Palladium-niobium bimetallic doped organosilica membranes for H₂/CO₂ separation

Hengfei Zhang, Yibin Wei, Hong Qi *

State Key Laboratory of Material-Oriented Chemical Engineering, Membrane Science and Technology Research Center, Nanjing Tech University, Nanjing, 210009, China

ARTICLE INFO

Keywords:
Bimetallic doping
Organosilica membrane
Palladium
Niobium
Gas separation

ABSTRACT

In this work, high-performance palladium-niobium doped 1,2-bis(triethoxysilyl)ethane (Pd–Nb-BTESE) membranes were prepared for H₂/CO₂ separation by using the sol-gel method. Nb was first incorporated into the organosilica networks in the form of Nb–O–Si covalent bonds, while Pd nanoparticles were successfully embedded into the networks with size of 5–10 nm. Based on the synergistic effects of Pd–Nb doping, the as-prepared membranes showed more appropriate structures for H₂/CO₂ separation. By controlling the same doping amount of Nb and changing Pd doping contents (n(Pd): n(Si) = 0.05–0.4), we found that the Pd-Nb-BTESE membrane with higher Pd doping content showed higher H₂/CO₂ permselectivity and stronger H₂ adsorption capacity. The H₂/CO₂ separation performance of all the prepared Pd–Nb-BTESE membranes surpass the upper bound 2008. The membrane with n(Pd): n(Si) of 0.4 showed a superior H₂/CO₂ permselectivity of 107 and a high H₂ permeance of 1.12 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹. Our findings provide novel insights into tailoring and functionalizing organosilica membranes through bimetallic doping for practical applications.

1. Introduction

Membrane-based gas separation technology has been considered more advantageous over conventional gas separation methods such as pressure swing adsorption, cryogenic distillation and solvent absorption, due to its low energy consumption, low operating cost and small footprint [1]. Microporous ceramic membranes have attracted much attention in the applications of separating small gas molecules under harsh industrial conditions because of their excellent thermal, mechanical and chemical stability [2]. In recent years, amorphous silica membranes with tunable microstructures have become some of the most important members in the ceramic membrane family owing to their unique permeance and molecular sieving capability for small gases separation [3]. As the first generation of amorphous silica membranes, tetraethoxysilane (TEOS) derived silica membranes have been extensively studied [4,5]. However, it was found by many researchers that the pure silica membranes were unstable under hydrothermal conditions, which limits their practical applications [6,7]. In the past decade, hybrid organosilica membranes with the incorporation of hydrophobic organic groups derived from bridged silsesquioxane have been proven themselves more hydrothermally stable in applications of pervaporation and gas separation [8,9]. Among organosilica membranes, 1,2-bis(triethoxysilyl)ethane (BTESE)-derived organosilica membranes with ethylene-bridged networks provide well-defined pore structures, which make them promising for small gases separation under hydrothermal conditions [10].

H₂/CO₂ separation under varying hydrothermal conditions is crucial for addressing the global challenges associated with energy security (e.g. hydrogen production) and climate change (e.g. pre-combustion carbon capture) [11–13]. Although pure BTESE-derived organosilica membranes usually exhibited acceptable hydrothermal stability and high H₂ permeance in H₂/CO₂ separation, the permselectivity of pure BTESE-derived membranes were still unsatisfied to meet the requirements for such applications. Metal doping is one of the efficient approaches to improve H₂/CO₂ permselectivity for silica-based membranes. Most metal (e.g. Al, Nb and Zr) dopants could endow silica-based membranes with denser structures, leading to a significant increase in their H₂/CO₂ permselectivity [14–16]. For example, ten Hove et al. reported a Zr-doped BTESE membrane with H₂/CO₂ permselectivity of 16, which was four times as much as that of their pure BTESE membrane [16]. They believed that the improved H₂/CO₂ permselectivity was ascribed to the formed denser structure caused by Zr doping.

Moreover, metal dopants such as Pd and Mg not only tailor the silica-based networks but also trigger interactions with H₂ or CO₂ molecules...
which confers the membranes with benefits for improved \( \text{H}_2/\text{CO}_2 \) permeselectivity\cite{17-19}. Karakilik et al.\cite{18} found Mg-doped silica membranes could show extremely high \( \text{H}_2/\text{CO}_2 \) permeselectivity (above 350). Because the doped Mg could provide abundant basic sites on the membrane pores, \( \text{CO}_2 \) molecules could strongly adsorb onto the sites and consequently blocked them for further permeation, resulting in a low \( \text{CO}_2 \) permeance of the membrane. In addition to hindering \( \text{CO}_2 \) permeation, doping Pd into silica-based networks could efficiently improve the \( \text{H}_2 \) permeance since Pd has strong adsorbability and solvability towards \( \text{H}_2 \)\cite{20}. However, it should be noted that Pd doping generally shows poor compatibility with silica-based networks causing non-selective interfacial voids, which counteracts the increase of \( \text{H}_2/\text{CO}_2 \) permeselectivities\cite{21}. Therefore, the strategy of monometallic doping is still limited to simultaneously improve \( \text{H}_2 \) permeance and \( \text{H}_2/\text{CO}_2 \) permeselectivity for silica-based membranes.

Apart from monometallic doping, Prof. Da Costa’s group first proposed the concept of bimetallic doping and they developed a series of bimetallic doped silica membranes derived from TEOS such as the palladium-cobalt doped (Pd–Co–TEOS)\cite{22}, the iron-cobalt doped (Fe–Co–TEOS)\cite{23,24} and the lanthanum-cobalt doped (La–Co–TEOS)\cite{25}. Co was selected as one of components in these bimetallic doped silica membranes for the improvement of hydrothermal stability, and the introduction of Pd, Fe or La into Co-TEOS membranes further confers the membranes with improved gas separation performance. Hence, bimetallic doping (i.e. introducing two different metal dopants with specific functions) is feasible to improve the overall performance of silica-based membranes. Very recently, Zhang et al.\cite{26} reported La–Y bimetallic doped BTESE membranes for the application of pervaporation desalination. They found that La and Y could both form Si–O–M (M represents La and Y) bonds in the BTESE-derived organosilica networks and their membranes could exhibit excellent desalination performance.

In contrast of improving the hydrothermal stability of TEOS-derived silica membranes, synergic effects of bimetallic doping may be utilized for improving \( \text{H}_2 \) permeance and \( \text{H}_2/\text{CO}_2 \) permeselectivity of more hydrothermal stable BTESE-derived organosilica membranes\cite{27,28}. Previously, we found niobium-doped BTESE (Nb-BTESE) membranes could show relatively high \( \text{H}_2/\text{CO}_2 \) permeselectivities and low \( \text{H}_2 \) permeances due to the dense structure caused by Nb–O–Si covalent bonds\cite{29}. However, palladium-doped BTESE (Pd-BTESE) membranes exhibited an opposite result (i.e. poor \( \text{H}_2/\text{CO}_2 \) permeselectivity yet high \( \text{H}_2 \) permeance), which is attributed to the larger pore size and an enhanced \( \text{H}_2 \) adsorbability by Pd nanoparticles\cite{19}. Here, we propose a novel strategy of preparing the palladium-niobium bimetallic doped organosilica (Pd–Nb–BTESE) membranes to improve both \( \text{H}_2 \) permeance and \( \text{H}_2/\text{CO}_2 \) permeselectivity by taking advantages of the two metal dopants. To our best knowledge, this is the first attempt that investigates the effects of bimetallic doping on gas separation performance of organosilica membranes. We hypothesized that the introduction of Pd into BTESE network increases the \( \text{H}_2 \) permeance due to its strong adsorption and permeability for \( \text{H}_2 \) and the Nb doping could maintain the permeselectivity of Pd–Nb–BTESE membranes. By controlling the same doping content of Nb, we compared the structural changes and the gas separation performances of the Pd–Nb–BTESE membranes prepared with different Pd doping content. This work may provide useful insights into designing high-performance silica-based membranes for \( \text{H}_2/\text{CO}_2 \) separation.

2. Experimental

2.1. Synthesis of Pd–Nb-BTESE sols

1,2-bis (triethoxysilyl) ethane (BTESE, purity 97%, ABCR) was used as precursor. Niobium penta (n) butoxide (NPB, purity 99%, ABCR) and palladium chloride (PdCl\(_2\), purity 98%, Merck) were used as Nb and Pd sources, respectively. To synthesize Pd–Nb-BTESE sols, 5 mL BTESE and 5 mL ethanol anhydrous (EtOH, purity 99.9%, Merck) were first mixed in a nitrogen glove-box. 0.5 mL hydrochloric acid solution (1 mol L\(^{-1}\)) was drop-wise added into the BTESE-ethanol mixture under vigorous stirring in an ice bath. The mixture was then refluxed in a water bath at 60 °C for 90 min to obtain BTESE sol. Subsequently, a mixture of 3.75 mL NPB, 25 mL ethanol and 0.3 mL HCl solution (1 mol L\(^{-1}\)) was drop-wise added into the BTESE sol. The Nb-containing mixture was then refluxed at 60 °C for an additional 90 min to obtain Nb-BTESE sol. Next, 0.2368 g PdCl\(_2\) was dissolved with 0.25 mL concentrated hydrochloric acid (HCl, 36.46 wt%) in a water bath at 60 °C for 40 min. Finally, the PdCl\(_2\) solution by diluting with 25 mL ethanol and as-prepared Nb-BTESE sol were mixed and then refluxed in a water bath at 60 °C for 90 min to obtain Pd–Nb–BTESE sol. The molar ratio of the as-prepared sol is n (Pd):n (Nb):n (HCl):n (H\(_2\)O):n (EtOH): n (Si) = 0.5:0.33:0.14:1.63:34.81:1, which is marked as Pd–Nb–BTESE-0.5. By increasing the content of Pd, the other three sols with molar ratios of n (Pd):n (Nb):n (Si) = 0.1:0.33:1, 0.2:0.33:1 and 0.4:0.33:1 were prepared and marked as Pd–Nb–BTESE-0.1, Pd–Nb–BTESE-0.2 and Pd–Nb–BTESE-0.4, accordingly. The molar ratio of ingredients for the Pd–Nb-BTESE sols can be found in Table S1.

2.2. Preparation of Pd–Nb-BTESE powders and membranes

Pd–Nb-BTESE sols were dried at room temperature (25 °C) for 24 h to prepare xerogels. Then, the obtained xerogels were ground into fine powders and calcined in \( \text{H}_2/\text{N}_2 \) (2:3, molar ratio) atmosphere at 400 °C for 3 h with the same heating and cooling rate of 0.5 °C·min\(^{-1}\). The powder samples were prepared and used for characterization to indicate the properties of the corresponding membranes.

Pd–Nb–BTESE membranes were prepared by single dip-coating the as-prepared sols onto home-made disk-type mesoporous γ-Al\(_2\)O\(_3\) supports (thickness: 2.5 mm, diameter: 42 mm, pore size: 5 nm). Before coating the membranes, the as-prepared sols were aged for 24 h at –20 °C. The dip-coating process was implemented at a withdrawal speed of 12 mm·s\(^{-1}\) by using a MEMPIDS coating unit (Pervatech B.V., The Netherlands). The membranes were finally calcinated by the same procedure as the powders. The whole membrane preparation procedure is schematically given in Fig. 1.

2.3. Membrane characterization and gas permeation measurement

An X-ray diffractometer (XRD, MiniFlex 600, Rigaku) was used to detect phase composition of Pd–Nb–BTESE powders, using a Cu Kα radiation operated at 40 kV and 15 mA. Fourier transform infrared (FTIR) spectroscopy (NICOLET 8700, Thermo Nicolet Corporation) was used to analyze the chemical structures of the powders. The cross-sectional morphologies of the membranes were observed by a scanning electron microscopy (SEM, S-4800, Hitachi) with the accelerating voltage of 7 kV. Morphological characteristics of Pd–Nb–BTESE powders were carried out by a high-resolution transmission electron microscope (HRTEM, JEM-2000CX, JEOL). Chemical compositions of Pd–Nb–BTESE powders were analyzed by an X-ray photoelectron spectrometer (XPS, ESCALAB250xi, Thermo Scientific) equipped with a monochromatic Al Kα X-ray source (1486.6 eV). The microstructures of the as-prepared membranes were evaluated by characterizing their corresponding powders through N\(_2\) adsorption-desorption isotherms (ASAP 2020, Micromeritics) at –196 °C. Pore size distributions were calculated by the non-local density functional theory method (NLDFT). Gas adsorption capabilities of the powders were analyzed by \( \text{H}_2 \) and \( \text{CO}_2 \) gas adsorption isotherms measured at 25 °C. Before gas adsorption measurement, samples were degassed under vacuum at 200 °C for 12 h.

Single gas permeation measurement was conducted in a dead-end modular set-up at 300 °C. Prior to measurements, temperature and pressure were kept at 300 °C and 0.3 MPa for 30 min until gas permeation reached a steady state. The single gas permeances of \( \text{He}, \text{H}_2, \text{CO}_2, \text{N}_2, \text{CH}_4 \) and \( \text{SF}_6 \) were respectively measured. The gas permselectivity is
equal to the permeance ratio between two gases.

3. Results and discussion

3.1. Chemical composition analysis of Pd–Nb-BTESE membranes

Fig. 2 shows the XRD patterns of Pd–Nb-BTESE powders with different Pd/Si molar ratios. No silicon- or niobium-related diffraction peaks were found for all samples, indicating that the BTESE-derived organosilica networks were amorphous. This result also implied that the doped niobium existed in the organosilica networks as an amorphous phase or the size of crystalline niobium compounds were too small to be detected by XRD, which agrees with a previous report by Pereira et al. [30]. In contrast to the doped Nb, the characteristic peaks centered at 40.14°, 46.7° and 68.18° 2θ correspond to (111), (200) and (220) planes suggesting the formation of Pd (0) in the four organosilica networks [31]. According to Scherer’s equation, the crystal size of the doped Pd for the four membranes were similar of about 20 nm. In addition, the relative intensity of those full Pd characteristic peaks for Pd-Nb-BTESE samples increased with the increase of Pd content, which indicates that Pd were successfully doped into the corresponding organosilica networks.

FTIR spectra were used to study the chemical states of the four Pd–Nb-BTESE membranes (Fig. 3). The four powder samples showed similar FTIR spectra, which confirm that chemical structures of the four Pd-Nb-BTESE membranes are similar. The peaks at 3450, 1628, 1045, 775 and 680 cm⁻¹ are assigned to Si–OH stretching vibrations, H–O–H deformation vibrations, Si–O–Si asymmetric stretching vibrations, –CH₂ rocking vibrations and Si–C stretching vibrations, respectively [32,33]. The weak peak appearing at 1410 cm⁻¹ corresponds to bending asymmetric vibrations of –CH₂ for Si–CH₂–CH₂–Si, confirming the existence of ethane-bridged silsesquioxane [32]. To study the influence of bimetal doping on chemical composition for organosilica networks, FTIR spectra of BTESE, Pd-BTESE, Nb-BTESE and Pd–Nb-BTESE were compared in
organosilica networks. Fig. 4 shows the Pd 3d and Nb 3d XPS spectra of Pd-BTESE powders and the deconvolutions details of O1s are given in Fig. 5 and Table 1. It can be seen that the percentages of Nb–O–Si for all the four samples remain constant (~7%). This result indicates that the contents of Nb–O–Si in the four Pd–Nb-BTESE networks are almost the same.

### 3.2. Morphological and structural analysis of Pd–Nb-BTESE membranes

Fig. 6 shows the TEM images of the four Pd–Nb-BTESE powders. Uniformly distributed black particles with size of about 5–10 nm were clearly observed in the four organosilica networks. In Fig. 6d, the distance of lattice fringe for the black nanoparticles was 0.196 nm corresponding to (200) plane of Pd (0) [41], which confirmed that the embedded black nanoparticles in the organosilica networks were Pd nanoparticles. It was observed that the Pd nanoparticle size did not vary with the increase of the concentration of doped Pd, but a higher Pd doping content resulted in the increased density of Pd nanoparticles in the corresponding organosilica networks.

Fig. 7 shows the cross-sectional SEM images of the four Pd–Nb-BTESE membranes. All these membranes exhibit an asymmetric structure including a α-Al2O3 support layer, a γ-Al2O3 intermediate layer and a Pd–Nb-BTESE separation layer. The Pd–Nb-BTESE layers of the four membranes have a similar thickness of about 170 nm. Fig. S5 shows the surface morphology of Pd–Nb-BTESE-0.4 membrane that the membrane surface is smooth and defect free.

N2 adsorption-desorption experiments were conducted to determine the effects of the bimetallic doping on microstructural changes of the organosilica networks. The N2 adsorption-desorption isotherms of Pd–Nb-BTESE powders are shown in Fig. 8. All samples reached high adsorption capacities rapidly at a very low relative pressure region matching well with the characteristics of type I isotherms, confirming that the Pd–Nb-BTESE membranes have microporous structures [42]. However, Pd–Nb–BTESE-0.1, 0.2 and 0.4 showed small hysteretic loops at the 0.4–0.7 relative pressure indicating some mesopores exist in the Pd–Nb-BTESE networks. The detailed pore structure information of Pd–Nb-BTESE powders is given in Table 2. Pd–Nb-BTESE-0.05 powders exhibited the highest Brunauer-Emmett-Teller surface area (S BET, (233 m² g⁻¹)) and the largest total pore volume (V total, 0.129 cm³ g⁻¹). As Pd doping content increased, S BET and V total of the prepared Pd–Nb–BTESE powders both showed a decreasing trend. When the n (Pd) : n (Si) rose to 0.4, the S BET and V total values of the sample were 177 m² g⁻¹ and 0.108 cm³ g⁻¹, respectively. This result could be attributed to the increased density of Pd nanoparticles in Pd–Nb-BTESE networks. Pd nanoparticles could competitively occupy pore volume in the Pd–Nb-BTESE networks, resulting in the decrease of S BET and V total.

In addition, the N2 adsorption-desorption isotherms of BTESE, Pd–BTESE and Nb–BTESE powders were shown in Fig. S6. The N2 adsorption-desorption isotherm of BTESE powders shows a type I isotherms suggesting the microporous structure. Compared with the BTESE powders, the Pd–BTESE powder exhibits a higher N2 adsorption capacity and has a large hysteretic loop at the range of 0.4–0.9 relative pressure, indicating some mesopores exist in the Pd–BTESE network. This result implied that doping Pd led to a larger pore size of the BTESE network.
The nitrogen adsorption-desorption isotherm of Nb-BTESE powders is almost undetectable. The detailed $S_{BET}$ and $V_{total}$ of the three samples are given in Table S2. The $S_{BET}$ and $V_{total}$ of Nb-doped BTESE powders are not available due to its dense structure. In contrast to the Nb-BTESE networks, the Pd-BTESE powders showed larger $S_{BET}$ of 507 m$^2$ g$^{-1}$ and $V_{total}$ of 0.354 cm$^3$ g$^{-1}$ than those of pure BTESE ($S_{BET}$ of 360 m$^2$ g$^{-1}$ and $V_{total}$ of 0.205 cm$^3$ g$^{-1}$). These results are in agreement with our previous monometallic doped BTESE work [19, 29]. Therefore, compared with the two types of monometallic doped BTESE networks, the relatively moderate $S_{BET}$ and $V_{total}$ of the as-prepared Pd–Nb-BTESE networks suggested that Pd–Nb bimetallic doping may present a better balance between the permeance and permselectivity in H$_2$/CO$_2$ separation.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Assignment</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Nb-BTESE-0.05</td>
<td>532.7</td>
<td>1.9</td>
<td>Si–O–Si</td>
<td>92.9</td>
</tr>
<tr>
<td></td>
<td>531</td>
<td>0.94</td>
<td>Nb–O–Si</td>
<td>7.1</td>
</tr>
<tr>
<td>Pd-Nb-BTESE-0.1</td>
<td>532.7</td>
<td>1.75</td>
<td>Si–O–Si</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td>531</td>
<td>0.91</td>
<td>Nb–O–Si</td>
<td>7.0</td>
</tr>
<tr>
<td>Pd-Nb-BTESE-0.2</td>
<td>532.7</td>
<td>1.85</td>
<td>Si–O–Si</td>
<td>92.9</td>
</tr>
<tr>
<td></td>
<td>531</td>
<td>0.9</td>
<td>Nb–O–Si</td>
<td>7.1</td>
</tr>
<tr>
<td>Pd-Nb-BTESE-0.4</td>
<td>532.7</td>
<td>1.76</td>
<td>Si–O–Si</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>531</td>
<td>0.94</td>
<td>Nb–O–Si</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Note: BE and FWHM represent binding energy and full width at half maxima, respectively.

Fig. 5. Deconvolution of the XPS O1s peak of Pd–Nb-BTESE powders.

Table 1 lists the XPS deconvolution details of O1s peaks of Pd–Nb-BTESE powders.

N$_2$ adsorption-desorption isotherm of Nb-BTESE powders is almost undetectable. The detailed $S_{BET}$ and $V_{total}$ of the three samples are given in Table S2. The $S_{BET}$ and $V_{total}$ of Nb-doped BTESE powders are not available due to its dense structure. In contrast to the Nb-BTESE networks, the Pd-BTESE powders showed larger $S_{BET}$ of 507 m$^2$ g$^{-1}$ and $V_{total}$ of 0.354 cm$^3$ g$^{-1}$ than those of pure BTESE ($S_{BET}$ of 360 m$^2$ g$^{-1}$ and $V_{total}$ of 0.205 cm$^3$ g$^{-1}$). These results are in agreement with our previous monometallic doped BTESE work [19, 29]. Therefore, compared with the two types of monometallic doped BTESE networks, the relatively moderate $S_{BET}$ and $V_{total}$ of the as-prepared Pd–Nb-BTESE networks suggested that Pd–Nb bimetallic doping may present a better balance between the permeance and permselectivity in H$_2$/CO$_2$ separation.

To further explore the porous structures of the as-prepared membranes, the pore size distributions (PSDs) of Pd–Nb–BTESE powders were calculated by the NLDFT method (Fig. 9). The pore size distributions of all samples are multimodal containing a main microporous region and a partial mesoporous region, indicating that micropores are predominant and a small amount of mesopores exist in these networks. The main pore sizes of the Pd–Nb–BTESE networks were centered at 6.01, 5.94, 5.84 and 5.96 Å as the n (Pd): n (Si) increased from 0.05 to 0.4, respectively. When n (Pd): n(Si) ratio is below 0.2, the pore sizes of the corresponding networks decrease as the Pd doping contents increase. However, at a high Pd doping content (n (Pd): n(Si) = 0.4), the pore size of Pd–Nb–BTESE-0.4 sample increases, which may be ascribed to the formation of larger pores caused by the high density of Pd nanoparticles.

3.3. Gas separation performance of Pd–Nb–BTESE membranes

Fig. 10 shows the kinetic diameter of gases dependency on single gas permeances for Pd–Nb–BTESE membranes. The permeances of the four Pd–Nb–BTESE membranes exhibited a decreasing tendency as the kinetic diameter of gases increases, except for H$_2$ permeance of Pd–Nb–BTESE-0.4 membrane. This result indicated that Pd–Nb–BTESE membranes possess molecular sieving characteristics. Among the four membranes, Pd–Nb–BTESE-0.05 membrane showed the highest gas permeances to all tested gases except for H$_2$. Both Pd–Nb–BTESE-0.1 and Pd–Nb–BTESE-0.2 membranes showed relatively low permeances to the tested gases. Pd–Nb–BTESE-0.2 membrane exhibited the lowest permeances to all gases, which agrees with the aforementioned pore size analysis. Interestingly, He, CO$_2$, N$_2$ and CH$_4$ permeances of Pd–Nb–BTESE-0.4 membrane were between those of Pd–Nb–BTESE-0.2 and Pd–Nb–BTESE-0.05, and Pd–Nb–BTESE-0.4 membrane showed the highest H$_2$ permeance.

Table S3 lists the permeances of H$_2$ and CO$_2$ and the H$_2$/CO$_2$ permselectivities for the as-prepared Pd–Nb–BTESE membranes. All H$_2$/CO$_2$ permselectivities of the four membranes are much greater than the Knudsen diffusion factor (4.7), suggesting that all the prepared Pd–Nb–
Fig. 6. HRTEM images of (a) Pd–Nb-BTESE-0.05, (b) Pd–Nb-BTESE-0.1, (c) Pd–Nb-BTESE-0.2 and (d) Pd–Nb-BTESE-0.4 powders (the inset of Fig. 6d is the HRTEM image for Pd nanoparticles in high-magnification).

Fig. 7. SEM images of (a) Pd–Nb-BTESE-0.05, (b) Pd–Nb-BTESE-0.1, (c) Pd–Nb-BTESE-0.2, (d) Pd–Nb-BTESE-0.4 membranes.
BTESE membranes could be used for H$_2$/CO$_2$ separation. Pd–Nb-BTESE-0.05 membranes showed H$_2$ permeance of $8.7 \times 10^{-11}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and H$_2$/CO$_2$ permselectivity of 40, respectively. Although H$_2$ permeances of Pd–Nb-BTESE-0.1 and Pd–Nb-BTESE-0.2 membranes did not increase, H$_2$/CO$_2$ permselectivities of the two membranes reached up to 53 and 54, respectively. Pd–Nb-BTESE-0.4 membrane not only showed the highest H$_2$ permeance ($1.12 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), but also the highest H$_2$/CO$_2$ permselectivity (107). The H$_2$ and CO$_2$ permeation mechanisms of Pd–Nb-BTESE-0.4 membrane have been discussed in Supporting Information (See Fig. S7). The H$_2$ molecules pass through Pd–Nb-BTESE-0.4 membrane by activated diffusion, while CO$_2$ molecules through the membrane are dominated by surface diffusion mechanism. The Pd–Nb-BTESE-0.4 membrane showed stable performance and good reproducibility (Fig. S8 and Fig. S9).

To further explain the results of single gas permeation of the as-prepared Pd–Nb-BTESE membranes, H$_2$ and CO$_2$ adsorption experiments for the corresponding Pd–Nb-BTESE powders were conducted. The four Pd–Nb-BTESE samples with different Pd-doping contents exhibited different H$_2$ adsorption isotherms, while CO$_2$ adsorption isotherms for all samples almost remained the same (Fig. 11). Obviously, the H$_2$ adsorption isotherms of all Pd–Nb-BTESE powders experienced dramatically increase at low absolute pressures (~50 mm Hg), and H$_2$ adsorbabilities gradually became stronger with the increase of Pd doping content. This result suggested that the high density Pd nanoparticles in Pd–Nb-BTESE-0.4 network dominated its H$_2$ adsorption process, which indirectly explains that Pd–Nb-BTESE-0.4 membrane has the highest H$_2$ permeance. In addition, to further reveal the H$_2$ adsorbability of Pd in the organosilica network, the H$_2$ adsorption isotherms of Pd-BTESE, Nb-BTESE and BTESE were provided in Fig. S10. Both Nb-BTESE and BTESE samples showed a very low H$_2$ adsorption capacity, suggesting that Nb and BTESE cannot contribute to the high H$_2$ adsorption capacity of Pd–Nb-BTESE powders. However, Pd-BTESE sample showed a high H$_2$ adsorption capacity and the characteristic of H$_2$ adsorption isotherms is same as the Pd–Nb-BTESE powders. This
result demonstrated that the doped Pd govern the H$_2$ adsorption capacities of the Pd–Nb–BTESE samples, which agrees with previous reports that metal Pd generally exhibits strong adsorbability toward H$_2$ for Pd-doped organosilica membranes [19].

According to the deep understanding of monometallic doped BTESE membranes (i.e. Pd- or Nb-doped membranes) and new findings presented in this work, the structural evolution of Pd–Nb–BTESE network from pure BTESE is schematically illustrated in Fig. 12. The pure BTESE-derived organosilica networks with relatively high pore volume and large pore size usually exhibit high H$_2$ permeances and low H$_2$/CO$_2$ permeselectivities [43]. The introduction of Nb could form new covalent bonds Nb–O–Si into the BTESE-derived networks and make the structures become much denser [29]. As a result, H$_2$ permeances of Nb-doped BTESE membranes are often very low, while of these membranes always exhibit high H$_2$/CO$_2$ permeselectivities. The mechanism of bimetallic doing into BTESE network is that when incorporated Pd into Nb-induced dense organosilica networks, the formed Pd nanoparticles can not only inhibit excessive densification of the Nb-doped networks but also functionalize the networks with H$_2$ preference. The increased Pd content conferred Pd–Nb–BTESE membranes a stronger H$_2$ adsorbability which is beneficial to improve the H$_2$ permeance. Therefore, we believe that the synergetic effects of bimetallic doping with Pd and Nb confers BTESE-derived organosilica membranes with moderate structures and excellent H$_2$ separation performance.

Fig. 13 compares the H$_2$/CO$_2$ separation performance (H$_2$ permeance and H$_2$/CO$_2$ permeselectivity) of the as-prepared Pd–Nb–BTESE membranes with other silica-based membranes reported in literature, where the commonly adopted upper bound 2008 is marked [44]. The detailed operational parameters and the separation performance of those membranes are provided in Table S4. It can be seen that the traditional SiO$_2$ membranes exhibit the excellent H$_2$/CO$_2$ separation performance, but it is well-known that these membranes suffer from poor hydrothermal stability under steam conditions for practical applications [5]. Only Co–SiO$_2$ membrane was tested with H$_2$/CO$_2$ binary gas, which shows a H$_2$/CO$_2$ selectivity of 40 but an extremely low H$_2$ permeance [45]. Compared with SiO$_2$ membranes, organosilica-based membranes generally exhibit enhanced hydrothermal stability but their H$_2$/CO$_2$ separation performance are not ideal enough. Most pure BTESE-derived membranes exhibited low H$_2$/CO$_2$ permeselectivities that are below Knudsen diffusion factor (4.7) [43,46]. Monometallic doping strategy was found to be effective for improving either H$_2$ permeance or H$_2$/CO$_2$ permeselectivity of BTESE-derived membranes [16,19,28,29,47]. In addition, although the bimetallic doped TEOS-derived silica membranes exhibited improved hydrothermal stability, they did not display impressive H$_2$/CO$_2$ separation performance that their permeselectivities were close to upper bound 2008 [22,23,25,48]. We note that the H$_2$/CO$_2$ permeselectivities of all the Pd–Nb–BTESE membranes in this work are far above the upper bound 2008, and the optimal membrane (i.e. Pd–Nb–BTESE-0.4) showed a very competitive H$_2$/CO$_2$ separation performance compared with that of reported silica-based membranes in literature.

4. Conclusions

Bimetallic doped BTESE-derived organosilica membranes were prepared by using the sol-gel method and the synergetic effects of Pd–Nb bimetallic doping on the organosilica networks were investigated. By controlling the same Nb doping content, the influences of different Pd doping contents (n (Pd): n (Si) = 0.05, 0.1, 0.2 and 0.4) on microstructures and H$_2$/CO$_2$ separation performances of the as-prepared Pd–Nb–BTESE membranes were compared. As evidenced by a series of characterization, the same amount of Nb was first coaxially incorporated into the four networks through the formation Nb–O–Si bonds, while metal Pd was doped into the networks in the form of nanoparticles. These Pd nanoparticles with size of ~5–10 nm were uniformly embedded into the as-prepared Pd–Nb–BTESE networks, for which the densities of Pd nanoparticles increases with the Pd doping content increases.

The bimetallic doping mechanism for the Pd–Nb–BTESE was established. Compared with Pd- or Nb-doped membranes, the four bimetallic doped membranes showed more moderate microporous structures and improved H$_2$/CO$_2$ separation performances. We found that tuning the Pd doping content was crucial for tailoring the pore sizes and the H$_2$ adsorption capacities of the Pd–Nb–BTESE networks, which eventually contributes to the H$_2$/CO$_2$ separation performance of the corresponding membranes.

In addition, H$_2$/CO$_2$ separation performances of the four Pd–Nb–BTESE membranes are all far above the upper bound 2008. Pd–Nb–BTESE-0.4 membrane exhibits superior H$_2$/CO$_2$ separation performance with H$_2$ permeance of 1.12 × 10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and H$_2$/CO$_2$ permeselectivity of 107, which is very competitive over that of reported silica-based membranes in literature. Thus, this work may signify an important step toward designing and developing high-performance organosilica membranes that challenge trade-off effects for practical H$_2$/CO$_2$ separation.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hengfei Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. Yibin Wei: Methodology, Investigation, Formal analysis, Writing - review & editing. Hong Qi: Investigation, Resources, Supervision, Writing - review & editing.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21490581), China Petroleum & Chemical Corporation (317008-6) and Guangxi Innovation Driven Development Foundation (317008-6). This work is supported by the National Natural Science Foundation of China (21490581), China Petroleum & Chemical Corporation (317008-6) and Guangxi Innovation Driven Development Foundation (317008-6).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2020.110279.

References