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Influence of synthesis and operating parameters on silicalite-1 membrane properties

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ABSTRACT

The present study deals with the synthesis of nanostructured silicalite-1 membranes on porous α-Al_2O_3 supports by a hydrothermal method. Different parameters including the synthesis conditions (temperature and alkalinity) and operating conditions (temperature and pressure) were investigated. The membranes were characterized by X-ray diffraction and scanning electron microscopy techniques. The optimum synthesis temperature and alkalinity were determined to be 160 °C and pH = 11, respectively. The permeability of CO_2 and CH_4 through the optimized membrane was determined by the pressure drop method. The results revealed that the main effective separation mechanism was adsorption. The permeation of CO_2 and CH_4 declined with increasing temperature, whereas high feed pressures enhanced the single gas flux. The CO_2 and CH_4 permeability values at 30 °C and 2 bar were 1.62×10^{-7} and 2.07×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, respectively. Furthermore, the response surface methodology analysis confirmed the significance of all the variables and the proposed model. Excellent correlation between the experimental and predicted data ($R^2 = 0.99$) was obtained, confirming that response surface methodology is a powerful tool for modeling nanostructured silicalite-1 membrane processes.

1. Introduction

In the past decade, significant progress has been made in the fields of membrane synthesis, transport, and separation principles. Zeolites have attracted great attention for industrial applications because of their remarkable properties [1]. Several reviews on zeolite membranes have focused on the synthesis and application of membranes for gas separation [2–4]. Zeolites exhibit uniform pore size, regular pore structure, and high chemical and thermal stability, which are all desired properties for membrane applications [5]. Since the synthesis of the first zeolite in 1948, several types of zeolites have been reported [6]. Mordenite framework inverted (MFI)-type zeolites are one of the most versatile frameworks, with applications in the highly selective separation of chemicals, such as hydrocarbons [7] and CO_2 [8–10], as well as a number of catalytic processes [11–13]. The MFI structure contains two zeolites: silicalite-1 and ZSM-5. Silicalite-1 is a siliceous material, more hydrophobic and less acidic than ZSM-5. A variety of methods can be used for zeolite membrane synthesis, such as hydrothermal [14–16], secondary growth [17], and microwave methods [18]. The hydrothermal method is the most common technique because of its simplicity and straightforwardness [19]. The use of different chemical

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sources and crystallization conditions, including the alkalinity, temperature, aging time, organic structure–directing agents, and silica precursors [20], influences the formation of silicalite-1 crystals. In particular, the temperature and alkalinity influence the crystal growth and nucleation rate [21].

Different types of zeolites, including MFI [22], Linde Type A [23], and mordenite [24], have been used for gas separation applications. However, MFI membranes are the most popular due to the vast literature available on their preparation, their suitable pore size for industrial applications (0.55 nm), easy synthesis, possibility of chemical modification, and high thermal and chemical stability [25]. The adsorption properties of each gas affect their diffusion through MFI membranes. The flux through the membrane is also influenced by the operating temperature and pressure [21]. Asaeda and Yamasaki [26] synthesized a porous silica membrane and showed that the permeance and selectivity toward CO_2 and CH_4 decreased with increasing temperature in the range of 27–227 °C.

To optimize membrane processes, the effects of the operating parameters and morphological features, such as the temperature, pressure, kinetic diameter of the permeating species, and crystallization time, on the membrane performance have been widely reported [27,28]. Most studies on gas separation have been carried out by a one-factor-at-a-time approach, in which one single parameter is systematically varied, whereas the other factors are fixed. Such one-factor-at-a-time methods fail to consider the possible interactions between parameters [29]. Therefore, statistical design of experiment (DOE) and response surface methodology (RSM) approaches are much needed to evaluate the effect of operating variables and their potential synergy/antagonism on the membrane performance [30]. Furthermore, research reports related to the application of RSM for the optimization of nanostructured silicalite-1 membranes are rare.

In this study, nanostructured silicalite-1 membranes were synthesized on porous α-Al_2O_3 supports by a hydrothermal method. The effect of alkalinity and temperature on the membrane morphology was investigated. The permeability of CO_2 and CH_4 gases as a function of the operating temperature and pressure was determined. Furthermore, a quadratic model was proposed based on an RSM approach to study the effect of process variables on the permeation flux through the nanostructured silicalite-1 membranes.

2. Materials and methods

2.1. Membrane preparation

Nanostructured silicalite-1 membranes were synthesized on homemade porous α-Al_2O_3 supports by a hydrothermal method. The synthesis solution was prepared as follows: a certain amount of aluminum hydroxide ($Al(OH)_3$, Merck) was dissolved in distilled water in a tightly covered polypropylene beaker and stirred for 15 min. Then, the appropriate amount of tetrapropylammonium hydroxide (TPAOH, 1.0 M, Sigma–Aldrich) was added and the solution stirred for 15 min. Tetraethyl orthosilicate (TEOS, >98%, Merck) was dissolved in distilled water and stirred for 15 min. This second solution was added dropwise to the first one under vigorous stirring. The molar composition of the final solution was 1.0TPAOH:3.24TEOS:0.03Al$(OH)_3$:400H_2O. The final mixture was then stirred for 1.5 h until it became transparent. A disk support (α-Al_2O_3) was placed inside a Teflon-lined stainless-steel autoclave completely filled with the synthesis solution. The hydrothermal process was carried out in an oven for 12 h. The recovered membranes were washed with distilled water several times and dried at room temperature (25 °C) for 24 h. The dried membranes were calcined at 450 °C for 8 h. The calcination process was carried out at a rate of 0.5 °C min^{-1} and cooled to room temperature at a rate of 1 °C min^{-1}. The samples (S_1–S_9) were synthesized according to Table 1.

2.2. Setup

In general, two methods are frequently used for permeation measurements through zeolite membranes: the pressure drop (PD) and concentration gradient (CG) methods. In the first method, a pressure gradient is applied to both sides of the membrane, whereas in the CG method a CG is the driving force resulting from a sweep gas flow at the permeate side. Researchers have described the effect of such a sweep gas on the feed permeability [31]. The PD method is simple, rapid for single gas permeation measurements, and more suitable for industrial operation. Furthermore, the PD method is capable of detecting viscous flow effects in the case of large defects in the membrane structure [32]. Therefore, the PD method was selected for this study. Fig. 1 shows the experimental setup. To control the operating temperature, the module was placed in an oven. In all the experiments, the feed pressure was fixed and the permeate side was vacuumed before each test. No sweep gas was used. CO_2 and CH_4 gases with purity of 99.99% were supplied by Technical Gas Services. The permeate gases were collected in a fixed volume vessel and the pressure changes in the vessel were monitored during the tests. The permeability of the gas was calculated by the following equation:

$$Q = \frac{V_c}{S_m R T_0 (P' - P'')} \left(\frac{dP''}{dt} \right) \quad (1)$$

where V_c is the vessel volume (m^3), S_m is the membrane surface area (m^2), P' and P'' are the feed and permeate

Table 1
Different temperatures and pH levels for membrane preparation.

Membrane no.	Synthesis temperature (°C)	pH
S_1	160	11
S_2	170	11
S_3	180	11
S_4	160	9
S_5	170	9
S_6	180	9
S_7	160	13
S_8	170	13
S_9	180	13

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