Synthesize of PDMS/Silver-Nanoparticle Composite and Applications in Gas Separation

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Abstract

We introduce and characterize a nano-composite membrane containing poly-dimethyl-siloxane and silver nano-particles which is used for gas separation **.**The separation of olefin/paraffin hydrocarbons occurs because of “facilitated transport” phenomena. Fabrication of this nano-composite includes “in situ” reduction of silver salts to gain silver Nanoparticles.

There are a number of published papers and patents on using facilitated transport for gas separation in which there’s no use of PDMS’s unique chemical and physical properties as a matrix for metal-nanoparticles. [1], [2], [3], [4], [5], [6], [7]

The nano-composite was characterized using UV-Vis spectroscopy and tensile test. UV spectroscopy results show absorption peak in range of 415-420 nm that is an evidence for presence of silver nano-particles in the polymer and stress-strain curves resulting from tensile test indicate nano-composite’s enhanced mechanical properties compared to pure PDMS.

Keywords: facilitated transport, olefin/paraffin separation, Fick’s law, PDMS

Introduction

Olefins, especially ethylene and propylene, are large-volume industrial chemicals that are produced commercially by the separation from petroleum refining, natural gas liquids, and on-purpose chemical syntheses. A key step is the separation of the corresponding (same carbon number) paraffins from the olefins, conventionally done by fractional distillation. However Due to the very close relative volatilities of the olefins and their corresponding paraffins, separation by distillation, while widely practiced industrially, is energy and capital intensive. [1]

The membrane technique has made significant progress during past several decades in separating gaseous mixtures such as nitrogen/oxygen. But the typical gaseous separation membrane does not usually succeed in separating olefin/paraffin mixture due to their similar molecular and physical properties. However if a facilitated transport phenomenon is applied to the membrane technique it will be possible to selectively separate olefin from the mixture at an acceptable rate. [2]

In the present work we introduce a nanocomposite membrane for facilitated transport of olefin hydrocarbons with long term operation and stability. In addition, owing to the use of PDMS and in situ reduction, the provided process is cheap and easy and the resulting product has no limitation such as working only under wet condition, necessity to add volatile plasticizer or requiring a feed stream saturated with steam. Thus it is practical and suitable for industrial application.

The profound value of the present work lies in the importance of olefin/paraffin separation in petrochemical industry and the high cost, complexity of old methods and low efficiency of previous membrane techniques.

For example the distillation method currently used in the art needs to operate a distillation column, which has about 120 to 160 stages at a low temperature of -30^{o}C and a high pressure of about 20pa for the separation of ethylene/ethane and about 180 to 200 stages for propylene/propane separation at -30^{o} C. [2] In addition high reflux ratio results in large energy requirements, and large-diameter, heavy walled columns, because of the large internal hydraulic traffic. [1]

It is estimated that over 230 trillion BTU/year are consumed in industrial countries for olefin/paraffin separations. [3]

One of the first separation membranes using facilitated transport phenomenon is the supported liquid membrane, in which a metal salt is dissolved in a solvent (such as water) and acts as a carrier capable of reacting selectively and reversibly with unsaturated olefin molecules. [4] These membranes are generally successful in selectively separating olefin from the mixture. However they apply facilitated transport efficiency only under a wet condition; thus it is not possible for the mentioned membranes to maintain their efficiency during a long term operation due to the eventual loss of solvent.

In order to overcome this issue in liquid supported membrane and similar ion exchange membranes, there has been developed a method for supplementing a solvent periodically in order to keep the membrane at a constant wet condition; however it is impossible to apply such methods in a practiced manner and the membranes are typically unstable.

Attempts have been made to develop processes for fabrication of water-free membranes utilizing facilitated transport. [5],[6],[7] For example Kraus et al. worked on processing a water-free immobilized liquid membrane for facilitated transport of unsaturated hydrocarbons. [8] However the selectivity of their product for a dry ethylene/ethane mixture is too low (about 10) for practical use; furthermore the plasticizer of polymer becomes lost with time and the membrane shows no selectivity. On the other hand, Pinnau et al. have developed a solid polymer electrolyte membrane containing a carrier complex in the form of an ionic metal salt which is solved not in water but in a solid polymer. [9] The resulting membrane shows a high initial selectivity (50 or more) but the selectivity decreases over time due to the tendency of Ag ions to be reduced and agglomerated. Furthermore chemically unstable silver ions easily react with sulfur-containing compounds, acetylene or hydrogen gas which exist in a dry hydrocarbon gas mixture.

In recent years Char and coworkers synthesized a silver nanoparticle/polymer nanocomposite membrane. [2] The membrane separates olefin/paraffin mixture using facilitated transport; but instead of using Ag ions, silver neutral nanoparticles are used as carriers. To prevent nanoparticles from self assembling, they are coated with a coating agent prior to being solved in polymer solution. The resulting membrane has excellent long term operation characteristics and good stability. We used the concept of nanocomposite membrane, combined with in situ method to produce the present membrane.

Since PDMS is an inert and easy to fabricate rubbery polymer the process is simple, highly reproducible and practical for industrial applications.

Separation of olefin/paraffin hydrocarbons using resulting nanocomposite has the potential to be used as an alternative to distillation method of separation and the replacement of traditional cryogenic methods with membrane based separations can dramatically cut costs.

Theory

The total diffusion of olefin molecules through nanocomposite membrane is modeled with combination of two different mechanisms. [10]

The first mechanism is diffusion in accordance to Fick's first law:

$$J = \bar{P} \times \frac{\Delta P}{l}$$

Where J is the rate of diffusion, $\bar{P}$ is permeability and is defined as the product of diffusivity and solubility constants, ΔP is pressure applied and l is thickness of the membrane. [11] Permeability is mainly a function of molecular size and physical properties. This transport method is applied to both olefin and paraffin and the permeability for the two is almost the same.

The other predominant diffusion mechanism is facilitated transport in which carriers act only with reactive species (olefins). Nanoparticles near the membrane surface form unstable chemical bonds with olefins and they will then pass these molecules to other nanoparticle sites. The advantage of facilitated transport is that both permeability and selectivity (ratio of olefin/paraffin permeabilities) can be increased.

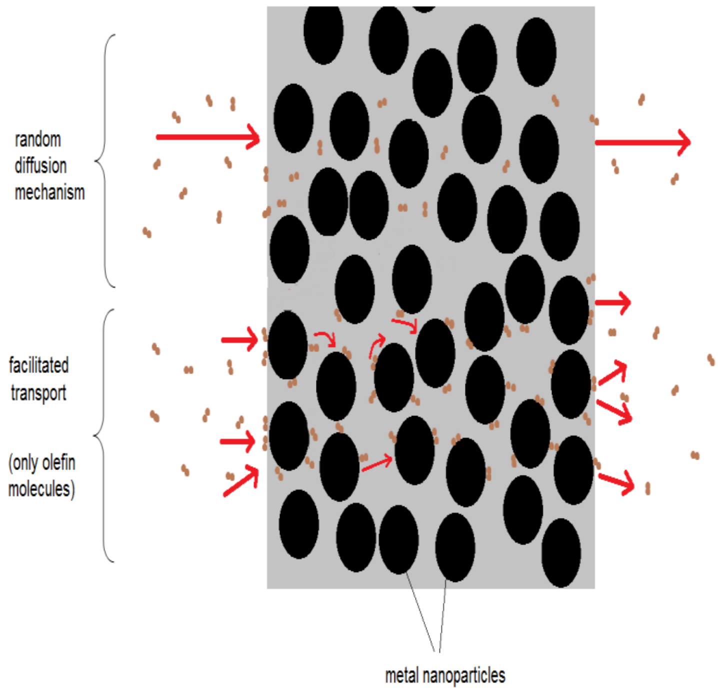

Figure1: Diffusion mechanisms in nanocomposite membrane

Experimental Part

PDMS or Poly-Dimethyl-Siloxane is used for over three decades. From its inception, its capability as an easily formed elastomer is demonstrated as a material of choice for experimentalists. PDMS is used in a variety of applications, including, material, medical, mechanical and microfluidics to mention a few.

PDMS is formed by mixing certain quantity of two part starting material, usually referred to as Part-I and Part-II. The two parts when mixed, out-gassed and annealed, within 60 minutes produce a highly transparent film, normally referred to as PDMS.

The novelty of this work is the addition of silver salt to PDMS mixture before being cured and optimizing the performance of reducing agents in order to produce a nano-composite consisting of silver nanoparticles as hardener. Furthermore attempts have been made to maximize the percentage of nanoparticles in mixture in order to for facilitated transport phenomena to occur.

Result of experimental work was a nano-composite having 0.6 % wt silver nanoparticle and young modulus of more than four times the pure PDMS. UV-spectroscopy results confirmed the formation of silver nano-particles with dimensions less than 100nm.

Conclusion

The concept of using metal nanoparticles in polymers -especially PDMS- adding antibacterial, strengthening or optical properties to resulting composites was a great field of research for material scientists in recent years. In this work, effects of adding silver nano-particles were investigated. Silver as a nobel metal has chemical characteristics such as stability in polymer matrix and capability of forming unstable chemical bonds with olefin molecules making it an ideal case for facilitated gas separation.

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