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(54) **Method and apparatus for ammonia synthesis at atmospheric pressure**

Verfahren und Vorrichtung zur Ammoniaksynthese bei Atmosphärendruck

Procédé et dispositif de synthèse d'ammoniac à pression atmosphérique

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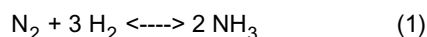
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Description

[0001] The present invention relates to a method for synthesizing ammonia from its elements (H_2 and N_2) at atmospheric pressure. This was achieved in a prototype solid state proton (H^+) conducting cell-reactor.

[0002] The development of a successful process for ammonia synthesis from its elements:



is considered a landmark in heterogeneous catalysis. The Haber process which involves reaction of gaseous nitrogen and hydrogen on a Fe-based catalyst at high pressures (15 - 30 MPa), was developed at the beginning of the twentieth century after an extensive search for an active catalyst (1).

[0003] Even from early studies, it was realized that the conversion is limited by thermodynamics. The gas volume decreases with reaction. Hence, very high pressures have to be used in order to push equilibrium to the right according to the Le Chatelier principle.

[0004] The reaction is exothermic (109 kJ/mol at 500°C) and therefore conversion increases with decreasing temperature. In order to achieve however, industrially acceptable reaction rates, the reaction temperature must be high. The trade-off solution is to operate at temperatures in the range of 430 - 480°C, at which the equilibrium conversion is of the order of 10 - 15% (1).

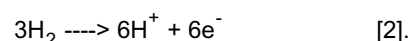
[0005] The present method refers on an alternative route to ammonia synthesis at atmospheric pressure via the use of solid state proton (H^+) conductors by which the requirement for operation at high pressures is eliminated. The method involves the process steps of present claim 1.

[0006] Solid electrolyte cells have been used so far in heterogeneous catalysis in order to a) study the mechanism of catalytic reactions (2, 3), b) electrochemically alter reaction rates (4,5) and c) cogenerate electricity and useful chemicals (6). The solid electrolytes used in most of the above applications were oxygen ion conductors.

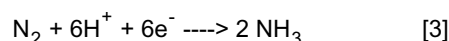
[0007] In the last decade however, materials that exhibit protonic conductivity in the solid state have been introduced into catalysis research (7). These H^+ conductors are particularly useful because they can operate at temperatures in which many industrial hydro- and dehydrogenation reactions take place. Furthermore, in contrast to oxidation reactions, a number of industrial hydrogenations (ammonia, methanol production) are equilibrium limited at the operating conditions.

[0008] A model process using solid state proton conductors to obtain conversions higher than those predicted by the reaction equilibrium, has been proposed in the past (8-10). It is possible to use two configurations. The double and the single chamber configuration.

[0009] In the double chamber configuration (Figure 1) a vessel 1 has been divided into a hydrogenation reaction chamber 2 and into a chamber containing a hydrogen atmosphere 3, using a proton conducting solid electrolyte ($SrCe_{0.95}Yb_{0.05}O_3$) 4. Two porous polycrystalline palladium (Pd) films served as electrodes. The working electrode 5 was deposited in chamber 2 and served also as catalyst for the reaction of ammonia synthesis. The counter electrode 6 was deposited in the other side of the solid electrolyte, i.e. in chamber 3. These two electrodes are connected with Au wires 7 in a galvanostat - potentiostat 8. The cathode (chamber 2) was exposed to a gaseous stream containing nitrogen diluted in helium while the anode (chamber 3) was exposed to a hydrogen stream. The gaseous H_2 passing over the anode of the proton-conducting cell-reactor, will be converted to H^+ :

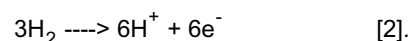


The protons (H^+) are transported through the solid electrolyte to the cathode where the half-cell reaction:

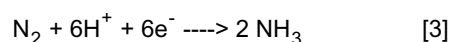


takes place. Thus, reaction [1] is again the overall reaction.

[0010] In the single chamber configuration (Figure 2) a reaction vessel 1 contains a proton conducting solid electrolyte ($SrCe_{0.95}Yb_{0.05}O_3$) 2. Two porous polycrystalline palladium (Pd) films were used as electrodes. The working electrode 3 was deposited in the one side of solid electrolyte and served also as catalyst for the reaction of ammonia synthesis. The counter electrode 4 was deposited in the other side of the solid electrolyte. These two electrodes are connected with Au wires 5 in a galvanostat - potentiostat 6. In the following a gaseous mixture containing nitrogen and hydrogen diluted in helium are fed to the reaction vessel. The gaseous H_2 passing over the anode of the proton-conducting cell-reactor, will be converted to H^+ :



The protons (H^+) are transported through the solid electrolyte to the cathode where the half-cell reaction:



takes place.

[0011] Hence, according to another aspect of the present invention, there exists an electrochemical cell as claimed in claim 6.

[0012] Specifically, this single chamber configuration is simpler than the double chamber configuration because of the fact that the complexity of the separation of the two chambers is avoided.

[0013] The ceramic material was a strontia-ceria-yttria (SCY) perovskite of the form: $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$. This perovskite is a solid with good mechanical strength and with high protonic conductivity [11]. The electrode preparation and characterization procedure has been described in detail elsewhere [12].

[0014] Figure 3 shows the dependence of the rate of NH_3 formation in a double chamber cell on $I/2F$, where I is the imposed current and F is Faraday's constant. Assuming that the SCY is solely a proton conductor, the ratio $I/2F$ is equal to the electrochemical molar flux of hydrogen through the solid electrolyte. The cell was kept at 570°C . A mixture of 1.8% N_2 in He was passing over the cathode at a volumetric flowrate of $8.3 \times 10^{-8} \text{ m}^3/\text{s}$ and atmospheric total pressure. A flow of $5.0 \times 10^{-7} \text{ m}^3/\text{s}$ of 100% H_2 at atmospheric pressure was maintained over the anode. At $I=0$, no products were formed. Upon imposing a current through the cell, NH_3 appeared at the cathode and after a transient period of 2-6 minutes, a steady state rate of NH_3 formation was established.

[0015] The data points in Figure 3 represent steady state rates. The two dotted lines of Figure 3 are based on thermodynamic calculations and are presented for comparison of the present results with those that would have been obtained in a conventional catalytic reactor (CCR) in which gaseous H_2 rather than electrochemical H^+ were used. Specifically, the curve denoted as CCR represents the maximum rate of NH_3 formation attained in a CCR that operates at 570°C and at atmospheric pressure and in which the same amounts of N_2 and H_2 as in the present experiments, are introduced. It can be seen that the NH_3 rates attained experimentally exceed the CCR rates by at least three orders of magnitude. Similarly, the curve denoted as PCCR (pressure in a conventional catalytic reactor) represents the total pressure at which a CCR should operate in order for the NH_3 conversion to be as high as that reported here.

[0016] Figure 4 shows the dependence of the rate of NH_3 formation in a single chamber cell on $I/2F$, where I is the imposed current and F is Faraday's constant. The cell was kept at 600°C . A gas mixture of N_2 (0.5%), H_2 (10%) in He was fed in the reaction vessel at a volumetric flowrate of $3.3 \times 10^{-7} \text{ m}^3/\text{s}$ and atmospheric total pressure. At $I=0$, no products were formed. Upon imposing a current through the cell, NH_3 appeared at the cathode and after a transient period of 2-6 minutes, a steady state rate of NH_3 formation was established.

[0017] The data points in Figure 4 represent steady state rates. The two dotted lines of Figure 4 are based on thermodynamic calculations and are presented for comparison of the present results with those that would have been obtained in a conventional catalytic reactor (CCR) in which gaseous H_2 rather than electrochemical H^+ were used. Specifically, the curve denoted as CCR

represents the maximum rate of NH_3 formation attained in a CCR that operates at 600°C and at atmospheric pressure and in which the same amounts of N_2 and H_2 as in the present experiments, are introduced. It can be seen that the NH_3 rates attained experimentally exceed the CCR rates by at least two orders of magnitude. Similarly, the curve denoted as PCCR (pressure in a conventional catalytic reactor) represents the total pressure at which a CCR should operate in order for the NH_3 conversion to be as high as that reported here.

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Claims

1. A process for synthesizing ammonia at atmospheric pressure which comprises passing a nitrogen-containing feed gas in contact with a cathodic electrode having a first catalyst comprising a palladium containing metal composition, wherein said first catalyst is deposited on a first surface of a proton conducting solid electrolyte; passing a hydrogen-containing gas such as diatomic hydrogen or steam in contact with second catalyst anodic electrode deposited on a second surface of said solid electrolyte wherein said second catalyst is capable of dissociating hydrogen comprised in the hydrogen-containing gas to form protons and said first catalyst is capable of promoting the hydrogenation of nitrogen to ammonia; and applying a voltage between said first and said second catalyst through said solid electro-

lyte, such that proton ions are transported through the solid electrolyte and contact said nitrogen to form ammonia.

2. The process according to claim 1, wherein said solid electrolyte comprises strontia, ceria and ytterbia ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$). 5
3. The process according to claim 1, wherein said hydrogen-containing gas comprises hydrogen-containing compound selected from water, methane, natural gas and alkanes. 10
4. The process according to claim 1, wherein said solid electrolyte comprises any material exhibiting protonic conductivity. 15
5. The process according to claims 1 or 2, wherein both said first and second surfaces of the solid electrolyte are exposed to the same gaseous mixture that contains both said nitrogen-containing and hydrogen-containing gases. 20
6. An apparatus for the electrochemical synthesis of ammonia comprising a chamber in which is arranged an electrode | solid electrolyte assembly made of a strontia-ceria- ytterbia perovskite of the form $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ as solid electrolyte on either side of which have been deposited porous polycrystalline palladium films. 25 30

Patentansprüche

1. Verfahren zur Ammoniaksynthese unter Luftdruck, ein Stickstoffgasgemisch, das eindringt, kommt in Kontakt mit einem kathodischen Elektroden welches metallisches Palladium enthält und bildet die erste katalytische Schicht. Dieses kathodische Elektrode hat sich in der ersten Schicht eines festen Elektrolyten /Protonenleiters abgelagert. Ein Wasserstoffgasgemisch in Form von zweiatomigem Wasserstoff oder Wasserdampf kommt in Kontakt mit der zweiten katalytischen Schicht, welches das anodische Elektrode bildet und ist auf der zweiten Schicht des vorgenannten festen Elektrolyten / Protonenleiters abgelagert. Dieses anodische Elektrode ist imstande den Wasserstoff im Gasgemisch zu spalten, um Protonen zu bilden. Die erste katalytische Schicht ist imstande, die Stickstoffhydrierung in Ammoniak voranzutreiben. Die Anwendung eines Potentials zwischen dem ersten und zweiten Katalysator treibt den Transport der Protonen voran durch den festen Elektrolyten, welche mit dem Stickstoff in Kontakt kommen und somit Ammoniak bilden. 35 40 45 50 55
2. Verfahren nach Anspruch Nr. 1, wobei der feste

Elektrolyt aus Strontium, Cerium, und Ytterbium ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$) **gekennzeichnet** ist.

3. Verfahren nach Anspruch Nr. 1, wobei wasserstoffhaltiges Gasgemisch aus einer wasserstoffhaltigen Verbindung gekennzeichnet ist, die Wasser, Methane, Erdgas und Alkanen enthält.
4. Verfahren nach Anspruch Nr. 1, wobei der feste Elektrolyte aus irgendeinem Material **gekennzeichnet** ist, welches in festem Zustand Protonenleiter ist.
5. Verfahren nach den Ansprüchen 1 oder 2, wobei die erste und zweite Schicht des festen Elektrolyten demselben reagierenden stickstoff- und wasserstoffhaltigen Gasgemisch ausgesetzt werden.
6. Ein Apparat für die elektrochemische Ammoniaksynthese welches aus einer Kammer **gekennzeichnet** ist in dem eine Anordnung aus Elektrode / fester Elektrolyt aufgestellt ist und der feste Elektrolyt aus Strontium-Cerium-Ytterbium der Form $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$ hergestellt ist, bei dem in jeder Seite poröse polykristallische Palladium Membrane aufgestellt sind.

Revendications

1. Une procédure de synthèse d'ammonia à la pression atmosphérique, qui comprend un passage de gaz de fourniture contenant d'azote au contact avec d'électrode cathodique qui a un premier catalyseur avec un palladium inclus contenant de composition métallique, où le premier catalyseur susnommé est posé sur une première surface d'électrolyte solide conduisant des protons; un passage de gaz contenant d'hydrogène, comme d'hydrogène diatomique ou de vapeur d'eau, au contact avec d'électrode anodique comprenant un deuxième catalyseur déposé sur une deuxième surface d'électrode solide susnommé, où le deuxième catalyseur susnommé est capable de rompre l'hydrogène qui existe au gaz contenant d'hydrogène, pour qu'il forme des protons, et le premier catalyseur susnommé est capable d'avancer l'hydrogénation d'azote à d'ammonia; et une application de voltage entre le premier et le deuxième catalyseur susnommé à travers l'électrolyte solide susnommé, bien que les ions des protons se transportent à travers l'électrolyte solide et contactent l'azote susnommé bien qu'ils forment d'ammonia.
2. La procédure selon la revendication 1, où l'électrolyte solide susnommé contient strontia, ceria et ytterbia ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$).

3. La procédure selon la revendication 1, où le gaz susnommé contenant d'hydrogène, comprend de contenant d'hydrogène choisi de l'eau, du méthane, du gaz naturel et des alcanes. 5
4. La procédure selon la revendication 1, où l'électrolyte solide susnommé comprend quelconque matière qui exhibe de conduction protonique.
5. La procédure selon les revendications 1 ou 2, où tous les deux, premier et deuxième surface de l'électrolyte solide, sont exposées à la même mixture des gaz qui contient tous les deux gaz susnommés contenant d'azote et d'hydrogène. 10 15
6. Un appareil pour la synthèse électrochimique d'ammonia, qui comprend une chambre dans laquelle un assemblage d'électrode | électrolyte solide, fabriqué de strontia-ceria-ytterbia perovskite de la forme de $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{Yb}_{0.05}\text{O}_3$, comme d'électrolyte solide, sur quelque côté duquel un film poreux polycristallin de palladium est posé, est arrangé. 20 25 30 35 40 45 50 55

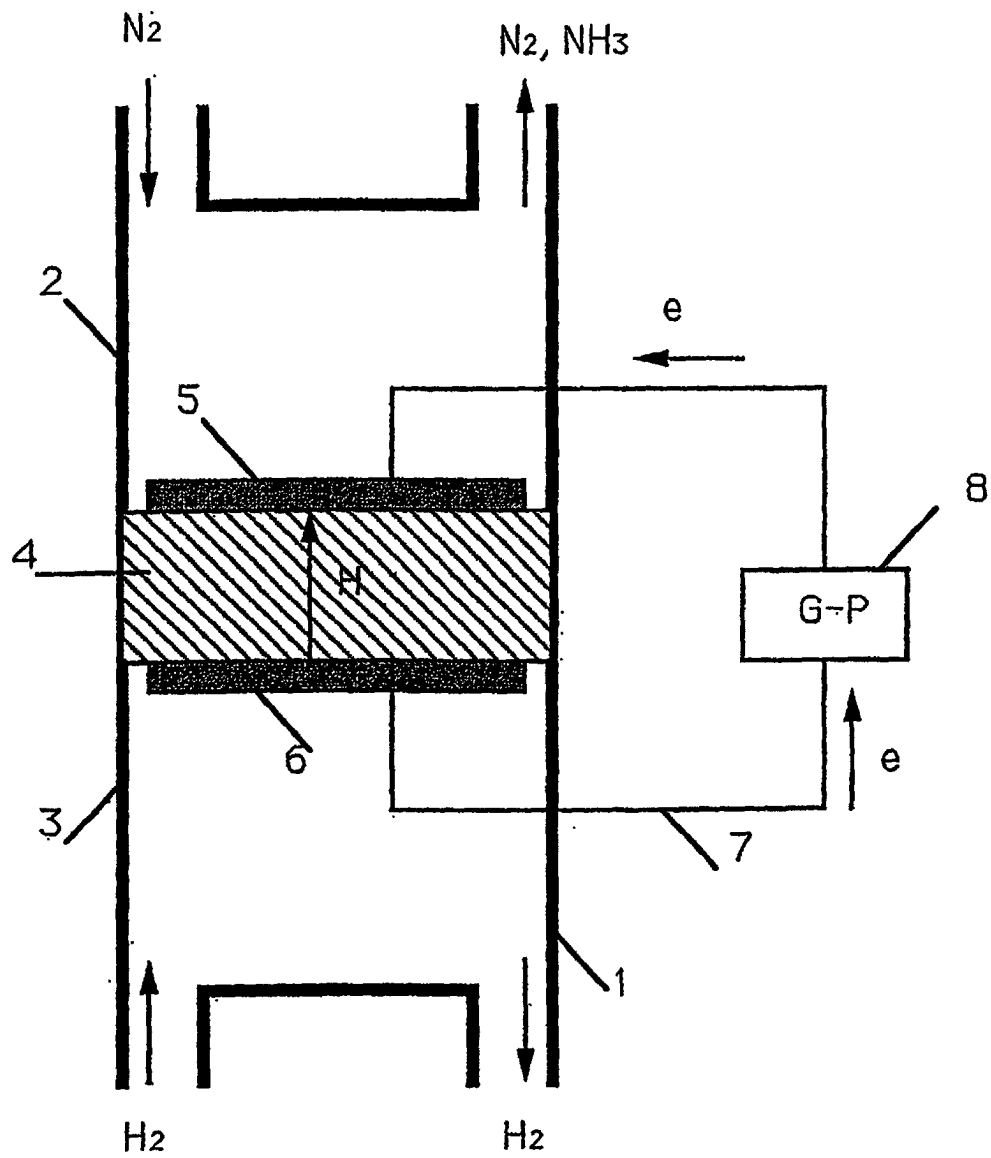


Figure 1

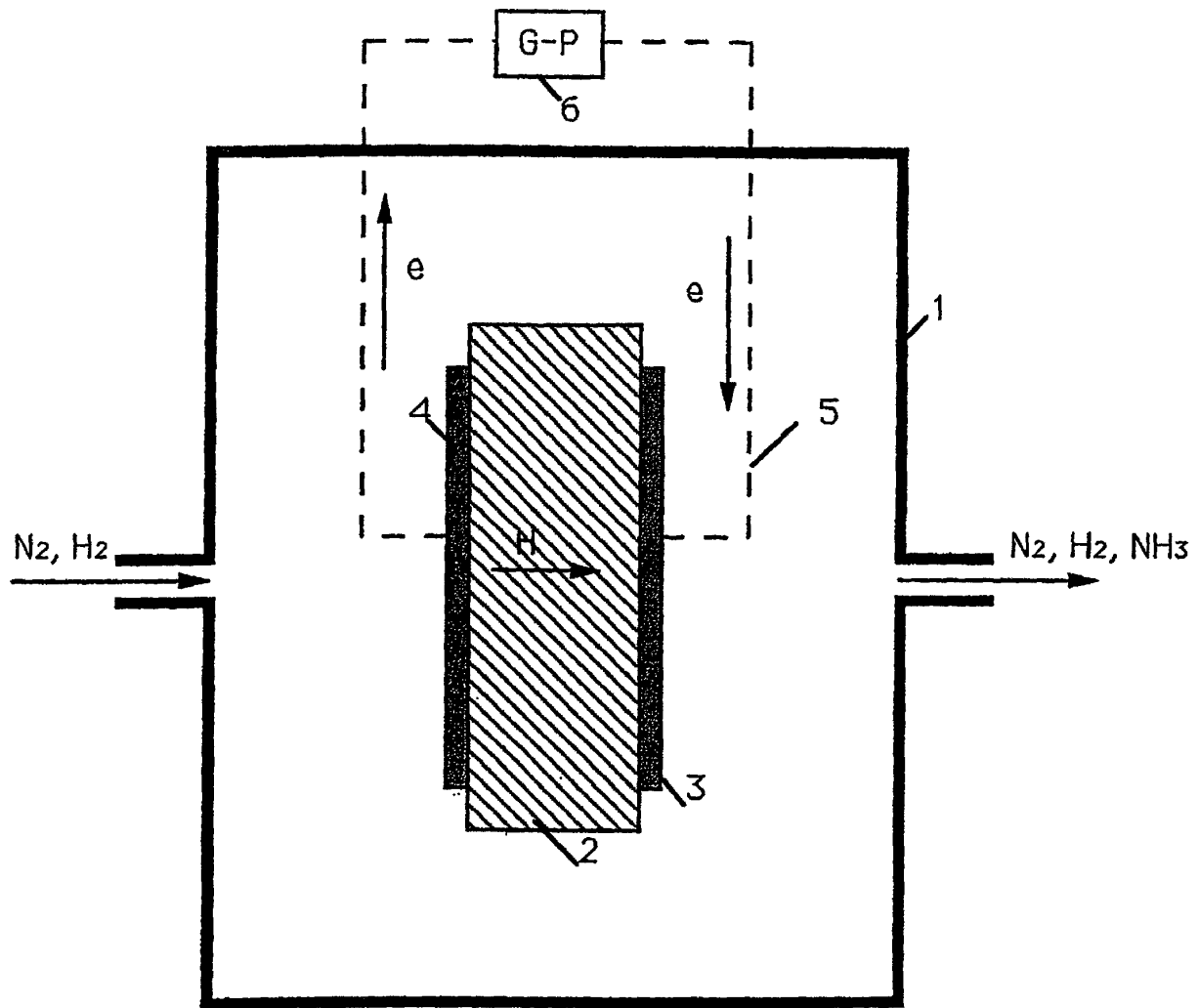


Figure 2

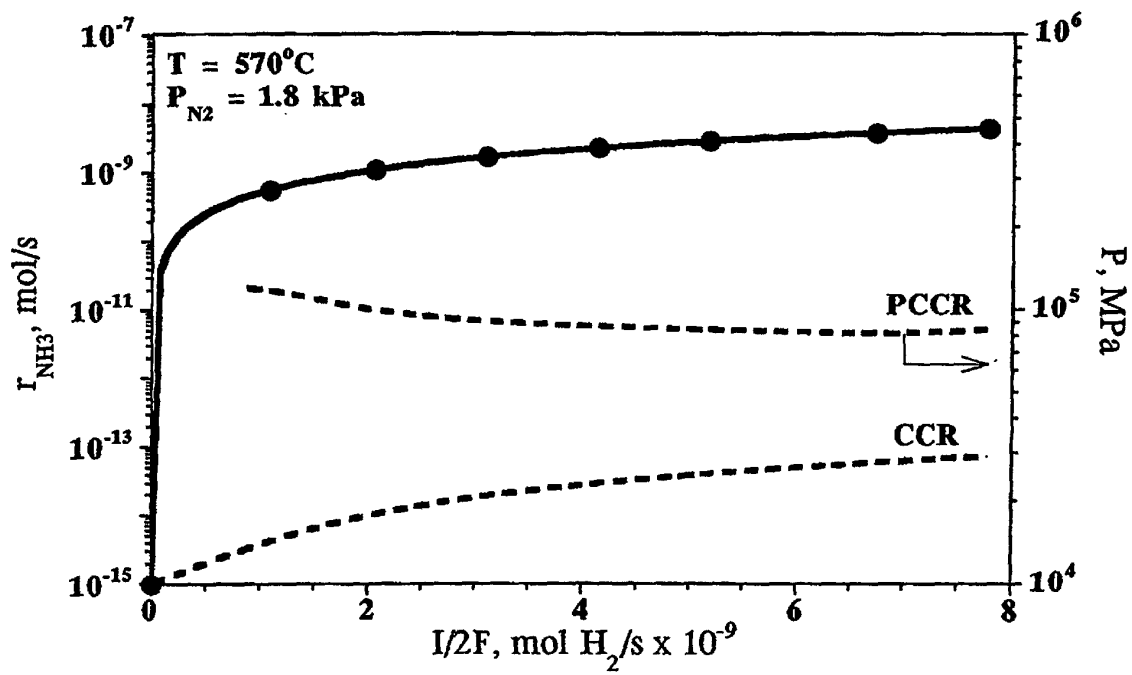


Figure 3

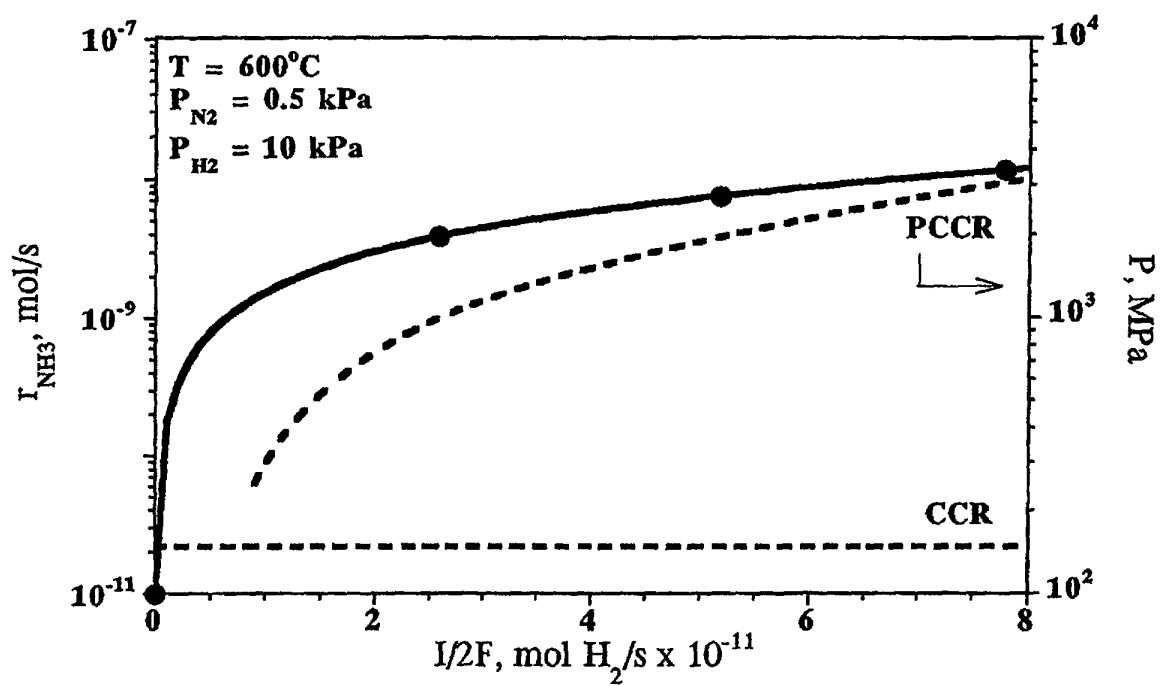


Figure 4