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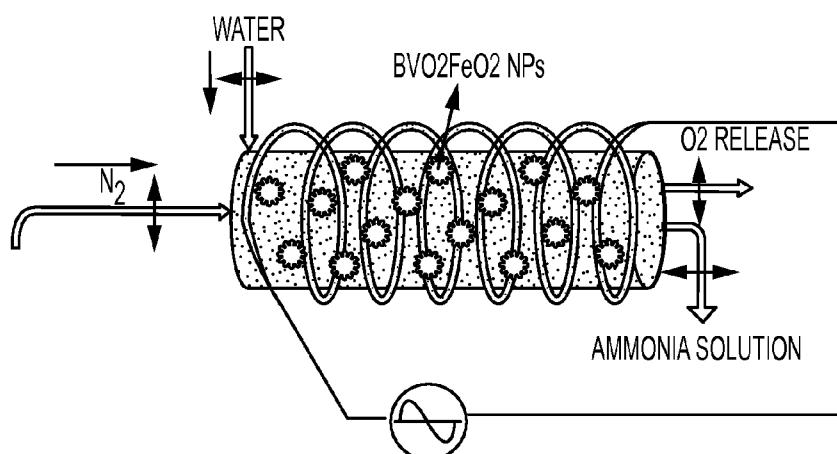
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**FIG. 3**

(57) **Abstract:** Disclosed herein are methods and systems to produce ammonia from nitrogen and water. In an embodiment, a method of producing ammonia involves contacting nitrogen, water, and at least one superparamagnetic catalyst to form a mixture, and exposing the mixture to a fluctuating magnetic field. In some embodiments, the superparamagnetic catalyst is BVO_2FeO_2 .

METHODS AND SYSTEMS FOR PRODUCING AMMONIA

RELATED APPLICATION

[0001] This application claims priority to Indian Patent Application No. 3476/CHE/2014, filed July 14, 2014, entitled, “Methods and Systems for Producing Ammonia,” the contents of which are herein incorporated by reference.

BACKGROUND

[0002] Ammonia synthesis is an important industrial process. Ammonia is produced in huge quantities worldwide, for use in the fertilizer industry, as a precursor for nitric acid and nitrates for the explosives industry, and as a raw material for various industrial chemicals. The dominant ammonia production today is the energy intensive Haber-Bosch process invented in 1904 which requires high temperature (500 °C) and/or high pressure (150–300 bar). However, in practice, both high pressures and temperatures are used due to a sluggish reaction rate. Due to overall low reaction efficiency when hydrogen and nitrogen are first passed over the catalyst bed, most ammonia production plants utilize multiple adiabatically heated catalyst beds with cooling between beds, typically with axial or radial flow. These steps are not economical due to increased operational and capital costs. Thus, it is desirable to produce ammonia efficiently and economically.

SUMMARY

[0003] Disclosed herein are methods and systems to produce ammonia from nitrogen and water. In an embodiment, a method of producing ammonia involves contacting nitrogen, water, and at least one superparamagnetic catalyst to form a mixture, and exposing the mixture to a fluctuating magnetic field.

[0004] In an additional embodiment, a method of preparing a catalyst involves contacting vanadium pentoxide with a first base to form a first reaction composition,

contacting the first reaction composition with boric acid to form a second reaction composition, contacting the second reaction composition with a second base to form a third reaction composition, contacting the third reaction composition with a bidentate ligand to form a fourth reaction composition, and contacting the fourth reaction composition with Fe_2O_3 to form the catalyst. In some embodiments, the catalyst produced herein is a superparamagnetic catalyst.

[0005] In a further embodiment, a reactor system for producing ammonia from nitrogen includes a closed reaction vessel configured to receive nitrogen, water, and a superparamagnetic catalyst, and at least one current carrying element arranged in proximity to a surface of the reaction vessel and configured to provide a fluctuating magnetic field.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 depicts a diagram of a reactor system to produce ammonia from nitrogen and water according to an embodiment.

[0007] FIG. 2 represents a putative structure of BVO_2FeO_2 according to an embodiment.

[0008] FIG. 3 represents an illustrative diagram of a reactor system to produce ammonia from nitrogen and water, according to an embodiment.

[0009] FIG. 4 depicts an X-ray diffraction pattern of BVO_2FeO_2 according to an embodiment. XRD of BVO_2FeO_2 indicates it is a polycrystalline material and was acquired on a Xperts Pananalytical X-Ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) with scanning range (2θ) of 10 to 90. The peaks 2θ at 25.00, 33.31, 34.80 and 61.40 correspond to vanadium iron oxide, iron borate, iron vanadium oxide and vanadium borate; pcpdf files are – 38-1372, 76-0701, 75-0317 and 17-0311; corresponding Millar indices (h k l) values are (1 2 0), (1 0 4), (3 1 1) and (1 0 4).

[0010] FIG. 5 shows vibrating sample magnetometer measurements of BVO_2FeO_2 catalyst according to an embodiment.

[0011] FIG. 6 shows schematics of the reaction mechanism of water and nitrogen to form ammonia according to an embodiment.

DETAILED DESCRIPTION

[0012] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0013] Disclosed herein are methods and systems to produce ammonia from nitrogen and water. In some embodiments, a method of producing ammonia involves contacting nitrogen, water, and at least one superparamagnetic catalyst to form a mixture, and exposing the mixture to a fluctuating magnetic field. The nitrogen may be from any source, such as natural gas, air, flue gas, and the like.

[0014] FIG. 1 depicts an illustrative diagram of a reactor system **100** in accordance with a specific embodiment of the present disclosure. System **100** may be utilized for a one-step process for the production of ammonia from nitrogen and water. The reactor system (or apparatus) **100** generally comprises a reaction vessel **101**, an inlet valve for nitrogen **102**, an inlet valve for water **103**, and a current carrying element **104**. A pair of outlet valves for O_2 gas **105** and ammonia **106** may be present in the reaction vessel **101**. The inlet valves may be configured to allow entry of nitrogen and water into the reaction vessel. Further, the catalyst BVO_2FeO_2 **107** may be disposed within the reaction vessel.

[0015] In some embodiments, the reactor system **100** comprises at least one current carrying element **104** arranged in proximity to a surface of the reaction vessel and configured to provide a fluctuating magnetic field. Current carrying elements may include,

for example, substrates having conductive or magnetic properties. Further, current carrying elements may be configured to generate magnetic fields of various strengths. The greater the current flow and coil density, the stronger the magnetic field. For instance, coil density may be high in order to produce a uniform magnetic field. In addition, the quantity of power required to achieve a particular magnetic field may depend on various factors, including the scale, structure, and location of the current carrying element with respect to the reaction vessel.

[0016] In other embodiments, the reactor system described herein may further include at least one thermoelectric couple, at least one pressure gauge, at least one temperature controller, at least one cooling system, at least one mechanical stirrer, or any combination thereof. In some embodiments, the current carrying element may be in close proximity to the reaction vessel. In other embodiments, the current carrying element may form a circular coil around a reaction vessel, as illustrated in FIG. 1. According to some embodiments, the strength of a magnetic field generated by the current carrying element may have various strengths, such as about 0.1 millitesla to about 1 tesla, about 0.1 millitesla to about 0.5 tesla, about 0.1 millitesla to about 0.1 tesla, about 0.1 millitesla to about 10 millitesla, about 0.1 millitesla to about 1 millitesla, or any range between any two of these values (including endpoints). The current carrying elements may be energized using various methods, including, without limitation, direct current, alternating current, and high-frequency alternating current. According to embodiments, the high-frequency alternating current may have various values, such as about 25 hertz (Hz) to about 1 megahertz, about 25 hertz to about 500 kilohertz, or about 25 hertz to about 100 kilohertz. Specific examples include, but are not limited to, about 25 hertz, about 100 hertz, about 500 hertz, about 1 kilohertz, about 100 kilohertz, about 200 kilohertz, about 300 kilohertz, about 400 kilohertz, about 500 kilohertz, and about 1 megahertz, or any range between any two of these values (including

endpoints). In some embodiments, the electric current may have various values, such as about 0.1 ampere (A) to about 100 A, about 0.1 ampere to about 50 A, about 0.1 ampere to about 30 A, or about 0.1 ampere to about 1 A. Specific examples include, but are not limited to, about 0.1 A, about 1 A, about 5 A, about 10 A, about 20 A, about 50 A, and about 100 A, or any range between any two of these values (including endpoints).

[0017] The reactor system described herein may be a batch reactor system or a continuous flow reactor system. In some embodiments, the reaction vessel is configured to maintain a substantially constant pressure of nitrogen during the reaction process. For example, nitrogen may be present at various pressures, such as a pressure of about 1 millibar to about 1 bar, about 1 millibar to about 500 millibars, about 1 millibar to about 100 millibars, or about 1 millibar to about 10 millibars. Specific examples include about 1 millibar, about 5 millibars, about 10 millibars, about 15 millibars, about 20 millibars, about 100 millibars, about 200 millibars, about 300 millibars, about 400 millibars, about 500 millibars, and about 1 bar, or any range between any two of these values (including endpoints).

[0018] The catalyst **105** that may be used in the reaction system **100** may be a superparamagnetic catalyst, such as BVO_2FeO_2 , BVOFe_3O_4 , $\text{BTiO}_2\text{Fe}_2\text{O}_3$, $\text{BCrO}_2\text{Fe}_2\text{O}_3$, and any combination thereof. In some embodiments, the catalyst may be in the form of nanoparticles. The catalyst described in the embodiments herein may be unsupported or may be supported by distribution over a surface of a support in a manner that maximizes the surface area of the catalytic reaction. A suitable support may be selected from any conventional support, such as polymer membrane or a porous aerogel. For example, the catalyst may be coated on a polymer membrane and woven into a 3D mesh and introduced in the reactor system **100**.

[0019] In some embodiments, the catalyst described herein may be present in the reaction mixture at various concentrations, such as about 0.1 mole percent to about 1 mole percent, about 0.1 mole percent to about 0.5 mole percent, or about 0.1 mole percent to about 0.2 mole percent of the total reaction mixture. Specific examples include, but are not limited to, about 0.1 mole percent, about 0.2 mole percent, about 0.5 mole percent, about 0.7 mole percent, and about 1 mole percent, or any range between any two of these values (including endpoints).

[0020] In some embodiments, the water may be present in the reaction mixture at various concentrations, such as about 99 mole percent to about 99.9 mole percent, about 99 mole percent to about 99.6 mole percent, or about 99 mole percent to about 99.3 mole percent of the total reaction mixture.

[0021] In some embodiments, the reaction mixture is exposed to a fluctuating magnetic field for various periods of time, such as about 30 minutes to about 3 hours. In some embodiments, the reaction mixture is exposed to a fluctuating magnetic field for about 30 minutes to about 2 hours. In some embodiments, the fluctuating magnetic field is applied for about 30 minutes to about 1 hour. In some embodiments, the reaction mixture is exposed to the fluctuating magnetic field for about 30 minutes, about 45 minutes, about 1 hour, about 1.5 hours, about 2 hours, about 3 hours, or any value or range of values between any of these values (including endpoints). At the end of the reaction process, the superparamagnetic catalyst may be recovered by applying a magnetic field. For example, a bar magnet may be used to collect BVO_2FeO_2 particles at the end of the reaction and reused.

[0022] BVO_2FeO_2 may act as a solid-state source of electrons in liquids, enabling a new pathway for induction catalytic reduction in which electrons are directly ejected into reactants. This approach may be particularly advantageous to achieve induction chemical reduction of otherwise difficult-to-reduce species, such as N_2 that bind only weakly to most

surfaces, such as V used as a catalyst in the experiments, that combines with the proton generated (H^+) at the catalytic site. Further, H^+ and OH^- may be generated from water by the same catalyst. The mechanism is illustrated in FIG. 6.

[0023] The methods disclosed herein may produce aqueous ammonia. Processes for removal of ammonia from dilute aqueous solutions are well known in the art and may be performed by stripping with an inert gas such as air, nitrogen, or the like and then extracting the ammonia from the gas by absorption in an acidic medium. The gas, after passing through the ammonia absorbing medium is recycled so that the stripping is performed in a closed loop. The stripping may be performed at pH 10.5-11.5 and at 140-180 °F. The pH of the aqueous waste may be adjusted by adding caustic soda solution. A commonly used acidic medium for absorption of ammonia from the gas is aqueous sulfuric acid. During absorption the acid solution is recirculated to allow a build-up of ammonium sulfate until a portion of the salt may be crystallized. Mother liquor is then fortified with acid and recycled.

[0024] Also disclosed here are methods to prepare a catalyst. In some embodiments, the method involves contacting vanadium pentoxide with a first base to form a first reaction composition, contacting the first reaction composition with boric acid to form a second reaction composition, contacting the second reaction composition with a second base to form a third reaction composition, contacting the third reaction composition with tetramethylethylene diamine (TEMED) to form a fourth reaction composition, and contacting the fourth reaction composition with Fe_2O_3 to form the catalyst. In some embodiments, the catalyst produced herein is a superparamagnetic catalyst.

[0025] In some embodiments, vanadium pentoxide is mixed with a first base to form a first reaction composition, and mixing may be performed for various periods of time, such as for about 3 minutes to about 30 minutes, about 3 minutes to about 20 minutes, about 3 minutes to about 15 minutes, or about 3 minutes to about 10 minutes. The first base may

generally be any base, such as NaOH, KOH, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, or NH_4OH , or any combination thereof. Mixing may be performed by generally any technique, such as stirring, shaking, sonication, and the like.

[0026] In some embodiments, the first reaction composition is mixed with boric acid to form a second reaction composition, and mixing may be performed for various periods of time, such as for about 3 minutes to about 30 minutes, about 3 minutes to about 20 minutes, about 3 minutes to about 15 minutes, or about 3 minutes to about 10 minutes. Mixing may be performed by generally any technique, such as stirring, shaking, sonication, and the like.

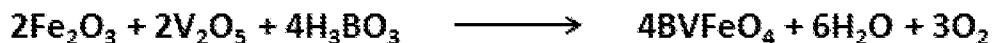
[0027] In some embodiments, the second reaction composition is mixed with the second base to form a third reaction composition. Non-limiting examples of second base are sodium borohydride, KOH, LiOH, $\text{Mg}(\text{OH})_2$, NH_4OH , and any combination thereof. Mixing may be performed for various periods of time, such as for about 30 minutes to about 60 minutes, about 30 minutes to about 50 minutes, about 30 minutes to about 40 minutes, or about 30 minutes to about 35 minutes. This mixing may be performed at generally any temperature, such as a temperature of about 70 °C to about 120 °C, about 70 °C to about 100 °C, about 70 °C to about 90 °C, or about 70 °C to about 80 °C. Mixing may be performed by generally any technique, such as stirring, shaking, sonication, and the like.

[0028] The third reaction composition may optionally be cooled to room temperature, and mixed with a bidentate ligand to form a fourth reaction composition. Non-limiting examples of bidentate ligand include acetylacetonate, phenanthroline, an oxalate, tetramethylethylene diamine (TEMED), trimethylene diamine, and any combination thereof. Mixing may be performed for various periods of time, such as for about 2 minutes to about 15 minutes, about 2 minutes to about 10 minutes, about 2 minutes to about 5 minutes, or about 2 minutes to about 3 minutes. In some embodiments, the bidentate ligand may be

TEMED, and TEMED solution may be diluted with water to a final concentration of about 1-5% (v/v) and mixed with the third reaction composition.

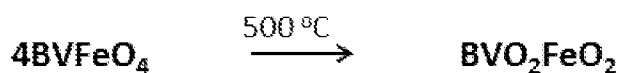
[0029] In some embodiments, the fourth reaction composition is mixed with Fe_2O_3 for various periods of time, such as for about 10 minutes to about 60 minutes, about 10 minutes to about 50 minutes, about 10 minutes to about 40 minutes, or about 10 minutes to about 30 minutes. In some embodiments, the Fe_2O_3 described herein may be dissolved in H_2O_2 , such as 10% (v/v) H_2O_2 before mixing with the fourth reaction composition.

[0030] After the mixing the fourth reaction composition with Fe_2O_3 , the solvent may be removed or evaporated. This step may be performed by generally any known process, such as heating, rotary evaporation, air drying, Soxhlet extraction, reflux condenser, or evaporating in an oven until the solvent is substantially evaporated. For example, the solvent may be heated to an elevated temperature, such as about 80 °C, about 100 °C, about 120 °C, or about 130 °C, using a reflux condenser. The reaction process may be outlined as follows:



[0031] In some embodiments, the BVFEO_4 obtained may be further subjected to the steps of washing, filtering, and drying. Drying may be generally performed in a hot air oven by heating to an elevated temperature, such as a temperature of about 80-120 °C for various periods of time, such as for about 30 minutes to about 60 minutes. After drying, the BVFEO_4 powder may be heated, such as in a furnace, to an elevated temperature, such as a temperature of about 500 °C to about 800 °C, for various periods of time, such as for about 5 minutes to about 1 hour, about 5 minutes to about 45 minutes, about 5 minutes to about 30 minutes, or about 5 minutes to about 15 minutes. Specific examples include, but are not limited to, about 5 minutes, about 10 minutes, about 15 minutes, about 30 minutes, about 45 minutes, and about 1 hour, or any ranges between any two of these values (including their endpoints).

[0032] In some embodiments, the BVFeO_4 obtained after heating is subjected to ethanol washing in the presence of oxygen. This step converts BVFeO_4 to BVO_2FeO_2 . This process may impart a superparamagnetic property to the catalyst.



[0033] The BVO_2FeO_2 catalyst obtained by the methods disclosed herein may be a nanoparticle having an average diameter, such as an average diameter of about 1 nanometer to about 50 nanometers, about 1 nanometer to about 40 nanometers, about 1 nanometer to about 25 nanometers, or about 1 nanometer to about 10 nanometers. Specific examples include, but are not limited to, about 1 nanometer, about 5 nanometers, about 15 nanometers, about 25 nanometers, and about 50 nanometers, or any range between any two of these values (including their endpoints). A putative structure of BVO_2FeO_2 catalyst is shown in FIG. 2.

EXAMPLES

EXAMPLE 1: Preparation of the catalyst BVO_2FeO_2

[0034] About 2 grams of vanadium pentoxide was dispersed in 50 mL of 1N sodium hydroxide in a flat bottom flask and sonicated for 5 cycles (700 watts; 3 minutes per cycle). About 2 grams of boric acid was added to the above mixture and again sonicated for 5 cycles. To this resulting mixture, about 50 mL of 0.1 N sodium borohydride was added slowly and stirred vigorously using a magnetic stirrer for 30-40 minutes at 100 °C. After cooling the mixture, about 20 mL of 2% TEMED (2 mL TEMED in 100 mL of deionized water) was added and the mixture was stirred for 5 minutes. To this mixture, about 1 gram of Fe_2O_3 in 10 % H_2O_2 was mixed, and the solution was stirred vigorously using a plastic overhead stirrer for 30 minutes. The solution was transferred to a Soxhlet apparatus and maintained at 100 °C until all the excess solvent was evaporated. The residue was washed with distilled water until a pH of 7 was reached. After filtering, the residue powder was dried

in a hot air oven at 100 °C for 30 minutes. Finally, the recovered compound was heated in a furnace for 10 minutes at 700 °C, removed, and about 10 mL of ethanol was added immediately. The catalyst thus prepared was characterized by X-ray diffraction (FIG. 4) and used for experiments described below.

EXAMPLE 2: Production of ammonia from nitrogen and water

[0035] About 500 milligrams of BVO_2FeO_2 catalyst prepared in Example 1 was dispersed in 50 mL of water in three neck flask, connected to N_2 cylinder and a gas collection chamber. The flask was subjected to fluctuating magnetic field by supplying an electric current of 230V, 50 Hz, 210 mA for 60 minutes (magnetic field about 1000 μT). Ammonia obtained was confirmed by NMR. The BVO_2FeO_2 catalyst was recovered using simple magnets (0.03T) for reuse.

EXAMPLE 3: Production of ammonia from nitrogen and water

[0036] The apparatus was set up as described in Example 2 and various parameters were changed to analyze the effect on the yield of ammonia. Table 1 shows the yield of ammonia obtained in response to various amounts of catalyst used. The volume of water (50 mL), exposure time (60 minutes), and the chamber pressure (1.2 bar of nitrogen) were kept constant in all the experiments.

TABLE 1

S.No	Time of exposure (min.)	Catalyst (mg.)	Volume of water (mL)	Ammonia/water yield (in mL)	Remaining solution	Ammonia yield(%)
1	60	100	50	$9.5/27.8 \pm 0.3$	37.3 ± 0.4	25.33
2	60	200	50	$14.55/20.8 \pm 0.3$	35.4 ± 0.3	40.84
3	60	300	50	$19.15/13.1 \pm 0.3$	32.3 ± 0.2	59.5
4	60	400	50	$20.75/7.5 \pm 0.3$	28.3 ± 0.2	73.4
5	60	500	50	$23.45/2.1 \pm 0.3$	25.6 ± 0.3	91.76

[0037] The process was repeated and the time of exposure to fluctuating magnetic field was varied. The volume of water (50 mL), catalyst (500 milligrams), and the chamber pressure (1.2 bar of nitrogen) were kept constant throughout the process. The percent yields of ammonia are shown in Table 2.

TABLE 2

S.No	Time of exposure (min.)	Catalyst (mg.)	Volume of water (mL)	Ammonia/water yield (in mL)	Remaining solution	Ammonia yield(%)
1	30	500	50	15.35/19.65 $\pm$ 0.3	35 $\pm$ 0.2	43.71
2	60	500	50	23.45/2.05 $\pm$ 0.3	25.5 $\pm$ 0.2	91.76
3	90	500	50	24.15/1.25 $\pm$ 0.3	25.4 $\pm$ 0.2	94.88
4	120	500	50	24.15/0.85 $\pm$ 0.3	25 $\pm$ 0.2	96.4

[0038] Further, the process was repeated and the chamber pressure was varied. The volume of water (50 mL), catalyst (500 milligrams), and exposure time to fluctuating magnetic field (60 minutes) were kept constant throughout the process. The percent yields of ammonia are shown in Table 3.

TABLE 3

S.No	Chamber pressure (bar)	Ammonia/water yield (in mL)	Remaining solution	Ammonia yield(%)
1	1.02	11.15/20.3 $\pm$ 0.3	35.1 $\pm$ 0.3	31.62
2	1.05	13.65/19 $\pm$ 0.3	32.7 $\pm$ 0.15	41.59
3	1.10	16.45/13.7 $\pm$ 0.3	30.2 $\pm$ 0.2	54.3
4	1.15	20.15/9.3 $\pm$ 0.3	29.5 $\pm$ 0.2	68.15
5	1.20	23.45/2 $\pm$ 0.3	25.5 $\pm$ 0.3	91.76

[0039] These studies demonstrated that higher catalyst loading, increased exposure time to fluctuating magnetic field, and higher chamber pressure increased ammonia yield.

EXAMPLE 4: Analysis of energy consumption during production of ammonia from nitrogen and water

[0040] The energy consumption to produce ammonia (91% yield) was measured by varying the amount of catalyst and keeping other parameters, such as chamber pressure (1.2 bar), water volume (50 mL), and magnetic field strength (1000 microtesla) constant.

TABLE 4

S.No	catalyst weight (milligram)	exposure time for 91% yield (minutes)	power required for 1 kilogram of NH ₃	power consumption (MWh) per ton
1	100	217	39.4	39.4
2	200	134	24	24
3	300	92	16.8	16.8
4	400	75	13.6	13.6
5	500	60	10.8	10.8

[0041] The energy consumption to produce ammonia (91% yield) was also measured by varying the reaction chamber volume and keeping other parameters, such as chamber pressure (1.2 bar), water volume (50 mL), catalyst amount (500 milligrams), and magnetic field strength (1000 microtesla) constant.

TABLE 5

S.No	reaction chamber volume (mL)	exposure time for 91% yield (minutes)	power required for 1 kilogram of NH ₃	power consumption (MWh) per ton
1	250	60	10.8	10.8
2	500	40	7.25	7.25
3	1000	25	4.5	4.5

[0042] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments

described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0043] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0044] As used in this document, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0045] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0046] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0047] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (example, bodies of the appended claims) are generally intended as "open" terms (example, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (example, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even

if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (example, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0048] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0049] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed

range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0050] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

CLAIMS

What Is Claimed Is:

1. A method of producing ammonia, the method comprising:

contacting nitrogen, water, and at least one superparamagnetic catalyst to form a mixture; and

exposing the mixture to a fluctuating magnetic field to produce ammonia.
2. The method of claim 1, wherein contacting nitrogen, water, and at least one superparamagnetic catalyst comprises contacting nitrogen, water, and BVO_2FeO_2 .
3. The method of claim 1, wherein exposing the mixture to the fluctuating magnetic field to produce ammonia comprises exposing the mixture to the fluctuating magnetic field to produce aqueous ammonia.
4. The method of claim 1, wherein exposing the mixture to the fluctuating magnetic field comprises exposing the mixture to the fluctuating magnetic field in a closed reaction vessel.
5. The method of claim 1, wherein exposing the mixture to the fluctuating magnetic field comprises exposing the mixture to the fluctuating magnetic field in a closed reaction vessel having at least one inlet and at least one outlet.
6. The method of claim 4, further comprising maintaining a substantially constant pressure of nitrogen in the closed reaction vessel.
7. The method of claim 6, wherein exposing the mixture to the fluctuating magnetic field comprises maintaining nitrogen in the closed reaction vessel at a pressure of about 1 millibar to about 1 bar.

8. The method of claim 1, wherein contacting nitrogen, water, and at least one superparamagnetic catalyst to form the mixture comprises contacting nitrogen and water with the superparamagnetic catalyst which is present at about 0.1 mole percent to about 1 mole percent of the mixture.

9. The method of claim 1, wherein contacting nitrogen, water, and at least one superparamagnetic catalyst comprises contacting nitrogen, water, and BVO_2FeO_2 nanoparticles.

10. The method of claim 9, wherein contacting nitrogen, water, and at least one superparamagnetic catalyst comprises contacting nitrogen, water, and BVO_2FeO_2 nanoparticles coated on a polymer membrane.

11. The method of claim 1, wherein exposing the mixture to the fluctuating magnetic field comprises exposing the mixture to the fluctuating electromagnetic field generated by an electrical current of about 0.1 ampere (A) to about 100 A, and having a frequency of about 25 hertz to about 1 megahertz.

12. The method of claim 11, wherein exposing the mixture to the fluctuating magnetic field comprises exposing the mixture to the fluctuating electromagnetic field of about 0.1 millitesla to about 1 tesla.

13. The method of claim 1, wherein exposing the mixture to the fluctuating magnetic field comprises exposing the mixture to the fluctuating magnetic field for about 30 minutes to about 3 hours.

14. The method of claim 1, further comprising performing the contacting and exposing steps as a batch process or a continuous process.

15. A method of preparing a catalyst, the method comprising:

contacting vanadium pentoxide with a first base to form a first reaction composition;

contacting the first reaction composition with boric acid to form a second reaction composition;

contacting the second reaction composition with a second base to form a third reaction composition;

contacting the third reaction composition with a bidentate ligand to form a fourth reaction composition; and

contacting the fourth reaction composition with Fe_2O_3 to form the catalyst.

16. The method of claim 15, wherein contacting vanadium pentoxide with the first base comprises contacting vanadium pentoxide with NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, NH_4OH , or any combination thereof.

17. The method of claim 15, wherein contacting vanadium pentoxide with the first base comprises mixing vanadium pentoxide and the first base for about 3 minutes to about 30 minutes.

18. The method of claim 15, wherein contacting the first reaction composition with boric acid comprises mixing the first reaction composition and boric acid for about 3 minutes to about 30 minutes.

19. The method of claim 15, wherein contacting the second reaction composition with the second base comprises contacting the second reaction composition with sodium borohydride, KOH , LiOH , $\text{Mg}(\text{OH})_2$, NH_4OH , or any combination thereof.

20. The method of claim 15, wherein contacting the second reaction composition with the second base comprises mixing the second reaction composition with the second base for about 30 minutes to about 60 minutes at a temperature of about 70°C to about 120°C .

21. The method of claim 15, wherein contacting the third reaction composition with the bidentate ligand comprises mixing a cooled third reaction composition with the bidentate ligand for about 2 minutes to about 15 minutes.

22. The method of claim 15, wherein contacting the fourth reaction composition with Fe_2O_3 comprises mixing the fourth reaction composition with Fe_2O_3 for about 10 minutes to about 60 minutes.

23. The method of claim 15, wherein contacting the fourth reaction composition with Fe_2O_3 comprises mixing the fourth reaction composition with Fe_2O_3 dissolved in 10% H_2O_2 .

24. The method of claim 23, wherein contacting the fourth reaction composition with Fe_2O_3 further comprises isolating the catalyst by evaporating a solvent after the contacting step.

25. The method of claim 24, wherein isolating the catalyst further comprises washing the catalyst, filtering the catalyst, and drying the catalyst.

26. The method of claim 25, wherein drying the catalyst further comprises heating the catalyst to a temperature of about 500 °C to about 800 °C for about 5 minutes to about 30 minutes.

27. The method of claim 26, wherein heating the catalyst further comprises contacting the catalyst with ethanol to convert the catalyst to a superparamagnetic catalyst.

28. The method of claim 26, wherein heating the catalyst further comprises contacting the catalyst with ethanol to convert the catalyst to BVO_2FeO_2 nanoparticles.

29. A reactor system for producing ammonia from nitrogen, the reactor comprising:

a closed reaction vessel configured to receive nitrogen, water, and a superparamagnetic catalyst; and

at least one current carrying element arranged in proximity to a surface of the reaction vessel and configured to provide a fluctuating magnetic field.

30. The reactor system of claim 29, wherein the catalyst is BVO_2FeO_2 nanoparticles.

31. The reactor system of claim 29, wherein ammonia comprises aqueous ammonia.

32. The reactor system of claim 29, wherein the reactor system is a batch reactor system or a continuous reactor system.

33. The reactor system of claim 29, further comprising at least one inlet valve and at least one outlet valve.

34. The reactor system of claim 33, wherein the inlet valve is configured to allow entry of nitrogen into the reaction vessel.

35. The reactor system of claim 29, wherein the reaction vessel is configured to maintain a constant pressure of nitrogen during a reaction process.

36. The reactor system of claim 29, further comprising a thermoelectric couple, a pressure gauge, a temperature controller, a cooling system, a mechanical stirrer, or any combination thereof.

37. The reactor system of claim 29, further comprising nitrogen, water, and at least one superparamagnetic catalyst.

38. The reactor system of claim 29, further comprising aqueous ammonia.

39. The reactor system of claim 29, further comprising nitrogen, water, at least one superparamagnetic catalyst, and ammonia.

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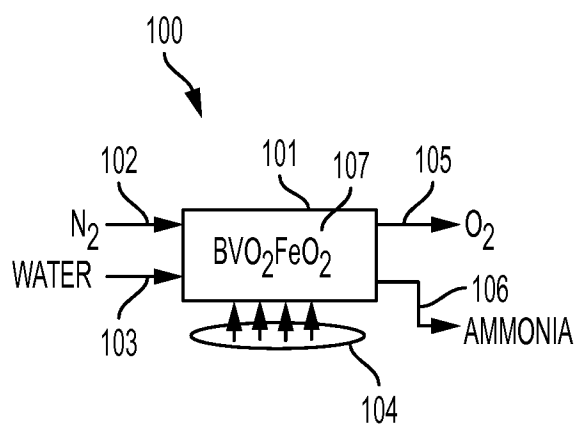


FIG. 1

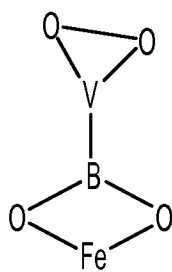


FIG. 2

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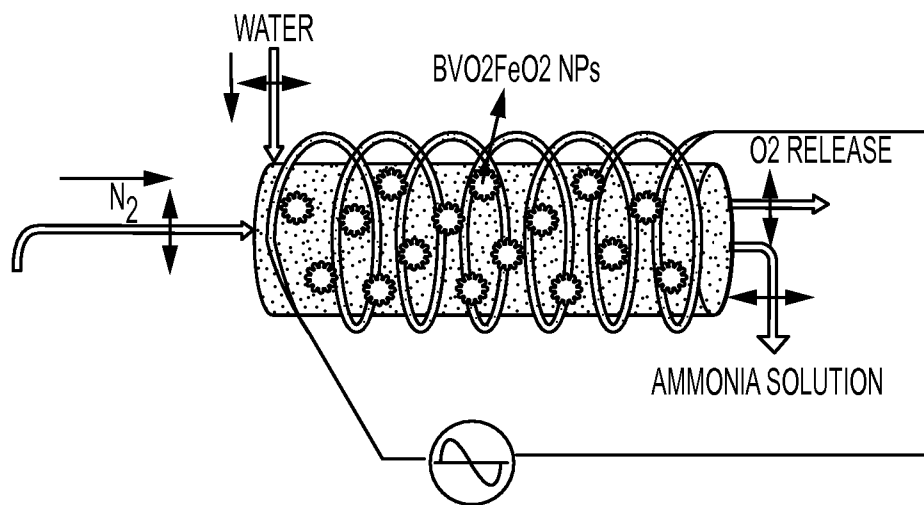


FIG. 3

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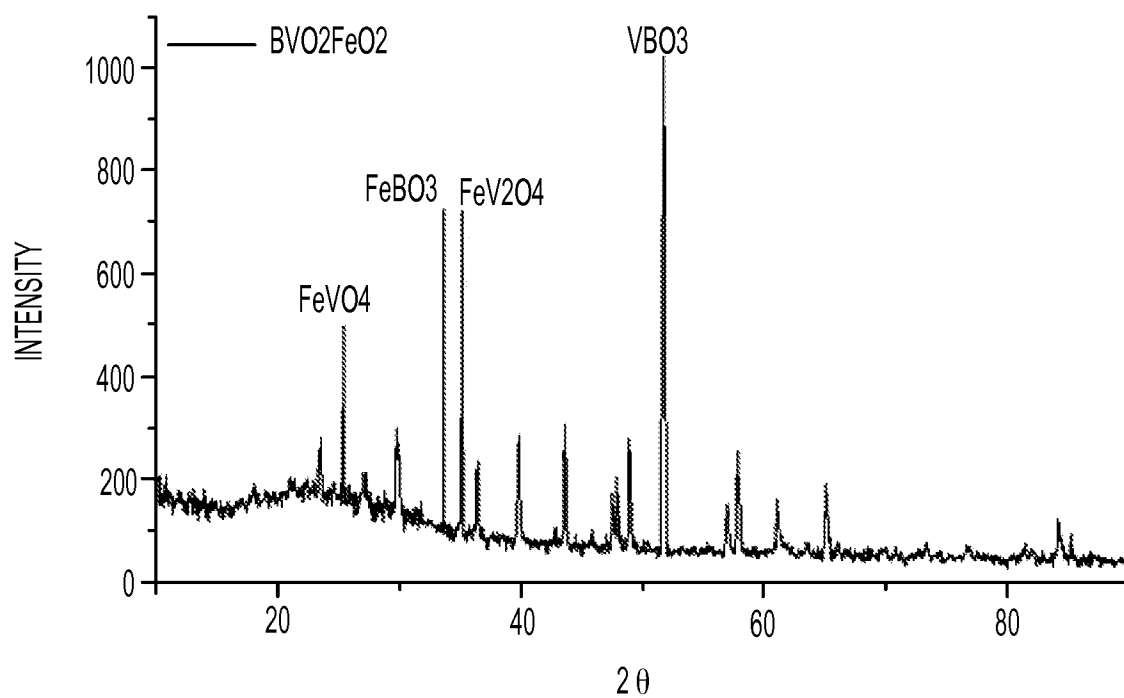
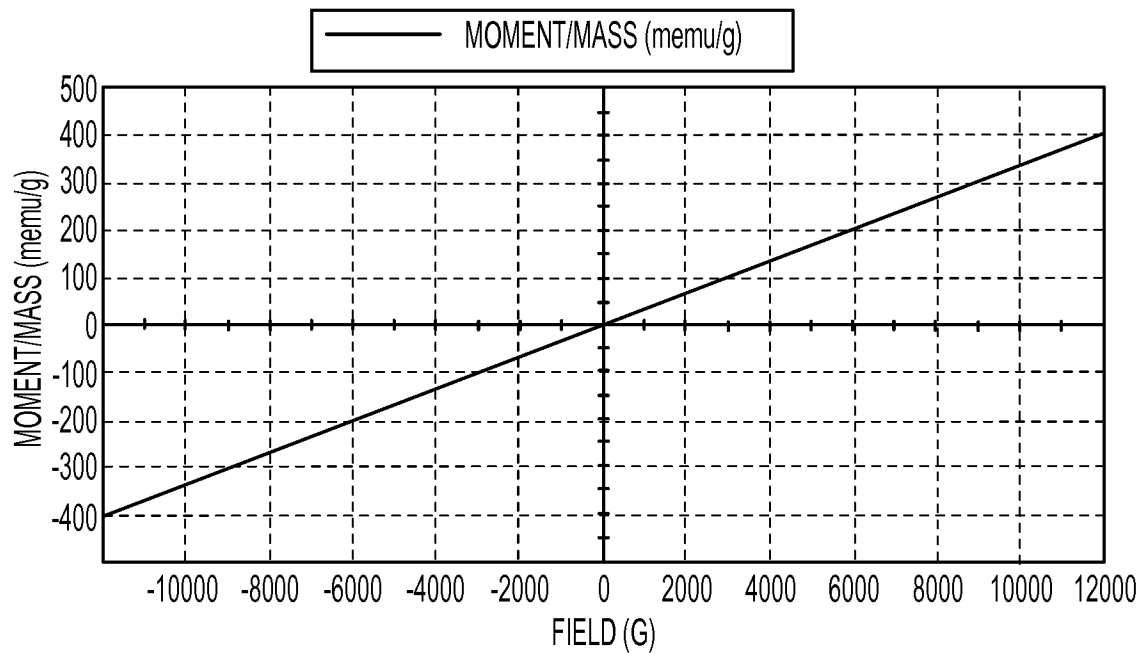


FIG. 4

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AREA-1ST QUAD.: 0.27537 erg/g	AREA-2ND QUAD.: 951.13E-6 erg/g	AREA-3RD QUAD.: 3.6089 erg/g
AREA-4TH QUAD.: 3.6693E-3 erg/g	AREA-TOTAL: 3.8889 erg/g	COERCIVITY (Hci): 4.0044 G
MAGNETIZATION (Ms): 0.40659 emu/g	Mass: 70.900E-3 g	RETENTIVITY (Mr): 132.99E-6 emu/g

FIG. 5

REPLACEMENT SHEET

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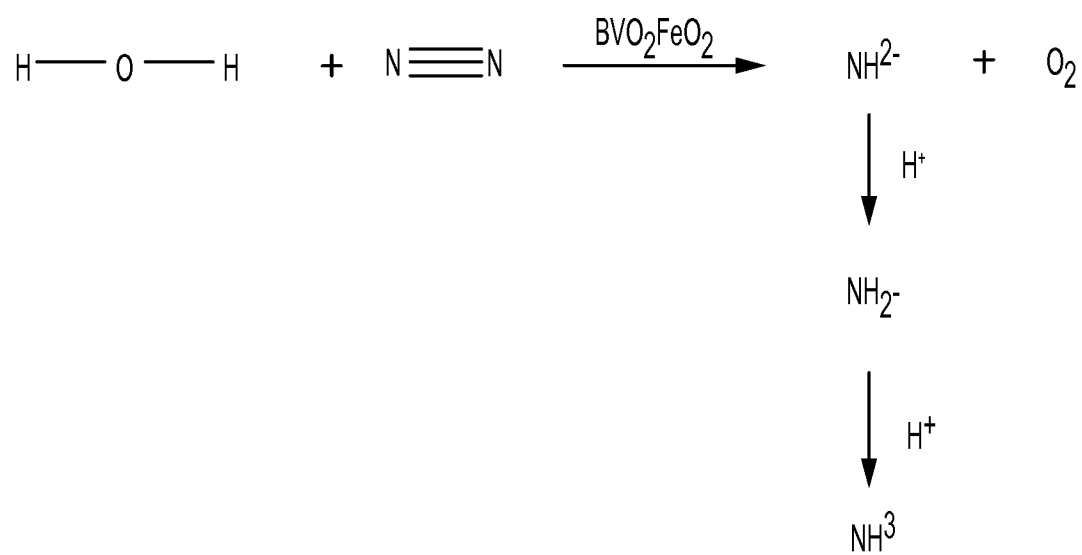


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/40294

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01C 1/00 (2015.01)

CPC - C01C 1/12; C01B 3/025; C01C 1/022

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CPC (C01C1/12; C01B3/025; C01C1/022; C01P2006/42; B01J2219/0854; B01J2219/0877; B01J35/0033; B01J19/087)

IPC: C01C 1/00 (2015.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC (423/352; 423/360; 423/359; 423/362; 422/148; 423/361; 502/522; 422/148)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Search
terms:synthesize ammonia water nitrogen reactor superparamagnetic magnetic field fluctuate catalyst make produce generate prepare
NH3 catalyze NH4+ vessel H2O plant chamber housing change vary swing alternate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/0243828 A1 (GORDON et al.) 6 October 2011 (06.10.2011) para [0003]; abstract	1-14 and 29-39
A	US 3,965,246 A (HINRICHS) 22 June 1976 (22.06.1976) col 2, ln 7-66; claim 1	1-14 and 29-39
A	US 2013/0053471 A1 (STUDART et al.) 28 February 2013 (28.02.2013) para [0005], [0006]	1-14 and 29-39
A	US 2012/0308467 A1 (CARPENTER et al.) 6 December 2012 (06.12.2012) para [0015]-[0017]	1 and 29
A	DE 102,008,011,005 A1 (MATSCHINER) 4 December 2008 (04.12.2008) para [0016]-[0018]; abstract; claim 1, 5 and 7	1 and 29

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

4 November 2015 (04.11.2015)

Date of mailing of the international search report

08 DEC 2015

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/40294

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-14 and 29-39, directed to a method and a reactor system for producing ammonia from nitrogen.

Group II: Claims 15-28, directed to a method of preparing a catalyst.

The inventions listed as Group I-II do not relate to a single special technical feature under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

****for continuation, please see additional sheets at the end****

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-14 and 29-39

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/40294

Continuation of Box II (Lack of Unity):

Special Technical Features:

Group I does not require contacting vanadium pentoxide with a first base to form a first reaction composition; contacting the first reaction composition with boric acid to form a second reaction composition; contacting the second reaction composition with a second base to form a third reaction composition; contacting the third reaction composition with a bidentate ligand to form a fourth reaction composition; and contacting the fourth reaction composition with Fe_2O_3 to form the catalyst, as required by Group II.

Group II does not require a closed reaction vessel configured to receive nitrogen, water, and a superparamagnetic catalyst; and at least one current carrying element arranged in proximity to a surface of the reaction vessel; and exposing the mixture to a fluctuating magnetic field to produce ammonia, as required by Group I.

Common Technical Features:

Group I and II share the technical feature of a catalyst. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by US 3,965,246 A (Hinrichs). Hinrichs teaches a catalyst (col 2, ln 7-23; abstract).

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.