The Implementation of a Carbon Precursor to Produce ZSM-5 Membranes for the Separation of Isomers in the Pervaporation System

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ABSTRACT: The separation of p-xylene from its bulkier m-xylene and o-xylene is of great importance in the petrochemical industry. This paper presents the experimental results of the separation of xylene isomers using a zeolite carbon composite membrane in a pervaporation system. The preparation method involves the use of an inexpensive carbon precursor, sucrose, to avoid the lengthy conventional preparation methods used in the literature (e.g., hydrothermal synthesis). The composite membranes that were prepared exhibited a separation performance with a p-xylene/o-xylene separation factor of 5.35 and permeability of 76 g/m² h for 95% o-xylene at 25 °C. The preparation procedure was designed from an economical perspective to facilitate any possible future commercialization.

1. INTRODUCTION

Obtaining a pure isomer is very important in the industrial production of polyethylene terephthalate, which is used mostly in the production of plastic bottles. The forms of xylene, that is, o-, m-, and p-xylene, are used as raw materials to produce phthalic anhydride, isophthalic acid, and terephthalic acid, respectively. Consequently, all of the isomers of xylene are used to produce plastics and rubber, and they also are used as additives to gasoline. Obtaining these substances with high levels of purity will enhance the efficiency of the process, thereby decreasing the associated costs. Table 1 shows that the xylene isomers, that is, p-xylene, m-xylene, and o-xylene, have similar boiling points, which makes it difficult to separate them by conventional methods. In a physical mixture, p-xylene is expected to permeate through a ZSM-5 membrane because its kinetic diameter is estimated to be 0.58 nm, while both m-xylene and o-xylene have kinetic diameters of 0.68 nm, which are larger than the 0.6 nm pores of ZSM-5. Therefore, this mixture is an excellent candidate for use in testing hydrophobic membranes, such as ZSM-5 zeolite membranes, in a pervaporation (PV) system. Because of the hydrophobic property and pore size of ZSM-5, it has been used extensively in organic separation processes. Conventional methods used to produce ZSM-5, that is, in situ and secondary growth procedures, are complex and require a long period of time because they involve the preparation of the synthesis gel solution. In this paper, a straightforward preparation method is used to produce ZSM-5 membranes for use in separating isomers. The preparation method was achieved by using a low-cost carbon precursor in the preparation process to block any defects, which is similar to the preparation approaches we reported in our previous work to synthesize zeolite A, mordenite, and clinoptilolite membranes. The results reported in this paper indicate that effective membranes were synthesized. This allows the production of ZSM-5 membranes without using the hydrothermal synthesis, which is replaced with the direct use of synthetic or natural zeolites.

2. RESULTS AND DISCUSSION

In order to examine the sustainability of the ZSM-5 structure during the conditions of the pyrolysis, ready-made zeolite powder was tested by X-ray diffraction (XRD) analysis (PANalytical, Empyrean XE) before and after exposure to these conditions. Figure 1 shows that there was a perfect match between the key peaks of the XRD patterns before and after pyrolysis, which confirmed the thermal stability of ZSM-5.

The scanning electron microscope (SEM), (JEOL, JSM-IT300) images, Figure 2, clearly show the zeolite crystals with significant quantity are deposited on the surface but no defined boundaries of the ZSM-5 layer are evident as it was expected to be internal with the support. Also, an electron-dispersive X-ray (EDX) spectrometer equipped with an INCA x-act detector was obtained from Oxford Instrumentation and used for further characterization. The EDX spectrometer indicated that the major components in the membrane that had been prepared were carbon, silica, and alumina. Figure 3 shows that there was good coverage of the stainless-steel support by the zeolite–carbon with XRD pattern presented in Figure 4, which demonstrate and represent the key peaks of ZSM-5 that
matches the standard sample in Figure 1 (at $2\theta = 8, 8.9$ and 23). Also, the carbon curve is presented in the XRD pattern as shown in Figure 4 (from $2\theta = 5$ to $\sim 10$). It was difficult to measure the thickness of the membrane, but the mass of carbon–zeolite was determined based on the weights of the disks before and after synthesis, as shown in Table 2.

To obtain clear and reliable results, $p$-xylene and $o$-xylene were chosen because of the greater difference in their boiling points (5.5 °C). This facilitated the analysis of the products using gas chromatography, which was expected to yield easily distinguished peaks in the pattern of the product. The $p$-xylene/$o$-xylene mixture came in contact with the membrane at different feed concentrations and temperatures. For comparison purposes, the prepared carbon–zeolite membrane was tested at four different concentrations, that is, 95, 90, 80, and 70 wt % $o$-xylene, and Table 3 provides the results.

The data show a diffusion preference for $p$-xylene, which was attributed to its smaller kinetic diameter than that of $o$-xylene. In general, these membranes had modest performances in terms of fluxes and separation factors. The low separation factors probably were due to the unavoidable pinholes on the surface of the membrane and due to the long duration of the runs, where the close sizes of the ZSM-5 pores and the kinetic diameter of $p$-xylene have a negative role in narrowing the

| component | CAS reg. no. | supplier       | assay % | BP (°C)$^a$ | kinetic diameter (nm) | analysis method |
|-----------|--------------|----------------|---------|-------------|-----------------------|-----------------|
| $p$-xylene| 106-42-3     | Supelco        | ≥99.5   | 138.3       | 0.58                  | GC$^a$          |
| $m$-xylene| 108-38-3     | Supelco        | ≥99.5   | 139.1       | 0.68                  | GC$^a$          |
| $o$-xylene| 95-47-6      | Supelco        | ≥99.5   | 144.4       | 0.68                  | GC$^a$          |
| ethanol   | 64-17-5      | Supelco        | ≥99.9   | 78.3        | 0.43                  | GC$^a$          |
| cyclohexane| 110-82-7     | Supelco        | ≥99.9   | 81          | 0.6                   | GC$^a$          |
| phenol    | 108-95-2     | Sigma-Aldrich  | ≥99     | 182         | 0.66                  | GC$^a$          |
| sucrose   | 57-50-1      | Sigma-Aldrich  | ≥99.5   | NA          | NA                    | GC$^a$          |

$^a$Gas chromatograph. $^b$The pressure for the measurement of boiling temperature was 101.3 kPa.
diffusion preferences. In order to determine the permeation mechanism, other pure feeds with different kinetic diameters, that is, ethanol (0.43 nm), cyclohexane (0.6 nm), and phenol (0.66 nm), were evaluated four times at 25 °C as illustrated in Figure 5. The ZSM-5 pores, with diameters possibly in the range 0.6 ± 0.02 nm, very likely were obtained. The permeability trend was decreasing as the kinetic diameters of the pure compounds were increasing. The sharp decrease in the permeability of cyclohexane probably was due to it having a larger kinetic diameter than the ZSM-5 pores (0.6 nm). This was attributed to the size exclusion behavior (molecular sieving mechanism). Thus, the presence of compounds with molecules larger than 0.6 nm on the permeate side possibly was due to the adsorption and affinity of these molecules toward the structure of ZSM-5. Another potential reason these molecules were present in the permeate side was the unavoidable cracks and pinholes in the membrane.

We investigated the effect of sucrose on the separation factor and permeability of the membrane. Figure 6 shows the results of the evaluation of the concentrations of sucrose in water, that is, 50–75% sucrose. The trends in the Figure 6 indicate that the concentration of the sucrose precursor solution was related directly to the separation factor and related inversely to the overall flux. This was attributed to the formation of more structures because the concentration of the precursor increased as the d-spacing values decreased gradually from 3.21 to 3.11 (Figure 7). The d-spacing values of the membranes prepared at different sucrose concentrations were estimated by Bragg’s formula, that is, \( d = \frac{\lambda}{2 \sin \theta} \).

The temperature effect was evaluated by using a constant feed composition of 50 wt %. Figure 8 shows that the temperature was proportional to the permeate flux, while the separation performance did not show any noticeable change in that range. The feed temperature had a slight effect on the permeate fluxes due to the effect of the temperature on fugacity on the liquid side of the membrane.

After the synthesis of the ZSM-5 carbon composite membranes using porous, stainless-steel supports, the fabrication process was repeated several times to evaluate the repeatability of their performances at 50 °C, as shown in Table 4. The results indicated that the preparation method resulted in a steady performance, which was estimated using the deviation data variances (\( S^2 \)) and calculated using eq 1. The membranes had permeate fluxes and selectivities within variances of 0.41 and 0.013, respectively.

\[
S^2 = \frac{\sum_{i=1}^{n} (X_i - X_{avg})^2}{n - 1}
\]

Figures 9–11 shows that the durabilities of these membranes also were tested and assessed for 100 h. These figures show a comparison between the xylene fluxes that had been conducted at two different temperatures, that is, 25 and 50 °C. In general, the permeation flux of each isomer decreased over time in the temperature range that was

| feed (wt %) | permeate (wt %) | permeate flux (g/m² h) | separation factor |
|------------|----------------|-----------------------|------------------|
| p-xylene   | o-xylene       | p-xylene o-xylene     |                  |
| 5          | 95             | 21.61                 | 76.04            | 5.35 |
| 10         | 90             | 23.49                 | 84.16            | 2.82 |
| 20         | 80             | 40.67                 | 59.33            | 86.27 | 2.64 |
| 35         | 65             | 64.65                 | 53.35            | 92.27 | 1.62 |
| 50         | 50             | 59.32                 | 40.67            | 112.67 | 1.46 |

Figure 5. Dependency of permeability on kinetic diameter for different compounds.

Figure 6. Effect of different sucrose concentrations on membrane performance at 50 °C.

Figure 7. XRD patterns of carbon samples prepared at different precursor concentrations.

Table 3. Evaluation of Carbon–Zeolite Membranes Using ZSM-5 after Post-Treatment with Sucrose as a Carbon Precursor with Different Feed Compositions at 25 °C

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investigated due to the concentration polarization on the membrane surface. The PV flux increased as the temperature increased for all of the isomers. Numerous studies have reported similar temperature dependence of the permeation flux through Mobil Five (MFI) membranes within this temperature range.\textsuperscript{1,4,12,14} The selectivity of the membrane prepared in this study were compared with those presented in the literature as shown in Table 5.

### 3. CONCLUSIONS

In order to avoid the complexity of preparing ZSM-5 membranes by the conventional method, that is, hydrothermal synthesis, an easy and less time-consuming method using an inexpensive carbon precursor was evaluated for xylene separation at different feed temperatures in the range of 25−50 °C. The results indicated that the overall fluxes increased as the temperature increased without affecting the separation factor. As indicated from this study, the concentration of the carbon precursor is important in defining the performance of the membrane, and it was observed that the separation factor of the membrane was improved slightly by increasing the concentration of the precursor. This improvement was attributed to formation of dense structures at the higher concentrations of the precursor as indicated by the d-spacing. However, there was a noticeable trade-off between the separation factors and the overall fluxes. Therefore, the performance of these membranes could be optimized for a given system by changing the concentration of the precursor that is used. A noticeable decrease in the PV flux was observed over time, which was attributed to the polarization of the concentration on the membrane in the feed flow side. The overall fluxes of the pure xylene isomers at 25 °C in the first 20 h decreased in the order of p-xylene > m-xylene > o-xylene. The preparation methodology was repeated several times to ensure the repeatability aspect, and it resulted in a stable performance with permeate flux and separation factor variances of 0.41 and 0.013, respectively. The procedure presented in this study for preparing ZSM-5 flat membranes yielded membranes that provided competitive performances to those presented in the literature.\textsuperscript{4,7,17,18,21} However, the main objective of this study was to implement a simple preparation
procedure that avoids the lengthy, conventional preparation methods described in the literature for the preparation of ZSM-5 membranes.

4. EXPERIMENTAL SECTION

Similar to our previous work, the lengthy preparation methods used in in situ and secondary growth methods were avoided by using the following synthesis method. First, equal weights of preformed synthetic ZSM-5 (obtained from Eka Nobel) and deionized water were mixed to form the ZSM-5 paste. Then, 0.4 g of the ZSM-5 paste was applied on a support disc, and the disc was placed in a low vacuum system for 5 min. The support metal used in this study were circular, porous, stainless-steel disks with a diameter of 20 mm, thickness of 1.5 mm, and porosity of 0.5 μm (obtained from Aegis Advanced Materials Ltd., UK). The porous metal coated with the ZSM-5 paste was allowed to dry for 1 h. A 50% sucrose solution was prepared by mixing 2 g of sucrose (obtained from Fisher Scientific UK, Ltd.) with 2 g of distilled water. A 0.45 g quantity of the sucrose solution was used to cover the ZSM-5 paste that had been in the low vacuum system for 5 min, and then, the disc was heated at the rate of 5 °C/min in a tubular furnace, followed by the pyrolysis process for 4 h at 550 °C. The carbon–zeolite membrane (ZSM-5) that was produced was glued onto a nonporous, stainless-steel washer using the two-component adhesive epoxy Araldite Rapid (obtained from Fisher Scientific UK, Ltd.), resulting a membrane surface area of 16 mm in diameter. Subsequently, Teflon rings were used to fit the membrane between the two compartments of the membrane cell, and the membrane was clamped. Figure 12 shows the PV system that was used in this study to evaluate the membranes that were prepared. A pump was used to feed the feed mixture of p-xylene/o-xylene to the membrane compartment at the rate of 130 mL/min. Then, the permeation process occurred due to the driving force caused by the difference in the partial pressures, where the pressure on the permeate side was set to 8 Pa. The permeate that was in the vapor phase was collected by condensing it with cold media, that is, liquid nitrogen traps. The PV process was conducted with different feed compositions using a total volume of 200 mL. The performance of each membrane used in the process described above was estimated in terms of separation factor ($\alpha_{ij}$) (eq 2) and total flux ($F$) (eq 3)

$$\alpha_{ij} = \frac{W_{p,j} W_{f,i}}{W_{f,j} W_{p,i}}$$  

(eq 2)

$$F = \frac{m_s}{A \Delta t}$$  

(eq 3)

where ($W_i$) and ($W_p$) are the weight compositions of the binary components of the mixture; ($W_{p,i}$) and ($W_{f,j}$) are the weight compositions of the permeate and feed, respectively; ($m_s$) is the weight of the collected permeate sample; ($A$) is the surface area of the activated membrane; and ($\Delta t$) is duration of the experiment.

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**Notes**

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