



Enhanced pervaporative desulfurization by polydimethylsiloxane membranes embedded with silver/silica core–shell microspheres

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ABSTRACT

Pervaporative desulfurization based on membrane technology provides a promising alternative for removal of sulfur substances (as represented by thiophene) in fluid catalytic cracking (FCC) gasoline. The present study focused on the performance enhancement of polydimethylsiloxane (PDMS) membrane by incorporation of core–shell structured silver/silica microspheres. A silane coupling agent, N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TSD), was used to chelate the Ag⁺ via its amino groups and attach the silver seeds onto the silica surface via condensation of its methoxyl groups. The resultant microspheres were characterized by Zeta-potential lifetime spectroscopy (ZetaPALS), inductively coupled plasma optical emission spectrophotometer (ICP), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The Ag⁺/SiO₂–PDMS composite membranes were prepared by blending PDMS with the as-synthesized silver/silica microspheres. PALS analysis was used to correlate the apparent fractional free volume with permeation flux. The sorption selectivity towards thiophene was enhanced after incorporation of silver/silica microspheres due to the π -complexation between the silver on the microsphere surface and the thiophene molecules. The pervaporative desulfurization performance of the composite membrane was investigated using thiophene/n-octane mixture as a model gasoline. The composite membrane exhibited an optimum desulfurization performance with a permeation flux of 7.76 kg/(m² h) and an enrichment factor of 4.3 at the doping content of 5%.

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1. Introduction

Automobile exhaust, as well as flue gas, has become the main source of sulfur oxide compounds in atmosphere, resulting in acid rain covering most part of the earth [1,2]. Moreover, sulfur poisoning also causes the deterioration of de-NO_x SCR (selective catalytic reduction) catalysts, thus creating more negative effects [3]. Gasoline desulfurization is attracting increased attention due to the urgent requirements for reduction/elimination of sulfur emissions. Many countries or regions have launched stringent programs step-by-step to pursue a sulfur-free gasoline environment. The European Union stipulates that the limitation of sulfur in gasoline should be minimized to 10 ppm since 2009 [4]. The California Reformulated Gasoline Regulations (CaRFG) requires the content cap limits of 30 ppm and 20 ppm from the end of the years 2005 and 2011,

respectively [5]. China's gasoline standard for motor vehicle executing from 2010 sets the sulfur content limitation down to 150 ppm, and the capital city Beijing has executed a standard of 50 ppm locally from 2008 [6]. The worsening environment and stricter restrictions make it more and more urgent to develop efficient technologies for sulfur removal from gasoline [7–9].

Besides reforming and isomerization oils, fluid catalytic cracking (FCC) gasoline takes 30–40% (78% in China) of the total commercial gasoline pool, and is the dominant sulfur contributor up to 85–95%. The main sulfur-containing components in FCC gasoline include thiophenes, mercaptans, sulfides, disulfides and its derivatives. By traditional Merox technology, mercaptans can be removed easily after conversion. The removal of thiophenes is more difficult than that of other sulfur-containing components [10,11].

Currently, hydrodesulfurization (HDS) is the most commonly used desulfurization technique [12]. However, the HDS suffers from high cost of hydrogen and the notable decrease of octane number of gasoline after treatment [13]. In addition, thiophenes are one of the most, if not the most, difficult of impurities to remove from gasoline by conventional hydrotreatment. Recently, alternative technologies, such as adsorption [14], biological method [15],

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extraction method [16], and pervaporation method [17], have been identified and developed for gasoline desulfurization.

Pervaporation is a membrane-based process which has been proved to be efficient in the separation of organic containing mixtures, especially in the fields of organic solvent dehydration, dilute organics (hazardous substances) removal from water and organic–organic separations for its lower energy consumption, high efficiency and environmental benignity [18–20]. The S-Brane™ technology developed by W.R. Grace & Co., CT, USA, is a well-known pervaporation-based industry-scale process for selective removal of sulfur-containing hydrocarbon molecules from FCC and other naphtha streams with a production of 300 barrels/day [21]. Pervaporative desulfurization, either applied alone or coupled with the conventional hydrodesulfurization process, can reduce the capital expenditure and operating cost without scarifying the octane number.

Polydimethylsiloxane (PDMS), polyethyleneglycol (PEG), polyimide (PI) and polyurea/urethane (PUU) are the most widely studied materials for pervaporative desulfurization. PDMS possesses a solubility parameter $(15.5(\text{kJ}/\text{cm}^3)^{1/2})$ suitable for preferable transport of thiophene from gasoline. The enrichment factor of recently developed PDMS-based membranes is around 4.2–4.9 and the flux is in the range of $1.5\text{--}5.37\text{ kg m}^{-2}\text{ h}^{-1}$ for desulfurization of thiophene/n-octane model gasoline [22–25]. To improve the stability of PDMS membrane in gasoline as well as its performance, various inorganic particles are incorporated into the polymer matrix. Organic–inorganic hybrid materials can preserve chemical reactivity and flexibility of the organo-functional groups, while strengthen the mechanical and thermal stability [26]. The swelling degree and free volume parameters of the polymer matrix can be modified by adding inorganic particles due to the mutual affect between the two parts, therefore the pervaporation performance can be improved.

Adsorbents containing transition metals (e.g., Ag, Cu, Ni, Ce and Pd) have been proved to be sulfur-selective and capable of preferably retaining thiophenic compounds by π -complexation [24,27,28]. Among these metal species, silver exhibits excellent adsorption property towards sulfur components in fuels. It has been demonstrated that incorporation of AgY zeolite and Ag_2O into PDMS matrix could increase the permeation flux from $3.3\text{ kg m}^{-2}\text{ h}^{-1}$ to $8.1\text{ kg m}^{-2}\text{ h}^{-1}$ while remaining the enrichment factor at ~ 3.5 [23,29]. The performance of these composite membranes incorporated with silver-containing-particles can break the upper bound of the trade-off curve for pure PDMS membrane.

In this study, silver/silica microspheres were fabricated by a facile procedure, and then filled into PDMS matrix. The bare silica microspheres were firstly prepared through a sol–gel method based on the Stöber reaction using tetraethyl orthosilicate (TEOS) as the silica precursor [30]. Silver nitrate (AgNO_3) was employed as the silver precursor and N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TSD) was used as the functional silane coupling agent performing as a chelator for silver and an anchor to carry the silver seeds onto the silica surface. The present preparation route was featured by the simultaneous fulfillment of chelation function and modification function by mixing TSD and silver precursor together to form silver-TSD chelates ($\text{Ag}^+[\text{NH}_2\text{--CH}_2\text{--CH}_2\text{--NH--}(\text{CH}_2)_3\text{--Si}(\text{OCH}_3)_3]$) in ethanol solution followed by mixing with silica suspension. The silver species were efficiently allocated onto the surface of the silica microspheres. The chemical composition and morphology of the as-synthesized silver/silica microspheres were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasmaoptical emission spectrophotometer (ICP) and transmission electron microscopy (TEM) and particle size distribution was measured. The potential application of the as-synthesized silver/silica microspheres in membrane desulfurization through the π -complexation between Ag^+ and thiophene

was investigated by blending with PDMS. The pervaporative performance of the silver/silica-doped PDMS membranes was tested for thiophene/n-octane model gasoline.

2. Experimental

2.1. Materials

N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TSD) (Sigma–Aldrich Co.), tetraethyl orthosilicate (TEOS), ethanol, aqueous ammonia and silver nitrate (The GuangFu Fine Chemical Research Institute, Tianjin, China) were used to prepare the silver/silica microspheres. TSD and polydimethylsiloxane (PDMS, viscosity 5000 mPa s), dibutyltin dilaurate (Beijing Chemical Company, China) and n-heptane (The GuangFu fine chemical research institute, Tianjin, China) were used for the preparation of the active layer of the PDMS composite membranes. Asymmetric PES ultrafiltration membrane with a molecular weight cut-off of 100 kDa (MegaVision Membrane Engineering & Technology Co., Shanghai, China) was used as the support layer. Thiophene and n-octane (GuangFu fine chemical research institute, Tianjin, China) were chosen as the representative components to formulate a model gasoline. All the reagents were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of bare silica microspheres

Bare silica microspheres were prepared according to the Stöber method [30]. Typically, 6 mL of TEOS was added into a mixture of 100 mL ethanol, 10 mL water and 7.5 mL 25% aqueous ammonia under vigorous stirring at room temperature for 24 h to get a white turbid suspension (marked as suspension A).

2.3. Preparation of silver/silica core–shell microspheres

A stock solution of 25 mM AgNO_3 was prepared in ethanol, to which a desired amount of TSD was added at a TSD: AgNO_3 mole ratio of 1:1.05 under stirring at room temperature until a clear yellow chelate solution was obtained (marked as solution B). Then, a desired amount of solution B was added slowly into suspension A under vigorous stirring at room temperature. The monosized core–shell silver/silica microspheres were separated from the mother suspension by centrifugation (9000 rpm/8 min), washed alternatively and repeatedly with ethanol and deionized water. Then, the microspheres were dried in a vacuum oven at 30°C for 24 h, heated at 50°C for 4 h and at 150°C in a Muffle furnace for another 4 h. The as-synthesized microspheres were stored in dust-free and dry environment before being used for preparation of silver/silica–PDMS hybrid desulfurization membranes.

2.4. Fabrication of silver/silica–PDMS desulfurization membranes

PDMS and TSD were dissolved in n-heptane at a mass ratio of 1:0.1:2.5 to form a homogenous solution under stirring at room temperature, to which the silver/silica microspheres were added. The mixture was stirred and treated sonically to enhance the dispersion of silver/silica microspheres. The catalyst, dibutyltin dilaurate, was then added into the above suspension with a weight ratio of 0.01 to PDMS. After degassing, the solution was cast onto the PES support. The composite membrane was first dried in air for 24 h and then placed in a 75°C oven to complete cross-linking and evaporate the residual solvent. All membrane samples were stored in dust-free and dry environment before being used in pervaporation experiments. For simplicity, the as-prepared membrane samples were designated as $\text{Ag}^+/\text{SiO}_2\text{--PDMS--X}$, where X in the range of

3–10% indicated the weight ratio of silver/silica microspheres to PDMS in the membrane. The thickness of the active PDMS layer of the composite membranes was in the range of 13–16 μm as observed by field emission scanning electron microscopy (FESEM).

Following the similar procedure for preparation, Ag^+/SiO_2 -PDMS homogeneous membranes without PES support for characterization purpose were fabricated except that the solutions were cast on a glass plate instead of the PES support.

2.5. Characterization of the silver/silica core-shell microspheres

The silver content in the microsphere was measured by Inductively Coupled Plasmaoptical Emission Spectrophotometer (ICP, ICP-9000 (N + M), USA Thermo Jarrell-Ash Co.). The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 diffractometer using Cu K α radiation to determine the crystallite size and identity of the bare silica and silver/silica microspheres. The crystallite size of the Ag_2O nanoparticles on the silica surface was estimated by Debye-Scherrer equation $L = 0.89\lambda / (B \cos\theta)$ where L was the average size of the crystalline domains, λ was the wavelength of the X-ray source (1.54056 Å), B is the full width half maximum of the XRD line in radians. The surface property of the microsphere was characterized by X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer PHI 1600 ESCA system with a monochromatic Mg K α source and a charge neutralizer. Transmission electron microscopy (TEM, JEOL JEM-100CXII) and high resolution TEM (HRTEM, FEI Tecnai G2 F20) were employed to observe the microstructure of the microspheres. The particle size distributions of the bare silica and silver/silica microspheres were measured using a zatePALS/BI-9000 particle size distribution analyzer (Brookhaven Instruments Co., New York, USA).

2.6. Characterization of the membranes

Fourier transform infrared (FT-IR) spectra of the Ag^+/SiO_2 -PDMS composite membranes were recorded on a Nicolet-560 FT-IR spectrometer equipped with a horizontal attenuated transmission accessory. The cross-section of the composite membrane was observed using field emission scanning electron microscope (FESEM, Nanosem 430, FEI Co., USA) operated at 10.0 kV, and all specimens were freeze-fractured in liquid nitrogen and then sputtered with gold before observation.

2.7. Free volume characteristics analysis

Positron annihilation lifetime spectroscopy (PALS) measurements were carried out using a fast-fast system with a resolution of 200 ps (full width at half maximum for the ^{60}Co prompt γ -rays, under ^{22}Na window settings). Ag^+/SiO_2 -PDMS hybrid membranes with different silver/silica contents were cut into 1 cm \times 1 cm pieces. The positron source was sandwiched between two membrane pieces. The thickness of the membrane sample for PALS measurement was in the range of 1.2–1.4 mm. All the measurements were conducted at 25 °C. Approximately 1 million counts were collected in each spectrum and five spectra were repeated for each sample. The spectra were resolved by LT-v9 program. The correlations between the radius of the free volume cavity (r_3 , r_4), the lifetime of o-Ps (τ_3 , τ_4) and the corresponding intensities (I_3 , I_4) were obtained according to the procedure described earlier [31].

2.8. Pervaporative desulfurization experiments

The desulfurization performance of the Ag^+/SiO_2 -PDMS composite membrane was investigated using thiophene/n-octane mixtures as the model gasoline. The pervaporation experiments were carried out on a membrane module which was identical to

that described earlier [31]. The effective area of the membrane was 25.6 cm 2 . The thiophene/n-octane mixture was fed into the upstream side under ambient pressure and the vacuum on the downstream side was maintained at 0.33 kPa by a vacuum pump. The permeate was collected in a liquid nitrogen cold trap and weighed. The permeation flux (J , kg/(m 2 h)) was defined as:

$$J = \frac{Q}{A \times t}$$

where Q (kg) was the total amount of the permeate collected during the experimental period (t , h), and A (m 2) was the effective membrane area. The flux was further normalized to the membrane thickness which was estimated based on the cast thickness and the swelling degree. The normalized flux was denoted as J_N (kg $\mu\text{m}/\text{m}^2$ h), $J_N = J \times l$, where l (μm) was the membrane thickness in swollen state.

The feed and permeate compositions were analyzed by gas chromatography (GC, Agilent 6890, Agilent Technologies Co., Ltd.) equipped with a 50 m long PONA capillary column (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China) and a flame ionization detector (FID, Agilent Co.). The temperatures for injector, detector and oven were set at 200 °C, 250 °C and 80 °C, respectively. The separation selectivity of the Ag^+/SiO_2 -PDMS composite membrane was expressed by the enrichment factor of thiophene (β), defined as:

$$\beta = \frac{\omega^P}{\omega^F}$$

where ω^F and ω^P referred to the weight fractions of thiophene in the feed and permeate, respectively.

2.9. Sorption behavior and swelling property

The Ag^+/SiO_2 -PDMS-X homogenous membranes without PES support were weighed carefully before being immersed in the feed mixture at 33 °C. The swollen membrane samples were taken out from the feed mixture after a certain period of immersion time and wiped with tissue paper to remove the surface liquid before being weighed. The degree of swelling (DS, %) was calculated as:

$$\text{DS}(\%) = \frac{W_S - W_D}{W_D} \times 100$$

where W_D and W_S were the weights of the dried and swollen membranes, respectively. The absorbed liquid in the swollen membrane was removed by a vacuum pump and condensed in a liquid nitrogen cold trap. The composition of the liquid absorbed by the membrane was analyzed by HP6890 gas chromatography. The sorption selectivity (α_S) was calculated by:

$$\alpha_S = \frac{\omega^M}{\omega^F}$$

where ω^M and ω^F were the weight fraction of thiophene in the absorbed liquid and feed, respectively. According to the solution-diffusion model, the diffusion selectivity (α_D) could be determined from enrichment factor of the membrane (β) and the sorption selectivity (α_S), $\alpha_D = \beta/\alpha_S$, based on the assumption of equilibrium sorption on the membrane surface at the feed side [18].

3. Results and discussion

3.1. Analysis of silver species deposited on the silica surface

The silver/silica core-shell microspheres were characterized by XRD, ICP and XPS to investigate the chemical composition and the crystallinity of the silver shell. Fig. 1 showed the XRD pattern of the silver/silica microsphere. Both silver oxide (Ag_2O) and silver

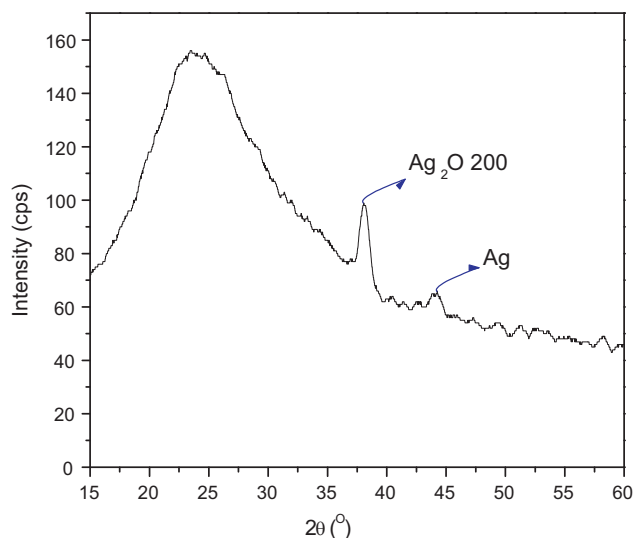


Fig. 1. XRD pattern of the as-synthesized silver/silica microspheres.

(Ag⁰) were present in the diffractogram at $2\theta = 38.13^\circ$ and 44.38° , respectively [32,33], revealing that there were two states of silver element (Ag⁺ and Ag⁰) coexisting in the silver shell. Furthermore, the relatively large width of the band indicated that Ag₂O particles in the shell were relatively small in size [34]. The crystallite size of the Ag₂O nanoparticles on the silica surface was determined by the Scherrer equation to be approximately 16 nm, and its crystalline interplanar spacing was 2.3578 Å.

To study the weight ratio between Ag⁺ and Ag⁰ existing in the silver shell, ICP and XPS measurements were performed on the silver/silica microspheres. The ICP result of the silver/silica microspheres demonstrated that the weight ratio between the total content of silver element and SiO₂ was about 0.168. Figs. 2 and 3 showed the XPS survey and the high-resolution XPS spectra for silver element on the microsphere surface. The XPS spectra again confirmed the coexistence of two chemical states of silver, Ag⁺ and Ag⁰ on the core-shell microsphere surface. The bonding energies of the Ag(3d_{5/2}) for the silver element at different chemical states (Ag⁺ and Ag⁰) were 367.8 eV and 368.2 eV, respectively, which were in accordance with the data reported in the literature [35,36]. Based on the deconvolution analysis of the high-resolution spectra for silver element (Ag(3d_{5/2})), it was found that the weight ratio between

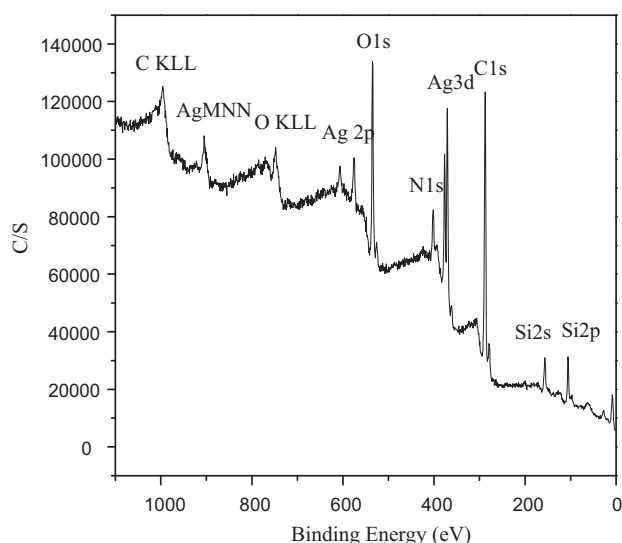


Fig. 2. Survey XPS spectrum of the silver/silica microspheres.

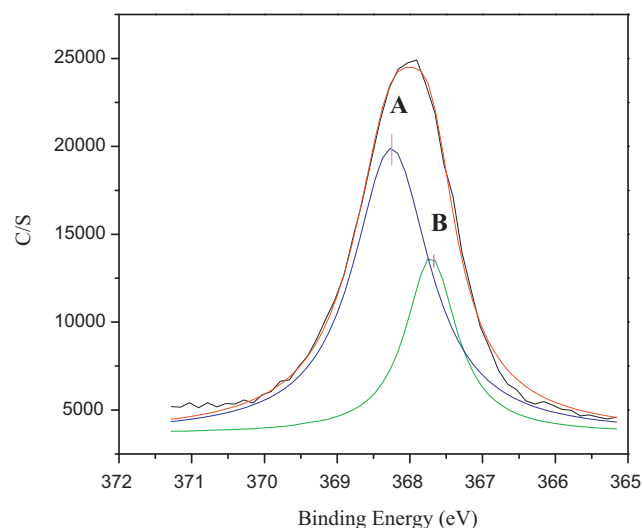


Fig. 3. High-resolution XPS spectra of Ag (3d_{5/2}) for the silver/silica microspheres wherein the peak A and B were assigned to Ag⁰ and Ag⁺, respectively.

Ag⁺ and Ag⁰ content on the silver/silica microsphere surface was 1:1.667, that is, 62.5% of the silver concentration on the surface was in its oxide state. The weight ratio of SiO₂ to Ag₂O could be estimated to be 1:0.1353 by combining the results of ICP and XPS analysis, suggesting that a quite amount of Ag₂O nanoparticles were formed on the silica surface.

3.2. Morphology of the silver/silica microsphere

Transmission electron microscopy images of the bare silica and the silver/silica microspheres were shown in Fig. 4. From Fig. 4(a) and (b) with a magnification of 4000×, it could be clearly observed that both the bare silica microspheres and the silver/silica core-shell microspheres were monodispersed and had a spherical morphology with a diameter of ~660 and ~690 nm, respectively. A rougher surface for silver/silica microsphere was found. The enlarged images of the silver/silica microsphere (10,000×, Fig. 4(c)) and its further enlarged surface images (20,000×, Fig. 4(d); 200,000×, Fig. 4(e)) obviously displayed a homogeneous distribution of the silver nanoparticles on the silica surface. The Ag₂O nanoparticles in the silver shell could be identified from Fig. 4(e) with an observed diameter of ~14 nm, a size similar to the result of XRD analysis (size of Ag₂O, ~16 nm). The interplanar spacing of the Ag₂O crystallite was also measured directly by the enlarged TEM image, an interplanar spacing of 2.46 Å (7.38 Å/3) being obtained which was in good agreement with that measured by XRD. The number of Ag₂O nanoparticles on one silica support sphere could then be deduced from the above XPS and TEM characterization, approximately 6500 Ag₂O nanoparticles per silica microsphere.

Besides the average sphere size observed by TEM, the size distributions of the bare silica and the silver/silica core-shell microspheres were further analyzed by a zetaPALS/BI-9000 particle size distribution analyzer. As shown in Fig. 5, the size distributions of the silica and the core-shell microspheres were fairly uniform with a narrow dispersity, indicating that silver-doping process did not significantly affect the structure of the monodispersed microspheres. The average microsphere sizes and the polydispersity parameters measured by the particle size distribution analyzer were 651 nm, 0.005 for bare silica and 677 nm, 0.096 for silver/silica, respectively. The moderate increase in the average size of silver/silica microspheres compared with the bare silica confirmed the fabrication of the core-shell structure. The thickness of the silver shell of 15–16 nm deduced from the size variation

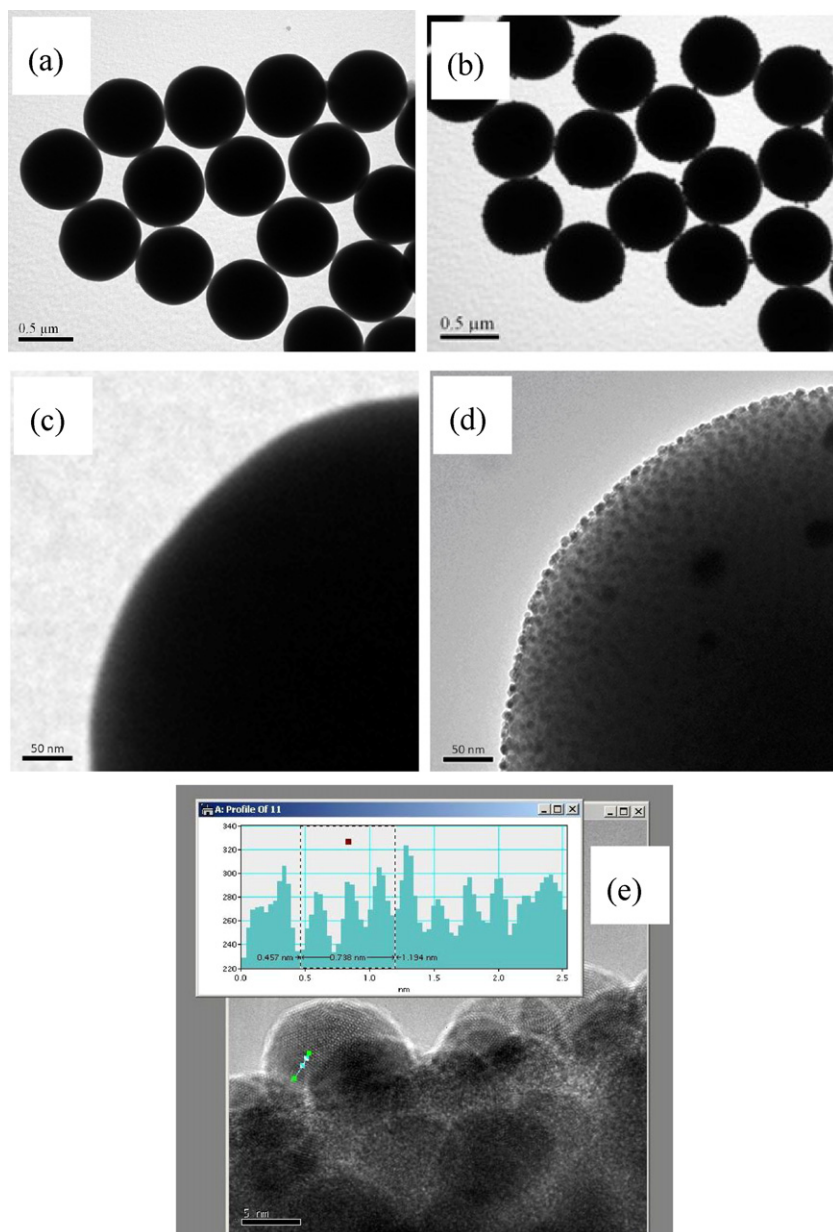


Fig. 4. TEM images of the bare silica microspheres (a and c), the silver/silica core-shell microspheres (b and d), and the enlarged surface structure of the silver shell (e).

before and after silver loading revealed a monolayer of the silver nanoparticles.

It has been proved that transition metal-containing adsorbents were sulfur-selective by retaining thiophenic compounds by π -complexation bonds. This π -complexation showed promise in desulfurization since, on one hand, π -complexation bonds are stronger than van der Waals force and electrostatic force involved in physisorption, and on the other hand, they are weak enough to be broken simply by raising temperature or decreasing pressure. Therefore, it was reasonable to suppose that the Ag_2O nanoparticles exposed on the core-shell microspheres were available and efficacious for selective separation of thiophene in the modeling gasoline, which was investigated by pervaporative desulfurization tests presented below.

3.3. Morphology of the composite membranes

The structure of Ag^+/SiO_2 core-shell filled PDMS composite membranes was investigated by FESEM and FT-IR. Fig. 6(a) showed

the cross-section morphology of the Ag^+/SiO_2 -PDMS membranes. A dense PDMS top layer with a uniform thickness of about 14 μm was firmly adhered on the PES support without any splits. From the enlarged image of the top layer shown in Fig. 6(b), it could be seen that silver/silica microspheres were well monodispersed in the PDMS top layer without aggregates.

The FTIR spectra of homogeneous PDMS membrane and Ag^+/SiO_2 -PDMS membranes were recorded and compared in Fig. 7. Except for the characteristic bands of PDMS and those of silica appeared after doping of the core-shell microspheres, no new absorption bands were found in the composite membrane, indicating that the inorganic microspheres were only physically blended with the PDMS polymer matrix without strong chemical interactions.

3.4. Swelling and sorption behavior of the composite membranes

The swelling property and sorption capability of the Ag^+/SiO_2 -PDMS composite membranes for thiophene in the

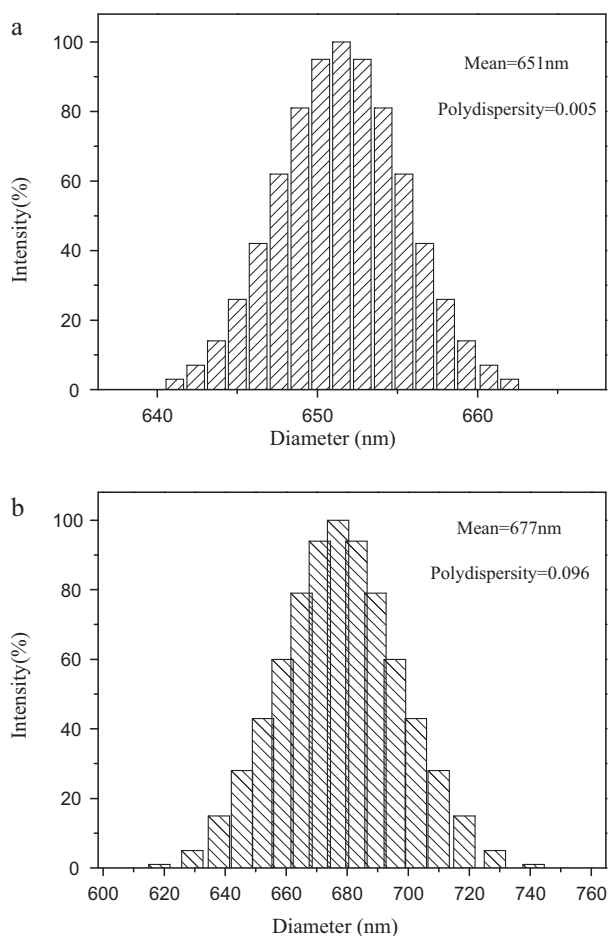


Fig. 5. Size distribution analysis of bare silica microspheres (a) and silver/silica microspheres (b).

modeling gasoline (thiophene/n-octane mixture) were investigated by static adsorption experiments. As shown in Fig. 8, the addition of silver/silica microspheres significantly decreased the swelling degree of PDMS membrane. With the microsphere content in the membrane increasing to 10%, the swelling degree was reduced by ~18% compared to pristine PDMS membrane. As described in experiment section, the sorption selectivities (α_S) of the Ag^+/SiO_2 -PDMS membrane were calculated and shown in Fig. 9 versus the microsphere content. It was found that the pristine PDMS control membrane showed an unfavorable sorption selectivity towards thiophene. The addition of silver/silica microspheres changed the adsorption behavior of the membrane reversely to a positive sorption selectivity larger than 1 due to the preferential adsorption of the microspheres towards thiophene via π -complexation between Ag^+ and thiophene. Moreover, with the increase of the silver/silica content, the adsorption selectivity increased. The diffusion selectivity and the overall desulfurization performance in terms of flux and enrichment factor were discussed as follows.

3.5. Desulfurization performance of the Ag^+/SiO_2 -PDMS composite membranes and free volume characteristics analysis

The addition of silver/silica microspheres improved the sorption selectivity of PDMS membrane efficiently as proved by sorption tests. In order to evaluate the desulfurization property of Ag^+/SiO_2 -PDMS membranes, pervaporative desulfurization experiments were carried out systematically. Fig. 10 showed the

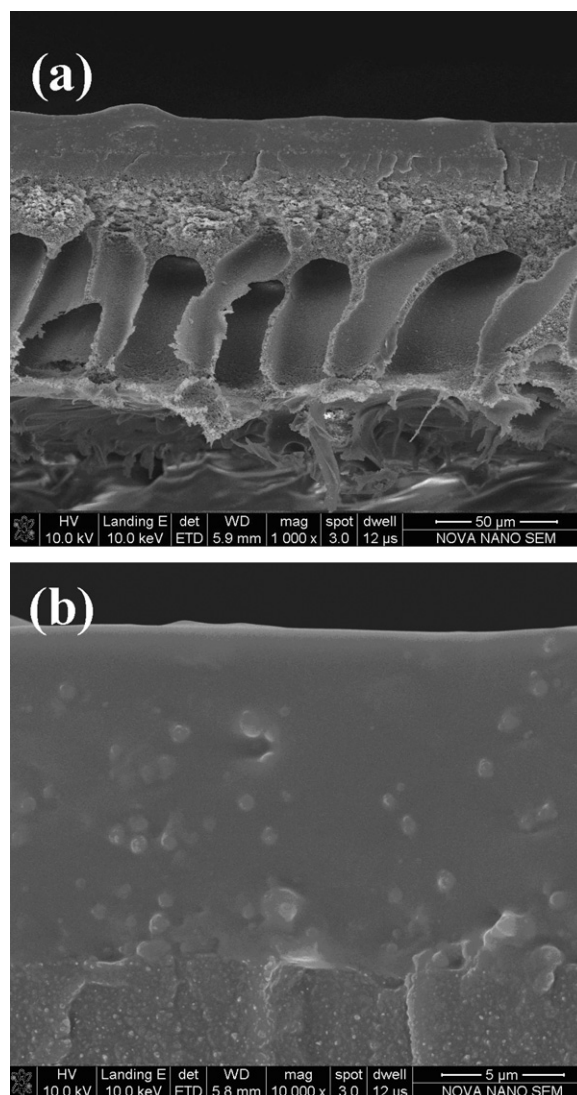


Fig. 6. FESEM images of Ag^+/SiO_2 -PDMS composite membrane.

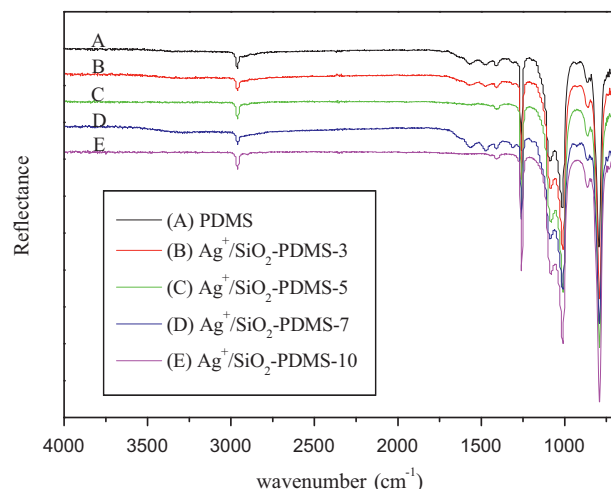


Fig. 7. FT-IR spectra of homogeneous PDMS and Ag^+/SiO_2 -PDMS membranes.

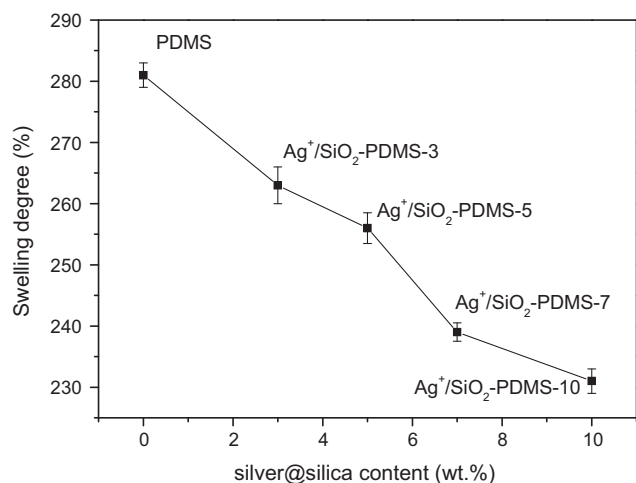


Fig. 8. Effect of silver/silica content on the swollen degree of the Ag^+/SiO_2 -PDMS composite membranes.

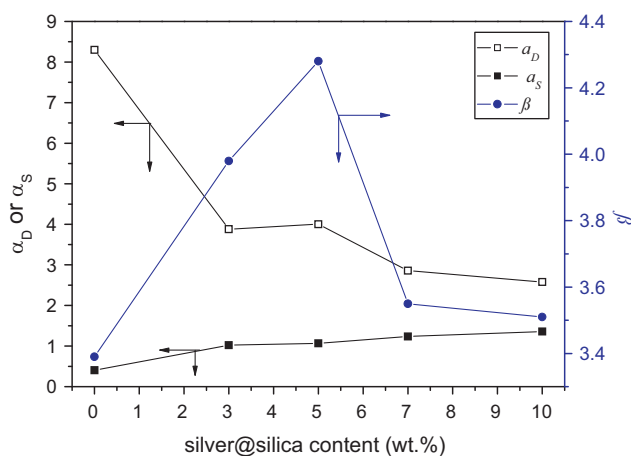


Fig. 9. Effect of silver/silica content on the sorption selectivity, diffusion selectivity and enrichment factor.

variation in enrichment factor and permeation flux (J and J_N) as a function of the microsphere content in the membranes for a feed of 1300 ppm thiophene in n-octane at 306 K with a flow rate of 40 L/h. Both the permeation flux (J) and the thickness-normalized flux (J_N) increased with increase of the microsphere content and the variation trends were similar with each other. A considerable increase in enrichment factor was found at lower microsphere contents while a decrease occurred at higher microsphere contents. The highest enrichment factor ($\beta=4.3$) was achieved when the microsphere content reached 5%. The diffusion selectivity for the composite membrane was calculated from the sorption selectivity and the enrichment factor and plotted in Fig. 9. The diffusion selectivity for all the membranes was higher than the corresponding sorption selectivity, revealing that the diffusion process exerted more influence on the mass transport of thiophene and n-octane across these PDMS-based membranes. Contrary to the variation trend of

Table 1

The o-Ps lifetime data and free volume parameters for Ag^+/SiO_2 -PDMS membranes.

Silver@silica content (%)	τ_3 (ns)	r_3 (nm)	I_3 (%)	τ_4 (ns)	r_4 (nm)	I_4 (%)	f_{v4}	f_v
0	1.18	0.1931	4.4	3.17	0.3741	18.7	0.0410	0.0423
3	1.38	0.2195	6.0	3.36	0.3862	24.8	0.0598	0.0625
5	1.52	0.2349	4	3.5	0.3947	24.4	0.0628	0.0065
7	1.47	0.2303	5.5	3.61	0.4013	23.4	0.0633	0.0661
10	1.41	0.2231	6.9	3.82	0.4034	23.6	0.0649	0.0681

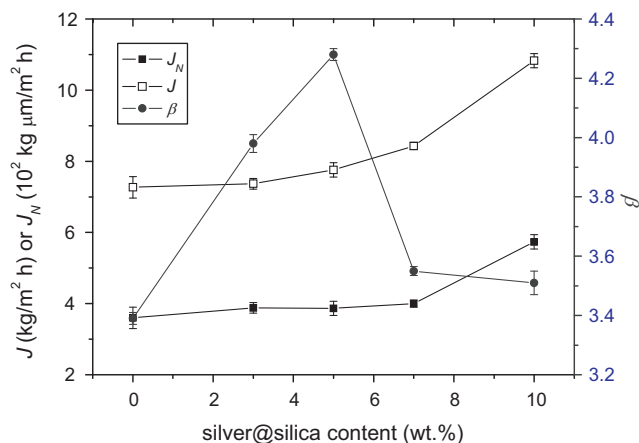


Fig. 10. Effect of silver/silica content on the pervaporation performance of the Ag^+/SiO_2 -PDMS composite membranes.

the sorption selectivity, the diffusion selectivity decreased with the increase of silver/silica content.

PALS analysis was applied to reveal the relationship between membrane structure and the desulfurization performance in terms of free volume which governed the transport behavior of membrane. The lifetimes and free volume parameters of the Ag^+/SiO_2 -PDMS active layers were listed in Table 1. It has been found that there are two types of free volume pores in polymer-based dense membranes, i.e., network pores reflected by lifetime τ_3 and aggregate pores reflected by lifetime τ_4 [37]. The network pores refer to the interstitial small cavities in the cross-linked site while the aggregate pores refer to the free volume between the clusters of networks and the interface of organic-inorganic phases in hybrid materials. r_3 and r_4 are the radii of the two free volume cavity calculated from their individual lifetime. The fractional free volume (f_v) increased monotonically with the silver/silica content, especially for the fractional free volume of aggregate pores (f_{v4}) which was resulted from the incompatibility between PDMS polymer segments and the inorganic microspheres. When the filler was incompatible with the polymer, void tended to occur at the organic-inorganic interface, leading to an increase in free volume of the system and, consequently, resulting in an increase in permeation flux but a decrease in enrichment factor. In summary, the addition of the silver/silica microspheres into the PDMS polymer system improved the enrichment factor towards thiophene. However, voids tended to occur at the organic-inorganic interface with the increasing content of microspheres, which led to an increase in permeation flux but a decrease in enrichment factor. Therefore, there existed an optimal content of the added silver/silica microspheres, and this optimum appeared at the addition amount of 5% where a permeation flux of 7.76 $\text{kg}/(\text{m}^2 \text{ h})$ and an enrichment factor of 4.3 were achieved for the Ag^+/SiO_2 -PDMS-5 membrane.

Table 2 summarized some pervaporative desulfurization results of a number of typical PDMS-based composite membranes. For the desulfurization of the thiophene/n-octane model gasoline, the enrichment factors of PDMS-based composite membranes reported

Table 2

Pervaporation performance of PDMS-based composite membranes for desulfurization of thiophene/n-octane model gasoline.

Membrane	Thiophene content in feed (ppm)	Permeation flux (kg/(m ² h))	Enrichment factor	Reference
PDMS/PAN	3640	1.5	4.9	[22]
PDMS-Ag ₂ O/PAN	2630	2.85	4.46	[23]
PDMS-Ni ²⁺ Y/PS	1310	3.26	4.48	[24]
PDMS/ceramic	1050	5.37	4.22	[25]
Ag ⁺ /SiO ₂ -PDMS/PES	1300	7.76	4.3	This work

in the literature were 4.2–4.9, while the fluxes varied from 1.5 to 5.37 kg m⁻² h⁻¹. There usually exists a “trade-off” effect between the flux and the enrichment factor, that is, a high flux which is required in practical industrial production is often obtained by sacrificing the enrichment factor. The flux of the Ag⁺/SiO₂-PDMS membranes prepared in this work reaches a high level of up to 7.76 kg m⁻² h⁻¹ at the cost of only a little decrease of enrichment factor (4.3).

4. Conclusions

Highly monodispersed silver/silica core-shell microspheres were prepared through a one-step method using TEOS as silica precursor and TSD as a bifunctional mediator. On one hand, TSD confined the Ag seeds efficiently by the chelating effect between Ag⁺ in AgNO₃ solution and the NH₂-CH₂-CH₂-NH-(CH₂)₃- group of TSD via amino groups. On the other hand, TSD incorporated the resultant Ag seeds onto the TEOS-derived silica core surface via the hydrolysis and condensation of its three methoxyl groups. XRD, XPS and TEM characterizations found that the Ag₂O nanoparticles with a size of 15–16 nm dispersed uniformly and compactly on the surface of the silica core. The as-synthesized Ag⁺/SiO₂ microspheres were utilized in the membrane desulfurization by blending with PDMS. The organic solvent-resistant property, the sorption selectivity and the overall desulfurization performance of the Ag⁺/SiO₂-PDMS composite membranes were all improved remarkably. The optimal performance for thiophene/n-octane model gasoline was achieved by the Ag⁺/SiO₂-PDMS-5 membrane containing 5% of silver/silica core-shell microspheres with a flux of 7.76 kg m⁻² h⁻¹ and an enrichment factor of 4.3.

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