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# Application of a CHA-type zeolite membrane to the esterification of adipic acid with isopropyl alcohol using sulfuric acid catalyst

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ABSTRACT

CHA-type zeolite membranes show extremely high dehydration performance and high acid stability. This study applied the membrane to the esterification of adipic acid with isopropyl alcohol using sulfuric acid as the catalyst. The membrane was placed in the vapor phase to avoid direct contact with sulfuric acid, and water vapor was removed by vapor permeation. A numerical kinetic model was constructed to understand the effect of dehydration by the membrane, and the experimental results were compared with the model predictions. The yield of diisopropyl adipate increased from 56% to 98% by membrane assistance. Moreover, the ester was produced in the high efficiency (yield > 90%) despite the small membrane (35–80 cm$^2$ per kg of reactant), since the permeation flux of the membrane was significantly high. These results suggest that assistance by a CHA-type zeolite membrane is effective for the ester condensation reaction of adipic acid with isopropyl alcohol. This paper also discussed the stability of the membrane under the reaction conditions.

## 1. Introduction

Inorganic membranes have been prepared from various materials such as palladium alloys, microporous silica, molecular sieve carbon, zeolites, and solid oxides. As the thermal and chemical stabilities of these membranes are higher than those of polymeric membranes, they can be applied to membrane reactors.

Membrane reactors are categorized by the catalytic activity of the membrane [1,2]. Catalytically active membranes work as catalysts and separators, while catalytically inert membranes shift chemical equilibria in the desired direction by removing the products or byproducts [3–8]. Hydrogen-permeable membranes have been applied in hydrogen production [3,4], and water-permeable membranes have been used to study esterification reactions [5–9].

Zeolite membranes are often used for membrane-assisted esterification [6–9] because they have high permeability or high acid stability. For example, the permeation flux of an A-type zeolite membrane was found to be 0.14 mol m$^{-2}$ s$^{-1}$ for a 78 mol% ethanol solution at 348 K [10]. But, the acid stability of the membrane was very low [11]. Although T-, MOR-, and SOD-type zeolite membranes have high acid stabilities [12–14], their permeation flux was much lower than that of the A-type zeolite membrane. These studies suggest that membranes with high permeation flux and acid stability are necessary for membrane-assisted esterification.

CHA-type zeolite membranes have been investigated in our previous research [15–17]. The membranes showed extremely high dehydration performance and excellent acid stability. The permeation flux was more than 0.2 mol m$^{-2}$ s$^{-1}$ for a 78 mol% ethanol solution at 348 K [17], and the separation factor was more than 10,000 for 10 h in an acid solution at pH 2 [15]. In the present study, the CHA-type zeolite membrane was applied in the esterification of adipic acid with isopropyl alcohol. Notably, sulfuric acid, one of the strongest acids that can destroy zeolite frameworks, was used as the catalyst. Hence, the membrane was placed in the vapor phase to avoid direct contact with sulfuric acid, and water was removed through the membrane by vapor permeation.

This study examined the esterification of adipic acid and isopropyl alcohol with and without membrane assistance, and a numerical kinetic model was constructed to discuss the effect of membrane dehydration on the esterification reaction. In addition, membrane stability was discussed.

## 2. Kinetics

Since adipic acid is dibasic, it is esterified by isopropyl alcohol in two stages, as follows

$$A + I \underset{k1/K1}{\overset{k1}{\leftrightarrows}} M + W, \qquad (1)$$

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$$\mathrm{M}+\mathrm{I}\ \underset{\overset{\rightarrow}{k2/K2}}{\overset{k2}{\leftarrow}}\ \mathrm{E}+\mathrm{W}, \tag{2}$$

where A, I, M, W, and E indicate adipic acid, isopropyl alcohol, mono-esterified adipic acid (intermediate), water, and diisopropyl adipate, respectively. $k$ and $K$ are the rate constant and equilibrium constant, respectively. Since the reaction rate is influenced by the amount of added catalyst, the rate for Eqs. (1) and (2) are given by

$$R_1 = w\left(k_1 C_A C_I - \frac{k_1}{K_1} C_M C_W\right), \tag{3}$$

$$R_2 = w\left(k_2 C_M C_I - \frac{k_2}{K_2} C_E C_W\right), \tag{4}$$

where $w$ and $C_i$ are the amount of added catalyst and the concentration of component $i$. The changes in the concentration of each component are described as follows:

$$\frac{dC_A}{dt} = -R_1, \tag{5}$$

$$\frac{dC_I}{dt} = -R_1 - R_2, \tag{6}$$

$$\frac{dC_M}{dt} = R_1 - R_2, \tag{7}$$

$$\frac{dC_E}{dt} = R_2, \tag{8}$$

$$\frac{dC_W}{dt} = R_1 + R_2 \tag{9}$$

When a membrane is used for water removal, changes in the water concentration include the dehydration rate $R_W$, as follows:

$$\frac{dC_W}{dt} = R_1 + R_2 - R_W \tag{10}$$

The dehydration rate $R_W$ is given by

$$R_W = \frac{k_W S \Delta P_W}{V}, \tag{11}$$

where $k_W$, $S$, $\Delta P_W$, and $V$ are the water permeance of the membrane, effective membrane area for permeation, partial pressure difference of water across the membrane, and total weight of reaction substrates, respectively. $V$ is decreased by membrane dehydration. Assuming that only water molecules can permeate through the membrane, the time course of $V$ is described as follows:

$$V = V_0 - M_W \int_{t=0}^{t} k_W S \Delta P_W \, dt, \tag{12}$$

where $V_0$ is the initial weight of the substrates.

## 3. Experimental section

### 3.1. Membrane preparation

A polycrystalline CHA-type zeolite layer was formed on the outer surface of a porous α-$Al_2O_3$ tube by the secondary growth of seed crystallites [15–17]. A synthesis gel for the secondary growth was prepared by mixing colloidal silica (Catalysts and Chemicals Industry Corp. Ltd., Cataloid SI-30), aluminum nitrate (Wako Pure Chemicals Industry), potassium hydroxide (Wako Pure Chemicals Industry), strontium nitrate (Wako Pure Chemicals Industry), and distilled water. The molar composition of the gel was $12SiO_2$: $1Al_2O_3$: $2K_2O$: 1SrO: $8KNO_3$: $780H_2O$. The porous α-$Al_2O_3$ tube was used as the support, and the properties were as follows: outside diameter = 2.0 mm, inside diameter = 1.6 mm, porosity = 39%, and mean pore diameter = 0.14 μm. The outer surface of the support tube was rubbed with CHA-type zeolite crystallites to implant seeds for nucleation. The support tube was added to an autoclave filled with the synthesis gel. The autoclave was placed in an oven at 413 K for 20 h to form the polycrystalline CHA-type zeolite layer on the support tube. After the autoclave was cooled in a water bath for 10 min, the composite membrane was washed with distilled water and dried overnight in air to obtain the CHA-type zeolite membrane, as shown in Fig. 1.

### 3.2. Pervaporation and vapor permeation tests

One end of the tubular membrane was connected to a stainless steel tube with a sealant (Varian, Torr Seal), and the other end was sealed. The effective membrane area for permeation was 1.9 $cm^2$. The membrane was used for the measurement of pervaporation, vapor permeation, and membrane-assisted esterification. For the vapor permeation tests (Fig. 2), the membrane was placed within the heating region in a flask, into which isopropyl alcohol solution (50 g) was added. For the pervaporation tests, the amount of the solution was increased to 200 g, and the membrane was immersed in the solution. For both the experiments, helium was introduced into the inside of the membrane at 1.0 mL $min^{-1}$ as the standard, and the

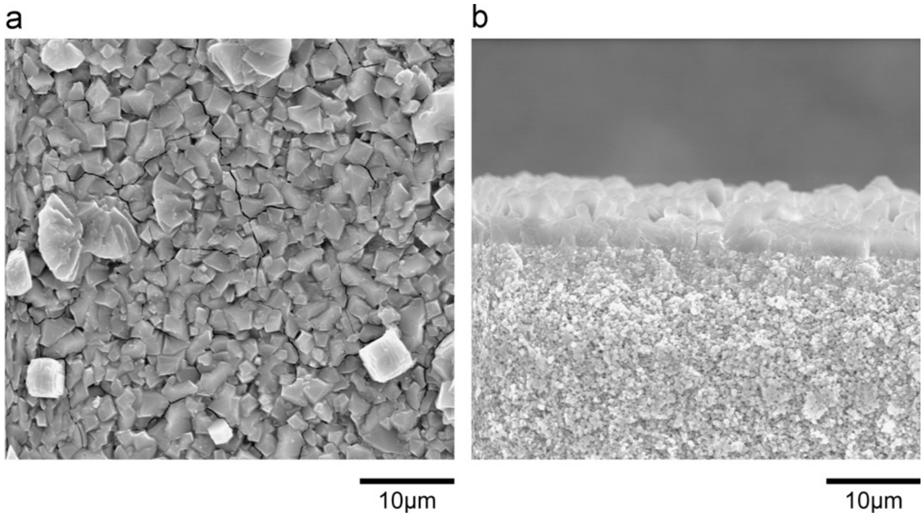

**Fig. 1.** Morphologies of the top surface (left) and fractured section (right) of the CHA-type zeolite membrane.