High efficiency ester condensation using hydrophobic zeolite membranes

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Abstract−We successfully developed zeolite membranes with hydrophilic character, by choosing appropriate zeolites in terms of hydrophilicity and high acid tolerance. We evaluated thus developed membranes by their pervaporation (PV) performance, dehydration from acidic organic solvent. The zeolite membranes we developed, based on merlinoite (MER), chabazite (CHA) or phillipsite (PHI), are shown to exhibit stable dehydration performance, respectively. We successfully applied the membranes to the selective removal of water in an ester condensation reaction starting from a stoichiometric mixture of a carboxylic acid and an alcohol. The availability of pervaporation-assisted ester condensation reaction was validated by various kinds of combinations of carboxylic acid and alcohols, which implies the general availability of pervaporation-assisted process intensification by zeolite membranes.

Key words: Zeolite Membranes, Pervaporation, Dehydration, Ester Condensation

INTRODUCTION

Separation via pervaporation (PV) and vapor permeation (VP) by membrane offers an energy-saving alternative over conventional distillation processes, and various kinds of organic membranes as well as inorganic membranes have been developed for the purpose [1,2]. Inorganic membranes are sometimes more convenient than organic ones because of chemical, mechanical, and thermal stability in PV and VP. Among inorganic membranes, recent progress in zeolite membranes has been promising as was proved by a commercialization example of alcohol dehydration. In this case, membranes consisting of LTA type Na substituted zeolite (NaA zeolite) have been used, which have been benefited by higher separation factor (more than 5000) as well as higher permeate flux, up to (more than $2 \, kg \, m^{-2} h^{-1}$) in separating water over ethanol [3].

However, there is a major limitation with NaA zeolite membranes in the attempt of extensive use other than alcohol dehydration, namely, acid-sensitivity of the zeolite itself. Various kinds of efforts have been made to utilize the excellent performance of the zeolite membranes even under acidic conditions. Among them, the use of membranes consisting of acid-tolerant zeolites is a straightforward solution to maximizing the advantages of PV by zeolite membranes. So far, some membranes have been proposed. Kalipcilar et al. prepared SSZ-13 zeolite membranes, which permeated water to concentrate aqueous nitric acid solution [4]. Masuda et al. treated silicalite-1 with hydrogen peroxide, which permeated mainly water during pervaporation from acetic acid aqueous solution [5]. Tanaka et al. prepared T-zeolite membrane which showed more resistance to acid compared with the NaA zeolite membranes they had prepared [6].

Even though, it is still challenging for zeolite membranes to maintain their performance with keeping direct contact with acidic solvents, especially with the coexistence of catalysts as they often shows strong acidity.

In principle, hydrophilic zeolites are regarded to be acid sensitive (except silicalite-1 treated with hydrogen peroxide), as they contain more Al in cage and alkali ions such as Na and/or K ion is also contained to compensate the charge neutrality. As Na ion tends to leach during close contact with acid solution, acid tolerance and hydrophilicity are a kind of trade-off. Still, there is an opportunity to find an appropriate hydrophilic zeolite membrane, as cage structure is also considered to be responsible for acid tolerance.

In this paper, we attempted to develop hydrophilic acid-tolerant zeolite membrane that could survive under acidic reaction condition - the acidity stems from substrate and/or catalyst. We selected appropriate zeolites in terms of hydrophilicity and high acid tolerance. Next, we developed zeolite membranes based on what we selected, and evaluated them by pervaporation performance. Finally, they were applied to various kinds of pervaporation-aided ester condensation reactions where total conversion to corresponding esters was attempted by shifting the equilibrium via selective water removal, as shown in Eq. (1).

$$R_1\text{-OH} + R_2\text{-COOH} \rightleftarrows R_2COOR_1 + H_2O \qquad (1)$$
(Equilibrium shift via water removal)
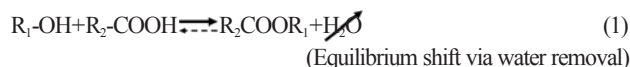
Ester condensation reactions are familiar among organic chemical processes. Due to their reversible nature, removing water from the reaction system is mandatory to achieve 100% conversion, and extensive effort has been reported to conduct the condensation reaction starting from stoichiometric reactant mixture, such as applying multiphase system and/or stripping water by distillation during the reaction. A multiphase system requires careful design of reactants/ product/water phase separation. Distillation condition may not be applicable for the reactions with thermally sensitive materials [7-14].

Pervaporation and/or vapor permeation using chemoseparative membranes have also served as an effort to remove water from the reaction system. Organic membranes as well as inorganic membranes including zeolite membranes have been applied to the purpose. But the pervaporation-aided process so far has been conducted more than at 340 K mainly because of insufficient water removing performance of membranes, namely lower flux, insufficient separatability. Also, it is preferable to apply VP as membrane separation because of low acid tolerance of these zeolite membranes [6, 15-21]. Considering that one of the advantages of PV-aided separation is working temperature, it is beneficial for the reactions with thermally sensitive materials. The zeolite membranes we report here open a new opportunity for pervaporation-aided chemical process intensification, leading to wide application not only for ester condensation reactions but also other dehydration-aided chemical processes at nearly room temperature.

EXPERIMENTAL SECTION

1. Zeolite Screening

We chose zeolite from three points of view - channel size comparison with permeate molecules, chemical affinity by adsorption measurements of water and organic compounds (s. a. alcohol), and chemical stability measurement against acid via X-ray diffraction measurements. Channel size comparison was conducted by using zeolite tables [22]. Vapor adsorption measurements were conducted by using BELSORP 18 (Nihon-Bel) and XRD profiles were recorded with BRUKER AXS M21X with CuKα radiation. Acid tolerance test was conducted by immersing each zeolite into 0.1 N of hydrochloric acid aqueous solution at 353 K for 1 h.

2. Zeolite Membrane Preparation

We prepared zeolite membranes on the outer surface of porous mullite tubes (PM tube, Nikkato Co.), whose chemical content is SiO_2 67% and Al_2O_3 33%, having 44% porosity and nominal pore diameter 1.8×10^{-3} mm. The tubes were 70-mm long having an inside diameter of 7.0 mm and an outside diameter of 10 mm. We applied the secondary crystal growth of the seed crystals which were rubbed on the porous surface. Zeolite membranes we prepared were MER, PHI, CHA, faujasite (FAU), MFI (both ZSM-5 and silicalite-1), and MFI treated with H_2O_2. Zeolite membranes were prepared by secondary growth method. Seed crystals of each zeolite were prepared in our laboratory, and accommodated into pore structure in the membrane support followed by secondary zeolite crystalline growth under hydrothermal condition. Detailed preparation procedure is described elsewhere [23-27].

3. Zeolite Membranes Evaluation by PV

PV experiments were conducted batch-wise on a laboratory scale. The zeolite membranes were capped with stainless steel-made caps and tubings. We interconnected the stainless steel-made component and the zeolite membrane with silyl functionalized urethane resin, commercially available. The urethane resin swells with organic solvents and tightens the gap during the pervaporation as well as the reactions.

We mainly evaluated pervaporation performance with equimolar mixture of ethyl acetate, acetic acid, ethanol and water (each organic chemical was purchased from Wako). Each membrane was set in a 12-member parallel organic reaction system (CCX-1000,

EYELA Co.), in which identical temperature control and mixing performance was validated. The inside of each membrane was evacuated and another series of test tubes served as traps for the permeate, which was immersed in a liquid nitrogen bath. The capped zeolite membranes were immersed into ca. 0.02 L of the mixture, and pervaporation was conducted by evacuating the inside of the membranes. The permeate was trapped separately in each test tube with liquid nitrogen. Content of the permeate was weighed, diluted with acetonitrile (Wako) and organic species (ethanol, acetic acid and ethyl acetate) were analyzed by DBWAX-ETR column (J and W capillary column) attached in GC-17A (Shimadzu), using FID detector. The amount of water was estimated from mass balance. PV from methanol aqueous solution was also tested for MER membranes.

4. PV Assisted Ester Condensation Reaction

We conducted stoichiometric ester condensation reactions from equimolar mixtures of alcohols and carboxylic acids, and zeolite membrane was immersed into the reactant solution. Catalysts used were Amberlyst 15(H) and Scandium Tri-fluoromethanesulfonate $(Sc(OTf)_3)$. The reaction temperature was kept at 313 K or 323 K during the reaction. Pervaporation via zeolite membrane was conducted by evacuating the inside of each zeolite membrane tube, and the permeate vapor was trapped separately in each test tube with liquid nitrogen. Both permeate and batch contents were analyzed by FID-gas chromatograph, by the same manner as pervaporation evaluation.

RESULTS AND DISCUSSIONS

1. Zeolite Selection

The first zeolite selection was conducted by the size of zeolite cage - as LTA zeolite, used for dehydration of alcohol, has 0.42 nm channel size, zeolite with similar cage diameter was selected, as MER, PHI, and CHA (Fig. 1). All of these zeolites show hydrophilic adsorption character. Acid tolerance was characterized via powder XRD, which revealed differences among FAU, CHA, MER and PHI. For MER and PHI the XRD intensity was maintained after acid treatment, while a little deterioration was observed for CHA and more severe deterioration with FAU [23].

Fig. 2 shows a comparison of pervaporation performance among zeolite membranes for equimolar mixture of ester condensation reac-
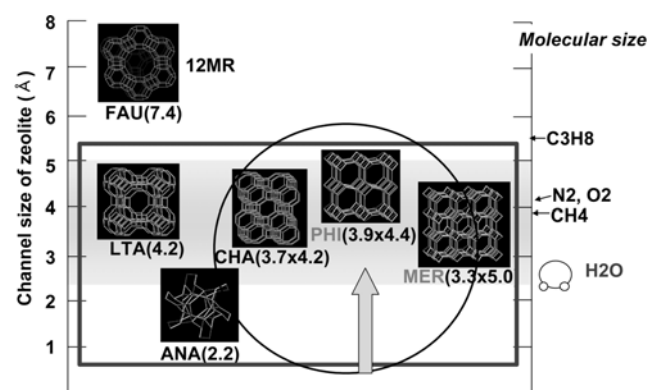

Fig. 1. Selection of zeolite by comparison of channel size and size of molecule.
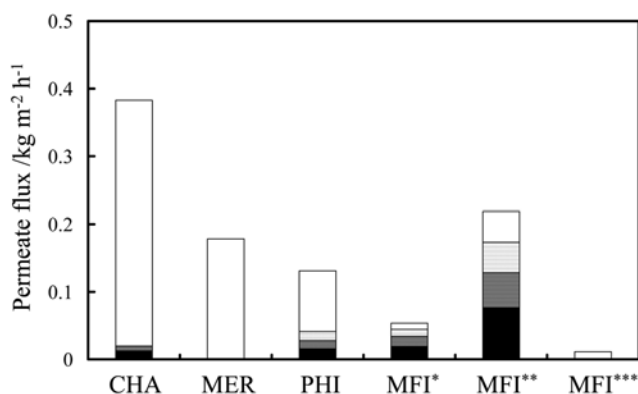
Fig. 2. Comparison of membrane pervaporation performances. Pervaporation was conducted at 313 K by immersing zeolite membranes into equimolar solution of water (□), ethanol (▨), acetic acid (▥) and ethyl acetate (■). Three different types of MFI membranes were used; ZSM-5 (Si/Al= 300), denoted as MFI*: silicalite-1, denoted as MFI: silicalite-1 with hydrogen peroxide treatment, denoted as MFI***. Membrane performances were compared at two hours.**

tion solution (namely, water, ethanol, acetic acid and ethyl acetate) at 313 K. FAU membrane leaked within one hour after starting pervaporation, and it is not presented. FAU zeolite with low Si/Al ratio was observed to be acid sensitive by the powder diffraction data, and the result is consistent with it [23]. CHA membranes and MER membranes exhibited excellent dehydration properties for both flux and water selectivity among these membranes. It is reasonable to regard why CHA membrane worked stably was because of weak acidic condition during the PV compared with zeolite acid tolerance test by powder form. PHI membrane also showed good dehydration property, although the selectivity is not quite excellent compared with CHA and MER membranes. Results are summarized in Table 1, where separation factor a is defined as follows:

$$\alpha = (F_{H2O}/F_{organic})/(B_{H2O}/B_{organic}) \qquad (2)$$

where F_{H2O} [kgm^{-2}h^{-1}] is the flux of permeated water, $F_{organic}$ [kgm^{-2}h^{-1}] is that of other organic compounds (ethanol, acetic acid and ethyl acetate), B_{H2O} [kg] is the amount of water in the batch and $B_{organic}$

Table 1. Comparison of membrane performance (cf. Fig. 2)

Membrane species	Total initial flux (kg m^{-2} h^{-1})	Separation factor α
CHA (Si/Al=2.34)	0.38	520
MER (Si/Al=2.34)	0.18	2200
PHI (Si/Al=2.78)	0.13	24
MFI (ZSM-5) (Si/Al=300)	0.05	2.3
MFI (silicalite-1)	0.22	2.8
MFI (silicalite-1, H$_2$O$_2$ treated)	0.01	25<
MER^a (Si/Al=2.34)	0.21	22

The experimental conditions were the same as Fig. 2 except MER^a: pervaporation was conducted from an equimolar mixture of methanol and water at 313 K.

[kg] is that of other organic compounds in the batch, respectively. The separation factors were 520 for CHA membranes and more than 2200 (organic substrates were under the detection limits by the gas chromatograph we used) for MER membranes, respectively, with reasonable flux (0.2-0.4 kgm^{-2}h^{-1}).

We also examined the pervaporation performance of MER membranes for methanol-water mixture, as they exhibited the best pervaporation performance among four hydrophilic zeolite membranes (MER, CHA, PHI, and H$_2$O$_2$ treated MFI). Results are also shown in Table 1. MER membranes exhibited good separation factor in methanol dehydration, as the separation factor was 20 and comparable to zeolite T membranes [28]. Compared with organic polymer membrane, permselectivity of water is excellent for zeolite membranes [2,31,32]. For example, silicone rubber composites have been used for the separation of hydrophilic VOCs separation, whose separation factor has been in the range of 5-10, even though promising results have been obtained by dispersing zeolite particles in the membrane [1].

High water permselectivity shown in pervaporation from organic/water separation comes from both hydrophilicity of zeolite itself and the size of cage, as the size of zeolite cage is 0.33 nm×0.50 nm for MER, which is smaller than most organic molecules (Fig. 1). This difference in pervaporation performance between CHA, MER and PHI has not been well understood yet, but it might arise during the membrane preparation; sizes of the seed crystals were different between CHA and MER (both less than 1 mm) and PHI (ca. 15 mm), hence it may be hard to incorporate PHI seed crystals into porous mullite tubes whose nominal pore diameter is 1.8×10^{-3} mm.

Also, the secondary growth condition was different between MER, CHA and PHI; thicker slurry was preferred as PHI membranes' precursor. These differences during membrane preparation may alter the dehydration performance. Generally, zeolite membrane consists of packed polycrystalline over the support, and seed crystals are considered to promote multinucleation to produce tiny crystallines over the membrane [2,31,33,34].

In the case of PHI membrane, it is likely that multinucleation of PHI crystalline is less controllable, which leads to larger intraparticle vacancies to deteriorate membrane performance. Considering these differences in preparation procedure, the performance of PHI membrane can be intensified by optimizing preparation condition, at least comparable with MER and CHA membranes. We regard that the difference in acid tolerance reflected that of membrane selectivity between CHA and MER, as powder diffraction data and acid tolerance test indicated MER to be more acid tolerable [23,27].

These performances are comparable to MOR membrane, ZSM-5 membrane reported by Li et al. or zeolite T membranes reported by Cui et al., even though it is hard to compare the performance directly because of the difference of experimental condition (both set-up and the feed content). One of the characteristics of our CHA, MER and PHI membranes is the potentially larger aqueous flux: our pervaporation evaluation was conducted at lower temperature, 313-323 K, while other zeolite membranes were mainly evaluated at around 343 K [28-30]. MFI membranes with high Si/Al ratio (Si/Al=300) or all-silica (silicalite) content showed mainly organic preferences. The performance of silicalite membrane treated by hydrogen peroxide exhibited hydrophilic character, which is consistent result with Masuda et al. [5].
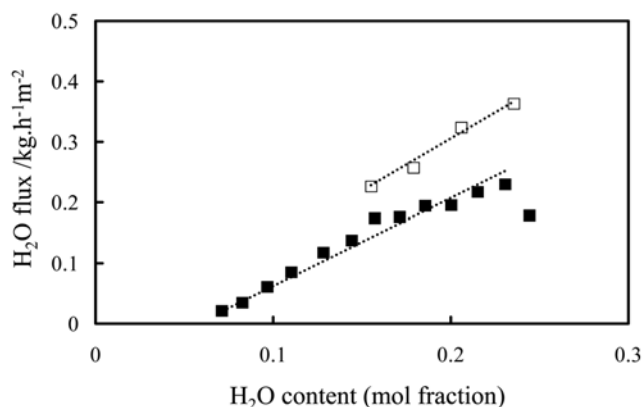
Fig. 3. Correlation between water permeate flux and water content in the solution for pervaporation via CHA (□), and MER (■) membranes. The initial condition (feed content and pervaporation temperature) was the same as Fig. 2.
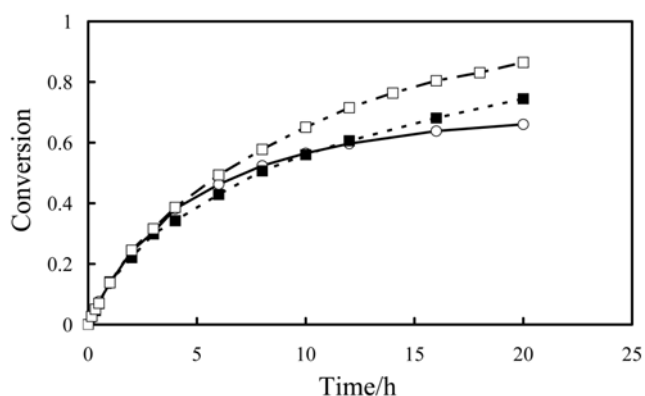

Fig. 4. Pervaporation assisted ester condensation reaction between ethanol and acetic acid at 313 K. The initial condition was the equimolar mixture of ethanol and acetic acid. Conversion was defined as (amount of ethyl acetate (mol)/(amount of ethyl acetate (mol)+amount of acetic acid (mol)). The membranes used for pervaporation were CHA (□), and MER (■) membranes. Blank test (non-pervaporated batch) was also conducted (○).

There was a good correlation between the amount of water in the flux and water content of the solution for MER and CHA membranes, and the performance of these membranes was kept stable at least 100 h of PV operation. The water flux dependence on water content in the feed is shown in Fig. 3 for MER and CHA membranes. The water flux was proportional to the water content in the feed, a consistent tendency with other hydrophilic membranes such as NaA zeolite, zeolite T, and Al-rich ZSM-5 membranes, which have shown similar proportional tendency with feed at low water content (lower than 20 wt%) [28,29,31]. In our case, the maximum water content in the feed (initial water content in the feed was 0.25 by mole fraction) corresponds to 8.5 wt% of water that confirms consistency.

2. Ester Condensation Reaction Results

We conducted ester condensation from equimolar mixture of ethanol and acetic acid by applying pervaporation via MER, CHA and PHI membranes, as the promotion effect was expected to be visible with membranes with higher water flux. That is, the reaction pro-

ceeds rightward by the equilibrium shift via water removal in Eq. (1):

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O \qquad (1)$$
(Equilibrium shift via water removal)
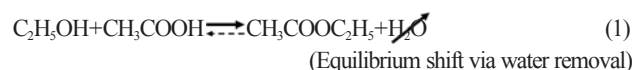
The results are shown in Fig. 4. In all three cases, pervaporation via CHA membrane, or MER or PHI membrane, condensation reaction proceeded more than equilibrium conversion (estimated to be 0.66 at 20 h after the reaction started), as water was selectively removed by pervaporation. The promotion of ethyl acetate yield was more visible with CHA membrane, in which the conversion reached 0.86 at 20 h. The initial reaction rates were nearly identical whether or not pervaporation worked during the reactions. The promotion of ethyl acetate yield became visible when the water removal via pervaporation became apparent. The reaction profile can be deter-

Table 2. Reaction results of pervaporation assisted ester condensation

Substrate			Ester yield (%)*, Time (h)	
Alcohol	Acid	Catalyst		Membrane
Methanol	Acetic acid	Sc(OTf)$_3$	98 (74) 47	CHA
Ethanol	Cyclohexane Carboxylic acid	Sc(OTf)$_3$	85 (59) 28	MER
	Acetic acid	Amberlyst (15H)	92 (68) 20	CHA
	Propanoic acid	Sc(OTf)$_3$	96 (73) 95	PHI
	Pentanoic acid	Sc(OTf)$_3$	87 (62) 76	PHI
	Hexanoic acid	Sc(OTf)$_3$	98 (88) 94	PHI
2-Propanol	Acetic acid	Sc(OTf)$_3$	82 (62) 47	CHA
Ethanol	Benzoic acid	Sc(OTf)$_3$	61 (60) 42**	MER
t-BuOH	Acetic acid	Sc(OTf)$_3$	0 (0) 47	MER
Phenol	Acetic acid	Sc(OTf)$_3$	4 (4) 48	MER

*Ester yields are estimated combining batch reactor contents and trapped permeate analyses. Yield in ( ) means non-pervaporation aided results. Reaction Temperature was 323 K, except methanol reaction (313 K).
**This reaction was conducted in acetonitrile solution due to poor solubility of benzoic acid. Other reactions were conducted under crude condition.

mined by the catalyst activity, equilibrium constant, and water removal flux. The reaction system with CHA membrane benefited by larger water removal flux that made the promotion effect more visible [16,26].

Table 2 summarizes the reaction results with various kinds of substrates. As a general trend, those reactions with fast initial reaction rates were promoted effectively by pervaporation, such reactions between primary or secondary alcohols and light carboxylic acids. In these cases, the reaction profiles were similar to Fig. 4, which shows that the effect of pervaporation becomes visible after the system reaches equilibrium.

It should be noted that ester condensation using methanol was successfully conducted, in which water removal by distillation cannot be applied because of lower boiling point of methanol. The separation factor of water from water-methanol equimolar mixture was 20, and such permselective performance worked beneficially for this reaction.

By contrast, promotion effect by pervaporation was not visible for those reactions with slower initial rate. As a nature of pervaporation, the amount of water flux depends on the water concentration in the solution. Reactions should proceed for water to accumulate in the reaction solutions so that the water removal via pervaporation works. One of the solutions to accelerate these slow reactions is to design a catalyst - zeolite membrane integrated reactor, so that the water concentration around the zeolite membrane can be promoted.

CONCLUSION

We successfully developed a brand new type of acid tolerant hydrophilic zeolite membrane consisting of MER, CHA and PHI membrane. Among these, MER, CHA showed excellent and stable and reasonable performance during pervaporation of water from equimolar solution of ethanol, acetic acid, ethyl acetate and water, as separation factor (α) was more than 500 and the water flux was 0.38 kgm^{-2}h^{-1} at 313 K. Also, MER membrane showed good separatability between water and methanol, whose separation factor was more than 20, and showed potential ability to condense hydrogen peroxide aqueous solution via pervaporation. PHI showed good performance during the same process, even though there seems to be more room for membrane performance optimization.

Thus developed membranes were applied to pervaporation-aided ester condensation reaction in which selective water removal promoted ester yield. By applying thus developed zeolite membranes, we have successfully developed a reaction system that enables stoichiometric ester condensation via continuous dehydration by pervaporation via zeolite membrane. Zeolite membranes we developed enabled effective water removal at nearly room temperature, even methanol was contained in the reaction system. The availability of pervaporation-assisted ester condensation reaction has been validated by various kinds of combination of carboxylic acid and alcohols, which implies the general availability of pervaporation-assisted process intensification by zeolite membranes.

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