Review Article

A Review on Catalytic Membranes Production and Applications

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Abstract

The development of the chemical industry regarding reducing the production cost and obtaining a high-quality product with low environmental impact became the essential requirements of the world in these days. The catalytic membrane is considered as one of the new alternative solutions of catalysts problems in the industries, where the reaction and separation can be amalgamated in one unit. The catalytic membrane has numerous advantages such as breaking the thermodynamic equilibrium limitation, increasing conversion rate, reducing the recycle and separation costs. But the limitation or most disadvantages of catalytic membranes related to the high capital costs for fabrication or the fact that manufacturing process is still under development. This review article summarizes the most recent advances and research activities related to preparation, characterization, and applications of catalytic membranes. In this article, various types of catalytic membranes are displayed with different applications and explained the positive impacts of using catalytic membranes in various reactions. Copyright © 2017 BCREC Group. All rights reserved.

1. Introduction

Nowadays, the membrane technologies are used in the most of the engineering approaches for the transport of substances between two sides through permeable membranes. The membrane is a selective barrier which can select one substance to pass through it and prevent the passing of other substances, or it can pass all substances except one substance. Generally, gaseous or liquid separations processes use membrane technologies [1].

In view of the rapid evolution in chemicals industries for various chemicals production to eliminate the production problems and improve the product quality needs to substantially small, clean, safe and good energy efficient technology. Recently, huge researchers efforts are devoted to catalytic membrane reactors, as a kind of membrane reactors, which is considered multi-functional catalytic reactors merging a membrane-based separation and chemical reaction in one single unit. An appropriate design for catalytic membrane reactor leads to improve the yield, reactants conversion and decrease downstream separation costs. According to that, the catalytic membrane reactors became an attrac-

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tive alternative compared to traditional reactors due to their characteristics properties. The catalytic membrane reactors separate the final products from the reaction stream and enhance the reaction conversion by eliminating the thermodynamic equilibrium. These features lead to improve the overall effects such as net reaction rate, residence time, conversion, selectivity and yield [2,3].

Accordingly, the catalytic membranes reactors are considered as a potential technology in different industrial fields including biotechnology, pharmaceutical sector, petrochemical, chemical plants, energy and environmental applications, etc. Also, the catalytic membrane reactors follow the process intensification strategy; this process is an innovative alternative for sustainable growth depending on design strategy to obtain benefits in manufacturing and processing. These benefits base on the reduction of industrial equipment size, decrease in capital costs, energy consumption, environmental impact, increase the efficiency of the industrial plant, safety controls, and industrial automatization improvement [5].

The choice of catalytic membrane type depends on several parameters like the productivity, separation selectivity, membrane lifetime, mechanical and chemical perfection at the operating conditions and cost [6]. According to these parameters the catalytic membranes can be classified to organic (polymeric) and inorganic (ceramic and metal) depending on the chemical process requirements. Polymeric membranes commonly operate at temperature don't exceed 300 ᵒC. Inorganic membranes can operate at high temperatures; they indicate wide tolerance to pH and high resistance to chemical degradation. Most of applications of inorganic membranes have been made on reactions of small molecules or for decomposition reactions at high temperatures.

Other classification of the catalytic membranes can be considered according to the roles of membranes to three types extractor, distributor, and contactor catalytic membranes. The extractor catalytic membrane role is to select or remove one of the products from the reaction medium to enhance the reaction yield. Distributor catalytic membranes role is to enter the one of the reactants especially gases in dosing that may react in successive reactions. The contactor catalytic membrane role is to intimate excellent contact between reactants and catalyst, where reactants are fed separately in either side of the membrane or by forcing them to pass together through catalytic pores of membranes [2,5,6]. In spite of the great features which is characterized by catalytic membranes, but there are some disadvantages like the high capital costs for catalytic membrane fabrication process. Table 1 illustrates advan-

Table 1. Advantages and disadvantages of catalytic membranes

Catalytic membrane type	Advantages	Disadvantages
Organic Catalytic Membranes (Polymeric catalytic membranes)	• The polymeric membranes have low cost as compared with metallic or ceramic. • The technology to fabrication of catalytic polymeric membranes is much better developed than the inorganic and metallic membranes. • Catalytic polymeric membranes mainly operating at low temperatures. • Less stringent demands for the materials required in the module construction	• Manufacturing cost of the membranes preparation and modules • Limited membrane life time • According to the chemical reaction processes and complexity of the process that can lead to more difficult modeling and prediction. • Polymeric membranes have less resistant to high temperature and aggressive chemicals than inorganic or metallic membranes.
Inorganic Catalytic Membranes (Ceramic and Metallic)	• Resistance to aggressive Environments • High thermal stability • Resistance to high pressure	• High capital costs • Brittleness • Generally low permeability of the highly selective (dense) membranes at medium temperatures • Difficult membrane-to-module sealing at high temperatures

tages and disadvantages of catalytic membranes.

The novelty of this review article is shed light on the most different methods for catalytic membrane production whether polymeric membranes or inorganic (ceramic and metal) membranes with different applications in chemical reaction and in industry. Also, the paper discussed the methods of catalyzation of the polymeric membranes and the most characterization methods. This review also is adopted a realistic study for the production of hydrogen in large scale using catalytic membranes. The objective of this review is to shed light on the catalytic membranes in terms of methods of preparation, characterization and fields of applications.

2. Catalytic Membrane Framework

The catalytic membranes can be made from organic (polymers) or inorganic materials according to their applications.

2.1. Polymeric membranes

Various polymers can be used to prepare different kinds of membranes as shown in the Table 2. The polymers which are used in membrane preparation may be glassy or rubbery polymers [7]. Usually, when rubbery polymers are used in membrane preparation can provide high permeability with a relatively low selectivity while using glassy polymers in membrane preparation can provide high selectivity and lower permeability with high product purity [1].

2.1.1. Polymeric membrane preparation

Polymeric membranes are prepared by phase inversion technique depends on the phase separation of polymer solutions forming coagulated polymer films called a membrane [1]. In phase inversion method a polymer is dissolved in an appropriate solvent and fabricated according to the wanted membranes configurations. The flat sheet membrane is prepared by spreading as a film on a plate, a belt, or a fabric support, while the hollow fiber or tubular polymeric membranes are prepared by spinning process using a spinneret block or an extruder to produce the hollow fiber or tubular shape [8]. The immersion precipitation step occurs, when the liquid film, fibers or tubes, causing separation of the homogeneous polymer solution into two phases; a polymer-rich solid phase and a solvent-rich liquid phase. The precipitated polymer forms a structure containing a network which may be either symmetric and porous or asymmetric with a more

Table 2. Different polymeric materials and their applications

Polymers materials	The main application
Cellulose acetate (CA) and its derivatives	RO, UF, MF, GS, FO
Polyethylene (PE)	RO
Poly(vinyl chloride) (PVC)	UF
Poly(vinylidene fluoride) (PVDF)	PV, GS
Polytetrafluroethylene (PTFE)	MF
Polyacrylonitrile (PAN)	UF, MF, ED, MD
Poly(vinyl alcohol) (PVA)	MF, MD
Polypropylene (PP)	UF
Poly(methyl pentenal) (PMP)	PV
Poly(ethylene tere phtalate) (PET)	MD
Poly(butylene tere phtalate) (PBTP)	GS
Polycarbonate (PC)	MF
Polydimethylsiloxane (PDMS)	GS
Polytrimethylsilyl propyne (PTMSP)	MF
Polysulfone (PSU) & PES	GS, UF, FO
Poly(phenylene oxide) (PPO)	GS, PV, UF
Polyamide (PA)	UF
Poly(etyher block amide) (PEBA)	UF, GS, RO
Polyphosphazene (PPN)	RO, UF
Poly(ether ether ketone) (PEEK)	GS, UF
	GS, PV

RO is reverse osmosis, UF is ultrafiltration, MF is microfiltration, GS is gas separation, MD is membrane distillation, ED is electrodialysis, PV is pervaporation, NF is nanofiltration, and FO is forward osmosis.

or less dense skin at one or both surfaces of a porous bulk phase [9].

Generally, phase separation mechanisms can be subdivided into three main categories according to the parameters that induce demixing [10]. First, temperature-induced phase separation (TIPS) depends on changing the temperature at the interface of the polymer solution, where the heat can be exchanged and demixing can be induced. Secondly, reaction induced phase separation (RIPS) is another mechanism where the original polymer solution can be exposed to a reaction which leads to phase separation. Thirdly, diffusion induced phase separation (DIPS) is the most common technique, depends on contacting a polymer solution to a vapor or liquid, where the diffusional mass exchange can lead to a change in the local composition of the polymer film and demixing can be induced [10].

DIPS has three types of techniques [10], i.e. (1). Coagulation by absorption of nonsolvent from a vapor phase. The polymer solution, which contains solvent and nonsolvent (such as additives) exposes to a vapor phase of the used nonsolvent or another one, where the polymer solution absorbs the nonsolvent, which leads to coagulation of polymer solution to form membrane film [10]; (2). Evaporation of solvent: the solvent and nonsolvent, which is considered components of polymer solution evaporate to the air, which leads to coagulation and formation of the membrane film; (3). Immersion into a nonsolvent bath: the polymer solution is immersed in a coagulation bath contains nonsolvent, where the solvent dissolves in the nonsolvent such as water and leaves the polymer solution to coagulate and form the membrane film. The combinations of the techniques are performed to achieve the desired membrane.

These techniques are schematically represented in Figure 1 [11].

Phase inversion technique also can be used in the preparation of various membranes configurations such as flat sheet, hollow fiber, multi holes hollow fiber and tubular polymeric membranes using different processes like casting process and spinning process. It involves many steps namely; material selection, drying process, dope solution preparation, casting or hollow fiber spinning, phase separation process, and surface treatment [9]. Figure 2 illustrates the polymeric membranes preparation process for different applications.

2.2. Catalyzation of polymeric membranes

There are two main types of polymeric catalytic membrane reactors (PCMRs): (a) Membrane-embedded catalysts: where the membrane is prepared to contain the catalyst into its backbone; (b) Membrane-assisted catalysts, where the catalyst is applied on the membrane surface by grafting or precipitation (deposition) processes and the membrane is considered a carrier of catalysts.

2.2.1. Membrane-embedded catalysts

The catalyzation of the polymeric membrane can be performed by blending process. Blending is the physical mixture of two (or more) polymers to obtain the requisite properties. The blending process can be performed between polymers with a liquid catalyst such as sulfuric acid or solid catalysts like nanomaterials, such as TiO_2, Al_2O_3, and different kinds of resins using various techniques of blending [12].

Blending with nanomaterials can provide membranes with some benefits like [13,14]: (a).
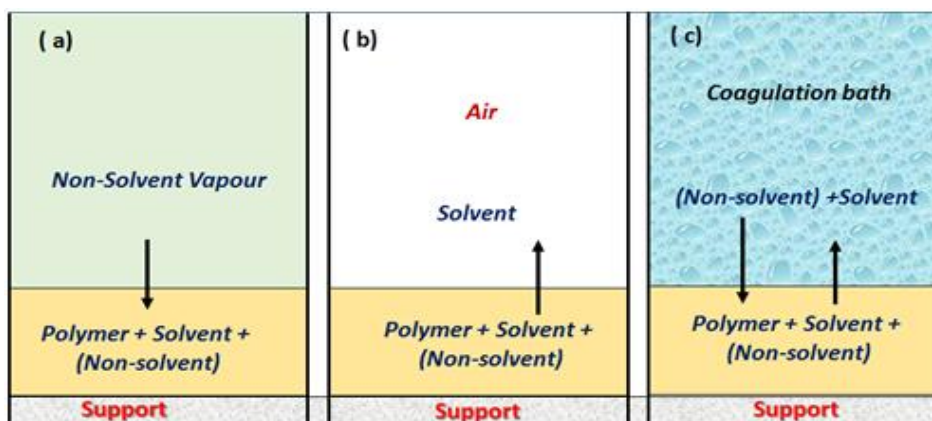
Figure 1. Schematic representation of three DIPS processes; (a) Precipitation with nonsolvent vapor, (b) evaporation of solvent, (c) immersion precipitation [11]

Lower agglomeration and corrosion of the nanomaterials / polymeric blend membrane; (b). Controlled the nanosize of membrane pores with different interaction between polymer and nanomaterials; (c). The embedding nanomaterials into the membrane matrix can enhance the transport of molecules through the membrane and mechanical stability; (d). The polymer produced dielectric environment around the nanomaterials, which leads to modification in the electronic and optical responses for the membrane.

The development of porous PVDF catalytic membrane by blending polymeric solution with Fe_2O_3 and multiwall carbon nanotubes (MWCNTs) provided good removal of humic acid using the catalytic oxidation of organic pollutants [15]. The porous catalytic membrane can be used in the degradation of organic contamination on the membrane surface and inside the pores by utilizing the oxidation power of generated hydroxyl radical [16,17]. Embedding nanoparticles (such as carbon nanotubes (CNTs), Fe_2O_3, TiO_2, Al_2O_3, etc.) into the polymer matrix can improve the membrane performance according to permeate flux and rejection percentage. The addition of multiwall carbon nanotubes (MWCNTs) into the polysulfone matrix improved the membrane permeability and decreased contact angles [18,19,20]. Also, the addition of multiwall carbon nanotubes into PVDF matrix improved the permeate flux and rejection of bovine serum albumin [21,22]. Embedding the metal oxide into the polymeric ma-

trix has positively impacted membrane characteristics due to enhancement in the fouling resistance. The antifouling properties of PVDF membranes were improved after Al_2O_3 addition [23]. Also, metal oxides have the ability to catalyze the degradation reactions of some organic pollutants by producing OH^- radicals during advanced oxidation processes [11,24]. The iron oxide minerals have confirmed high efficiency in catalyzing Fenton-like oxidation reactions during water remediation. However, immobilization of iron oxides like Fe_2O_3 nanoparticles on the PVDF membrane to be used in dechlorination of trichloroethylene (TCE) at a near neutral pH; the TCE conversion reached to 100 % depending on iron and H_2O_2 ratio. Accordingly, the addition of nano-particles and metal oxides into polymeric membranes providing advanced treatment process by reducing the membrane fouling with subsequent cost savings with a merit for organic compounds degradation [15].

Figure 3 illustrates the inclusion of nanoparticles in the polymers by blending process. Vatanpoura *et al*. [10] studied the addition of TiO_2 nanoparticles on polyether sulfone membrane, which enhanced the performance of the membrane [10].

2.2.2. Membrane-assisted catalysts

The catalyzation of the polymeric membrane, in this case, is carried out by two processes; grafting process or precipitation (deposition) process [7].
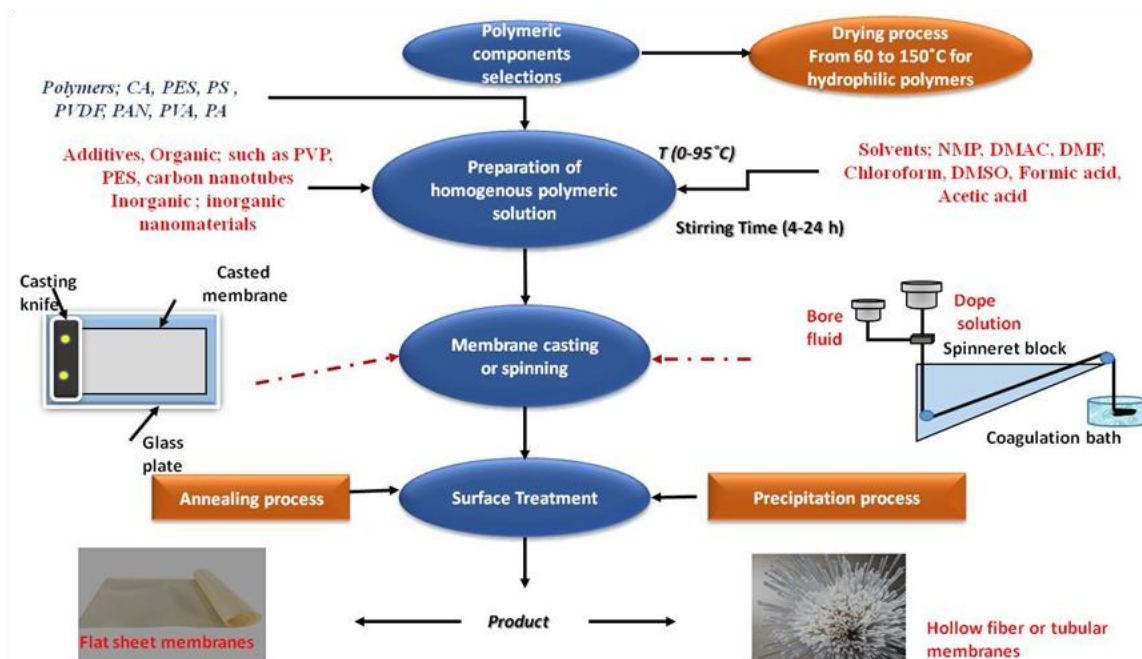

Figure 2. Polymeric membranes preparation process

2.2.2.1. Grafting process

Grafting is a process to modify the polymers surface by covalently bonded of monomers onto the polymer chain. The factors which can control grafting include the nature of the backbone, monomer, solvent, initiator, additives, temperature, etc. The nature of the polymer backbone plays an important role in grafting according to the ability of accepts or resists the grafting reaction. In the case of styrene grafting to polyethylene, the addition of methanol or methanol with sulfuric acid along with the monomer increases the viscosity in the amorphous region, thus increasing the grafting rate [7]. The monomer reactivity is important in grafting process and respects on polar and steric nature, swellability of backbone in the presence of the monomers and concentration of the monomers. The effect of solvent in grafting mechanism depends on determination of solvent which can carry the monomers, thus the choice of solvent based on the solubility of the monomer in solvent, the swelling properties of the polymer backbone, the miscibility of the solvents if more than one is used, the generation of free radical in the presence of the solvent, etc. Alcohols mostly used in grafting process for styrene because alcohols can swell the backbone effectively and can dissolve the styrene so it can easily diffuse into the polymeric structure. Also, the grafting process can not occur without an initiator, and its nature, concentration, solubility, as well as function, must be considered. The temperature during grafting step is one of the important factors that can control the kinetics of graft copolymerization and generally the yield of grafting increases with increasing temperature [7,25].

Two major types of grafting may be considered: (a). Grafting with a single monomer; where the grafting occurred in a single step; (b). Grafting with a mixture of two (or more) monomers, in this case, the two various monomers are grafted side by side to get the required specification, this type of grafting can produce the bipolar membranes [7].

In free radicals grafting way, the free radicals are formed from the initiators and transferred to the substrate to react with the monomer to produce the graft copolymers [26]. The development of atom transfers radical polymerization (ATRP) offers an effective means for the design and fabrication of functional catalytic membrane. The ATRP grafting of the polymeric membrane provides brushes onto membrane surface and pores which can carry appropriate catalytic sites for various applications. Functional catalytic polymeric membranes are considered contactor membranes and they are the central elements in different membrane applications such as fuel cells, gases reactions, adsorption, and pervaporation [27].

Atom transfers radical polymerization (ATRP) is used to prepare proton exchange membranes according to improve the proton transfer efficiency in fuel cells [28]. For example, ATRP grafting for Nafion series can change the molecular architecture and membrane morphology of it. The synthesis of amphiphilic segmented copolymers involving of both hydrophilic and hydrophobic segments exhibits a promising strategy in building ordered proton conducting channels attributed to their unique self-assembly property [27].

In the preparation of proton exchange membranes (PEMs), the hydrophobic polymer ma-
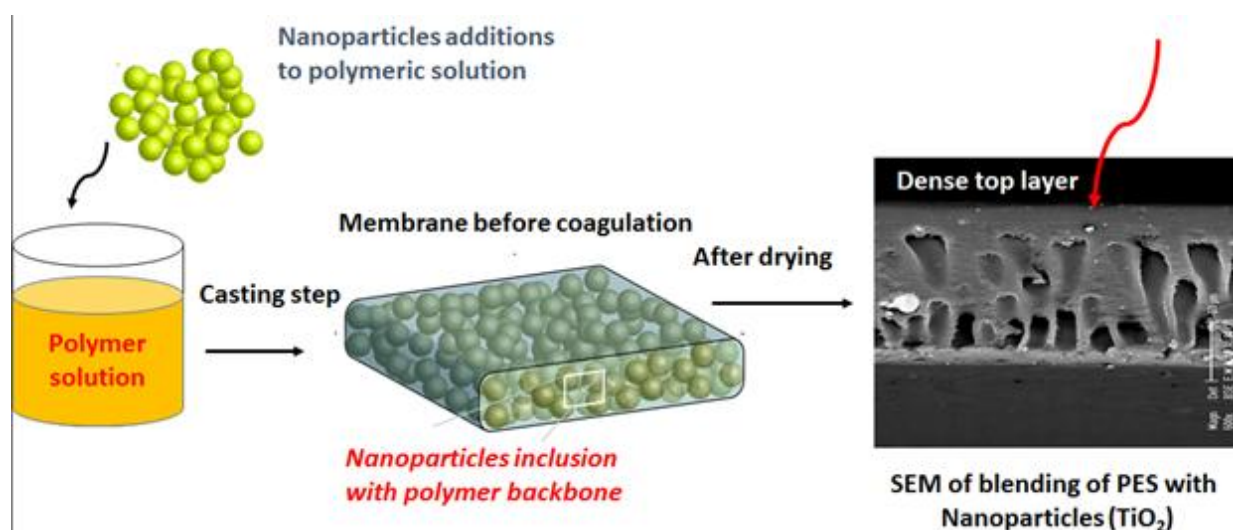

Figure 3. Method for inclusion of nanoparticles in polymeric membranes

trices with distributed initiating functionalities generally include the poly(vinyl chloride) (PVC), poly(vinylidene) (PVDF), poly(vinylidene difluoride-co-chlorotrifluoro ethylene) (PVDF-co-CTFE), and aromatic polymers attitude either bromomethyl or chloromethyl. The inclusion of hygroscopic compounds into the neat polymer membranes can improve the proton conductivity, water retention, mechanical strength at high temperatures and enhance the efficiency of the fuel cell in applications at higher temperatures [29,30].

Inorganic substances, including ZrO_2, TiO_2, and SiO_2 [31,32] are promising selections for mixing with the grafting copolymer matrix. Using hydroxyl [33] or tetraethoxysilane (TEOS) functional groups for subsequent cross linking or sol-gel reactions as a block to the side chain can improve the performance of grafting and it is a perfect way to obtain PEMs with high conductivity and enhanced stability [34].

For another application of grafted catalytic membrane, Casimiro *et al.* [35] studied the esterification of lauric acid to methyl laurate. The authors used poly(vinyl alcohol) (PVA) supported catalytic membranes grafted by mutual *γ*-irradiation method using two distinct cross linking agents, adipic acid (AA), and succinic acid (SA), and a commercial ion exchange resin as catalyst. Esterification by pervaporation techniques was used, thus the membrane was selective to remove produced water from the reaction mixture [35].

2.2.2.2. Precipitation (deposition) process

Precipitation process or deposition depends on the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces. Wang *et al.* [36] studied a novel method in to deposit the nanoparticles on the polymeric membrane surface using the roll to roll process [36]. Polymer membranes have low fabricating costs due to use the roll-to-roll fabrication process [37,38]. Also, this process can be applied for nanoparticle alignment on membrane support and pattern printing on membrane films [39]. Wang *et al.* [36] synthesized zeolite on polymer supports, where a dehydration / rehydration system was developed to reduce the synthesis time of zeolites formation with crystallization times of <2 h [36]. This time was enough to applicable for roll-to-roll fabrication to produce flat-sheet zeolite polymeric membrane and this membrane was tested for CO_2/N_2 gas separation [36,40]. The system consists of two moving rollers, a fixed column dipping in a reactor of the aluminosili-

cate gel, and a stirrer for stirring the gel. Nonwoven fabric band was rolled on to the two rollers and fixed column as shown in Figure 4. The rotation of rollers in clockwise fashion, so the nonwoven fabric band moves through the gel from right to left. The nanozeolite seed particles were coated into the PES support, where all of them were stapled onto the band of nonwoven fabric during the rolling process through the reactive aluminosilicate gel.

Mashentseva *et al.* [41] described the effect of deposition of Au- and Ag-based nanotubes on the polyethylene terephthalate track-etched membranes [41]. The PET film was irradiated with Kr ions and etched in sodium hydroxide solution 2.2 M at 85 ℃ for 75 s to provide formation of cylindrical pores in size of the 100±5 nm and the deposition of Au and Ag nanotubes were carried out by low electrodeposition technique. In recent days, the embedded of noble gold and silver nanotubes (NTs) in porous membranes are an important trend of functional composites to their unique properties and potential application in sensors [42] or electrochemical electrodes [43], heterogeneous catalysts [44] and in flow through reactors, also in medicine [41,45].

Also, there are many reasons to prefer using of nanoporous track-etched membranes as nanocatalyst support; large surface area of the internal pores leads to more effective loading of the nanocatalyst. Also, no separation required for the catalyst from the reaction mixture at the end of the reaction and finally, the reaction takes place on the membrane surface and inside the pores due to the excellent contact between catalyst and reactants [46]. Gold and silver nanoparticles and nanotubes can be used as the suitable catalyst for reduction of the wide range of the nitroaromatic compounds, CO oxidation [47,48].

Mashentseva *et al.* [41] used the single step catalytic hydrogenation of P-nitrophenol (4-NP) to P-aminophenol (4-AP) by reducing agent sodium borohydride in aqueous solution to test the catalytic membrane activity. All tested membranes exhibited quite a good stability and the activity of catalytic membrane had no any significant decrease after reuse at least 5 cycles [41].

2.3. Inorganic catalytic membranes

Inorganic membranes are mainly used in liquid filtration, but there is a trend to develop inorganic membranes for high quality gas separation for sustainable energy production. The most common materials used in the prepa-

ration of inorganic membranes are carbon, zeolite, ceramic membranes and metallic [49].

Inorganic membranes have strong advantages in chemical and engineering processes [50]; such as high thermal stability compatible with temperature ranges of (300-800) °C. Accordingly, It can be applied in the food industry and pharmaceutical due to its inertness and biocompatibility. However, ceramic membranes have good mechanical strength at high operational pressures. this kind of membranes are easy purification and cleaning after fouling. They have long life time and easy incorporation of additional phases with catalytic activity in certain processes. But the disadvantages related to the high capital costs or the fact that fabrication process which is still under development continuously vanishes due to the technological achievements in the area [50].

2.3.1. Ceramic catalytic membrane

Ceramic membranes are considered as a permselective barrier or a fine sieve. The permeation factor in the porous ceramic membrane is controlled by the membrane thickness, pore size, and porosity of the membrane. Ceramic membrane is considered as composite membrane due to use different mixtures of inorganic materials. Generally, ceramic membranes can be fabricated by a support layer, a thin skin layer which is a selective layer and the layer which can carry the catalyst [51]. The most methods are used in ceramic membranes fabrication is slip casting, extrusion, pressing,

these methods are followed by heat treatment and surface treatment.

The most common materials used in the ceramic membranes fabrication are alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), silica (SiO_2), or a combination of these metal oxides. Ceramic membranes can be divided into three types according to the pore size. The macroporous membranes provide high permeability, and they are used as a support in the synthesis of composite catalytic membranes, or as a distributor of reagents. Mesoporous membranes have high permeability and low selectivity and are used in the synthesis of composite membranes. The third one, microporous membranes have low pore size diameter with a potential use in molecular sieve separation. The geometric configurations for ceramic membranes are flat membrane, tubular, multichannel monolith and hollow fiber. The most ceramic configuration is hollow fiber or tubular membrane according to the high surface-to-volume ratios compared to other membrane configurations. It can be applied in industrial processes such as corrosive fluids filtration, high temperature reactors, fuel cells, and as a catalytic contactor membrane with high catalytic activity [51].

Khajavi *et al.* [52] studied preparation of nonpermselective sulfated zirconia catalytic membrane to be applied in a catalytic membrane reactor. The authors prepared membrane using the sol-gel method at low sintering temperatures. While, the fabrication of the catalytic layers of sulfated zirconia with gradient composition on the surface improved the
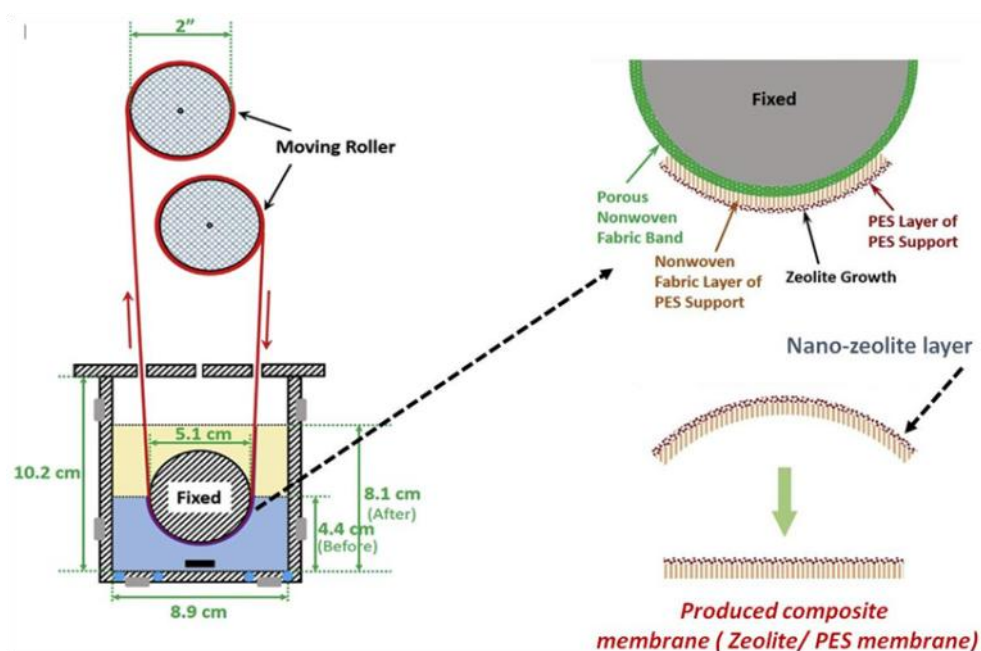
Figure 4. Method for inclusion of nanoparticles in polymeric membranes

support to achieve the catalytic membrane has uniform structure, appropriate crack-free surface, and desirable crystalline phase. The results, in this case, indicated that the catalytic top layer has a mesoporous structure which is perfectly suitable for catalytic applications [52].

2.3.2. Metal catalytic membrane

Metal membranes are dense membranes and can be used for hydrogen separation from gas mixtures and as catalytic membranes in the gases reactions area. Palladium and its alloys are the dominant materials for fabrication of this type of membranes due to its high solubility and permeability of hydrogen [49].

Palladium is very expensive material due to low availability in nature. The recent way to overcome the cost of metal membranes, the palladium is used as a thin layer coating on the supported membrane, which may be ceramic or polymeric membranes. The merits of using thin coating layer of metal are decreasing in material costs, improving in resistance to mechanical strength and high permeating flux. On the other hand, tantalum, vanadium, nickel, and titanium can be used as dense membranes selectively permeable only to hydrogen as alternative materials with respect to the palladium and its alloy [49].

According to the high cost of metal membranes, the researches tend to deposit the metals nanoparticle on the polymeric surface. Soukup *et al.* [53] investigated the deposition of metallic nanoparticles from solution directly on electrospun fibers; monometallic palladium as platinum catalysts was supported on poly (2,6-dimethyl-1,4-phenylene) oxide electrospun mats. The catalytic activity of platinum catalysts in the total oxidation reaction of methanol increased with the increasing size of Pt-based nanoparticles [53].

2.4. Catalytic membrane characterization

Most common characterization tests for catalytic membranes are Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), thermo-gravimetric analysis (TGA), scanning electron microscope (SEM), atomic force microscope (AFM), and contact angle. Also, mechanical properties must be characterized such as tensile strength and elongation to indicate the ability of the membrane to carry loads like pressure especially when it will be used in the gases reaction [1].

The Fourier transform infrared spectroscopy (FT-IR) test is a technique which is used to in-

dicate the catalytic sites in the catalytic membrane after grafting process, precipitation of catalyst on the membrane surface and blending of the catalyst during the membrane preparation step [8]. For example, Fayyazi *et al.* [54] studied preparation of catalytic polysulfone membrane, where the chloromethylation is preliminary step for functionalization of polysulfone membrane. This step was confirmed qualitatively by a FT-IR technique, which displayed clearly the presence of methylene groups in the polymer backbone after chloromethylation step that was observed at 2993 cm^{-1} related to methylene group CH_2 [54].

Thermo gravimetric analysis (TGA) analysis indicates the change in physical and chemical properties of membrane before and after catalyzation as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss) to indicate the effect of catalyzation process on the membrane efficiency. Jaleh *et al.* [55] tested the irradiated PVDF by TGA to indicate the thermal stability of the membranes after grafting by irradiation step. The thermo-degradation of PVDF was observed at 420 °C, while after irradiation of PVDF the thermos degradation increased to 460 °C. The grafting of PVDF by irradiation improved the thermal stability of the catalytic membrane [55].

The nuclear magnetic resonance (NMR) analysis is used to determine the percentage of catalysts supported on the membrane surface. Fayyazi *et al.* [54] tested the prepared catalytic polysulfone membrane by H-NMR to determine the percentage of chloromethylation on the membrane surface. H-NMR spectra indicated that; the polysulfone construction provided two readings 6.8-7.9 ppm according to phenyl group hydrogens and 1.67 according to methyl groups. The appearance of the peak at 4.56 ppm proved that chloromethylation of PSf has occurred and the percentage of chloromethylation was estimated by the area of the peaks at 4.56 ppm and 1.67 ppm which was about 12 % [54].

A scanning electron microscope (SEM) is used for the evaluation of membrane morphology before and after catalyzation step to indicate the effect of catalyst loading on the membrane structure. Casimiro *et al.* [35] studied preparation of catalytic polyvinyl alcohol (PVA) membranes. The PVA polymer was dissolved in water at 80 °C with succinic acid, adipic acid and 0.5 g ion exchange resin. The polymeric solution was exposed to *γ*-irradiation for grafting

step. The prepared membrane was tested by SEM, where the images demonstrated that the presence of asymmetric membranes composed of two distinct layers; a polymeric selective layer and a catalytic layer with resin spherical particles [35].

The atomic force microscope (AFM) is used to indicate the surface roughness of membrane before and after catalyzation process. Alpatova *et al.* [15] prepared PVDF catalytic membrane by blending multiwall carbon nanotubes with Fe_2O_3 under sonication process. AFM testing of the prepared catalytic membrane was studied, which indicated that the addition of Fe_2O_3 has been slightly effected on the membrane surface roughness compared with the prepared membranes without any addition [15].

The contact angle test is carried out on the membrane surface to indicate the nature of surface before and after catalyzation according to its hydrophilicity or hydrophobicity. Alpatova *et al.* [15] tested the contact angle of the prepared blend PVDF membranes with nanoparticles (multiwall carbon nanotubes with Fe_2O_3) and without nanoparticles. The results indicated that the PVDF membrane was a hydrophobic membrane with high contact angle ($95.6\pm2.1^{\circ}$), while after nanoparticles addition the hydrophilicity of the membrane increased due to decrease in the contact angle below 90° for all tested membranes [15].

3. Classifications of Catalytic Membranes According to Their Applications

The catalytic membranes can be divided to three different kinds according to the roles of the catalytic membrane in a membrane reactor; extractor catalytic membrane, distributor catalytic membrane and contactor catalytic membrane.
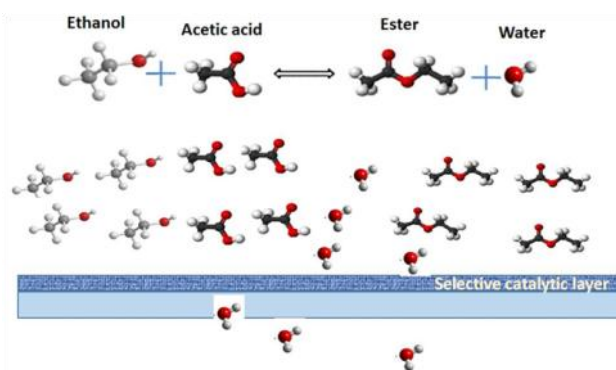
3.1. Extractor catalytic membrane

In this type of catalytic membrane; the membrane withdraws a reaction product from the reaction zone acting as an extractor for the product, which leads to high conversion due to the shift effect in the thermodynamic equilibrium. Generally, this type is a selective membrane for one of the products. The most using the extractor catalytic membrane are in esterification and dehydrogenation reactions where these are required selective removal of produced water from reaction or hydrogen respectively. Figure 5 indicates the schematic drawing for the extractor catalytic membrane function for the esterification reaction. Esterifica-

tion reactions by pervaporation membrane is an application uses extractor catalytic membrane. The membrane, in this case, is a hydrophilic dense membrane and contain sulfonic group as a catalytic site in the backbone of the membrane. The membrane extracts the produced water from the reaction leading to increasing the conversion by breaking the thermodynamic equilibrium of the reaction. Most extractor catalytic membranes are dense membranes and the transport mechanism depends on the principle of solution/diffusion through the bulk of the material. The permeation through the membranes implies that the molecule of selected gas or liquid is adsorbed on the membrane surface, and dissolves in the membrane material, then diffuses through the membrane and desorbs on the other side [56].

3.2. Distributor catalytic membrane

In distributor catalytic membrane, the membrane allows to one of the reactants to pass in doses with a controlled form to the reaction zone as shown in Figure 6. A controlled dosing of reactants (mostly the gases) to the reaction zone permits enhancing the reaction selectivity. This type of catalytic membrane can be used in gas phase reaction to maintain the mixture below the explosion limits. Selective oxidation and hydrogenation reactions can be performed using this type of catalytic membrane due to the exceptional performance of the membrane [57,58].

Kertalli *et al.* [59] investigated direct synthesis propylene oxide using distributed catalytic membrane. The reactor was designed to the coupling of two sequential reactions H_2O_2 synthesis and propylene epoxidation. The feed was oxygen and hydrogen in excess, they flew to the shell tubular reactor then they flew

Figure 5. Schematic drawing for the extractor catalytic membrane function in the esterification reaction [56]

through the catalytic membrane in doses. The catalytic layer of the membrane was Pd/SiO_2 in the top layer of the membrane, where hydrogen and oxygen react to form H_2O_2 while the bottom layer of the membrane was titanium silicalite to catalyze the reaction between H_2O_2 with propylene and produce propylene oxide [59].

The methanol is used as the best solvent for the direct synthesis of propylene oxide because it has high reaction rates and high hydrogen solubility [60]. The results in this work indicated that the conversion of hydrogen to form H_2O_2 increased depending on the catalyst thickness, also the conversion of H_2O_2 to propylene oxide increased by increasing the thickness layer of the catalyst as shown in Figure 7.

3.3. Contactor catalytic membrane

The contactor catalytic membranes are used to facilitate the contact between the reactants and catalyst. In this membrane, the membrane can be intrinsically active as a catalyst or the catalyst can be supported onto the membrane matrix. There are two possible modes for con-
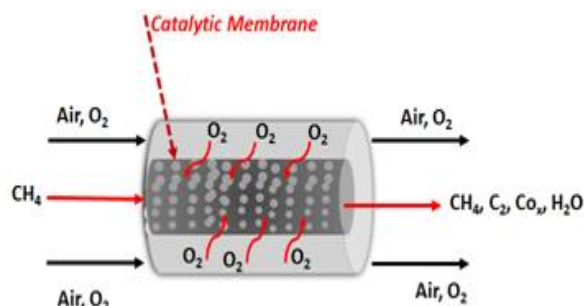

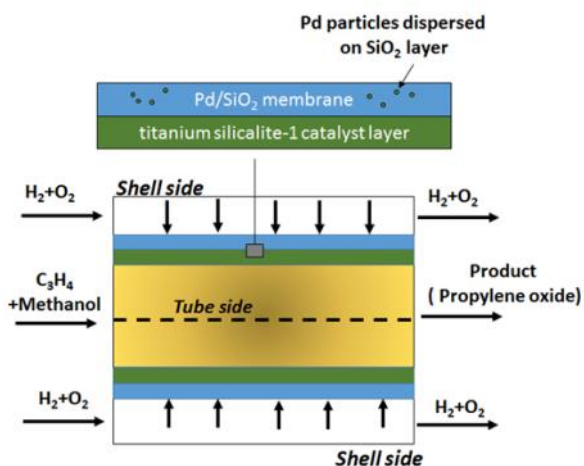**Figure 6.** Schematic drawing for the distributor catalytic membrane function

Figure 7. Direct synthesis of propylene oxide using distributor catalytic membrane [60]

tactor catalytic membranes work. The first mode is the interfacial contactor membrane, where the reactants are separately medicated from each side of the membrane (lumen/shell side), and they react over the catalytic site as shown in Figure 8.

This mode is usually used in reactions with immiscible reactants. Also, there is no restriction in the use of gaseous reactants because there is no danger of explosive formation or flammable atmospheres [61]. The second mode is the flow through catalytic contactor membrane. A mixture of reactants is forced to flow through the nonpermeability selective catalytic porous membrane. The membrane pores provide a region where the reaction will take place. The catalyst sites are supported into the membranes pores while the reactants flow through the pores to permit the excellent contact between catalyst and reactants. This mode leads to the fastest reaction with a short residence time of reaction [2,5,62]. A scheme of the second mode of flow through contactor catalytic membrane is depicted in the Figure 9.

Also, the contactor catalytic membrane can have separation properties, which can separate one of the products from the reaction region. There are two types of membranes used as contactor catalytic membrane: (i) Membranes intrinsically active for catalytic reactions, such as perosvkites or ion/electron conducting ceramics, metallic dense membranes, zeolites, metal oxide compounds, etc. (ii) The inert membranes with an incorporated catalytic active sites as shown in Figure 10 [2,5].
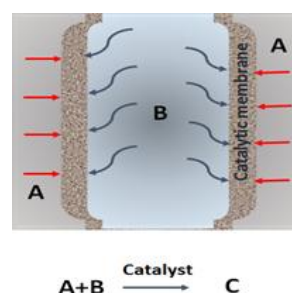

$$A + B \xrightarrow{\text{Catalyst}} C$$
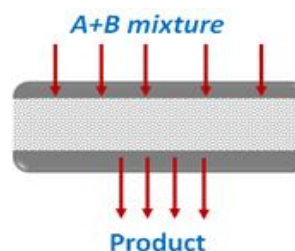
Figure 8. Interfacial membrane contactor

**Figure 9.** Flow-through membrane contactor

There are many aspects must be taken into consideration when the contactor catalytic membrane is chosen to perform any reaction. These aspects are catalyst stability on the membranes, size or shape of catalyst particles, distribution of the catalyst along membrane surface and the stability of catalyst under reaction conditions, also the ability of the catalyst to regeneration. The introduction of catalyst on membranes can be applied by covalent binding, electrostatic interactions, weak interaction (Van de Waals or hydrogen bonds) or physically embedded in the matrix of casting membrane materials [4]. The contactor catalytic membrane can be applied in gas-gas applications, liquid-liquid applications or gas-liquid reactions [9,62].

The transfer mechanism in the porous flow through catalytic membrane relies on the Knudsen diffusion due to the small of the mean free path of molecules compared to the pore diameter of the membrane. The molecules undergo many more collisions with each other than with the walls of the membrane [5].

4. Applications of Catalytic Membranes and Case Studies

4.1. The Suzuki reaction

The Suzuki reaction is the organic reaction that is classified as a coupling reaction where the reactants are a boronic acid with a halide catalyzed by a palladium. Fayyazi *et al*. [54] studied the Suzuki reaction of idobenzene and phenyl boronic acid. The membrane was prepared as blend membrane from polysulfone and Pd(II) and treated for 12 min under ultrasonic irradiation and stirred for 5 h at room temperature. The homogenous solution was casted onto a glass substrate and immersed in water coagulation bath. In this study biphenyl was produced by passing iodobenzene and phenyl boronic acid in water as solvent through the cata-
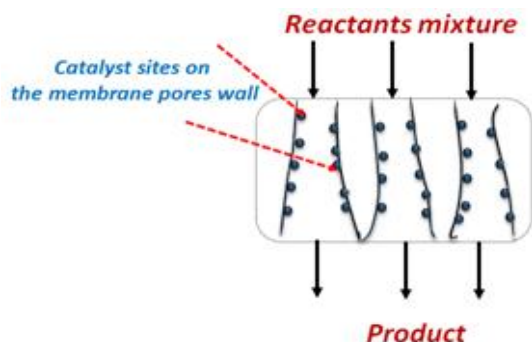
Figure 10. Flow-through catalytic membrane, the catalytic sites supported on the pores wall

lytic membrane, where the reaction could occur on the catalyst layer directly without any need to separate products from the catalyst. The produced results indicated good catalytic activity and the catalyst was stable enough to be reused over 30 times without any significant loss of productivity [54].

Gu *et al*. [48] developed flow through catalytic membrane using grafting step on microfiltration polyether-sulfone and precipitate the Palladium catalyst on the surface by soaking the membrane in $K_2[PdCl_4]$ (0.05 mol/L) in H_2O/methanol (1/1 volume ratio) for 90 min, then the membrane was rinsed by ionized water, finally, the reduction step was occurred by soaking the membrane in $NaBH_4$ for one hour, the photo of prepared composite Pd/PES catalytic membrane is illustrated in Figure 11. The authors studied the Suzuki-Miyaura cross-coupling between 1-iodo-4-nitrobenzene and phenyl-boronic acid using colloidal Pd catalyst without membrane and in a batch system. This reaction provided conversion 100% at a temperature of reaction 80 °C for reaction time 5 h, with 87 % selectivity of the cross coupling by-products. While, using catalytic membrane provided 100 % conversion at room temperature and residence time 9 seconds with 100 % selectivity of cross coupling by-products [48]. The residence time of reactants in the membrane was very short, so the formation of the homo-coupling byproduct was prohibited. Really, the highest catalytic membrane reactivity improves the selectivity of the process [63,64].

4.2. Dehydrogenation reactions

Dehydrogenations reactions are the very important reaction in chemical industries, where dehydrogenations of alkanes and ethylbenzene as an example have a great industrial importance in the petrochemical industries especially in the manufacture of plastics, synthetic rubbers, etc. Also, the dehydrogenation of cyclohexane to benzene has conceivable importance for hydrogen storage and renewable energy applications due to the cyclohexane is considered a chemical source of hydrogen [65].

Most problems of dehydrogenation reactions are endothermic and equilibrium-limited, and should be, performed at comparatively high temperatures to increase the reactions rates and to shift the conversion to a good level. Also, the thermal cracking at the high reaction temperatures can occur and lead to the production of undesired by-products, which cause catalyst deactivation due to the formation of carbon precipitated [53,66].

Catalytic membrane reactors can be used to overcome these problems, where the reactions can be carried out at low temperatures, the selectivity of gas increases to values above 75 % and the membrane-assisted reaction system to achieve high conversion with minimal hydrocarbon. Thus, the production of undesired by-products is reduced and the stability of the catalyst is increased, allowing long cycles between regenerations [49]. Table 3 indicates some studies on the application of catalytic membranes on dehydrogenation reactions.

Jeong *et al.* [65] studied the dehydrogenation of cyclohexane in a catalytic membrane reactor to produce benzene and hydrogen. The prepared membrane was zeolite membrane which was shaped on a porous a-Al$_2$O$_3$ support tube and the catalyst Pt/Al$_2$O$_3$ impregnated on the tubular membrane. The results indicated that the conversion of cyclohexane in the membrane reactor increased due to the instantaneous removal of hydrogen and benzene from the reaction media. The conversion of cyclohexane using the prepared catalytic membrane reached to 72.1 % at 473 K [65].

4.3. Hydrogenation reactions

Partial hydrogenation is considered an important process for multiple-unsaturated hydrocarbons in the petrochemical industry, such as purification of alkene feed streams and production of commodity chemicals from alkynes, dienes, and aromatics. The selection of catalyst type in this process is very important. The catalyst selectivity is the main target because this process is often run at low temperatures and low hydrogen partial pressures. Therefore, using the polymeric catalytic membrane in the application of partial hydrogenation is a prom-

ising way due to operation at low temperatures and the limitation of mass transfer imposed by the catalytic polymer membrane matrix that may actually be advantageous [68].

Some authors studied the selective hydrogenation in the gas phase in a catalytic membrane made of polymers, where the catalysts were deposited on its surface. Liguori *et al.* [69] studied partial hydrogenation reactions of 1,5-cyclooctadiene over hybrid inorganic/polymeric catalytic membranes. The palladium nanoparticles (4.6 nm) were grown into a hybrid zirconia/polyvinyl alcohol matrix, to be suitable in partial hydrogenation reactions in the liquid phase under smooth conditions. The reaction conversion reached to 87.7 % with 78.4 % selectivity to cyclo-octene under 5 bars hydrogen, during the reaction, there was no observation of by-products such as the isomerization of 1,3- or 1,4-cyclo-octadiene products [69].

Wehbe *et al.* [70] studied the hydrogenation of nitrates solutions using mesoporous flow-through catalytic contactor membranes. Nitrates are the main compounds in fertilizers, and they are used in an excessive amount which leads to contaminating the surface and ground water [70]. Catalytic hydrogenation of nitrates provides a smart solution to water de-nitrification, where the nitrates are decreased into a harmless product and nitrogen. The most using catalyst for this process is supported palladium catalysts promoted by copper [68].

Wehbe *et al.* [70] used commercial porous alumina tubes with an asymmetric structure consisted of 3 γ-alumina layers. The pore size decreased (12, 0.8, and 0.2 μm) from shell to lumen side, while a final mesoporous layer (lumen side) made of γ-alumina with pores of

Figure 11. Prepared composite Pd / PES catalytic membrane [54]

Table 3. Some studies on the application of catalytic membranes on dehydrogenation reactions [67]

Membrane System	Reaction
Pd-Alloy membrane reactor	Dehydrogenation of hydrocarbons
Pd-Rh foil membrane	Dehydrogenation of cyclohexanediol to pyrocatechol
Pd-Ru-Ni Alloy membrane	Dehydrogenation of isopropanol
Pt/Al$_2$O$_3$-Pd membrane	Dehydrogenation of cyclohexane to benzene

25, 10, or 5 nm. The Pd and Cu catalysts were precipitated simultaneously in the membrane using the evaporation-crystallization technique. The rate of nitrate disappearance increased with the trans-membrane flow rate, with low contact time. The accumulation of nitrates over the membrane increased the concentration polarization, where the nitrate accumulation in the catalytic zone led to an increase in the reaction rate and the nitrate conversion reached to 92 % [70].

Wang *et al*. [40] prepared new kind of catalytic membrane can be used in wastewater treatment, where the polyvinylidene fluoride (PVDF) / polymethacrylic acid (PMAA) blend membranes were prepared by blending PVDF polymer powders with PMAA microspheres, produced from distillation precipitation polymerization, the blend polymers mixed with dimethyl-formamide for 6 h at 60 °C. The prepared polymer solution was casted on a glass plate and the immersion precipitation of the membrane has occurred in coagulation water bath. Then the prepared membrane was soaked in sodium hydroxide solution (0.1 M) for 12 h to convert PMAA into carboxylate [40]. The membrane was washed and soaked in palladium chloride solution (4 mM) at pH 4 for 48 h to immobilize the Pd catalyst into the membrane. The hydrogenation reaction of *p*-nitrophenol to *p*-aminophenol in aqueous solution with $NaBH_4$ as a reductant was carried out by a cross-flow filtration mode through the compo-site membrane consisting of a tangential flow and a penetrative flow process as shown in Figure 12. The results indicated that the reaction provided an extremely high rate of *p*-aminophenol degradation at 20 min, where the conversion of *p*-nitrophenol reached to 99.8 % using the composite membrane with a Pd loading of 0.38 mg/g [40].

4.4. Esterification reaction

Esterification is a chemical reaction producing esters, it is a reversible, and very slow reaction. It must use a mineral liquid acid catalyst (e.g. sulfuric or hydrochloric acid) to orient the reaction in the forward direction, which leads to equipment corrosion, neutralization of the reaction mass and difficulty in the catalyst separation [71]. Pervaporation membrane reactor (PVMR) is a catalytic extractor membrane, where the coupling of pervaporation with esterification in PVMR is an ideal candidate used to enhance the esterification process and overcoming its disadvantages. Esterification-pervaporation coupled reactors are also anticipated to provide time saving, low energy consumption, clean operation and minimum waste [72].

Sorribas *et al*. [56] performed esterification reaction of acetic acid with ethanol using pervaporation catalytic membrane. The membrane was mixed matrix membranes and prepared using commercial polyimide with the addition of the metal organic to improve the hydrophilicity of the membrane [56]. The metal organic are crystalline porous materials that fit organic-inorganic hybrid compounds, so the size, shape and chemical functionalities of the metal organic cavities can be easily adjusted by choosing the appropriate linker-metal couples [73]. The results of this study indicated that the prepared catalytic membrane reactor provided conversion reached to 72 % using molar ratio 3:1 ethanol to acetic acid and at reaction time 1.5 h and temperature 50 °C [56].

Another best alternative is esterification using flow though catalytic membrane. El-Zanati *et al*. [71] developed esterification reaction of ethanol and fatty acid using flow-through catalytic membrane. The polyethersulfone membrane was prepared by phase inversion
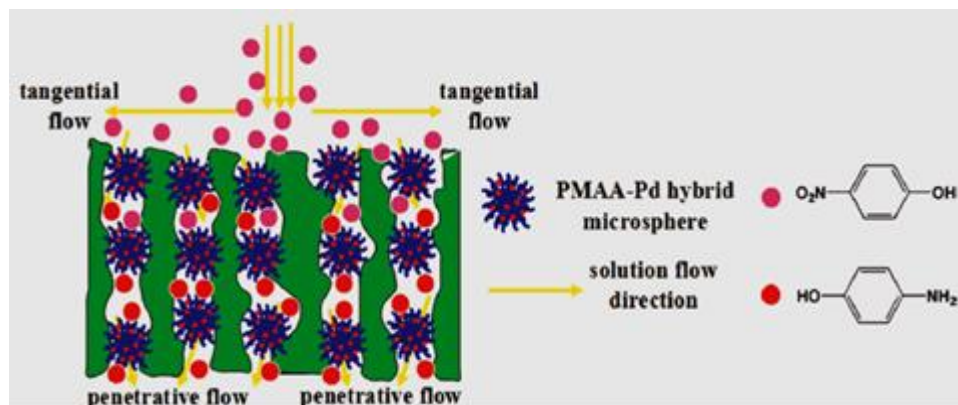

Figure 12. Schematic diagram of cross flow catalysis [70]

method. The membrane was grafted under cationic polymerization using styrene as a monomer for grafting process [71]. The grafted membrane has more than 100 repeated catalytic chain units inside each pore of the membrane, which made each pore of the membrane as a micro-reactor; this led to very fast reaction within low residence time. The conversion of the fatty acid to ester reached to 99 % at reaction time 10 seconds. The reactants are forced flow through the catalytic sites in membrane pores, the produced water from the reaction was adsorbed on the catalytic sites, so the reversibility of the reaction was prevented. Figure 13 indicates the schematic drawing of flow-through contactor catalytic membrane and the adsorbed water on the catalytic sites. After a certain time, the membrane was regenerated to activate the catalyst sites and reuse the catalytic membrane [71].

Also, the author designed and fabricated the integrated pilot unit for esterification / regeneration unit as shown in Figure 14, which afforded a high esterification reaction conversion of (96-98) % for esterification of acetic acid and a fatty acid with ethanol, respectively. The production cost was calculated for this process to be $1.4/gallon, which is promising to be a competitor fuel with respectable benefits margin, compared with the world price of biodiesel which is ranged from $3.86/gallon to $4.2/gallon [71].

4.5. Photocatalytic reactions
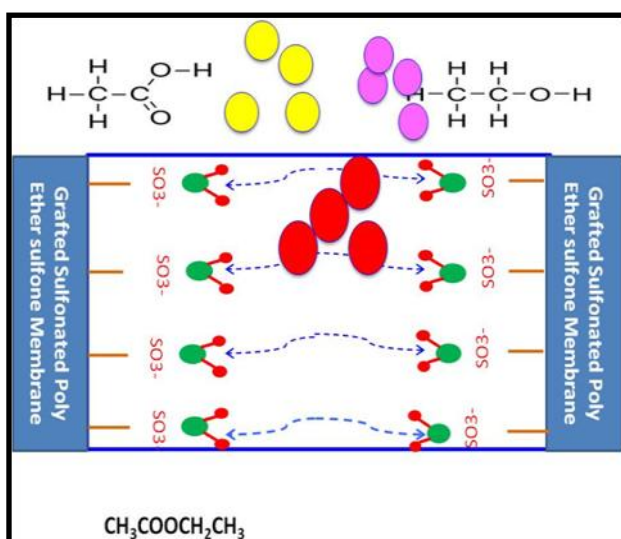
Nowadays, the photo-catalytic degradation

Figure 13. Schematic drawing of esterification reaction using contactor catalytic membrane [71]

has a great attention as an alternative method in the removal of environmental pollutants in aqueous or gaseous media. Generally, advanced oxidation processes depend on the addition of oxidizing agents (hydrogen peroxide, ozone, or molecular oxygen itself) in the presence of a catalyst, ultraviolet radiation (UV) or both, has led to photo-catalytic oxidation processes. This method of oxidation has been offered as a feasible alternative for the decontamination of either waste water or drinking water for human uses, which can be used for the degradation of the different toxic organic compounds particularly chlorinated ones [74].

Photo-catalytic polymeric composite membranes were prepared by photo-polymerization and photo-crosslinking of a blend composing of acrylic monomers, a photo-initiator and the photo-catalyst or photo grafted onto both sides of a perforated polyester support. Figure 15 illustrates the schematic drawing for photo-catalysis using photo-catalytic membrane. Some parameters can effect on the photo-catalytic membrane performance such as porosity, which must be controlled in membrane surface coating during membrane preparation to optimize the conditions of the photo-crosslinking [75].

The immobilization of photo-catalyst into porous membranes can provide effective industrial applicability of these membranes. Buscio *et al.* [76] studied removal of red dye using flow-through photo-catalytic membrane, where titanium dioxide was the loaded catalyst and the degradation of dye by oxygen reached to 87 % at 50 ppm of red dye [76]. Also, Li *et al.* [77] prepared sand-wished nanofiber photocatalytic membrane made from three layers upper and lower layer of polymethylmethacrylate (PMMA) and $H_4SiW_{12}O_{40}$ blended nanofibers, while the middle layer was polyvinyl alcohol (PVA), the membranes were prepared by electrospinning technique, the photooxidative degradation of azo-dyes was studied and the membrane provided 72.9 % within 30 min degradation of the organic dye [77].

5. Case Study: Palladium Membrane Reactor for Large Scale Hydrogen Production [78]

This case study provides an overview of the developed palladium membrane reactor as a catalytic membrane at Energy research Centre of the Netherlands (ECN) for large-scale hydrogen production. The ceramic tubular membrane was used and the dense layer of Pd alloy have been made on ceramic supports with low

electroplating on a 1 m² scale with thickness 3-6 µm as shown in Figure 16. In the production step up to 90 cm ceramic tubes was used to produce high selectivity from 1000 to 7000 and high hydrogen permeance 34 - 48 $Nm^3/m^2.h.bar^{0.5}$ at 450 °C. Using catalytic membrane reactor is possible to shift the methane conversion beyond chemical equilibrium by means of hydrogen removal [78].

The aim of this study [78] was: (a). Development of a hydrogen catalytic membrane reactor for chemicals production especially industrial hydrogen production; (b). Construct and test a hydrogen catalytic membrane reactor that can produce delivers 5 Nm^3/h. This study was applied in the Netherlands in: large scale hydro-

gen production for the ammonia process; power generation with integrated CO_2 capture; small scale on-site hydrogen supply; and dehydrogenations.

The actual industrial consumption was 458 PJ/year and the estimated energy saving potential was 24 PJ/year with total saving potential 5 %. Using hydrogen catalytic membrane reactor in the ammonia process reduced the production units. The conventional process needs desulfurization step, two reformers steps, high temperature shift, low temperature shift, CO_2 removal and methanation. The alternative method just need desulfurization step and catalytic membrane reactor unit, which led to energy saving about 12 % as shown in Fig-
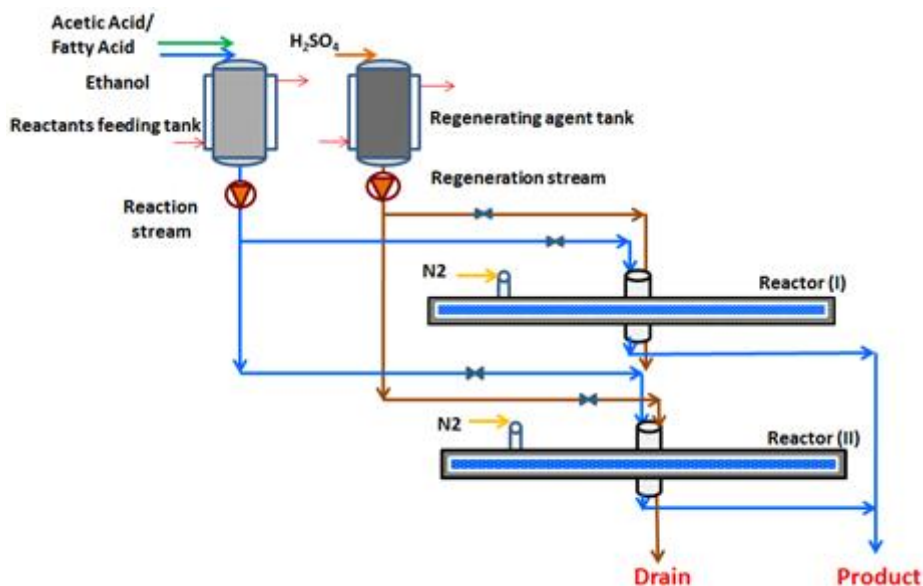
Figure 14. Schematic flow sheet of esterification prototype unit for reaction and regeneration using catalytic membrane [71]
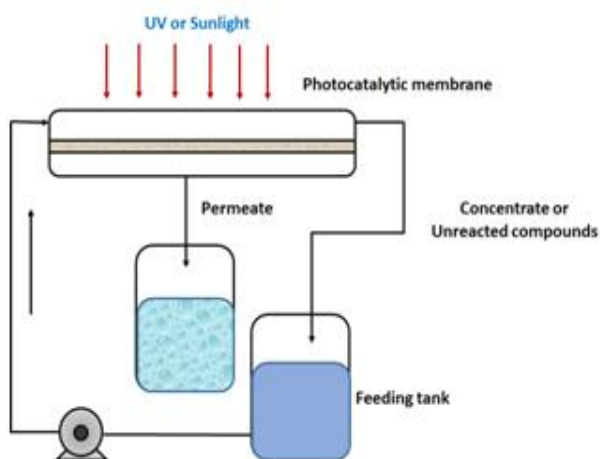
Figure 15. The schematic drawing for photocatalysis using photo-catalytic membrane [74]
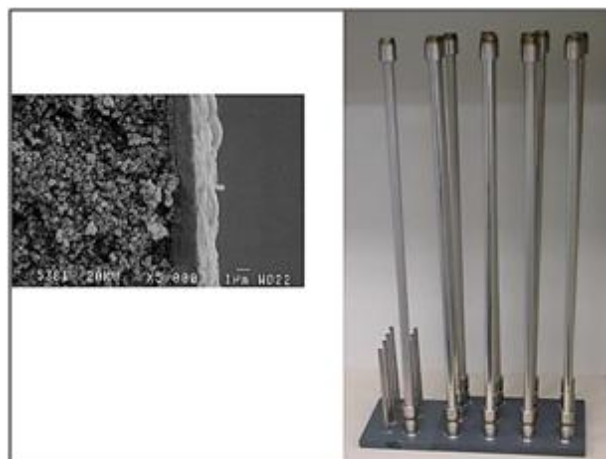
Figure 16. Pd tubular catalytic membrane [78]

ure 17. The capture of CO_2 using conventional production process increased the energy consumption from 16 to 40 %. Meanwhile, usage of catalytic membrane reactor process reduced the cost of CO_2 capture to 50 %. The new process provided 97 % CH_4 conversion at low temperature (500-650) °C, high H_2 recovery more than 98 %, high selective membrane operating at (500-650) °C. The process membrane permeability was 50 $m^3/m^2h.bar^{0.5}$. The membrane approximately price is 1400 euro/m^2 and the life time of membrane was approximately 3 years. Also, multitube membrane reactors must be used for membrane reforming and membrane water gas shift at operating conditions 600 °C and 40 bars [78].

6. Conclusions

In this review article, catalytic membranes kinds; polymeric and inorganic membranes preparations and characterization have been addressed. Classification of catalytic membranes according to their applications has been displayed. Catalytic membranes classified to three types; extractor, distributor and contactor catalytic membranes. The applications of catalytic membranes in some reactions have been exhibited, which indicated that the catalytic membrane can be considered as an alternative way compared with traditional methods. The catalytic membrane has many advantages like breaking the thermodynamic equilibrium limitation, increasing conversion rate, reducing the recycle and separation costs. The main disadvantages of catalytic membranes are the high capital costs for fabrication which is still under development. Some application cases, such as using catalytic membranes in Suzuki reactions, provided conversion of up to 100 % in 9 seconds with a selectivity of byproduct 100 %. Also, using flow-through catalytic contactor membrane in esterification reaction provided conversion 99 % at low residence time 10 sec with selective of produced water on the catalytic sites. Using catalytic membranes in hydrogenation and dehydrogenation reactions provided good yield and intimate an excellent contact between catalysts deposited on the
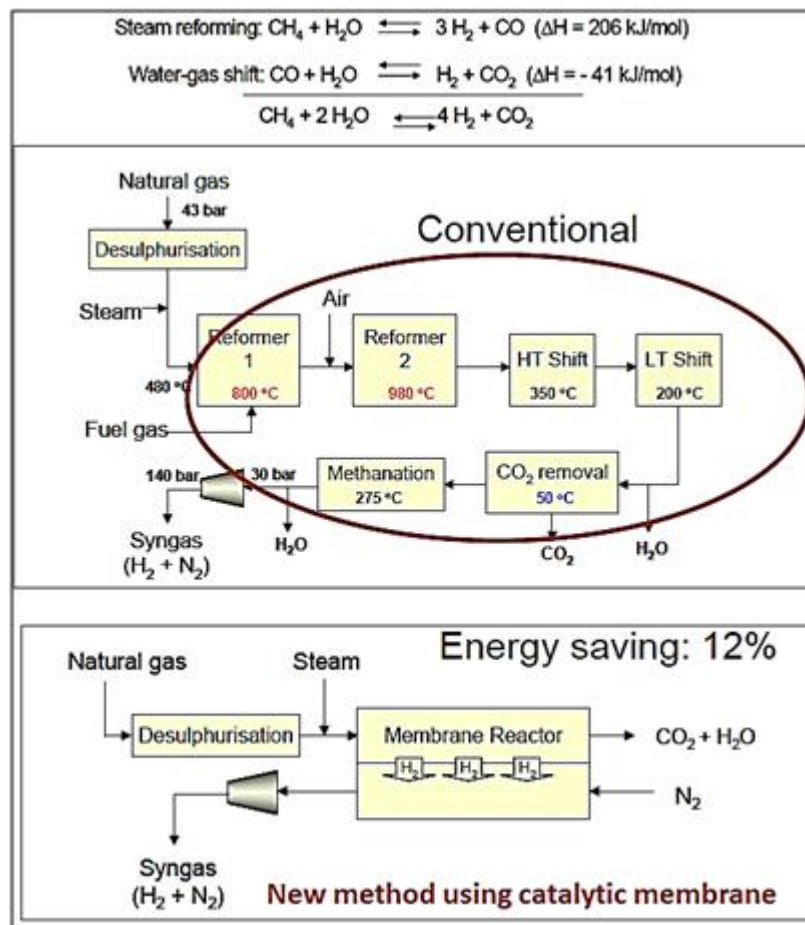

Figure 17. Flow sheets for comparison between conventional and catalytic membrane reactor process in hydrogen production [78]

membrane surface and reactants whether the gases or liquids. Moreover, the catalytic membrane can be used in photo-catalytic reactions by immobilization of photo-catalyst into porous membranes; this type of catalytic membrane performed an excellent degradation of dyes. The case study of palladium membrane reactor for large scale hydrogen production at Energy Research Centre of the Netherlands was exhibited, where using catalytic membrane provided 97 % CH_4 conversion at low temperature (500-650 °C), and high H_2 recovery more than 98 %.

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