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Building movable bridges in membrane matrix by polyrotaxane crosslinking for sulfur removal

Ligang Lin^{a,b,*}, Meimei Dong^{a,b}, Chunyu Liu^{a,b}, Hui Sun^{a,b}, Longhui Zhang^{a,b}, Chao Zhang^{a,b}, Panshan Deng^{a,b}, Yingna Li^{a,b}

^a State Key Laboratory of Hollow Fiber Membrane Materials and Processes (Tianjin Polytechnic University), Tianjin 300187, PR China
^b Department of Environmental and Chemical Engineering, Tangshan College, Tangshan 063000, PR China

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ABSTRACT

Sulfur removal from gasoline by pervaporation (PV) membrane has attracted considerable attention. A novel strategy has been proposed to improve the desulphurization performance by building movable bridges in PV membrane matrix. Based on the designed polyrotaxane (PR) crosslinking agent, the EC membranes with PR bridges are fabricated. The selectivity and permeation flux of fabricated membranes are 8.1 and 3.5 kg/(m² h), respectively. The membrane performance is at higher level compared with the literature data, which is markedly related with the movable bridges in membrane matrix.

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1. Introduction

Sulfur compounds in gasoline are the main source of sulfur oxides (SO_x) , which are head-scratching pollutants for air pollution. Sulfur removal from gasoline has been motivated by the worldwide concerns [1,2]. New efficient desulphurization technologies are of great urgency [3]. PV membrane has been proposed as a promising desulphurization way, and the related research involves in membrane material, process optimization, etc.

However, the current PV performance for desulphurization does not meet the requirements for large-scale applications. The challenging problem is the trade-off phenomenon between selectivity and flux. High flux is always significant for the scale-up application. However, high flux often leads to lower selectivity for PV membranes. The recent research attempts to modify the membrane materials to attain higher PV performance [4].

Crosslinking and filling modification have been reported to increase the PV performance. The polydimethylsiloxane membranes filled with AgY zeolites [5], Ag_2O [6] and Ni²⁺Y zeolites [7] were reported for sulfur removal. For all cases, the flux-selectivity trade-off was found. By crosslinking modification, Lin and Kong [8] and Qi et al. [9] increased the selectivity of polyethylene glycol and polydimethyl-siloxane membrane, respectively. The fixed crosslinking junction

E-mail address: phdlinligang@163.com (L. Lin).

http://dx.doi.org/10.1016/j.matlet.2014.04.036 0167-577X/© 2014 Elsevier B.V. All rights reserved. confined the flux at low level. In brief, the reported modification research on PV membranes is still far from satisfactory performance for scale-up of sulfur removal by PV process.

To solve the challenging problem of PV performance, we propose a new strategy to achieve high performance by building movable bridges in membrane matrix. Polyrotaxane (PR), which possesses sliding or rotating cyclic molecules along the chains, is an interesting supramolecular material [10]. The crosslinking points with dynamical properties are expected to be favorable in achieving higher selectivity and higher flux.

In current work, the PR crosslinking agent is prepared. By designed crosslinking reaction, the EC membranes with PR bridges will be fabricated. The application characteristic of membranes will be investigated.

2. Materials and methods

Materials: EC was from the Shanghai Changwei Company (China). Gasoline feed (after alkali cleaning process) was obtained from General Petrochemical Works of ShengLi Oilfield (China). All other reagents were bought from Sinopharm Chemical Reagent Corporation (China). All the solvents used in experiments were of analytical reagent (A.R.) grade.

Membrane preparation: The PR used in this work was prepared by the reported way [11]. The PR crosslinking agent was prepared by introducing double bond onto PR. Under nitrogen atmosphere, 1.2 mL of allyl glycidyl ether was dissolved into DMF solution





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^{*} Corresponding author at: State Key Laboratory of Hollow Fiber Membrane Materials and Processes (Tianjin Polytechnic University), Tianjin 300187, PR China. Tel.: +86 22 83955808; fax: +86 22 83955055.

(7 mL). At 353 K, the reaction was carried out for 10 h, and then the solution was cooled down to ambient temperature. When acetone (50 mL) was added into the solution, white precipitate was obtained. The precipitate should be cleaned by acetone for three times. Through vacuum drying for 24 h, the PR crosslinking agent can be obtained for the following experiments. The EC polymer mixed with PR crosslinking agent and benzophenone as photo initiator dissolved in mixed solvent (50 V% ethanol and 50 V % benzene) to obtain a homogenous solution at 298 K. The polymer content was at 11 wt%. After filtration and degassing, the polymer solution was cast onto glass plate. The solvent was evaporated at 343 K for 24 h, and then crosslinked under ultraviolet light. The optimal crosslinking conditions will be analyzed in Section 3.

PV measurements and analysis: For the PV measurements, a permeation cell with 25.3 cm² of effective membrane area was used. The flux (*J*) and selectivity (α) can be obtained following the reported way [12].

By Varian3800 GC, the detailed components distribution of gasoline sample can be obtained. The selectivity of each sulfur component was defined as the peak area ratio of permeate sample to feed sample.

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Characterization: The infrared spectra were presented by TEN-SOR37 FT-IR. All NMR spectra were obtained on a Bruker AM-300 spectrometer. Sample concentrations were about 0.7% (w/v) in DMSO-d6.

3. Results and discussion

Building of movable bridges in membrane matrix by polyrotaxane: Fig. 1 gives evidence and analysis for the building of movable bridges in membrane matrix by polyrotaxane. The molecular structure and ¹H NMR spectra of prepared PR are shown in Fig. 1 (a). Compared with α -cyclodextrin (α -CD), the peaks of PR show shifted position, increased intensity and broadened shape, which result from the increased electron cloud density in α -CD cavity caused by threaded polymer chains. The NMR provides supporting evidence for threaded polymer architectures. The XRD pattern of PR (Fig. S1 in Supplementary data) provides additional evidence. Compared with those peaks of α -CD and PEG, the appeared strong peak at around 20° for PR is assigned to the characteristic channeltype crystalline structure from the threaded PEG chains into α -CD cages [13]. The PR crosslinking agent (PR=) was prepared by



Fig. 1. Analysis of PR characteristics: (a) ¹H NMR spectra of PR and α-CD; (b) Schematic diagram of bridges in EC membrane matrix; and (c) FT-IR spectra of raw PR and PR=.

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