

Xylene isomerization in an extractor type catalytic membrane reactor

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Abstract

A zeolite/alumina pore plugging membrane was used to successfully separate xylene isomers. It was then applied, as a selective membrane, in an extractor type catalytic membrane reactor (CMR), used to enhance the xylene isomerization reaction selectivity towards *para*-xylene. The results of the CMR in different configurations (permeate-only and combined permeate-and-retentate mode) were compared to conventional fixed-bed reactor results. In both cases, the selectivity was significantly enhanced (up to 100% in permeate-only mode). In the combined mode, the CMR also provided a net increase in productivity over the conventional reactor.

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1. Introduction

In 2003, the worldwide demand for xylenes was about 22 million tons, with *para*-xylene (a precursor to polyesters) holding 80% of the market share [1]. Principal sources of xylene isomer mixtures are catalytically reformed naphthas and pyrolysis distillates [2], with the distribution of xylene isomers being approximately 50–60% of *meta*-xylene and 20–25% *ortho*- and *para*-xylenes. In order to meet the *para*-xylene demand the much less used *ortho*- and *meta*-xylenes are converted via the xylene isomerization reaction, a major industrial process for this aromatic [3]. Xylene isomerization is a thermodynamic equilibrium restricted reaction, and therefore, total conversion is impossible in conventional conditions. Equilibrium product distributions in the standard state (atmospheric pressure) for temperatures 250–1500 K, range from 63–47% for *meta*-xylene, 13.4–30% for *ortho*-xylene and 23.6–23% for *para*-xylene [4].

Separation of *para*-xylene from its isomers is essential, but is difficult due to their close boiling points. *Para*-xylene ($T_b = 411.3$ K) and *meta*-xylene ($T_b = 412.1$ K) are normally separated by crystallization, selective adsorption or chromatographic techniques. Recent research efforts focus on

using MFI-zeolite membranes for xylene separation, a potentially more energy-efficient separation method [5–8]. The MFI-zeolite pore structure consists of straight, circular pores (0.54 nm × 0.56 nm), interconnected with sinusoidal, elliptic pores (0.51 nm × 0.54 nm) [9]. These pore sizes are close to the kinetic diameter of *para*-xylene ($d_k = 0.58$ nm), and it is expected that its bulkier isomers ($d_k = 0.68$ nm) would diffuse at a slower rate, and adsorb to a lesser extent in the MFI framework due to their size and shape [6].

A number of research groups have carried out studies in this area with different results. Baertsch et al. [5] studied permeation of *p*- and *o*-xylene through silicalite-1 membranes containing large amounts of non-zeolite pores. They found that for a mixture of ~3 mol% *p*-xylene, 3 mol% *o*-xylene and 94 mol% He over the temperature range 380–480 K, no separation occurred. Keizer et al. [10] reported separation factors of *p/o*-xylene as a function of time between 298 and 473 K and gave values of ~1 at 298 K to >200 at 375–415 K with a maximum at ~400 K. The separation factor was 25 at 473 K. The partial pressures of components in the feed were low (*p*-xylene 0.31 kPa, *o*-xylene 0.26 kPa). A maximum *p*-xylene flux at 400 K was said to be due to opposing effects of adsorption and diffusion. Gump et al. [9] studied the fluxes of aromatic molecules (*p*-xylene, *o*-xylene and benzene), through several molecular sieve membranes (SAPO-5, SAPO-11

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and mordenite) as well as three types of MFI membranes (silicate-1, ZSM-5 and boron substituted ZSM-5), as a function of pressure and temperature. They found that surface diffusion and what they identified as *activated gas transport* were the controlling mass transfer mechanisms for MFI membranes. Boron-substituted ZSM-5 membrane displayed the highest *p*-/*o*-xylene separation, up to 60, obtained at 425 K for partial feed pressures of 2.1 kPa per isomer. Higher pressures of *p*-xylene were reported to distort the membrane framework, leading to higher *o*-xylene permeation and reduced separation.

An extensive study of xylene vapour permeation was performed by Xomeritakis et al. [6,11,12]. Single gas permeation tests at feed partial pressures of 0.86 and 0.64 kPa for *p*- and *o*-xylene were done in the temperature range 295–548 K for c-oriented MFI membranes. It was found that *p*-xylene permeance displayed weak temperature dependence, while *o*-xylene permeance displayed a minimum at 373 K. Also, as the partial pressure of *p*-xylene in the feed mixture was increased from 43 to 430 Pa, the *p*-/*o*-xylene separation factor dropped from 48 to 3. In order to get rid of defect influence, Sakai et al. [7] used self-supporting MFI-zeolite membranes of a thickness between 60 and 130 μm . The *p*-xylene permeation flux showed a maximum at 473 K and a partial pressure at 0.3 kPa, and was described by the competitive effects between equilibrium adsorption and diffusivity. The permeation of *m*- and *o*-xylene was small, and almost constant between 473 and 673 K. The separation factors of *p*- to *m*-xylene and *p*- to *o*-xylene reached a maximum value of 250 at 473 K. On the other hand, high-pressure, high-temperature gas separation of xylenes were carried out by Hedlund et al. [13] using ultra thin MFI films (0.5 μm) on porous α -alumina supports produced by a two-step support masking technique, and a monolayer of colloidal nucleation seeds, followed by in situ hydrothermal growth. High-permeance values were obtained (up to 0.6 $\mu\text{mol}/(\text{s m}^2 \text{ Pa})$ at 373 K), together with *p*-/*o*-xylene separation factors somewhat lower than expected (3–17) [14]. Similar interesting results were obtained recently by Lai and co-workers [15,16].

Separation of *para*-xylene from its isomers is therefore possible through MFI-zeolite membranes. However, the presence of defects shows a strong influence on separation factors found in the literature, particularly at higher temperatures. In particular, supported zeolite films may suffer from defects opening during calcinations or temperature increase, as a consequence of the difference in thermal expansion coefficient between the zeolite and the support [7]. We show here the use of a zeolite/alumina nanocomposite membrane of the *pore-plugging* type.

Catalytic membrane reactors (CMRs) have been classified, in previous publications from our team, into three groups, depending on the function of the membrane: extractor, distributor and contactor [17]. By using a membrane capable of separating *p*-xylene from the mixture

of the three isomers, we propose to study the behaviour of the catalytic reaction taking place in the CMR. Therefore, this paper reports on the use of an extractor type CMR for the selectivity enhancement of the *meta*-xylene isomerization reaction towards *para*-xylene. Nevertheless, whereas extractor CMRs are commonly reported to enhance conversion, this work concentrates on improving selectivity.

2. Experimental

2.1. Materials

The MFI-zeolite membrane was synthesized in the wall of a porous ceramic tubular support (Pall-Exekia T1-70), consisting of three macroporous α -alumina layers (from outer to inner side, respective average pore sizes: 12, 0.8, 0.1 μm and thicknesses 1500, 40, 20 μm). It had an outer diameter of 10 mm, inner diameter of 7 mm and an effective membrane length of 13 cm. The MFI membrane was obtained by synthesis of zeolite crystals inside the pores of the macroporous tubular support (*pore-plugging* method) [18,19]. The MFI-zeolite precursor solution was obtained by mixing silica (Aerosil 380) and a template (tetrapropylammonium hydroxide, TPAOH). After a 3-day ageing period, the solution was poured in a Teflon-lined autoclave containing the porous ceramic tube. Hydrothermal synthesis was then performed at 443 K for 3 days, and the membrane was calcined at 773 K under airflow. Low-temperature butane/hydrogen separation through the membrane showed it could be considered close to defect-free (i.e. the transport through the membrane is controlled by the micropores of the MFI structure).

The *catalyst* (Pt on zeolite) was a commercial xylene isomerization catalyst (ISOXYL) from Süd-Chemie. The catalyst was diluted with kaolin to 5 wt.% of the original and extruded into ca. 2-mm pellets, with a lab-scale extruder. The same mass of 2.18 g of the obtained solid was used in every experiment. Before catalytic use, the solid was activated in situ under H_2 flow at 673 K for 3 h.

Anhydrous xylene isomers were purchased from Sigma-Aldrich: *meta*-xylene >99%, *para*-xylene >99% and *ortho*-xylene 97%.

2.2. Set-up

Fig. 1 shows a schematic diagram of the experimental set-up used for the separation tests, as well as the catalytic membrane reactions. The xylenes were fed as gas phase diluted in nitrogen, using two saturators in series. The temperature in the first saturator was kept 5 K higher than the second one, in order to ensure precise vapour saturation. The flow through the compartments could be either co- or counter-current (valve 3). The carrier gas, and sweep gas flow rates were controlled with Brooks mass flow controllers (FC). The internal pressure was measured with the help of a

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