

Thin Pd membrane on macroporous stainless steel tube filter by an in-situ multi-dimension plating mechanism

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1. Experimental process

1.1 The preparation of aluminum hydroxide sols

The preparation schematic of aluminum hydroxide sol is shown in Fig. 1. At beginning, the aqueous solution of ammonium carbonate (0.6 M) was slowly titrated into the aqueous

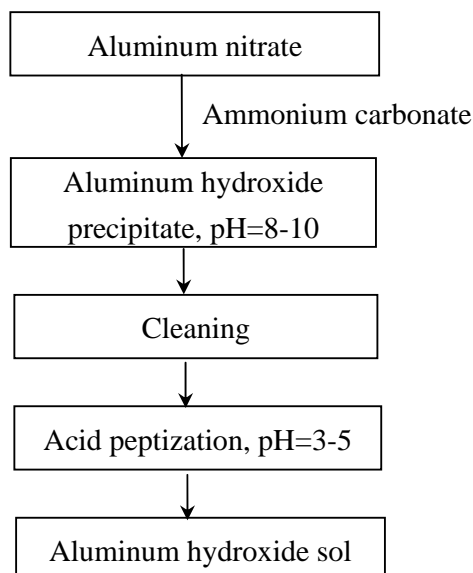


Fig. 1 Preparation procedure of aluminum hydroxide sol

solution of aluminum nitrate (0.4 M) at the room temperature. The aluminum hydroxide solid gradually precipitated with the addition of ammonium carbonate solution. The final pH value was controlled to be 8-10. After stirring for 3 h, the aluminum hydroxide precipitate was separated from the solution by vacuum suction filtering. Subsequently, the precipitate was cleaned using distilled water for several times. After that, the as-cleaned precipitate was mixed into distilled water (0.2 M). While strongly stirring, the 1.0 M nitric solution was titrated into the mixture system. The final pH value was controlled to 3-5. The peptization process was performed at the steady temperature of 353 K and has been continuously conducting for 6 h. At last, the stable aluminum hydroxide sol was prepared well.

1.2 The detailed composition of activating solution and plating solution

The activating solution and plating solution were bought from Okuno Chemical Industries Co., Ltd. (JAPAN). The homepage of this company is "<http://www.okuno.co.jp/>". The telephone number of foreign department is +81-06-203-6667. The commercial name of the activating solution was OPC-50 inducer A, OPC-50 inducer C, and OPC-150 cryster MU. The commercial name of the plating solution was PALLA TOP A and PALLA TOP B. The detailed composition of these commercial solutions from the company is displayed in the following table.

Solution name	Composition and properties
OPC-50 inducer A	Palladium salt, 0.78w%; boric acid salt, 2.4w%; Organic chemical, 1w%; de-ionized water, 95.82 w%; orange to red color; d, 1.023 g/ml.
OPC-50 inducer C	NaOH, 3.1w%; boric acid salt, 18w%, de-ionized water, 78.9w%; without to dilute yellow color; d, 1.149 g/ml.
OPC-150 cryster MU	C ₂ H ₁₀ NB and de-ionized water, without color.
PALLA TOP A	Palladium salt aqueous solution
PALLA TOP B	Reductant aqueous solution

Due to the protection of company patents, we cannot know more detailed composition about these solutions. But all these solutions are commercially available, so it is easy for the other researcher to conduct research work using these solutions.

1.3 The detailed conditions of activating and plating

The activating solution I was prepared by mixing 50 ml OPC-50 inducer A, OPC-50 inducer C and 900 ml water together. The activating solution II was prepared by mixing 150 ml OPC-150 cryster MU with 850 ml water. The activating solution III was prepared by mixing 30 ml OPC-150 cryster MU with 970 ml water. Firstly, the tube filter after jamming was dipped into activating solution I for 6 min at 313 K. Continuously, the tube filter was put into activating solution II for 5 min at 298 K. At last, the tube filter was put into the activating solution III for 1 min at 298 K. After water rinsing, the tube filter can be submitted to Pd membrane plating.

The plating solution was prepared by mixing 100 ml PALLA TOP A, 100 ml PALLA TOP B and 800 ml water together. The Pd concentration was about 2 g/L. The first step of Pd plating was carried out at 313 K and pH=7. The second step of Pd plating was carried out at 323 K and pH=6. The HCl and NaOH were used to modify the pH value of the plating solution.

1.4 The measurement of membrane thickness

The membrane thickness was measured by using three methods at the same time. Firstly, the membrane thickness was confirmed by the Pd concentration decrease in the plating solution (ICPS-7000, SHIMADZU). As for this method, before activating and plating, we coated organic film on the dense tube surface where we did not want to plate Pd membrane.

The Pd membrane could not be plated the organic membrane. The schematic is shown in **Fig. 2**. From this figure, we can easily find that the plating area inside the plating solution is determined when the level of plating solution was at the zone of organic film. Therefore, the plating area we obtained is relatively exact.

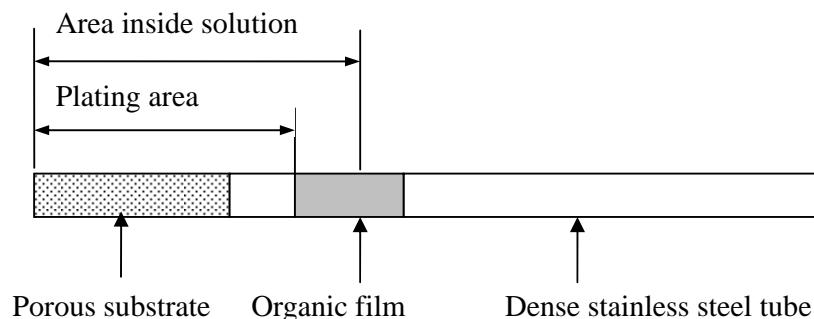


Fig. 2 The schematic of effective plating area

Secondly, we measured the mass increase of the tube filter before and after plating Pd membrane. Combined with the plating area determined by first method, the membrane thickness could also be obtained.

Thirdly, a smaller and thinner stainless steel sheet (which possesses big surface area and smaller mass) with designated area was used as thickness indicator. We activated and plated the sheet under the same condition of Pd membrane preparation experiment. Combined the designated area with the mass increase, we could obtain the Pd membrane thickness easily. Due to the exactly designated plating area and the smaller original mass of the smaller sheet, the method is more correct.

In our experiments, the thickness from these three methods is almost same (about 6 μm).

2. Pd membrane reactor configuration for steam reforming of CH_4

The membrane reactor was constructed using the as-synthesized Pd membrane, whose apparent thickness was about 6 μm . The membrane reactor configuration is shown in **Fig. 3**,

which is a double tubular type reactor. The outside tube is dense stainless steel tube and the inside tube is the as-synthesized palladium composite membrane tube in the same axis. The nickel-alumina based catalyst (Osaka Gas Company) is packed into the annulus volume between these two tubes. The temperature controlling thermocouple is placed in the middle of the membrane. The temperature measuring thermocouple is placed on top of the tube

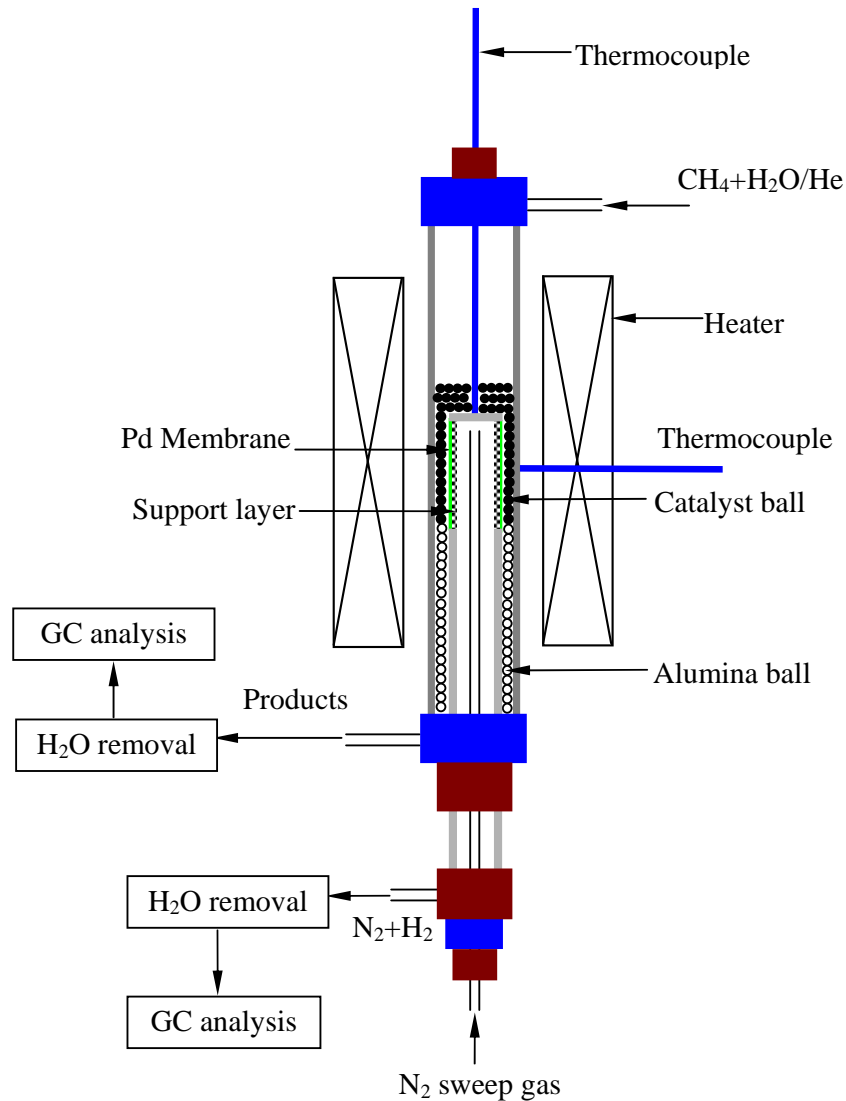


Fig. 3 Configuration of membrane reactor for steam reforming of methane to produce hydrogen

membrane. At the lower place of the reactor, a slim stainless steel tube is plugged into the membrane tube for introducing nitrogen sweep gas. The gas mixture of methane and steam is introduced into the annulus volume reaction space from the higher inlet of outside tube. The gas product from the reaction annulus reaction zone and the permeated gas from the inside membrane tube, after removed of water, are introduced to GC analysis system to determine the gas composition and calculated the reaction performance.