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COMPOSITE SUPPORTED LIQUID MEMBRANE CONTAINING MIMIC ENZYME FOR CO_2 CAPTURE

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ABSTRACT

Current technologies for capturing carbon from flue gas are plagued by high capital, energy and chemical costs, etc. Here, we report a composite supported liquid membrane containing mimic enzyme that may provide a possible solution to these issues. This composite membrane has two highly permeable silicone layers which immobilize the mimic enzyme (Zn-cyclen complex) solution in the pores of a cellulose acetate nanofiltration membrane. The schematic is showed in Fig.1. The membrane couples the selectivity of liquid sorbents and energy-efficiency of membrane separation without absorbent regeneration unit. The prepared Zn-cyclen complex was characterized by ^{1}HNMR and dissociation constant (pKa). The contact angles of the cellulose acetate support membrane and the prepared composite membrane were tested. CO_2 separation performances of the membranes were studied in a plate-and-frame membrane module system. The membrane system presents a CO_2/N_2 selectivity of 94 and a CO_2 permeance of 1.33 [m^3 (STP)/(m^2 bar h)] with a very small amount of 0.0052 M mimic enzyme. This composite supported liquid membrane shows the advantages of low cost, simple production procedure and high CO_2 separation performance.

Keywords: CO_2 capture, Post combustion, Composite supported liquid membrane, Mimic enzyme, hydrophobic photopolymerizable silicone

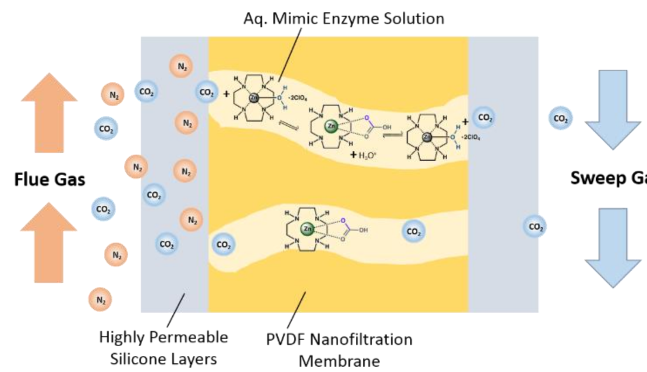

Fig. 1 Schematic of the composite supported liquid membrane separating CO_2.

1. INTRODUCTION

CO_2 capture from the flue gas of coal-fired power plants, which is one of the biggest carbon sources, is highly desirable. However, current systems have the drawbacks of high capital, energy and chemical costs [1, 2]. Membrane technology is well recognized to be environmentally friendly and less energy intensive. But it has a very small share in the market because of the high cost and the performance bounded by the Robeson limit (Permeability must be sacrificed for selectivity and vice versa) [3].

The liquid membrane system facilitated by immobilized carbonic anhydrase (CA) shows a dramatic increase in CO_2 selectivity over other gases, meanwhile, maintains high permeance [4, 5]. CA was found from mammal body to catalyze hydration of CO_2 fast and reversibly with minimal heat of reaction. While the enzyme's inactivation and instability are the major drawbacks of this type of membrane.

The enzyme inspired complexes of zinc (II) and other metals have been reported to mimic the activity and the catalytic mechanism of CA [6-8]. These mimic enzyme are cost-effective and more durable/stable at drastic conditions. A mimic enzyme promoted facilitated transport membrane for CO_2 capture was developed by Saeed and Deng [9]. A CO_2 permeance of 0.69 [m^3(STP)/(m^2 bar h)]and a CO_2/N_2 selectivity of 107 were reported with the catalysis of Zn-cyclen mimic enzyme. However, there must be abundant water in contact with CO_2 for the hydration of CO_2 in the system, in which the mimic enzyme functioning as a catalyst. Later they added carbon nanotubes into PVA-mimic enzyme membrane layer to enhance the hydration of CO_2 [10]. CO_2 permeance and CO_2/N_2 selectivity was increased by 30% and 15%, respectively. However, there is still a great potential to improve the CO_2 separation performance. Because the zinc containing enzyme can hydrate CO_2 in unprecedented rate ($K_{cat}=10^6\ s^{-1}$) [11].

Here we report a composite supported liquid membrane containing Zn-cyclen complex mimic enzyme for CO_2 capture from flue gas. This composite membrane has two highly permeable silicone layers which immobilize the mimic enzyme solution in the pores of a cellulose acetate nanofiltration membrane. The hydrophobic silicone can prevent the loss of carrier solution, meanwhile, keep sufficient water inside the membrane system for CO_2 hydration. The Zn-cyclen complex was selected as the mimic enzyme because of its small molecular structure, low reaction heat, high hydrophily and kinetic rate constant [7]. The Zn-cyclen complex was characterized by ^{1}HNMR and dissociation constant (pKa). The contact angles of the cellulose acetate membrane and the prepared composite membrane were tested. CO_2 permeance and selectivity were studied in a plate-and-frame membrane module system.

2. EXPERIMENTAL

2.1 Synthesis and Characterization of Zn-cyclen mimic enzyme

The preparation method of Zn-cyclen is according to the procedure described by Zhang, et al. [12]. Macrocyclic scaffold of aneN4 and $Zn(ClO_4)_2 \cdot 6H_2O$ were mixed and heated in ethanol solution. The product of Zn-cyclen was precipitated and collected after the reaction. The prepared Zn-cyclen was verified with ^{1}H NMR (Advance 400, Bruker). The 1D ^{1}HNMR spectra of Zn-cyclen in D_2O were recorded at 25°C.

2.2 Dissociation experiment

Zn-cyclen complex is attached with OH^- to catalyze the hydration reaction of CO_2 [12]. In order to insure the mimic enzyme solution provides sufficient OH^- ions for Zn-cyclen complex, the acid base titration was performed with a potentiometric titration meter (ZDJ-5, Shanghai Leici Instrument Factory). 30g of the mimic enzyme aqueous solution with 10 mg Zn-cyclen was titrated by 0.1M NaOH solution at a rate of 0.2 ml/min. The titration procedure was controlled by the computer. The pKa values were calculated in the software as a pH at half- equivalence [13].

2.3 Membrane preparation

A hydrophilic cellulose acetate membrane (11107-47-N, Sartorius) was employed as the support to immobilize Zn-cyclen complex solution. The nominal pore size is 0.22 µm, the thickness is 80-100 µm. A hydrophobic photopolymerizable silicone (Semicosil® 949UV, Wacker) was coated over the two sides of cellulose acetate membrane as the protective layer. 0.0052 M Zn-cyclen complex solution was used as the solute. Its pH value was adjusted by 0.1 M NaOH solution. The cellulose acetate membrane was vacuum degassed for 2 h, then dipped into the Zn-cyclen complex solution for 24 h. The fully soaked cellulose acetate membrane was wiped with paper tissue very gently to remove the surplus Zn-cyclen complex solution on the membrane surfaces. At this stage, a hydrophobic photopolymerizable silicone was coated on two surface of the cellulose acetate membrane.

2.4 contact angle test

The hydrophilic cellulose acetate membrane and the prepared composite membrane with hydrophobic silicone were tested for water contact angles, employing an optical contact angle measurement instrument (Dataphysics OCA40 GmbH, Filderstadt) with the sessile drop method. Though this system allows for estimation of contact angles with 0.1° accuracy. The uncertainty up to ±5° were reported [14]. So five measurements for each sample were carried in this study to minimize experimental errors.

2.5 Permeation test

CO_2 separation tests of the membranes were performed in a plate-and-frame membrane module system. The membrane gas system was built according to the process described by Deng, et al. [15]. The gases of 12.5 vol.% CO_2 and balanced N_2 were from gas cylinders. A membrane was sandwiched between the permeate chamber and the feed gas chamber, supported by a plastic mesh (329238, EXPO·NET) and sealed with rubber O-rings. Both feed gas and sweep gas were saturated with water vapor by bubbling through water bottles. The flow rates were determined by the mass flow controllers. A counterbalance valve was used to adjust the pressure of the feed gas. The gas compositions at the outlets of the permeate chamber and the feed gas chamber were analyzed by a gas chromatograph (9790 Ⅲ, FuLi Analytical Instrument). The CO_2 permeant flux and selectivity were determined by measuring the CO_2 concentration at the two outlets of the membrane module. Sweep gas of He was fed on permeant side for better recording of fluxes and gas compositions. The gas permeance was defined as the flux divided by the partial pressure differences between the upstream and downstream of the membrane and presented in units of [m^3(STP)/(m^2 h bar)]. The selectivity was calculated from the permeance of CO_2 divided by the permeance of N_2.

3. RESULTS AND DISCUSSION

3.1 Characterization and evaluation of the mimic enzyme

The prepared Zn-cyclen complex was verified by ^{1}HNMR. The results agree well with the literatures [6]. The Zn-cyclen complex is split to be doublet, and the ligand alone is a singlet peak at 2.66 ppm.

In aq. Zn-cyclen complex solution, either water molecule or OH^- ion can be attached to Zn-cyclen complex. However, only OH^- attached Zn-cyclen is active for CO_2 hydration reaction. So the pH value of the aq. Zn-cyclen complex solution should be maintained to ensure a sufficient supply of OH^- ions. The dissociation constant (pKa) is defined as the pH value at which 90% of the mimic enzyme is attached with OH^- [9]. The potentiometric titration was performed to determine pKa. So the Zn-cyclen complex solution can afford sufficient OH^- ions when maintaining its pH value higher than the pKa value.

The curve of the Zn-cyclen complex solution titrated by NaOH is showed in Fig. 2. For a potentiometric titration measurement, the pKa value is usually determined graphically by considering the pH value at the half volume of titrant to correspond to an equivalence point [13]. The pKa is calculated to be 7.82 from Fig. 2, which agrees well with the literatures [10]. It shows the mimic enzyme solution must be maintained at the pH value higher than 7.9 to ensure the activation of the Zn-cyclen complex.

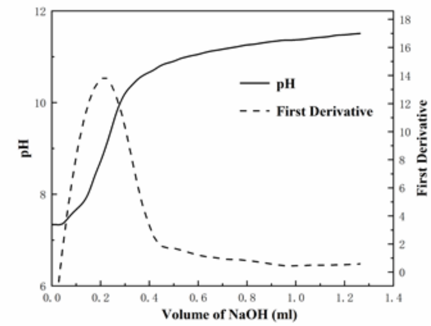

Fig. 2 Curve of Zn-cyclen complex solution titrated by NaOH.

3.2 Membrane preparation and contact angle test

This composite membrane has two highly permeable silicone layers which seals the Zn-cyclen complex solution in the pores of a cellulose acetate nanofiltration membrane. The pH value of Zn-cyclen complex solution was adjusted by 0.1 M NaOH solution to 9, at which Zn-cyclen complex solution shows a high CO_2 permeance and selectivity in the study of Saeed and Deng [9].

In this composite membrane system, the Zn-cyclen complex solution is filled in the pores of the cellulose acetate support membrane. The fully filled pores can prevent the other gases than CO_2 in the feed gas to permit though the membrane. So the hydroscopicity of the membrane is essential for the CO_2 selectivity. Meanwhile, abundant water is also prerequisite for the hydration reaction of CO_2. While the inverse property is required for two silicone layers coated. These two layers are supposed to seal the Zn-cyclen complex solution inside the pores. It prevents mem brane degradation by protecting the Zn-cyclen complex solution from the deactivation or entrainment with the gas stream. So the coated layers have to be hydrophobic to separate the solution and gas streams. The cellulose acetate membrane and the coated silicone layers were tested for the water contact angles. Their average contact angles are 46.7° and 113.9°. So the cellulose acetate membrane shows good hydrophily, and the silicone layer of the composite membrane is quite hydrophobic.

3.3 CO_2 permeance and selectivity

The CO_2 permeance and selectivity are the essential properties for the membrane gas separation system, which were tested in a plate-and-frame membrane module system. When the operating parameters are 100 ml/min flow rate of the feed gas, 200 ml/min flow rate of the sweep gas, 0.1 bar pressure of the feed gas and 0.0052 M concentration of the Zn-cyclen complex solution, the CO_2 permeance is 1.33 [m^3(STP)/(m^2 bar h)]. It is about half higher than the CO_2 permeance of the PVDF hollow fiber membrane with MEA absorbent solution [16], and 2 times higher than the CO_2 permeance of the hollow fiber liquid membrane containing CA solution [17]. Both of the CO_2 permeances were simulated and verified by experiments with a hollow fiber membrane module. The CO_2/N_2 selectivity is 94, which is close to the value in the study of Saeed and Deng [9].

A composite supported liquid membrane using PVDF membrane instead of cellulose acetate was studied as well. Its CO_2 permeance and selectivity are 1.28 [m^3(STP)/(m^2 bar h)] and 81, which both are lower than the membrane with cellulose acetate. This decrement might be caused by the different hydrophilia of two membranes, as the contact angle of the PVDF membrane is 56.8° higher than the cellulose acetate membrane of 46.7°. We speculate the cellulose acetate membrane pores are more fully filled by the mimic enzyme solution, which can obstruct N_2 flow.

4. CONCLUSIONS

We have demonstrated a novel composite supported liquid membrane containing mimic enzyme for CO_2 capture, which is mechanically robust, chemically stable, highly permeable, environmentally benign and cost efficient. The mimic enzyme is immobilized in the pores of a cellulose acetate nanofiltration membrane coated by two highly permeable silicone layers. This stable structure presents a high permeable CO_2 permeance of 1.33 [m^3(STP)/(m^2 bar h)] and a CO_2/N_2 selectivity is 94.

The composite membrane system shows potential for significant decreases in costs and energy penalties. The cellulose acetate membrane and silicone employed in our composite membrane are widely used in industries with low cost for filter and seal, respectively. With the addition of a very small amount of 0.0052 M mimic enzyme, the membrane system can separate CO_2 at a low pressure of 1-3 bar without an absorbent regeneration unit, which is reported to account for the majority of energy consumption for the leading technology of amine-based absorption.

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