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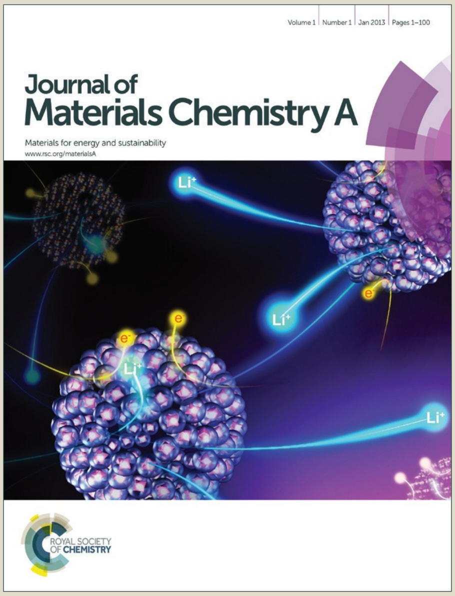

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ARTICLE TYPE

Synthesis of zeolite membrane as a protective layer on metallic Pd composite membrane for hydrogen purification

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Palladium composite membranes are widely used in hydrogen purification process due to its excellent hydrogen permeability and selectivity. However, they could irreversibly lose hydrogen permeability when exposed to a small amount of impurity gases, which severely limits its applications. Here, a seed-free hydrothermal method was successfully developed to synthesize a zeolite membrane on the surface of an ultra-thin metallic Pd composite membrane to give a protection from impurity gases. The impurity gases with kinetic diameter larger than zeolite pore size were obstructed from being direct contact with Pd composite membrane. The presence of the protective zeolite membrane distinctly suppressed the hydrogen permeance decline in 5% propylene/hydrogen mixture, which greatly enhanced the stability of Pd membrane. From the results of SEM and XRD, the acid pretreatment before the secondary hydrothermal growth process and the rotary state were beneficial to synthesize thin and uniform zeolite membrane. With prolonging synthesis time, the protective effects of zeolite membrane were significant enhanced due to the reduction of defects.

Introduction

In recent years, the Pd and Pd alloy composite membranes are known for their excellent hydrogen permeability and selectivity, and they are widely used in hydrogen purification process, especially in production of ultra-pure hydrogen (≥99.9999%)[1-3]. In addition, Pd membranes are also desired to be used in the separation of alkanes or olefins from hydrogen waste gases in refineries to obtain pure hydrogen and valuable chemical products simultaneously, such as propylene and isobutene[4]. However, the low hydrogen permeability and the poor stability of Pd membrane severely limit its applications. The Pd membrane could irreversibly lose hydrogen permeability when exposed to the atmosphere with some impurity gases, such as sulfur compounds[5], CO, CH_4, unsaturated hydrocarbon[6], alcohols and ether. The strong adsorption of these impurity gases and the formation of Pd_4S or PdC could inhibit the hydrogen dissociation and recombination reactions on the Pd membrane surface[7, 8], and thus decreasing the hydrogen permeability and selectivity. The permeation of weakly adsorbing molecules (e.g. hydrogen at 295 K) can drop over two orders of magnitude in the presence of strongly adsorbing molecules (e.g. n-butane at 295 K)[9]. Surprisingly, most reports to date discuss the influences of these impurity gases on hydrogen permeance[10-14], while quite little is known about the protection of Pd membranes. The Pd membrane could be protected from being directly exposed to the atmosphere of impurity gases by coating a protective layer. Zeolite membrane is an excellent candidate due to its molecular sieving capability and unique adsorption properties.

In this paper, we developed an in-situ hydrothermal synthesis method without seed introduction to synthesize zeolite membrane on as-synthesized ultra-thin metallic Pd composite membranes, which was very different from that on porous supports. Firstly, the synthesis of the zeolite membrane should keep the surface of the Pd membrane intact. Otherwise, the Pd membrane will lose the hydrogen selectivity. Secondly, a very thin zeolite membrane (less than 3 μm) would be necessary to minimize the additional resistance of hydrogen permeation. Finally, homogeneous crystal structures are difficult to obtain because it is impossible to introduce specific crystal seeds to the surface of compact and nonporous metallic substrate like Pd membrane. Therefore, synthesis of thin and defect-free zeolite membranes on metallic membranes is challenging and promising. Moreover, the effect of a zeolite membrane on hydrogen permeance and the protection of zeolite-Pd composite membrane from propylene were also investigated.

Experimental Section

Preparation of Pd composite membrane

The Pd composite membranes were prepared by a modified electroless plating method[15]. The synthesis procedures comprised: (i) washing a 50 mm long porous ceramic tube (12 mm in diameter) supplied by Nanjing University of Technology as the substrate by ethanol and then by boiling deionized water, (ii) pre-seeding Pd nuclei on the outer surface by an active treatment comprising successive immersions of the support in the acidic stannous chloride and acidic palladium chloride baths, (iii) electroless depositing Pd membrane on the outer surface by controlling the auto-catalyzed reduction of Pd precursor in the presence of hydrazine as a reducing agent and EDTA to stabilize the palladium complex and (iv) thermal treatment by nitrogen flow at 400 °C for 2 h. Finally, a dense Pd layer having a thickness of about 7 μm was uniformly prepared on the porous alumina substrate.

Synthesis of zeolite membrane

The hydrothermal synthesis solution was prepared by adding 50ml silicate solution to 50 ml aluminate solution with stirring. The aluminate and silicate solution were prepared by dissolving 0.3 g aluminate powder and 5.6 g silica sol (30 wt% SiO_2) to sodium hydroxide aqueous solution (5.56 mol/L) at room temperature, respectively. The molar ratio of this mixture solution was $50Na_2O : Al_2O_3 : 5SiO_2 : 1000H_2O$, which was used to synthesize LTA zeolite membrane reported elsewhere[16]. After an additional 10 h stirring, the resulting solution was transferred to a Teflon autoclave. The pretreated and untreated Pd composite membranes supported by ceramic tubes were sealed with Teflon caps at both ends and located vertically in the Teflon autoclave. The hydrothermal synthesis was performed in a rotary furnace (2.3 rotations per minute) at 90 °C for 3 h under autogenous pressure. Subsequently, when the autoclave cools down to room temperature, the Pd composite membrane was rinsed with distilled water for several times until the pH value reached 7 and then dried at 150 °C for 4 h. In this way the zeolite-Pd composite membrane was obtained.

Acid pretreatment

Before hydrothermal synthesis, the Pd membrane was immersed in diluted hydrochloric acid solution (pH=6) for 15 min and then rinsed with distilled water for several times until the pH value reached 7.

Permeation measurements

The Pd composite membrane was positioned in a stainless steel reactor and sealed by the graphite O-rings. Prior to the permeation experiments, the absence of leakage was verified by N_2 pressure test at room temperature. The membrane was then heated slowly under N_2 (200 ml/min) to 400 °C, at which temperature the atmosphere was changed to H_2 (200 ml/min). Then the Pd composite membrane was activated at 450 °C and kept at this temperature until the H_2 permeance was stable. The initial H_2 permeance and the H_2 permeance after introduction of 5 % propylene/hydrogen mixtures (200 ml/min) were measured at 400 °C. The transmembrane pressure difference as the driving force was kept at 0.1 MPa. The H_2 flow rates at the permeate side were measured with a soap-film flowmeter. The furnace was controlled by a temperature programming controller and a heating rate of 1 °C/min was used in all experiments.

Characterizations

The crystal structure of zeolite membranes was checked by X-ray diffraction (XRD). XRD measurements were conducted on a PANalytical X'pert diffractometer (Cu Ka, 40 kV, 40 mA). The zeolite samples were scrapped from the as-synthesized zeolite-Pd membranes after hydrothermal synthesis. The surface morphology and membrane thickness of zeolite membranes were characterized by a scanning electron microscopy (SEM, JSM-7800F).

Results and discussion

Synthesis of zeolite membranes described recently can be widely classified into two categories: in situ and secondary (or seeded) growth. The secondary (or seeded) growth technique is a two-step technique, involving initial ex-situ seeding of a support by previously synthesized zeolite crystals followed by hydrothermal crystallization. This method offers greater flexibility in controlling the orientation of the zeolite crystals and the microstructure of the zeolite membrane. With the in situ technique, the support surface is directly contacted with the zeolite precursor solution. Under appropriate conditions, zeolite crystals nucleate on the support and grow to form a continuous zeolite layer. A number of papers are dedicated to the growth of zeolite membranes on different substrates, including porous supports and metals, directly from hydrothermal precursor gels or solutions without seed introduction by both conventional[17-19] and microwave-assisted hydrothermal synthesis[20]. However, the success of in situ methods in yielding uniformly and defect-free zeolite membrane is limited due to the insufficient understanding of nucleation and growth processes in hydrothermal systems, especially on metallic support surfaces. Thus the morphology, crystal structures and uniformity of zeolite membrane are very sensitive to synthesis conditions and methods.

Compared to the porous support, including porous ceramic or stainless support, the adhesion between zeolite membrane and metallic surface is much weaker. Nonetheless, zeolite membranes are successfully synthesized on non-porous metal substrates, such as gold[21], copper[22], nickel and metal alloy[23] via particular pretreatment. In order to enhance the adhesion, the support surface is always pretreated by silane coupling agents. For example, 3-aminopropyltriethoxysilane (APTES) is introduced to form a covalent linker between zeolite membrane and support[24, 25]. And meanwhile thiol-organosilane is used to yield a negatively charged interface which facilitates the adsorption of zeolite crystals[26, 27]. However, in our case, Pd composite membrane plays a key role in hydrogen perm-selection, so it should be kept out of contamination and damage from organic agent. Herein, diluted acid was chosen as pretreatment agent. The damage of acid treatment on Pd membrane was proved to be negligible from our experimental results which showed that the permeance of hydrogen and nitrogen of the Pd membrane before and after acid treatment did not change.

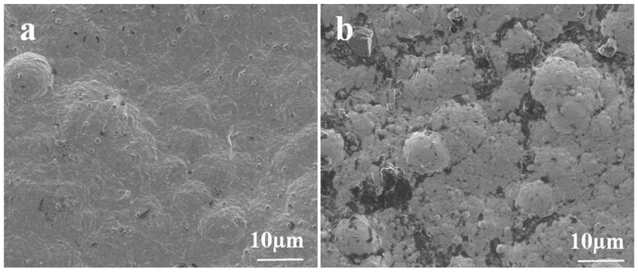

Fig. 1 SEM images of zeolite-Pd composite membranes prepared by hydrothermal synthesis for one time (a) pretreated by acid; (b) without pretreatment.

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Fig. 1 exhibits the SEM images of zeolite-Pd composite membranes prepared by hydrothermal synthesis for one time with and without acid pretreatment. It can be seen that the zeolite membrane synthesized on acid pretreated Pd membrane is uniform and continuous, while the one without pretreatment is discontinuous. The black areas shown in Fig. 1 (b) are the surface of uncovered Pd membrane. There are many large spherical zeolite clusters on the surface of untreated Pd membrane. According to Valtchev et al.[23], the metal surface tension and wettability of the metal have an effect on zeolite membrane formation. Under the same conditions, zeolite membrane formation can be observed on metal substrates with high values of the surface tension, such as Cu, Ni, and Ag. While on low surface tension metal substrates, such as Pb and Sn, the zeolite membrane is hardly formed. Moreover, the mechanism of zeolite membrane formation depends on the substrate surface activity. The substrate plastic deformation, i.e. the high density of substrate surface defects, is one of the dominant parameters for good adhesion and mechanical stability[22]. The imperfections are favourite locations for zeolite nucleation and stimulate the formation of zeolite crystals. The acid treatment of metal substrates leads to a partial destruction of the surface of Pd membrane, thus promoting the formation of zeolite membrane.

The secondary growth of zeolite on the basis of in-situ or seeded hydrothermal synthesis was first reported by Tsapatsis et al. to address the challenge of producing thin and defect-free membranes[28]. The initial step was to prepare nanocrystalline zeolite. This thin film was composed of zeolite clusters with inter-zeolitic porosity, which was then used for further membrane formation. This approach served to decouple the nucleation and crystal growth steps. In our experiment, the hydrothermal synthesis procedure was repeated for the second time, following the same steps of the first time except for the acid pretreatment. Two zeolite-Pd membranes were prepared. One was pretreated by acid before the primary growth and the other was pretreated only before the secondary growth step. Fig. 2 (a,b) shows the surface morphology of secondary hydrothermal synthesized Pd membrane pretreated by acid before the primary growth, which is synthesized on the basis of zeolite-Pd membrane in Fig. 1 (a). It can be found that many thread-ball-like or flower-like zeolite crystals with 1 to 3μm diameter are heterogeneously dispersed on the surface of the first zeolite layer. It indicates that the zeolite crystals do not grow well to form uniform membrane in the secondary hydrothermal growth process. In comparison, uniform and continuous zeolite membrane are observed in Fig. 2 (c,d) when the Pd membrane pretreated by acid before the secondary hydrothermal synthesis, i.e. it is synthesized after acid treatment of as-synthesized zeolite-Pd membrane shown in Fig. 1 (b). It indicates that the second zeolite growth step is essential in zeolite crystallization. Zeolite membrane with specific crystal structures is formed after the second zeolite growth. In addition, acid treatment before the second zeolite growth stage is more effective than that before the first zeolite growth step to get a more homogeneous zeolite layer.

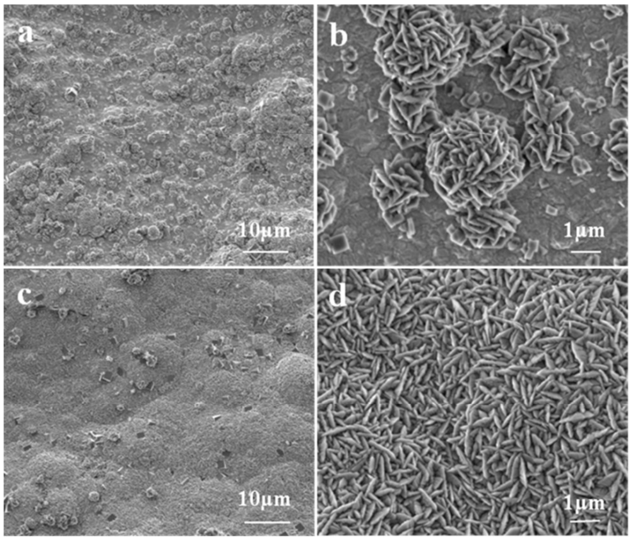

Fig. 2 SEM images of the surface morphology of zeolite-Pd composite membranes pretreated by acid before the primary (a,b) and the secondary hydrothermal synthesis procedure (c,d), b and d give the corresponding higher magnification images.

As mentioned above, the zeolite membrane was prepared by using a rotary autoclave. For comparison, the synthesis of zeolite membrane was also carried out in a static autoclave at the same conditions. The surface images in Fig. 3(a,b) show that many thread-ball-like or flower-like zeolite crystals with 4 μm diameter are loosely attached on the surface when the hydrothermal synthesis is performed in the static autoclave. Many defects and gaps can be detected among the zeolite crystals. The thickness of the zeolite layer is about 5 μm from the cross section images in Fig. 3(c). According to Kundu et al.[29], thread-ball-like particles are hydroxy sodalite which has a six-membered oxygen aperture with a kinetic window diameter of 2.65 Å. In principle, only very small molecules can access and enter the cages, making hydroxy sodalite a potential candidate in separation of small molecules[30]. However, it could not be used as a molecules separation material unless continuous and compact hydroxy sodalite zeolite membranes are formed.

When the hydrothermal synthesis is performed in rotary autoclave, the spherical zeolite crystals expand and connect together to form a planar and continuous rice-like zeolite membrane which is shown in Fig. 3(d,e). From Fig. 3(f), an about 1 μm thickness continuous and compact zeolite membrane is successfully synthesized on the surface of Pd membrane. The rotary state could provide effective mixing of the synthesis solution and improve the mass transfer from the solution to the stagnant layer on the Pd membrane by keeping the solution at a homogeneous concentration[31]. In addition, mixed solution can ensure a better heat transfer from the walls of the autoclave to the center where the Pd membrane is placed. As crystallization is a thermally sensitive process, providing a more homogenous temperature inside the autoclave can significantly help the formation of uniform and continuous zeolite membrane.

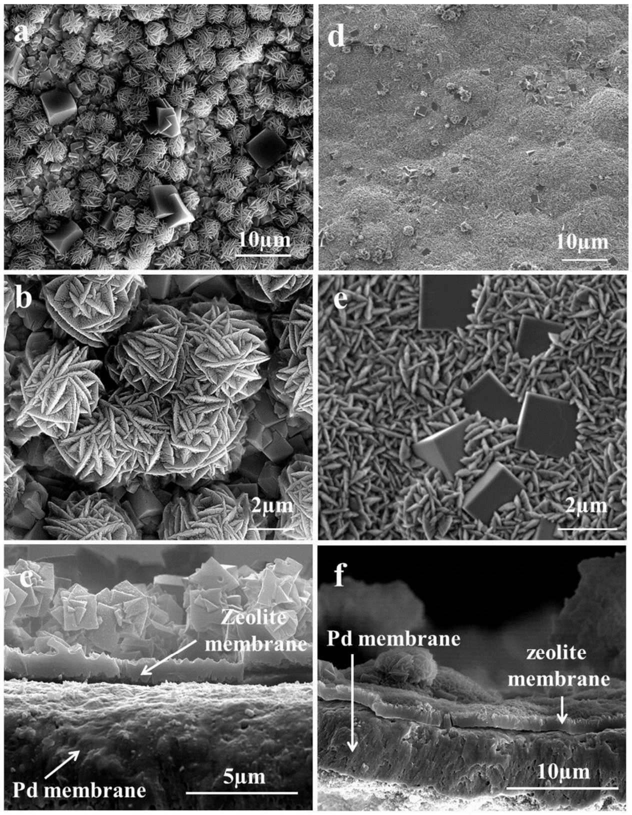

Fig. 3 SEM images of zeolite-Pd membranes prepared by hydrothermal synthesis in static state (a,b,c) and in rotary state (d,e,f); b and e give the corresponding higher magnification images; c and f show the cross section morphology.

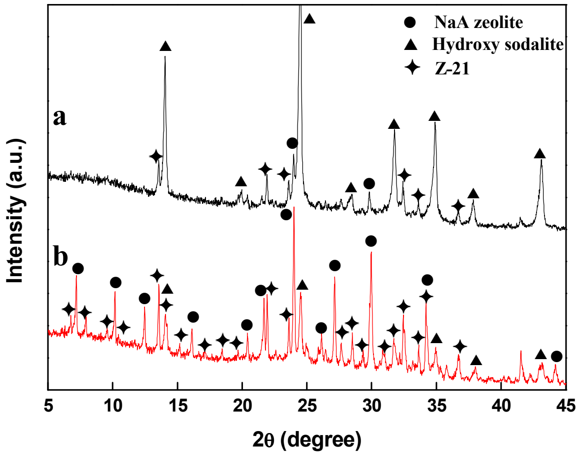

Fig. 4 XRD patterns of zeolite powders scrapped from (a) zeolite-3h and (b) zeolite-6h.

The zeolite-Pd membrane with longer hydrothermal synthesis time was also prepared to investigate the change of crystal structure during the process. The primary hydrothermal synthesis processes of two Pd membranes were both carried out at 90 °C for 3 h in rotary state. Then these Pd membranes with the first zeolite layer were subjected to the secondary hydrothermal synthesis at 90 °C for 3 h and 6 h in rotary state after acid pretreatment, named by zeolite-3h and zeolite-6h, respectively. The crystal structures of the zeolite membrane were identified by XRD shown in Fig. 4 using the zeolite powders scrapped from zeolite-Pd membranes. According to references and standard diffraction patterns, zeolite-3h consists of hydroxy sodalite[32] and a small amount of two foreign phases, i.e. zeolite NaA and Z-21[33]. The quantity can be identified in the following orders: hydroxy sodalite > Z-21 > NaA. This result is consistent with the presence of a small amount of cubic inclusions embedding in the hydroxy sodalite membrane shown in Fig. 3(e). Zeolite crystallization is partially dependent on the Si/Al ratio in the solution. The Si/Al ratios of these three zeolites are all 1. Since there are no special seed crystals on the substrate, it is more easily to form mixture phase zeolite crystals. The formation of mixture phases is also related to alkaline conditions. Pure phase hydroxy sodalite always exists under the strongest alkaline conditions of 16 M NaOH[34]. The strong alkaline conditions favor the formation of pure hydroxy sodalite. In our case, the 6 M NaOH concentration facilitates the formation of mixture zeolite crystal phases.

Generally, the growth of crystals is governed by a nucleation-dissolution-recrystallization growth mechanism in hydrothermal synthesis[35, 36]. Firstly, a layer of amorphous crystal nuclei is formed during the initial hydrothermal process, which is shown in Fig. 1. The possible growth mechanism of the crystal nuclei could be Ostwald ripening which has been widely reported in the nucleation and growth process of zeolite membrane[37-39]. It can lead to dissolution of the very small crystals and growth of almost equally sized crystals. The crystals become larger and more stable at the expense of the dissolution of smaller and less stable particles. Another possible zeolite growth mechanism is reported by T. Bein[40]. Amorphous gel particles (40-80 nm) are formed in the clear aluminosilicate solution during aging process at room temperature. Then nucleation and crystallization of zeolite crystals are achieved inside the gel particles. In the course of crystal nuclei growth, the amorphous gel zeolite particles maintain their average size until they completely convert into zeolite crystalline. Large zeolite crystals are formed after subsequent hydrothermal synthesis. Secondly, the crystal nuclei dissolve and recrystallize during the secondary hydrothermal process. The crystal growth of this recrystallization process is oriented. There is an intrinsic tendency for the nucleation growth along special direction to form crystalline zeolite. Finally, the zeolite crystals continue growth, and the continuous zeolite membrane is formed. During this process, the defects and cracks among the crystals gradually diminish. With prolonging the hydrothermal time, the basic conditions and precursor concentration in the solution change, which is mainly responsible for the crystal transformation. When the hydrothermal synthesis time is prolonged to 6 h, most of hydroxy sodalite crystallines transform to zeolite NaA and Z-21. It demonstrates that the crystal transitions inside the crystalline and crystal dissolution in strongly basic synthesis solution occur in extended synthesis

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time. Various zeolite crystals with large pore size could also form, for example Z-21 in our case, especially in seeding-free hydrothermal synthesis process. The kinetic diameters of zeolite NaA and Z-21 are 0.41[41] and 1.7 nm[42], respectively. In this case, the impurity gases with kinetic diameters smaller than 0.41 or 1.7 nm may diffuse through these crystals. Therefore, the synthesis of defect-free and homogeneous zeolite membrane without crystal transformation is crucial for gas separation. The synthesis conditions and synthesis methods need to be optimized to suppress undesirable crystal transformation in further investigations.

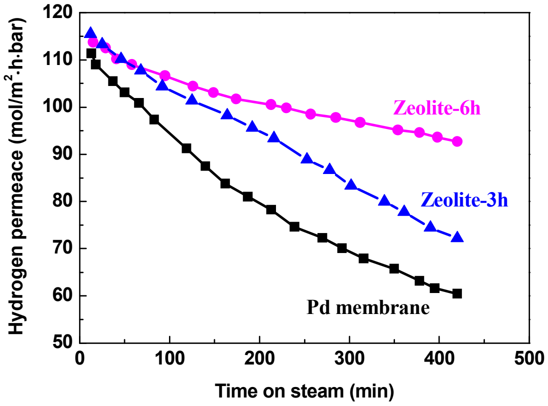

Fig. 5 Effects of 5% propane/hydrogen mixtures on hydrogen permeance of Pd composite membrane and zeolite-Pd composite membranes at 400°C.

The separation of hydrogen from refinery gas by Pd membrane is considered to be an efficient method to recover pure hydrogen and valuable products, e.g. propylene from propane dehydrogenation process. The effects of propylene on the hydrogen permeance of Pd membrane and the protective effects of zeolite membrane are investigated. The variations of hydrogen permeance of Pd membranes with and without zeolite protective layer are concluded in Table 1. After activation in pure hydrogen at 450 °C for more than 100 h, the hydrogen permeance of the Pd membrane, zeolite-3h and zeolite-6h are stable at 295.0, 213.3 and 210.9 mol/m^2·h·bar at 400 °C, respectively. Then the 5 % propylene/hydrogen mixtures (200 ml/min) are introduced into membrane reactor. It is worth to note that the permeability of Pd membranes is stable after acid pretreatment and hydrothermal synthesis of zeolite membrane.

After exposure to the mixture gas for 10 min, the hydrogen permeance of Pd membrane, zeolite-3h and zeolite-6h fall down 62.2, 45.8 and 46.1 % compared to the original flux in pure hydrogen, respectively. This decline is mainly caused by the concentration polarization. The accumulation of propylene near the membrane surface will prevent the adsorption and dissociation of hydrogen on Pd membrane[43].

Experimental results show that the hydrogen permeance of Pd membrane cannot recover to original level, even purged in pure hydrogen for more than 10 h at higher temperature (450 °C) after exposure to mixture gas for 420 min. That indicates the irreversible propylene adsorption and destruction are largely responsible for hydrogen permeance decline. It was found that propylene was dissociative chemisorbed on Pd membrane, and that carbon-carbon bonds were cleaved at temperatures above 199 °C[6]. The destruction of Pd membrane was also caused by the dissolution of carbon atoms in the Pd lattice. The crystalline phase structure of Pd membrane was face-centered-cubic (fcc). The XRD results (not shown here) showed that the structure of Pd membrane before and after zeolite hydrothermal synthesis did not change. But shoulders appeared at metallic Pd peaks after the hydrogen permeation test in 5 % propane/hydrogen mixtures. That indicated some $Pd_{1-x}C_x$ phases were formed on Pd membrane, which was responsible to the decrease of hydrogen permeance[7]. However, the losses of hydrogen permeance for zeolite-Pd membranes were smaller than Pd membranes, and those shoulders were not found on the used zeolite-Pd membranes, indicating the zeolite membrane could suppress the adsorption propylene and the formation of $Pd_{1-x}C_x$. The hydrogen permeance was plotted as a function of the exposure time to 5 % propylene/hydrogen mixtures in Fig. 5. In the period of 420 min exposure to mixture gases, the hydrogen permeance of Pd membrane without zeolite membrane protection quickly declined from 111.4 to 60.4 mol/m^2·h·bar (45.8 % reduction). While zeolite-3h and zeolite-6h slowly declined from 115.5 to 72.2 mol/m^2·h·bar (37.5 % reduction) and 113.7 to 92.7 mol/m^2·h·bar (18.5 % reduction), respectively.

Table 1 The variations of H_2 permeance of Pd membranes with and without zeolite protective layer at 400°C.

Membranes	Initial H_2 permeance at 400°C and 0.1MPa (mol/m^2·h·bar)	H_2 permeance after exposure to the mixture for 10 min (mol/m^2·h·bar)	H_2 permeance after exposure to the mixture for 420 min (mol/m^2·h·bar)	H_2 permeance reduction during the exposure to the mixture (%)[a]
Pd membrane	295.0	111.4	60.4	45.8
Zeolite-3h	213.3	115.5	72.2	37.5
Zeolite-6h	210.9	113.7	92.7	18.5

[a] H_2 permeance reduction=(H_2 permeance after exposure to the mixture for 10 min-H_2 permeance after exposure to the mixture for 420 min)/H_2 permeance after exposure to the mixture for 10 min*100%.

It indicates that the zeolite coating on Pd membrane can efficiently protect the Pd membrane, and zeolite-6h is more effective than zeolite-3h. The adsorption and desorption properties of propylene on zeolite membrane may be in relation to the crystal phase, zeolitic pores and membrane defects. Mass transport of single-component gas molecules through good quality zeolite membranes with no defects is mainly controlled by the diffusivity of the gas molecule through the zeolitic pores and the adsorption affinity between the gas and the zeolite framework[44, 45]. The kinetic diameter of propylene (0.45 nm) is larger than the pore size of the zeolite NaA (0.41 nm) and hydroxy sodalite (0.265 nm) but smaller than that of Z-21 (1.7 nm). The propylene molecular should not permeate through defect-free NaA or hydroxy sodalite zeolite membrane, but could get through any defects on zeolite membrane and the pores of Z-21. From XRD results, most crystals are hydroxy sodalite on zeolite-3h, while zeolite NaA with some Z-21 crystals are formed on zeolite-6h. That illustrates the hydrogen permeance loss is responsible for large defects on zeolite-3h and Z-21 formation on zeolite-6h. Compared to zeolite-3h, more efficient protective effect of zeolite-6h may attribute to significant reduction of defects. Furthermore, the preferential adsorption of propylene molecules within the cavity of zeolite crystals or in the defects and cracks may also play an important role in the protection of Pd membrane. The zeolite membrane as an adsorbent can preferentially adsorb propylene molecules to give Pd membrane a protection. Therefore, a zeolite protective layer, which is able to prevent impurity gases from being in contact with Pd membrane, could efficiently avoid the fatal destruction. However, it is reported that defects or cracks formation are easily occurred[46], and all membranes possess unavoidable defects due to intercrystalline porosity which are formed during the membrane growth[44, 47]. Any progresses in suppressing defects and large pore size zeolite crystals formation will be desirable and exciting.

Conclusions

An about 1 μm zeolite membrane as a protective layer was successfully synthesized on the surface of metallic Pd composite membrane for hydrogen purification. A developed seed-free hydrothermal synthesis method was used to synthesize zeolite membrane at 90 °C with acid pretreatment in rotary state. Crystal transformation and defects reduction on zeolite membrane were detected by extending the synthesis time. The presence of zeolite protective layer distinctly suppressed the hydrogen permeance loss from 45.8 to 18.5 % reduction in 5 % propylene/H_2 atmosphere, which greatly enhanced the stability of Pd membrane.

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Graphical and textual abstract

An about 1μm zeolite membrane as a protective layer was successfully synthesized by a developed seed-free hydrothermal synthesis method on the surface of metallic Pd composite membrane for hydrogen purification. The zeolite membrane, which was used as an "Armor", could give a good protection to Pd membranes, significantly suppressing hydrogen permeance loss. The formation of any defects and any crystals with large pores on zeolite membrane will impair the protective effect.