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Catalytic MFI zeolite membranes supported on α-Al_2O_3 substrates for m-xylene isomerization

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ABSTRACT

MFI zeolite membranes were synthesized on α-alumina substrates by in situ hydrothermal crystallization. The separation of p-/o-xylene (PX/OX) mixtures was performed to evaluate the quality of MFI zeolite membranes. EDS analysis showed that aluminum from the substrate was incorporated into the zeolite structure during membrane synthesis. The negatively charged aluminosilicate framework possessed ion-exchange properties due to the presence of charge-balancing cations, which could produce acidic sites for xylene isomerization. A membrane with a PX permeance of 2.58×10^{-8} mol/m^2 s Pa and a PX/OX separation factor of 19.3 at 300 °C was modified by H^+ ion-exchange treatment and used for the isomerization of m-xylene (MX). The effects of the operating temperature, feed flow rate and sweep flow rate on the membrane reaction were investigated. For MX isomerization, a high PX selectivity of 92.1% and a MX conversion of 6.5% were achieved at 270 °C over the catalytic membrane.

1. Introduction

Zeolite membranes have been extensively studied due to their well-defined pore size and high thermochemical stability [1]. MFI-type zeolite membranes are considered an alternative material for the separation of xylene isomers, which is performed to obtain p-xylene, an important stock in the chemical industry. MFI zeolites have an average pore size of 5.5 Å, which is similar to the kinetic diameter of p-xylene (PX) (~5.8 Å) but smaller than that of o-xylene (OX) and m-xylene (MX) (~6.8 Å). Therefore, due to molecular sieving through zeolitic pores, defect-free MFI zeolite membranes have high permselectivity for PX over OX and MX.

Recent studies on the synthesis of MFI zeolite membranes [2] have shown that the membranes can be used for the separation of xylene isomers, and high separation selectivity for PX can be obtained. Furthermore, MFI zeolite membranes have been used for xylene isomerization [3–7], which could significantly enhance the PX yield. van Dyk et al. [3] investigated MFI zeolite membrane packed with a commercial catalyst and achieved greater PX productivities than that of a conventional packed-bed reactor. Yeong et al. [4] studied MX isomerization in an acid-functionalized silicalite-1 zeolite membrane reactor and obtained an MX conversion and PX yield of 52% and 32%, respectively, at 450 °C. In our group, MFI zeolite membranes packed with H-ZSM-5 catalyst particles were used for the isomerization of xylene [5], and the experimental data were compared to those obtained from membrane reactors produced using different catalyst packing methods. Compared to a catalyst in contact with α-Al_2O_3 substrate, superior results were obtained when the loaded catalyst was in contact with the zeolite layer. These findings were attributed to the effective removal of PX using the latter packing method. The experimental results suggested that a bifunctional membrane displaying PX selective separation and isomerization catalytic activity could enhance xylene isomerization by immediately removing PX from the system.

Al-substituted MFI zeolite (namely ZSM-5) membrane could be used as a bifunctional membrane to simultaneously separate PX and isomerize xylene. Tarditi et al. [8] performed xylene isomerization in a Ba^{2+} ion-exchanged ZSM-5 zeolite membrane reactor and found that the PX production rate increased to approximately 28% compared with a fixed-bed reactor at 370 °C. However, the quality of ZSM-5 membranes is difficult to control due to the introduction of Al in the MFI zeolite framework. Noack et al. [9] suggested that aluminum present in synthesis solution could affect the growth of defect-free MFI membranes because the surface charge of the zeolite framework becomes more negative when the Al content is high. Min et al. [10] reported that the ideal permselectivity of PX/MX on ZSM-5 membrane at 100–300 °C was less than 2. Tarditi et al. [11] used ZSM-5 membranes for the separation of xylene isomers at 150 °C, and PX/OX and PX/MX separation factors of only 8 and 6.9, respectively, were obtained. The lower separation performance of ZSM-5 membranes would affect the efficiency of membrane reactors for the enhancement of xylene isomerization. Furthermore, when ZSM-5 membranes are used for xylene isomerization, PX generated in the channels of the catalytic membranes can be converted

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into by-products on the permeate side because the catalytic activity of the membrane exists throughout the separation layer. Therefore, a bi-layered catalytic membrane composed of a catalytic layer and an inert separation layer may provide superior isomerization results. Mabande et al. [12] prepared bi-layered Al-ZSM-5/silicalite-1 membranes by secondary growth; however, the aforementioned synthetic method produced membranes with a modest separation factor for PX/OX.

Pure-silica (silicalite) membranes exhibit excellent performance for xylene separation [13–15]. α-Alumina substrates are generally used to support the zeolite layer, which can result in the incorporation of aluminum into the zeolite framework during membrane synthesis [16–18]. Incorporated aluminum may have minor effects on the separation performance of the zeolite layer because aluminum tends to accumulate in the intermediate layer near the alumina substrate. It would be very interesting if the aluminum-incorporated zeolite framework within the membrane layer could serve as a catalytic media for xylene isomerization. In this way, catalytic membranes with high separation performance could be obtained. Therefore, in the present study, we activated the catalytic activity of MFI zeolite membranes by subjecting the membrane to H^+ ion-exchange treatment and used the H^+ ion-exchanged MFI (H-MFI) zeolite membranes for MX isomerization. We aimed to reveal whether the catalytic membranes exhibited better catalytic performance in xylene isomerization.

2. Experimental

2.1. Membrane synthesis and ion-exchange

Pure-silica MFI membranes were synthesized on disk-shaped α-Al_2O_3 substrates by in situ hydrothermal crystallization. The substrates had an average pore size of about 100 nm and a porosity of about 30%. The synthetic precursor was prepared by dissolving sodium hydroxide pellets (99.99%, Aldrich) and fumed SiO_2 (99.98%, Aldrich) in 1 M tetrapropylammonium hydroxide (TPAOH) solution (Aldrich) at 80 °C. The synthetic solution had a molar composition of $1(TPA)_2O{:}6.66SiO_2{:}0.35Na_2O{:}92.2H_2O$. Hydrothermal crystallization was carried out at 180 °C for 5 h. The as-made membranes were calcinated at 450 °C for 8 h to remove the template. The active membrane area was about 2.54 cm^2. Details of the synthetic procedure have been reported in our previous papers [19,20].

H-MFI zeolite membranes were prepared using an ion-exchange method described in the literature [21]. Fresh MFI zeolite membranes were immersed into excess 1 M NH_4Cl and stirred at 80 °C for 24 h. Ammonium ions (NH_4^+) were fully exchanged with charge-balancing sodium ions (Na^+) in the aluminum-containing zeolite framework. The ion-exchanged membrane was rinsed with deionized (DI) water and dried in an oven at 60 °C overnight. To generate acidic sites (H^+) in the zeolite framework, the ion-exchanged membranes were calcinated at 500 °C for 5 h.

2.2. Membrane separation and reaction

Fresh MFI zeolite membranes and H-MFI zeolite membranes were examined in the separation and isomerization of xylene. The membrane was sealed by graphite rings and mounted in a stainless steel cell, which was placed in a temperature-controlled furnace. A helium stream was saturated with xylene vapor in a saturator and diluted with an additional helium stream. The xylene-containing helium stream was introduced onto one side of the zeolite membrane (feed side), while the other side of the zeolite membrane (permeate side) was swept by a helium stream. PX (99%) and MX (99%) were purchased from Alfa Aesar, and high purity helium (99.999%) was used as a carrier or sweep gas. Both sides of membrane were maintained at atmospheric pressure. The experimental apparatus used for membrane separation and reaction has been described in our previous paper [5]. The products obtained from separation or isomerization were analyzed with an on-line gas chromatograph (GC, GC2014, Shimadzu) equipped with a flame ionization detector (FID) and a KR-B34 capillary column (Keepring). The pipe connected to the GC was wrapped with heating tape and maintained at 125 °C to prevent product condensation. The conversion, selectivity, and yield of the membrane reactions were calculated according to the combination of components present in the permeate and retentate. In some cases, the PX selectivity was calculated using only the components present in the permeate or retentate. The formulas used to calculate the PX selectivity based on permeate, retentate or the combination are given as follows,

$$S_P = \frac{M_P^{PX}}{M_P^{Products}} \quad (1)$$

$$S_R = \frac{M_R^{PX}}{M_R^{Products}} \quad (2)$$

$$S_C = \frac{M_P^{PX} + M_R^{PX}}{M_P^{Products} + M_R^{Products}} \quad (3)$$

where M_P^{PX} and $M_P^{Products}$ are the molar flow rates of PX and the total products present in the permeate, respectively, and M_R^{PX} and $M_R^{Products}$ are the molar flow rates of PX and the total products present in the retentate, respectively.

To evaluate the membrane performance, the separation factor for component i over component j was defined as

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad (4)$$

where x_i and x_j are the molar composition of component i and j in the feed stream, and y_i and y_j are the molar composition of i and j in the permeate stream, respectively.

2.3. Characterization

Single-gas nitrogen permeation measurements were carried out at room temperature to evaluate the membrane density. The feed and permeate pressure were set to 240 kPa and 101 kPa, respectively. Prior to measurement, the membranes were flushed with N_2 at 300 °C for 2 h to remove any adsorbed components from the micropores. The gas flow rate through the membrane was measured using a soap bubble flowmeter.

The structures of the samples were determined by X-ray diffraction (XRD, D8-Advance, Bruker). The textures of the membranes were observed by field emission scanning electron microscopy (FESEM, S-4800, Hitachi), and the distribution of elements in the membranes was detected by energy dispersive spectroscopy (EDS, Noran NSS 2.2, Thermo Scientific). Acidic sites on the samples were determined by NH_3 temperature-programmed desorption (TPD, TP-5080, TianJin Xianquan-Instrument Co., Ltd.). Physically adsorbed NH_3 was removed by helium at 500 °C for 1 h. NH_3-TPD experiments were carried out by heating the samples from 100 to 600 °C at a rate of 10 °C/min. The stream was monitored continuously with a thermal conductivity detector (TCD) to determine the rate of ammonia desorption.

3. Results and discussion

3.1. Membrane characterization

Fig. 1 shows the XRD patterns of MFI membranes before and after ion-exchange treatment. After ion-exchange, the membranes