



Sulfur removal from fuel using zeolites/polyimide mixed matrix membrane adsorbents

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ARTICLE INFO

Article history:

Received 5 May 2011

Received in revised form

29 November 2011

Accepted 2 December 2011

Available online 13 December 2011

Keywords:

MMMs

Sulfur

Adsorption

Zeolites

Polyimide

ABSTRACT

A novel membrane adsorption process was proposed for the sulfur removal from fuels. The mixed matrix membranes (MMMs) adsorbents composed of polyimide (PI) and various Y zeolites were prepared. By the detailed characterization of FT-IR, morphology, thermal and mechanical properties of MMMs adsorbents, combining the adsorption and desorption behavior research, the process–structure–function relationship was discussed. Field-emission scanning electron microscope (FESEM) images show that the functional particles are incorporated into the three-dimensional network structure. MMMs adsorbents with 40% of zeolites content possess better physical properties, which was confirmed by mechanical strength and thermo stability analysis. Influence factors including post-treatment, content of incorporated zeolites, adsorption time, temperature, initial sulfur concentration as well as sulfur species on the adsorption performance of MMMs adsorbents have been evaluated. At 4 wt.% zeolites content, adsorption capacity for NaY/PI, AgY/PI and CeY/PI MMMs adsorbents come to 2.0, 7.5 and 7.9 mgS/g, respectively. And the regeneration results suggest that the corresponding spent membranes can recover about 98%, 90% and 70% of the desulfurization capacity, respectively. The distinct adsorption and desorption behavior of MMMs adsorbents with various functional zeolites was markedly related with their various binding force and binding mode with sulfur compounds.

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1. Introduction

During recent years, increasing attention has been paid to the environment issue caused by sulfur compounds in transportation fuels which is the main source of SO_x in air. Numerous governments worldwide will adopt new regulations which limit the sulfur concentration in fuel at 10 ppm or less in the near future [1,2]. On the other hand, hydrocarbon fuels are ideal hydrogen source of fuel cell system. However, even the trace of sulfur compounds in fuels can poison the catalysts and electrodes in fuel cell stack, which needs to reduce the sulfur level in hydrocarbons fuels to less than 0.1 ppmw [3,4].

It is well known that sulfur removal from fuel can be achieved by catalytic hydrodesulfurization (HDS). However, this conventional hydrotreating process results in a significant reduction of octane number due to the saturation of olefins. Meanwhile, it is difficult for HDS to remove thiophenic species, which are main sulfur

compounds in fuels [5–7]. Under above circumstances, quite a number of novel non-HDS desulfurization methods have emerged, including oxidation [8], extraction [9], biodesulfurization [10], adsorption [11–14] and membrane desulfurization [15], etc. Among these processes, the adsorption approach is rather attractive, because it does not need to consume H₂ and can be operated at ambient or rather low temperature and pressure. However, the now developed adsorption desulfurization process was usually in fixed bed or fluid bed operation. During those operation circumstances, the leakage of adsorbent particles with flowing fuel is inevitable. To prevent the leakage of particles, the size of used adsorbent particle is usually requested at larger level, which means lower specific surface for adsorption.

In current work, the membrane adsorption process has been proposed for the sulfur removal from fuels. Membrane adsorption can take advantage of adsorption process and membrane technique. The inorganic adsorbent particles can be incorporated into the three-dimensional network structure of porous polymeric membranes, hence the mixed matrix membranes (MMMs) adsorbents. Membrane adsorption process with MMMs adsorbents can prevent the leakage of adsorbent particles and also grant the size of them at micrometer level, which means the larger specific surface area. On the other hand, for membrane adsorption process, it is

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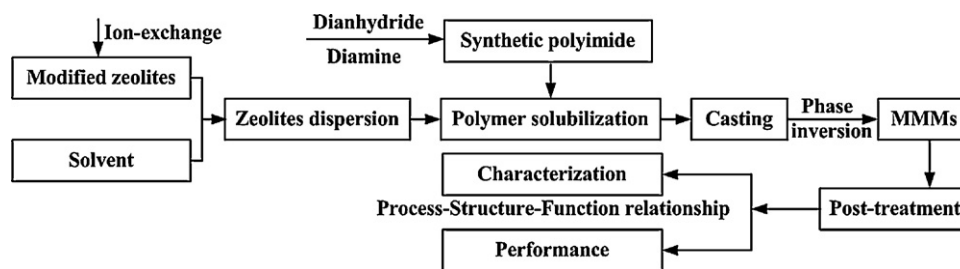


Fig. 1. Flow diagram for MMMs adsorbents preparation procedure.

convenient to carry out on-site operation for future scale-up application. During recent years, the reported desulfurization research based on membrane technique involves pervaporation [16] and membrane extraction [17], etc. Until recently the report about the membrane adsorption for desulfurization is quite insufficient.

In this study, the mixed matrix membrane adsorbents for desulfurization have been prepared using polyimide (PI) as matrix material and various Y zeolites as adsorptive functional materials. The effects of post-treatment, content of incorporated zeolites, adsorption time, temperature, initial sulfur concentration as well as sulfur species type on the adsorption performance were investigated. By the detailed analysis of FT-IR, morphology, thermal and mechanical properties of MMMs adsorbents, the process-structure-function relationship was obtained.

2. Materials and Methods

2.1. Materials

NaY zeolites, used as a starting material for making ion-exchanged zeolites, was purchased from QiLu Petrochemical Catalyst Plant (China). Thiophene and dibenzothiophene (typical sulfur species) were from Chengdu Kelong Chemical Reagent Corporation and Shouferu Reagent Corporation, respectively. n-Heptane and n-octane (typical hydrocarbons) were from Tianjin Kemiou Chemical Reagent Corporation, respectively. Silver nitrate and cerium nitrate was from Tianjin Yingda Chemical Reagent Corporation and Tianjin Jinke Fine Chemistry Institute, respectively. Other reagents were from Sinopharm Chemical Reagent Corporation. All chemicals used were of analytical reagent (A.R.) grade and used without further purification. The monomer of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) was from Beijing Multi. Technology Co., Ltd., 4,4'-diamino-3,3'-dimethyldiphenylmethane (DMMDA) from Shanghai EMST Corporation. And the monomers were purified by recrystallization. N,N-dimethylformamide (DMF) was purified on distillation under reduced pressure.

2.2. Mixed matrix membrane adsorbents preparation

Fig. 1 shows a flow diagram for the MMMs adsorbents preparation procedure. The detailed methods and conditions for every involved procedure are presented in the following sections.

2.2.1. Synthesis of polyimide

BTDA–DMMDA polyimide was prepared by a two-step solution-imidization route. The diamine was dissolved in DMF, and then the diamine was gradually added into the solution. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 13 wt.%, respectively. The mixture reacted for 10 h at room temperature producing a viscous polyamic acid solution. The chemical imidization was carried out with acetic anhydride and pyridine at room temperature for 14 h. The reaction mixture was then added to

ethanol solution. The precipitate was collected by filtration, washed with water, and dried in vacuo at 150 °C to obtain the solid of polyimides.

2.2.2. Ion-exchange zeolites preparation

Liquid-phase ion-exchange process was used for the preparation of AgY zeolites. NaY zeolites were used as the starting material. NaY particles were added to silver nitrate solution in a stirred vessel. The mixture was stirred for certain time. After the ion-exchange treatments, the samples were filtered, washed, and dried at 80 °C. The silver ion loaded zeolites were calcined at 400 °C for 3 h. The optimal preparation conditions for AgY zeolites have been determined through the orthogonal experiments with adsorption capacity as investigation index. The optimal preparation conditions for AgY were as follows: 0.15 mol/L of silver nitrate solution, 1.0 of Ag⁺/Na⁺ mole ratio, 5 h of ion-exchange time and 20 °C of ion-exchange temperature. CeY zeolites were prepared following the same procedure mentioned above. Cerium nitrate solution was used for the liquid-phase ion-exchange process. The corresponding optimal preparation conditions for CeY were as follows: 0.10 mol/L of cerium nitrate solution, 10 of Ce³⁺/Na⁺ mole ratio, 4 h of ion-exchange time and 90 °C of ion-exchange temperature.

2.2.3. Fabrication of mixed matrix membranes

Certain contents of zeolites were dispersed into the mixed solvent (DMF + THF (tetrahydrofuran)) in a stirred vessel. The mixture was stirred 4 h and then sonicated for 0.5 h to break the clusters of particles and to assure the particles well dispersed. Then PEG-400 was added to the mixture in order to improve the membrane morphology. Finally, PI, which has been dried in a vacuum oven at 120 °C for 24 h, was gradually added to the mixture and stirred for 24 h to ensure complete dissolution of polymer. Before casting, the solution was degassed. All membranes were made by phase inversion technique. The solution was cast on a glass plate and immersed into a water coagulation bath. During this process, solvent exchange occurred and the solidified membrane formed with porous structure. To ensure that all of the solvent in the membrane structure was removed, membranes were immersed in the water bath for 24 h. Before performance investigation, the solvent post-treatment and baking post-treatment of MMMs adsorbents needs to be carried out, and the specific post-treatment conditions will be mentioned in Section 3.2.1. Membranes were prepared with zeolites loadings of 0 wt.%, 18 wt.%, 30 wt.%, 40 wt.% and 50 wt.%.

2.3. Adsorption experiments

Adsorption experiments were performed by a batch method. An organic solution consisting of n-heptane and thiophene was used as model gasoline fuel, and n-octane and dibenzothiophene as model diesel fuel. The model solution and certain amount of membranes were mixed in a conical flask in shaking machine for a desired time at given temperature of 25, 40 and 60 °C. The liquid phase was separated from the membrane adsorbent, and the sulfur concentration

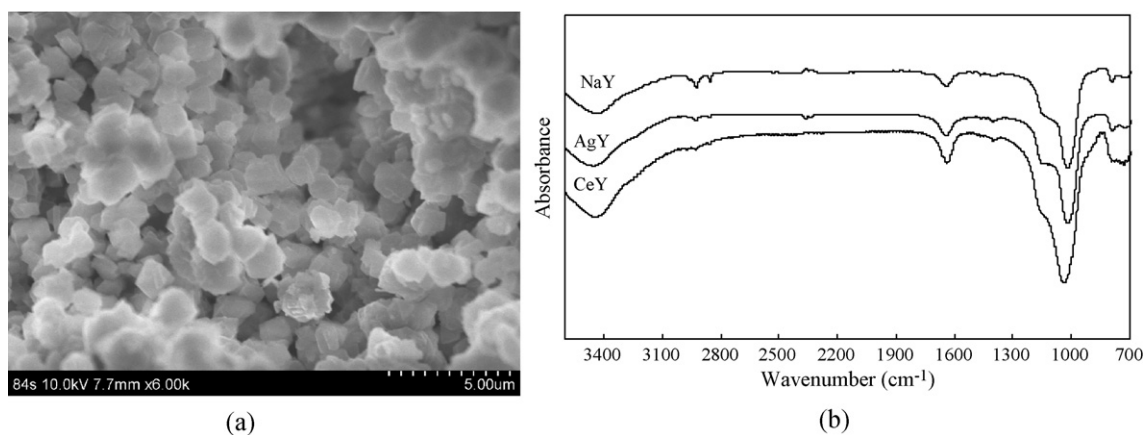


Fig. 2. Surface morphology and FT-IR spectra of zeolites: (a) FESEM; (b) FT-IR spectra.

in the solution was analyzed by Micro-Coulometric Analysis Instrument (Jiangsu, China). The adsorption capacity with unit of mg S/g was calculated.

2.4. Desorption/regeneration experiments

Regeneration of spent adsorbent was performed by solvent washing. In the solvent washing method, ethanol used as desorption agent was mixed with spent MMMs adsorbents in a conical flask in shaking machine at 65 °C. The sulfur concentration of washing solvent is analyzed using the sulfur analyzer at intervals until the concentration is stable. The adsorption capacity of regenerative MMMs adsorbents was tested to compare with the fresh samples. The regeneration was repeated five times to investigate the practical application potential of MMMs adsorbents.

2.5. Characterization

The infrared spectra of prepared MMMs adsorbents were obtained by KBr method on a TENSOR37 FT-IR. The microscopic morphology of zeolites and various membrane samples was characterized by field-emission scanning electron microscope (FESEM), carried out on Hitachi S-4800 at 10 kV. Thermal gravimetric analysis (TGA) was performed on both the raw PI membranes and zeolites/PI matrix membranes 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, with a nitrogen flow rate of 50 mL/min. The mechanical properties of the MMMs adsorbents with different loading of zeolites were tested with M350-10 kN testing machine (Testometric Company).

For convenient comparative analysis on the physical properties of MMMs adsorbents, the surface morphology and FT-IR spectra of zeolites were presented in Fig. 2. Fig. 2(a) presents the regular surface morphology with polyhedral shape, with about 5–8 μm of particle diameter. From the FT-IR spectra in Fig. 2(b), the characteristic peak of various Y zeolites was at 1036 cm⁻¹ corresponds to the stretching vibrations of the zeolites structure framework. The IR analysis demonstrated that no change occurs on the bands of the AgY and CeY compared with original NaY-zeolites, which indicating that the ion-exchange modification by silver ion and cerium ion on NaY has little influence on the chemical structure of zeolites framework.

3. Results and discussion

3.1. Characterization

To observe clear process-structure-function relationship, the non-functionalized PI membranes and functionalized zeolites/PI MMMs adsorbents have been characterized by FT-IR, morphology, thermal and mechanical properties.

3.1.1. FT-IR analysis

FT-IR spectra of raw PI and zeolites/PI MMMs adsorbents are shown in Fig. 3. For the raw PI membranes, the band at 1774 cm⁻¹ (characteristic imido II band) and 1717 cm⁻¹ (characteristic imido III band) corresponds to the symmetrical and asymmetrical stretching vibrations of the two C=O groups at five-membered imine ring, respectively. The band at 1368 cm⁻¹ can be assigned 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. From the spectra of zeolites/PI MMMs adsorbents, all characteristic imido bands are retained. By the comparative analysis, a new kind of peak appears at 990–1010 cm⁻¹ for the MMMs adsorbents, which corresponds to the stretching vibrations of the zeolites structure framework (as seen in Fig. 2). From Fig. 3, the intensity of zeolites characteristic peak increases with the increasing zeolites content in MMMs adsorbents.

3.1.2. Morphology analysis

For the membrane adsorption process, it is obvious that the morphology strongly affects the transport properties of small molecules

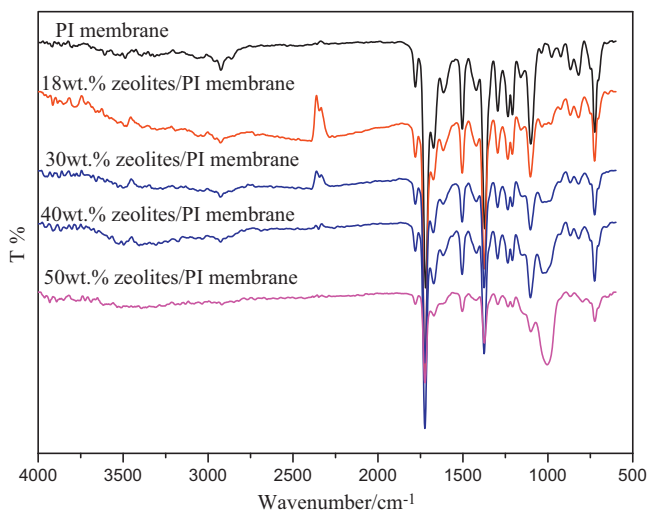


Fig. 3. FT-IR spectra of raw PI and zeolites/PI MMMs adsorbents.

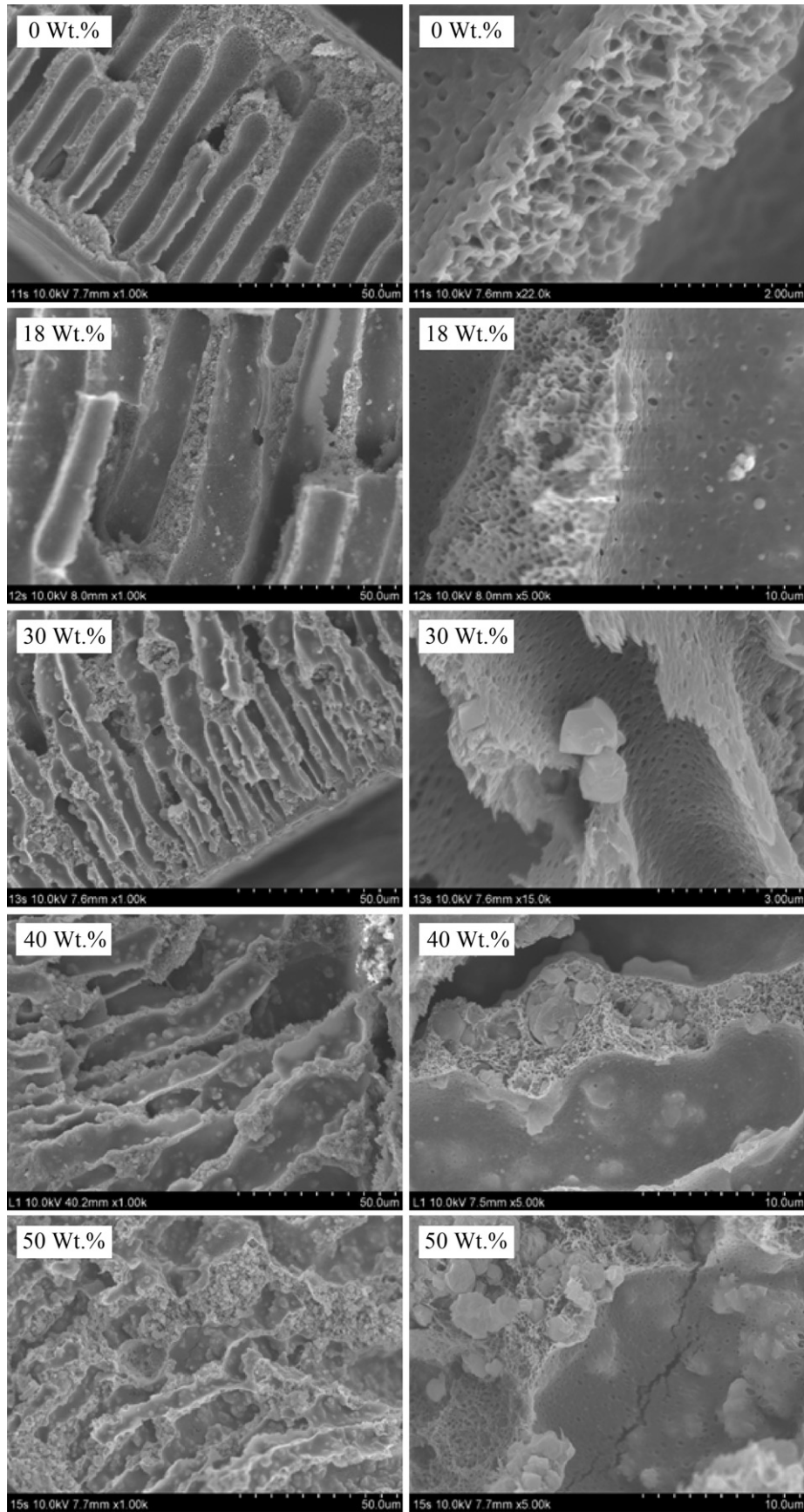


Fig. 4. FESEM images of cross-sections of raw PI and zeolites/PI MMMs adsorbents: (1) 0 wt.%, (2) 18 wt.%, (3) 30 wt.%, (3) 40 wt.%, and (5) 50 wt.% taken at various magnification.

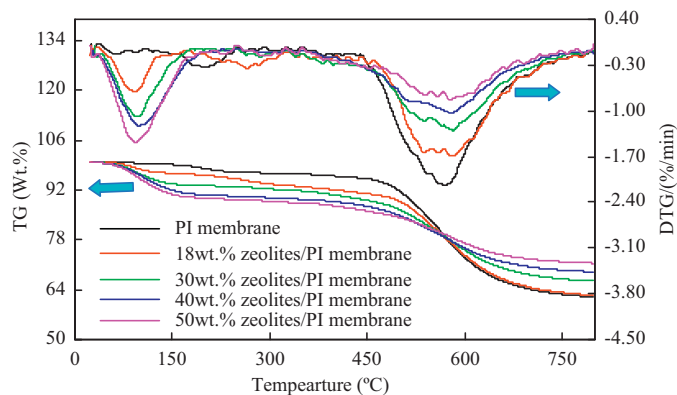


Fig. 5. Thermal degradation of raw PI and zeolites/PI MMMs adsorbents.

in MMMs adsorbents. The cross-section morphology at various magnifications of raw PI and zeolites/PI MMMs adsorbents have been observed, and the FESEM images are shown in Fig. 4.

The FESEM images in Fig. 4 show that raw PI membranes as well as the MMMs adsorbents have abundant finger-like and sponge-like pores, which is sound structure to ensure the contact between the incorporated zeolites particles and liquid fuel flowed through. From the MMMs adsorbents images in Fig. 4, the zeolites particles are dispersed and incorporated in the polymer matrix, and the particles tend to be re-agglomerated when the filling amount of zeolites in MMMs adsorbents is increased.

Obvious changes can be seen from the images of MMMs adsorbents with the increasing zeolites content. The finger-like pores become fewer and irregular, especially when the zeolites content comes to 50%. At 50% of zeolites content, part of the molecular interface and network between the polymer and particles becomes disconnected, even defect has appeared, which means the poor mechanical strength and practical applicability. Distributing filler particles into three-dimensional network structure throughout the MMMs adsorbents is a key factor to achieve outstanding separation properties. From FESEM images it is concluded that MMMs adsorbents with 40% of zeolites content possess better conditions. This will be further proven by practical performance investigation as well as mechanical strength and thermo stability analysis.

3.1.3. Thermal properties analysis of MMMs adsorbents

The thermal properties of raw PI and zeolites/PI MMMs adsorbents were characterized by TGA analysis, and the results are illustrated in Fig. 5.

From Fig. 5, the weight loss (TG) and derivative weight loss (DTG) curves of raw PI membrane shows one major weight loss at 570.6 °C, corresponding to the thermal decomposition temperature. For MMMs adsorbents with various zeolites contents, two peaks appear. They are 92.7 °C and 577.3 °C for 18 wt.% hybrid membrane, 96.1 °C and 582.3 °C for 30 wt.% hybrid membrane, 98.7 °C and 581.1 °C for 40 wt.% hybrid membrane, 93.9 °C and 577.1 °C for 50 wt.% hybrid membrane, respectively. The weight loss at about 92–99 °C is attributable to the desorption of the adsorbed water in zeolites, and the values of the weight loss (3.47%, 7.19%, 10.04%, 10.67%) increases with the increasing zeolites content (18 wt.%, 30 wt.%, 40 wt.%, 50 wt.%) in MMMs adsorbents. The above conclusion verifies more zeolites particles existed in MMMs network with higher zeolites content, which is in good accordance with the FT-IR analysis (Fig. 3) as well as the FESEM images (Fig. 4).

It is obvious from Fig. 5 that the thermal decomposition temperatures of MMMs adsorbents (except for the membranes with 50 wt.% zeolites content) are higher than that of raw PI membrane. The interaction between organic PI material and inorganic zeolites restricts the thermal motion of polymer, and increases the needed

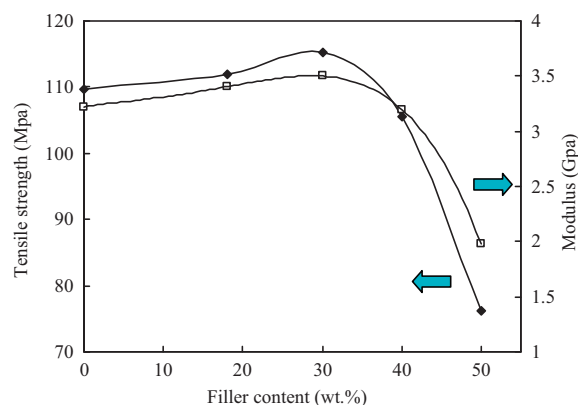


Fig. 6. Effect of content of incorporated zeolites on the mechanical properties of MMMs adsorbents.

energy for the movement and segmentation of polymer chains, which enhances the thermal stability of membranes. However, the MMMs adsorbents with 50 wt.% of zeolites content have lower decomposition temperature than raw PI and other MMMs adsorbents. As mentioned during FESEM analysis, overmuch inorganic particles in polymer tend to agglomerate, which can not assure the effective inorganic/organic interfacial binding, even defect has appeared.

3.1.4. Mechanical properties of MMMs adsorbents

The effect of content of incorporated zeolites on the tensile properties of MMMs adsorbents is shown in Fig. 6.

As shown in Fig. 6, it can be observed that both the tensile strength and modulus of MMMs adsorbents increased first and declined then with the increasing contents of incorporated particles. Obviously, the addition of inorganic particles enhanced the mechanical strength of the MMMs adsorbents within certain range. However, the strength of the MMMs adsorbents decreased significantly when the content of incorporated particles is 50%. When the content of incorporated particles is at lower level, the polymer is the main composition part of the hybrid membrane, and the zeolites particles can be incorporated into polyimide membrane matrix very well, which assured the sound interfacial behavior of inorganic/organic phase. When the content of incorporated particles come to 50%, the interfacial defects between inorganic particles and polymer appear, which brought the significant negative influence on the tensile strength of the prepared MMMs adsorbents. The conclusion corresponds to the discussions on morphology and thermal properties analysis.

In summary, the MMMs adsorbents with 40 wt.% of filling content, which incorporate abundant zeolites particles, show sound morphology, thermal and mechanical properties. During the following performance research, MMMs adsorbents with 40 wt.% of zeolites content are used if no special clarification.

3.2. Adsorption studies

Detailed adsorption studies have been carried out on the prepared MMMs adsorbents to discuss their adsorption behavior. The schematic diagram of membrane adsorption process is shown in Fig. 7. The functional particles are incorporated into the three-dimensional network structure. When the liquid fuel passes through the interconnected pores, the sulfur compounds are adsorbed onto the surface of functional particles and polymer pores, hence the desulfurization realizes. The effects of post-treatment, content of incorporated zeolites, adsorption time,

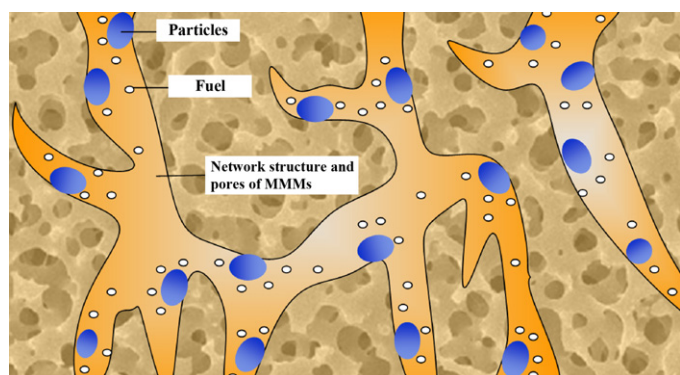


Fig. 7. The schematic diagram of membrane adsorption process.

temperature, initial sulfur concentration as well as sulfur species type on the adsorption performance will be investigated.

3.2.1. Effect of post-treatment of MMMs adsorbents on adsorption performance

As illustrated in the flow diagram for MMMs adsorbents preparation procedure, the post-treatment of MMMs adsorbents needs to be carried out before performance investigation. Table 1 shows the effect of post-treatment of MMMs adsorbents on adsorption performance. The experiments were conducted at 25 °C with model fuel (thiophene and n-heptane) feed. MMMs adsorbents with 40 wt.% AgY content were used as representative samples. The MMMs adsorbents were first post-treated by ethanol solvent, and then baked. The specific conditions of post-treatment are listed in Table 1.

From Table 1, the post-treatment of MMMs adsorbents can increase the adsorption capacity effectively. Under subsequent baking post-treatment at 90 °C, the solvent post-treatment increases adsorption performance of MMMs adsorbents significantly. It can be seen from Table 1 that the adsorption capacity obtains obvious increase through baking post-treatment at 250 °C. In fact, during the preparation process of MMMs adsorbents, the coagulation bath is water, which is usually unfavorable for the adsorption. The adsorbed water and intercalated water within zeolites pores can occupy the available surface for adsorption, even hinder the entrance of sulfur compounds into zeolites pores. Solvent post-treatment can replace and remove part of adsorbed water, while most of the intercalated water within zeolites needs to be expelled by baking post-treatment at higher temperature.

The baking post-treatment requires the MMMs adsorbents to be thermal-resistant, which is one of the reasons why PI is used

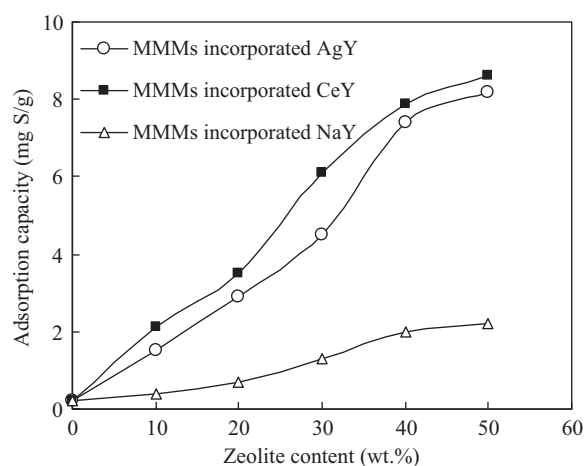


Fig. 9. Effect of the content of incorporated zeolites on adsorption capacity of MMMs adsorbents.

as matrix material in this research. It is well known that PI has excellent thermal resistance, which has also been verified by the thermal properties analysis in Section 3.1.3. It is noteworthy that the microscopic morphology of MMMs adsorbents through baking post-treatment at 250 °C remains regular without collapse structure, as is shown in Fig. 8.

3.2.2. Effect of content of incorporated zeolites on adsorption performance

The zeolites particles are the functional particles which were used to remove the sulfur compounds from liquid fuel by adsorption. Fig. 9 presents the effect of the content of incorporated zeolites (NaY, AgY and CeY) on the adsorption capacity of MMMs adsorbents. The experiments were conducted at 25 °C with 500 mg/L of initial sulfur concentration.

From Fig. 9, it can be seen that the adsorption capacity of the MMMs adsorbents increases with the increasing content of various incorporated zeolites particles. Obviously, more zeolites particles meant more contact area of sulfur compounds to them, hence higher adsorption performance. Considering the practicability, it is not suggested to adopt higher content of incorporated particles since they can bring negative influence on the mechanical strength of MMMs adsorbents, as is mentioned in Section 3.1.4.

From Fig. 9, when the content of incorporated zeolites is 40%, the corresponding adsorption capacity for NaY/PI, AgY/PI and CeY/PI MMMs adsorbents come to 2.0, 7.5 and 7.9 mg S/g, respectively. The results indicated that the adsorption performance of functional

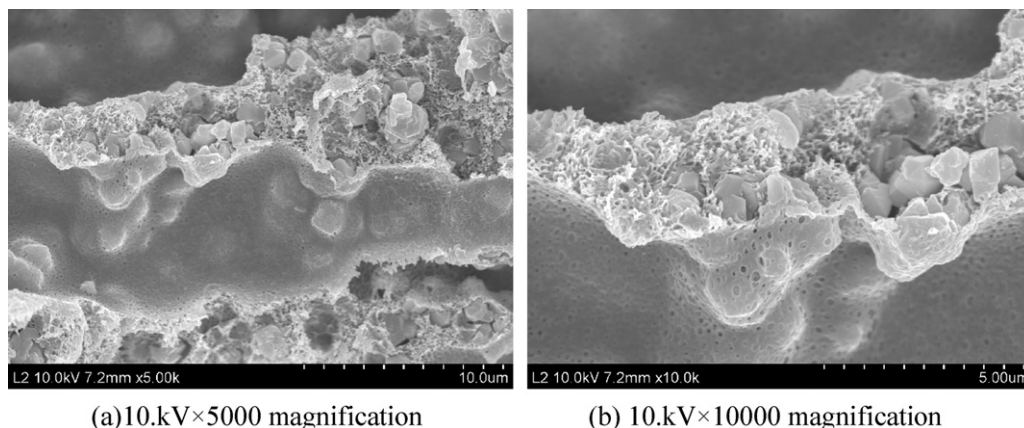


Fig. 8. Cross-section of MMMs adsorbents through baking post-treatment at 250 °C.

Table 1
The effect of post-treatment of MMMs adsorbents on adsorption performance.

Solvent post-treatment		Baking post-treatment		Adsorption capacity (mg S/g)
Whether or not	Time (h)	Baking temperature (°C)	Time (h)	
No	–	90	12	0.9
Yes	4	90	12	3.6
No	–	250	4	7.5
Yes	4	250	4	7.6

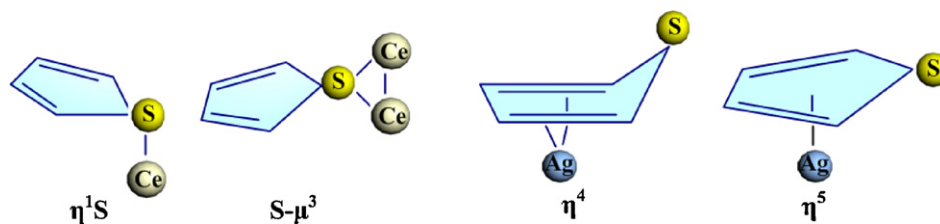


Fig. 10. Known adsorption configurations of thiophenic compounds with metal species on the surface of zeolites.

Table 2
Adsorption performance comparison for zeolites and membranes.

	PI membranes	AgY/PI MMMs adsorbents	AgY
Adsorption capacity (mg S/g membrane)	0.2	7.5	–
Adsorption capacity (mg S/g zeolites)	–	18.8	21.6

particles has been increased significantly through silver and cerium ion-exchange modification on NaY zeolites.

The distinct adsorption performance of MMMs adsorbents with various functional zeolites was markedly related with the binding force between sulfur compounds and the functional particles. For NaY, desulfurization relies on the physical adsorption of zeolites pore channels, which bind with sulfur by weak Van der Waals force. That weak binding causes low adsorption selectivity for sulfur, hence the low desulfurization performance. However, for the ion-exchange modified AgY and CeY zeolites, the adsorption mechanism is different. In fact, 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. As is shown in Fig. 10, thiophene can act either as an n-type donor by donating the lone pairs of electrons that lie in the plane of the ring to the adsorbent (direct S-M σ bond) or as a π -type donor by utilizing the delocalized π electrons of the aromatic ring (π bond) to form a π -type complex with the metal ions. Ag^+ can combine with thiophenic sulfur mainly by π bonds and form π -type complexes (η^4 or η^5 configurations), while Ce^{4+} prefers to combine by the direct σ bond ($\eta^1\text{S}$ or S- μ^3 configurations) [18]. Obviously, the strength follows the order: S-M coordination > π -complexation > Van der Waals force, which corresponds to the distinct adsorption performance for MMMs adsorbents with various functional zeolites.

It is interesting to discuss the adsorption contribution. Table 2 presents the performance comparison among AgY zeolites, AgY/PI MMMs adsorbents and PI membranes. From Table 2, compared with zeolites and MMMs adsorbents, PI membranes have lower adsorption capacity, which means that the sulfur adsorption performance of MMMs adsorbents mainly depends on the incorporated zeolites. The base PI membrane matrix contributes to the immobilization of zeolites and to the three-dimensional porous channel. Meanwhile, the theoretical adsorption capacity of AgY/PI MMMs adsorbents is 18.8 mg S/g zeolites, which is lower than the

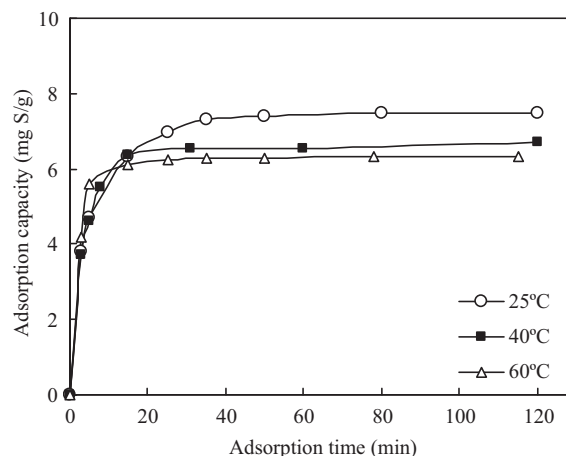


Fig. 11. The adsorption curves of MMMs adsorbents under various temperatures.


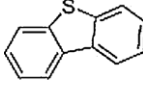
experimental value of AgY (21.6 mg S/g zeolites). In fact, for the MMMs adsorbents with 40 wt.% AgY content, part of the zeolites can be imbedded into the base membranes and be absent contact with the sulfur compounds. Therefore, the effective content of zeolites can not reach to 40 wt.%.

3.2.3. Effect of adsorption time

The adsorption curves of MMMs adsorbents under various temperatures are presented in Fig. 11. The experiments were conducted at 500 mg/L of initial sulfur concentration level of model fuel (thiophene and n-heptane). MMMs adsorbents with 40 wt.% AgY content were used as representative samples.

It is observed from Fig. 11 that the adsorption capacity of the MMMs adsorbents increases first and then tends to adsorption equilibrium with the increasing adsorption time. The thiophene adsorption was fast, and the adsorption equilibrium is achieved at 50 min, 31 min and 20 min under 25°C, 40°C and 60°C, respectively. The increased adsorption time means more sulfur compounds adsorbed onto MMMs adsorbents, hence the increasing adsorption capacity. At higher experiment temperature, the saturation adsorption capacity was lower, which is resulted from the thermodynamic adsorption process (intrinsic exothermic [19]) of thiophene species on functional zeolites incorporated in MMMs adsorbents.

Table 3
Adsorption performance comparison for different sulfur compounds.

Sulfur species	Structure	Charge on S atom	Feed type	Feed composition	Adsorption capacity (mg S/g)
Thiophene		-0.159	Model gasoline	Thiophene/n-heptane	7.5
Dibenzothiophene		-0.211	Model diesel	Dibenzothiophene/n-octane	8.3

3.2.4. Effect of initial sulfur concentration on desulfurization performance

Considering the various sulfur content level of worldwide refineries, Fig. 12 reveals the desulfurization performance of MMMs adsorbents under various initial sulfur concentrations. The experiments were conducted at 25 °C with model fuel (thiophene and n-heptane) feed. MMMs adsorbents with 40 wt.% AgY content were used as representative samples.

It is observed from Fig. 12 that the MMMs adsorbents can reduce the sulfur concentration to less than 1 mg/L for the fuel feed with 100 and 300 mg/L of initial sulfur concentration. At 80 min of adsorption time, the adsorption capacity of MMMs adsorbents under 500 and 1000 mg/L initial sulfur concentration was 7.5 and 9.0 mg S/g, respectively. Under same MMMs adsorbents amount and fuel volume, higher sulfur concentration in feed means easier touch of sulfur compounds with MMMs adsorbents than that under lower sulfur concentration, hence the different adsorption capacity at the same adsorption time.

3.2.5. Adsorption performance comparison for different sulfur compounds

Type of sulfur compounds in fuel is also important investigation subject for the desulfurization technology. Relevant research [20,21] reveals that primary sulfur species in gasoline and diesel fuel are thiophenic sulfur compounds. The main goal for desulfurization of liquid fuel is to remove the thiophene species. Table 3 shows the adsorption capacity of MMMs adsorbents for different sulfur species. The experiments were conducted at 25 °C with 500 mg/L initial sulfur concentration level. MMMs adsorbents with 40 wt.% AgY content were used as representative samples.

As depicted in Table 3, the adsorption capacity of MMMs adsorbents for dibenzothiophene is higher than that for thiophene, which

is consistent with the higher electron density of S atoms for dibenzothiophene. The results suggest that the MMMs adsorbents have higher desulfurization performance for diesel fuel. Based on molecular orbital calculations, Yang et al. [22] showed that the methyl groups in the substituted thiophenic compounds can enhance the electron back-donation process during π -complexation and, thus, results in higher energies of adsorption

3.3. Desorption studies

One of the challenging problems on adsorptive desulfurization is regeneration of the MMMs adsorbents. Generally, there are two techniques for regeneration of the adsorbent, the thermal treating and the solvent washing. In this study, desorption attempts have been conducted for MMMs adsorbents incorporated with various Y zeolites by solvent washing, which is convenient for on site operation during future scale-up of membrane adsorption process. There are some other advantages of solvent washing for the regeneration of spent MMMs adsorbents. On the one hand, regeneration by solvent washing is an environmentally benign method because it avoids the emissions of SO_x generated by oxidative regeneration or H_2S generated in the reductive regeneration [23]. On the other hand, the organic sulfur compounds can be recovered by separating them from the solvent and the concentrated sulfur compounds can be treated in small HDS reactors to remove sulfur and the remaining organic moiety can be blended with the fuel. The adsorption capacities of the regenerated MMMs adsorbents under various regeneration times are given in Fig. 13.

From Fig. 13, the adsorption capacity of the MMMs adsorbents decreases after the first regeneration, and then remains stable during the successive regenerations. Comparing with the fresh MMMs adsorbents, the spent membranes with incorporated AgY, CeY and NaY zeolites can recover about 90%, 70% and 98% of the desulfurization capacity, respectively. The desorption efficiency of MMMs adsorbents with typical Y zeolites follow the order:

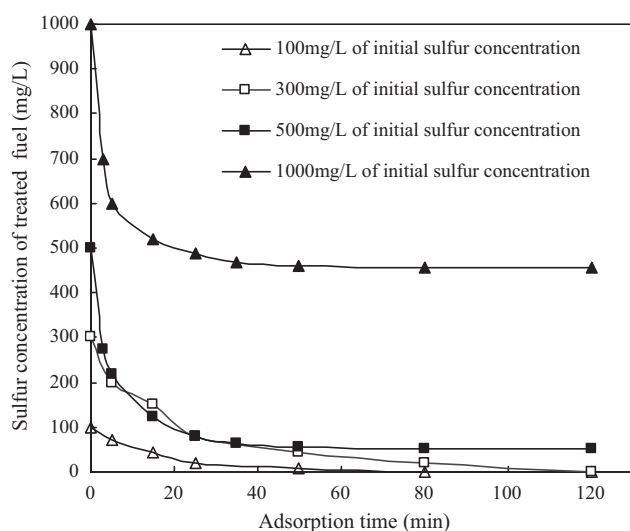


Fig. 12. Effect of initial sulfur concentration on desulfurization performance of MMMs adsorbents.

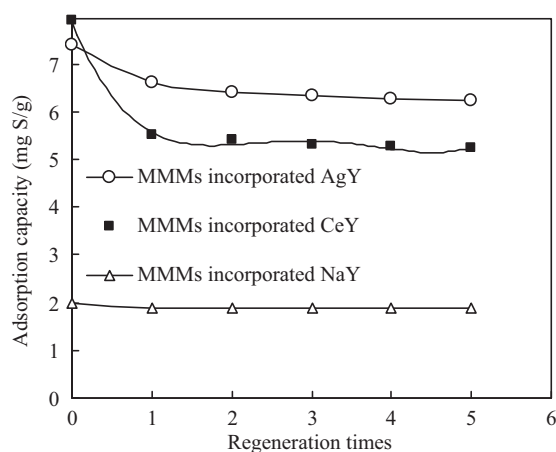


Fig. 13. Effect of regeneration times on the adsorption capacity of MMMs adsorbents.

NaY > AgY > CeY, which is the reverse as that found in adsorption capacity (Fig. 9). The different desorption efficiency of various zeolites can be explained in terms of the binding force between sulfur compounds and the incorporated zeolites. As discussed in Section 3.2.2, the strength of the binding force follows the order: S-M coordination > π -complexation > Van der Waals force. It is more difficult to break the stronger binding force, hence the more difficult desorption.

4. Conclusions

Sulfur removal from transportation fuels has gained increasing attentions. In current work, a novel membrane adsorption process was proposed for the sulfur removal from fuels. The MMMs adsorbents for desulfurization have been prepared using PI as matrix material and various Y zeolites as adsorptive functional materials. By the detailed characterization of FT-IR, microscopic structure morphology, thermal and mechanical properties of MMMs adsorbents, combining the adsorption and desorption behavior research, the process-structure-function relationship was discussed. From FESEM images it is concluded that MMMs adsorbents with 40% of zeolites content possess better conditions, which was confirmed by mechanical strength and thermo stability analysis. Influence factors including post-treatment, content of incorporated zeolites, adsorption time, temperature, initial sulfur concentration as well as sulfur species on the adsorption performance of MMMs adsorbents have been evaluated. The adsorption capacity of MMMs adsorbents increased with the increasing filling content and initial sulfur concentration as well as decreasing temperature. At 40 wt.% zeolites content, the adsorption capacity for NaY/PI, AgY/PI and CeY/PI MMMs adsorbents come to 2.0, 7.5 and 7.9 mg S/g. MMMs adsorbents have higher desulfurization performance for diesel fuel than that of gasoline. The regeneration results suggest that the spent membranes with incorporated AgY, CeY and NaY zeolites can recover about 90%, 70% and 98% of the desulfurization capacity, respectively. The distinct adsorption and desorption behavior of MMMs adsorbents with various functional zeolites was markedly related with their various binding force with sulfur compounds.

Acknowledgements

The authors acknowledge support of this work by National Natural Science Foundation of China (no. 21006070) and Tianjin Natural Science Foundation, China (nos. 11JCZDJC23700, 11JCZDJC21200). This project is also supported by Research Fund for the Doctoral Program of Higher Education (no. 20091201120002) and State Key Laboratory of Hollow Fiber Membrane Materials and Processes (Tianjin Polytechnic University).

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