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Hollow fiber membranes with polyimide matrix for sulfur-free hydrogen source

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ABSTRACT

Sulfur-free hydrogen production is significant for sustainable energy such as fuel cell to avoid poisoning catalysts. The hollow fiber membrane is proposed as sulfur trapper for the hydrocarbon fuels. Hollow fiber membranes with polyimide (PI) matrix and adsorptive zeolites fillers are fabricated by dry–wet spinning with subsequent imidization process. By detailed investigation of FT-IR, thermal degradation cures, morphology and sulfur trapping performance, the molecular structure, thermostability and adsorption channels of membranes have been analyzed. The hollow fiber membranes have abundant pores, and the zeolites particles are incorporated in the three-dimension polymer matrix. The inlet fuel can be desulfurized to below 0.1 mg L^{-1}, which means that the outlet fuel can be used as sulfur-free hydrogen source for fuel cell applications. Excellent sustainability of the system with hollow fiber configuration show attractive on-board application potential.

Introduction

Hydrogen (H_2) production has attracted worldwide attention for its broad application potential. Hydrogen is the cleanest sustainable energy, which can solve the local problems connected with air quality [1,2]. Fuel cell is a promising way for efficient and reliable energy utilization. Hydrogen can be produced from a variety of resources including fossil fuels, biomass, and other renewable energy technologies, such as wind, solar, geothermal, and hydro-electric power. Liquid hydrocarbons fuels like gasoline are the primary source of industrial hydrogen. For the automotive fuel cells and military fuel cells, liquid hydrocarbon fuels are ideal choice due to their higher energy density, ready availability, and proven safety for transportation and storage [3]. By well-known steam reforming process, the hydrocarbons fuels can be converted to hydrogen for fuel cell applications [4–6].

However, the liquid hydrocarbon fuels usually contain certain sulfur compounds which are poisonous to both the catalysts used in fuel processor (such as reforming catalysts and water–gas-shift catalysts in hydrocarbon-based fuel cell system) and the electrode catalysts in fuel cell stack [7]. To prevent the catalysts in fuel cell systems from poisoning by sulfur containing substances, the hydrocarbon fuels for hydrogen production should be sulfur-free (less than 0.1 mg L^{-1}) [8]. Therefore, sulfur removal from traditional liquid hydrocarbon fuels has been a challenging problem.

To provide a method integrated with fuel cell system easily for on-line run, herein we propose hollow fiber membranes for

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the sulfur removal process. Membrane separation processes underwent a rapid growth over the past few decades. It is known that the membrane method presents superiority such as high efficiency, ease of on-board implementation and low cost. Especially, the membranes in hollow fiber configuration show large surface area per unit volume, low module volume and low cost of operation [9]. Compared with the conventional sorption desulfurization process in packed bed mode, the adsorptive hollow fiber membranes also show short diffusion path length and less leakage of particles. Moreover, the membranes can be used for large scale production since they can easily be scaled up to industrial volumes by multiplying the number of modules. That technology flexibility is also attractive.

Liquid hydrocarbon fuel is composed of complex organic compounds [10]. It is necessary to design membrane matrix with excellent solvent resistance performance. In current work, the PI polymer was synthesized as membrane matrix. The hollow fiber membranes with PI matrix and zeolites functional fillers are fabricated for sulfur removal from hydrocarbon fuels. The molecular structure, morphology, and desulfurization performance of hollow fiber membranes will be investigated. The sustainability of the system will be discussed.

Experimental

Materials

The monomers of pyromellitic dianhydride (PMDA) and 4,4′-diaminodiphenyl ether (ODA) were from Sinopharm Chemical Reagent Corporation (China). And the monomers were purified by recrystallization with acetic anhydride and ethanol. NaY zeolites were purchased from QiLu Petrochemical Catalyst Plant (China). Thiophene and *n*-heptane were from Tianjin Kemiou Chemical Reagent Corporation. Dibenzothiophene was from Shouerfu Reagent Corporation (China). Silver nitrate was from Tianjin Yingda Chemical Reagent Corporation. Other reagents were all from Sinopharm Chemical Reagent Corporation (China).

Membrane preparation

A simple and inexpensive method was proposed for the preparation of hollow fiber membranes with polyimide matrix. With PMDA and ODA monomers, the nascent polyamide acid (PAA) solution was prepared with the steps as follows. The PMDA was dissolved in NMP, and then the ODA was gradually added into the solution. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 12 wt%, respectively. The mixture reacted for 8 h at 25 °C. And then the AgY zeolites under various loading were added into above mixture. The mixture was stirred for 4 h and then sonicated for 0.5 h to assure the particles well dispersed. After degasification of the dope solution, the nascent PAA hollow fiber membranes were prepared by a dry–wet spinning process, as shown in Fig. 1. During the spinning, the fiber was extruded under nitrogen pressure. Bore fluid in spinneret is water. The fibers were immersed into precipitation bath (water, 25 °C).

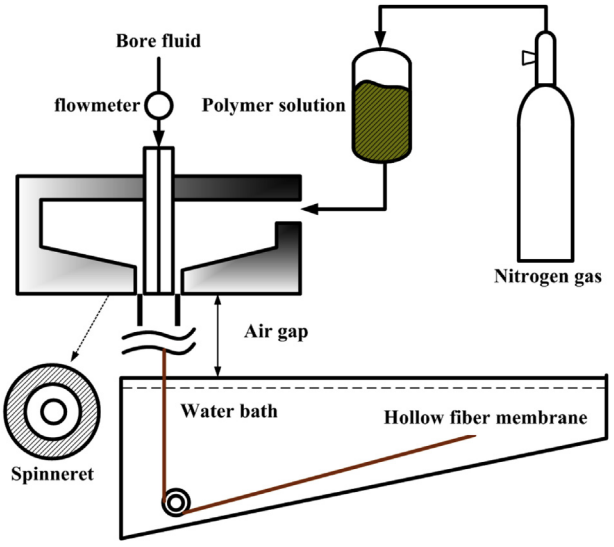

Fig. 1 – Schematic diagram of the spinning process for hollow fiber membranes.

During this process, solvent exchange occurred and the solidified hollow fiber membrane formed with porous structure. After 24 h, the membranes was collected and dried at 250 °C for 3 h to conduct the imidization.

Through above thermal imidization treatment, the synthetic procedure from PAA to PI was conducted. Then, the hollow fiber membranes with PI matrix can be obtained, and the evidence will be provided in the following section.

In addition, the AgY zeolites were prepared by ion-exchange steps as follows. NaY particles were added to silver nitrate solution (0.15 mol/L) in a stirred vessel. 1.0 of Ag^+/Na^+ mole ratio was under work. After 5 h of ion-exchange reaction under 20 °C, the samples were filtered, washed, and dried at 80 °C. The silver ion loaded zeolites were calcined at 400 °C for 3 h before usage.

Adsorption and regeneration experiments

The sulfur removal performance of membranes was obtained by dynamic adsorption experiments. The experiments were performed in hollow fiber modules in a continuous manner (details seen in Sulfur removal from fuel for hydrogen source). In all cases, a flow rate of 50 mL h^{-1} for the feed fuel was used. The sulfur trapping and adsorption experiments were conducted at 25 °C with 500 mg L^{-1} of inlet sulfur concentration level. When the fuel feed consisting of hydrocarbons and thiophenic sulfur compounds passed through the membranes, the sulfur compounds can be adsorbed, and the sulfur concentration of the outlet solution was analyzed by Micro-Coulometric Analysis Instrument (Jiangsu, China). Once the outlet sulfur concentration is found over 0.1 mg L^{-1}, the regeneration is necessary.

Regeneration of membranes was performed by solvent washing under 65 °C. Ethanol used as desorption agent, and the sulfur concentration of washing solvent is analyzed using the sulfur analyzer at intervals until the concentration is stable. The adsorption capacity of regenerative membranes was tested to compare with the fresh samples. The

regeneration was repeated four times to investigate the practical application potential.

Characterization

The infrared spectra of prepared membranes were obtained by KBr method on a TENSOR37 FT-IR. The microscopic morphology of hollow fiber membrane was characterized by field-emission scanning electron microscope (FE-SEM), carried out on Hitachi S-4800. Thermal gravimetric analysis was performed using NETZSCH STA 409 PC/PG. The samples were heated from 35 to 800 °C at a heating rate of 10 °C/min, under nitrogen atmosphere.

Results and discussion

Molecular structure and thermostability of prepared membranes

In this work, a simple way was proposed for the preparation of membranes with PI matrix. By immerse precipitation phase separation method, the nascent membranes with PAA matrix were prepared. With the following imidization treatment, PI membranes can be obtained. Fig. 2 presents the molecular structure analysis on raw PAA, raw PI and zeolites/PI membranes.

For PAA membranes, the typical peaks at 1710 cm^{-1} and 1659 cm^{-1} were ascribed to the stretching vibration of C=O group in COOH and CONH-, respectively. The band at 1543 cm^{-1} corresponds to the stretching vibrations of C–N groups in CONH-. By comparison on those peaks in PAA and PI, it is clear that the "amide" band disappears through the imidization treatment. For both the raw PI membrane and zeolites/PI membranes, four characteristic "imido" bands can be observed. The band at 1774 cm^{-1} (characteristic imido I band) and 1717 cm^{-1} (characteristic imido II band) correspond to the symmetrical and asymmetrical stretching vibrations of the two C=O groups in five-membered imine ring, respectively. The band at 1368 cm^{-1} can be ascribed to the stretching vibration of C–N group, which is characteristic imido III band. The characteristic imido IV band can also be found at 719 cm^{-1}, which corresponds to the deformation vibration of imine ring. More importantly, a new peak appears at 990–1010 cm^{-1} for the zeolites/PI membranes, which corresponds to the stretching vibrations of the Y zeolites framework. The results give evidence on the successful immobilization of adsorptive functional materials into PI base matrix. Additional evidence will be provided in the following morphology analysis.

Fuel, which is treatment system in this work, is composed of complex organic compounds. It is well known that PI has super solvent resistance performance, which is one of the reasons why PI is designed as matrix material. To achieve higher separation performance, thermal treating is necessary for the membranes with zeolites. The thermal degradation cures in Fig. 3 give the reason. From Fig. 3, the weight loss for zeolites at about 50–150 °C is attributable to the desorption of combined and adsorbed water in framework. Before used for separation, the membranes should be treated under high temperature to eliminate the influence of combined water in zeolites. The thermal degradation curve of zeolites/PI membrane shows two weight loss peaks. Except the corresponded peak for embedded zeolites, another major weight loss at 450–700 °C can be ascribed to the thermal decomposition of PI matrix. From Fig. 3, thermal degradation curve of raw PI membrane shows one major weight loss, corresponding to the thermal decomposition temperature. Both the raw PI membrane and zeolites/PI membrane show excellent thermostability.

Porous channels of hollow fiber membranes

The hollow configuration of membranes provides convenient fluid pathway, which is favorable for the online operation and process scale-up. However, the micro structure of membranes is also significant since the micro pores provide space and porous channels for the adsorption function.

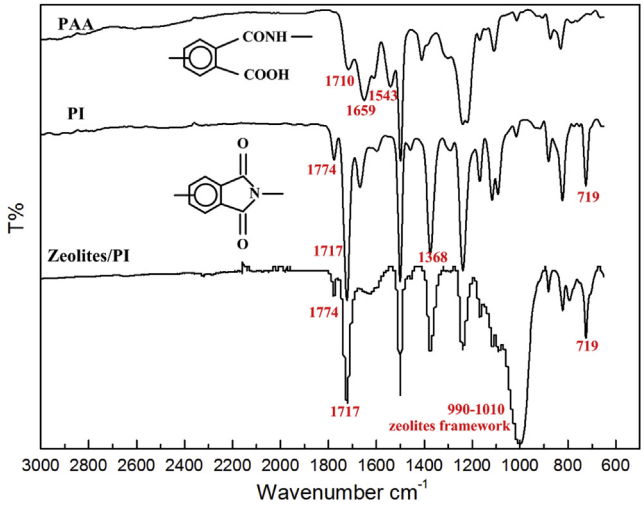

Fig. 2 – FT-IR spectra of PAA, PI and zeolites/PI membranes.

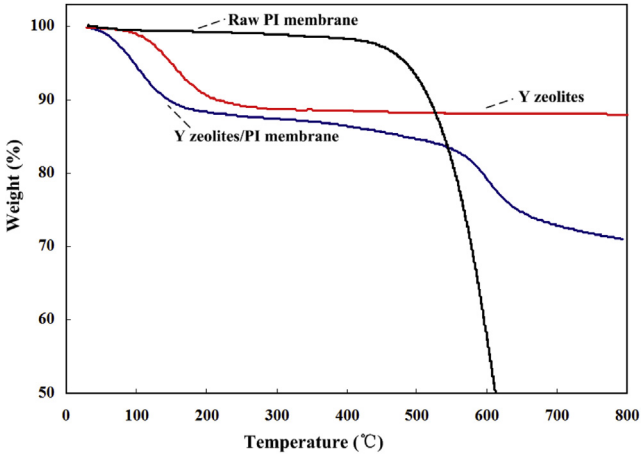

Fig. 3 – Thermal degradation of raw PI, raw zeolites and zeolites/PI membranes.

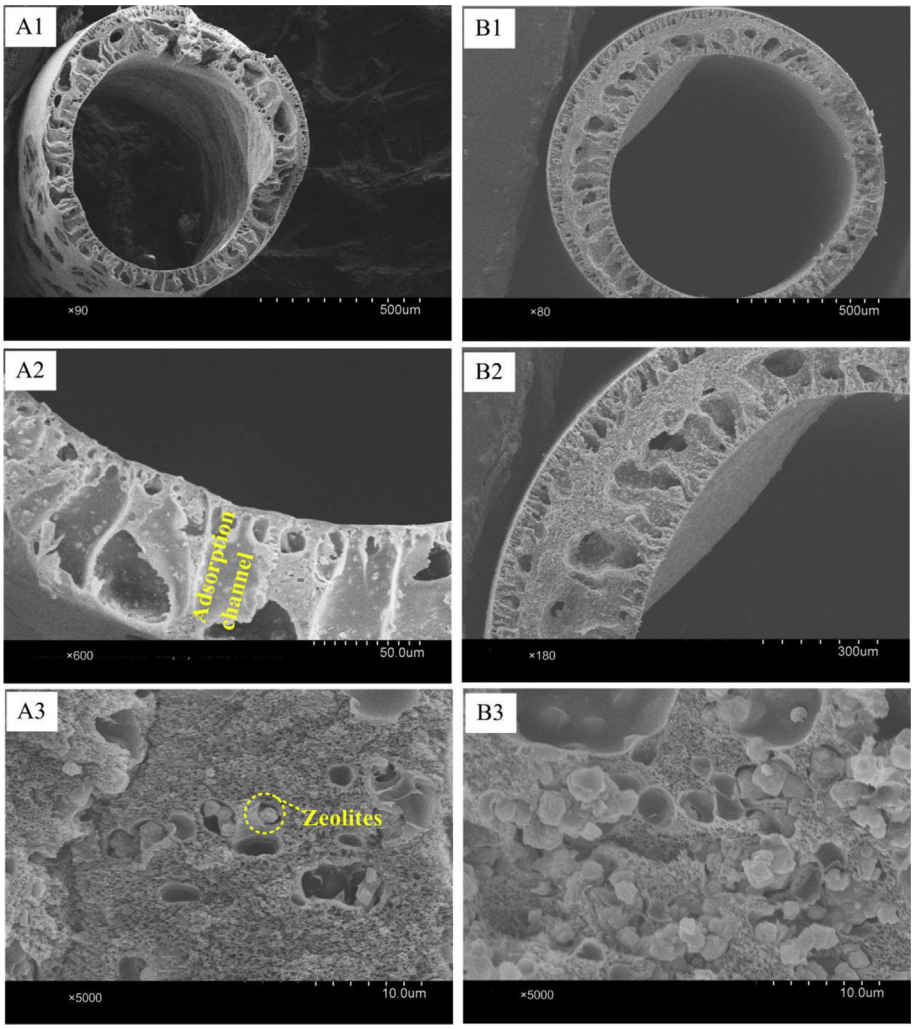

Fig. 4 – FESEM images of hollow fiber membrane: (A) Membranes with 10% zeolites loading under various magnification, (B) Membranes with 20% zeolites loading under various magnification.

The FESEM images of prepared hollow fiber membranes under various zeolites loading are shown in Fig. 4. It can be seen from Fig. 4 that the membranes have abundant pores, which provide necessary adsorption channels. From the magnified images (Fig. 4A2 and A3, Fig. 4B2 and B3), the AgY zeolites particles are dispersed and incorporated in the polymer matrix. The conclusions are in good accordance with the FT-IR analysis. The three-dimension pore channels ensure the

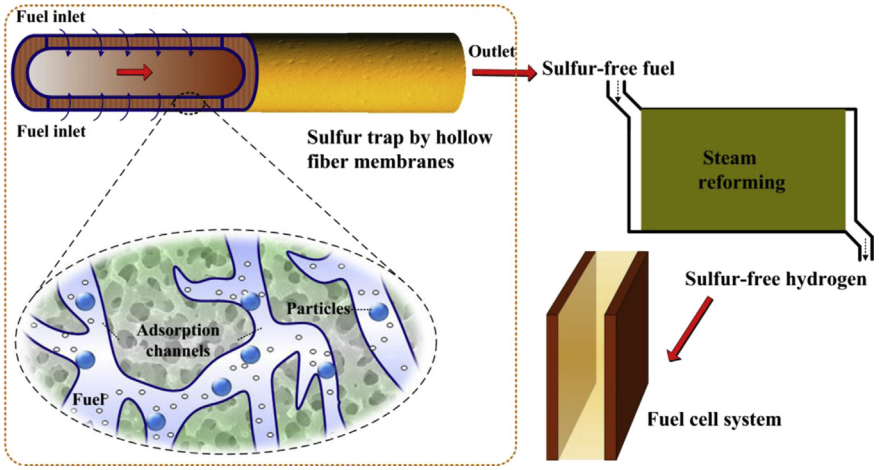

Fig. 5 – The schematic diagram of hollow fiber membrane for sulfur-free hydrogen source.

Table 1 – Adsorption contribution and effects of zeolites content.

Zeolites content (%)	Adsorption capacity (mg S g^{-1})
0	0.16
5	6.41
10	12.84
15	10.01
20	4.22

contact between the incorporated zeolites particles and the liquid fuel flowing through. And the sulfur adsorption and removal from the fuel can be achieved during the process. It is also worth mentioned that increasing zeolites loading in membrane matrix can resulted in the agglomeration of zeolites particles. That has negative influence on the connection between polymer and inorganic fillers. For practical applicability, 10% of zeolites loading was proposed in this work if no special declaration.

Sulfur removal from fuel for hydrogen source

The prepared hollow fiber membranes are designed as sulfur trapper from hydrocarbon fuel for hydrogen source, and the schematic diagram is shown in Fig. 5.

From Fig. 5, membrane filtration was carried out in a continuous manner. When the fuel feed consisting of hydrocarbons and thiophenic sulfur compounds passed through the hollow fiber membrane, in which the zeolites as enabling materials, the sulfur compounds can be adsorbed and trapped. The sulfur concentration of the outlet solution can be analyzed by Micro-Coulometric Analysis Instrument.

Effect of content of incorporated zeolites

As discussed on the porous channels of hollow fiber membranes, zeolites loading has significant influence on the membrane performance. Table 1 shows the effect of the content of incorporated zeolites on the adsorption capacity. During the experiments, the initial sulfur concentration was 500 mg L^{-1}.

From Table 1, compared with hybrid membranes, raw PI membranes show low adsorption capacity, which means that the incorporated zeolites particles play main contribution for the sulfur adsorption. It can be seen that the adsorption capacity of the hybrid membranes increases with the increasing zeolites content. Zeolites/PI membranes with 10wt.% of particles content show the highest performance. Under a certain filling degree, more zeolites particles in porous channels mean more contact opportunity of sulfur compounds with the fillers, hence higher adsorption capacity. However, higher zeolites contents such as 15wt.% and 20wt.% bring decreased performance from Table 1. Under higher content, the agglomeration of zeolites particles has negative influence on the porous channels. Part of the network between the polymer and particles becomes disconnected, even defect has appeared, which is unfavorable for the contact of sulfur compounds with the fillers. The results correspond to the discussions on morphology analysis (Fig. 4). Considering the practicability, 10 wt.% of zeolites content is suggested.

It is noteworthy that the above adsorption experiments were conducted under convective style. The corresponding adsorption capacity was calculated based on the dynamic breakthrough experiments. Different with the experiment phenomena under batch style, the adsorption performance was affected by zeolites and adsorption channels. Under batch style, the adsorption isotherm and adsorption kinetics curves are shown in Fig. 6. From Fig. 6, the adsorption capacity of membranes increases firstly and then tends to adsorption equilibrium with the increasing adsorption time. Under various concentration conditions, the adsorption capacity remains at high level. However, the adsorption capacity under convective operation style (Table 1) was less than that under batch style (Fig. 6) with the same sulfur concentration condition. The results were from the short retention time under convective style. Part of the zeolites particles were absent on contact with the fuel. This was particularly true for the membranes with higher zeolites content.

Sulfur removal performance for different sulfur compounds

The fabricated membrane adsorber has unique advantages such as multiple function sites, easy in-line operation, etc. The membrane adsorber is expected to work in an efficient way, and the breakthrough curves for the adsorptive sulfur removal from the fuel with different sulfur compounds by fabricated hollow fiber membranes is shown in Fig. 7.

From Fig. 7, it is evident that the inlet fuel with 500 mg L^{-1} of sulfur concentration is desulfurized to below 0.1 mg L^{-1} for all cases, which means that the outlet fuel can be used as

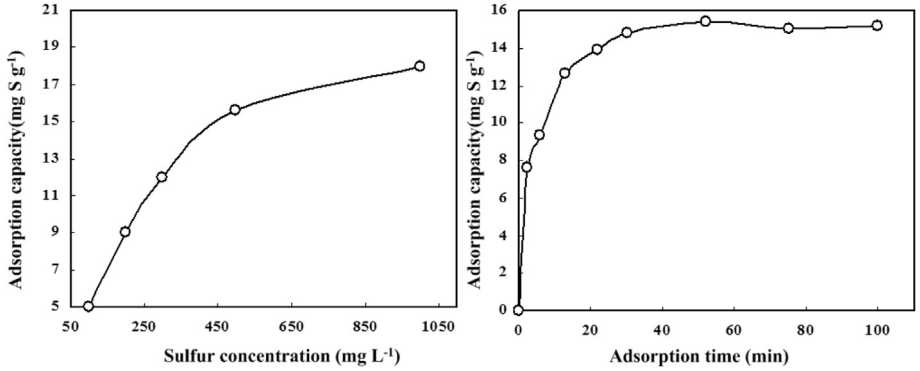

Fig. 6 – The adsorption isotherm and adsorption kinetics curves.

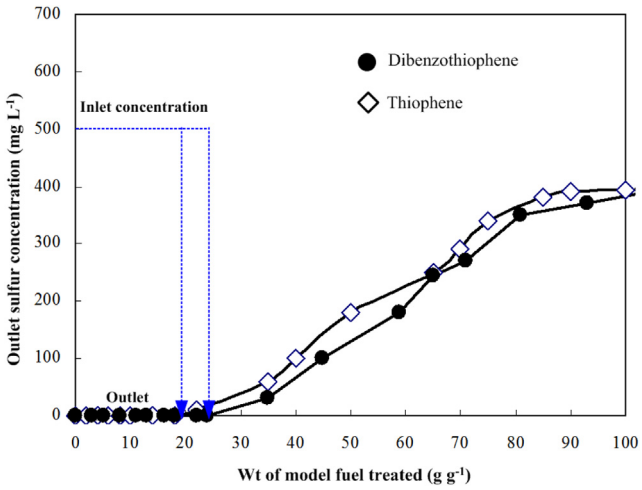

Fig. 7 – Sulfur removal performance of hollow fiber membrane.

sulfur-free hydrogen source. In fact, the adsorption behavior of membranes embedded with AgY zeolites was markedly related with the binding mode between sulfur compounds and the fillers. In this work, the AgY zeolites were embedded as functional fillers. It is known that thiophenic sulfur compound has two lone pairs of electrons on the sulfur atom: one pair lies on the six-electron π system and the other lies in the plane of the ring. The Ag^{+} on the surface of zeolites can combine with thiophenic sulfur by π bonds [11]. The excellent adsorption performance of zeolites/PI membranes was due to the strong π-complexation binding force.

As depicted in Fig. 7, the sulfur removal performance for dibenzothiophene is higher than that for thiophene, which suggests that the membranes have higher desulfurization performance for diesel fuel. The results are from the higher electron density of S atoms for dibenzothiophene. The methyl groups in the substituted thiophenic compounds can enhance the electron back-donation process during π-complexation adsorption [12].

Sustainability of the system

From above analysis, the hollow fiber membrane adsorber can remove sulfur in fuel in an efficient way. The outlet fuel is expected as sulfur-free hydrogen source for fuel cell applications (Fig. 5). The advantages of hollow fiber membranes include their large surface area per unit volume, low separation module volume, low cost of operation and ease of on-board implementation, which provides convenience for the integration with fuel cell systems. The sulfur-free fuel can be obtained at the outlet of membrane process. And then the sulfur-free hydrogen can be generated by the steam reforming, which is a well-known technology. The proposed hollow fiber membrane are expected to be applied as sulfur trap before the reformer for fuel cells on-board or on-site, and it may be applied in a periodically replaceable form.

One of the challenging problems on membrane adsorber is the regeneration and repetitive usage. In the present work, the solvent washing combined with thermal treating was conducted for the spent membranes. From above TGA analysis (Fig. 3), the fabricated membranes have super thermostability. It is also well known that PI, which is matrix material, has super solvent resistance performance. The membranes can be long-term used under high temperature and solvent circumstances. The regeneration experimental results are presented in Table 2, and experiment conditions are shown in the experimental section.

Table 2 – The regeneration efficiency of membrane adsorber.

Regeneration times	Adsorption capacity (mg S g^{-1})	Regeneration efficiency (%)
0	12.84	–
1	11.87	92.5
2	11.53	89.8
3	11.79	91.9
4	11.64	90.7

From Table 2, the adsorption capacity of the membrane adsorber decreases after the first regeneration, and then remains stable during the successive regenerations. Compared with the fresh membranes, the spent membranes can recover about 90% of the desulfurization capacity by regeneration. It was obvious that the prepared membrane adsorber can be regenerated effectively.

Conclusions

Sulfur-free hydrogen is significant for sustainable energy such as fuel cell. An efficient strategy for sulfur-free hydrogen source is proposed from membrane viewpoint. The zeolites/PI membranes with attractive application potential are fabricated by a simple way. The sulfur compound in hydrocarbon fuels can be trapped in an efficient way, which means that the hollow fiber membrane can solve the challenging sulfur poisoning problem on the catalysts in fuel cell stacks.

Acknowledgments

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