Investigation of New Ammonia Synthesis Process Utilizing Vanadium-Based Hydrogen Permeable Alloy Membrane

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The possibility of a new ammonia synthesis process has been investigated by utilizing V-based alloy membrane under moderate temperature and pressure conditions. Three membrane samples with different coating conditions of Pd-Ag alloy on the outlet side surface have been tested. It is found that the deposition of Pd-Ag alloy on the outlet side surface is needed for V-based alloy membrane for hydrogen permeation at 623 K. While keeping the hydrogen permeation condition, nitrogen gas is flowed to the outlet side surface of the membrane samples, and the reaction gas is bubbled into distilled water to detect ammonia formation by using Nessler’s reagent. Ammonia is not synthesized for the membrane sample coated thickly with Pd-Ag alloy on the outlet side surface, indicating that Pd-Ag alloy does not have a dissociation ability of nitrogen molecule. In contrast, ammonia is formed for the membrane sample coated in a grid pattern with Pd-Ag alloy on the outlet side surface. In this case, both V-based alloy and Pd-Ag alloy coexist on the outlet surface, and hydrogen atoms permeating through the membrane and nitrogen atoms dissociated on the surface of V-based alloy probably react with each other to form ammonia. [doi:10.2320/matertrans.MB201507]

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1. Introduction

Although over 78% of the atmosphere is composed of nitrogen, it exists in an unusable gaseous form chemically and biologically. It is difficult to use N2 directly by plants because plants can only use fixed nitrogen. The breakthrough in nitrogen fixation has taken place a century ago, by the well-known Haber-Bosch process. Nitrogen fertilizer has supported approximately 27% of the world’s population over the last century, equivalent to around 4 billion people born since 1908.1)

On the other hand, it is recently planned that the hydrogen is shipped in the form of liquid hydrogen or chemical carrier. Ammonia (NH3) has been concerned as a liquid chemical hydrogen carrier together with cyclohexane, methylcyclohexane and methanol since 1990’s. Ammonia as hydrogen carrier having a high hydrogen capacity of 17.6 mass% can be easily stored and transported in liquid because ammonia gas is liquefied by pressurizing up to 8.57 MPa at 293 K.2) Thus, ammonia is very important not only for chemical fertilizer but also for hydrogen energy carrier.

For the Haber-Bosch process, however, high temperature (~773 K) and high pressure (15–30 MPa) conditions are required,3) which increases the requirement for special equipment and construction materials, resulting in high cost of the end product. Thermodynamically, ammonia synthesis is exothermic process so that it is more favorable to carry out at low temperatures, but the rate of synthesis reaction on the iron catalyst is significantly decreased.4) In order to reduce the energy required with synthesis as well as the cost of the end product, it is essential to introduce new ammonia synthesis process.

In the Haber process, the following eight elemental steps are considered to proceed.5)

\[
\begin{align*}
H_2 & \rightleftharpoons H_{2,ad} & (1) \\
N_2 & \rightleftharpoons N_{2,ad} & (2) \\
H_{2,ad} & = 2H_{ad} & (3) \\
N_{2,ad} & = 2N_{ad} & (4) \\
N_{ad} + H_{ad} & = NH_{ad} & (5) \\
NH_{ad} + H_{ad} & = NH_{2,ad} & (6) \\
NH_{2,ad} + H_{ad} & = NH_{3,ad} & (7) \\
NH_{3,ad} & = NH_3 & (8)
\end{align*}
\]

It is widely recognized that the dissociation of the triple bonded N2 molecule into N atoms (step (4)) is the rate-limiting process of the total reaction of ammonia synthesis.5,6) However, there is another opinion about the rate-limiting step. Kitano et al. suggest that the step (5) is the rate-limiting process of ammonia synthesis when the activation energy for the dissociation of N2 molecule is greatly reduced by good catalyst.7) Here, if the former idea is correct, the catalytic activity for dissociation of nitrogen molecule is very important to enhance the kinetic of step (4) reaction.

By the way, hydrogen permeable metal membranes are important materials for hydrogen separation and purification technologies.8–10) For example, Pd-based alloy (e.g., Pd-Ag and Pd-Cu alloys) membranes are widely used practically for the separation and purification of high purity hydrogen gas.9) Group 5 materials (vanadium (V), niobium (Nb) and tantalum (Ta)) are promising materials for next generation hydrogen separation membranes, because of their lower cost and higher hydrogen permeability than currently used Pd-based alloys.11) In our previous study, the hydrogen permeability of V-based alloy membranes have been investigated, and V-Fe alloy has been designed and
developed, which shows extremely high hydrogen permeability together with strong resistance to hydrogen embrittlement and good durability.12) Figure 1(a) shows a schematic illustration of hydrogen permeation process through metal membrane. As shown in this figure, active atomic hydrogen is continuously supplied to the outlet side surface through the metal membrane.

Also, vanadium is known to have a dissociation ability of nitrogen molecule into nitrogen atoms.13) When nitrogen gas is flowed on the outlet side surface of the V-based hydrogen permeable alloy membrane, strong N≡N bond will be dissociated by the catalytic activity of vanadium, and atomic nitrogen is supplied to the outlet side surface of the membrane. Thus, the hydrogen and the nitrogen atoms coexist on the outlet side surface of the membrane. When energy is high enough to proceed steps (5)–(7), the hydrogen and nitrogen atoms on the surface react with each other to form ammonia, as shown in Fig. 1(b).

In this study, the possibility of the idea of new ammonia synthesis process by utilizing V-based hydrogen permeable alloy membrane has been investigated in a fundamental manner.

2. Experimental Procedure

2.1 Adoption of V-based alloy and experimental condition

In this study, atomic hydrogen is supplied through V-based hydrogen permeable alloy membrane. Here, vanadium is known to be very sensitive to hydrogen embrittlement. In order to prevent brittle failure of the vanadium membrane, the hydrogen concentration must be controlled and kept below the critical value of the ductile-to-brittle transition hydrogen concentration (DBTC, i.e., 0.2 (H/M)).14) For this purpose, the measurement of the hydrogen solubility, i.e., the pressure-composition-isotherms (PCT), is very important. The alloying effects on the hydrogen solubility have been investigated and discussed for the V-5 mol% alloy (X = Mo, Cr, Fe, Co) by Suzuki et al.12) It is found that the alloying effects of iron and cobalt into vanadium are much larger than that of chromium or molybdenum. In other words, iron and cobalt are effective alloying elements to improve the resistance to hydrogen embrittlement of vanadium and hence high hydrogen pressure can be applied to the membrane. Therefore, in this study, V-Fe alloy is selected as the hydrogen permeable metal membrane in order to prevent the hydrogen embrittlement.

According to the thermal equilibrium, almost all ammonia is decomposed above about 673 K in moderate pressure. Therefore, the low temperature is preferred for ammonia synthesis reaction. In contrast, the hydrogen permeability through V-Fe alloy membrane decreases with decreasing temperature. For these reasons, the temperature for ammonia synthesis experiment is set to be 623 K in this study.

Figure 2 shows the PCT curves for V-10 mol%Fe alloy at 623 K together with that for pure V for comparison. As shown in Fig. 2, the hydrogen solubility of V-10 mol%Fe alloy is reduced compared to that of pure V, and the hydrogen concentration in V-10 mol%Fe alloy is kept below the DBTC (i.e., 0.2 (H/M)) even applying 0.4 MPa of hydrogen pressure at 623 K. Therefore, the inlet hydrogen pressure applied in this study is determined to be 0.4 MPa, and the outlet hydrogen pressure is set to be 0.1 MPa so that high hydrogen flux through the membrane is expected with this pressure condition at 623 K.

2.2 Sample preparation

The ingot of V-10 mol%Fe alloy is melted by using a tri-
are furnace in a purified argon gas atmosphere. The purity of the raw materials used in this study are 99.9 mass% for vanadium and 99.99 mass% for iron. According to the V-Fe equilibrium binary phase diagram, this alloy is composed of a single phase with simple bcc crystal structure.

The as-cast ingot is cut into disks with about φ12 mm in diameter and 0.5 mm in thickness, and they are annealed in vacuum at 1273 K for 24 h.

They are polished mechanically by alumina abrasive papers followed by the final polishing with 1 µm alumina powders. The final thickness of the samples is approximately 0.41–0.48 mm. Subsequently, Pd-27 mol% Ag alloy is deposited at 573 K on the inlet side surface of each sample for about 200 nm in thickness by using an RF magnetron sputtering apparatus. This palladium layers act as catalyst to eliminate the impediment barrier for hydrogen dissociation and dissolution reactions on the inlet side surface. In this study, three different samples are prepared by changing the morphology of the Pd-Ag alloy deposition on the outlet side surface as shown in Table 1. There is no Pd-Ag alloy deposition layer for sample A, but for sample B, Pd-Ag alloy is coated thickly on the outlet side surface. On the other hand, the sample C is prepared by masking its outlet side surface with a Ni mesh (diameter is 74 µm, aperture ratio is about 40%) during the sputtering of Pd-Ag alloy on the outlet side surface. The SEM image of the morphology of the outlet side surface of sample C is shown in Fig. 3. The area ratio of Pd-27 mol% Ag alloy is estimated to be about 54% using Image J software.

### 2.3 Hydrogen permeation test

A schematic illustration of the apparatus for hydrogen permeation test and ammonia synthesis experiment used in this study is shown in Fig. 4. The V-10 mol% Fe alloy membrane is sealed with VCR fittings and set in an electric furnace.

Prior to the ammonia synthesis experiment, the hydrogen permeation test is performed at 623 K. High purity hydrogen gas is introduced into both inlet and outlet sides of the membrane sample.

By opening V1 valve in Fig. 4, the inlet pressure is regulated to 0.4 MPa. Outlet pressure is kept to be 0.1 MPa by using check valve (V4). V2 valve is closed in order not to introduce nitrogen gas into the system, and three-way valve (V3) is switched toward the mass flow-meter (MFM) side. The hydrogen fluxes, \( \dot{J} \), permeated through the membrane with a unit area within a unit time are measured by the conventional gas permeation method using the MFM. It is divided by the inverse of the membrane thickness, 1/\( L \), in order to estimate the normalized hydrogen flux, \( \dot{J} \cdot L \). It is noted that the atomic hydrogen flux, mol H m\(^{-2}\) s\(^{-1}\), is evaluated in this study, which is twice as large as the gaseous hydrogen flux, mol H\(_2\) m\(^{-2}\) s\(^{-1}\). A detailed explanation of the hydrogen permeation test is given elsewhere.\(^{15} \)

### 2.4 Ammonia synthesis and detection

After hydrogen permeation test, the ammonia synthesis experiment is performed at 623 K. While keeping the inlet hydrogen pressure at 0.4 MPa, V2 valve shown in Fig. 4 is opened and nitrogen gas of 0.1 MPa is flowed on the outlet side surface of the membrane. Then, V3 valve is switched toward the distilled water side, and the reaction gas with mixture of hydrogen and nitrogen is bubbled in the 50 mL of distilled water. The flow rate of nitrogen gas is controlled to the same amount of hydrogen permeation flux. After ammonia synthesis experiment, the bubbled water is analyzed by using Nessler’s reagent. 2 mL of Nessler’s reagent is added into 10 mL of bubbled water, and the color change of the water is observed. If ammonia is synthesized and trapped in the distilled water, the color of the water will change to deep yellow.

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**Table 1** Coating conditions of Pd-27Ag on the sample surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd-27 mol% Ag coating thickness (nm)</th>
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<tr>
<td></td>
<td>Inlet side</td>
</tr>
<tr>
<td>A</td>
<td>200</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
</tr>
<tr>
<td>C</td>
<td>200</td>
</tr>
</tbody>
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**Fig. 3** SEM image of the outlet side surface of V-10 mol% Fe sample coated in a grid pattern with Pd-27 mol% Ag (sample C).

**Fig. 4** Gas line diagram of the apparatus used for the hydrogen permeation test and ammonia synthesis experiment.
After the ammonia synthesis experiment, V2 valve is closed and V3 valve is switched toward the MFM side, and the hydrogen permeation test is performed again.

3. Results and Discussion

3.1 Hydrogen permeability

Figure 5 shows the time dependence of the normalized hydrogen flux, $J\cdot L$, for sample A at 623 K. As shown in Fig. 5, it is evident that the hydrogen flux is almost zero from the beginning. Then, the hydrogen permeation test is performed for sample B, and the result is shown in Fig. 6 with open circles (○). In contrast to sample A shown in Fig. 5, the hydrogen flux is sufficient and becomes constant value of about $37.5 \times 10^{-6}$ mol H m⁻¹ s⁻¹ after about 300 min. From these results of the hydrogen permeation tests for sample A and sample B shown in Fig. 5 and Fig. 6 respectively, the Pd overlayer on the outlet side surface of V₂-based alloy membrane is requisite for hydrogen permeation.

Figure 7 shows the time dependence of the normalized hydrogen flux for sample C (open circle (○)). As similar to sample B, the hydrogen flux is sufficient and becomes constant value for about $16.8 \times 10^{-6}$ mol H m⁻¹ s⁻¹ after about 200 min. However, the $J\cdot L$ value for sample C is only about 45% as much as that for sample B shown in Fig. 6. As mentioned before, the area ratio of Pd-27Ag alloy on the outlet side surface of sample C is about 54% as shown in Fig. 3. From these results for sample A, B and C, the hydrogen will permeate through only the area coated with Pd-27Ag alloy on the outlet surface.

The time dependences of the hydrogen flux after the ammonia synthesis experiment, i.e., blowing nitrogen gas to the outlet side surface, for sample B and C are shown in Figs. 6 and 7 with solid circles (●), respectively. It is interesting that the normalized hydrogen flux through the membrane increases after blowing nitrogen gas in both cases of sample B and C. For example, in case of sample C, the hydrogen flux increases by about 1.4 times after blowing nitrogen gas. The reason of the increment of hydrogen flux due to nitrogen flow remains unclear. Further investigation on the sample surface such as XPS analysis will be needed to clarify the cause of this behavior.

3.2 Ammonia detection by Nessler’s reagent

Figure 8 shows the comparison of the color change by adding Nessler’s reagent into the solutions, (a) distilled water, (b) distilled water dissolving reaction gas of sample B and (c) distilled water dissolving reaction gas of sample C. Comparing Fig. 8(a) and Fig. 8(b), the color of the solution for sample B is similar to that of distilled water, indicating that ammonia is scarcely synthesized with sample B. From these results and the fact that the outlet side surface of sample B is covered thickly with Pd-Ag alloy, it is considered that Pd-based alloy does not have a dissociation ability of triple bonded nitrogen molecule.
Fig. 8  Color changing of the solutions by adding Nessler’s reagent; (a) distilled water without dissolving reaction gas, and (b) distilled water dissolving reaction gas of sample B, and (c) distilled water dissolving reaction gas of sample C.

On the contrary, as shown in Fig. 8(c), the color of the solution changes into light yellow, indicating that ammonia is synthesized with sample C. In this case, both V-Fe alloy and Pd-Ag alloy coexist on the outlet side surface of sample C in a grid pattern. Therefore, hydrogen atoms permeating through the part of Pd-Ag alloy and nitrogen atoms dissociated from nitrogen molecule on the part of V-Fe alloy react with each other to form ammonia. Thus, there is a possibility that ammonia can be synthesized under moderate temperature and pressure conditions by utilizing V-based hydrogen permeable alloy membrane.

However, the yield of ammonia formation in this study is very low according to the color change of the solution by the Nessler’s reagent. As mentioned before, there are two opinions about the rate-limiting step for ammonia synthesis reaction. One idea is that the dissociation of nitrogen molecule (step (4)) is the rate-limiting step. The other one is that the combination of Nad and Had to form NHad (step (5)) is the rate-limiting step. Assuming that the catalytic activity of vanadium is high enough for N2 dissociation, it is possibly that the kinetics of the combination of Nad and Had may be low and the reaction is not promoted under the temperature and pressure condition in this study. In this case, the destabilization of the adsorbed nitrogen atom (Nad) may enhance the reaction rate of step (5) because the interaction between vanadium and nitrogen is too strong, which makes the progress of the reaction more difficult. For example, designing alloys which have lower affinity with absorbed atomic nitrogen (Nad) on the surface will be needed in order to improve the reaction yield. Also, optimization of the temperature and pressure conditions may be necessary.

In this paper, thermodynamic property about each steps of ammonia synthesis reaction cannot be discussed because only single temperature and pressure condition is adopted. Further investigation for the ammonia synthesis will be needed, for example, thermodynamic analysis, quantitative measurements of ammonia formation, research for the optimum condition and alloy composition as well as the optimum surface morphology.

4. Summary

The possibility of the new ammonia synthesis process has been investigated by utilizing V-based alloy membrane under moderate temperature and pressure conditions. It is found that the Pd coating is necessary on the outlet side surface of V-based alloy membrane for the hydrogen permeation reaction at 623 K. During the hydrogen permeation, nitrogen gas is flowed on the outlet side surface of the membrane sample, and the ammonia is detected by using Nessler’s reagent. As a result, ammonia is scarcely synthesized for the membrane coated thickly with Pd-Ag alloy on the outlet side surface, indicating that Pd-Ag alloy does not have a dissociation ability of triple bonded nitrogen molecule. In contrast, ammonia is formed for the membrane coated in a grid pattern with Pd-Ag alloy on the outlet side surface. In this case, both V-based alloy and Pd-Ag alloy coexist on the outlet side surface of the membrane. Therefore, active atomic hydrogen and nitrogen probably coexist on the outlet side surface, and react with each other to form ammonia.

However, the yield of ammonia formation is not enough under the condition tested in this preliminary study. Further investigation will be needed.

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REFERENCES