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Application of a sodalite membrane reactor in esterification—Coupling reaction and separation

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A R T I C L E I N F O

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ABSTRACT

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Keywords: Membrane reactors Pervaporation Esterification Hydroxy sodalite A tubular hydroxy sodalite (SOD) membrane was successfully applied in the esterification of acetic acid with ethanol and acetic acid with 1-butanol, to selectively remove water by pervaporation and to overcome the thermodynamic equilibrium limitation of the esterification. The reactions were carried out using equimolar solutions of acetic acid with the appropriate organic alcohol at 363 K using Amberlyst 15 as acid catalyst. The hybrid process drove the esterification reactions almost to completion. The special feature of the SOD-membrane is that it showed absolute selectivity towards water and retained its stability under the reaction conditions. The membrane exhibited a stable water pervaporation performance at pH values above 2.9 for acetic acid–water mixtures.

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1. Introduction

Hybrid processes combining reaction and separation are becoming increasingly popular in chemical industry [1–5]. In these, the use of membranes and membrane technology for the selective separation of products from equilibrium limited media to shift equilibria towards higher reaction yields is being progressively recognized [6-16]. Esterification is a classical case of an equilibrium limited reaction [17]. Traditionally the equilibrium limitation is overcome by either using an excess amount of the alcohol or by separating the by-produced water from the reaction through reactive distillation or reactive stripping [18,19]. While the use of excess alcohol may increase the operation costs on the downstream reagent recovery and result in unwanted ether formation [20], reactive distillation is only useful when the products and reactants are not close boiling liquids [19]. In this respect, the use of membrane reactors is attractive as the process efficiency is not limited by the thermodynamic equilibrium conversion while the process costs can be reduced due to the smaller amounts of reactants required and the higher conversions obtained [21-25].

In integrating reaction and membrane separation, typically pervaporation is coupled with the chemical reaction [7,26–33]. In contrast to distillation which is based on the difference in volatilities of the substances, pervaporation solely relies on the solubility and transport rate of each compound. Conventionally membrane reactors are configured as either a batch reactor, where the reaction takes place, followed with an external pervaporation unit built in the recycle to continuously remove water from the reactor [34], or as an integrated unit where both reaction and separation take place simultaneously [35]. Both configurations have been widely studied in the literature [34]. Next to esterification, other types of equilibrium limited reactions such as etherification and condensation reactions have been investigated [36].

Here we report on the esterification in a membrane reactor of acetic acid with ethanol and with 1-butanol to produce ethyl acetate and butyl acetate, respectively, using Amberlyst 15 as catalyst. A tubular hydroxy sodalite membrane has been used as a highly water selective membrane for water permeation. Hydroxy sodalite (H-SOD) is a zeolite-like material, consisting of sodalite cages only [37]. The material does not contain distinct pores or channels, but consists of an array of cages connected to each other through 4- and 6-rings. The 4-rings are too small to allow permeation of any molecule, but the diameter of the 6-rings is large enough (0.27 nm) to allow only very small molecules such as water (kinetic diameter: 0.265 nm) to pass through [37-39]. Owing to the unique window diameter of the material, absolute separation of water from various organic alcohol streams has been achieved [38]. In using membranes under esterification conditions, it is vital that the membrane preserves its structural integrity. Therefore, a hydroxy sodalite membrane was applied in dehydration of concentrated acetic acid solutions to study its stability under acidic conditions [40].

2. Experimental

2.1. Membrane preparation

A hydroxy sodalite tubular membrane was made according to a previously reported procedure [41] by means of hydrothermal synthesis on the inner surface of an α -alumina tubular support



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Table 1

 α -Alumina support properties.

Provider	Inocermic
Number of layers	3
Pore diameter top layer	200 nm
Surface treatments	None
Outer diameter	7 mm
Inner diameter	5 mm
Length permeable section	5 cm

purchased from Inocermic. The support properties are given in Table 1. The synthesis gel was prepared by mixing silicate and aluminate solutions with the final gel molar composition being 5SiO₂:Al₂O₃:50NaO₂:1005H₂O. After the hydrothermal treatment at 413 K for 3.5 h, the tube was thoroughly washed with water and dried under dry air flow overnight. Following, single gas permeation measurements using He and N₂ were conducted to verify formation of a closed membrane prior to use in the esterification reactions. As water acts as a template during synthesis, the sodalite cages are fully occupied with water. Therefore neither He nor N₂ should be able to permeate through the cages, unless through membrane defects. At room temperature and under a cross membrane pressure of 0.5 MPa, the membranes were impermeable to nitrogen, and the helium permeance was as low as $\sim 10^{-10}$ mol s⁻¹ m⁻² Pa⁻¹. This was used as a test of membrane quality before coupling it with the reaction section.

2.2. Pervaporation membrane reactor

The experimental set-up used for the reaction-pervaporation experiments is schematically depicted in Fig. 1. The esterification was carried in a 250 ml round bottom flask fitted with a reflux condenser. The flask was inserted in a thermostatic water bath and its temperature was regulated using a thermocouple. 1 mol ethanol or 1-butanol were initially added to the reactor with Amberlyst 15 as catalyst (loading: 100 g/l solution) and heated to the reaction temperature. An equimolar amount of acetic acid was heated separately, and after reaching the reaction temperature it was added to the reactor. Simultaneously, the reaction mixture was started to be continuously pumped through the pervaporation unit at a rate of 50 ml/min. This time was noted as the starting time of the experiment. The conventional esterification reactions were carried out until equilibrium was reached. In membrane facilitated experiments, the time at which the reaction was started parallel to the start up of the membrane system was noted at the starting time of the experiment.

The tubular membrane was initially sealed in a stainless steel membrane module, with the membrane on the inner side of the tube facing the feed ($A = 15.0 \text{ cm}^2$ effective membrane surface area and a selective layer thickness of about 1 µm [38]); the module was placed in the oven of the pervaporation set-up and was controlled to maintain the same temperature as the reaction medium.

The feed pressure was regulated using a backpressure controller and kept at 0.5 MPa to ensure a liquid phase feed at the exercised temperatures. A two-stage vacuum pump was used to evacuate the permeate side. The pressure at the permeate side was kept at a constant value of 300 Pa and was monitored using a digital vacuum gauge installed between the vacuum pump and the cold traps. The temperature of the feed inside the membrane cell and the permeate temperature were measured using two thermocouples. At steady state conditions, the flux through the membrane was determined by the rate-of-rise method described elsewhere [38].

Samples were withdrawn from both the reactor and the permeate side at regular intervals and immediately quenched for analysis using a GC (HP 6890, column: HP-FFAP) equipped with a thermal conductivity detector (TCD).

3. Reactor model

The model reactions which have been used to describe the esterification reactions investigated in this study can be generally expressed as:

$A + B \Leftrightarrow E + W$

where A is acetic acid, B is the alcohol, being either ethanol or butanol, E is the ester and W is the water.

For sole esterification, when an excess of the alcohol is used and if the selectivity of the desired production is 100%, the conversion of the limiting reactant acetic acid, *X*, can be expressed in the ratio of the acid to ester:

$$\frac{\text{acid}}{\text{ester}} = R_1 = \frac{1-X}{X} \tag{1}$$

$$X = \frac{1}{R_1 + 1} \tag{2}$$

Hence,

Table 2 gives the reaction mixture composition in the feed at time t_1 . When pervaporation is coupled with esterification, water is removed from the reaction system, and the composition of the reaction changes as given in Table 2. In the pervaporation-aided



Fig. 1. Schematic drawing of the pervaporation set-up (V, valve; PI, pressure indicator; TR, temperature recorder; BPC, back pressure controller; CT, cold trap).

(4)

Table 2Feed composition and reaction composition in the coupled membrane reactor.

Time (h)	Amount (mol)					
		Acetic acid	Alcohol	Ester	Water	
Feed	t = 0	N ₀	N ₀	0	0	
Batch reactor	$t = t_1$	$N_0(1-X)$	$N_0(1-X)$	N_0X	N_0X	
Coupled reactor	$t = t_1$	$N_0(1-X)$	$N_0(1-X)$	N_0X	N_0Y	

esterification the ratio of ester to water is equivalent to:

$$\frac{\text{ester}}{\text{water}} = R_2 = \frac{X}{Y}$$
(3)

$$Y = \frac{R_1}{R_2}$$

Hence,



Fig. 2. Concentrations of acetic acid (\Box) and ethyl acetate (a) and butyl acetate (b) (\bigcirc) in reaction mixture as a function of reaction time without water removal (*T*=363 K, equimolar feed). The solid lines were calculated according to the kinetic model.

Using calculated *X* and *Y* values from the experimentally determined concentrations, the amount of water removed (N_w) can be determined:

$$N_{\rm w} = N_0(X - Y)(\rm{mol}) \tag{5}$$

with N_0 being the initial amount of acetic acid.

The liquid reaction volume changes from the feed volume V_0 to V_1 . If the volume of the removed water is V_2 , and assuming additive properties, then:

$$V_0 = V_1 + V_2$$
 (6a)

$$V_2 = \text{Molar volume liq water} \times N_0(X - Y)$$
(6b)

For simple first order behaviour in the reactants and products, the rate of the reversible esterification can be written as:

$$r_{\text{est}} = k_1 \left[\frac{N_0(1-X)}{V_1} \right] \left[\frac{N_0(R_1-X)}{V_1} \right] - \frac{k_1}{K_{\text{eq}}} \left[\frac{N_0 X}{V_1} \right] \left[\frac{N_0 Y}{V_1} \right]$$
(7)

and substitution in the molar balance for a batch reactor leads to:

$$\frac{dX}{dt} = \frac{N_0 k_1}{V_1} \times \left[(1 - X) \cdot (R_1 - X) - \frac{X \cdot Y}{K_{\text{eq}}} \right]$$
(8)

The equilibrium constant, K_{eq} , is determined from the composition of the reaction mixture in the batch experiment without water removal (so $R_2 = 1$, Y = X, and $V_1 = V_0$) at equilibrium:

$$K_{eq} = \left\{ \frac{[E][W]}{[A][B]} \right\}_{eq}$$
(9)

The forward rate constant k_1 is determined from the early stages of the reaction ($t \sim 0$). Both parameters were estimated simultaneously by nonlinear Least Squares Analysis, applying Athena Visual Studio (www.athenavisual.com).

In the coupled reaction system, the water removal rate at any time *t* can be expressed as:

$$R_{\rm H_2O} = \frac{dN_{\rm w}}{dt} = N_0 \frac{d(X - Y)}{dt} \,({\rm mol}/{\rm min}) \tag{10}$$

If all water is removed through the membrane, the flux can be determined as:

$$J = \frac{R_{\rm H_2O}}{A} \tag{11}$$

where J is the water flux through the membrane, and A is the effective membrane surface area. Now the calculated flux can be compared with the measured flux through the membrane.

As hydroxy sodalite is a highly water selective membrane with water selectivity values of above 1,000,000, the permeation of the organic components need not to be considered.

4. Results and discussion

4.1. Heterogeneous catalytic reactions

The catalytic activity of Amberlyst 15 and the thermodynamic equilibrium conversion were determined from the batch reactor operation. As shown in Fig. 2, in case of ethanol esterification with acetic acid, after 2 h of reaction at 363 K equilibrium was reached, while 1-butanol esterification with acetic acid required 7 h at 363 K. The equilibrium constant, K_{eq} , and forward rate constant, k_1 , of each reaction were determined at 343 K and 363 K (Table 2). Table 3.

4.2. Membrane activity

The esterification reactions were carried out in the absence of the catalyst with the addition of freshly synthesized hydroxy sodalite crystals (10 wt.%). In case of ethanol esterification after 8 h

Table 3

Equilibrium constant and forward rate constant in the esterification of acetic acid with ethanol and 1-butanol with Amberlyst 15 as catalyst.

Esterification	T=343	<i>T</i> =343 K		3 K
	Keq	k_1 (l/mol min)	Keq	k_1 (l/mol min)
Acetic acid with ethanol Acetic acid with butanol	3.16 2.73	0.003 0.037	4.85 3.51	0.045 0.103

of experiment only a 17% conversion was reached, the same as in a blank run without any catalyst (Fig. 3). Similarly, for butanol esterification, after 8 h of reaction, a 14% conversion was reached which is the same as without catalyst. Thus, hydroxy sodalite behaves as an inert by showing no catalytic activity in either esterification reaction.

4.3. Pervaporation-aided esterification

In Fig. 4a and b the concentration profiles of acetic acid, water and ethyl acetate and butyl acetate in the pervaporation-assisted



Fig. 3. Conversion of acetic acid with ethanol (a) and with 1-butanol (b) in a blank run without catalyst (\bigcirc), and in an experiment in the presence of hydroxy sodalite crystals (\bullet), *T* = 363 K.



Fig. 4. Concentration of acetic acid (\Box) , ethyl acetate (a) butyl acetate (b) (\bigcirc) , and water (\triangle) in the reaction mixture with pervaporation through a hydroxy sodalite membrane as a function of reaction time (*T* = 363 K, equimolar feed). The solid lines were calculated according to the kinetic model.

reactor configuration are presented. The water concentration profile in the membrane reactor initially showed an increase until it reached a maximum, after which it started to decline continuously until it almost reached zero. This indicates that at the beginning of the reaction, the rate of water formation is faster than its removal from the reaction mixture.

In the pervaporation-aided esterification of both ethanol and butanol with acetic acid, the concentration profiles show a steady continuous decline in the amount of acetic acid followed simultaneously by the continuous increase of the ester content. The conversion of acetic acid to ethyl acetate increased from 67% to 98% (Fig. 5a) and in case of butyl acetate, conversion was enhanced from 62% to 92% (Fig. 5b). In both reactions, the water removal overcame the equilibrium limitation and drove the reaction towards completion. The conversion profiles in Fig. 5 indicate that the esterification of ethanol initially does not proceed much different from the batch experiment, while that of butanol shows a faster conversion in time. Fig. 6 shows the development of water activity as



Fig. 5. Conversion of ethanol (a) or 1-butanol (b) as function of time with (\blacksquare) and without pervaporation (\Box). The solid lines were calculated according to the kinetic model.

function of time in the mixture. Similar to the concentration profile of water formation (Fig. 4), evolution of water activity follows the same pattern whereby it increases with increasing water concentration and declines when membrane reaches steady state in removing water as it is being produced.

Fig. 7 shows the water flux through the membrane measured experimentally in comparison with the calculated flux values obtained from conversion data assuming that all water permeated through the membrane. For approximately the first 2 h of the experiment, the flux through the membrane is significantly lower than the flux values calculated based on conversion, while at longer time there is still a steady water flux through the membrane. The high 'fluxes' in the beginning are attributed to the increased volume of the reaction system in which water can be present in the vapor phase, constituting an apparent water disappearance in the initial phase of the process. The steady but low water removal through the membrane finally drives the reaction slowly to completion. The experimental flux values are in-line with earlier reports with this



Fig. 6. Evolution of water activity as function of time in the esterification of (a) ethanol with acetic acid and (b) butanol with acetic acid.

membrane type [38,41], showing a proportionality with the water concentration. This explains the long tailing of the process towards completion.

Hydroxy sodalite is exemplary in demonstrating the potential of membranes for in situ separation of products in reactions. The unique property of hydroxy sodalite in comparison with the other widely studied membranes in hybrid processes [26–33] is its virtually 100% selectivity in removing water solely on the basis of molecular sieving [38–40]. No traces of the other components were detected in the permeate (water selectivity~ 1,000,000). This in terms of industrial applicability gives sodalite the advantage of producing pure water at the permeate side, which eliminates the need of further downstream recovery or cleaning with direct reflections in the operation costs.

Compared to other hydrophilic inorganic membranes [42], sodalite also demonstrates a good stability under the ruling reaction conditions. The acidic conditions lead to the loss of membrane integrity in most hydrophilic membranes due to the leaching of the framework aluminum by the attack of hydroxonium ions [43].



Fig. 7. Water 'flux' through the membrane measured experimentally (\triangle) , and water removal rate calculated from the conversion data (\blacktriangle) for the esterification of ethanol with acetic acid (Fig. 4a).

Under mild acidic conditions, $pH \ge 2.9$, sodalite does not deteriorate in quality. Fig. 8 illustrates a hydroxy sodalite membrane performance in permeating water in different acidic solutions over prolonged operation times. The flux through the membrane remained stable through the process; no traces of acetic acid were detected at the permeate side. Although hydroxy sodalite is a hydrophilic material (Si/Al=1), its window openings are too narrow for aluminum to be leached out. In addition, the cages are at full saturation with water which almost fully occupies the space, and thus does not ease the attack of the dissociated OH⁻ groups. However, if the pH is decreased severely (Fig. 9), the framework exterior is weakened by the initial breakage of Si-O-Al bridges [28]. Under esterification conditions, the amount of acid present is counterbalanced by the other components throughout the reaction. Nevertheless, at the initial stages of the reaction when 50 mol% of the solution consists of acetic acid, long-term exposures under these conditions can initiate the disintegration of the membrane. Therefore it is crucial for the catalyst to be active enough in boosting the rate.

Selectivity, membrane stability and flux are three dominating factors which are crucial to membrane applications. A combination of the three is seldom offered by one specific membrane. Li et al. have recently reported on the synthesis of long-term stable membranes under reactive conditions. While the membranes show good flux values, they preserve their intactness under the reaction conditions [44]. Other reports indicate different results, while in most studies the importance of high flux values is empha-



Fig. 8. Membrane stability in pervaporative dehydration of water/acetic acid mixtures with feed water content of 93 mol% (\blacklozenge), 87 mol% (\blacksquare), 83 mol% (\blacktriangle), 80 mol% (\blacklozenge); $T_{\text{feed}} = 473 \text{ K}, P_{\text{feed}} = 2.2 \text{ MPa}, P_{\text{perm}} = 300 \text{ Pa}$. One hydroxy sodalite membrane was used in the whole series.



Fig. 9. Membrane stability in pervaporative dehydration of water/acetic acid mixtures with feed water content of 69 mol% (×), 49 mol% (+), 15 mol% (\bigcirc); T_{feed} = 473 K, P_{feed} = 2.2 MPa, P_{perm} = 300 Pa. For each condition a new membrane was used.

Table 4

Collection of membranes published in the literature tested for H₂O permeation under reactive conditions.

Membrane	Reaction type	$Flux (kg m^{-2} h^{-1})$	Selectivity	Reference
NaA	Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate, ethyl acetoacetate and diethyl malonate	0.104	124,000	[45]
Zeolite T	Esterification of acetic acid and ethanol	0.81	830	[46]
MOR	Esterification of acetic acid and ethanol	0.075	164	[42]
Zeolite A	Esterification of acetic acid and ethanol	0.150	92	[42]
NaA	Esterification of lactic acid and ethanol	0.12	1000	[47]
PVA	Acetylation of benzyl alcohol	0.54	640	[31]

sized, other focus on membrane stability [30–33]. It is often the process requirements which indicate a membrane's specific properties which can be utilized. In processes, where product loss does not govern the process costs, high flux values may be more desired compared to a case in which downstream separation of permeate or product loss can be detrimental to the process. Table 4 gives a summary of some of the most studied membranes under reactive conditions with their flux and selectivity values. Compared to these membranes, sodalite has the remarkable capability of being purely water selective.

5. Conclusions

Pervaporation-aided esterification of acetic acid with ethanol and with 1-butanol was successfully carried out using equimolar solutions of acid and base at 343 K and 363 K using Amberlyst 15 as catalyst. A hydroxy sodalite membrane was used to selectively remove water during reaction to enhance product formation, overcoming the equilibrium limitation. In the reaction system the membrane was capable of removing water at a rate compatible with its formation. In both reactions, conversion was increased by 30% almost reaching completeness. The water selectivity in these experiments was above 1,000,000. The reactor model to predict conversion and concentration profiles of the reactions was in good agreement with the experimental results.

Despite the hydrophilic nature of hydroxy sodalite, the membrane showed a good stability under the reaction conditions. Stand alone experiments of water pervaporation through a sodalite membrane in acetic acid/water solutions with $pH \ge 2.9$ proved the membrane to be stable for long operation duration. Below this pH the membrane disintegrated after a certain time.

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