Preparation and high CO$_2$/CH$_4$ selectivity of ZSM-5/Ethyl cellulose mixed matrix membranes

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Abstract

It is known that natural gas is extracted with a large amount of CO$_2$, which reduces the amount of heat generated during the combustion of natural gas. How to remove some of the CO$_2$ from the natural gas is a problem that needs to be solved. The significant breakthroughs of the membrane technology, specifically the mixed matrix membrane (MMM) has revealed a promising CO$_2$/CH$_4$ separation performance. In this study, a series of ZSM-5/EC mixed matrix membranes with ethyl cellulose (EC) as matrix and ZSM-5 as inorganic dispersant in tetrahydrofuran were prepared under high speed and ultrasonic vibration-assisted, the ZSM-5/EC membranes were fabricated by using the casting solution. The successful ZSM-5/EC mixed matrix membranes were confirmed by Fourier transfer infrared (FTIR) and Scanning electron microscopy (SEM). The ZSM-5/EC membranes exhibited good membrane forming ability, heat resistance and mechanical properties; The CO$_2$/CH$_4$ selectivity of the ZSM-5/EC membranes were 10.7, 15.4, 19.7, 25.5 and 11.7, respectively, increased up to 1.3, 1.9, 2.4, 3.1 and 1.4 times as compared to pure EC (8.20) with a feed composition of 50:50 for CO$_2$/CH$_4$.

Introduction

Membrane technology has emerged as a leading tool worldwide for effective CO$_2$ separation because of its well-known advantages, including high surface area, compact design, ease of maintenance, environmentally friendly nature, and cost-effectiveness [1]. Many different types of membranes such as polymeric [2], MOFs [3], carbon material [4, 5], zeolite [6] and MMMs [7–9] are synthesized for the separation of CO$_2$ from different gas mixtures. Inorganic fillers in mixed-matrix membranes improve gas permeability and/or selectivity, outperforming polymeric membranes. Combined with relatively economical and simple scaling-up compared to inorganic membranes, mixed-matrix membranes could potentially be a next-generation membrane concept for gas separation applications [10]. The high permeability and selectivity of MMMs by incorporating different types of fillers exhibit the best performance for CO$_2$ separation from natural gas [1]. In the past few years, Silica (SiO$_2$) nanoparticles were first functionalized using (3-aminopropyl) triethoxysilane (APTES) and then utilized as filler for the preparation of poly (ether-block-amide) (Pebax™-1074) based mixed-matrix membranes (MMMs). The permeation experiments exhibited that the incorporation of 12.5 wt% of amine-functionalized SiO$_2$ nanoparticles into the Pebax matrix raises the CO$_2$ permeability and ideal CO$_2$/CH$_4$ selectivity about 100 and 32%, respectively [11]. Combination of the polyimide 6FDA-mPD (6FDA = 4,4′-hexafluoroisopropylidene diphthalic anhydride and mPD = m-phenylenediamine) and crystallites of the metal-organic frameworks (MOFs) MIL-101(Cr) or MOF-199 (HKUST-1, Cu-BTC) produces mixed-matrix membranes (MMMs) with excellent dispersion and compatibility of the MOF particles within the polymer matrix. Permeation tests of a
binary CO$_2$/CH$_4$ (50/50) gas mixture showed a remarkable increase of CO$_2$ permeabilities for MIL-101(Cr) @6FDA-mPD and significantly higher selectivities for MOF-199@6FDA-mPD [12].

Nevertheless, it is still a big challenge to resolve the weak interaction between fillers and the polymer phase, which will weaken the mechanical strength and long-term separation performance of MMMs. This problem has improved well now. Functionalized UiO-66 MOF particles were covalently grafted with hydride-terminated polydimethylsiloxane (PDMS) via postsynthetic modification (PSM). These PDMS-coated MOF particles (termed here ‘corona-MOF’) were used in the preparation of mixed matrix membranes (MMMs). The PDMS MMMs showed distinct separation features in a single-gas permeation test, displaying much higher CO$_2$ gas permeation with no decrease in selectivity when compared to MMMs prepared with unmodified UiO-66 particles [13]. Hybrid Polymer/Metal Organic Framework (MOF) membranes were prepared by in situ growth (ISG) of HKUST-1 within the pores of polyimide membranes. To improve the performances of ISG membranes, chemical modification was performed. Aryl carboxylic acid moieties were introduced to polyimide P84 ultrafiltration membranes allowing coordination of the HKUST-1 directly on to the polymer. Chemically modified ISG membranes outperformed non-modified [14].

Ethyl cellulose (EC) has a pivotal position in gas separation due to its complete source [15], low price [16], easy film formation [17] and good gas separation performance [18, 19]. To improve the gas separation performance of pure EC membranes, the group previously studied the composite modification of ethyl cellulose by the ionic liquid 1-allyl-3-methylimidazolium tetrafluoroborate. The membrane separation of carbon dioxide and nitrogen, compared with pure ethyl cellulose membranes, the permeability of carbon dioxide and the separation coefficient of the two were greatly improved [20]; Then studied the ethyl cellulose graft ionic liquid Gas separation membranes with a PCO$_2$/PCH$_4$ of 18.8 (9 for pure EC) and a PCO$_2$ of 198.9 Barrer (46.8 Barrer for pure EC membrane). In contrast, the environmental life of the membranes was significantly improved [20].

Solvents and dissolution in general, have been an integral part of numerous industries for hundreds of years. Particularly in the chemical industries, solvents are important auxiliaries in processes, and most of the manufacturing methods require various kinds of solvents [21]. With the development of time, the use of green solvents is becoming more widespread. Dimethyl isosorbide (DMI) a well-known biobased high boiling green solvent was used for the first time in the preparation of poly(vinylidene fluoride) and poly(ether sulfone)-based membranes. The membranes revealed different structures and a tunable pore size in the range of ultrafiltration (UF) and microfiltration (MF) that render them ideal for applications in water treatment processes [22]. S Park and A Alammar have reported high-performance TFC membranes fabricated solely from sustainable resources such as plant-based monomers (priamine, tannic acid), green solvents (p-Cymene, water) and recycled polymer waste (PET). They found that control over the selectivity of the membrane (cut-off between 236 and 795 g mol$^{-1}$ at 80:20. This is different from the purity and type of ethyl cellulose used in the literature, resulting in a certain deviation from the literature. Toluene and isopropanol are not plasticizers. ZSM-5 was purchased from Suzhou Zhiting New Material Technology Co., Ltd. ZSM-5 molecular sieve is pure silicon type, and the average pore size of the ZSM-5 molecular sieve is 0.5 A. The

2. Experimental section

2.1. Materials

Ethyl cellulose (EC) was purchased from Shanghai Darui Fine Chemicals Co., Ltd. The ethyl cellulose we used was 45–55 MPa.s, purity 95%, and contains 5% toluene/isopropanol = 80:20. This is different from the purity and type of ethyl cellulose used in the literature, resulting in a certain deviation from the literature. Toluene and isopropanol are not plasticizers. ZSM-5 was purchased from Suzhou Zhiting New Material Technology Co., Ltd. ZSM-5 molecular sieve is pure silicon type, and the average pore size of the ZSM-5 molecular sieve is 0.5 A. The
purity of ZSM-5 molecular sieve is 99%. Tetrahydrofuran (THF) of analytically pure was purchased from Tianjin Kaitong Chemical Reagent Co., Ltd. The purity of THF is 98%, and was employed after distillation. H₂ and CO₂/CH₄ mixtures were purchased from Daqing Xuelong Petrochemical Technology Development Co., Ltd.

2.2. Preparation of ZSM-5/EC mixed matrix membranes

Ethyl cellulose (1.8 g) was placed in a flask and dissolved in THF (20 ml) at room temperature under high speed and ultrasonic vibration-assisted. ZSM-5 of various qualities (contents: 1%, 18.2 mg; 3%, 55.7 mg; 5%, 94.7 mg; 8%, 156.5 mg; 10%, 200.0 mg) was dispersed into THF by ultrasonic vibration-assisted for 1 h, and then it was added the ethyl cellulose solution, followed under high speed and ultrasonic vibration-assisted for 2 h to get a uniformly mixed casting solution. The uniformly mixed casting solution was filtered by 200 mesh filter and then spread on clean glass plates and evaporating solvents at room temperature. Finally, the obtained homogeneous membranes (recorded as: EC-ZSM1, EC-ZSM3, EC-ZSM5, EC-ZSM8, EC-ZSM10) were dried under vacuum at 25 °C for 12 h.

2.3. Characterization of the membranes

Infrared spectra were recorded on a Fourier transform infrared spectrometer (Spectrum Two, PE company, Waltham, Massachusetts, USA). SEM analysis has also been performed to determine the surface morphology of pure EC and ZSM-5/EC mixed matrix membranes. Membranes have been cracked in liquid nitrogen and sputtered with the small layer of gold. After that, these membranes have been analyzed by scanning electron microscope (JSM-6490, JOEL Japan) at the distance of 10 mm and current of 90 mA.

2.4. Thermal properties analysis

The thermogravimetric analyzer (Q5000IRS type, American TA Co., Ltd) was used to test the thermal performance of the pure EC membrane and the mixed matrix membranes. During the test, the membranes were heated to 600 °C, and the temperature change when ZSM-5 molecular sieve was added to decompose 5% is analyzed. And the change of the membranes in residual quantity at 600 °C.

2.5. Mechanical properties analysis

A membrane tensile testing machine (CH-1-B hand-type, China Jinan Sanquan Zhongshi Experimental Instrument Co., Ltd) was used to test the mechanical properties of the membranes. The thickness of the membranes were measured by a thickness gauge (thickness gauge was purchased from Shanghai Liuling Instrument Factory, model was CH-1-B hand-type millimeter thickness gauge, the graduation value was 0.001 mm, the measurement range was 0–1 mm, the error was about ± 0.007 mm).

2.6. Gas separation

The test of mixed gas permeation was measured a differential pressure gas transmission instrument (GTR-11MH type, GTR TEC Corporation, Kyoto, Japan; the test area was 0.785 cm². The instrument test temperature was 34 °C, and the test pressure was maintained at 49 KPa, the content of the mixed gas was the same, the test pressure was 0.1 MPa. The carrier gas was H₂, and the pressure was 0.5 MPa). The permeability coefficients of the mixed gases were measured by gas chromatographic method using the differential pressure gas transmission instrument (GTR-11MH type), and the gas permeability coefficient P was calculated by the following relation (1) [20]:

\[ P = \frac{q \times K \times \frac{1}{a \times p \times t}}{(\text{ml} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1})} \]  \hspace{1cm} (1)

where, q is transmission volume (ml), K is auxiliary positive coefficient (the fixed value is 2), it is the setting point instrument by factory, L is film thickness (cm), p is permeability pressure (cmHg), t is measurement time (s) and a is the area of the gas permeation film (the fixed value is 0.785 cm²).

In this experiment, the gas separation factor was calculated by the following relation (2) [20]:

\[ \alpha = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \] \hspace{1cm} (2)

where \(P_{\text{CO}_2}\) and \(P_{\text{CH}_4}\) correspond to single gas CO₂ and CH₄, them can be calculated from equation (1).
3. Results and discussion

3.1. Characterization of the EC and ZSM-5/EC membranes

FTIR was used to determine the molecular structure of ZSM-5, pure EC membrane and ZSM-5/EC mixed matrix membranes. As shown in figure 1, all the mixed matrix membranes show the wagging vibrational peak of the T-O-T (T is Si) of the ZSM-5 appeared at 801 cm$^{-1}$, and the vibration absorption peak of the five-member ring structure in the 552 cm$^{-1}$ was also observed. The above-infrared absorption peaks are more potent with the increase of the doping content of the ZSM-5. Simultaneously, the –OH peak at 3474 cm$^{-1}$ broadened with the addition of ZSM-5 and shifted to the lower frequency band. Because –OH group in ZSM-5 and –OH group in ethyl cellulose passed hydrogen bonds are connected. Therefore, it can be considered that the mixed matrix membranes contain ZSM-5.

The membrane morphology of hybrid membranes was investigated in detail, and figure 2 presents the optical picture of pure EC membrane and ZSM-5/EC mixed matrix membranes. As shown in figure 2, pure EC membrane is colourless and transparent, with the increase of ZSM-5, the transparency of the mixed matrix membranes become lower and lower, which is caused by the blocking of ZSM-5. The mixed matrix membranes show the same excellent flexibility as the pure EC membrane and repeatedly curled without deformation and breakage.

To further observe the distribution of ZSM-5 in the mixed matrix membranes, the study of morphology of membranes were investigated by SEM analysis. Figure 3 shows the surface morphology of (a) pure EC membrane, (EC-ZSM1(b), EC-ZSM3(c), EC-ZSM5(d), EC-ZSM8(e), EC-ZSM10(f)) ZSM-5/EC mixed matrix membranes. According to figure 3, the surface of pure EC membrane is dense and flat; at the content of ZSM-5 of 1% (figure 3(b)) and 3% (figure 3(c)), there is no apparent difference between the mixed matrix membranes and pure EC membrane, and the surface of the membrane is dense and flat; the presence of ZSM-5 of 5% (figure 3(d)) can be seen in the mixed matrix membranes, which is evenly dispersed in the EC matrix, while the particle size is small and homogeneous. The ZSM-5 can be seen in the mixed matrix membranes with the content of 8% (figure 3(e)) and 10% (figure 3(f)) of ZSM-5, the overall increase in particle size. With the increase of the ZSM-5 content, the presence of the become more and more apparent, but still uniform distribution with no agglomeration phenomenon, indicating that the experiment using high-speed stirring assisted by ultrasonic oscillation method can get a homogeneously mixed matrix membranes of EC doped ZSM-5 [27, 28].

In the cross-sectional SEM images of ZSM-5/EC membranes (figure 4), the bright point and continual area with some bright lines are the stacking ZSM-5 sheets with wrinkles on them. These phenomena can be observed more clearly from cross-section image. And these phenomena can indicate the uniform distribution of ZSM-5 in the mixed matrix membranes [28].

![Figure 1. FT-IR spectra of ZSM-5, pure EC membrane and ZSM-5/EC membranes.](image)
Figure 2. The optical photos of pure EC membrane (a) and ZSM-5/EC mixed matrix membranes (EC-ZSM1 (b), EC-ZSM3 (c), EC-ZSM5 (d), EC-ZSM8 (e), EC-ZSM10 (f)).

Figure 3. The surface SEM images of pure EC membrane (a) and ZSM-5/EC mixed matrix membranes (EC-ZSM1 (b), EC-ZSM3 (c), EC-ZSM5 (d), EC-ZSM8 (e), EC-ZSM10 (f)).
3.2. Thermal properties analysis of the pure EC membrane and ZSM-5/EC mixed matrix membranes

Thermogravimetric analysis curves of the pure EC membrane and the ZSM-5/EC mixed matrix membranes are presented in figure 5(a) corresponded to the full graph from the starting temperature of room temperature to 600 °C, and figure 5(b) corresponded the enlarged graph from 375 °C to 600 °C. The experimental results show that the shape of the whole weight loss curves of pure EC membrane and ZSM-5/EC mixed matrix membranes is very similar, while the difference is that the temperature of mixed matrix membrane at 5% weight loss (324 °C–327 °C) is slightly higher than that of pure EC membrane (322 °C); after 380 °C, with the increase of the doping amount of ZSM-5, the residual amount in mixed matrix membrane is increased. This phenomenon due to the good thermal stability of ZSM-5, which doesn’t
break and tensile strength of the mixed matrix membranes decreased when the doping of ZSM-5 exceeded 5%.

3.4. Gas separation properties of membranes
The prepared ZSM-5 mixed matrix membranes was tested for the separation performance of CO2 and CH4 mixed gas with a mixing ratio of 1:1. The influence of ZSM-5 doping amount on the permeation of CO2 and CH4 as the doping amount of ZSM-5 increases is presented in figure 5. According to the figure 5, the permeation of both gases continued to decrease with the increase of the loading content of ZSM-5, compared to the pure EC membrane; but the decrease of CH4 was higher than that of CO2. The gas permeability reached a minimum when the ZSM-5 loading was 8% and then increased simultaneously. This phenomenon may be because the introduction of ZSM-5 blocked the gas channels in the original EC membrane, causing the CO2 and CH4 permeation to drop to a certain extent; especially for CH4 with large molecular size. When the doping amount of ZSM-5 exceeds 8%, the permeation amounts of CO2 and CH4 increase, which might be due to the defects between the ZSM-5 and polymer chains caused by the high content of ZSM-5 in the mixed matrix membrane. Therefore, the amount of CO2, CH4 permeation increases and the separation coefficient decreases [33, 34].

However, with the increase of ZSM-5 loading, its separation performance has increased significantly. When loading content is 8%, the separation factor of CO2 and CH4 reaches the highest value (PCO2/PCH4 = 25.5), which is 3.12 times of pure EC membrane (PCO2/PCH4 = 8.2), as shown in figure 6. This phenomenon may be that although the added ZSM-5 blocks its gas paths to a certain extent, the reduction of the gas paths makes CO2 with a smaller molecular size have a higher gas permeability than CH4 with a larger molecular size, so the separation factor of CO2/CH4 has been dramatically improved. The data is summarized, as shown in table 2. At the same time, the gas permeability performance of the prepared ZSM-5/EC mixed matrix membranes is consistent with the theoretical doping amount, during pyrolysis step, the EC and ZSM-5 were degraded to their constituent entities. The ash left at the end of test con...
compared with the Robeson Upper Bound (1991). As shown in figure 8, although it has not reached the Robeson Upper Bound (1991) [35], it has been very close, and the mixed matrix membranes with 1%, 3%, 5% and 8% ZSM-5 loading are better than pure EC membranes. In general, the prepared ZSM-5/EC mixed matrix membranes can make up for the shortcomings of the current commercial EC membranes that show insufficient separation coefficient during the separation of CO₂ and CH₄.

### Figure 6.
CO₂ permeability of pure EC membrane and ZSM-5/EC mixed-matrix membranes.

### Figure 7.
CO₂/CH₄ separation factor of pure EC membrane and ZSM-5/EC mixed-matrix membranes.

### Table 2.
CO₂ permeability and CO₂/CH₄ separation factor of pure EC membrane and ZSM-5/EC mixed-matrix membranes.

| Samples   | PCO₂(barrer) | PCH₄(barrer) | PCO₂/PCH₄ |
|-----------|--------------|--------------|-----------|
| EC        | 45.3 ± 2.3   | 5.5 ± 0.3    | 8.2 ± 0.3 |
| EC-ZSM1   | 42.6 ± 3.0   | 4.0 ± 0.3    | 10.7 ± 0.5|
| EC-ZSM3   | 36.9 ± 2.7   | 2.4 ± 0.2    | 15.4 ± 0.4|
| EC-ZSM5   | 27.6 ± 2.5   | 1.4 ± 0.1    | 19.7 ± 0.6|
| EC-ZSM8   | 15.3 ± 1.6   | 0.7 ± 0.06   | 25.5 ± 0.5|
| EC-ZSM10  | 16.5 ± 1.3   | 1.4 ± 0.08   | 11.7 ± 0.3|

Note:

* 1 barrer = \(10^{-10}\) cm³(STP) × cm × cm⁻² × s⁻¹ × cmHg⁻¹.
3.5. Drawbacks and limitations
The solvent used in this study is tetrahydrofuran, which is not a green solvent. This is contrary to the concept of green chemistry, and we will look for environmentally friendly green solvents in our future experiments.

The aging of gas separation membranes was not studied due to the epidemic, and we will add the relevant contents in our future work.

4. Conclusions
The elongation at break of ZSM-5/EC mixed matrix membranes with 1%, 3% were 22.36% and 24.53% and the tensile strength of ZSM-5/EC mixed matrix membranes with 1%, 3% were 47.58 MPa and 50.52 MPa. The elongation at break and tensile strength of ZSM-5/EC mixed matrix membranes with 1%, 3% were significantly better than the pure EC membrane (21.56%, 44.53 MPa). The mechanical property test showed that the elongation at break and tensile strength of the ZSM-5/EC mixed matrix membranes increased when the doping amount of ZSM-5 was low. The elongation at break and tensile strength of the ZSM-5/EC mixed matrix membranes with 5%, 8% and 10% were 11.23%, 7.56% and 4.16% and the tensile strength of ZSM-5/EC mixed matrix membranes with 5%, 8% and 10% were 35.23 MPa, 25.34 MPa, 19.26 MPa. The elongation at break and tensile strength of ZSM-5/EC mixed matrix membranes with 1%, 3% were significantly weaker than the pure EC membrane (21.56%, 44.53 MPa). The mechanical property test showed that with the doping amount of ZSM-5, the increase of the elongation at break and tensile strength of ZSM-5 showed a decrease. CO₂/CH₄ separation factor of ZSM-5/EC mixed matrix membranes with 1%, 3%, 5%, 8% and 10% were 10.7, 15.4, 19.7, 25.5 and 11.7 respectively. CO₂/CH₄ separation factor of ZSM-5/EC mixed matrix membranes were significantly better than the pure EC membrane (8.2). The gas separation performance showed that the addition of ZSM-5 improved the separation performance of CO₂/CH₄ in no small extent.

Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

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