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Supported Ionic Liquid Membrane in Membrane Reactor

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Abstract. Membrane reactor is a device that integrates membrane based separation and (catalytic) chemical reaction vessel in a single device. Ionic liquids, considered to be a relatively recent magical chemical due to their unique properties, have a large variety of applications in all areas of chemical industries. Moreover, the ionic liquid can be used as membrane separation layer and/or catalytically active site. This paper will review utilization of ionic liquid in membrane reactor related applications especially Fischer-Tropsch, hydrogenation, and dehydrogenation reaction. This paper also reviews about the capability of ionic liquid in equilibrium reaction that produces CO_2 product so that the reaction will move towards the product. Water gas shift reaction in ammonia production also direct Dimethyl Ether (DME) synthesis that produces CO_2 product will be discussed. Based on a review of numerous articles on supported ionic liquid membrane (SILM) indicate that ionic liquids have the potential to support the process of chemical reaction and separation in a membrane reactor.

INTRODUCTION

Membrane-based separation processes have found many applications in fields such as water, energy, chemical, petrochemical and pharmaceutical industries [1]. Recently, membrane technology has rapid development primarily due to its advantages and potential to various applications in various sectors[2-4]. One potential membrane application in industrial equipment is membrane reactor to boost the performance equilibrium-limited reaction [5-6].

Membrane reactor (MR) is a device that integrates a membrane with a reactor. The membranes may serve as a product separator, reactant distributor, catalyst support or combination of them. The integration of selective separation layer and chemical reactions in a single step has various advantages, such as selective removal of intermediate (or final) product, control the addition of a reactant, control the contact between gasses and catalysts, and the combination of several reactions in one system [7]. As a result, improvement in conversion and yield and/or reduction in the capital and operational cost can be achieved [1, 8]. According to IUPAC, membrane reactor itself is a device to simultaneously perform a reaction (steam reforming, dry reforming, auto-thermal reforming, etc.) and membrane-based separation in the same physical device [9].

In general, membranes used to make the membrane reactor can be classified in homogeneous or heterogeneous, symmetric or asymmetric in structure, solid or liquid membrane. They can have positive or negative charge and can be neutral or bipolar [10, 11]. In all cases, driving force present as the pressure gradient, concentration, etc., is applied to induce permeation through the membrane. There are many concepts to classify membrane reactor, for example, reactor design (extractors, distributor, or contactors), membrane material (inorganic and organic), morphology (porous and dense), types of reactions (Fischer-Tropsch, dehydrogenation, hydrogenation, isomerizations, and esterifications) membrane role in catalytic conversion (inert or catalytic membranes), and position in the configuration (catalyst in/near/before/behind the membrane) [12, 13].

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To improve the performance of membrane reactor, many researchers added a magical chemical that can support the separation process and chemical reactions that occur. Ionic liquids, considered to be a relatively recent magical chemical, have a large variety of applications in all areas of the chemical industries. Ionic liquid (IL) is a salt compound of organic or inorganic which has a melting point below 100°C, other than that IL has high resistance to thermal, chemical and physical force. It also has high viscosity, possesses catalytic properties, environmentally friendly solvents, and high conductivity [14-17]. Based on a various and tunable characteristic that are owned by IL, it can be integrated into membrane reactor employing a role of catalyst, membrane or even both.

This paper will discuss the potential of supported ionic liquid membrane for the application of membrane reactor. Several reactions that have been studied and the corresponding ionic liquid used will be discussed in detail. Moreover, some potential and possible future development of supported ionic liquid membrane in membrane reactor will also be discussed.

The Functions of Ionic Liquid in Membrane Reactor

In the last decade, ionic liquids (ILs) have become a topic of many researchers as media in a chemical reaction, separation process, supported membrane reactor, supported liquid phases for membrane separation even as gas and liquid chromatographic stationary phases [18-20]. IL applied to improve membrane reactor performance to this date is still being developed by researchers. Generally, IL itself is already widely used in a lot of technologies such as a liquid membrane (emulsion liquid membrane (ELM), bulk liquid membrane (BLM), and supported liquid membrane (SLM)) [21, 22]. Liquid membrane technologies still have many weaknesses because it uses toxic and volatile carrier in the form of organic solvents. To handle these problems, supported IL is needed to convert the chemical reaction and separation into "green processing" (environmentally friendly). Using IL can also make the reaction process and separation much more effective and efficient [23]. In addition to liquid membranes, IL also supports the performance of the solids membrane porous and non-porous, organic and inorganic membrane [24]. IL is applied to improve some membrane reactors performance especially in Fischer-Tropsch, Hydrogenation, and Dehydrogenation. IL can act as a contactor in membrane reactor, membrane separator, and even increasing the catalytic performance of reaction. Common IL is usually used shown in Fig. 1.

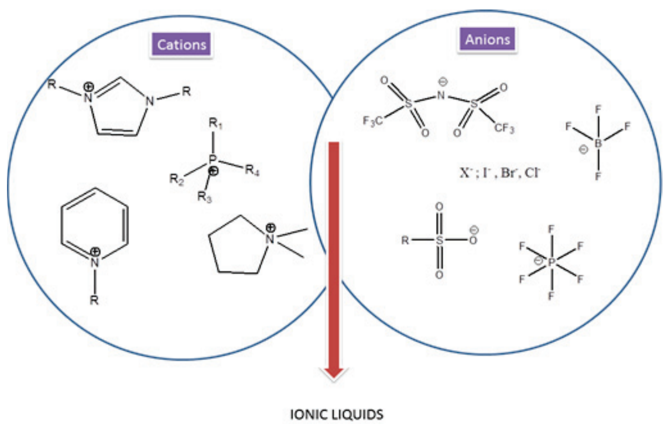

FIGURE 1. Common ILs are used to support perfomance of membran reactor.

There are so many ILs used in the membrane reactor to increase the performance of reactor, such as cations framers : [25] 1-ethyl-3-methylimidazolium, [bmim]: 1-*n*-butyl-3-methylimidazolium, [OMIM]: 1- *n*-octyl-3-methylimidazolium, [DMIM]: 1-*n*-decyl-3-methylimidazolium, [dodecylMIM]: 1-*n*dodecyl- 3-methylimidazolium, [BDMIM]: 1-*n*-butyl-2,3-dimethylimidazolium, [TEA]: tetraethylammonium, [TBA]: tetrabutylammonium, [mbpy]: 4-methyl-*N*-butyl-pyridinium, [DAMI]: 1,3-di(*N*,*N*-dimethylaminoethyl)-2-methylimidazolium, [C8Py]: *N*-octylpyridinium, [BMMIM]: 1-*n*-butyl-2,3-dimethylimidazoliium, [BMIMOH]: hydroxyl-functionalized butyl- 3-methylimidazolium and anions frames are used [BF_4]: tetrafluoroborate, [PF_6]: hexafluorophosphate, [NTf_2]: trifluoromethanesulfonimide, [OTf]: triflate, [$N(CN)_2$]: dicyanamide, [HSO_4]: hydrogen sulphate, [$EtOSO_3$]: ethyl sulphate, [$BuOSO_3$]: butyl sulphate, [$HexOSO_3$]: hexyl sulphate [17, 20, 26-30].

Ionic Liquid Membrane to Fischer-Tropsch Reaction

Membrane reactor that uses IL is still being developed. For example, Fischer-Tropsch reaction to produce medium up to long chain hydrocarbon compounds to produce renewable fuels from H_2/CO and/or H_2/CO_2 syngas precursor. The common IL used is 1-alkyl-3-methylimidazolium bis (trifluoromethane sulfonyl) imidate. This IL type is an effective catalyst for Fischer-Tropsch (FT) reaction, yielding olefins, oxygenates, and paraffin (C7-C30) [31, 32]. The nanoparticles of catalyst are easily prepared by the decomposition of $[Co(CO)_8]$ in the IL membrane reactor at 150°C and can be reused at least three times if they are not exposed to air [33]. Scheme of fluidized bed IL membrane dual type Fischer-Tropsch reactor is shown in Fig. 2.

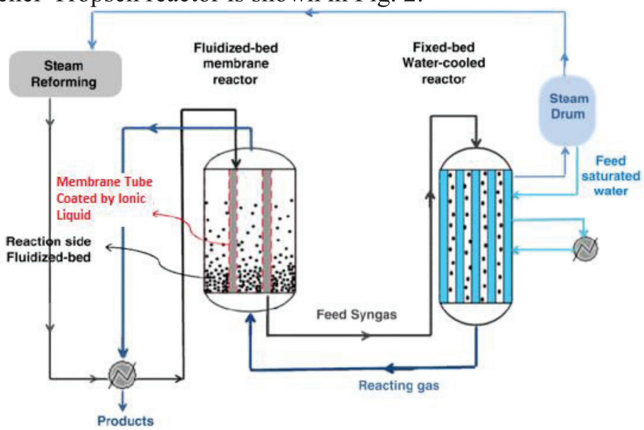

FIGURE 2. Scheme of fluidized bed ionic liquid membrane dual type Fishcer-Tropsch reactor. Adapted from [34]

Other researchers are also used IL as supported in membrane reactor for Fishcer-Tropsch, Silva and coworkers have been done Fishcer-Tropsch reaction in 1-n-butyl-3-methylimidazolium hexafluorophosphate and bimetallic Co/Pt metal [31] . IL acts as an adequate media for the chemical (bottom-up) and physical (top-down) generation of surface "clean" metal NPs. In Fischer-Tropsch reactor, the reactant involved such as CO, which is processed in IL and blended with Co catalyst [29, 35]. Co based catalyst is used $[Co_2(CO)_8$, because its thermally stable property so that it can acted as a selective catalyst in Fischer–Tropsch reaction at 150 °C and can be reused at least three times. The types of IL that has the potential in Fischer–Tropsch are $[BMIM][BF_4]$ and $[BMIM][PF_6]$ with conversion % e.g. 68% and 70 % [36, 37].

Ionic Liquid Membrane to Dehydrogenation Reaction

Ionic liquid has the potential in dehydrogenation reaction. Several researchers have been worked by IL assisted membrane reactor for dehydrogenation. Marcos et al. [38] used supported IL membranes reactor for propane/propylene separation from dehydrogenation reaction using $AgBF_4$ dissolved in [BMIM][BF4] as a carrier solution. It was found that under similar operation conditions, the permeability of the gaseous components in mixed gas experiments was about 6.1% lower for propane and 15% higher for propylene than in pure gas experiments. Moreover, it was observed that Ag^+-SILMs systems are suitable to separate C_3H_8/C_3H_6 gas mixtures since it is possible to obtain a permeate stream with pure enough propylene to be used in most of the propylene applications. In different work, Marcos et al. [39] showed that an increase in silver concentration in the membrane would increase propylene permeability because more carriers are available for propylene transport. On the other hand, although propane should not be affected by the presence of silver ions in the membrane, the permeability of propane is slightly increased when silver salt is added to the membrane because the high flux of propylene can sweep some propane molecules dissolved in the membrane. Development of economically viable propane/propylene separation processes is becoming increasingly important, but it is extremely challenging due to the physicochemical similarities between those two molecules [40, 41]. Therefore, the study of propane-propylene separation process using SILMs still needs further improvements.

Furthermore, other researchers have been used IL to develop the production of hydrogen from ammonia-borane. Ammonia borane (AB) is a potential chemical hydride storage medium so that in the reactor will produce hydrogen in high purity [42-44]. Therefore, to develop the performance reactor of fuel based AB is needed a solvent to increase of dehydrogenation more selective [45]. The solvent has promoted IL and It has the extent and rate of hydrogen release are significantly increased. The IL usually is used [BMIM][Cl] (1-butyl-3-methylimidazole), because of its properties such as non-nucleophilic bases such as proton sponge, 8 and transition metal catalysts [46, 47]. Thus, AB and IL are blended with good ratio mixture to get high H_2 production, which ratio is 50%:50% [46, 48].

TABLE 1. Performance of various Ionic Liquid for dehydrogenation reaction

Ionic Liquid	Catalyst	Condition of Reaction or Separation	% Conversion or Performance Indicator (H_2 release)	Reference
[BMIM[[BF_4]	$AgBF_4$	pure gases and with a 50:50 C_3H_8/C_3H_6 gas mixtures	6.1% lower for propane and 15% higher for propylene	[38]
[BMIM][BF_4]	$AgBF_4$	80% polymer(PVDF-HFP)-20% IL;50/50%v/v C_3H_8/C_3H_6 mixtures	Obtaining C_3H_6 permeabilities upto 6630 barrer and C_3H_8/C_3H_6 selectivities over 700 combined with good long term stability	[39]
[BMIM][Cl]	[Rh(COD)Cl]$_2$	AB (150 mg), [bmim][Cl] (150 mg) and 2.5 mol% Rh(COD)Cl]$_2$ (1) (60 mg) using an automated gas burette; 85°C	Equivalen of H_2 is 2	[45]
[BMIM][Cl]	N/A	95 °C and 22 h	5.4 wt % H_2, Equivalen of H_2 is 1.6	[46]
1,3-chloropropylsilane	PbS nanoparticles	30°C	Yield % H_2 is 95 %	[49]
[BMMIM][Cl]	N/A	Experimental data at 85°C for AB/[BMMIM][Cl] (50:50) mixture	Equivalen of H_2 is 2.34	[50]
[BMMIM][Cl]	N/A	0.3:1 (IL:EDB);140°C	Equivalen of H_2 is 3.90 with 6.5 wt% H_2	[51]
[BMMIM][Cl]	N/A	Ratio of AB: [BMMIM] [Cl] is 0.154 mol/mol	15.1 wt% H_2 and equivalen H_2 is 2.31	[52]
[BMIM][BF_4]	N/A	120°C	Yield % H_2 is 86 %	[53]
1,3-chloropropylsilane	PbS nanoparticles	dehydrogenation of HCOOH/HCOONa at 40 °C	Yield % H_2 is 97 %	[54]
[BMIM][PF_6]	Pt/AC	Substrate: tetralin; 60 min.; microwave heating	70%	[55]

Basically, dehydrogenation of AB can be thermal induced, so in H_2 production conditionally the AB is homogeneous using solvent. Therefore, Ionic Liquid is needed since it has good thermal stability. Moreover, modified IL with PbS based catalyst as the active sites have been successfully prepared using a facile and environmentally-friendly approach [49]. Some kinds of IL has been used for hydrogenation reaction e.g. 1-butyl-2,3-dimethylimidazolium chloride ([BMMIM] [Cl]), 1-butyl-2,3-dimethylimidazolium acetate ([BMMIM][CH_3COO]), 1-butyl-3-methylimidazolium acetate ([BMIM][CH_3COO]), and 1-butyl-3-methylimidazolium methyl sulfonate ([BMIM][OMs]) is compared and the mixture [BMMIM][Cl] [51, 57]. The initial reactant is used to produce H_2 does not only AB, but can be used from ethylene diamine bisborane. Using various IL has lead reactor performance to produce H_2 6.5 %wt at 140°C. IL will support of separation of H_2 in reactor more selective, so the yield of H_2 is maximum. The other IL that has been tested for dehydrogenation are butyronitrile side chains (1-(butyronitrile)-3-methylimidazolium chloride) and diethylamino functionalized ethyl side chains (1-(N,N-diethyl-2-amino)ethylene-2,3-dimethylimidazolium chloride) [51]. Based on explained above, exhibited of potential IL in membrane reactor to dehydrogenation especially for H_2 production. The best type of IL has used BMIM cation with various anions. Summary of various IL performances for dehydrogenation reactions is showed in Table 1.

Ionic Liquid Membrane to Hydrogenation Reaction

Additionally, IL membrane reactor is also used in the hydrogenation reaction of unsaturated hydrocarbons into saturated hydrocarbons. IL-coated Pd catalyst is placed in the membrane reactor [58, 59]. Development of hydrogenation reaction with IL membrane reactor also assured the authors today because metallic Pd-Ni will be trapped in the IL as a unique stabilizer agent thereby increasing the stability and catalytic activity of this nanomaterial. The report uses imidazolium-based IL on a single stabilizing agent, Pd(0)-Ni (4.9 ± 0.8 nm) produced in [BMI][PF_6] (or [BMI][BF_4]) on the reduction of Pd(acetylacetonate)$_2$ by molecular hydrogen (4 atm, constant pressure) at 75°C [60, 61]. Scheme of IL membrane reactor used in the hydrogenation reaction is shown in Fig. 3.

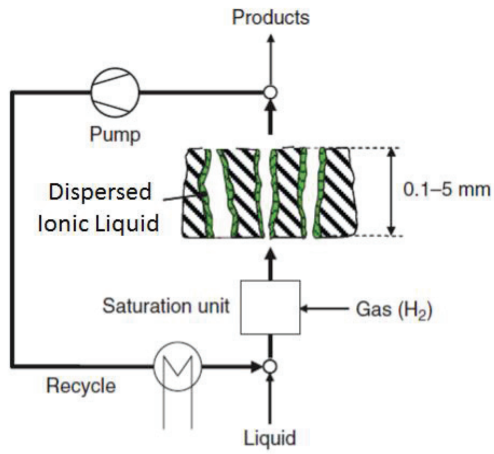

FIGURE 3. Scheme of ionic liquid membrane reactor used in the hydrogenation reaction with a Pd catalyst which has been coated by the ionic liquid is placed in the membrane reactor. Adapted from [8]

IL supported membrane not only is used for hydrogenation of unsaturated hydrocarbon but also is used for asymmetric hydrogenation of benzalacetone, which is [p-$CH_3C_6H_6SO_3$] based IL [62]. IL can be used as supported of hydrogen reactor for the asymmetric compound, because it has good physic and chemical properties, moreover IL can be acted as immobilize chiral catalysts so that the hydrogenation will running efficient and easily for the recycle of chiral catalysts [63-65]. The length of alkyl chain in IL will take effect with its hydrophobicity characteristic in the dissolving of reactant. Therefore, many researchers are developed modifying of IL to get the best performance in hydrogenation with a specific substrate. Moreover, the catalyst is used to asymmetric hydrogenation should be noted, the specific catalyst used Ru (ruthenium).

Zhang et al. [66] have also studied of influence IL supporter reactor in asymmetric hydrogenation. They are used Rh catalyst - diphosphine (S,S)-MeDUPHOS ligand, phosphine-phosphoramidite ligands (Sa,Sc)- MATPHOS[67], and (Sa,Rc)-Xyl-QUINAPHOS [68] with solvent [NTf_2]/s$ScCO_2$ (EMIM:1-ethyl-3-methyl-imidazolium; Tf: trifluoromethanesulfonyl) to asymmetric hydrogenation. Based on their research has shown that IL has good potential to hydrogenation reaction with addition supported with catalyst is specific, and the best performance and high conversion while catalyst ligand is used (Sa,Sc)-MATPHOS.

The other research [69] has been done catalytic hydrogenation of g-valerolactone (GVL) used IL solvent and [Rh(cod)$_2$][BF_4] as a catalyst. Based on Stradi and coworkers [69] have been done the highest conversions were achieved by using [Rh(cod)$_2$][BF_4] as catalyst precursor and formic acid as H_2 donor at 80 °C, with the molar ratio of HCOOH/ substrate between 5:1 and 6:1. Furthermore, Upadhyay et al.[70] have successfully synthesized of Ru/Ti-x catalyst for IL supported CO_2 hydrogenation reaction. Their result is showed that Ru/Ti-x catalytic with IL supported reactor system offered the hydrogenation reaction in a more optimized way to achieve maximum selectivity (high TON/TOF value of formic acid), even the catalyst can be used eight times. IL can support transformation of CO_2 to methane, Melo et al.[71] research has good result effect of imidazolium-based ionic liquid media and ruthenium nanoparticles as catalyst in CO_2 hydrogenation. They are used [OMIM][NTf_2], 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide, moreover getting the yield % of methane about 69% with the condition of reaction at 40 bars of H_2 pressure, adding 40 bars of CO_2 pressure, and at 150 °C [71]. The other performances of IL in membrane hydrogenation reactor are showed in Table 2.

TABLE 2. Performances of Ionic Liquid supported hydrogenation reactor

Ionic Liquid	Substrate	Catalyst	Conversion	Reference
[BMIM][BF_4]	1-hexane	Pd or Ru nanoparticles	>99%	[72]
(S,S)-DPENDS [disodium salt of sulfonated (S,S)-1,2-diphenyl-1,2-ethylenediamine]	benzalacetone	[TPPTS: P(m-C6H4SO3Na)3]-stabilized Ru	99.5%	[62]
chiral ionic liquid-supported complex	4-chloroacetophenone	ruthenium	98%	[73]
[NTf_2]/scCO_2 (EMIM: 1-ethyl-3-methyl-imidazolium; Tf: trifluoromethanesulfonyl)	enol ester 1-(trifluoromethyl)vinyl acetate	Rh-catalyzed	90–70%	[66]
tetraethylammonium 4-hydroxyvalerate ([TEA][HV]), tetrapropylammonium 4-hydroxyvalerate ([TPrA][HV]), and tetrapentylammonium 4-hydroxyvalerate ([TEA][HV])	g-valerolactone-	[Rh(cod)$_2$][BF_4]	>99%	[69]
1,3-dimethylimidazolium methylphosphite([DMIM][$MeHPO_3$])	acetylene	Pd/SiO_2	96.1%	[74]
[BMMIM][NTf_2]	Ethylene Diamine Bisborane	Pd- and Ru-Nanoparticles	72%	[75]
[DAMI][$CF_3CF_2CF_2CF_2SO_3$]	CO_2	Ru/TiO_2	70%	[70]
[omim][NTf_2], 1-octyl-3-methylimidazolium bistrifluoromethanesulfonylimide	CO_2	ruthenium nanoparticles	Yield of methane (69%)	[71]

Ionic Liquid Membrane Potential for CO_2 Byproduct Reaction

The main IL membrane nowadays is designed towards CO_2 removal [30, 76]. Regarding clean air, the increasing atmospheric concentrations of greenhouse gasses, specifically CO_2, is of particular concern [15, 77]. There is a lot of functional ILs that gives excellent and selective CO_2 permeation. This progress can be integrated into membrane reactor because reactions that utilize membrane reactor.

Reactions employed in membrane reactor usually limited by equilibrium, produces smaller and/or poisoning byproduct that can be easily removed. From those reasons, IL may be promising in equilibrium reaction that produces CO_2 product so that the reaction will move towards product. One promising reaction that fit both criteria is water gas shift reaction in ammonia production. CO is converted into CO_2 and H_2 using steam and then bulk CO_2 from reaction mixture is separated to prevent catalyst poisoning and transferred to urea production line [78]. Another possible reaction is direct DME synthesis from syngas which produces CO_2 byproduct [79].

Raeissi and Peters [80] studied the gas solubility of H_2 and CO_2 using [C_nMIM][NTf_2]. The experiment result showed that the solubility of CO_2 is strongly influenced by pressure and temperature. The ionic liquid ([NTf_2] and [BMIM][NTf_2]) has CO_2 solubility up to 60 molar percent, which is significantly higher than other studied ionic liquids. In contrast, hydrogen solubility is an order of magnitude lower than CO_2 solubility. Related to an operation condition, increased temperature will increase hydrogen solubility while reducing CO_2 solubility. Pressure increase will significantly increase CO_2 solubility while only add little additional H_2 solubility. These properties are specifically favorable for steam reforming-water gas shift (SR-WGS) reaction since it produces hydrogen and CO_2 as showed in equation 1-3.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{3}$$

SR-WGS reaction usually carried out in two-step conversion to maximize its conversion. Membrane reactor has been widely studied in this reaction to simplify the process into one-step operation [81, 82]. However, most WGS membrane reactors are using H_2 separation membranes [83-85]. SILM membrane reactor has the potential not only to increase the reaction but also to minimize CO that hardly removed from the gas mixture and usually undesirable.

CONCLUSION

Based on a review of numerous articles on SILM indicate that ILs have the potential to support the process of chemical reaction and separation in a membrane reactor. Kind of IL has the potential to support the membrane reactor is imidazolium derivative compounds which are substituted alkyl group on the atoms N such as nMIM based cation with anions framers BF_4, PF_6, NTf_2 . The length of alkyl chain in IL will take effect with its hydrophobicity characteristic in the dissolving of reactant, furthermore to improve thermal stability, chemical and physic stability of IL. Therefore, many researchers are developed modifying of IL to get the best performance in Fischer-Tropsch, dehydrogenation, and hydrogenation with a specific substrate, even for CO_2 byproduct reaction. Moreover, the catalyst is used from the specific reaction which has an important role to note with coordinated with IL in membrane reactor system to get the best performance, the specific catalyst used e.g. Ru, Pd, Co, and Rh. IL membrane reactor provided an exciting prospect for the membrane reactor technology and applied in various industries involving chemical reactions.

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