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Deposition of TS-1 zeolite film on palladium membrane for enhancement of membrane stability

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Abstract

A thin TS-1 zeolite film was successfully fabricated on palladium membrane using an assembly method combined with secondary growth technique. The preparation of TS-1-Pd composite membrane involved three stages: (1) deposition of palladium layer on porous alumina support through electroless plating; (2) assembly of silicalite-1 zeolite seeds on the palladium layer; (3) growth of TS-1 layer from the zeolite seeds over the top surface of the palladium layer using hydrothermal synthesis method. The detailed microstructure of the TS-1-Pd composite membrane was examined by SEM, EDX, XRD, FT-IR and UV-vis. This architecture allows the composite membrane to remain stable for 10 days of hydrogen permeation tests at 773 K and tolerate 30 cycles in gas exchanging tests, even for 5 days of hydrogen permeation tests at 423 K. Furthermore, the presence of a TS-1 zeolite film on palladium membrane effectively

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protected the palladium membrane from the contamination from the hydrocarbon, therefore greatly enhanced its operation stability.

Keywords: Palladium membrane; Zeolite; Thin film; Hydrogen separation; Stability

1. Introduction

Hydrogen as a clean energy carrier has drawn much attention in the last decades [1-6]. For production of hydrogen, a variety of techniques have been developed, such as steam reforming of hydrocarbons, partial oxidation of fossil fuels, electrolysis of water, etc. However, hydrogen is not the only product from above mentioned methods. Therefore, obtaining highly pure hydrogen from the gas mixtures is the key point. Membrane technologies are expected to play a key role in separation and purification of hydrogen. Among various H₂-permeable membranes [7], palladium and palladium alloy membranes seems to be excellent candidates for applications in hydrogen separation and purification [8-14], fuel cells [15, 16], steam reforming [17-19] and H₂-related reactions [20-22] due to their excellent hydrogen permselectivity.

Based on the configuration, palladium-based membranes can be classified as two main types, palladium foil [23] and supported palladium membrane [24-31]. Compared to palladium foil, the supported palladium membrane has attracted intense interest owing to its low cost, excellent H₂ permeability and high physical strength. Despite extensive contributions which have been made on the preparation of supported palladium membranes, the membrane stability is still an obstacle for their applications in industries [32-35]. For instance, most studies focused on the preparation of

palladium-based membrane on the outer surface of porous support [36-40]. Under such way, the palladium membranes can be easily polluted and scratched during the operation, resulting in a decrease of their H₂ permeation performance and stability, even failure.

On the other hand, palladium membranes are often exploited for dehydrogenation process of hydrocarbons, such as dehydrogenation of propane to propylene [41] and dehydrogenation of ethylbenzene to styrene [42, 43]. By combining separation and catalytic functionalities in a single membrane reactor, instantaneous removal of hydrogen in the reaction zone by permeation through a membrane can increase the conversion. However, degradation of palladium membrane is often observed when they were applied to separate hydrogen from those carbon-containing gas mixtures. During the separation process of hydrogen, the palladium layer directly exposed to the feeding gas was prone to be contaminated and poisoned by carbon, resulting in a loss of hydrogen permeability [44, 45].

Recently, a novel strategy to enhance the stability of palladium membrane has been reported, in which a zeolite film as a protective layer was deposited on the surface of palladium membrane. This sandwich-like structure significantly improved the membrane stability. Abate et al.[46] reported that a TS-1 zeolite film was fabricated on the palladium membrane by secondary growth technique, including seeding of palladium membrane with TS-1 nanocrystals followed by hydrothermal synthesis. During the seeding process, polymers have to be used to increase the adhesion between TS-1 particles and the palladium membrane. Yu et al. [47] used the dilute acid to

pre-treat palladium membrane to form the imperfections of palladium membrane. This morphology will improve the adhesion of zeolite film on the palladium membrane. Evidently, fabricating a continuous and compact zeolite film on a palladium membrane is quite challenging, owing to their different chemical characteristics.

This paper presents a novel method to fabricate a TS-1 zeolite film on the palladium membrane using an assembly method combined with secondary growth technique to enhance the membrane stability. The microstructure and morphology of the TS-1-Pd composite membrane were characterized by SEM, EDX, XRD, FT-IR and UV-vis. The membrane stability was evaluated by long-term operation test, gas exchange cycling test. Moreover, the effect of propylene on hydrogen permeation properties of the TS-1-Pd composite membrane was also investigated.

2. Experimental

2.1 Materials

N_2H_4 , Na_2EDTA , SnCl_2 , HCl , NH_4OH , and TEOS , which were used for synthesis of palladium membrane and TS-1 zeolite film, were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. The tetrapropyl ammonium hydroxide (TPAOH, 20 wt.%) was prepared in the laboratory. The PdCl_2 was provided by Shanghai Jiuling Chemical Co. Ltd. A porous alumina tube (O.D. 13 mm, I.D. 9 mm, length 75 mm, nominal pore diameter 200 nm) was provided by Foshan Ceramics Research Institute of China.

2.2 Fabrication of TS-1-Pd composite membrane

Fabrication of palladium membrane. The palladium membrane was fabricated on the porous alumina support by electroless plating. Prior to plating, the substrate was

activated by a $\text{SnCl}_2/\text{PdCl}_2$ method at room temperature. The activation process was composed of a two-step immersion sequence in an acidic SnCl_2 solution (2 g/L), followed by an acidic PdCl_2 solution (0.2 g/L). Then the palladium membrane was prepared by electroless plating at 318 K using the plating solution [48] containing PdCl_2 (3.5 g L^{-1}), Na_2EDTA (30 g L^{-1}), NH_4OH (15 M, 101 ml L^{-1}) and N_2H_4 (1 M, 16 ml L^{-1}).

Assembly of silicalite-1 (Sil-1) zeolite seeds on palladium membrane. The resulted palladium membrane was functionalized with 3-aminopropyltrimethoxysilane (APTMS). During this process, the palladium membrane was placed in APTMS solution of ethyl alcohol (1:40 v/v) in a sealed autoclave and was heated at 373 K for 4 h. The unreacted organic linkers were washed away from the surface palladium membrane with ethanol. Subsequently, the APTMS-treated palladium membrane was immersed in an autoclave containing 0.08 wt.% silicalite-1(Sil-1) zeolite suspension of ethanol for 4 h at 373 K to assemble the zeolite seeds on the membrane surface. The Sil-1 zeolite seeds were synthesized from a solution with molar composition of 25 TPAOH:100 TEOS:2700 H_2O at 368 K for 24 h as described by Zhang et al. [49].

Growth of TS-1 zeolite. After seeding palladium membrane, the TS-1 zeolite layer was grown on the top surface of the palladium membrane using hydrothermal synthesis from a synthesis solution with a molar composition of 1 TEOS: 0.01 TBOT:0.18 TPAOH: 250 H_2O [50, 51]. A seeded palladium membrane was immersed in the synthesis solution in a Teflon vessel, which was sealed in a stainless steel autoclave at 448 K for 72 h. Thereafter, the resulted TS-1-Pd composite membrane was rinsed with deionized water, dried overnight at 373 K and calcined for 6 h at 823 K in nitrogen

atmosphere to remove the organic template.

2.3 Characterization

The morphologies of silicalite-1(Sil-1) zeolite seeds, palladium membrane, the seeded palladium membrane with Sil-1 zeolites and the TS-1-Pd composite membrane were examined by field emission scanning electron microscopy (FESEM, Hitachi S-4800). The X-ray diffraction (XRD) analysis was carried out with a D/Max2400 Rigaku X-ray diffractometer using Cu K α radiation at 40 kV and 50 mA. Elemental composition of the samples was measured by Energy dispersive X-ray spectroscopy (EDXS, Bruker-quantax). Fourier transform infrared spectra (FT-IR) was recorded on an EQUINOX55 spectrometer (Bruker) using the KBr disk technique. The resulted samples were also analyzed by JASCO V-550 diffuse reflectance UV-vis spectrometer with BaSO₄ as the internal standard.

2.4 Permeation test

Permeation test of TS-1-Pd composite membrane was carried out in a stainless steel reactor described in previous report [48]. The membrane was sealed in the permeation module using graphite O-rings. The permeation module was placed in a temperature-programmable furnace and heated to the desired temperatures with a heating rate of 1 K min⁻¹. A set of thermocouples (K-type) within the permeation module were used to monitor the temperature during the permeation test. The gases (hydrogen, nitrogen and propylene) were introduced to the permeation module by the mass-flow controller. The hydrogen permeance at the permeation side was measured at desired temperature using a soap-bubble flow meter.

To investigate the membrane stability, the TS-1-Pd composite membrane was tested for 10 days at 773 K. In addition, the membrane was subjected to rapid changes in hydrogen and nitrogen for 30 cycles at 773 K. Furthermore, the chemical stability of the resulting membrane was tested with the treatment of propylene (30 ml/min) for 30 min at 703 K, followed by the measurement of hydrogen permeance.

3. Results and discussion

3.1 TS-1-Pd composite membrane

The preparation of TS-1-Pd composite membrane is illustrated in Fig.1. The preparation procedure involves three stages: (1) deposition of palladium layer on porous alumina support through electroless plating; (2) assembly of silicalite-1 zeolite seeds on the palladium layer; (3) growth of TS-1 film on the top surface of the palladium layer using hydrothermal synthesis method.

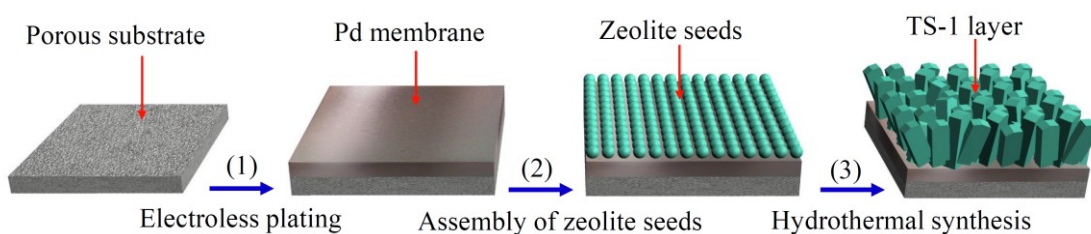


Fig.1 A schematic diagram of the preparation procedure for TS-1-Pd composite membrane.

For the preparation of palladium membrane on the non-conductive substrates including porous ceramic substrate or porous glass, electroless plating technique is one of the most effective methods in comparison with electroplating [52], chemical vapor deposition [53] and sputtering [23]. Fig.2a and b show that the non-conductive substrate

(porous alumina support) has smooth surface and nominal pore size of 200 nm. Fig.2c and d exhibit the SEM images of the palladium membrane prepared by electroless plating. A dense and smooth palladium layer was obtained on the alumina support (Fig.2c). No defects or cracks could be observed. As shown in Fig.2d, a palladium membrane with thickness of 6 μm was firmly connected to the substrate surface.

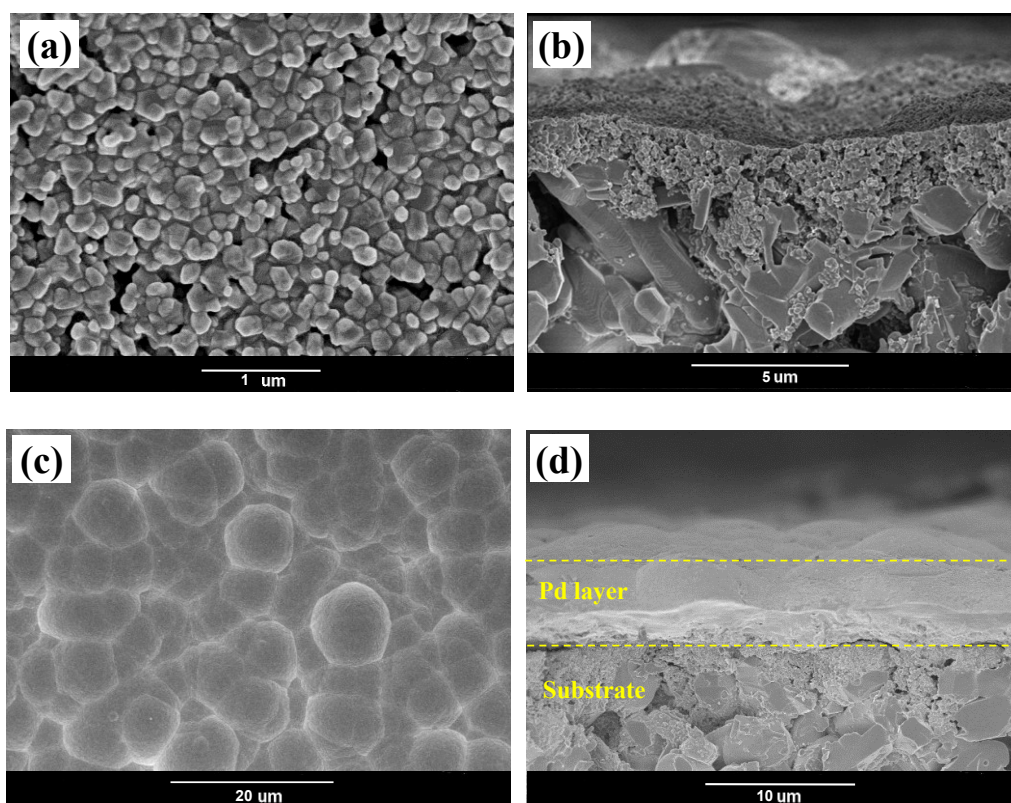


Fig.2 SEM images of porous substrate (a, b) and palladium membrane (c, d)

The secondary growth technique is a common method for the synthesis of zeolite films on substrates, involving deposition of zeolite seeds on a support followed by hydrothermal crystallization, due to its flexibility in controlling the orientation of the zeolite crystals and the microstructure of the zeolite film. A number of studies focused on the growth of zeolite film on different substrates, such as porous supports [50] and

non-porous metal substrates [54]. The seeding process of substrate plays a key role in the synthesis of the zeolite film by the secondary growth technique. The zeolite seeds will offer the crystal nuclei for the growth of zeolite film. In general, the zeolite seeds could be easily deposited on the porous substrate by dip-coating method mainly due to the capillary force. Nevertheless, this method is not very useful to deposit the zeolite seeds on the non-porous metal substrates, such as gold, copper and nickel. Therefore, pretreatments of the non-porous metal substrates are necessary. In our method, the surface of the resulted palladium membrane was pretreated with silane coupling agents (APTMS) to form a linker between the TS-1 zeolite and the palladium membrane.

Prior to depositing TS-1 zeolite film on the palladium membrane, Sil-1 zeolite seeds with particle size of 200~300 nm were prepared, as shown in Fig.3a. The Sil-1 zeolite seeds were then uniformly attached and assembled on the surface of the palladium membrane through APTMS linkers, as presented in Fig.3b. During the seeding process, the APTMS linkers can attach to palladium surface through the NH_2 groups, which is similar to that in the previous reports [55, 56]. The alkoxy silane group of the APTMS linkers tethered on the surface of palladium membrane will connect with the hydroxyl groups on the Sil-1 zeolite surface. These zeolite seeds will provide nuclei for further growth of TS-1 zeolite layer. In comparison, the palladium membrane was seeded without the assistance of APTMS. As presented in Fig.3c, only some Sil-1 zeolite particles scattered on the palladium membrane. This indicates that APTMS as a linker plays an important role in the seeding process of palladium membrane. The EDX analysis of the seeded palladium membrane shown in Fig.3d clearly indicates that

silicon (Si $K\alpha$) and palladium (Pd $L\alpha_1$) along with oxygen (O $K\alpha$) were detected. This result also confirmed that the Sil-1 zeolite seeds were dispersed on the surface of the palladium membrane.

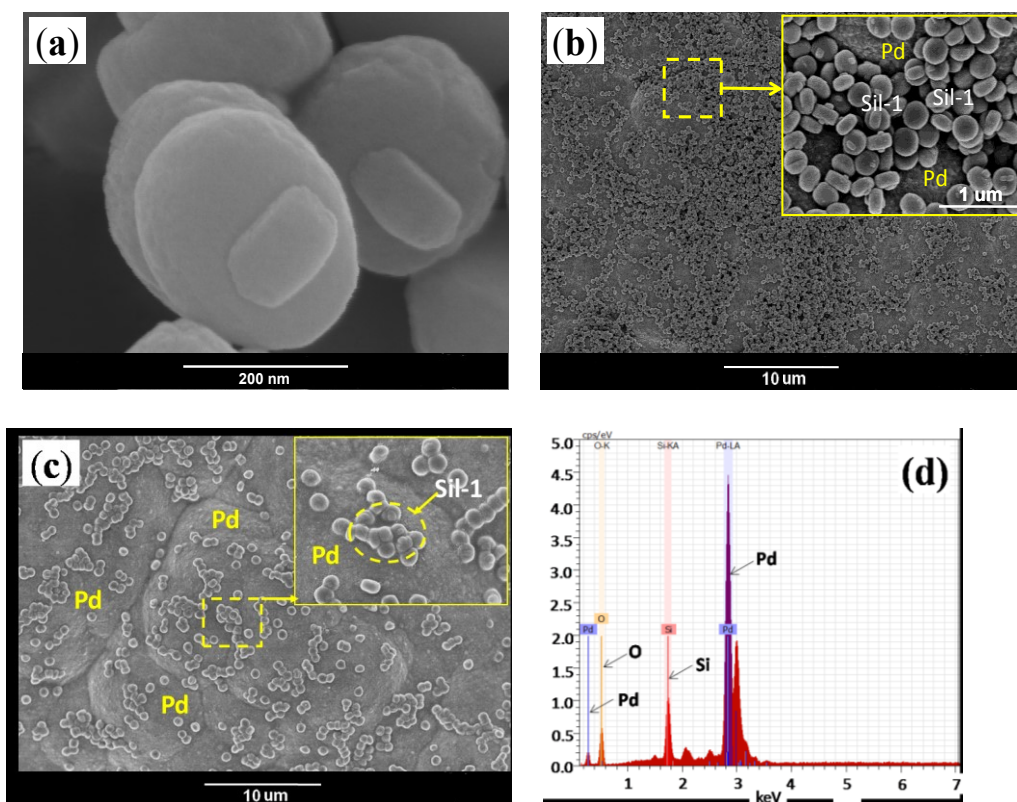


Fig. 3. SEM images of Sil-1 zeolite seeds (a), seeded palladium membrane with (b) and without (c) assistance of APTMS, respectively. EDX analysis of the seeded palladium membrane (d).

According to the dissolution-recrystallization growth mechanism for the synthesis of the zeolite by hydrothermal synthesis, the Sil-1 zeolite seeds on the palladium membrane will grow to a continuous TS-1 zeolite film. Fig. 4a presents the SEM image of the TS-1-Pd composite membrane. It reveals that the palladium membrane surface was fully covered with compact and well intergrown TS-1 zeolite crystals. No

palladium layer can be found. This indicates that the palladium layer will be protected very well by the zeolite layer. In contrast to the cross-sectional view of palladium membrane (Fig.2d), it can be clearly seen in Fig.4b that an additional TS-1 film with thickness of 2 μm was formed on the top surface of the palladium membrane. However, when the seeding process was carried out without the assistance of APTMS, obvious defects can be observed in the resulted TS-1 film, as displayed in Fig.4c. The palladium membrane was not fully covered by TS-1 zeolite crystals. This is attributed to the poor seeding of the palladium membrane, as shown in Fig.3c. In addition, compared to the secondary growth technique, TS-1 zeolite film was prepared on the palladium membrane using directly hydrothermal synthesis without seeding process. From the SEM image presented in Fig.4d, only some scattered TS-1 zeolites were deposited on the palladium membrane. It reveals that a continuous and dense TS-1 zeolite film could not be easily formed without zeolite seeds on the palladium membrane.

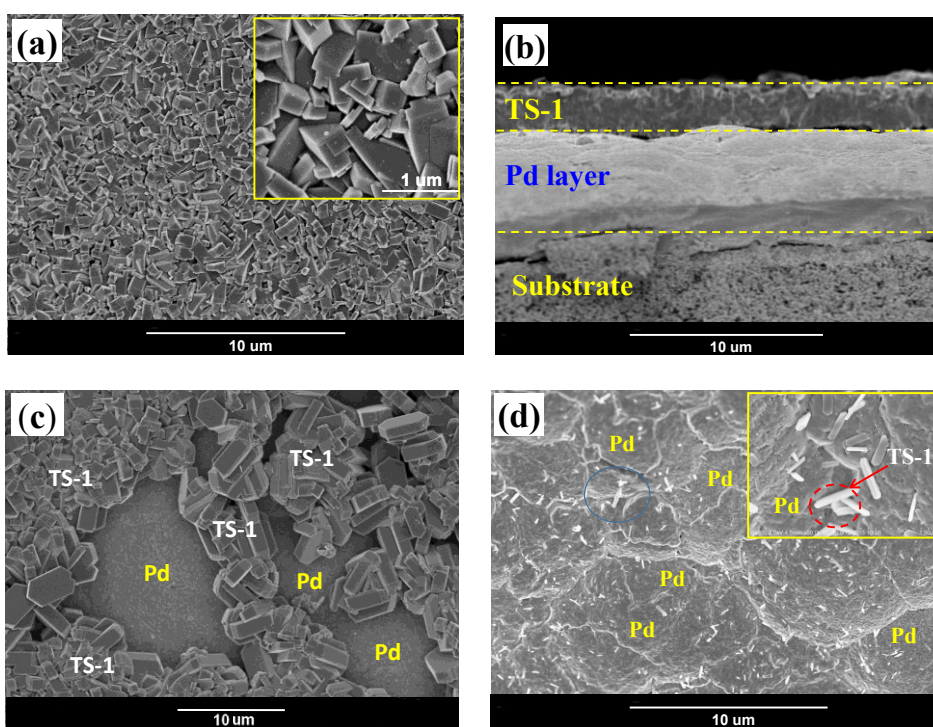


Fig.4. SEM images of TS-1-Pd composite membranes prepared by hydrothermal synthesis with (a, b) and without (c) assistance of APTMS and directly hydrothermal synthesis without seeding process (d), respectively.

To further understand the structure of the TS-1-Pd composite membrane, the elemental distribution of the composite membrane was studied by EDX lining analysis. As shown in Fig.5, the Pd signal between the TS-1 layer (Ti, Si and O signals) and the porous alumina support (Al signal) was clearly observed. This reveals that the TS-1-Pd composite membrane has sandwich-like structure, which is in good agreement with the SEM result displayed in Fig.2d.

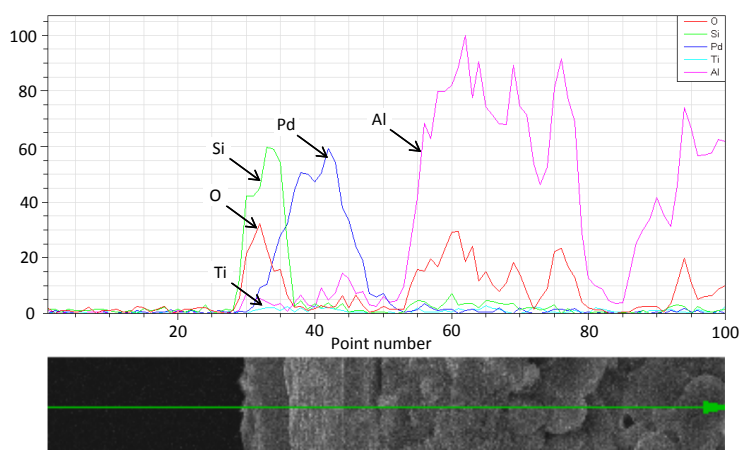
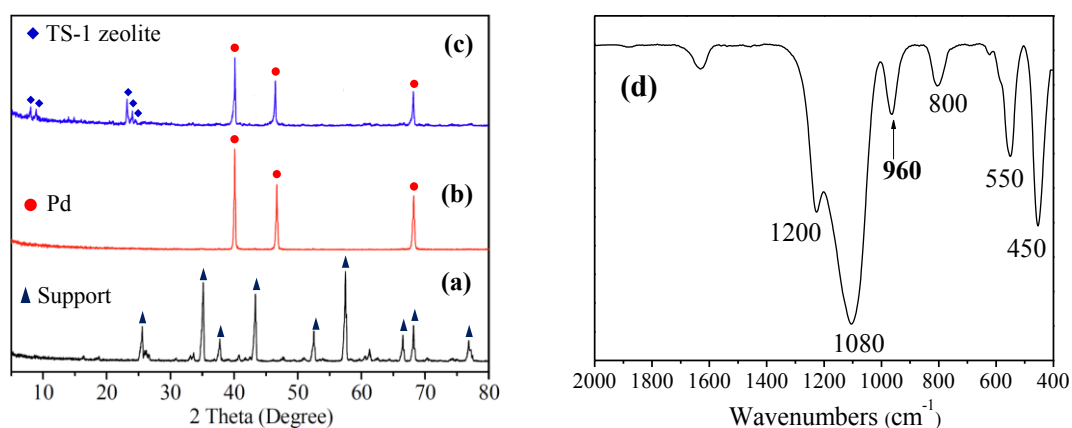


Fig.5. EDX lining analysis of the TS-1-Pd composite membrane.

The X-ray diffraction patterns have also confirmed the sandwich-like structure of the TS-1-Pd composite membrane, as shown in Fig.6a~6c. For the palladium membrane deposited on the porous alumina, only the characteristic peaks of pure palladium could be seen in Fig.6b, suggesting that the palladium layer is dense. After synthesizing TS-1 zeolite film, apart from typical palladium peaks, characteristic peaks of TS-1 zeolite

were also clearly observed in Fig.6c. This indicates that the TS-1 zeolite layer was successfully fabricated on the outer surface of palladium membrane. Moreover, no diffraction peak of alumina was detected on the TS-1-Pd composite membrane, suggesting the integrity of the palladium membrane was not affected during the formation of TS-1 zeolite layer by hydrothermal synthesis. Fig.6d shows FT-IR spectrum of the TS-1 zeolite powders collected at the bottom of synthesis autoclave. It indicates that absorption peaks at 1220 cm^{-1} , 1100 cm^{-1} , 800 cm^{-1} , 550 cm^{-1} and 450 cm^{-1} were clearly seen. These peaks were assigned to the characteristic bands of MFI zeolite [57]. Besides, the infrared signal at about 960 cm^{-1} is commonly originated from Ti-O-Si and often taken as the fingerprint of titanium substitution in the zeolite framework [58]. Moreover, Fig.6e presents the UV-vis spectrum of the TS-1 zeolite crystals. It can be found that the zeolite exhibits a dominant peak at 220-240 nm, which is assigned to the presence of the tetrahedral titanium in the zeolite framework. As expected, the characteristic adsorption peak of anatase TiO_2 at 330 nm was not observed, which confirms that the only tetrahedral coordinated titanium was formed in the zeolite framework [59].



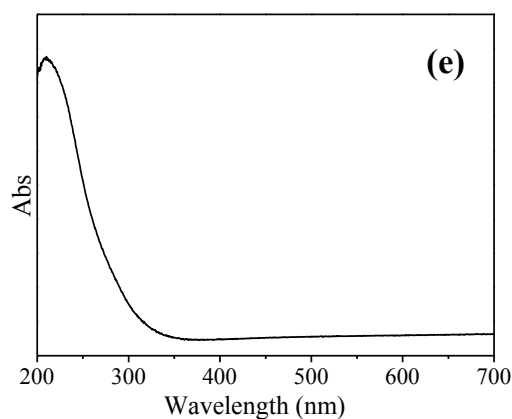


Fig. 6. The XRD patterns of alumina support (a), palladium membrane supported on alumina substrate (b) and TS-1-Pd composite membrane (c). FT-IR (d) and UV-vis (e) spectra of the TS-1 zeolite collected at the bottom of synthesis autoclave.

3.2 Hydrogen permeation performance

To investigate the effects of TS-1 zeolite film on the hydrogen transport properties and stability of the TS-1-Pd composite membrane, permeation tests were performed with H₂ and N₂ at temperature range of 423~773K. Fig.7 plots the H₂ permeation fluxes of palladium membrane before and after zeolite regrowth at various temperatures and pressure differences. The palladium membrane and resulted TS-1-Pd composite membrane have H₂ permeances of 2.05×10^{-6} and 0.54×10^{-6} mol m⁻² s⁻¹ Pa⁻¹, respectively. These permeance values are comparable to other hydrogen-permeable membranes (Table 1). After growth of TS-1 zeolite on the palladium membrane, an obvious decrease of hydrogen permeance for TS-1-Pd composite membrane was observed. This is attributed to the higher transport resistance across the compact TS-1 zeolite film. Yu et al. [46] reported that the presence of an additional zeolite film on top of the palladium membrane markedly decreased its hydrogen permeance. In addition, Ti element was introduced to synthesize TS-1 zeolite film. Fernandez et al. [65] reported that Ti has

strong chemical interaction with palladium, resulting in the low hydrogen permeance of palladium membrane.

Table 1 Comparison of hydrogen permeation flux for various hydrogen-permeable membranes

Membrane	Temperature (K)	Pressure difference (kPa)	H ₂ flux (mol m ⁻² s ⁻¹)	H ₂ /N ₂ Selectivity	Ref.
Pd/ZrO ₂ /PSS	773 K	100	0.083	160	[60]
MCM-22/silica/Al ₂ O ₃	473 K	100	0.007	50	[61]
silica	773 K	100	0.018	730	[62]
ZIF-90	473 K	100	0.021	17.5	[63]
Pd/NaA	723 K	50	0.079	608	[64]
Pd/YSZ	673	110	0.0734	320	[36]
Pd	773 K	100	0.205	886	This work
TS-1-Pd	773 K	100	0.054	268	This work

According to Sieverts' law, the hydrogen flux is proportional to the square root of hydrogen partial pressure (pressure exponent $n=0.5$) when bulk diffusion through palladium layer is the rate-controlling step. When the surface process is important, this exponent corresponds to $n=1$. Fig.7 shows that the hydrogen flux is linearly proportional to the pressure difference across the membrane at different temperatures, reflecting the n value=1. Factually, the pressure exponent often deviated from 0.5, as reported by many researchers [31, 37, 38, 46], the differences of n -values would be attributed to the differences in the preparation method, surface activity, membrane microstructure and mass transfer resistance for palladium composite membranes. It is believed that the existence of TS-1 film decreases the surface which may be reached by H₂, because part of the palladium membrane is shielded from the deposited zeolite

crystals. This causes the change of surface activity and mass transfer properties of the palladium membrane, resulting in the increase of n value. On the other hand, the H_2 permeation flux increases with temperature and activation energies of 15.4 and 13.7 kJ mol^{-1} were obtained for the palladium membrane and resulted TS-1-Pd composite membrane, respectively. These values are comparable to that reported in other publications [34, 46].

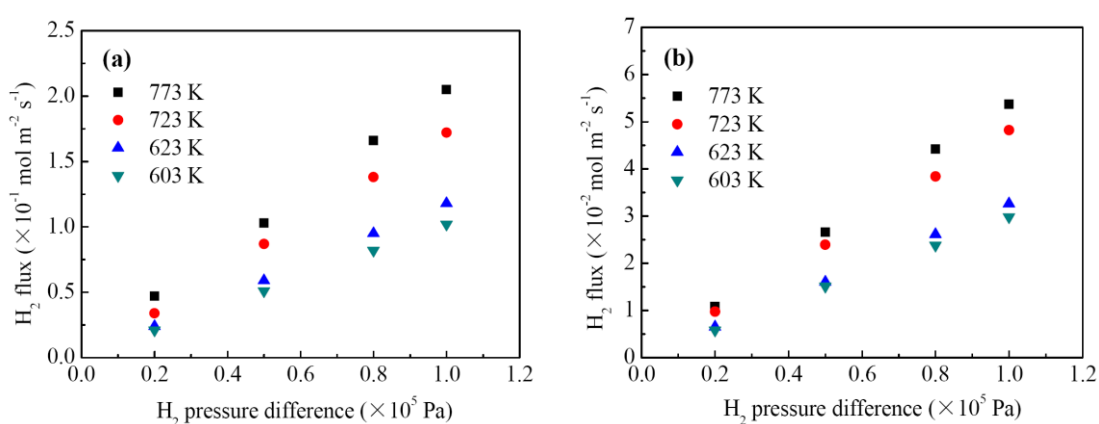


Fig. 7. The H_2 permeation fluxes of palladium membrane before (a) and after (b) zeolite regrowth at various temperatures and pressure differences.

Thermal and chemical stability of the palladium membranes remains as one of the major problems for their applications in industries. The formation of defects on palladium membranes has often been observed when undergoing thermal treatment for long-term operation and hydrogen absorption/desorption cycles [33]. To measure the stability of the TS-1-Pd composite membranes, long-term operation was carried out at 773 K and 423 K, as presented in Fig.8. The plots show that a stable hydrogen permeance was obtained during a continuous operation of 10 days at 773 K, even when the membrane was operated for 5 days of permeation at 423K which is below the

embrittlement temperature of palladium. In addition, the gas exchange cycle between hydrogen and nitrogen at 773 K and 100 kPa was also used to evaluate the stability of the resulting TS-1-Pd composite membrane. Fig.9 shows the hydrogen permeance almost kept unchanged after 30 cycles of the gas exchange between hydrogen and nitrogen. This indicates that the TS-1-Pd composite membrane has a good stability.

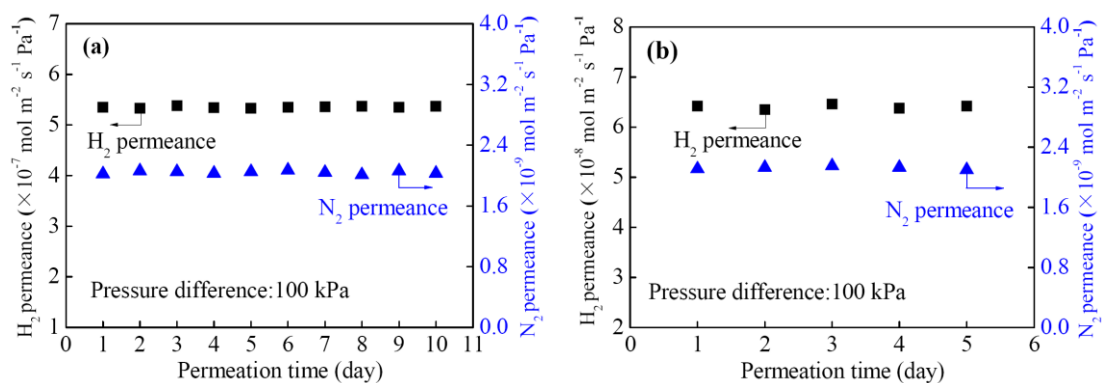


Fig.8. Long-term tests for the TS-1-Pd composite membrane at 773 K (a) and 423 K (b).

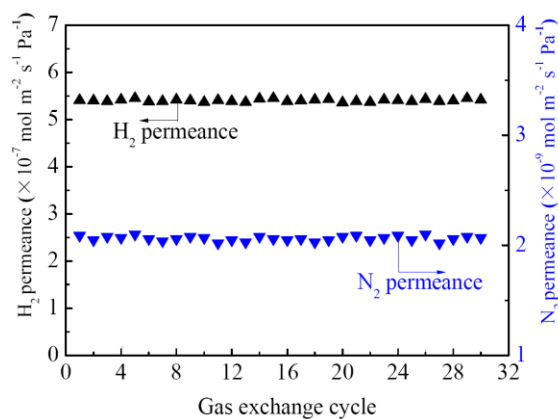


Fig.9. Gas permeances vs. gas exchange cycle between hydrogen and nitrogen at 773K for the TS-1-Pd composite membrane.

Furthermore, the effects of hydrocarbon on the hydrogen permeation performance of palladium composite membrane were investigated to determine the chemical stability of

the membrane. During the experimental process, propylene of 30 ml/min was introduced into permeate side of the membrane reactor for 30 min at 723 K. Then the gas flow was switched to the hydrogen from propylene, followed by measuring the hydrogen flux of the membrane. After the test, the hydrogen flux of the palladium membrane and TS-1-Pd composite membrane decreased 18% and 5% compared to the original hydrogen flux of the membranes, respectively, as shown in Fig.10. It revealed that propylene adsorption on the palladium membrane will affect the hydrogen permeability of the membrane. EDX analysis (not shown here) showed that a certain amount of carbon was observed on the membrane surface. This indicated that the palladium membrane was polluted by propylene, resulting in the decrease of the surface activity. Yu et al.[47] also found that some $\text{Pd}_{1-x}\text{C}_x$ phases formed on the palladium membrane after permeation test by propylene. However, the loss of hydrogen permeance for the TS-1-Pd composite membrane was much smaller than that for the pure palladium membrane. The results presented have demonstrated that the TS-1 zeolite layer as a protector was grown on the top surface of palladium membrane. This sandwich-like membrane configuration makes the TS-1-Pd composite membrane able to operate under harsh condition.

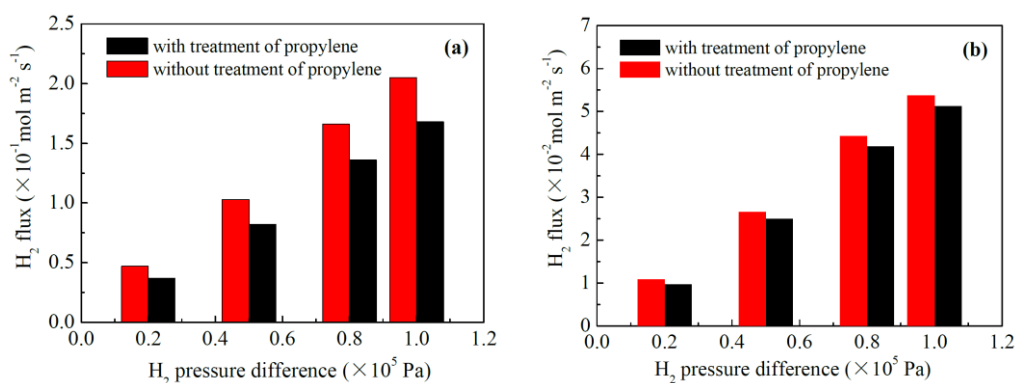


Fig.10. Effects of propylene on the hydrogen flux of pure palladium membrane (a) and TS-1-Pd composite membrane (b).

Reproducibility is a crucial factor for developing a novel fabrication method, which will influence the industrial mass production. A series of TS-1-Pd composite membranes were fabricated at the same synthesis condition. Table 2 lists the permeation test results of those TS-1-Pd composite membranes. The results show that all samples exhibited similar permeation selectivities and hydrogen fluxes at 773 K. In addition, the reproducibility was also evaluated by hydrogen permeation test at different temperatures and their distribution of data was shown in Fig. 11. The relative standard deviations in the H₂/N₂ selectivity were below 20%. The results of hydrogen permeation tests suggested that the reproducibility was acceptable for the fabrication method.

Table 2 The hydrogen permeation properties of the resulted TS-1-Pd composite membranes fabricated at same condition in permeation tests at 773 K.

Sample number	Temperature (K)	Pressure difference	H ₂ flux (mol m ⁻² s ⁻¹)	H ₂ /N ₂ Selectivity
1	773 K	100 kPa	5.41	268
2	773 K	100 kPa	5.92	244
3	773 K	100 kPa	4.98	205
4	773 K	100 kPa	5.15	221

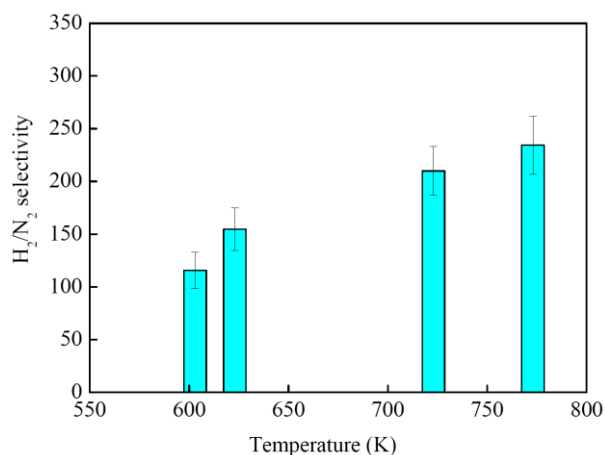


Fig.11. Reproducibility in fabrication of TS-1-Pd composite membranes that evaluated by hydrogen permeation tests at the temperature range of 603 K~773 K.

4. Conclusion

This work reports a novel method to fabricate a sandwich-like TS-1-Pd composite membrane to enhance the membrane stability. A continuous and compact TS-1 zeolite film was grown on the outer surface of palladium membrane using assembly method combined with secondary growth technique. The resulted TS-1-Pd composite membrane was stable for repeated cycling of gases and long-term operation at 773 K and 423 K. Furthermore, the existence of the TS-1 zeolite film can effectively suppressed the hydrogen flux loss from 18% to 5% reduction after pretreatment of the composite membrane in propylene atmosphere. In addition, the reproducibility in fabrication of TS-1-Pd composite membranes was acceptable, possessing a promising potential in the industry application.

Acknowledgments

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