Separation and Purification Technology 73 (2010) 32–37

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

A catalytic ZSM-5 membrane sandwiched with silicalite-1 layers for highly selective toluene disproportionation

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ARTICLE INFO

Keywords:
Zeolite
Membrane reactor
ZSM-5
Catalytic membrane
Disproportionation

ABSTRACT

A catalytic zeolite membrane composed of silicalite-1, ZSM-5 and silicalite-1 layers supported on a porous stainless support was prepared by hydrothermal synthesis (silicalite-1/ZSM-5/silicalite-1 membrane). The permeance of hydrogen, argon, nitrogen, *n*-butane and isobutane for silicalite-1/ZSM-5/silicalite-1 membrane was measured from 353 to 513 K. The permeance of these gases were from 5 to 25×10^{-8} mol/(m^2 s Pa) the same range as typical MFI-type membranes and the ratio of the permeance of *n*-butane to isobutane was 2 or less. The toluene disproportionation was examined at 673 K with silicalite-1/ZSM-5/silicalite-1 membrane as a membrane reactor as well as ZSM-5/silicalite-1 membrane and ZSM-5 powder. The products detected were benzene, *p*-, *m*- and *o*-xylene. The toluene conversion with two membrane reactors was less than 3%. At lower than 1% of toluene conversion, the selectivity of *p*-xylene for silicalite-1/ZSM-5/silicalite-1 was above 96% whereas that for ZSM-5/silicalite-1 membrane was below 89%. The silicalite-1 layers sandwiching the ZSM-5 layer probably suppressed the surface reaction on both ZSM-5 layers, which would achieve the significantly high selectivity of *p*-xylene in toluene disproportionation.

1. Introduction

The zeolite membrane allows both selective separation and selective reaction due to its pores near molecular size. In general, the thermal and chemical stability of zeolite membrane is distinctly better than that of organic membranes. From these advantages, zeolite membranes offer a potential as a new technology for specific separation and organic synthesis in the industrial chemical process [1]. The MFI-type zeolite such as ZSM-5 and aluminium-free silicalite-1 with a pore diameter of 0.58 nm can separate *p*-xylene (kinetic diameter of 0.585 nm) from *o*- and *m*-xylene (kinetic diameter of 0.685 nm) selectively utilizing the difference in size [2–4]. Therefore, MFI-type membrane works not only as a molecular sieving separator but also as a membrane reactor for various reactions such as methanol to olefin synthesis [5], alkylation of toluene [6] and xylene isomerization [7], whereby giving better product selectivity.

The reaction model of toluene disproportionation with ZSM-5 membrane is shown in Fig. 1(a). In the micropores and intercrystalline pores of ZSM-5, the selective formation of *p*-xylene with benzene proceeds. However, the acidic points existing on the external surface of ZSM-5 layer are still active but non-selective for the formation of xylenes [6]. The byproducts, *o*- and *m*-xylene, form on the surface of membrane and a part of byproducts permeates through ZSM-5 layer. As a result, the selectivity of *p*-xylene will decrease. To improve this disadvantage, silicalite-coated silica-alumina fine particles have been proposed. The particles show selective formation of *p*-xylene in the disproportionation of toluene, where the silicalite layer controlled the flux of reactants and products both inside and outside [8].

In this study, the silicalite-1/ZSM-5/silicalite-1 sandwich membrane is proposed for highly selective disproportionation of toluene. The concept of this membrane is shown in Fig. 1(b). The silicalite-1 layers on both sides of ZSM-5 layer are non-reactive and similar in permeation property to ZSM-5 layer. The surface silicalite-1 layer will inhibit the surface reaction on the ZSM-5 layer. On the other hand, the role of the base silicalite-1 is a kind of adhesive agent binding the ZSM-5 layer with the porous stainless steel support. This idea is based on the empirical fact that silicalite-1 is easier to be synthesized on the stainless support than ZSM-5. Consequently, the silicalite-1/ZSM-5/silicalite-1 membrane should realize the highly selective production of *p*-xylene. The silicalite-1/ZSM-5/silicalite-1 membrane proposed in this study was designed to achieve the highly selective formation of *p*-xylene in toluene disproportionation. Further, the membrane was expected to work as a separator for various compounds as well as the membrane reactor.

In this study, the silicalite-1/ZSM-5/silicalite-1 sandwich membrane was prepared by hydrothermal synthesis. The permeation

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doi:10.1016/j.seppur.2009.08.007

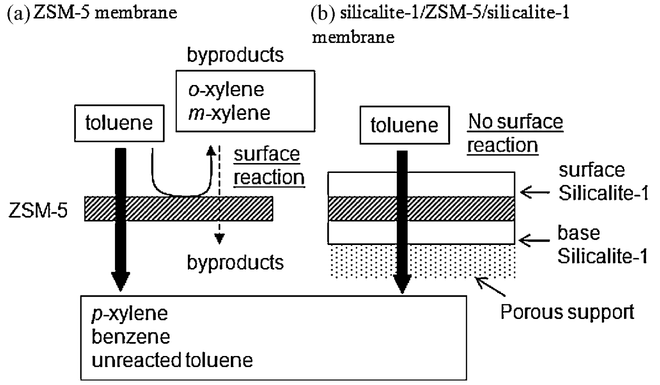

Fig. 1. Concept of silicalite-1/ZSM-5/silicalite-1 sandwich membrane for toluene disproportionation.

tests of usual gases and toluene disproportionation for this membrane were examined to evaluate the permeability of gases and the selectivity of toluene disproportionation.

2. Experimental

2.1. Synthesis of membrane

Sealant-free MFI-type zeolite membranes were prepared on the support by hydrothermal synthesis [9]. A porous stainless steel filter with 0.5 μm of an average pore size (SS-2F-05, Swagelok) was used for the support. The support was impregnated in 1 M NaOH aq. (NaOH: 96%, Wako Pure Chemical Industries, Ltd.), followed by 1 M HNO_3 aq. (Wako Pure Chemical Industries, Ltd.) as a pretreatment. For synthesis, the seed gel composing of tetraethoxysilane (TEOS, 95%, Wako Pure Chemical Industries, Ltd.): NaOH:tetrapropylammonium bromide (TPABr, 98%, Kanto Kagaku):H_2O = 1:0.0079:0.36:19.16 was used. TPABr was a template of zeolite. The silicalite synthesis solution was prepared by combining the seed gel, sodium hydroxide aqueous solution, TPABr and colloidal silica (Cataloidloid SI-30, Shokubai Kasei Co., Japan; 30.5 wt% SiO_2, 0.42 wt% Na_2O and 69.1 wt% H_2O). The final molar composition of the silicalite synthesis solution was Si:Na:TPABr:H_2O = 1:0.35:0.86:157. The ZSM-5 synthesis solution was prepared from the seed gel, sodium hydroxide aqueous solution, colloidal silica, TPABr and Aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, 98%, Wako Pure Chemical Industries, Ltd.) with the molar composition of Si:Na:TPABr:Al:H_2O = 1:0.35:0.12:0.0069:145.

At first, the silicalite-1 layer was synthesized on a porous stainless steel filter with the silicalite solution. For the preparation of first silicalite-1 layer, the surface of porous stainless steel filter was rubbed with silicalite-1 powders as a seed crystal. After the support was immersed in silicalite synthesis solution, hydrothermal synthesis of the silicalite-1 layer on support was carried out in autoclave at 453 K for 48 h. The silicalite-1 powder formed at the bottom of autoclave was used as a seed crystal. Next, the silicalite-1/support obtained was immersed in ZSM-5 synthesis solution and the hydrothermal synthesis of the ZSM-5 layer on the silicalite-1/support at 453 K for 48 h to make ZSM-5/silicalite-1 membrane [10]. The composite membrane was preferred to make ZSM-5 layer on stainless support because a single ZSM-5 layer on the stainless support had tended to be scaled in our preliminary experiment. In the case of the synthesis of silicalite-1/ZSM-5/silicalite-1 membrane, hydrothermal synthesis of silicalite-1 layer over ZSM-5/silicalite-1/support was conducted in the silicalite synthesis solution at 453 K for 48 h. After the synthesis of ZSM-5/silicalite-1 membrane and silicalite-1/ZSM-5/silicalite-1 membrane, the membrane prepared were calcined up to 693 K for 6 h to remove template.

The membranes prepared were observed by scanning electron microscopy (VE-7800, Keyence). The structure of zeolite was determined by XRD (RINT2100, Rigaku) using Cu-Kα radiation.

2.2. Gas permeation measurements

Single-gas permeation measurements were carried out with several gases. The membrane on porous stainless steel filter was build into Swagelok filter unit. The unit was put in the thermostat (L-75, Gasukuro Kogyo Co., Ltd.) controlled at a measurement temperature. Hydrogen, nitrogen, argon, *n*-butane and isobutane were supplied through a pressure regulator from the upstream of the filter unit. The pressure of non-permeate side was controlled by both the pressure regulator and the needle valve at the end of non-permeated line. The permeated gas flow rate was measured by using a soap-film flow meter. The temperature was from 353 to 513 K and the pressure difference was from 0.6 to 1.0 MPa.

2.3. Toluene disproportionation

After the gas permeation experiments, the sodium cation in ZSM-5 layer was exchanged with proton by ion-exchange method, where the membrane was submerged in 1 M ammonium nitrate (99%, Wako Pure Chemical Industries, Ltd.) aqueous solution at 323 K for 16 h, then dried at 333 K for 6 h and heated at 723 K for 2 h.

Fig. 2 shows the experimental apparatus for toluene disproportionation. The argon was supplied with the mass-flow controller (SECU-1, Estec Inc.) as a carrier gas. Toluene (99.99%, Wako Pure Chemical Industries, Ltd.) loaded in the saturator submerged in the water bath (LTB-125, As One Corporation) at 290 K was supplied as a saturated vapor with argon. The partial pressure of toluene in argon was 2474 Pa estimated by Antoine equation. The feed mixture containing toluene was preheated in the electric furnace to reaction temperature. The Swagelok filter unit containing membrane was placed in electric furnace as a membrane reactor. The toluene vapor was introduced to the shell side. The all amount of the feed mixture permeates through the membranes in the toluene disproportionation. The product was analyzed by gas chromatography with FID detector (GC-14, Shimadzu) and Bentone 34 +DNP column, and the flow rate of gases was measured by a soap-film flow meter.

For comparison, we conducted toluene disproportionation with proton exchanged ZSM-5/silicalite-1 membrane and ZSM-5 powder. ZSM-5 powder used was obtained during the hydrothermal synthesis of ZSM-5 layer. The method of experiment was almost the same as that for silicalite-1/ZSM-5/silicalite-1 membrane. In the case of ZSM-5/silicalite-1 membrane, this membrane was placed instead of silicalite-1/ZSM-5/silicalite-1 membrane. In the case of ZSM-5 powder, the power after ion-exchange was combined with glass beads was put in the Swagelok filter unit instead of membrane. Silica wool was placed around the catalyst bed to fix it.

3. Results and discussion

3.1. Physical properties of membrane

It is difficult to analyze the cross-section of silicalite-1/ZSM-5/silicalite-1 membrane because the membrane stuck in stainless support and cannot be split finely. We obtained the flake of silicalite-1/ZSM-5/silicalite-1 membrane and observed it although this flake would not show the actual membrane due to the lack of