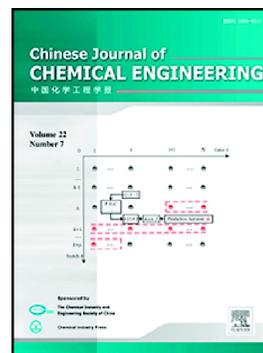


## Accepted Manuscript

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**Materials and Product Engineering**

Controlling pore structures of Pd-doped organosilica membranes by  
calcination atmosphere for gas separation<sup>☆</sup>

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**Abstract**

Pd-doped organosilica membranes were prepared by controlling calcination atmospheres (i.e. POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub>, POS-H<sub>2</sub>/N<sub>2</sub>) to tailor their networks for improving their gas separation performance. This study shows that Pd (II) could be only maintained under non-reductive calcination atmosphere, while inert and reducing calcination atmosphere is more beneficial to maintain organosilica moieties in POS networks. POS-H<sub>2</sub>/N<sub>2</sub> membrane showed the optimal H<sub>2</sub> separation performance that its permselectivities for H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/SF<sub>6</sub> are 15.0, 96.7, 173.0 and 3400.0, respectively. Moreover, it is found that H<sub>2</sub> molecules pass through the four membranes are based on activated diffusion, while CO<sub>2</sub> molecules permeation through POS-N<sub>2</sub> and POS-Air membrane is dominated by surface diffusion. This work may provide insight into the understanding of the calcination atmosphere effect on gas separation performance of metal-doped organosilica membranes.

**Keywords:** Pd doping; organosilica membrane; calcination atmosphere; gas separation.

## 1. Introduction

Over recent decades membrane-based technologies have been proven to be effective solutions to critical challenges that human beings are facing today, such as the efficient production of fuels, chemicals, renewable energy, and drinking water; as well as advanced environmental remediation and climate change mitigation [1-3]. Inorganic ceramic membranes exhibit excellent mechanical, thermal and chemical stability, which allow them to be promising for gas separation. Among the ceramic membranes, microporous silica-based membranes have drawn a great deal of attention for molecular sieving applications owing to their tunable pore size [4].

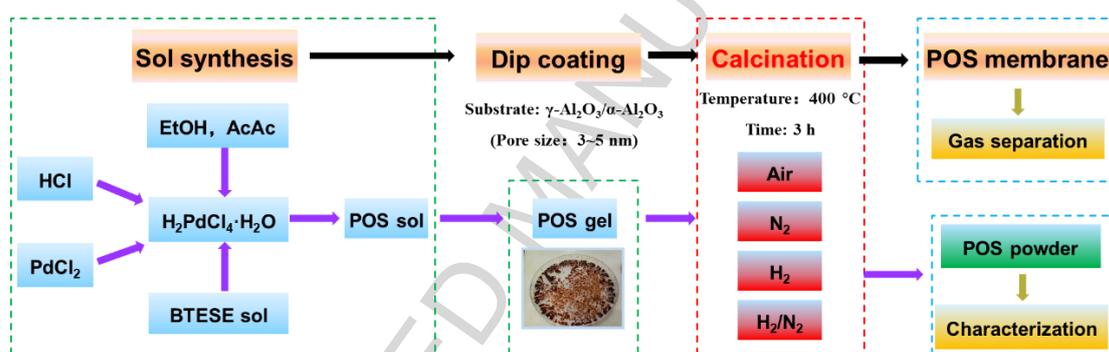
The first gas separation silica membrane was prepared by Uhlhorn et al. in 1989 [5]. Their membranes were asymmetric with a structure consisting of three layers including a macroporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support layer, a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> intermediate layer and a microporous silica separation layer, exhibiting excellent CO<sub>2</sub>/CH<sub>4</sub> separation performance. A few years later, de Vos et al. [6] reported an ultra-thin microporous silica membrane with superior hydrogen separation performance (H<sub>2</sub> permeance of  $5 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> and H<sub>2</sub>/CO<sub>2</sub> permselectivity of 71), which signify an important step toward industrial application of H<sub>2</sub>/CO<sub>2</sub> separation. However, many follow-up studies pointed out that microporous silica materials are unstable in a steam environment [7]. Si-O-Si groups in silica network can decompose into mobile silanol encountering H<sub>2</sub>O at high temperature, leading to the formation of non-selective pores [8]. Therefore, hydrothermal stability is another critical criterion

in addition to permeability and permselectivity, and the poor hydrothermal stability of silica membranes limits its real industrial application in H<sub>2</sub>/CO<sub>2</sub> separation.

In 2007, Castricum et al. [9] prepared an organic-inorganic hybrid silica membrane derived from the precursor 1, 2-bis(triethoxysilyl)ethane (BTESE) and the co-reactant methyltriethoxysilane (MTES), for n-butanol dehydration via pervaporation process. It is worth noting that the membrane showed not only the excellent separation performance (water flux of 10 kg·m<sup>-2</sup>·h<sup>-1</sup> and the separation factor ~ 1000) but also unprecedented hydrothermal stability. In a moderate steam atmosphere at 150 °C, 4% water flux decline of the membrane was found per month, and the water flux kept up to 5 kg·m<sup>-2</sup>·h<sup>-1</sup> after running 500 days. Inspired by this, Tsuru 's group [10] successfully prepared BTESE membranes used for gas separation for the first time, which can achieve ~10<sup>-5</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> level in H<sub>2</sub> permeance under hydrothermal conditions. The hydrothermal stability of amorphous silica-based membranes with an organic bridging group between two Si atom (also known as organosilica membranes) was then extensively studied proving their enhanced hydrothermal stability when compared with that of pure inorganic silica membranes and methylated silica membranes [11-16].

Among organosilica membranes, BTESE derived membranes with the ethylene-bridged network have been considered the most promising for H<sub>2</sub>/CO<sub>2</sub> separation under hydrothermal conditions [17]. The sol-gel method is commonly used to prepare silica-based membranes and the preparation procedure usually consists of

three steps including synthesis of sol, coating (e.g. spray and dip) and calcination (Fig. 1) [18]. The sol-gel chemistry controlled by synthesis parameters can ultimately affect the structure and properties of the membranes [19]. The sol needs to be carefully tuned prior to coating for avoiding sol permeation into the substrates. Calcination is the last step in forming the microporous structure and removing water and organic impurities [20]. It should be noted that the organic chains could be pyrolyzed under harsh calcination conditions and the calcination process of the preparation of silica-based membranes should be carefully selected [21].



**Fig. 1.** Schematic illustration for the preparation process of POS powders and membranes.

Although pure BTESE membranes exhibit good  $H_2$  permeability, its low  $H_2/CO_2$  permselectivity still remains challenging to meet the requirement of industrial application [22-24]. Doping metals such as Mg, Zr, Co, Pd, Nb and etc., into silica networks has been regarded as an effective strategy to improve hydrothermal stability and  $H_2/CO_2$  permselectivity of silica network [4, 25-30]. However, the trade-off between permeability, permselectivity and hydrothermal stability still exists in the

reported metal-doped organosilica membranes. The introduction of metals doubtless improves the complexity of the organosilica networks and leads to synergetic gas separation results [31]. More experimental and theoretical efforts are required to elucidate these new phenomena for designing and developing desirable membranes. Our recent studies [32, 33] confirmed that incorporating palladium (Pd) into BTESE-derived organosilica network could greatly improve the H<sub>2</sub> permeability of the membrane due to the high attraction of Pd to hydrogen atoms. Both metal dopant and organosilica network of a membrane are influenced by calcination process, but this effect on Pd-doped organosilica (POS) membrane are lack of investigation.

Therefore, in this study, we investigate the effect of four typical calcination atmospheres on the gas separation performance of the Pd-doped organosilica (POS) membranes. As illustrated in Fig 1, a POS sol, which has to be suitable for dip coating onto a substrate, was synthesized and characterized. Followed by a coating process, four POS membranes were fabricated by calcination in air, N<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> atmosphere, respectively. X-ray diffractometry (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and N<sub>2</sub> sorption measurements are used to investigate the chemical state and microstructure of the four membranes. Single-gas permeation of the four membranes was evaluated under different temperature. H<sub>2</sub> and CO<sub>2</sub> transport mechanism of the four POS membranes were explored and discussed.

## 2. Experimental

### 2.1. Materials

1, 2-Bis(triethoxysilyl)ethane (BTESE, 97% purity) from ABCR GmbH was used as the precursor. Palladium chloride ( $\text{PdCl}_2$ , purity > 98%) was purchased from Meryer. Ethanol anhydrous (EtOH) and acetylacetone (AcAc purity > 99%) were purchased from Shanghai LingFeng Chemical Reagent Co., Ltd. Concentrated hydrochloric acid (36-38 wt% aqueous solution) were purchased from Liyang Dongfang Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

### 2.2. Preparation of sols, gels and membranes

The details of the preparation procedure for the Pd-doped organosilica (POS) sols could be found in our previous studies [32, 33]. The composition of the obtained POS sol is BTESE: Pd: EtOH:  $\text{H}_2\text{O}$ :  $\text{H}^+$  = 1: 0.22: 94.71: 55.55: 0.68 (molar ratio). The molar ratio of Pd: Si = 0.11: 1. POS gels were prepared by drying the corresponding sols for 24 h in Petri dishes at ambient temperature. The obtained gels were then ground into fine powders and calcined under different atmosphere. Four calcination atmospheres, i.e. air,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{H}_2/\text{N}_2$  ( $n(\text{H}_2)$ :  $n(\text{N}_2)$  = 2: 3) were investigated, and the calcined powders were marked as POS-Air, POS- $\text{N}_2$ , POS- $\text{H}_2$  and POS- $\text{H}_2/\text{N}_2$ , accordingly, for further characterization. The calcination procedure includes a heating process with a rate of  $0.5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , dwelling for 3 h at  $400\text{ }^\circ\text{C}$  and a cooling process with a rate of  $0.5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

To prepare POS membranes, a POS sol was first diluted (Si concentration of 0.17

mol·L<sup>-1</sup>) and then dip-coated onto home-made mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> discs substrate with pore diameters of 3-5 nm in a clean room condition [14]. The dip-coating process was conducted using an automatic coating machine (Pervatech B.V., Netherland) at a withdraw speed of 1.2 cm·s<sup>-1</sup>. The coated membranes were first dried at 40 °C for 3 h in an oven. The POS-N<sub>2</sub>, POS-H<sub>2</sub>, POS-H<sub>2</sub>/N<sub>2</sub> and POS-air membranes were finally prepared based on the same calcination conditions as those used for the preparation of above-mentioned POS powders.

### 2.3. Characterization of powders and membranes

Particle size distributions of the freshly prepared sols were measured by a nanosizer (Zetatrak, NPA152, Microtrac Inc.) at 30 °C. The particle size distribution and mean particle size of sols were calculated by the Microtrac software. Thermal behaviors of the gel powders were evaluated by thermogravimetric analysis (TGA, STA-449-F3, Netzsch) with a heating rate of 10 °C·min<sup>-1</sup> from 20 °C to 800 °C under N<sub>2</sub> or air atmosphere. The crystalline structure of POS powder samples was analyzed by X-ray diffractometry (XRD, D8-Advance, Bruker) using a Cu K $\alpha$  radiation at 40 kV and 15 mA. Fourier transform infrared (FTIR) spectra was used to determine the chemical composition of the POS powders by a Thermo NICOLET 8700. Transmission electron microscope (TEM, JEM-200CX, JEOL) was used to image observe morphological characteristics of the POS structures. N<sub>2</sub> adsorption-desorption isotherms at 77 K were conducted using Micromeritics ASAP 2020 to evaluate microstructures of the POS powders. The powders were degassed under vacuum at

473 K for 12 h prior to measurements. Pore size distributions of the POS powders could be estimated via the N<sub>2</sub> adsorption-desorption isotherms based on cylindrical pore model.

#### *2.4 Gas permeation measurement*

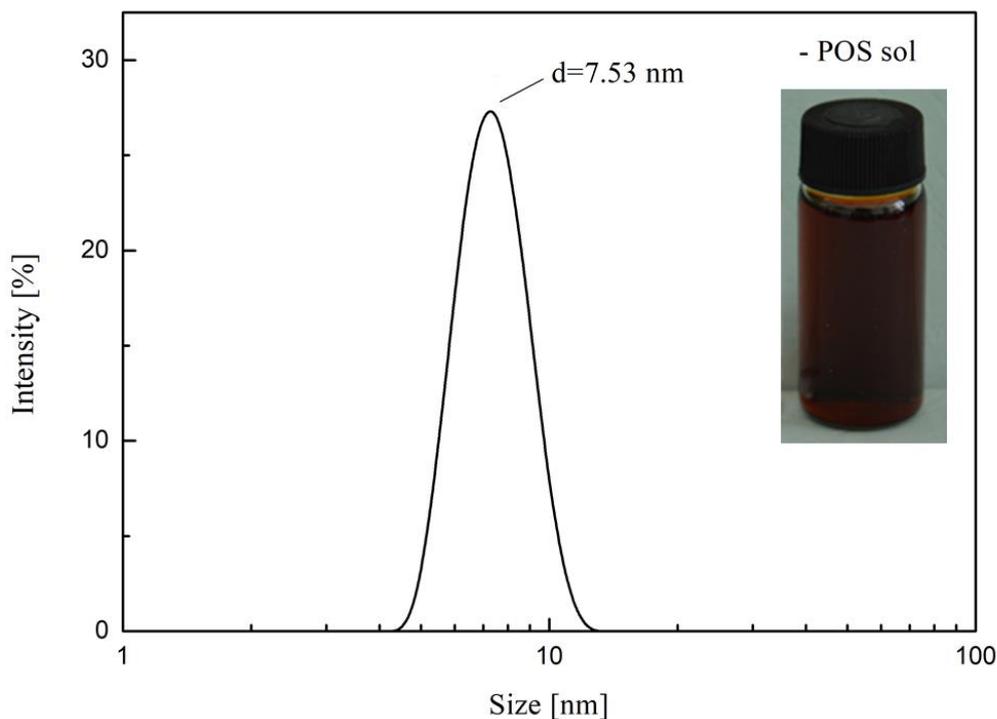
Single-gas permeation of as-prepared POS membranes was measured at 200 °C under a transmembrane pressure of 0.3 MPa using a dead-end mode apparatus. The membranes were tested using single gases with different kinetic diameters ( $d_k$ ) [He (2.55 Å), H<sub>2</sub> (2.89 Å), CO<sub>2</sub> (3.3 Å), N<sub>2</sub> (3.64 Å), CH<sub>4</sub> (3.8 Å), to SF<sub>6</sub> (5.5Å)]. The gas permselectivity, also known as ideal selectivity, was equal to the permeance ratio between two gases.

### **3. Results and Discussion**

#### *3.1. Sol-gel of POS*

Fig. 2 shows the appearance and particle size distribution of the as-prepared POS sol. It is observed that the sol is homogeneous in reddish brown color. We also found the sol could be stored at -16 °C for 14 months without any agglomeration, which indicates that the as-prepared sol is extremely stable. Because the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support layer has a pore size of 3–5 nm, to avoid sol permeating into substrates, sols with mean particle sizes larger than 5 nm and uniform particle size distribution are desirable for coating. The sol has a narrow unimodal particle size distribution with

5.62-11.70 nm and a mean particle size of 7.53 nm, which could be selected for membrane preparation.

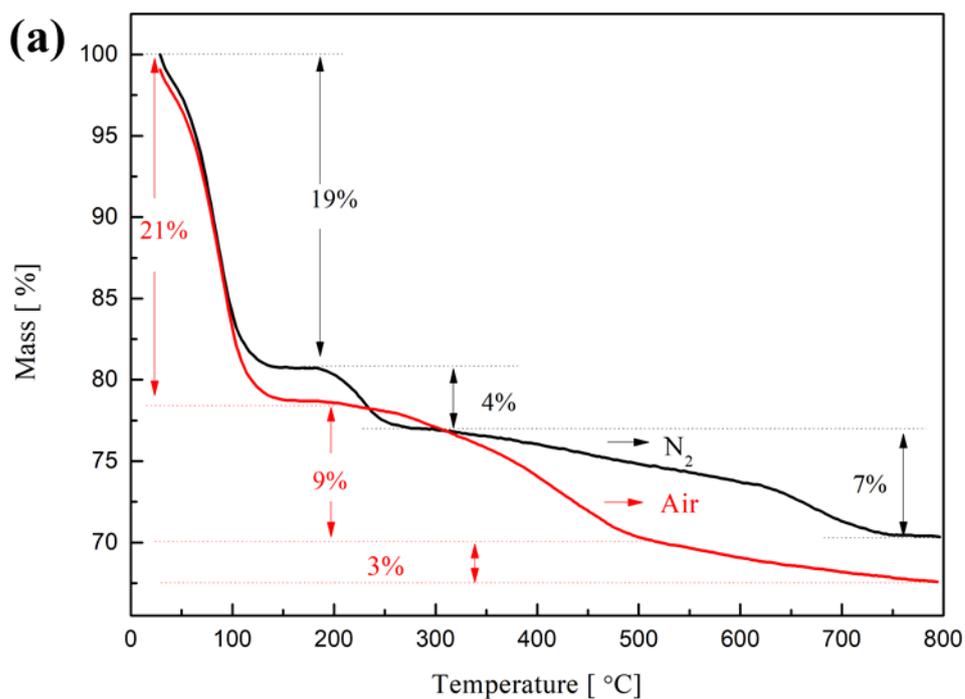


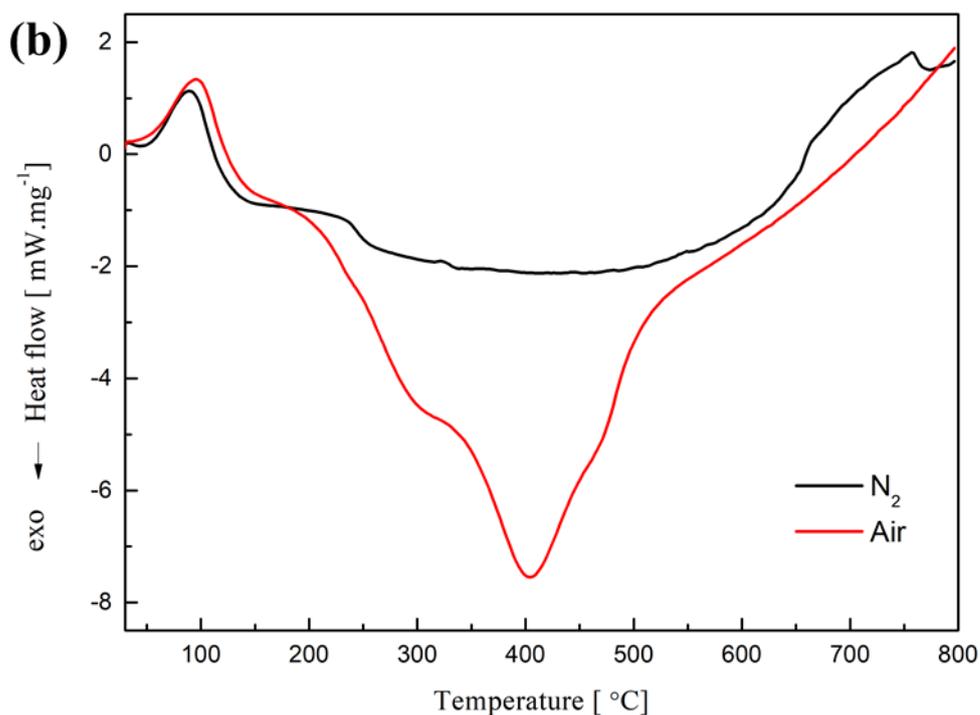
**Fig.**

## 2. Particle size distribution of the as-prepared POS sol.

Fig. 3 describes the thermal evolutions of the as-prepared POS gel under  $N_2$  and air atmosphere heating from 20 °C to 800 °C. The mass loss of POS gel measured under  $N_2$  and air atmosphere showed a similar tendency that a three-stage mass loss could be clearly observed from the TG curves. In the first stage, about 20 % of POS gel mass was lost when measured under air or  $N_2$  atmosphere between 80-130 °C, which was caused by the loss of physically adsorbed water and solvent. For POS gel measured under  $N_2$  atmosphere, 4 % and 7 % of mass loss were found in the temperature ranges of 200-250 °C and 250-800 °C, respectively. This might be attributed to the dehydroxylation and decomposition of the organic moieties,

respectively [21]. Notably, an exothermic peak was observed in differential scanning calorimetry (DSC) for the POS gel measured under air atmosphere at 406 °C, and the mass loss for the temperature



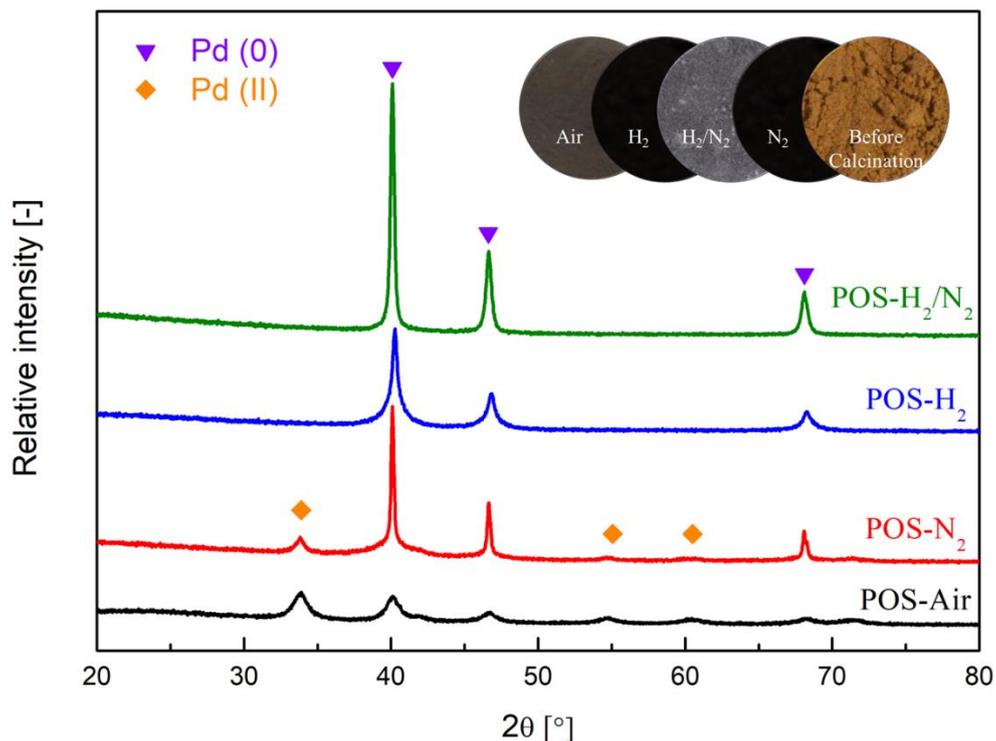


**Fig. 3.** (a) Thermogravimetric and (b) differential scanning calorimeter curves of the POS gels under air and N<sub>2</sub> atmosphere.

range of 130- 500 °C is 9 %. We attribute this to thermal oxidation decomposition, because  $\equiv\text{Si-C-C-Si}\equiv$  in the POS matrix could be decomposed under high-temperature oxidation condition. Therefore, to maintain the organic moiety in the network, the calcination temperature of POS membranes should be below 400 °C, which agrees with the other report [34]. It can also be deduced that the calcination atmosphere has a significant influence on the POS microstructures and the resultant gas separation performance.

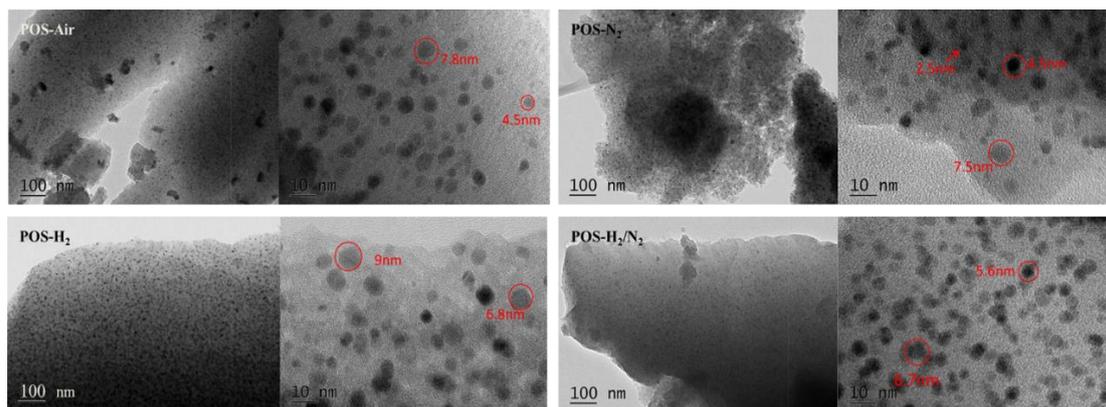
### 3.2. Characterization of POS membranes

It is commonly believed that the as-prepared POS powders could be characterized for reflecting the properties of the corresponding POS layer of as-prepared membranes [35]. Fig. 4 shows XRD patterns of the POS powders calcined under air, N<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> atmosphere. As can be seen from the optical photos of the POS powders (inset of Fig. 4), the colors of the calcined POS powders differ from the original color of POS gel powders, and the colors of POS powders calcined by different atmospheres are disparate as well. The POS gel powders before further calcination are brown in color, while POS-Air and POS-H<sub>2</sub>/N<sub>2</sub> powders are dark grey and grey-white, respectively. Moreover, POS-H<sub>2</sub> and POS-N<sub>2</sub> powders are close to black. The color differences between the four POS powders may indicate that the four POS powders have different chemical states or structures. In XRD patterns of the four powders, no diffraction peaks of crystalline SiO<sub>2</sub> were observed and Pd (0) characteristic peaks ( $2\theta = 40.1^\circ, 46.7^\circ$  and  $68.2^\circ$ ) were detected corresponding to the (111), (200) and (220) plane reflections of palladium [36]. Pd (0) in POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> samples are easily understood due to the H<sub>2</sub> reduced reaction. However, the existence of characteristic peak of Pd (0) in POS-N<sub>2</sub> and POS-Air samples may be attributed to the heat treatment which was also found by Yang et al. [37]. In addition, the characteristic peaks at  $34.2^\circ, 54.5^\circ, 60.2^\circ$  and  $71.5^\circ$  represents the existence of Pd (II) in POS-N<sub>2</sub> and POS-Air powders. This is because PdCl<sub>2</sub> was used as palladium source and Pd (II) could be maintained under non-reductive calcination atmosphere.



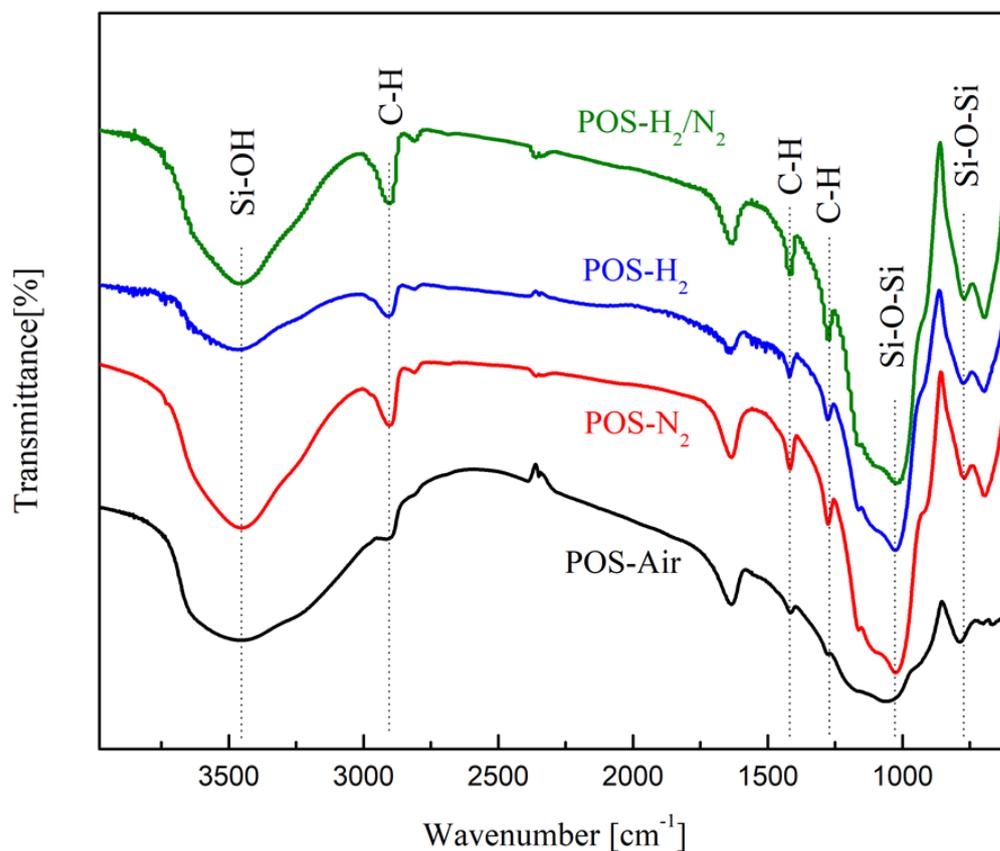
**Fig. 4.** XRD patterns of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> powders.

Fig. 5 shows TEM images of the POS powders calcined at the four atmospheres. It can be observed from each case that Pd particles with a size range between 2-10 nm are randomly dispersed in an organosilica network, indicating that Pd has been successfully doped into the amorphous silica matrix. However, the distribution of Pd particles in the four cases is different. Many large aggregations were found from POS-Air sample under low magnification observation. The metal aggregation phenomenon may be attributed to the transformation of single Pd into PdO and the decomposition of  $\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$  bonds [30]. Compared with the steric resistance of Pd aggregation was reduced in POS-Air, Pd particles were uniformly dispersed in the other samples.



**Fig. 5.** TEM images of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> powders.

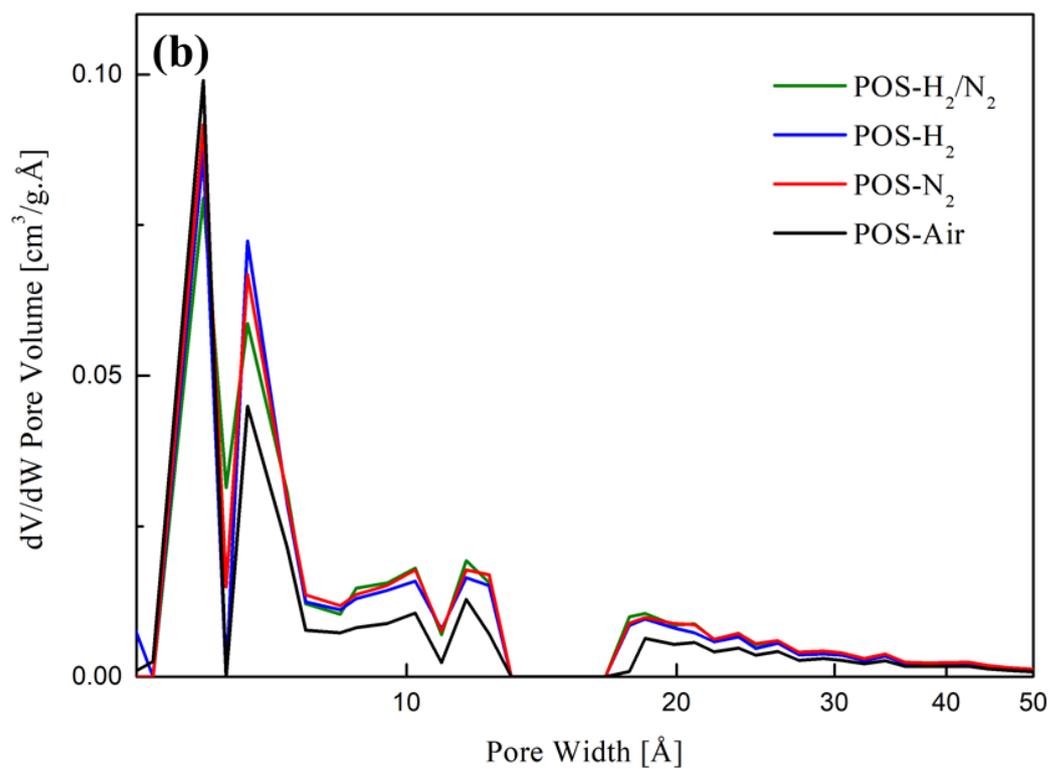
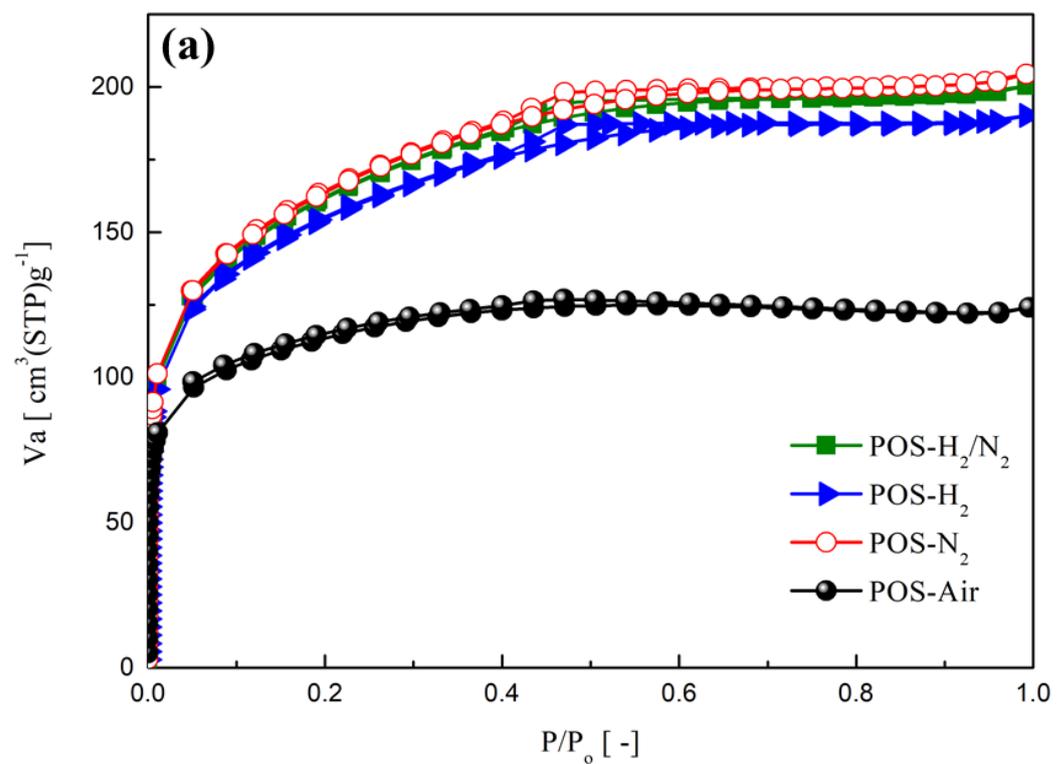
FTIR experiments were conducted to verify the chemical states of the four POS powder samples (Fig. 6). Characteristic peaks of POS samples at 3447, 2906, 1025 and 770 cm<sup>-1</sup> correspond to Si-OH stretching vibration, C-H symmetric stretching vibrations, Si-O-Si asymmetric stretching vibrations, and Si-C stretching vibrations, respectively [38]. The co-existence of the shear vibration peak at 1274 cm<sup>-1</sup> and the swing vibration peak at 1414 cm<sup>-1</sup> is ascribed to ≡Si-CH<sub>2</sub>-CH<sub>2</sub>-Si≡ bond, which suggests the presence of organosilica segment in the samples [25]. It is obvious that the intensity of ≡Si-CH<sub>2</sub>-CH<sub>2</sub>-Si≡ bond in POS-Air sample is the weakest in comparison with other POS powders calcined under inert or reducing gas atmosphere. Kanezashi et al. [39] also found that ≡Si-CH<sub>2</sub>-CH<sub>2</sub>-Si≡ bond may suffer from decomposition or carbonization when heated under air. Therefore, inert (N<sub>2</sub>) and reducing (H<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>) calcination atmosphere is more beneficial to maintain the organosilica moieties.



**Fig. 6.** FTIR spectra of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> powders.

To investigate the effect of calcination atmosphere on the microstructure of POS membrane, N<sub>2</sub> adsorption-desorption experiments of POS powders calcined under the four atmospheres were conducted. Fig. 7a shows the N<sub>2</sub> adsorption-desorption curves of POS powders calcined under the four atmospheres. The type I N<sub>2</sub> adsorption isotherms of the four powders were found and all POS powder samples match with typical characteristics of microporous structure that extremely fast adsorption occurs at low pressure. The small hysteresis loops appeared at  $P/P_0 = 0.45$  indicating that there is a certain amount of mesopores in the four POS powders. POS powders calcined under inert and reducing atmosphere exhibit similar N<sub>2</sub> adsorption capacity

(about  $180 \text{ cm}^3$ )



**Fig. 7.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distributions of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> powders.

**Table 1.** Pore structure data of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> powders.

	$S_{\text{BET}} [\text{m}^2 \cdot \text{g}^{-1}]$	$V_{\text{total}} [\text{cm}^3 \cdot \text{g}^{-1}]$	$V_{\text{micro}} [\text{cm}^3 \cdot \text{g}^{-1}]$	$V_{\text{micro}}/V_{\text{total}} [\%]$
POS-Air	410.18	0.19	0.64	0.87
POS-N <sub>2</sub>	547.37	0.31	0.76	0.71
POS-H <sub>2</sub>	507.18	0.29	0.77	0.71
POS-H <sub>2</sub> /N <sub>2</sub>	540.09	0.30	0.75	0.74

Note:  $S_{\text{BET}}$ ,  $V_{\text{total}}$ ,  $V_{\text{micro}}$  and  $V_{\text{micro}}/V_{\text{total}}$  represent Brunauer–Emmett–Teller (BET) specific surface area, total pore volume, micropore volume and microporosity, respectively.

(STP)  $\cdot \text{g}^{-1}$ ), while the N<sub>2</sub> adsorption capacity of POS-Air is much lower, only 125 cm<sup>3</sup> (STP)  $\cdot \text{g}^{-1}$ . The pore structure information derived from the N<sub>2</sub> adsorption-desorption results is given in Table 1. Similarly, specific surface area, total pore volume, average pore diameter and microporosity of POS powders calcined under inert and reducing atmosphere show nearly same values which are much different from those of POS-Air powder. Among the four samples, POS-Air powder has smaller specific surface area, total pore volume and average pore diameter but higher microporosity (0.87). The relatively small specific surface area and total pore volume of POS-Air sample may be ascribed to the decomposition of organic chains that determined by the aforementioned FTIR results. The consequent closure or collapse of pores leads to a denser structure of POS-Air membrane, in comparison with that of other POS membranes calcined under an inert or reducing atmosphere.

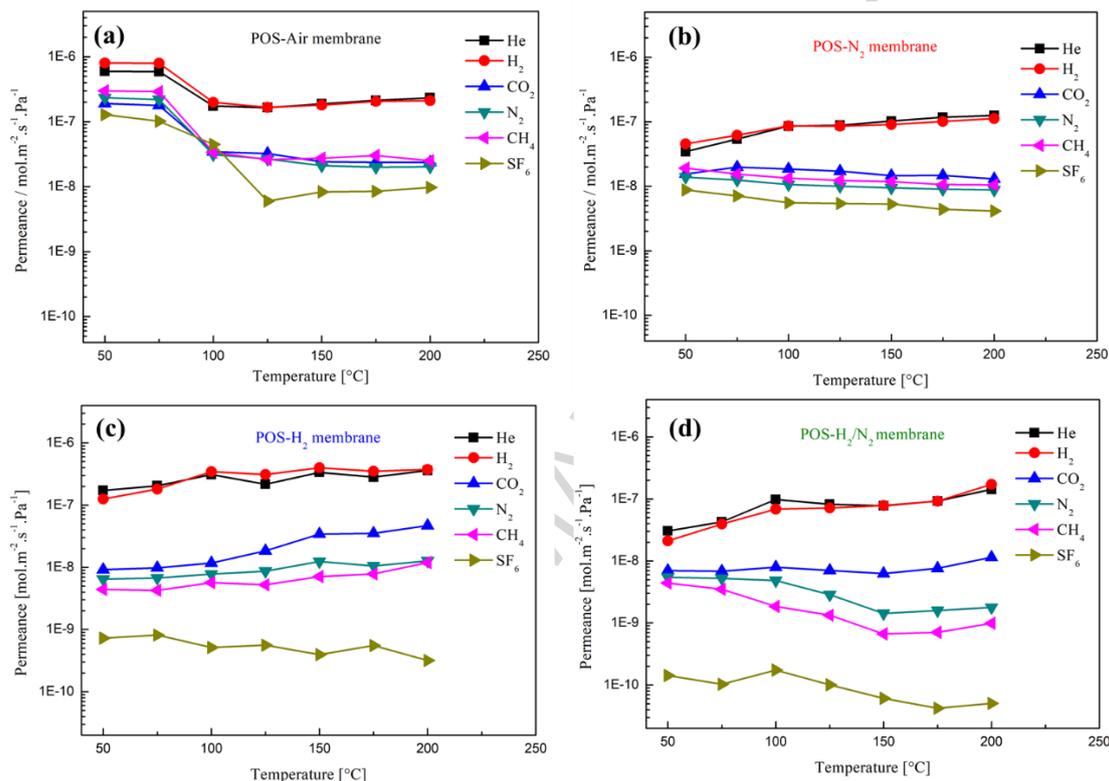
To further investigate pore size and its distribution of the as-prepared POS membranes, nonlocal density functional theory (NLDFT) model [40] analysis based on the  $N_2$  adsorption-desorption curve was applied. In Fig. 7b, the four POS powders have very similar multimodal pore size distribution and the pore size of the four samples is mainly distributed between 0.5 and 0.6 nm. A certain percent of mesopores with the pore size between 2 and 50 nm is found in each POS sample as well. It is observed that POS-Air sample has a higher ratio of micropores and a lower ratio of mesopores compared with those of other POS samples.

### *3.3. Gas separation performance of POS membranes*

#### *3.3.1. Single-gas permeation*

Single-gas permeances and permselectivities of the four POS membranes were studied at different temperature ranging from 50 to 200 °C. In Fig. 8a, POS-Air membrane measured at 50 °C exhibits the highest permeance to all testing gases. This result may be caused by the formation of large pores or defects when calcined under air.  $H_2$  and  $CO_2$  permeance of the membrane measured at 50 °C are  $8.01 \times 10^{-7}$  and  $1.91 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ , respectively. When the testing temperature is above 100 °C, the gas permeances of POS-Air membrane showed a downward tendency to all gases. At 200 °C,  $H_2$  and  $CO_2$  permeance declined to  $2.11 \times 10^{-7}$  and  $2.37 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ , respectively. These results suggest that gas permeance of POS-Air membrane is not stable, which might be attributed to the fracture of the organic chain

segment occurred during the calcination process under air atmosphere. Many small fragments (e.g. silanol groups) were generated during the calcination and moved by gas transport process to block micropores, resulting in gas permeance decline of POS-Air membrane [8].



**Fig. 8.** Single-gas permeances of (a) POS-Air, (b) POS- $\text{N}_2$ , (c) POS- $\text{H}_2$  and (d) POS- $\text{H}_2/\text{N}_2$  membranes tested under different temperature.

In contrast,  $\text{H}_2$  and He permeances of POS- $\text{N}_2$ , POS- $\text{H}_2$  and POS- $\text{H}_2/\text{N}_2$  membranes slightly increase with the increase of temperature (Fig. 8b-d). The  $\text{CO}_2$  permeance of the POS membrane calcined under inert atmosphere (i.e. POS- $\text{N}_2$ ) decreases slightly with the increase of the temperature, while  $\text{CO}_2$  permeance of the POS membrane calcined under reducing atmosphere (i.e. POS- $\text{H}_2$  and POS- $\text{H}_2/\text{N}_2$ ) increases. This

indicates that  $\text{CO}_2$  pass through these POS membranes is based on different mechanisms.  $\text{SF}_6$  molecules can permeate through the four POS membranes, which confirms the existence of mesopores in the membranes.

The four POS membranes measured at 200 °C exhibit good molecule sieving properties as the  $\text{H}_2$  permselectivities of these membranes are much higher than the corresponding Knudsen diffusion factors and the results are compared in Table 2. Among the four membranes, POS- $\text{H}_2/\text{N}_2$  membrane shows the best  $\text{H}_2$  separation performance that its

**Table 2.** Permselectivities of POS-Air, POS- $\text{N}_2$ , POS- $\text{H}_2$  and POS- $\text{H}_2/\text{N}_2$  membranes measured at 200 °C.

	$F_\alpha(\text{H}_2/\text{CO}_2)$	$F_\alpha(\text{H}_2/\text{N}_2)$	$F_\alpha(\text{H}_2/\text{CH}_4)$	$F_\alpha(\text{H}_2/\text{SF}_6)$
POS-Air	8.91	10.4	8.4	21.7
POS- $\text{N}_2$	8.6	12.8	10.7	27.1
POS- $\text{H}_2$	8.0	29.3	31.3	1170
POS- $\text{H}_2/\text{N}_2$	15.0	96.7	173.0	3340

Note:  $F_\alpha$  is permselectivity.

permselectivities for  $\text{H}_2/\text{CO}_2$ ,  $\text{H}_2/\text{N}_2$ ,  $\text{H}_2/\text{CH}_4$  and  $\text{H}_2/\text{SF}_6$  are 15.0, 96.7, 173.0 and 3400.0, respectively. Tsuru [41] well established a simple intraparticle-interparticle pore model to explain gas permeation performance of silica membranes, and we also supplemented and confirmed it with a new experimental investigation [42]. Briefly, in organosilica network, internal pores (also known as intraparticle pores) are formed by a  $\text{Si-O-Si}$  and  $\text{Si-CH}_2\text{-CH}_2\text{-Si}$  hybrid structure and unconnected pores (also known

as interparticle pores) are generated as voids between sol/gel particles. Small gas molecules (e.g. He and H<sub>2</sub>) can permeate through intraparticle pores and interparticle pores, larger gas molecules (in kinetic diameter, e.g. CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and SF<sub>6</sub>) may pass through organosilica membranes via interparticle pores. The mechanism is also applicable to explain the present study that calcination atmosphere can tailor the chemical state and porous structures of POS membranes for improving their permselectivities.

### 3.3.2. H<sub>2</sub> and CO<sub>2</sub> transport mechanism

Efficient separation of H<sub>2</sub> and CO<sub>2</sub> is of great importance for H<sub>2</sub> production in chemical industries. To further study H<sub>2</sub> and CO<sub>2</sub> transport mechanism through the as-prepared POS membranes, the relationship between gas permeance and temperature was studied. The gas permeance of the POS membranes can be calculated from equation 1 [43]:

$$F = F_0 \exp \left[ \frac{-(E_a - E_{ads})}{RT} \right] = F_0 \exp \left( \frac{-\Delta E}{RT} \right) \quad (1)$$

where  $F$  is gas permeance [ $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ],  $F_0$  the temperature independent parameter,  $R$  the gas constant [ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ],  $T$  the absolute permeation temperature [K] and  $\Delta E$  the apparent activation energy [ $\text{J} \cdot \text{mol}^{-1}$ ].

According to equation 1, the Arrhenius plots of H<sub>2</sub> and CO<sub>2</sub> permeances of the four membranes are shown in Fig. 9. The straight lines in the figures show linear fits to the

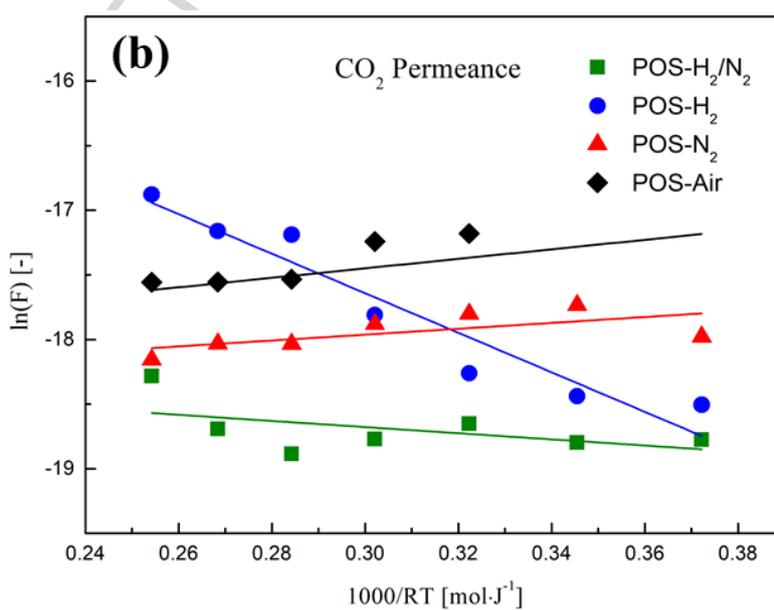
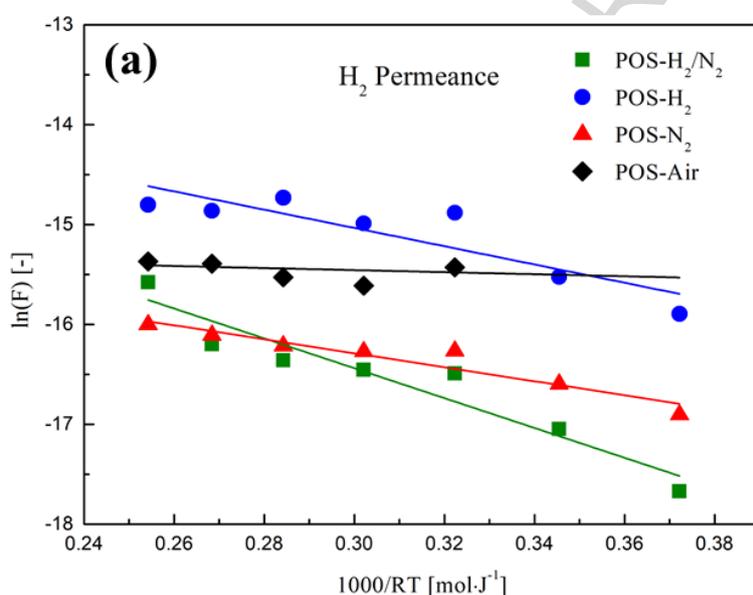
data with slopes equal to  $-\Delta E$  [ $\text{kJ}\cdot\text{mol}^{-1}$ ]. The positive  $\Delta E$  suggests that a gas permeation through a membrane obeys the activated diffusion mechanism, while the negative  $\Delta E$  suggests the process is mainly based on surface diffusion mechanism [44, 45]. The apparent activation energies for  $\text{H}_2$  and  $\text{CO}_2$  permeation through the four POS membranes are presented in Table 3. The four apparent activation energy values for  $\text{H}_2$  pass are positive, which implies that  $\text{H}_2$  molecules pass through our membranes by activated diffusion. Higher activation energy means higher repulsive forces need to be overcome by gas molecules through membrane pores. We found that the apparent activation energy for  $\text{H}_2$  molecules pass through the POS- $\text{H}_2/\text{N}_2$  membrane is much higher than that of the POS-Air membrane. This may indicate that POS-Air membrane has a looser porous structure than that of POS- $\text{H}_2/\text{N}_2$  membrane owing to the differences in the POS networks formed under the different calcination atmospheres.

**Table 3.** Apparent activation energy of  $\text{H}_2$  and  $\text{CO}_2$  through POS-Air, POS- $\text{N}_2$ , POS- $\text{H}_2$  and POS- $\text{H}_2/\text{N}_2$  membranes.

	$\Delta E_{\text{H}_2}$ [ $\text{kJ}\cdot\text{mol}^{-1}$ ]	$\Delta E_{\text{CO}_2}$ [ $\text{kJ}\cdot\text{mol}^{-1}$ ]
POS-Air	1.78	-6.36
POS- $\text{N}_2$	7.00	-2.27
POS- $\text{H}_2$	9.14	15.29
POS- $\text{H}_2/\text{N}_2$	14.96	2.37

Note:  $\Delta E_{\text{H}_2}$  and  $\Delta E_{\text{CO}_2}$  are the activation energy of  $\text{H}_2$  and  $\text{CO}_2$  pass through a membrane, respective.

Notably, POS-H<sub>2</sub>/N<sub>2</sub> and POS-H<sub>2</sub> membranes have positive apparent activation energies for CO<sub>2</sub> permeation, while POS-N<sub>2</sub> and POS-Air membranes have negative apparent activation energies for CO<sub>2</sub> permeation. This result suggests that the transport of the CO<sub>2</sub> molecules through POS-N<sub>2</sub> and POS-Air membrane is dominated by surface diffusion mechanism and the pores in the two membranes exhibited strong adsorption capacity to CO<sub>2</sub>.



**Fig. 9.** Temperature dependency of (a) H<sub>2</sub> and (b) CO<sub>2</sub> permeances of POS-Air, POS-N<sub>2</sub>, POS-H<sub>2</sub> and POS-H<sub>2</sub>/N<sub>2</sub> membranes

#### 4. Conclusions

Four POS membranes calcined under different atmospheres were successfully prepared to investigate the effect of calcination atmosphere (i.e. air, N<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub>) on gas separation performance of those membranes. A POS sol with a mean particle size of 7.53 nm was firstly synthesized for preparation of POS membranes. The TGA-DSC experiment of the POS gel was then conducted to confirm that calcination atmospheres have a significant effect on the chemical state and structure of the POS networks. XRD results confirm that Pd (II) could be only maintained under non-reductive calcination atmosphere (i.e. without H<sub>2</sub>). FTIR analysis suggests that inert and reducing calcination atmosphere is more beneficial to keep organosilica moieties in POS networks. N<sub>2</sub> adsorption-desorption experiments indicate that the pore size of the four membranes is mainly distributed between 0.5 and 0.6 nm with the existence of a certain amount of mesopores.

For gas separation performance, all four POS membranes measured at 200 °C exhibit good permeance to small gas molecules (i.e. He and H<sub>2</sub>) and the H<sub>2</sub> permselectivities of these membranes are much higher than the corresponding Knudsen diffusion factors. Among the four membranes, POS-H<sub>2</sub>/N<sub>2</sub> membrane shows the optimal H<sub>2</sub> separation performance that its permselectivities for H<sub>2</sub>/CO<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/SF<sub>6</sub> are 15.0, 96.7, 173.0 and 3400.0, respectively. In addition, the analysis of activation energies points out that H<sub>2</sub> molecules pass through the four membranes by

activated diffusion, while CO<sub>2</sub> molecules permeation through POS-N<sub>2</sub> and POS-Air membrane is dominated by surface diffusion.

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