12%). At the same time, the wall temperature of

the reactor was decreased to 130°C. From the data listed in Table 4, it is apparent that the same effects have been observed when introducing the BaTiO₃ spheres in the discharge gap by comparing the results from Reactor-1 to Reactor-2. Therefore, the reactor configuration is an important factor to be taken into account for plasma catalysis. It is quite possible that the stainless steel mesh electrode can also catalyze the reaction when it is exposed to the plasma activated N₂ and H₂ species in plasma.

In Table 4, the specific energy conversion for various catalyst and reactor configuration was also calculated. It can be seen that the specific energy of ammonia production can be reduced from 143 MJ/mol obtained for Reactor-1 and 100% BaTiO₃ PCPs is reduced by 56% to 81 MJ/mol when the Reactor-2 is used with 4.5 wt% catalyst occupying the DBD reaction space.

The 3rd reactor configuration as represented in Fig. 2 (c) when both electrodes are placed within the reactor space and therefore are in contact with PCPs and the catalyst. In this case, plasma could not be maintained because of arcing. Therefore, the experiments were not continued.

3.2.4. The effect of plasma power

The effect of plasma wall power on conversion was investigated using Reactor-1 and a mixture of catalyst (4.5wt% + 95.5 wt% BaTiO₃ spheres) at the fixed H₂/N₂ ratio of 3 and total gas flow rate of 25 ml/min. The conversion and ammonia concentration data were obtained after 24 h of continuous reaction. The results are shown in Fig. 7 which show near linear enhancement of conversion with wall-power. At the highest power input (195 W), the conversion is over 16% above the values achieved in current industrial ammonia production at high pressures and temperatures. At this conversion rate, the specific energy consumption is 137 MJ/mol which is very close to the result obtained for the lower wall power for the Reactor-1 configuration.

Fig. 7 The effect plug-in power on nitrogen conversion and ammonia concentration in the effluent gas using Reactor-1 (both electrodes are isolated) when $H_2/N_2 = 3/1$; Total flow rate: 25ml/min. Plasma reaction zone was filled with 4.5 wt% Catalyst + 95.5 wt% BaTiO₃ spheres.

3.2.5. Long term continuous operation

It is important to evaluate the long term operational characteristics of the process to identify any catalyst deactivation. Although the data supplied for ammonia synthesis was based on 24 h continuous operation, we have also investigated the catalyst and reactor performance over a period of 72 hours. In this study, the Reactor-2 electrode configuration was used and the catalyst system consisted of 4.5 wt% Ni/Si=1/4 Mw-ABC and 95.5 wt% BaTiO₃ as PCP (see Section 3.2.3). The results are shown in Fig.8 which indicates that there is no decay in catalyst or plasma activity over a period of 72 h. These results also justify the results on conversion that the data represent the steady state conditions.

Fig. 8 Effect of reaction time on the reaction activity of the mixture of catalyst with BaTiO₃ balls in a dielectric barrier discharge plasma using Reactor-2 configuration when H₂/N₂ = 3/1, Total flow rate: 25ml/min; Wall Power : 87W; Wall Temperature: 130°C. Catalyst mixture in the plasma zone consisted of 8 g (50 ml) catalyst Ni/Si=1/4 Mw ABC + 165 g (50 ml) BaTiO₃ spheres.

3.3. Effect of plasma reaction on catalyst

In Fig. 3, the XRD patterns of the catalyst are presented at various stages of preparation and after it was used in ammonia synthesis. The XRD based catalyst crystallite sizes (using the dominant band) are shown in Table 1. As seen from Fig. 3 and Table 1, the catalyst crystallite size (either as NiO or Ni) is significantly reduced after it was used in ammonia synthesis for 24 h. However, two new sharp bands associated with SiO₂ appear indicating increase in the crystallinity of the support as seen in the XRD-pattern of the spent catalyst Ni/Si=1/4 Mw ABCD. The examination of the TEM images (at magnification of 450k, the highest magnification available) of the fresh catalyst (Ni/Si=1/4 Mw ABC) and the spent catalyst (Ni/Si=1/4 Mw ABCD) indicates no obvious changes in the lamellar (bar-code) structure. It is therefore likely that the lamellae sheets of SiO₂ and catalyst (NiO/Ni) remain unchanged but the crystallite size within these lamellar sheets changes.

3.4. Mechanism of ammonia synthesis by the combination of DBD and catalyst

Ammonia is considered to be produced via the dissociative adsorption of N₂ and H₂, followed by stepwise addition, the hydrogenation of adsorbed N and the intermediates, NH and NH₂, over the surface of catalysts.³⁴ In contrast to the Haber-Bosch process, N₂ and H₂ molecules can be activated / dissociated in the gas phase under plasma conditions. Several research groups have demonstrated that ammonia formation is dependent on the type of reactor wall material in plasmas. The reactor wall is considered as catalyst to form adsorbed nitrogen atoms or molecular nitrogen ions in ECR plasma or glow discharge.^{17,15,35} Helden et al^{36,37} demonstrated that ammonia formation is strongly dependent on the fluxes of N and H radicals to the catalyst surface by using an Expanding Thermal Plasma (ETP) Technique. By optimizing the atomic N and H fluxes to the surface using an atomic N and H source, ammonia can be formed efficiently. However, it was also demonstrated that ammonia production is independent of wall material.^{13,36} It has been demonstrated that metals behave as a catalyst for ammonia production in plasmas.^{14-16,18,19,24,37} Ammonia is considered to be formed via NH radicals as an intermediate under plasma conditions. Some authors suggested that the NH radicals can be formed via ionization of nitrogen molecules (Reactions (1-6) below) by using radio frequency plasma, microwave plasma, ECR plasma, or ETP at low pressures.^{11,13,17,19,36,38}

In a DBD, the average energy of energetic electrons is in the range of 1 – 10 eV, which is higher than the dissociation energy of H₂ (4.52 eV) and N₂ (9.8 eV).²⁰ The ionization potential of N₂ is 15.6 eV, which is much higher than the average energy of energetic electrons in a DBD. So, the formation of NH via N₂⁺ route could be negligible in DBDs. In a non thermal plasma, highly energetic electrons are generated which can dissociate and excite N₂ and H₂ molecules, creating ground and excited hydrogen and nitrogen atoms and molecules (H, H₂; N(⁴S, ²D, ²P) and N₂ (A³Σ_u⁺)). It is these atomic and molecular species that are responsible for the formation of NH₃ in plasma.

The initial step for the electron-impact dissociation of H_2 is described as

and the initial step for the electron-impact dissociation of N_2 is described as

The activation of nitrogen (Reaction 8) is the key step of ammonia production in a DBD due to its high dissociation energy (9.8 eV). The excited nitrogen ($N_2(A^3\Sigma_u^+)$, 6.2 eV) can experience dissociation to form N radicals on the surface of catalysts, and this process can be catalyzed / promoted by the stainless steel mesh electrode or the nano-porous catalyst exposed to the plasma activated nitrogen and hydrogen species in a DBD. In this case, the stainless steel mesh electrode can be a catalyst for N_2 and H_2 activation. However, the difference between the surface area associated with the electrode and catalyst are vastly different and hence we can assume that the contribution to ammonia formation by the catalyst is more pronounced than the exposed electrode. However, the activation of nitrogen and hydrogen are closer to the electrode.

The NH radicals are produced by the reaction of N with H or H_2 (Reaction 9-13). Especially N (2D) is a key species for the formation of NH radicals because other excited states N(4S , 2P) are generally quenched rapidly at atmospheric pressure. These reactions may be promoted on the surface of catalysts or stainless steel mesh in plasma. The reaction of excited H with N_2 (Reaction 14) may occur, but this reaction is probably negligible considering the high dissociation energy of N_2 .

The NH radicals formed on the surface of catalyst can react with H₂ or H to form NH₂ radicals (Reactions 15-17), and then form NH₃ by stepwise addition reactions between NH₂ with H₂ or H radicals on the surface of catalyst (Reactions 18,19).

4. Conclusions

Principles of Process Intensification were applied to develop a sustainable small scale ammonia production method operating at 130-150 °C and 1 atm using low temperature plasma generated over a wide gap containing plasma catalysis promoters and a novel silica supported nickel catalyst. The characteristics of the catalyst were evaluated at various stages of processing. The highly porous catalyst is in the form of lamellae sandwiched between the support material obtained through the coassembly of the support (SiO₂) precursor and catalyst precursors (NiNO₃) in the precursor fluid.³³ This method already achieves ammonia concentrations reached in industrial scale production which is carried out at above 350 °C and 100 - 250 bar. The extended (upto 72 h) continuous processing time indicates that the plasma and catalyst activity are maintained and the catalyst structure does not change although XRD-based catalyst size reduces from ca. 3 nm to less than 1 nm after the reaction. It is shown that the reactor electrode configuration is important in achieving high conversions at lower temperatures and power consumption.

A mechanism for the reaction is proposed. The highly reactive species from hydrogen and nitrogen generated by the combination of dielectric barrier material and porous catalyst in a DBD can make ammonia synthesis possible at relatively low temperatures and atmospheric pressure. Applying higher dielectric constant material such as BaTiO₃ spheres in the discharge gap can enhance the ammonia concentration and nitrogen conversion at the reduced energy consumption for ammonia synthesis from nitrogen and hydrogen at low temperature and ambient pressure in a DBD. The

catalyst property and its distribution in the discharge gap play an important role in ammonia synthesis in plasma. Proper amount of catalyst in the mixture of catalyst and BaTiO₃ balls in the discharge gap can increase the ammonia concentration and nitrogen conversion significantly at low energy consumption. By exposing one of the two electrodes to the reactant gas and catalyst, the specific energy consumption can be reduced by ca. 60% for the same amount of ammonia production (6.4%) and the same level of nitrogen conversion (12%). Maximum conversion per pass through the DVB reactor with one expose electrode at wall power of 195W was 16% with corresponding ammonia concentration of 9%.

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