막촉매반응기를 이용한 수소생산

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Carbon-free Hydrogen Production Using Membrane Reactors

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요   약: 본 총설은 분리막기술이 적용된 수소생산에 대한 개론으로, 특히, 암모니아를 수소운반체로 이용하는 수소생산에 대한 연구결과를 중점적으로 서술하였다. 암모니아를 수소운반체로 적용한 수소생산은 추가적인 탄소생성이 없다는 점 외에 여러 측면에 있어 이점이 있다. 많은 연구들이 고순도 수소 분리 및 생산을 위한 분리막 개발을 위해 진행되고 있으며, 이들 중 팔라듐을 기본으로 한 분리막(예를 들어, 다공성 세라믹 또는 다공성 금속 지지체와 팔라듐 합금의 얇은 선택층으로 이루어진 분리막)에 대한 연구가 활발하다. 반면에, 효율적인 암모니아 분해를 위해서는 주로 루테늄 촉매가 적용되고 있으며, 루테늄과 지지체 및 촉진제로 이루어진 루테늄에 기반을 둔 촉매에 대한 연구발표가 다수 존재한다. 수소생산을 위한 분리막 반응기 형태로는 충전층, 유동층, 그리고 마이크로반응기 등이 있으며, 이들의 최적화 및 원활한 물질전달 연구는 현재진행형 이다. 또한, 높은 암모니아 분해율, 고순도 수소생산 및 높은 수소생산율을 얻기 위해 분리막과 촉매의 다양한 조합에 대한 연구 및 분리막과 촉매의 역할을 동시에 구현할 수 있는 분리막에 대한 연구가 발표되고 있다.

Abstract: This review focused carbon-free hydrogen productions from ammonia decomposition including inorganic membranes, catalysts and the presently studied reactor configurations. It also contains general information about hydrogen productions from hydrocarbons as hydrogen carriers. A Pd-based membrane (e.g. a porous ceramic or porous metallic support with a thin selective layer of Pd alloy) shows its efficiency to produce the high purity hydrogen. Ru-based catalysts consisted of Ru, support, and promoter are the efficient catalysts for ammonia decomposition. Packed bed membrane reactor (PBMR), Fluidized bed membrane reactor (FBMR), and membrane micro-reactor have been studied mainly for the optimization and the improvement of mass transfer limitation. Various types of reactors, which contain various combinations of hydrogen-selective membranes (i.e. Pd-based membranes) and catalysts (i.e. Ru-based catalysts) including catalytic membrane reactor, have been studied for carbon-free hydrogen production to achieve high ammonia conversion and high hydrogen flux and purity.

Keywords: Pd-based membranes, supported Ru catalysts, catalytic membrane reactor, carbon-free hydrogen production, ammonia decompositions

1. Introduction

Hydrogen, the highest energy content per unit of weight, is one of the candidates as an energy source for next generation. Production, separation and purification of hydrogen has been continuously kept the scientific attention[1-3].

Conventionally, hydrogen is produced by steam re-

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Table 1. Reactions to Produce Hydrogen from Methane, Methanol, and Ethanol[8]

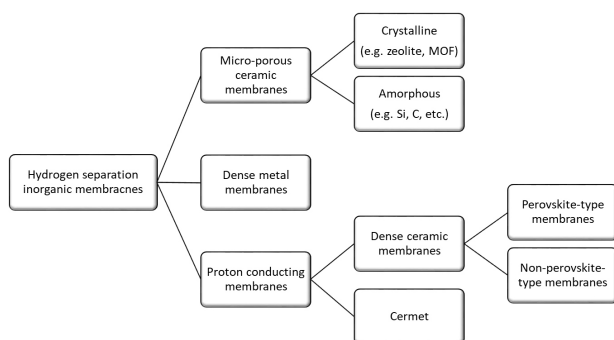| Reaction	$\triangle H_{298K}$ $(KJ \cdot mol^{-1})$
Water gas shift (WGS)	
$CO + H_2O = CO + H_2$	-41.1
Decomposition (Carbon production)	
$CH_4 = C + 2H_2$	75
Steam reforming (SR) reactions	
$CH_4 + H_2O = CO + 3H_2$	206.2
$CH_4 + 2H_2O = CO_2 + 4H_2$	164.9
$CH_3OH + H_2O = CO_2 + 3H_2$	49
$C_2H_5OH + H_2O = 2CO + 4H_2$	239.5
Partial and full oxidation reactions	
$CH_4 + 2O_2 = CO_2 + 2H_2O$	-14.4
$CH_4 + O_2 = CO_2 + 2H_2$	-71
$CH_4 + 1/2O_2 = CO_2 + 2H_2$	-35.6
$CH_3OH + 1/2O_2 = CO_2 + 2H_2$	-192.3
$C_2H_5OH + 1/2O_2 = 2CO + 3H_2$	-14.4
Autothermal reforming (ATR) reactions	339
$4CH_4 + 2H_2O + O_2 = 10H_2 + 4CO$	0
$4CH_3OH + 3H_2O + 1/2O_2 = 4CO_2 + 11H_2$	-50
$C_2H_5OH + 2H_2O + 3/2O_2 = 2CO_2 + 5H_2$	

forming reactions, partial oxidative reactions, and auto-thermal reforming reactions when various hydrocarbons such as methane, methanol, and ethanol are used as hydrogen carriers[4,5]. The main drawbacks of conventional reactors are equilibrium limited and produce a hydrogen rich gas mixture which is consequently required the hydrogen separation and purification steps[4,5]. The reactors consisted of hydrogen perm-selective membranes with catalysts provide a reduction of total reactor volume due to the elimination of the extra hydrogen purification units, a total capital cost reduction due to the milder operation conditions, and a circumvention of the thermodynamic constraint[4,6,7].

Depending on the types of hydrogen carriers, the relevant reactions for methane, methanol, and ethanol to produce hydrogen was shown in Table 1[8]. In conventional reactors, methane, methanol, and ethanol reforming require temperature above 800, 600, and 250-300°C, respectively, and those temperatures are dramatically decreased when membrane reactors, particularly Pd-based membranes in reactors, are used[8]. However, decreasing the reaction temperatures increase the potential formation of carbon deposition on the catalysts, and the ratio H_2O/C of 3-5 is also required to avoid carbon formation[9]. Using natural gas as methane source is carefully concerned due to H_2S poisoning on the surface of Pd-based membranes[10]. Methanol, which has also been known for a hydrogen storage medium, is successfully performed in membrane reactors at temperatures below 400°C[11]. Ethanol generally requires higher temperature than methanol, and ethanol reforming at moderate temperature produces the undesirable by-products, formaldehyde, methane, ethylene and carbon[12]. Membrane reactors for the reforming of hydrocarbons as hydrogen carriers demonstrate the improvement of hydrogen separation and purification, the reduction of by-product, the operation at lower temperatures, and the cost effectiveness.

Ammonia is a promising candidate as hydrogen carrier due to high energy density (12.8 GJ m^{-3}), easy of liquefaction at room temperature, and an inexpensive fuel (US$_{2012}$530/ton) that has a well-developed manufacturing-distribution infrastructure worldwide[13-15]. The use of ammonia as carbon-free hydrogen production has been repeatedly suggested. Ammonia catalytic decomposition ($NH_3 \leftrightarrow 1/2 N_2 + 3/2 H_2$) is an endothermic process, and it can apply to proton exchange membrane (PEM) fuel cell. A trace amount of ammonia after hydrogen production sharply degrades the performance of polymer electrolyte fuel cell, but alkaline fuel cells overcome the negative impact on performance until relatively high-volume fractions of ammonia (up to 9%)[16]. The safety of ammonia release at the level of immediately dangerous to life and health (IDLH) limit below 300 ppm should be aware[14].

Obviously, those works imply that the membrane technology is the key to advance the production of high purity hydrogen. This work reviews membrane technologies for hydrogen production. Specifically, it focuses for carbon-free hydrogen productions from am-

Fig. 1. Membrane types for hydrogen separation.

1. External diffusion
2. Dissociation
3. Dissolution
4. Internal diffusion
5. Association
6. Desorption
7. External diffusion

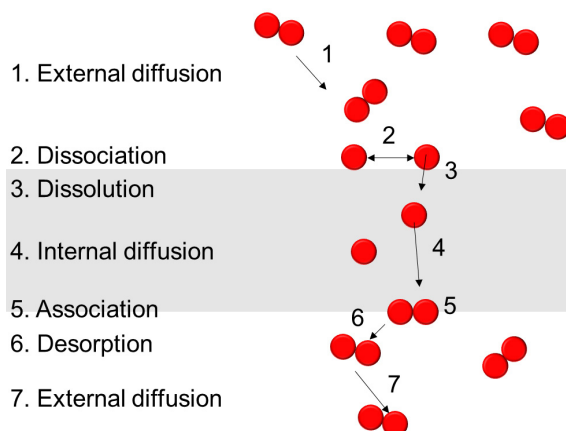Fig. 2. Solution-diffusion mechanism for hydrogen separation in metal membrane.

monia decomposition, which contains inorganic membranes for hydrogen separations, catalysts for ammonia decompositions, and the recent reactor configurations for carbon-free hydrogen productions including general reactor configurations.

2. Membranes for Hydrogen Separation

Membrane materials, specifically inorganics, for hydrogen separation can be classified as shown in Fig. 1 [4]. Dense metal membranes (mainly palladium-based) and proton conducting membranes show relatively high hydrogen selectivity, while dense metal membranes and microporous ceramic membranes show relatively high hydrogen flux.

Microporous membranes generally have a pore diameter smaller than 2 nm, and those are classified into crystalline (e.g. zeolite and metal-organic framework) and amorphous (e.g. silica, carbon, etc.)[4]. To overcome the limitations of microporous ceramic membranes (i.e. relatively low hydrogen selectivity by molecular sieving), the thin selective layers (i.e. thickness in the ranges of 1-10 μm) are deposited on porous ceramic membranes as supports[4,5].

As proton conducting membrane is concerned, a high purity H_2 stream can be recovered by dense ceramic membranes at the temperature of 900°C, and a high hydrogen flux can be obtained with high values for protonic and electronic conductivities[4]. Perovskite-type and non-perovskite-type membranes are a subcategory of dense ceramic membranes. Cermet membranes, which are a combination of a ceramic as a pure proton conductor and a metallic as a highly electron conductor, may provide the durability caused by the contact with catalyst particles in the fluidized suspension[4,8].

Dense metal membranes are commonly used for high purity hydrogen production, and it follows a solution-diffusion mechanism (Fig. 2)[5]. Palladium (Pd), which is the most well-known material used as dense metal membrane, has excellent permeability, high tolerance to hydrocarbon flows and self-catalyzing the H_2 dissociation reactions[5]. The embrittlement of pure Pd occurs below 298°C and 2 MPa of pressure[17]. Furthermore, the deposition of carbon and the irreversible sulfur poisoning occurs when hydrocarbons used as hydrogen carrier[8].

Pd alloy with various metals (i.e. aluminum, copper, indium, molybdenum, nickel, platinum, rhenium, rhodium, ruthenium, silver, titanium and tungsten) has been tested to overcome embrittlement and poisoning. Particularly, it is reported that when Pd alloy with silver, it diminishes hydrogen embrittlement[18] while when Pd alloy with copper or gold, it improves resistance to H_2S poisoning[19]. Currently, composite Pd-base membranes (i.e. porous ceramic or porous metallic supports with a thin selective layer) are developed for high hydrogen permeability, reasonable thermal stability, and proper mechanical strength. Performance of the

Table 2. Performance of Pd-based Membrane for Hydrogen Separation

Membrane material	Selective layer thickness (μm)	Operation temperature (°C)	H_2 Permeance (10^{-8} mol/m^2 s Pa)	Ideal selectivity	Ref.
ZIF-7/Al_2O_3	2	220	4.5	20.7 (H_2/N_2)	[20]
ZIF-90/Al_2O_3	20	200	21	17.5 (H_2/N_2)	[21]
SiO_2/Al_2O_3	0.02	600	70	100 (H_2/N_2)	[22]
Ni-SiO_2/Al_2O_3	0.3	500	20	400 (H_2/N_2)	[23]
Pd/TiO_2	13	648	16-64	1,000	[24]
Pd-Ag/MPSS	4	773	200	∞ (H_2/Ar)	[25]
Pd-Cu/Al_2O_3	3.5	623	42,700	7,000 (H_2/N_2)	[26]
Pd/SiO_2/PSS	6	773	270	450 (H_2/N_2)	[27]
Pd/NaAZ/PSS	199	723	110,000	608 (H_2/N_2)	[28]

MPSS: macroporous stainless steel, PSS: porous stainless steel.

selected membranes for hydrogen separation is shown in Table 2.

A variety of techniques (i.e. electroless plating (ELP), physical vapor deposition (PVD), chemical vapor deposition (CVD), pyrolysis, micro-emulsion technique, electroplating, solvated metal atom deposition and high velocity oxy-fuel spraying (HVOF)) are available for Pd deposition on porous ceramic or porous metallic supports[5]. One of the main methods, ELP, a heterogeneous oxidation-reduction reaction, has advantages (i.e. simple equipment, the absence of electrical source, and relatively low temperature) and disadvantages (i.e. longer preparation time, generation of hazardous liquid wastes). ELP consists of 1) seeding Pd fine particles on the sensitizing and activating support surface and 2) Pd layer plating on top of the activated surface[29]. The deposition of intermediate layers can smooth the initial rough surface of support[29]. Moreover, the pH of solution and temperature are important parameters for deposition[5].

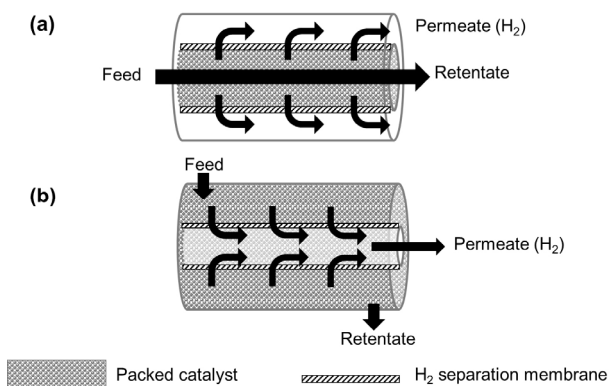## 3. Catalysts for Ammonia Decomposition

Catalysts for ammonia decomposition are divided into active component, support, and promoter. Various metals (i.e. Fe, Ni, Pt, Ru, Ir, Pd, Rh, etc) have been tested for active component[30]. Of the pure metals, it has been known that ruthenium is the most active

component, even though the precursor of the active component can affect the catalytic performance[13,31]. There can be a maximum Ru loading for ammonia conversion (e.g. a maximum Ru loading of 15 wt% reported by Yin et al.)[30]. Moreover, when carbon nanotube (CNT) and SiO_2 are used as support, Ru also show the most active for ammonia decomposition [30,32]. With respect to Fe catalysts, it is suggested that the active component is the unstable FeN_x[33]. If the cost is concerned, Ni can be an attractive alternative[30].

Supports are commonly employed to enhance the dispersion and surface area of the active component. Unusual but expectedly, the catalytic performance of Ru catalyst is support-dependent[30]. The support for excellent catalytic performance of Ru catalyst should possess basicity, conductivity, the high purity, high thermal stability, and the high dispersion of Ru, and specifically, the higher degree of graphitization as carbon materials.

Known efficient promoters for supported Ru catalysts are alkali, alkaline earth or rare earth metal ions [30]. The promotional effect is dependent on the adopted active component. It is reported that the higher the electronegativity of the promoter, the lower is the ammonia conversion. It has been found that KOH is effective for promoting Ru and Ni/ZrO_2[30].

Ru-based catalysts consisted of Ru, support, and pro-

Fig. 3. PBMR with catalysts packed (a) in the tube and (b) in the shell side.

Fig. 4. Catalysts in the tube side PBMR with (a) counter-current mode and (b) co-current mode.
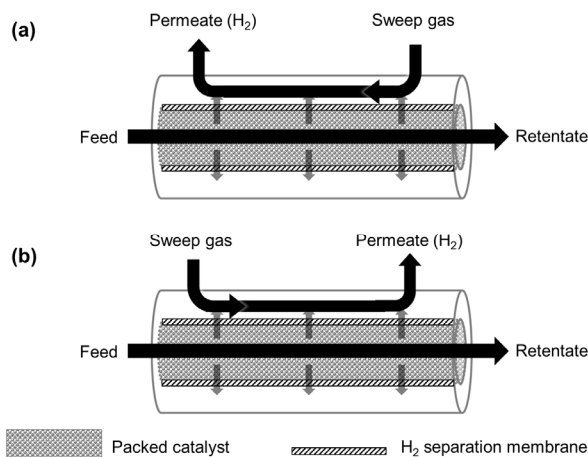
moter are the efficient catalysts for ammonia decomposition to generate carbon-free hydrogen. However, alternatives including Fe-based and Ni-based catalysts are continuously searched. The activities of Fe-based catalysts are much lower than those of Ru-based catalysts and Fe-based catalysts cannot supply the high purity of hydrogen until now[13]. Ni-based catalyst does appear to be a promising catalyst due to its cost advantage over Ru and relatively high activity for ammonia decomposition.

4. Reactor Configurations

4.1. Packed bed membrane reactors (PBMR)

PBMR is the simple and well-established configuration. The catalyst in PBMR can be located either in membrane tube or in the shell side. The generalized configuration of PBMR is shown in Fig. 3.

For less membrane surface area required for hydrogen separation, a sweep gas can be used in the permeation side of membrane to maintain the permeation hydrogen partial pressure as low as possible[4,5]. The sweep gases can be either reactive (e.g. air or oxygen) or inert (e.g. nitrogen). A sweep gas can be used in either co-current or counter-current mode (Fig. 4). Gallucci et al. mathematically simulate ethanol conversion and hydrogen recovery in different sweep gas modes, and they show that high pressure and high temperature lead higher ethanol conversion in the
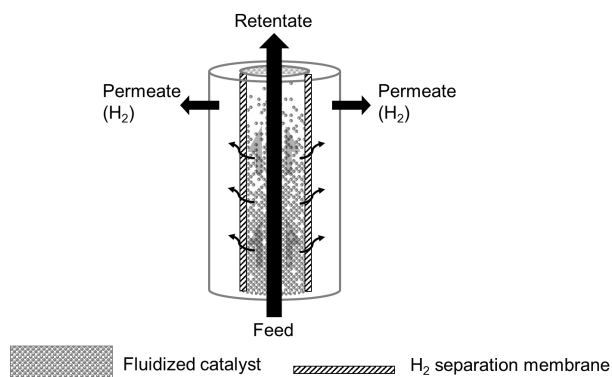
counter-current mode while the higher ethanol conversion is resulted at low pressure and low temperature in co-current mode[34]. Moreover, the differences in terms of ethanol conversion and hydrogen recovery between co-current and counter-current is negligible at a very large sweep gas flow rate compared to feedstock flow rate[34].

Decreasing the membrane thickness increases membrane flux, and the increasing membrane flux reduces membrane area required for separation[4,5]. However, the limitations of hydrogen transport through membrane is shifted to the limitation of hydrogen transport between the bulk of catalytic bed and the membrane wall (bed-to-wall mass transfer limitations, which is also called concentration polarization) when lower selective layer thickness is applied.

The pressure drop and temperature control are other limiting factors in association with PBMR. To decrease the pressure drop, the catalyst particles with large size need to be used, but this reflects in the intra-particle mass transfer, which results in the increasing membrane area for certain conversion and recovery[4,5]. A decrease of temperature on the membrane surface decreases the hydrogen flux through the membrane while an increase of temperature leads to membrane surface cracking, which subsequently decreases the perm-selectivity of membrane.
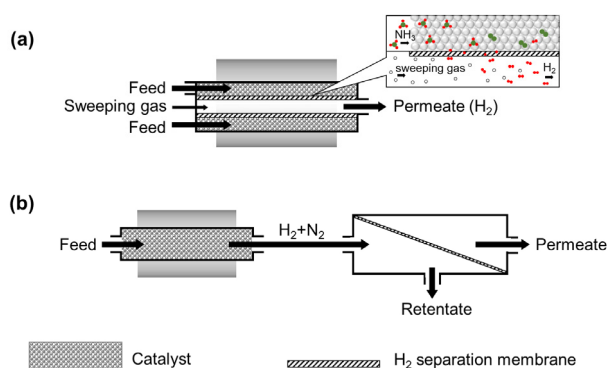
Fig. 5. Fluidized bed membrane reactor.

Fig. 6. The conceptual sketches of (a) membrane reactor for NH$_3$ decomposition and (b) NH$_3$ cracker integrated with a followed membrane separator.

To increase the membrane area per volume of reactor, multi-tube membrane housing and hollow fiber configuration are investigated[4]. In multi-tube membrane housing, the catalyst is loaded in the shell side of reactor while the membrane tubes are connected to a collector for the pure hydrogen[4,35].

4.2. Fluidized bed membrane reactors (FBMR)

FBMR, which is a bundle of hydrogen selective membrane immersed in a catalytic bed operated in the bubbling or turbulent regime, is shown in Fig. 5. The main advantages of using FBMR are 1) the reduction of bed-to-wall mass transfer limitation and 2) the operation at isothermal condition. Negligible pressure drop, flexible arrangement of membrane package, and improved fluidization behavior due to compartmentalization and reducing average bubble size are also beneficial[4,5]. On the other hand, the known disadvantages of FBMR are the erosion of inside reactor and catalyst attrition due to vigorous particle motion[5].

Two different membrane reactor configurations, which one is packed bed and the other is fluidized bed operated in the bubbling regime, are theoretically compared in case of hydrogen production via methane steam reforming[36]. It reports that both configurations suffer from mass transfer limitations, which FBMR is limited by mass transfer between bubble and emulsion, and PBMR is limited by mass transfer between catalytic bed and membrane wall (concentration polarization). However, mass transfer limitation for FBMR

can be resolved by breaking up of bubbles while it for PBMR cannot be easily avoided. Moreover, PBMR requires more membrane area with respect to FBMR.

4.3. Membrane micro-reactors

Membrane micro-reactor can improve mass and heat transfer using the micro-channels, remove mass transfer limitation (i.e. concentration polarization), and integrate different process steps in a small-scale devise[4]. Microchannel membrane reactor consists of a stainless-steel feed channel housing with six parallel channels and a ~1.4 μm thick self-supported Pd/Ag membrane was reported[37]. It reports that a permeance of hydrogen at 573 K is 1.7×10^{-2} mol m^{-2} s^{-1} Pa$^{-0.5}$, and the membrane endures differential pressure up to 470 kPa. Even though membrane micro-reactors ignore external mass transfer limitations, more research are required to optimization[4].

4.4. Membrane technologies for carbon-free hydrogen production

Interestingly, two systems, which one is membrane reactor for NH$_3$ decomposition (Fig. 6(a)) and the other is NH$_3$ cracker integrated with a followed membrane separator (Fig. 6(b)), are investigated[38]. It is noted that Fig. 6 is not the exact reactor configuration, but the conceptual sketches. In both systems, the ultra-thin Pd membrane, which is supported by porous ceramic tube modified with aluminum hydroxide gel, is used as the
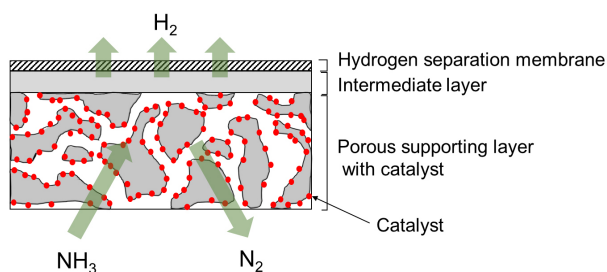
Fig. 7. The conceptual drawing of the catalytic membrane.

hydrogen permeation, and Ni/La-Al$_2$O$_3$ catalyst is used as ammonia decomposition[38]. Performance of membrane reactor for NH$_3$ decomposition shows high NH$_3$ conversion, but an unsatisfactory permeation due to low utilization of Pd membrane[38]. Comparatively, performance of NH$_3$ cracker integrated with a followed membrane separator shows high productivity of pure H$_2$[38].

A multifunctional membrane reactor with Pd membrane and Ru-carbon catalyst is evaluated[39]. The porous stainless steel is treated to generate a homogeneous oxide layer as an intermediate barrier layer and Pd is deposited on them[39]. This thin Pd layer on porous stainless steel is used as hydrogen permeation[39]. A carbon supported Ru is prepared by incipient wetness impregnation and NaOH is used as promotor. This Na/Ru-carbon catalyst is used for ammonia decomposition. The importance of porous stainless steel instead of non-porous stainless steel as support is addressed[39].

A bimodal catalytic membrane reactor (BCMR) consisting of Ru/γ-Al$_2$O$_3$/α-Al$_2$O$_3$ bimodal catalytic support and a hydrogen-selective silica membrane is proposed[40]. The conceptual drawing of the reactive membrane is shown in Fig. 7. TEM and SEM images in the study are clearly showed a single unit as a combination of catalytic support and a hydrogen-selective membrane[40]. The results show that H$_2$ permeance at 773 K is 6.2×10^{-7} mol m^{-2} s^{-1} Pa$^{-0.5}$, and ammonia conversion at 723 K after H$_2$ extraction is 95%[40].

Ru catalyst (i.e. the commercial Hypermec 10010 Ru catalyst) with Pd-coated membrane reactor equipped a three-zone heating control without sweep gas is also studied[41]. It performs the higher ammonia conversion (i.e. over 99.5%) and the hydrogen yield (i.e. around 87%) without heating the ammonia tank. Recently, it is reported that the higher ammonia conversion (i.e. 100%) is achieved by multi-stage fixed bed membrane reactors and there is a linear relationship between the number of beds and the feed temperature[42]. Moreover, it also shows that ammonia conversion in a single fixed bed membrane reactor is superior to that in a single fixed bed reactor.

5. Conclusions

Membrane technologies are one of key for hydrogen production. A Pd-based membrane, which is porous ceramic or porous metallic support with a thin selective layer of Pd alloy, shows high hydrogen permeability, reasonable thermal stability, and proper mechanical strength. For carbon-free hydrogen production from ammonia decomposition, Ru-based catalysts consisted of Ru, support, and promoter are the efficient catalysts, even though alternatives including Fe-based and Ni-based catalysts are continuously searched. PBMR is commonly operated with a sweep gas. FBMR has the advantages of the reduction of mass transfer limitation and the operation at isothermal condition, but it has the disadvantages of the erosion of inside reactor and the attrition of catalyst. In addition, membrane micro-reactor has been studied to improve mass and heat transfer using the micro-channels for reduction of mass transfer limitation (i.e. concentration polarization). Various types of reactors and combinations of membrane/catalyst (e.g. the ultra-thin Pd membrane supported by porous ceramic tube with Ni/La-Al$_2$O$_3$ catalyst, Pd membrane supported by porous stainless steel with Na/Ru-carbon catalyst, a hydrogen-selective silica membrane on top of Ru/γ-Al$_2$O$_3$/α-Al$_2$O$_3$ bimodal catalytic support, etc.) have been studied to reach higher ammonia conversion and the higher hydrogen flux and purity.

Acknowledgements

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