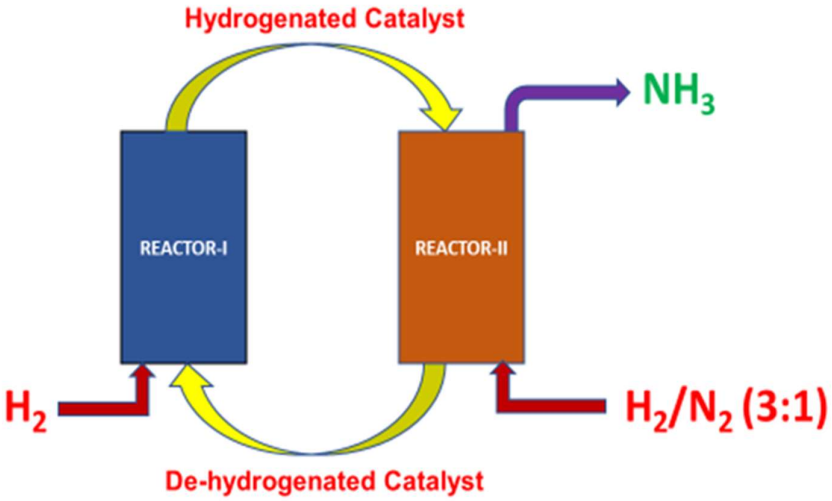

Fig. 1

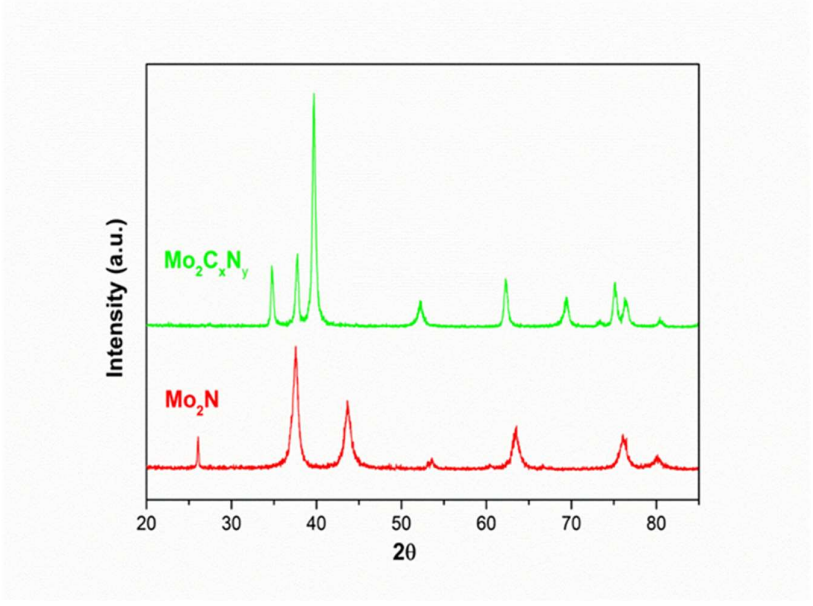

Fig. 2

(RICHA PANDEY) (IN/PA 826)
KRISHNA & SAURASTRI ASSOCIATES LLP

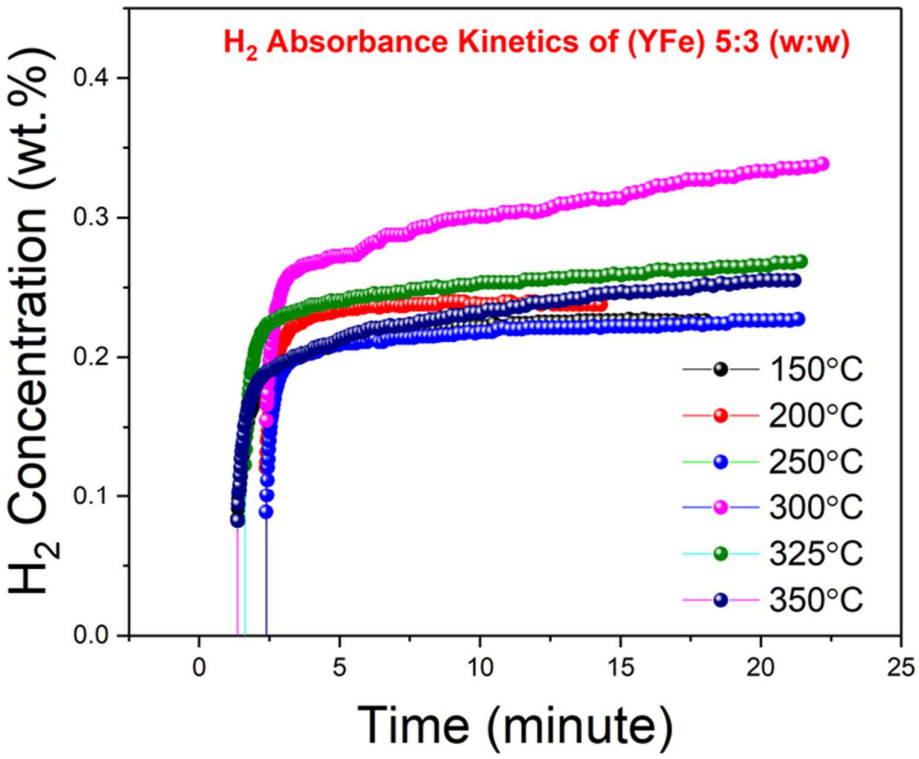

Fig. 3

(RICHA PANDEY) (IN/PA 826)
KRISHNA & SAURASTRI ASSOCIATES LLP

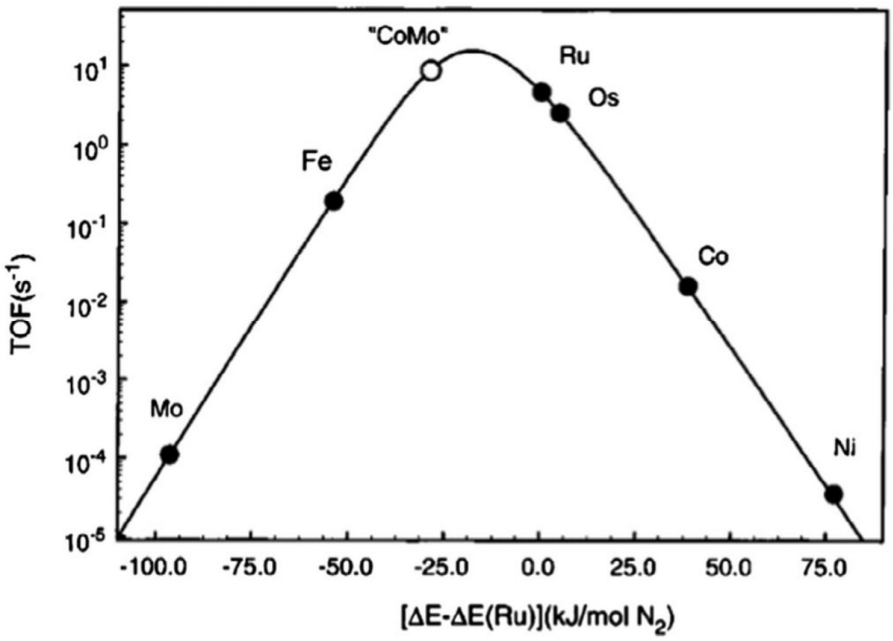

Fig. 4

(RICHA PANDEY) (IN/PA 826)
KRISHNA & SAURASTRI ASSOCIATES LLP

FORM 2

The Patent Act 1970
(39 of 1970)

&

The Patent Rules, 2003

COMPLETE SPECIFICATION
[See Section 10 and Rule 13]

CATALYST FOR SYNTHESIS OF AMMONIA, METHOD OF PREPARATION THEREOF AND METHOD OF SYNTHESIS OF AMMONIA

INDIAN INSTITUTE OF TECHNOLOGY PATNA, WHOSE ADDRESS IS INDIAN INSTITUTE OF TECHNOLOGY PATNA, BIHTA, PATNA, BIHAR - 801 106, INDIA

THE FOLLOWING SPECIFICATION PARTICULARLY DESCRIBES THE INVENTION AND THE MANNER IN WHICH IT IS TO BE PERFORMED.

Field of the Invention

The present invention relates to a catalyst for synthesis of ammonia, a method of preparation thereof, and a method of synthesis of ammonia.

Background of the Invention

Ammonia finds its use in fertilizers, household cleaning products, as a refrigerant, and as a reactant in several industrial manufacturing processes. Haber-Bosch process has been conventionally used for the synthesis of ammonia at an industrial scale. The method suffers from several disadvantages. The major drawback of the Haber-Bosch process is that it is energy intensive. It has been noted that the Haber-Bosch process has been updated since the last few decades, decreasing the energy consumption from 100 GJ $t_{NH_3}^{-1}$ to 26 $t_{NH_3}^{-1}$ (K.H.R. Rouwenhorst, et. al. 'Future Trends' in 'Techno-Economic Challenges of Green Ammonia as an Energy Vector', 2021), however, this process is still considered to consume about 2% of the total energy supply in the world and release more than 400 Mt. of CO_2, which accounts for 1.6% of total global CO_2 emissions (Shiming Chen, et. al. 'Horizons in Sustainable Industrial Chemistry and Catalysis' in 'Studies in Surface Science and Catalysis', 2019). Recently ammonia has gained more attention because of its high hydrogen storage capacity which could be used for transportation of hydrogen. (S.F.Yin, et. al., 10.1016/j.apcata.2004.09.020) Using Capcost_2017 program, Wang and Abild-Pedersen computed the equipment cost and the bare module cost as a function of operating pressure (10.1073/pnas.2106527118). A typical 63-m^3 ammonia synthesis vessel made of carbon steel needs about $5.34 million for operating at 350bar. Interestingly, the investment reduces to mere $0.15 million at operating pressures around 10 bar. Such analysis demonstrates the possibility to dramatically reduce the capital and operating cost when Haber-Bosch process could operate at lower reaction pressures.

Therefore, there is a need to provide a catalyst and a method for energy efficient synthesis of ammonia.

Summary of the Invention

The present invention relates to a catalyst for synthesis of ammonia. The catalyst comprises of molybdenum carbonitride and a hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), Lanthanum (La), or a combination thereof. These hydrides act as electrides and facilitate electron donation to nitrogen molecules for their bond dissociation.

The present invention also relates to a method of preparing a catalyst for synthesis of ammonia. The method comprises mixing the Molybdenum carbonitride and hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), Lanthanum (La), or a combination thereof.

Description of Drawings

Figure 1: Schematic outline of process for synthesis of ammonia as per the present invention.

Figure 2: X-ray diffractogram showing diffraction peak which confirms the synthesis of $Mo_2C_xN_y$.

Figure 3: H_2 absorption kinetics of $(AB)H_x$ (w: w ratio of 5:3).

Figure 4: volcano shape plot for different transition metals.

Description of the Invention

The present invention is directed to a catalyst comprising a combination of Molybdenum carbonitride and a hydride $(AB)H_x$ where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), Lanthanum (La), or a combination thereof. The hydride is preferably a Yttrium (Y) hydride doped with transition metals selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo), or a combination thereof.

Molybdenum carbonitride in the catalyst of the present invention is represented by the formula $Mo_2C_xN_y$, wherein x and y are positive integers. In an embodiment, the $Mo_2C_xN_y$ contains x = 2.32% and y= 7.44%.

Preferably, the transition metal A is Iron (Fe) and rare earth metal B is Yttrium (Y), i.e., the hydride is an Iron doped Yttrium hydride.

The Molybdenum carbonitride and iron-doped Yttrium hydride doped with transition metals selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo) or a combination thereof, is in a ratio of 50:50 (w:w).

Preferably, the catalyst of the present invention comprises Molybdenum carbonitride and Yttrium (Y) hydride doped with Iron (Fe), in a ratio of 50:50 (w:w).

Another embodiment of the present invention relates to a method of preparing a catalyst. The method comprises a step of mixing Molybdenum carbonitride and a hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni),

Cobalt (Co), Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), Lanthanum (La), or a combination thereof.

Preferably, the Molybdenum carbonitride and the hydride $(AB)H_x$ are mixed in a weight ratio of 50:50 (w:w).

Preferably, the method of the present invention comprises mixing Molybdenum carbonitride and Yttrium hydride doped with Iron (Fe) using ball mill, in a weight ratio of 50:50 (w:w).

To prepare the Molybdenum carbonitride, molybdenum pentachloride is dissolved in ethanol to obtain an alcoholic solution of molarity in a range of 1.35M to 1.55M, preferably 1.45M. To the alcoholic solution, urea is added in a molar ratio of urea: molybdenum in a range of 2 to 6, preferably 5, with stirring for a period in a range of 45 minutes to 90 minutes, preferably 1 hour, to obtain a solution. The solution is heated under N_2 gas flow in a tubular furnace for a period in a range of 160 minutes to 200 minutes (holding time), preferably 3 hours, at a temperature in a range of 750°C to 850°C, preferably 800°C, and a ramp rate in a range of 2°C/minute to 10°C/minute, preferably 4°C/minute, was used to reach to 800°C.

To prepare the hydride $(AB)H_x$, Yttrium (or Ce, La) is mixed with a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), or Molybdenum (Mo) in a ratio of 5:3 to obtain a mixture. The mixture is treated under hydrogen gas (H_2) at a temperature of 250°C to 350°C and a pressure of 15-20 bar.

Preferably, Yttrium is mixed with Iron (Fe) in a ratio of 5:3 to obtain a mixture. The mixture is treated under hydrogen gas (H_2) at a temperature of 250℃-350℃ and a pressure of 15-20 bar.

Yet another embodiment of the present invention relates to a method for synthesis of ammonia. Figure 1 provides a schematic outline of a process for synthesis of ammonia as per the present invention. The method comprises passing a rare earth metal, a transition metal and hydrogen through a hydride formation reactor, known as Reactor-I. The hydride obtained in the Reactor-I is passed along with a reactor gas mixture comprising nitrogen and hydrogen through a continuous flow fixed bed reactor (Reactor-II). The Reactor-II comprises a catalyst comprising Molybdenum carbonitride which along with the hydride from the Reactor-I catalyses the synthesis of ammonia. Both these reactors operate in a loop and hence the process is termed as "chemical looping method".

Preferably, the method comprises passing Yttrium (Y), Iron (Fe), and hydrogen through the Reactor-I, and passing the Yttrium (Y) hydride doped with Iron (Fe) obtained in the Reactor-I, along with a reactor gas mixture comprising nitrogen and hydrogen through a continuous flow fixed bed Reactor-II. The continuous flow fixed bed reactor comprises a catalyst comprising Molybdenum carbonitride. The Yttrium (Y) hydride doped with Iron (Fe) along with the Molybdenum carbonitride catalyse the synthesis of ammonia in Reactor-II.

Preferably, the reactor gas mixture comprises nitrogen and hydrogen in a ratio of 1:3. The reactor gas mixture is passed through the continuous flow fixed bed reactor at a flow rate in a range of 30-72mL/minute, at a reaction temperature from 300°C to

550°C, and at a pressure in a range of 1 to 5 bar. Preferably, the reactor gas mixture is passed through the continuous flow fixed bed reactor at a flow rate of 30 mL min^{-1}.

The catalyst as per the present invention has following advantages –

- The catalyst is employed to generate on-site NH_3 with the use of inexpensive metals such as Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo).
- Moreover, the operational reaction conditions for synthesis of ammonia as per the present invention are mild and hence, alleviate energy and cost burden, which is otherwise pertinent with the conventional methods.

Examples

The following examples illustrate the invention but are not limiting thereof.

Example – 1: Preparation of the catalyst as per the present invention

1. Synthesis of Molybdenum carbonitride

1gm of Molybdenum chloride was dissolved in 2.18 mL of ethanol to obtain an alcoholic solution of molarity of 1.40M to 1.50M. To the alcoholic solution, 1.10 gm of urea was added in a molar ratio of urea: molybdenum of 2 to 6 with stirring for 45 minutes to 90 minutes to obtain a solution. The solution was heated under N_2 gas flow in a tubular furnace for 160 minutes to 200 minutes (holding time) at 750°C to 850°C and the ramp rate of 2°C/minute to 10°C/minute was used to reach to 800°C to form Molybdenum carbonitride with the formula $Mo_2C_xN_y$ wherein x = 2.32% and y= 7.44%.

2.1 Selection of transition metal in hydride $(AB)H_x$

The desorption kinetics of Yttrium hydride (YH_x) was very fast under ammonia synthesis reaction conditions. To alleviate this issue, it has been doped with

transition metals. The selection of transition metals was based on volcano plot. The synergistic effect of the as-synthesized hydride was significantly more efficient in reducing the stability problem. However, to get better insight, Density functional theory (DFT) calculations are required.

The main challenge in ammonia synthesis reaction is to break strong bond between nitrogen molecule. To get optimum performance from any catalysts it should have small activation energy for nitrogen dissociation and also have weak bond with adsorbed nitrogen molecule so that it can easily desorbed NH_3 molecule from its surface. Keeping these two properties in the mind and by using volcano plot shown in the Figure 4, different transition metals have been selected to minimize the effect of linear scaling i.e. linear relationship between the activation energy for nitrogen dissociation and the binding energy of atomic nitrogen on the catalysts surfaces.

2.2 Synthesis of Iron (Fe) doped Yttrium (Y) hydride

0.8gm of Yttrium was mixed with 0.48gm of Iron (Fe) in a ratio of 5:3 to obtain a mixture. The mixture was treated under hydrogen gas (H_2) at a temperature of 200℃-350℃ and a pressure of 15-20 bar to form Iron (Fe) doped Yttrium (Y) hydride with the formula Fe-YH_x, wherein $0<x<3$.

Example – 2: CHN Analysis

CHN data reveals that $Mo_2C_xN_y$ contains x = 2.32% and y= 7.44%.

Catalyst	C(%)	N(%)
Mo_2N	0.16	9.27
$Mo_2C_xN_y$	2.32	7.44

The values of x and y are to simply exhibit the possible reactions. However, it is not limited to 2.32% or 7.44%. High amount of carbon in $Mo_2C_xN_y$ at initial stage observed to generate higher reaction rate of NH_3 synthesis. [ACS Appl. Energy Mater. 2020, 3, 7, 7167–7179]

Example – 3: Absorption kinetics

Figure 3 shows H_2 absorption kinetics of Y-Fe (w:w ratio of 5:3).

The hydrogen de/absorption kinetic and storage capacity were measured by a fully automatic Sieverts-type apparatus (model-Setaram-PCT Pro). In the sample tube, about 0.2-1g of sample was loaded. Then, leakage test was performed. And the H_2 storage capacity test was carried out at pressure of 15-20 bar and temperature 200-350°C. Importantly, the volume calibration was done at various temperature and pressure conditions. After the volume calibration, the hydrogen absorption and desorption measurement were performed with an initial hydrogen pressure up to 2MPa (for absorption) and 0.1 MPa (for desorption). These steps were repeated for each tested sample.

The value of x varies with the temperature conditions. For instance, at 300°C and 20 bar H_2, about 0.35 wt. % of H_2 is absorbed by Y-Fe in about 20 minutes.

Example – 4: Synthesis of Ammonia

Ammonia was synthesized in presence of only $Mo_2C_xN_y$ as catalyst (comparative route), and in presence of $Mo_2C_xN_y$ and Fe-YH_x as catalyst (synthesis route as per the present invention), under varying temperature and pressure conditions.

0.125gm of Molybdenum carbonitride and 0.125gm of Iron (Fe) doped Yttrium hydride as prepared in the steps above were added to a continuous flow fixed bed reactor. A reactor gas mixture comprising nitrogen and hydrogen in a ratio of 1:3 was passed through a continuous flow fixed bed reactor, at a flow rate of 30-75 mL/minute, at a reaction temperature of 300°C-600 °C, and at a pressure of 1-5 bar.

The Table 1 shows the results obtained with both the synthetic routes. The 'x' and 'y' have the same value for comparative catalyst and the catalyst of the present invention. Further, the ratio of $Mo_2C_xN_y$ to Fe-YH_x in the catalyst of the present invention in all the examples was 50:50

Catalyst	**Temperature(°C)**	**Pressure (bar)**	**Reaction Rate of NH_3 synthesis ($\mu molg^{-1}h^{-1}$)**
$Mo_2C_xN_y$ (Comparative Example)	350	1	102
$Mo_2C_xN_y$ + Fe-YH_x (present invention)	350	1	**211**

$Mo_2C_xN_y$ (Comparative Example)	400	1	140
$Mo_2C_xN_y$ + Fe-YH_x (present invention)	400	1	**306**
$Mo_2C_xN_y$ (Comparative Example)	450	1	198
$Mo_2C_xN_y$ + Fe-YH_x (present invention)	450	1	**393**
$Mo_2C_xN_y$ (Comparative Example)	400	3	140
$Mo_2C_xN_y$ + Fe-YH_x (present invention)	400	3	**519**
$Mo_2C_xN_y$ + Fe-YH_x (present invention)	500	1	**593**

Herein, synthesis of $Mo_2C_xN_y$ was carefully controlled to keep C:N {(2-5):1), w:w ratio} and their activity is mentioned in the Table 1. Further, it was observed that the addition of hydride composed of transition metals (TM) and rare earth metals facilitate NH_3 generation at relatively mild conditions (see Table 1).

It can be seen from the Table 1 above that the reaction rate of synthesis of ammonia was higher with the catalyst as per the present invention at all temperature and pressure conditions as compared to the comparative route. Also, high amount of carbon in $Mo_2C_xN_y$ at initial stage was observed to generate higher reaction rate of NH_3 synthesis. Most importantly, the catalyst ($Mo_2C_xN_y$ + Fe-YH_x) of the present invention demonstrated a rate of $519 \mu mol g^{-1} h^{-1}$, which is about 1.57-folds higher than

commercially used doubly-promoted Fe catalyst (Fe-K_2O-Al_2O_3) at ambient pressure and 400°C.

A maximum ammonia synthesis rate of $593 \mu mol g^{-1} h^{-1}$ was observed for as-developed catalyst ($Mo_2C_xN_y$ + Fe-YH_x) at ambient pressure and 500°C.

The Table 2 shows the results obtained with different weight ratio of hydride and carbonitride.

Wt.% of $Mo_2C_xN_y$	Wt.% of YH_x	**Reaction Rate of NH_3 synthesis ($\mu molg^{-1}h^{-1}$)**	Condition
5	95	448	T= 255°C P= 1bar
10	90	232	T= 200°C P= 1bar
90	10	165	T= 300°C P= 1bar
50	50	187	T= 300°C P= 1bar

It can be seen from the table above that the varying concentrations of the Molybdenum carbonitride and Yttrium hydride doped with Iron in the catalyst provide varying rates of synthesis of NH_3.

The foregoing description of the invention has been set merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to a person skilled in the art, the invention should be construed to include everything within the scope of the disclosure.

We Claim:

1. A catalyst comprising Molybdenum carbonitride and a hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), and Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), and Lanthanum (La), or a combination thereof .
2. The catalyst as claimed in claim 1, wherein the hydride is an Iron doped Yttrium hydride.
3. The catalyst as claimed in claim 1 or 2, wherein the Molybdenum carbonitride and the hydride are in a ratio of 50:50.
4. The catalyst as claimed in claim 1, wherein Molybdenum carbonitride and Iron doped Yttrium hydride are in a ratio of 50:50.
5. A method of preparing a catalyst, the method comprising a step of mixing the Molybdenum carbonitride and hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), and Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), and Lanthanum (La), or a combination thereof.
6. The method as claimed in claim in claim 5, wherein the Molybdenum carbonitride and Yttrium hydride doped with transition metals selected from Iron (Fe), Nickel (Ni), Cobalt (Co), and Molybdenum (Mo) are mixed in a weight ratio of 50:50.
7. The method as claimed in claim 5, wherein the Molybdenum carbonitride is prepared by a method comprising steps of
    a. dissolving molybdenum chloride in ethanol to obtain an alcoholic solution of molarity of 1.45M;

b. adding urea to the alcoholic solution in a molar ratio of urea: molybdenum of 5 with stirring for 1 hour to obtain a solution; and

c. heating the solution under N_2 gas flow for 3 hours (holding time) at 800°C at a ramp rate of 4°C/minute.

8. The method as claimed in claim 5, wherein the Yttrium (Y) hydride is prepared by a method comprising steps of

a. mixing Yttrium with a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), and Molybdenum (Mo) in a ratio of 5:3 to obtain a mixture; and

b. treating the mixture under hydrogen gas (H_2) at a temperature of 350°C and a pressure of 20 bar.

9. A method for synthesis of ammonia, the method comprising a step of passing a reactor gas mixture comprising nitrogen and hydrogen through a continuous flow fixed bed reactor wherein the continuous flow fixed bed reactor comprises a catalyst comprising Molybdenum carbonitride and a hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), and Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), and Lanthanum (La), or a combination thereof.

10. The method as claimed in claim 9, wherein the reactor gas mixture comprises nitrogen and hydrogen in a ratio of 1:3.

11. The method as claimed in claim 9, wherein the reactor gas mixture is passed through the continuous flow fixed bed reactor at a flow rate in a range of 30-72mL/minute, or 30 mL min^{-1}.

12. The method as claimed in claim 9, wherein the reactor gas mixture is passed through the continuous flow fixed bed reactor at a reaction temperature from 300°C to 550°C.

13. The method as claimed in claim 9, wherein the reactor gas mixture is passed through the continuous flow fixed bed reactor at a pressure in a range of 1 to 5 bar.

Dated this 14th day of October, 2022

For INDIAN INSTITUTE OF TECHNOLOGY PATNA
By their Agent



(RICHA PANDEY) (IN/PA 826)
KRISHNA & SAURASTRI ASSOCIATES LLP

ABSTRACT

CATALYST FOR SYNTHESIS OF AMMONIA, METHOD OF PREPARATION THEREOF AND METHOD OF SYNTHESIS OF AMMONIA

The present invention relates to a catalyst comprising a combination of Molybdenum carbonitride and a hydride $(AB)H_x$, where A is a transition metal selected from Iron (Fe), Nickel (Ni), Cobalt (Co), Molybdenum (Mo), or a combination thereof; B is a rare earth metal selected from Yttrium (Y), Cerium (Ce), Lanthanum (La), or a combination thereof. Ammonia was produced using these catalyst combinations in a continuous flow of (H_2:N_2 (3:1), flow rate ratio) operating at ambient pressure and temperature (350-500°C).