Journal of Hazardous Materials 187 (2011) 324–332

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

Ruijian Cao[a], Xiongfei Zhang[a], Hong Wu[a,b,*], Jingtao Wang[a], Xiaofei Liu[a], Zhongyi Jiang[a,c]

[a] *Key Laboratory for Green Chemical Technology, Ministry of Education of China, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China*
[b] *Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, PR China*
[c] *State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China*

ARTICLE INFO

*Article history:*
Received 26 October 2010
Received in revised form 5 January 2011
Accepted 6 January 2011
Available online 14 January 2011

*Keywords:*
Gasoline desulfurization
Pervaporation
Composite membrane
Silver/silica
Polydimethylsiloxane

## 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-(trimethoxysily)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-positron annihilation lifetime spectroscopy (ZetaPALS), inductively coupled plasmaoptical emission spectrophotometer (ICP), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The $Ag^+/SiO_2$–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/($m^2$ h) and an enrichment factor of 4.3 at the doping content of 5%.

## 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-NOx 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],

---

[*] Corresponding author at: Key Laboratory for Green Chemical Technology, Ministry of Education of China, School of Chemical Engineering and Technology, Tianjin University, Weijin Road 92#, Tianjin, Nankai District 300072, PR China. Tel.: +86 22 23500086; fax: +86 22 23500086.
*E-mail address:* wuhong2000@gmail.com (H. Wu).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.01.031

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$^{TM}$ 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 $(15.5\,(\mathrm{kJ/cm^3})^{1/2})$ 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 1.5–5.37 $\mathrm{kg\,m^{-2}\,h^{-1}}$ 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 $\mathrm{kg\,m^{-2}\,h^{-1}}$ to 8.1 $\mathrm{kg\,m^{-2}\,h^{-1}}$ while remaining the enrichment factor at $\sim$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-(trimethoxysily)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 ($Ag^+[NH_2–CH_2–CH_2–NH–(CH_2)_3–Si(OCH_3)_3]$) 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-(trimethoxysily)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 $Ag^+/SiO_2$–PDMS-X, where X in the range of