Facilitated transport of thiophenes through Ag_2O-filled PDMS membranes

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Abstract

Facilitated transport membranes of polydimethylsiloxane (PDMS) with silver oxide (Ag_2O) as the carrier were prepared and used for the separation of thiophenes/n-octane mixtures. The effect of the degree of Ag_2O loading, feed temperature on the pervaporation properties of Ag_2O-filled membranes was investigated experimentally. Ag_2O-filling leads to an increase in selectivity to thiophenes but a decrease in total flux simultaneously. Feed temperature shows different impact on selectivity of thiophenes for Ag_2O-filled and unfilled membranes because of the distinct transport mechanism within them. Selectivity-permeability trade-off was analyzed for Ag_2O-filled and unfilled membranes.

Keywords: Facilitated transport; Silver; Desulfurization of gasoline; Pervaporation

1. Introduction

Organosulfur impurities present in gasoline produce SOx in automotive exhaust and consequently lead to severe environmental problems. Worldwide concerns over environment have inspired an increasing interest both in academia and industry for deep desulfurization of gasoline [1, 2].

As a membrane based separation technique, pervaporation possesses great predominance and potential for desulfurization of gasoline, in which the separation mechanism is based on the difference of sorption and diffusion properties of the feed compounds. In our previous work [3, 4, 5], PDMS was selected for pervaporative desulfurization of model gasoline. PDMS/PAN composite membranes were prepared and characterized for the purpose. With n-octane/thiophene as the primary components making up model gasoline, the fundamental problems in relation to the mechanism and contributing factors in the desulfurization process of gasoline by pervaporation were investigated. Experimental results showed that PDMS membrane is selective for thiophenes and considerable fluxes were gained. However, the separation of thiophene/hydrocarbon mixtures has not been much effective because the physico-chemical properties of thiophenes and various hydrocarbons are not efficiently distinguishable.

According to the analysis of Robeson [6], greater permeability and higher selectivity couldn't be achieved simultaneously within solution-diffusion mechanism when using conventional polymeric membranes. But in heterogeneous membranes consisted of a polymeric phase and certain carrier particles, the reversible reactions between carrier and penetrant provide another transport mechanism through the membrane in addition to the solution-diffusion. Thanks to the complexation reaction between silver ion (Ag^+) and the double bonds of the solute, Ag^+ is mostly used as the carrier for the facilitated transport of unsaturated hydrocarbons [7, 8, 9]. Investigation

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on desulfurization of transport fuels by adsorption also confirmed the existence of strong π-complexation bond between Ag^+ and thiophene or substituted thiophenes [10, 11]. Therefore, Ag^+-containing salts or oxides could be reasonably employed to promote the transport of thiophenes within the membrane.

In current work, Ag_2O was taken as the filler for preparation of the fixed-site carrier PDMS membranes, in which the facilitated transport of thiophenes was expected. With the mixture of n-octane/thiophene/2-methyl-thiophene as the model gasoline, the pervaporative desulfurization performance of Ag_2O-filled membranes was investigated. Contributing factors including Ag_2O contents in the membranes, feed temperature were evaluated experimentally.

2. Experimental

Ethyl orthosilicate, dibutyltin dilaurate, n-heptane (Beijing Chemical Company, China) were purchased for the preparation of PDMS membrane. Silver oxide (Ag_2O, Beijing Beihua Fine Chemical Co. Ltd., China) was ground with a muller before used as the membrane filler. Asymmetric microporous PAN membrane (provided by Beijing Megavision Membrane & Engineering Co. Ltd., China) was employed as supports. n-Octane (China Medicine (Group) Shanghai Chemical Reagent Corporation), thiophene (Tianjin Chemical Company, China) and 2-methyl-thiophene (98% pure, Acros) were chosen as the representative components making up the model gasoline.

PDMS, crosslinking-agent ethyl orthosilicate and catalyst dibutyltin dilaurate were dissolved in n-heptane at ambient temperature. Silver oxide was added into the solution under stirring. The resulting suspension was then sonicated for 30 minutes to promote the dispersion of silver oxide powder. After degassed under vacuum, the solution is cast onto the PAN membrane. The membrane was first vulcanized under room temperature to evaporate the solvent, and then introduced into a vacuum oven to complete crosslinking. Membranes with the following degree of Ag_2O-filling were prepared and used in current work: 100 wt% PDMS-0 wt% Ag_2O, 98 wt% PDMS-2 wt% Ag_2O, 95 wt% PDMS-5 wt% Ag_2O, 92 wt% PDMS-8 wt% Ag_2O, 90 wt% PDMS-10 wt% Ag_2O.

Pervaporation experiments were carried out in a continually fed cell. Details of the apparatus and the measurement procedure are available elsewhere [3, 4]. Compositions of feed and permeate were analyzed by gas chromatography (HP6890, USA). Enrichment factor k_i defined as follows is adopted to characterize the separation performance of the membrane:

$$k_i = \frac{\omega_i^P}{\omega_i^F} \qquad (1)$$

where k_i is the enrichment factor for component i; ω_i^F and ω_i^P refer to the weight fraction of component i in the feed and permeate respectively.

3. Results and discussion

3.1 SEM analysis of Ag_2O-filled membrane

SEM characterization of the Ag_2O-filled membrane was carried out to investigate the dispersion of Ag_2O particles in the polymeric phase of the membrane. From the SEM photographs in Fig.1, it can be seen that the porous PAN substrate is covered by a flat faultless layer. In the dense top layer, Ag_2O particles are uniformly dispersed and well adhesive with PDMS matrix. No

nonselective voids could be found on the carrier-solute interface.

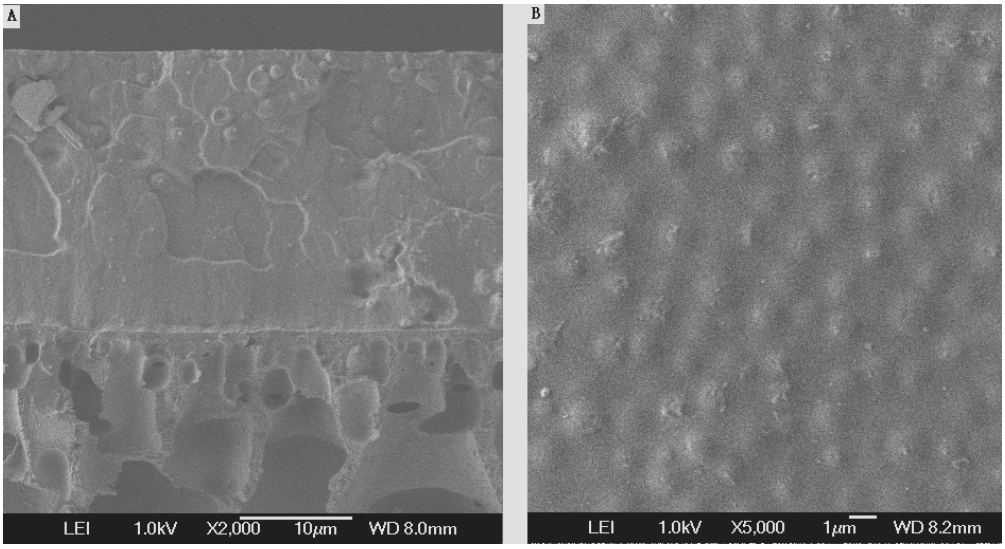


Fig.1. Cross-section and top surface morphologies of the Ag_2O-filled membrane.
95 wt% PDMS-5 wt% Ag_2O; (A) Cross-section and (B) top surface

3.2 Effect of Ag_2O contents on pervaporation properties

With n-Octane as the main component of gasoline, along with thiophene and 2-methyl-thiophnene as the representative organosulfurs present in gasoline, the sulfur removal performance of the membranes were investigated experimentally. The corresponding sulfur content in the feed is about 1000μg/g, with the mole ratio of thiphene and 2-methyl-thiophene 1:1.

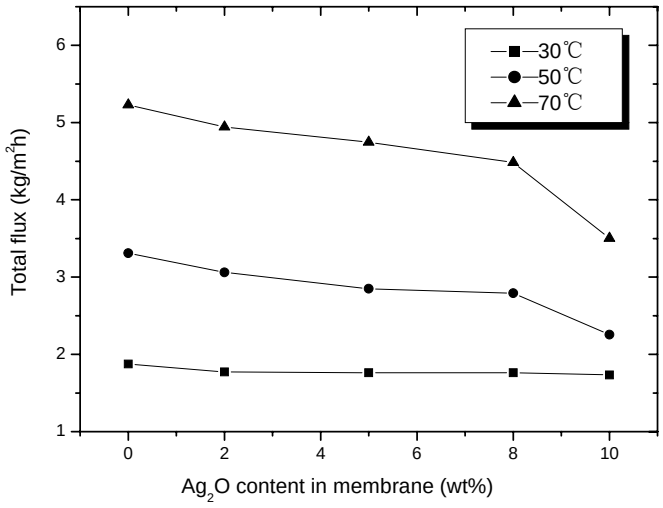
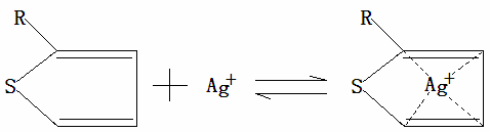


Fig.2. Effect of Ag_2O content on total flux

Fig. 2 demonstrates the effect of Ag_2O content on total flux of the model gasoline under different feed temperatures. It can be seen that, with the increase of Ag_2O loading in PDMS membranes, total fluxes decrease and higher feed temperature makes this trend more evident. Owing to the ultra low concentrations of thiophene and 2-methyl-thiophene in the model gasoline, the majority of feed and permeate is n-octane. Within the fixed-site carrier PDMS membranes, the

primary transport mechanisms for permeating molecules include the diffusion through the polymeric phase, diffusion through pores of the carrier, sorption onto the carrier, surface diffusion in the carrier and desorption from the carrier. For n-octane, the filled Ag_2O particles are inert and completely impermeable. The diffusivity of n-octane would decrease due to the tortuosity effect and the total flux decrease accordingly. Higher feed temperature would make the components more permeable through the membrane, which leads to a more prominent effect of the Ag_2O filling on the permeating flux.

On the other hand, a complexation reaction as Eq. (2) exists between Ag^+ ion and C=C double bonds in thiophenes:



（2）

According to RC circuit model [12, 13], the continuous reversible reaction between the carrier and solute would result in fluctuation of local concentration in the membrane, which leads to a higher free energy, a higher chemical potential and a higher flux for the desired component. Consequently, the above complexation would accelerate sorption onto and desorption from the carrier particles and facilitate transport of thiophenes. Selectivity to thiophenes would increase because of the facilitation effect in Ag_2O filled membranes. This is verified by the experimental findings shown in Figs. 3 and 4.

With the membranes having a normalized top layer of 15μm, when Ag_2O loading increases from 0 to 5 wt%, the total fluxes decrease from 3.31 to 2.85 kg/m^{2}h at 50℃, while the corresponding enrichment factors increase from 3.55 to 4.46 and from 2.24 to 2.61 for thiophene and 2-methyl-thiophene respectively.

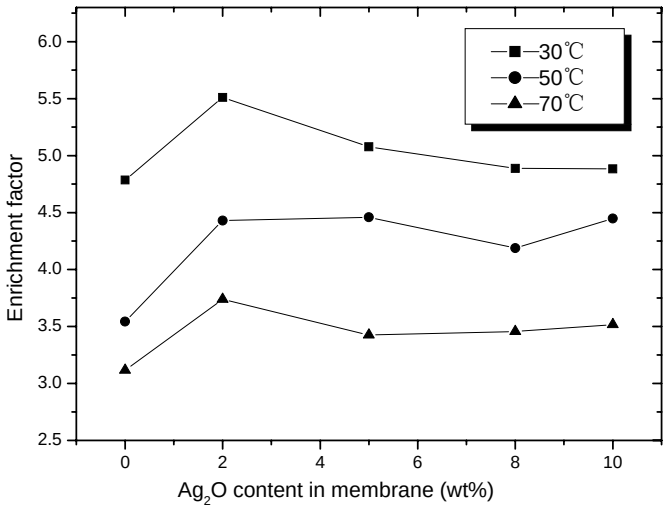


Fig.3. Profiles of thiophene enrichment factor with Ag_2O loading

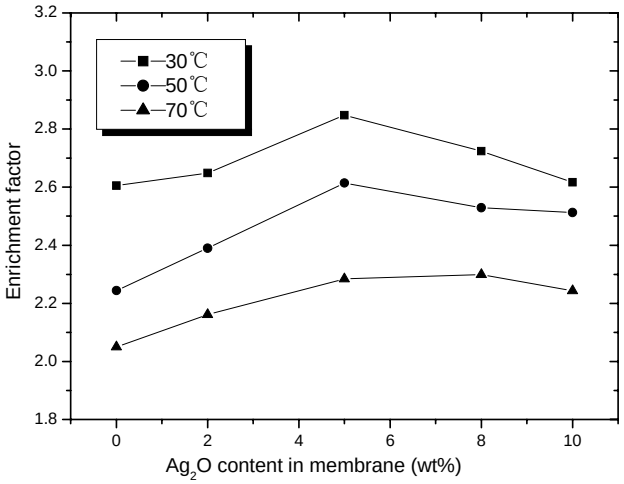


Fig.4. Profiles of 2-metyl-thiophene enrichment factor with Ag_2O loading

3.3 Effect of feed temperature on pervaporation properties

Effect of feed temperature on the pervaporative desulfurization efficiency using Ag_2O-filled PDMS membranes was also evaluated experimentally. Fig. 5 illustrates the total flux variation versus feed temperature. Without exception, all the experimental evidence confirms an increase in permeability with increasing feed temperature for both Ag_2O-filled and unfilled membranes. Two parallel impacts of temperature on the permeant and membrane should be responsible for this: one is the increase of the mobility of individual permeating molecules which promotes their movement both in the bulk feed solution and within the membrane, one is the enhanced mobility of the polymer segments which offers more free volume for permeating molecules to occupy. As a minor contributing factor, changes occurring on the carrier-polymer interface play a certain role in the results obtained.

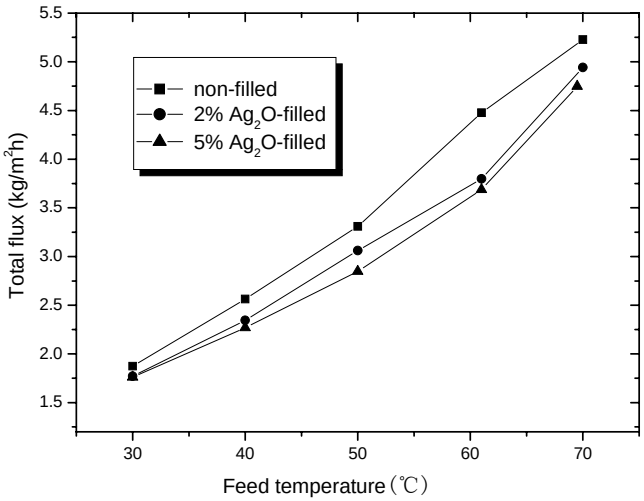


Fig.5. Temperature dependence of total flux in Ag_2O-filled and unfilled membranes

As shown in Figs. 6 and 7, the increase in the degree of swelling of the membrane with temperature results in a decrease in selectivity to thiophenes. Additionally, experimental results indicats that extent to which feed temperature affects the enrichment factors of thiophenes is different in filled and unfilled membranes. It is so mainly because the transport of thiophenes in Ag_2O-filled and unfilled membranes are dominated by different mechanism. Theoretically, the total flux of the permeant through the carrier-filled membrane is the sum of two different parts: one is the solution-diffusion flux of uncomplexed species, one is the facilitated flux of solute due to the carrier-solute complexation. In Ag_2O-filled PDMS membrane, the facilitated fluxes of thiophenes lie on the reversible reaction between Ag^+ and thiophenes, while the solution-diffusion fluxes of thiophenes in pure PDMS membrane are determined by the solution and diffusion properties theirof.

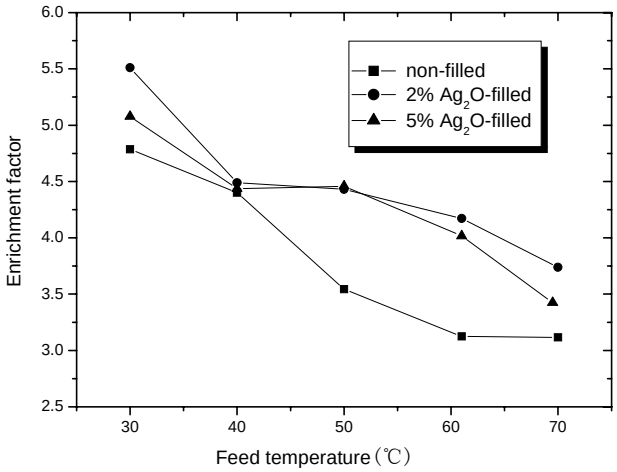


Fig.6. Effect of temperature on selectivity to thiophene

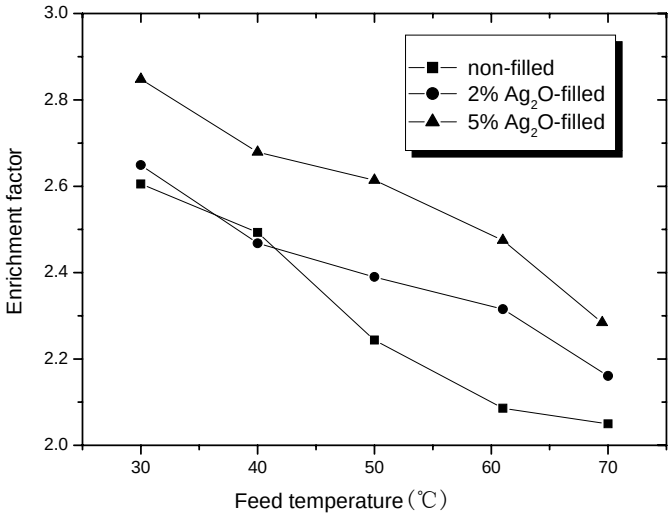


Fig.7. Effect of temperature on selectivity to 2-methyl-thiophene

3.4 The upper bound curve for thiophenes/n-octane separation

Using the data for a large number of membranes, Robeson qualitatively constructed an upper bound curve for gas separation process, in which the selectivity of the more permeable gas was plotted as a function of its permeability on a log-log scale [6]. Nearly all the data cluster below the upper bound implies that there is a trade-off for the polymeric membranes between the permeability and selectivity. However, it has been demonstrated that facilitated transport membranes would not comply with such a rule.

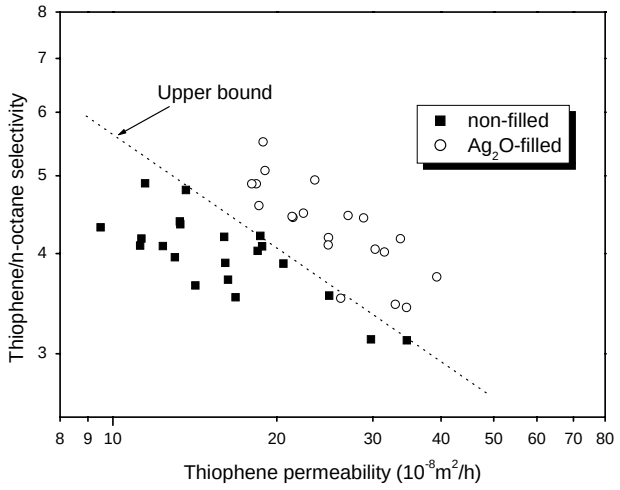


Fig. 8. Selectivity-permeability trade-off curve of PDMS membranes for separation of thiophene/n-octane mixtures

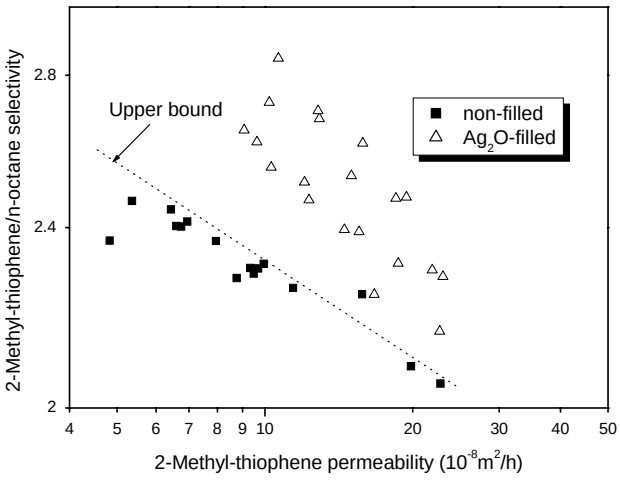


Fig.9. Selectivity-permeability trade-off curve of PDMS membranes for separation of 2-methyl-thiophene/n-octane mixtures

Based on the experimental data gained in our earlier work, the upper bound curves for separation of n-octane/thiophene and n-octane/2-methyl-thiophene mixtures using unfilled PDMS membranes are constructed. Just as shown in Figs. 8 and 9, Ag_2O-filled PDMS membranes can surpass the limit of the upper bound owing to the facilitated transport mechanism within the process. The above experimental results suggest that facilitated transport brings improvement in selectivity to thiophenes, but the total flux decrease slightly because of the tortuosity effect. In order to get more effective performance of facilitated transport for the solute, more active sites should be provided for the reversible complexation reaction between C=C bond and Ag^+ ion. But increasing the carrier loading would make the tortuosity effect sharpen. Accordingly, more fine Ag_2O powder with more specific area should be used. And more, relatively regular shape and unity of Ag_2O powder would reduce the sharpness of the powder surface and avoid the formation of "dead end", which to some degree reduce the tortuosity effect and eliminate the formation of voids on the carrier-solute interface.

4. Conclusions

Ag_2O powder was taken as the active filler to prepare PDMS/PAN composite membranes for the purpose of gasoline desulfurization. SEM characterization indicates that Ag_2O particles can uniformly disperse into the polymeric phase and are well adhesive with the PDMS matrix.

With n-octane and thiophenes making up model gasoline, the effect of the degree of Ag_2O loading, feed temperature on the pervaporation properties of Ag_2O-filled membranes was investigated experimentally. Ag_2O-filling leads to an increase in selectivity to thiophenes because of the facilitated transport of thiophenes induced by the complexation between Ag^+ and double bonds in thiophenes, as well as a decrease in total flux owing to the tortuosity effect of the impermeable Ag_2O particles. With the rise of feed temperature, the total flux increases but the selectivity to thiophenes decreases simultaneously. Because the transport of thiophenes in Ag_2O-filled and unfilled membranes were dominated by different mechanism, the extent to which feed temperature affects the selectivity to thiophenes is different. For the membranes with a normalized top layer of 15μm, when Ag_2O loading increases from 0 to 5 wt%, the total fluxes decrease from 3.31 to 2.85 kg/m^{2}h at 50℃, while the corresponding enrichment factors increase from 3.55 to 4.46 and from 2.24 to 2.61 for thiophene and 2-methyl-thiophene respectively.

Selectivity-permeability trade-off curves of PDMS membranes using both the earlier and current data were constructed for separation of thiophene/n-octane and 2-methyl- thiophene/ n-octane mixtures. Nearly all the data for Ag_2O-filled membranes locate above the upper bounds for pure PDMS membranes, which implies that Ag_2O-filling results in improvements in both selectivity and permeability for thiophenes.

Acknowledgement

The authors would like to express their gratitude to Ministry of Science and Technology of China for the financial support (National 973 Project, No. 2003CB615701).

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