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Review

Catalytically active membranes for esterification: A review

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ABSTRACT

Esterification is an important process in the food industry and can be carried out *via* homogeneous or heterogeneous catalysis. The homogeneous catalyst, despite providing high conversion, can cause corrosion in reactors, which is not observed with the use of heterogeneous catalysts. However, some of these catalysts require a high process temperature and may lose their catalytic activity with reuse. Thus, catalytic membranes have been proposed as a promising alternative. The combination of catalysis and separation in a single module provides greater conversion, reduction of excess reagents, compact industrial plant, making the process more efficient. Within this context, this work aims to present a literature review on the catalytic membrane for the synthesis of esters, improving the understanding of the production and development. This review examines the materials, catalysts used, and synthetic pathways. A comparison between the methods, as well as limitations and gaps in the literature, are highlighted.

1. Introduction

In recent years, an increasing interest in the application of catalytic membranes for ester synthesis is observed. Pervaporation (PV) is recognized as a viable high-performance membrane process for the separation of liquid mixtures. The use of PV with catalytic membranes for ester synthesis could be a competitive method compared to the conventional process, in which the synthesis is performed in batch or semi-batch reactors and the separation of products and by-products occurs in subsequent steps [1–3].

Like any membrane separation process (MSP), PV performance is based on two main parameters, selectivity, and permeability, which are directly related to the compounds to be separated, the operating conditions, and the chemical and physical characteristics of the membrane. The main advantages of PV include high membrane selectivity, reduced energy consumption, use of milder operating conditions, and compact design [4].

Generally, PV fractionates a liquid mixture by the difference in vapor pressure of the solutes. For such, the mixture to be separated is heated, and vacuum or carrier gas is used in the permeate side as a driving force to partially vaporize the substances of the mixture that cross the membrane and reach the permeate side, following the solution-diffusion transport mechanism [5]. Pervaporation can separate azeotropic mixtures, thermolabile products, and mixtures with compounds at low concentrations [6]. Main applications include organic solvents dehydration [7–10], separation of organic mixtures [11,12], and, more recently, the removal of water in esterification reactions [13–15].

Due to PV operating characteristics, the incorporation of catalysts directly on the membrane surface has been suggested as a promising alternative. The continuous removal of water produced in the reaction by PV can shift the thermodynamic equilibrium of the esterification reaction [16,17]. Thus, the deposition of catalysts transforms a PV membrane into a catalytic membrane combining the process of esterification and separation in a single step.

The integration of the PV system with a processing or chemical reaction unit is a strategy that allows the optimization of the synthesis processes and improves its general efficiency by increasing productivity, with less energy consumption and less waste generation in a more compact design [18,19]. Additionally, another attractive advantage of using a catalytic membrane in esterification reactions is the continuous removal of the water (by-product), which can lead to the maximum production of ester [16,17,20]. In summary, catalytically active membranes allow the catalysis and separation processes to occur in the same membrane, which has unique catalytic and selective layers. In this configuration, there is the advantage of *in-situ* removal of one of the reaction products, positively favoring reactions limited by equilibrium, as esterification reactions [20,21]. Since the membrane is hydrophilic,

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it shows higher water permeability [22]. Other medium components can also be removed and transferred to the permeate but in small concentrations. The most significant challenge in catalytic membrane synthesis is then the preparation of a membrane that presents concomitant high permeate flux and high water selectivity [17,20].

Two reviews published recently [23,24] describe well the characteristics of the catalytic membranes, the principles of operation, the influence of synthesis parameters in the membrane properties, characterization methods, and the applications of such membranes in several chemical processes. They provide a comprehensive view of the application of catalytic membranes in different applications in the chemical industry. However, none of them bring an in-depth comparison of the studies available in the literature on the application of catalytic membranes for esterification reactions related to using different catalysts, synthesis material, and process conditions. In this context, this review critically discusses the most used catalysts, synthesis materials, and the structure of the catalytic membrane for esterification, which are essential aspects for the production and application of catalytic membranes. Finally, future perspectives on the development of these membranes for esterification processes are presented.

2. Ester Synthesis

Esters are commonly used in the chemical, pharmaceutical, cosmetics, and food industries. According to a report published by the Global Industry Analyst, the valuation for the global aroma ingredients market is projected to reach USD 3.60 billion by 2026, being the esters responsible for a considerable revenue of about USD 1.00 billion [25]. The esters can be obtained by extraction and isolation of compounds from natural sources or produced through a chemical route, esterification, using chemical or biological catalysts [26–29].

Esterification is the condensation reaction between a carboxylic acid and an alcohol, forming an ester and water. The chemical catalyst can be either homogenous or heterogeneous. The homogeneous catalysts most employed in ester synthesis are chloric, sulfuric, phosphoric, and *p*-toluene sulfonic acid, mainly due to low cost and high conversion. However, hydrophilic acids like sulfonic and sulfuric acids present low activity and selectivity when used in reactions that produce water as a by-product [30]. Moreover, the application of these catalysts shows drawbacks because they cannot be reused, promote equipment corrosion, and require more purification stages [29,31,32]. In turn, heterogeneous catalysts (*e.g.*, zeolites [33–35], sulfatedzirconia [36,37], and acidified silica [38,39]) are not associated with corrosion of equipment and pipes and are easily separated from the reactional medium and recycled. Ion exchange resins (Amberlyst, Dower) have been widely used in organic synthesis [40–43]. These resins are composed of a matrix from divinylbenzene with active sites in the surface and present high thermal and mechanical stability and easy separation from the reaction medium [44]. Nevertheless, the heterogeneous catalysts show lower catalytic activity when compared to the homogenous catalysts. This fact motivates further investigations on the improvement of the catalytic activity of heterogeneous catalysts and studies related to their reuse [45].

The use of several catalysts and their synthesis routes to produce esters have been well reported in the literature in the past years, including the biocatalysts, which emerged as an alternative to traditional chemical adjuvants, mainly due to its high specificity and mild operational conditions of the process. Lipase (*e.g.*, Novozymes 435) is the most common biocatalyst applied in the industry forester production because it is easy to reuse and present reactional stability [46,47]. However, this type of catalyst still shows some limitations, such as enzyme denaturation, sensibility to alcohol concentration, and increased process cost [48].

Esterification is a reversible reaction influenced by the concentration and molar ratio of substrates and catalysts, temperature, and water content. It is common to use alcohol in excess to drive reaction equilibrium to product formation, although this practice results in high waste generation. The formation of water as a reaction byproduct in esterification is responsible for decreasing reaction rates and the generation of secondary products by the hydrolysis of the ester, resulting in a lower conversion profile. This is particularly observed in processes performed in batch reactors [29]. Hybrid processes have often been suggested for overcoming such drawbacks, in which the reaction and separation of products occur in the same device [15,16,29,41,49,50]. Another approach involves the use of reactive extraction intensified by a bifunctional solvent based on ionic liquids. In this case, the ionic liquid acts both as a solvent to the reaction medium and reaction catalyst. The produced ester is continuously extracted into an organic solvent while the acid, alcohol, and water are kept in the ionic liquid phase. Thus, the reaction equilibrium is shifted to the product formation, and conversion is improved [51].

3. Pervaporation Process

3.1. Basics of pervaporation

The PV process stands out due to the tailored selectivity and the possibility of separating azeotropic mixtures and heat-sensitive compounds. The PV (represented schematically in Fig. 1) is a membrane separation technique based on the transport mechanism known as solution-diffusion: (i) sorption of species into the membrane on the feed side; (ii) diffusion through the membrane; (iii) desorption at the permeate side. In this process, the liquid mixture is in direct contact with a nonporous barrier, and vacuum or inert gas flow is applied on the downstream side. The species that permeate the membrane vaporize, then they are collected in a condenser trap. The driving force for the separation process is the difference in the partial pressure of the species in the phases separated by the membrane. The use of a sweeping gas only becomes interesting if no extra condensation stage is required for the gas separation [52–54].

In terms of process, the liquid mixture is usually subjected to a temperature rise to the maximum saturation temperature of one of the components in the first stage of the separation process. The component with the highest diffusion rate and better affinity for the membrane is preferably absorbed by the barrier [22]. A concentration gradient is then created between both sides of the membrane. The compound desorption defines the third and final step of the separation process [1,55].

The performance of the PV process is commonly evaluated by the permeate flux (productivity) and the separation factor (selectivity) [56,57]. According to Eq. (1), the permeate flux, usually given as mass flux ($kg{\cdot}m^{-2}{\cdot}h^{-1}$), is characterized by the relationship between the mass of component(s) (m_{c1}) that permeate the membrane, the time (t) required for this, and the membrane area (A_m) [56,57].

$$J = \frac{m_{c1}}{A_m t} \tag{1}$$

The membrane selectivity is determined by the separation factor (α), given as the ratio between the mass ratios of the two components in the permeate and the feed stream [55,58], as described in Eq. (2).

$$\alpha = \frac{y_a/y_b}{x_a/x_b} \tag{2}$$

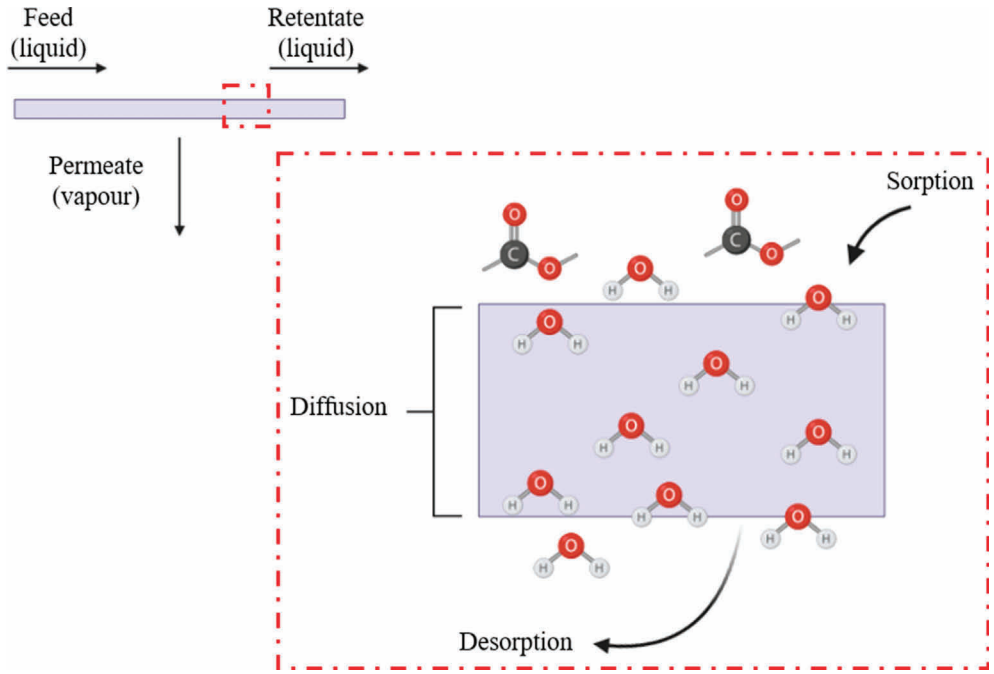

Fig. 1. Scheme of the pervaporation transport mechanism.

The separation factor is a dimensionless parameter. For values of α equal to 1, the separation of the mixture is not observed. In turn, when α tends to infinite, the process tends to the ideal separation. Feng and Huang [59] present a review of these PV process parameters.

Although most of the studies on PV use permeate flux and separation factor to describe the process behavior, these parameters are dependent on the composition of the feed mixture, the operation parameters, and membrane characteristics. Jyoti *et al.* [60] demonstrated, through mathematical equations, the interference of those parameters over the PV process performance. Baker *et al.* [4] suggest using permeability (component flux normalized by the membrane thickness and driving force) or permeance (component flux normalized by the driving force) and membrane selectivity (ratio of the permeabilities/permeances of two feed components) as parameters for evaluating the membrane performance. Still, according to Baker *et al.* [4], using these parameters allows studying membrane performance through their intrinsic parameters, enabling a more realistic analysis of the membrane and a better comparison between different studies.

3.2. Pervaporation in esterification reactions

Two process configurations have been investigated for the ester production by PV: (i) reactor and membrane separation module in distinct units; (ii) membrane module inside the reactor (Fig. 2). While the former configuration is more common in industrial applications, the second is a more recent approach, which integrates the reaction and separation steps. Some authors call this second configuration as inert membrane reactor (IMR) if the membrane is not catalytic (*i.e.*, inert), or catalytic membrane reactor (CMR) if the membrane has the catalyst in its structure [24].

The application of pervaporation with an inert hydrophilic polymer membrane in the dehydration of a reaction medium during the esterification was firstly proposed by Kita *et al.* [61]. The process was the esterification of oleic acid and acetic acid with ethanol using *p*-toluene sulfonic acid as a catalyst. Since then, the development of the membrane in terms of material, applications, and the optimization of operating conditions for the application of pervaporation in dehydration of a reaction media has been evolving. The main esters studied are used as flavor agents, solvents, and more recently biofuels. Table 1 indicates studies related to the application of inert membranes in esterification batch reactions.

High conversion of acid is achieved in the two system configurations under similar reaction conditions. Usually, the molar ratio between alcohol and acid is less than 3:1, but temperatures higher than 60 °C or long reaction times are needed for reaching high conversion.

An inert commercial pervaporation membrane was evaluated in organic synthesis processes. Chandane *et al.* [31] reported the stability of a commercial PVA/PES pervaporation membrane for the synthesis of isobutyl propionate. In the study, the inert membrane was used in 4 reaction cycles, under the same reaction conditions, maintaining the same conversion of propionic acid and physical stability.

It is noteworthy that few studies address the reuse of catalytic membranes, which is an important aspect considering their application in industrial processes. Among the studied parameters, selectivity, flux, and mechanical properties such as tensile strength may present a lower performance after the pervaporation process due to a plasticization effect and physical aging due to the presence of organic vapors [70–73]. The plasticization can increase the free volume and the sorption of feed components into the membrane [60]. Physical aging caused by the physical relaxation of polymeric chains may also occur [74].

The main limitation of using inert membranes in the esterification reaction is that the water generated is dispersed in the reaction mixture, reducing the conversion, usually requiring higher temperatures and time to favor the ester formation. Facing the limitation imposed by the esterification reaction equilibrium, the use of a catalytic pervaporation membrane has appeared as an attractive option [16]. The catalytic membrane has a layer containing catalysts, and a separation layer selective to water [75]. The catalyst layer incorporation in the membrane opens a new field of research area offering new alternatives to catalytic projects development. Since the esterification reaction occurs in the catalytic

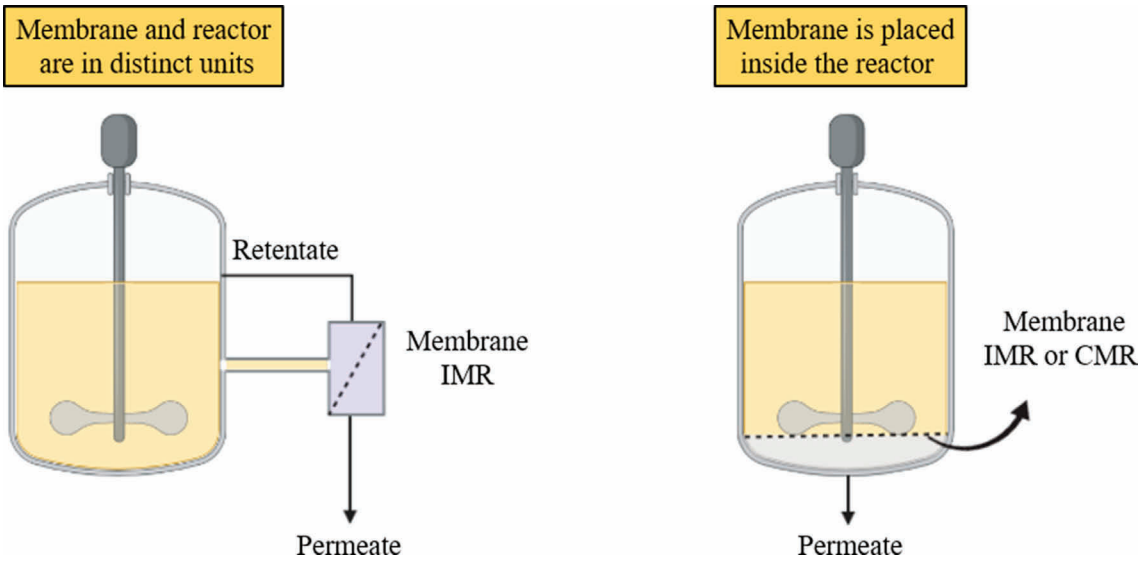

Fig. 2. Schematic illustrations of possible configurations of pervaporation membranes reactors for ester synthesis.

Table 1
Application of pervaporation with inert membranes in esterification batch reactions

Product	Catalyst	Configuration	[Alcohol:acid] molar ratio	Temperature/°C	Time/h	Conversion/%	Ref.
Isopropyl acetate	Amberlyst-15	Distinct units⑤	2:1	75	25	78	[62]
Ethyl lactate	Amberlyst-15	Distinct units⑤	3:1	75	~33	~90	[63]
Isopropyl propionate	Toluene sulfonic acid	Distinct units⑤	1.5:1	86	2.5	100	[64]
Isobutyl acetate	Dowex 50W-X8	IMR⑥	8:1	70	10	~80	[65]
Isobutyl acetate	Dowex 50W-X8	IMR⑦	1:1	70	10	~90	[65]
Ethyl oleate	SCER①	Distinct units	15:1	80	24	87	[66]
Isobutyl propionate	*p*-Toluene sulfonic acid	Distinct units	1:2	90	8	84.3	[67]
Propyl butyrate	*p*-Toluene sulfonic acid	Distinct units	2:1	80	7	96	[29]
Methyl acetate	Amberlyst-15	IMR	4:1	70	~5	99.2	[68]
Butyric acid/propanol	*p*-Toluene sulfonic acid	Distinct units	1:2	80	7	96.4	[29]
Isobutyl propionate	Cenosphere② and H_2SO_4	IMR	2.5:1	80	~6	92	[31]
Ethyl propionate	H3PW③	IMR	3:1	70	~6	93	[14]
Biodiesel	s-MWCNTs④	IMR	20:1	135	10	70	[69]

①SCER—sulfonated cation exchange resins, ②Cenosphere—waste material of thermal power plants, ③H_3PW—12-tungstophosphoric, ④s-MWCNTs—sulfonated multi-walled carbon nanotubes. ⑤PERVAP® 2201, ⑥ PERVAP® 2216, ⑦Nafion 117.

sites of the membrane, the water content in the reaction medium remains low as the membrane simultaneously removes the water generated by the reaction through a selective barrier, increasing the conversion rate and the overall conversion.

The first study published on the synthesis and application of a hydrophilic polymer membrane in an esterification process was carried out by David *et al.* [76]. This study showed the production of a pervaporation catalytic membrane composed of polyacrylonitrile (PAN) and PVA, and poly(styrenesulfonic acid) (PSSA) as a catalyst for propyl propionate synthesis. The results indicated good catalytic activity, but the membrane did not exhibit a good separation factor due to the weak mechanical resistance of the selective layer. This study opened a new research field on the development of more resistant and selective pervaporation catalytic membranes for use in esterification processes.

The interest in this issue can also be spotted by the number of patents filed. According to Spacenet's database, approximately 50% of the patents filed in the last 14 years regarding pervaporation catalytic membranes are related to the esterification process. From these patents, 44% are focused on the synthesis of porous catalytic membranes, 22% on the use of ionic liquids as a catalyst, and 44% on the use of a solid catalyst with sulfonic acid groups.

Accurate and reliable mathematical models have also been proposed for the design of catalytic pervaporation membrane systems applied to the esterification reactions. Mathematical models play an important role in the design, analysis, and optimization of the process [77]. However, only a few studies are available concerning the use of mathematical tools for esterification processes using catalytic membranes [16,78,79], thus indicating a growing and promising field.

When we consider the material used in pervaporation catalytic membranes applied in esterification processes, it is possible to notice that more than half of the studies published over the last 30 years have focused on polymeric membranes. Most studies are dedicated to investigate different polymers (56%) and hybrid materials (36%) for the synthesis of the pervaporation membranes. Only 8% of the studies focus on ceramic membranes. Hybrid materials enable the preparation of hydrophilic membranes with better mechanical resistance and higher selectivity to water when compared to pure hydrophilic polymeric membranes.

Hydrophilic polymers are commonly applied to the synthesis of pervaporation membranes for esterification processes. However, these membranes have presented some drawbacks of operation such as ease of swelling in the aqueous medium [80–82], poor thermal and mechanical properties [83], and low selectivity in aqueous solutions [84,85]. Alternatives have been proposed to overcome the limitations, such as the modifications in the membrane synthesis process using crosslinking [16,86], synthesis of

hybrid membranes (polymeric and inorganic) [87–89], and use of polymer blends (mixtures of two or more polymers) [90,91]. However, these strategies often lead to hydrophilicity reduction, a decrease in the permeate flux, and an increase in synthesis complexity.

Since the most recent developments on the pervaporation process applied in esterification reactions go in the direction of polymeric catalytic membranes, inorganic membranes, and hybrid membranes, we provide more detail in separate sections.

4. Membrane Materials Applied in Esterification Systems

The choice of membrane material designed for the esterification reactions is not only essential in terms of the selectivity and flux that can be obtained. Other factors, such as great affinity to the catalyst and decreased resistance to mass transfer in membranes with multiple layers, for example, should also be considered. The methods for preparing catalytic inorganic and polymeric membranes for several applications were recently discussed in detail by Abdallah *et al.* [23] and Qing *et al.* [24]. In the following sections, we discuss the membrane materials and synthesis specifically applied to esterification reactions.

4.1. Catalytic polymeric membranes

Polymers used to prepare catalytic membranes designed for pervaporation processes are easy to cast films, flexible, and have low cost compared to inorganic membranes [92]. Polymers can be classified regarding their physical state as rubbery or glassy materials, depending on their glass transition temperature and the ambient temperature [93]. If the synthesis material is rubbery, the resulting membrane commonly presents high permeability but low selectivity. Conversely, if a glassy polymer is used, the membrane shows a high selectivity but low permeability [1,94,95]. The physical state of the polymeric membrane at the operating temperature has been neglected in most studies, despite its large influence on the process performance [96]. Diffusion selectivity is related to the permeant size, feed composition, and mobility of the polymer chains that compose the membrane. Knowing the glass transition temperature (T_g) of the membrane material allows us to assess whether the loss of selectivity was caused by the increased flexibility of the polymer chains during the process or not.

Materials such as polyvinyl alcohol [86,97], chitosan [98], and sodium alginate [16] are commonly used in the synthesis of pervaporation catalytic membranes applied to dehydration of organic reaction media, mainly due to their hydrophilic properties and easiness to form the film. However, membranes composed only of those materials tend to swell. Catalytic polymeric membrane still suffers from low thermal resistance, ease of swelling in aqueous media, and high complexity in fabrication [23]. Thus, obtaining more resistant and permselective materials is a challenge in the synthesis of these membranes. Promoting polymer crosslinking, using polymer blends, and incorporating inorganic materials into the synthesis of these membranes are suggestions to overcome these drawbacks.

The addition of inorganic materials such as zeolites, carbon nanotubes, silica, graphene oxide, and titania to the polymeric solution used to prepare the membrane leads to the known mixed matrix membranes (MMMs) [99]. When metal–organic frameworks (MOFs) are used in MMM synthesis, the membranes are defined as MOF/MMM. The MMMs/MOF membranes present advantages like increased mechanical resistance and decreased swelling [100]. To date, only a few papers relate the use of this type of material in the synthesis of pervaporation catalytic membrane aimed at the synthesis of esters [68,89,101–103]. The use of MOFs HKUST-1 [104] and MIL-101 (Cr) [105] for ethyl acetate synthesis is reported in the literature. High selectivity and permeate flux were obtained, with conversions greater than 60%.

The adhesion of solid particles to the polymer matrix is a challenge in the production of MMMs. Some limitations of mixed matrices are the formation of non-selective voids, particle agglomerates, and the incompatibilities between the inorganic particle and polymer matrix. These limitations can lead to a reduction in the membrane mechanical resistance and loss of permeability and selectivity. Some strategies like adding the particles into the solvent before the polymer, using particles with the same polarity, *in-situ* particle synthesis within the polymer structure, and promoting thermal annealing have been used at membrane preparation to minimize these disadvantages [73,106,107]. Table 2 presents the most recent studies regarding catalytic polymeric membranes, with respective performance in the esterification conversion.

Zirconium sulfate is a heterogeneous catalyst that has been well explored for the synthesis of esters. Its layered structure makes it an ion exchanger with high catalytic activity and selectivity in esterification reactions [110]. Qing *et al.* [20] utilized the solution of zirconium sulfate and PVA forming a homogenous catalyst. This choice was based on previous studies by the same research group [71,97], which used heterogeneous catalysts in the catalytic layer of pervaporation membranes, and noted that porosity and access to catalytic sites should be improved.

High ester conversion rates are observed even with a low molar ratio between the alcohol and the acid, attributed to the characteristics of the catalyst in contact with the membrane material. Li *et al.* [16] performed a series of studies applying catalytic membranes made with PVA and PSSA with different catalyst concentrations and reported an increase in the ester production at higher catalyst content. At the same operational conditions, an increase in total flux and a decrease in tensile strength were observed. The authors attributed the flux increase to the higher PSSA concentration in the membrane matrix since the catalyst had a high affinity for both alcohol and water.

The use of sodium alginate (SA) in the synthesis of composite membranes for pervaporation is widely reported in the literature [29,67,108,111], but the presence of carboxyl and hydroxyl groups in the membrane structure turn it unstable in an aqueous medium [112]. Gao *et al.* [113] proposed the addition of carbon nanotubes to improve the chemical resistance of this type of membrane; more details are provided in the section on hybrid membranes.

The chitosan structure presents hydroxyls and amino groups that accept chemical modification by crosslinking, grafting, and blending with other polymers. The polycationic nature of the matrix supports polycation–polyanion bonds that can be used to improve the membrane mechanical properties due to the formation of complex and stable links with other cation groups. Several research groups have proposed membrane modification with polyelectrolytes [11,114,115]. Since the ionic groups used in this technique are commonly hydrophilic, they increase membrane resistance through the ionic crosslinking and make the membrane insoluble to most organic solvents. However, using this kind of additive is challenging, due to its natural ionic crosslinking characteristics [116].

Fig. 3 depicts the relation between conversion, flux, and separation factor of catalytic pervaporation membranes for ester production reported in publications over the last six years. We observed that the acid conversion follows the expected behavior for esterification reactions, *i.e.*, higher acid:alcohol ratio and longer reaction time led to higher acid conversion. Conversions are greater than 90% with small alcohol:acid molar ratio (less to 3:1) in esterifications that used pervaporation catalytic membrane. Also, higher

Table 2
Pervaporation catalytic polymeric membranes and respective conversions obtained in batch esterification reactions

Membrane composition	Esterification substrates	Catalyst	[Alcohol:acid] molar ratio	Temperature/°C	Time/h	Conversion/%	Ref.
PVA/PES	Acetic acid/*n*-butanol①	$Zr(SO_4)_2{\cdot}4H_2O$	1:1	85	45	100	[20]
PVA-SA/SPVA	Acetic acid/ ethanol①	Sulfoisophthalic acid	1:2	75	12	96.0	[17]
PVA	Propionic acid/ethanol②	Tungstophosphoric acid	1:3	70	~6	92.9	[14]
Chitosan	Levulinic acid/ethanol①	Sulfosuccinic acid	1:3	70	7	93.0	[98]
PVA/sodium alginate	Propionic acid/ethanol①	Poly(styrene sulfonic acid)	1:2	60	12	91.6	[16]
PVA/PES	Caproic acid/isobutanol②	Amberlyst 15	1:5	90	5	94.4	[108]
PVA	Acetic acid/ethanol①	PSSA-MA5	1:2	75	12	94	[109]

Note: PVA—polyvinylalcohol, PES—polyethersulfone, SA—sodiumalginate, SPVA—sulphonatedpolyvinylalcohol, PSSA-MA—poly(styrenesulfonicacid-*co*-maleicacid). ①Distinct units; ② CMR.

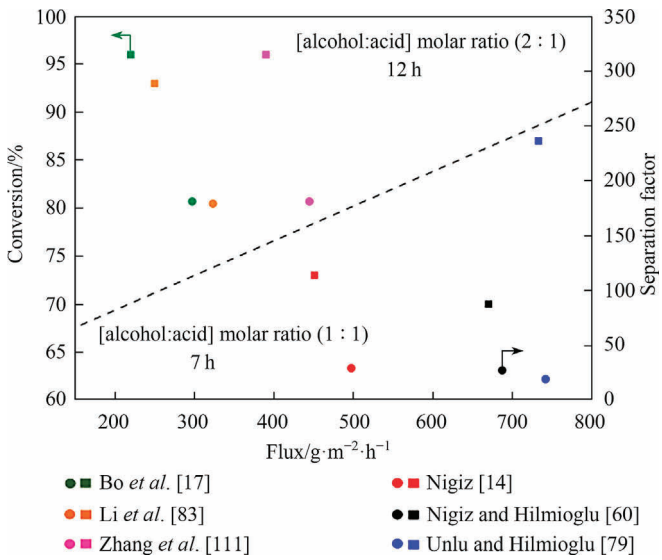

Fig. 3. Performance of pervaporation catalytic membranes in the synthesis of esters. Square markers stand for conversion (%). Circle markers stand for separation factors. Dotted line limits the experimental conditions: below the dotted line: [alcohol:acid] molar ratio 1:1 and 7 h reaction; above the dotted line: [alcohol:acid] molar ratio 2:1 and 12 h reaction.

conversion is accompanied by low flux and higher separation factors. These results show that higher selectivity favors higher conversions, but at the expense of lower fluxes, a behavior that is also observed with inert membranes.

The comparison of results obtained by different studies is important, but it is not straightforward due to the lack of standardization of test conditions. Besides, only a few studies report the reuse and the physical characteristics of the catalytic membranes after testing, which is an important factor for the analysis of the process viability and scale-up actions. From the few studies that report the membrane reuse, the pervaporation catalytic membranes showed an average of 4 reuse cycles, with a decrease in catalysis activity of approximately 10% [17,70,98].

4.2. Inorganic catalytic membranes

Inorganic membranes can be made from a variety of metal oxides, carbon, zeolites, or noble metals and alloys. Ceramic membranes made from metal oxides like alumina, zirconia, or titania usually present several advantages over polymeric materials, including high thermal and mechanical stability, high-pressure resistance, and feasibility to be operated above 300 °C [117]. Table 3 presents studies performed applying ceramic membranes in the esterification process.

The commercial availability of pervaporation ceramic membranes is still limited, with NaA type (Linda Type-A) zeolite being the most common and intended for solvent dehydration processes. The choice for zeolites is based on their microcrystalline aluminum–silicate structure with well-defined pore sizes and uniform distribution [64,118,119].

The cage structure of hydroxy sodalite allows only very small molecules such as helium, ammonia, and water to permeate between the cages. However, once water molecules pass through, other molecules cannot permeate until dehydration processes of this material occur [121].

Most of the inorganic membranes studied for the pervaporation in esterification processes are inert, either in the IMR configuration or in a membrane module separated from the reactor. Among the recent studies on the use of catalytic inorganic membranes in esterification, it is worth highlighting the results of Tanaka *et al.* [122] and Xu *et al.* [123]. Tanaka *et al.* [122] reported the use of zeolite T membrane for ethyl acetate esterification with 100% acetic acid conversion in 8 h. The active membrane of SO_4^{2-} / TiO_2 was used by Xu *et al.* [123] for biodiesel production, yielding 97.6% of conversion. However, the authors did not report the permeate flux and water selectivity.

The application of ceramic membranes in the pervaporation process is still modest because the first studies identified that the difficulty to form a suitable selective layer, without defects and mesopores, resulted in poor selectivity, brittle characteristics, and consequently operational limitations in the ester synthesis process [6,124]. However, the technology to prepare ceramic membranes has advanced significantly in the last years, which justifies further studies.

Table 3
Inorganic materials most studied in the synthesis of pervaporation membranes and respective conversions obtained in batch esterification reactions

Material	Esterification substrates	Catalyst	[Alcohol:acid] molar ratio	Temperature/°C	Time/h	Conversion/%	Ref.
Hydroxy sodalite	Acetic acid/ethanol①	Amberlyst-15	1:1	~90	10	98	[42]
Hydroxy sodalite	Acetic acid/butanol①	Amberlyst-15	1:1	~90	10	92	[42]
NaA zeolite	Acetic acid/*n*-propanol②	Ion-exchange resins	2:1	97	7	98.6	[120]
Zeolite	Oleic acid/ethanol①	Amberlyst-15	1:1	80	5	98	[41]
Zeolite	Oleic acid/methanol①	Amberlyst-15	1:1	80	5	96	[41]

①Distinct units; ②CMR.

4.3. Hybrid catalytic membranes

Hybrid membranes are considered emerging materials with potential characteristics to be used in pervaporation for esterification processes. The membranes are composed of a mixture of polymers and inorganic compounds intended to join the best qualities of both materials. Hybrid membranes show better mechanical resistance and chemical stability when compared to purely polymeric or inorganic membranes [6,125]. In this way, the interest in this kind of membrane has exponentially grown in recent years [126]. For the synthesis of hybrid membranes, physical methods, such as dip-coat process [127], electrospinning [128], dry immersion phase membrane (solution evaporation) [102], and wet phase inversion membrane [71,97] are examples.

In this context, Zhang *et al.* [71] prepared a layer-by-layer membrane by coating a catalytic layer containing polyvinyl alcohol and ion-exchange resins onto a dense polyvinyl alcohol (PVA)/ polyethersulfone (PES) separation membrane, using two synthesis methods—blending and wet phase inversion. They observed that the wet phase inversion method provided higher catalytic activity because the catalytic sites were more available to the reaction due to the porous structure (Fig. 4(b)), while in the blending approach, the polymer probably covered part of the catalyst sites resulting in a lower catalytic activity (Fig. 4(a)).

The addition of phosphotungstic acid, a heterogeneous catalyst, in a polymeric PVA solution was proposed by Shi *et al.* [129]. The authors observed an increase in thermal stability compared to a membrane without a heterogeneous catalyst. From the studies presented in sections 4.1 to 4.3, considering the process aspect, lower acid to alcohol molar ratio is used compared to conventional esterification processes. However, relatively high temperatures, above 60 °C, are used. High permeation selectivity with low flux was reported for some polymeric membranes. Hybrid membranes bring significant improvements in chemical and physical resistance. However, catalytic membrane synthesis is still a challenge since an ideal catalytic membrane should present high catalytic activity, flux, and selectivity. Despite the considerable advances in the area, it is clear that this field still needs to be further explored due to the complexity and multidisciplinary character of catalytic membranes synthesis.

Another significant aspect of catalytic membrane synthesis is the influence of the catalyst concentration on the membrane structure, which can affect mass transfer limitations and catalytic sites inactivation. These factors should be considered when choosing the membrane design. In the following section, research on membrane structure and its influence on the ester synthesis are presented.

5. Structure of Pervaporation Catalytic Membranes

The structure of catalytic membranes for esterification described in the literature is generally classified as concrete-like (single layer) and sandwich-like (multi-layer). A concrete-like structure presents dispersed fillers inside a homogenous polymeric matrix. In turn, the sandwich-type structure has two or more layers of polymeric, inorganic, hybrid material, or interlayered layers of these materials [6]. The structures are represented in Fig. 5.

5.1. Concrete-like structures

Several studies applied the concrete-like technique to synthesize membranes since this is a simple method to incorporate catalysts into the selective layer. The methods applied to obtain this membrane architecture include phase inversion [130] and electrospinning [131]. The catalyst is mixed in a polymeric solution that is cast on porous support [24], allowing the incorporation of enzymes, as well as liquid (*e.g.*, acids) and solid (*e.g.*, resins, TiO_2, and carbon nanotubes) catalysts [23].

Dense PVA membrane added with natural nanofiber-like palygorskite functionalized with ionic liquid PAL-PILS (1-butyl sulfonate-3-vinylimidazole hydrogen sulfate, 0.5%−3.0% (mass)) was proposed by Li *et al.* [132] (Fig. 6(a)). The authors observed an enhanced thermal stability of hybrid membranes. Higher tensile strength was obtained for membranes containing 0.5%, 1.0%, and 2.0% (mass) of PAL-PILS. Using 3.0% (mass) led to a lower tensile strength probably because of the undesirable agglomeration of the inorganic particles, as it was also observed in the SEM images of the membrane (Fig. 6). The particle agglomeration can cause interfacial voids on the membrane surface due to the deposition or accumulation of solid particles. Further, it can limit the mechanical resistance of the membrane.

The catalytic membrane PVA / SO_4^{2-} AAO was proposed by Sun *et al.* [101]. The polymeric PVA solution was coated on the surface of a porous AAO membrane. In turn, this polymeric solution penetrated the pores of the AAO membrane and formed an interface layer between the organic (PVA) and inorganic (AAO) phases (Fig. 7). A membrane more resistant to swelling with larger and straighter pores was obtained. However, the selectivity of these membranes decreased as the temperature increased to greater than 50 °C.

The incorporation of the catalyst in a polymeric matrix turns the membrane synthesis simpler, decreases the possibility of catalyst leaching, and does not significantly affect the membrane morphology (size and porosity). However, the addition of extra process steps and the decrease of the permeate flux and catalytic activity

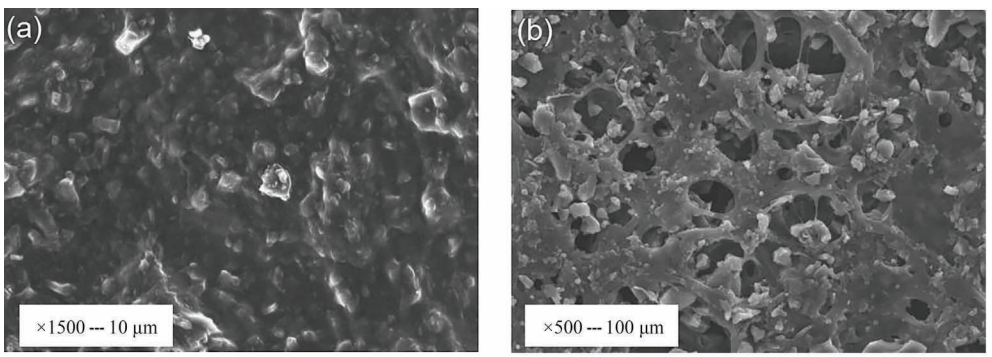

Fig. 4. SEM images of an ionic resin PVA membrane: (a) membrane prepared by dry phase inversion and (b) membrane prepared by immersion phase inversion. Reproduced from Ref. [71] with permission of Elsevier, copyright 2014.

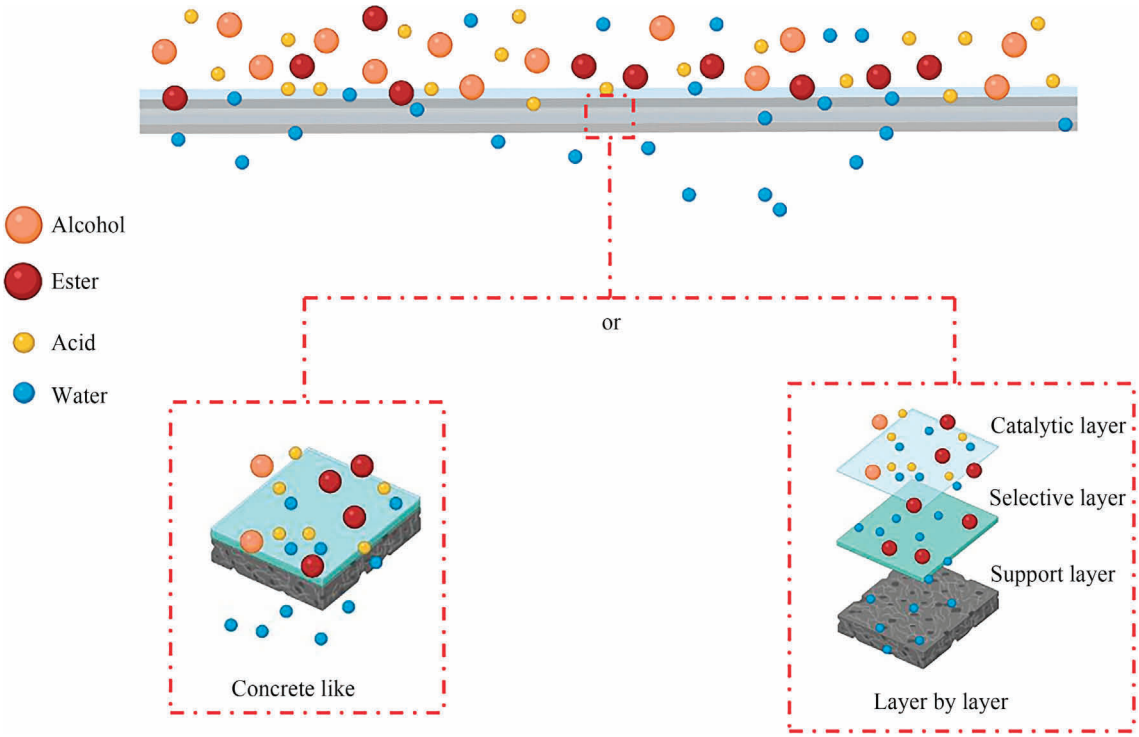

Fig. 5. Representation of the structure of pervaporation catalytic membranes: concrete-like structure and sandwich-like structure.

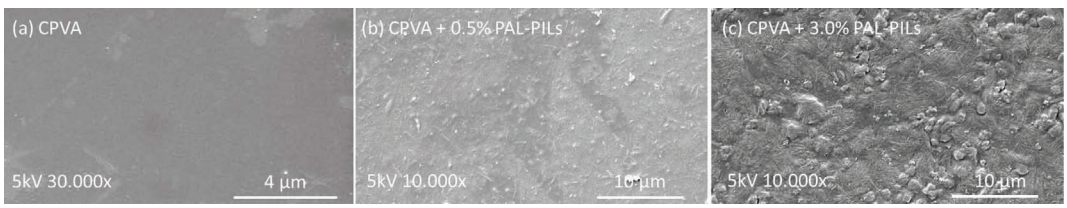

Fig. 6. SEM images of poly (vinyl alcohol)/palygorskite-poly (ionic liquids) hybrid catalytic membranes: (a) Crosslinked PVA membrane, without PAL-PILS; (b) CPVA with 0.5% (mass) of PAL-PILS; (c) CPVA with 3.0% (mass) of PAL-PILS.Reproduced from Ref. [132] with permission of Elsevier, copyright 2020.

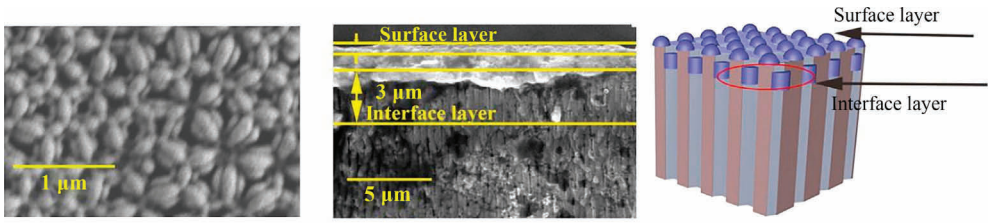

Fig. 7. SEM images of PVA / SO_4^{2-} AAO membrane with 3% (mass) PVA in the surface of the AAO layer. Reproduced from ref. [101] with permission of Elsevier, copyright 2020.

are considered drawbacks. The dense structure of concrete-like membrane design is still a challenge due to the mass transference resistance [24].

The application of electrospinning on membrane synthesis is an alternative because it generates dispersed fibers, increasing the membrane's catalytic surface area and decreasing diffusion resistance in the material. This technique was applied by Shi *et al.* [131] using a polymeric solution formed by PVA and phosphotungstic acid as a homogeneous catalyst. PVA mass content below 8% led to the irregular formation of beads and fibers due to the low solution viscosity, while content over 14% hampered the fibers obtaining because of the high solution viscosity. The application of 12% of PVA on membrane production led to higher contact surface area and reached higher conversion levels.

Although the advantages presented using liquid catalysts, such as easy solubility in the polymeric matrix, solid catalysts have attracted the attention of researchers because of the advantages associated with the utilization of hybrid membranes to the pervaporation process in the organic synthesis, already explored in the text. Zhang *et al.* [130] have reported the use of carbon nanotubes in PES and observed an increase in the mechanical strength of the membrane. This material shows high mechanical and thermal

stability (operating range up to 250 °C), high surface area, and many active sites that allow easy access for the reactants. However, the modification of this type of catalyst with sulfonic groups can be inefficient in an aqueous reactional medium (*e.g.*, esterification) due to the loss of catalytic activity caused by the leaching of sulfonic groups [133].

The formation of a single layer composed simultaneously of catalyst and selective barriers can present some disadvantages. For example, when the solid catalyst is used, the membrane may lose some catalytic sites due to leaching during the catalysis process or coating the solid catalyst with the polymeric material during membrane synthesis. The formation of a single dense block may not exhibit high catalytic activity due to the smaller surface area compared to more porous surfaces. In other words, membranes with a dense layer are more selective, while porous membranes have greater catalytic activity [24].

5.2. Sandwich-like structures

In this type of membrane architecture, the selective and catalytic layers are independent, allowing more freedom in the synthesis and optimization of each layer [24]. The interest in this type of membrane is growing mainly in the esterification processes, whether applying biocatalysts [97,134], homogeneous [70,71], or heterogeneous catalysts [13,71]. The use of lipases for the synthesis of esters was investigated by Zhang *et al.* [97] and Nigiz and Hilmioglu [134]. High conversion under mild reaction conditions (low temperature and absence of excess solvent) was possible. However, the formation of aggregates due to the agglomeration of enzymes on the catalytic surface was responsible for fouling. This agglomeration can affect the access of reagents to the catalytic sites of the membrane and decrease conversion.

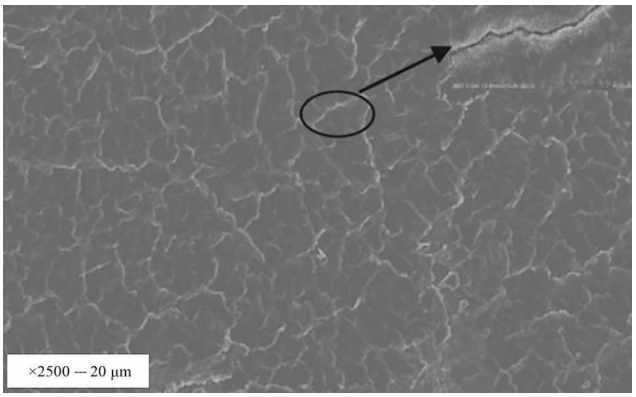

Fig. 8. SEM image of an ionic resin PVA membrane surface view of the PVA-SA/SPVA membrane with 20% SPVA. Reproduced from Ref. [17] with permission of Elsevier, copyright 2018.

Bo *et al.* [17] used SIPA (5-sulfoisophthalic acid) as a heterogeneous catalyst and observed cracks in the membrane surface (Fig. 8) when using a concentration greater than 20% in the polymeric solution of PVA/SA. The authors also observed that increasing the catalyst concentration above 20% caused no significant increase in conversion. They highlighted that increasing the amount of catalyst, the crosslinking of the membrane would also augment, which limits diffusion rates. The increase in catalytic sites could also be non-significant with the increase in catalyst concentration from 20% to 30%.

A membrane with a highly porous catalytic layer was proposed by Qing *et al.* [20], who obtained a layer with massive macrovoids and sponge pores (Fig. 9), with less resistance to mass transfer. The membrane was prepared by firstly casting a dense PVA selective layer on a PES microfiltration support; then, an aqueous solution containing PVA and $Zr(SO_4)\cdot 4H_2O$ homogeneous catalyst was cast on the dense PVA and immersed into an ethanol coagulation bath, which was responsible to promote the phase inversion. This strategy generated a highly spongy structure containing the macrovoids (Fig. 9(b)) [20].

The synthesis of membrane-containing solid catalysts can be facilitated by applying polymers with a film-forming profile (*e.g.*, PVA and PAN), and by using a polymer compatible with the catalyst to improve catalyst dispersion in the polymer matrix [135]. Li *et al.* [16] used PSSA and PVA and described that the compatibility between polymer and catalyst was responsible for the aspects of symmetry and uniformity of the membrane. Further, the authors observed that an increase in the catalytic layer thickness led to a 100% increase in flux, with the increase in the molar ratio of polymer and catalyst from 3:5 to 5:7. Usually, a thicker layer decreases the permeate flux, but the result was explained by the high hydrophilicity of the PSSA that readily absorbs the water and allows the increase of the permeate flux, keeping the membrane selectivity.

The use of sulfonic acid in esterification processes frequently presents a lower incidence of secondary reactions [136]. Bo *et al.* [17] used 5-sulfoisophthalic acid (SIPA) and PVA to create a catalytic layer and PVA-SA to make a selective layer for ethyl acetate production. It is necessary to observe that SIPA is a homogenous catalyst soluble in water with —COOH groups that can quickly form crosslinks with the –OH groups of PVA, reducing the mass transfer problems among reactants and catalysts. Besides, the presence of PVA in both layers favors their adhesion.

The application of ionic liquids like modification agents to catalytic membrane synthesis is also reported. Zhang *et al.* [70]

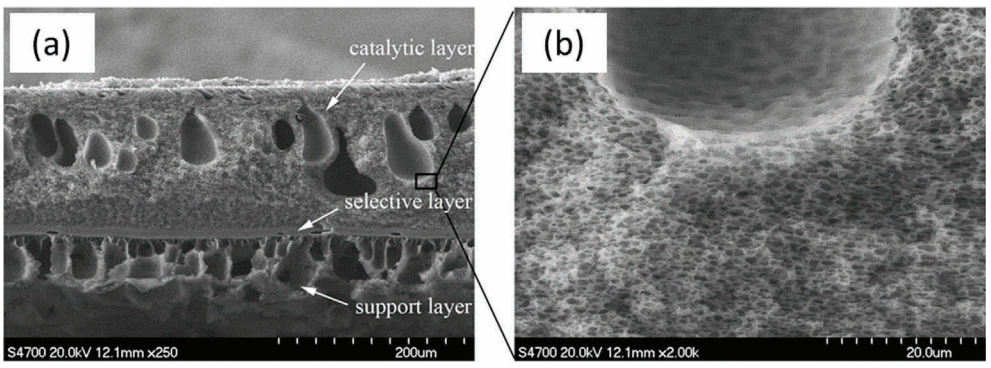

Fig. 9. SEM image of a catalytically active membrane with porous catalytic layer: (a) image of the cross-section indicating each layer (catalytic–$Zr(SO_4)\cdot 4H_2O$ embedded in PVA; selective – dense PVA, support–porous PES). (b) augmentation on the porous catalytic layer. Reproduced from Ref. [20] with permission of Elsevier, copyright 2017.

produced catalytic layers in PVA membranes with ionic liquids and used glutaraldehyde crosslinked PVA to create a separation layer. Ionic liquids have shown high catalytic activity [137] and present desirable characteristics for catalysts in the acid synthesis of esters [138–140]. However, the costs involved in using ionic liquids are high compared to other catalysts.

The deposition of porous layers has been studied [20,141] for enhancing membrane catalytic activity. The porous catalytic layer increases permeate flux and reduces the contact time between water and the produced ester, reducing hydrolysis. Besides, it offers a larger surface area for catalysis. However, the fouling on the membrane surface, the need for sufficient retention time for the reaction, and the resistance between the catalytic porous and selective dense layers are still issues to be solved. Membrane pore size and porosity should be optimized to overcome these issues. Zhang *et al*. [97] reported a series of studies about the synthesis of a porous catalytic layer applying the phase inversion technique. The authors observed that the presence of particles of the solid catalyst hindered the correct formation of the catalytic layer on the membrane.

Flux, selectivity, and high conversion are essential for the proper performance of the catalytic membrane. Most recent studies focused on the synthesis and application of configuration layer-by-layer with a porous catalytic layer, and a high-rate conversion of organic acid was found. However, the synthesis process still needs improvements. Single-layer configuration is simple to produce and yields high selectivity, but it usually contributes to lower flux.

6. Concluding Remarks and Perspectives

The application of catalytic membranes for simultaneous ester production and water separation is a promising alternative to improve the esterification conversion. This review presented an overview of the recent research studies involving the application of membranes in esterification, focusing on catalytic membranes, their structure, preparation, and the catalysts involved. The development of membranes with high catalytic activity, selectivity, and flux is still challenging. Studies on synthesis methods and the use of different catalysts reported conversions greater than 90% with a low acid:alcohol molar ratio. So far, the studies using layer-by-layer porous catalytic membranes have been more efficient for achieving high conversions (>90%) of organic acids, with a low resistance to mass transfer compared to concrete-like structures. The application of heterogeneous catalysts has also been promising since their use increases the mechanical resistance of the membrane and decreases swelling when compared to membranes using homogeneous hydrophilic catalysts. On the other hand, the catalytic activity of the membrane may decrease depending on the immobilization technique of the heterogeneous catalyst on the membrane surface. Nevertheless, further investigations are still needed to prepare more resistant and catalytically active membranes.

Most of the previous studies have focused on only one parameter, such as conversion, permeate flux, and selectivity, which are reported to range between 60%–90%, 200–800 $g \cdot m^{-2} \cdot h^{-1}$, and 30–250, respectively. Systematic investigations on reuse cycles, catalytic activity, flux, selectivity, structural characteristics, mechanical and chemical resistance, and membrane stability after use are still scarce. Knowledge of these aspects is essential to validate the viability of using these membranes in industry.

Several studies on the application of catalytic pervaporation membranes in esterification processes target the influences of the process variables and new potential applications. Materials and methods specifically designed for esterification are critical issues to overcome the limitations associated with the design and manufacture of these membranes. Even with the great potential of applying catalytic membrane in esterification reactions, most studies are carried out only on a lab scale. Future investigations should also focus on pilot studies and upscaling strategies of such membrane processes. The development of a more resistant polymeric membrane is also demanded. These membranes should provide easy access to the catalytic sites and need to be designed for esterification intensification. Additionally, an alternative hydrophilic catalyst that does not interfere in the membrane flux and decreases the diffusional resistance would reduce process costs while favoring scaling-up and industrial implementation of this technology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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