

Advances of zeolite based membrane for hydrogen production via water gas shift reaction

I G B N Makertihartha*, M Zunita, Z Rizki, and P T Dharmawijaya

Chemical Engineering Department, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, West Java, 40132, Indonesia

makertia@che.itb.ac.id

Abstract. Hydrogen is considered as a promising energy vector which can be obtained from various renewable sources. However, an efficient hydrogen production technology is still challenging. One technology to produce hydrogen with very high capacity with low cost is through water gas shift (WGS) reaction. Water gas shift reaction is an equilibrium reaction that produces hydrogen from syngas mixture by the introduction of steam. Conventional WGS reaction employs two or more reactors in series with inter-cooling to maximize conversion for a given volume of catalyst. Membrane reactor as new technology can cope several drawbacks of conventional reactor by removing reaction product and the reaction will favour towards product formation. Zeolite has properties namely high temperature, chemical resistant, and low price makes it suitable for membrane reactor applications. Moreover, it has been employed for years as hydrogen selective layer. This review paper is focusing on the development of membrane reactor for efficient water gas shift reaction to produce high purity hydrogen and carbon dioxide. Development of membrane reactor is discussed further related to its modification towards efficient reaction and separation from WGS reaction mixture. Moreover, zeolite framework suitable for WGS membrane reactor will be discussed more deeply.

1. Introduction

Hydrogen is the most abundant element on the planet. However, it can only be found naturally bonded with other elements and can be extracted from water, biomass, or hydrocarbons. Hydrogen combustion only produces water that it often referred as ‘clean energy’. Hydrogen is already produced around the globe at the annual capacity of 5 billion cubic metres. There are many uses of hydrogen mainly for reactant of various syntheses such as ammonia production for fertiliser (~50%), oil refining (~37%), methanol production (8%), and in the chemical and metallurgical industries (4%) [1]. Over the past few years, many countries have invested in hydrogen mainly for energy use.

Water gas shift (WGS) reaction is an important process for production of H_2 from syngas [2, 3]. WGS is an endothermic and equilibrium limited reaction. To achieve good reaction performance, namely high reaction rate and CO conversion, most of today’s WGS reaction employs two-step operation consists of high temperature shift (HT-WGS) and low-temperature shift (LT-WGS) [4]. The first step (HT-WGS) is operated using iron-based catalyst at high temperature range of about 350-400 °C to boost reaction rate but resulted in low equilibrium conversion. The second step (LT-WGS) generally operated using copper-zinc oxide catalyst at about 200-250 °C [5-7] to further boost the equilibrium conversion [8, 9]. This two-step conversion process is rather complex, high catalyst consumption and high steam recycling [10].



Due to the complexity of two-step conversion, membrane reactors that integrate hydrogen-selective membrane separation into reaction vessel have been investigated. The result shows that one-step operation shows great potential for CO deep conversion [11, 12]. Most WGS membrane reactors are using H₂ separation membranes [13-15]. The lack of H₂ due to removal results in high CO conversion at a given temperature, hence retentate stream consist mainly of CO₂ can be obtained. The process will be much simplified from two-step reaction process into a single stage shift reactor that produces high purity hydrogen without or with minimum further separation/purification step. This will also reduce the duty of the scrubbing system and high pressure CO₂ can be obtained which will minimize the cost of CO₂ capture [16]. Nevertheless, stability is one key issue of WGS membrane reactors. WGS reaction is conducted at relatively high temperature and pressure. Several harsh gasses such as steam and H₂S are also included. Therefore, WGS membrane reactors require high thermal, mechanical and chemical stability membrane. Pt and Pt alloys are the main selection of hydrogen selective membrane material due to their high performance. However, several disadvantages of using Pd-based membrane such as high cost and poor resistant to H₂S and CO make some researchers seek microporous inorganic membranes for hydrogen selective layer [10]. Pd-based membranes also have moderate durability and high brittleness that limit their practical applications[17]. SiO₂ membranes have been used for H₂ and other gas components separation and shows excellent performance [18].

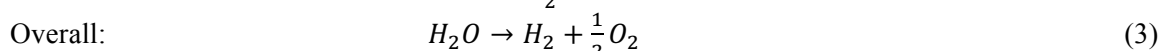
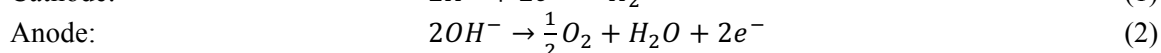
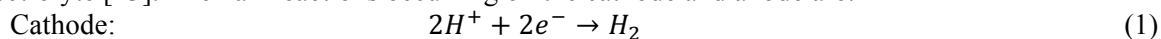
Membrane reactor for water gas shift reaction is one interesting technique to boost the production of hydrogen efficiently. However, the selection of selective hydrogen layer is still the main challenge to commercialize it. The potential of zeolite based membrane for gas separation has been demonstrated well by various authors [19-21]. Moreover, the high price of Palladium based membrane for hydrogen selective layer make zeolite more interesting choice. This paper will discuss about zeolite membrane reactor for water gas shift reaction. The progress, challenges, and effort given to commercialize said technology will be discussed.

2. General hydrogen production

Since hydrogen is not available in gas state, hydrogen has to be extracted from various compounds. The common compounds used to extract hydrogen are water and hydrocarbons. Hydrogen extraction from water uses electrolysis technology while water gas shift reaction is employed to extract hydrogen from hydrocarbons. While electrolysis offer direct high purity hydrogen at various scale, water gas shift route is more interesting route nowadays due to its lower cost.

2.1. Electrolysis of water

Water electrolysis unit at least consists of an anode, a cathode, power supply and an electrolyte [22]. Current is then applied to maintain the electricity balance and electrons flow to the cathode where it consumed by hydrogen ions (protons) to form hydrogen. To maintain electrical charge and valence, hydroxide ions (anions) transfer via electrolyte to the anode where it gives away electrons. Electrolytes may vary from traditional ion solution, polymer electrolyte membrane, and molten salt electrolyte [23]. The half reactions occurring on the cathode and anode are:



As can be seen, pure hydrogen and oxygen gas are formed in different electrodes so it needs no further separation process. The practical limitation of electrolysis of water to produce hydrogen is energy price in terms of electricity. Electrolysis of water is now mainly built to store energy generated from solar, wind, wave, etc. in form of hydrogen for later use.

2.2. Water gas shift reaction

Hydrogen is widely produced via steam reforming and water gas shift reaction from hydrocarbons. Natural gas (mainly consist CH₄) is the major source of hydrocarbon for steam reforming and WGS

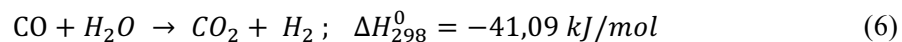
reaction due to its cheaper price and high H/C ratio compared with other hydrocarbons. High temperature is needed to break hydrocarbons into syngas (CO, H₂) via reaction (4). Carbon monoxide is further reacted with steam shifted into carbon dioxide and more hydrogen via reaction (5).



To produce high purity hydrogen from said reactions, further separation process should be performed [1]. To the date, amine absorption is the most competitive technology to purify hydrogen via CO₂ removal due to its maturity. However, membrane systems have the potential to be more economical in terms of both relative capital investment and unit recovery cost [24]. The detailed aspects of water gas shift reaction will be discussed in the following section.

3. Water gas shift for hydrogen production

The Water Gas Shift (WGS) reaction is one alternative pathway to produce hydrogen that is commonly chosen. Traditionally, WGS reaction is performed to produce hydrogen for ammonia production from synthesis gas [25]. WGS is a reaction that uses carbon monoxide gained from combustion of hydrocarbons via steam addition. The equation of WGS is shown in equation (6). The WGS reaction is an exothermic catalytic reaction which conversion is limited by the equilibrium condition [26].



The conventional WGS reaction has many drawbacks that need to be improved. In order to achieve both fast catalytic reaction and considerable conversion, the traditional WGS reaction was performed in two steps, using high temperature (300-400°C) prior to low temperature reaction (200-300°C) [27]. Furthermore, the products need to process further to separate the hydrogen from CO₂ and excess reactants.

Answering those problems, a membrane reactor is applied in WGS reaction. The idea of membrane reactor is to remove one of the products (hydrogen) after the reaction occurred. By then, the equilibrium will be shifted which gives better performance in term of conversion and product recovery [28-30]. Furthermore, a membrane reactor in WGS reaction eliminates the second reactor and further separation related to the product purification. The concept of membrane reactors have been applied to other critical reaction processes besides the WGS reaction [31, 32].

Table 1. Performance of Various WGS Membrane Reactor

Research Type *)	Membrane Material	Catalyst	Configuration	Max CO Conversion (%)	Max H ₂ Recovery (%)	Reference
E	Pd-Ag	Cu-Zn	Tubular	almost 100%	70%	[9]
E	Pd-based	Fe-Cr	Tubular**)	95	91,5	[27]
E	Pd-Ag	Pt-CeO ₂	Hollow Fiber	>60	ND	[33]
E+S	MFI Zeolite	Fe-Cr-Cu	Tubular	>95	>90	[16]
E+S	Pd-Ag	ND	Tubular	95,3	43	[34]
S	ND	ND	Shell and tube **)	> 95	ND	[35]
S	ND	ND	Tubular	>99	86,8	[36]

*) E = Experiment, S = Simulation

**) catalyst outside

The researches in membrane reactor have already been studied a lot via both experiments and simulations and several configurations have been proposed [29]. However, the tubular configuration is the most common with the process stream inside a tube [37, 16] while the reversal configuration has also been already performed [27]. The performance of several WGS membrane reactors is summarized in Table 1.

4. Zeolite membrane and modification

Among the materials that used in membrane reactor, zeolite becomes one favourable option due to its unique properties. Zeolite is known to be stable under harsh condition (e.g. chemical, high temperature and selective separation) [38, 39]. In addition, it also has unique properties that makes zeolite suitable in wide range of applications including membrane separation, integrated membrane reactor, electrode, chemical sensor and insulator[40].

The properties of zeolite membrane depend on the preparation method. Furthermore, the natural zeolites are not suitable for hydrogen separation [38]. Therefore, modifications are needed to customize and improve the properties of zeolite into specific required properties. The modifications can be a formation of composite materials or adjustment in synthesis technique. Feng [39] mentioned that the most attractive type of zeolite composites are the mixed membrane matrix (MMM) and metal organic frameworks (MOFs).

The most common method to prepare dense zeolite membrane is hydrothermal synthesis. Hydrothermal synthesis can be done with seeding (namely secondary growth method) and the heating procedure can be performed using microwave (microwave hearing). Zeolite membrane requires porous support to be attached to, which can be in the form of tubular, hollow fibre or any other membrane module configuration. The methods during synthesis process will determine how dense the zeolite membrane be thus affecting the separation performance [39].

Zeolite membrane and its derivatives have been widely studied in gas separation, especially for hydrogen. Several applications of zeolite membrane in hydrogen separation are summarized in Table 2.

Table 2. Zeolite Membrane for Hydrogen Separation

Type of Zeolite membrane	Compounds separated	Separation notes	Ref
Pd/Silicate-1 Zeolite	H ₂ /N ₂	High Selectivity H ₂ /N ₂	[41]
MFI Zeolite	H ₂ /CO ₂ +CO +H ₂ O	Very high selectivity for H ₂ O and moderate for CO and CO ₂	[42]
MFI-ZSM5	H ₂ /He	Separation factor below 2	[20]
Natural Zeolite	H ₂ /C1+C ₂ Hydrocarbon	High selectivity at ambient temperature and moderate to low at 500°C	[43]
Acrylate-zeolite MMM	H ₂ /CO ₂	more than 2 times selectivity increase	[44]
Hydroxy Sodalite Zeolite	H ₂ /CH ₄	17% selectivity increase	[45]

5. Application and performance of zeolite based membrane in hydrogen production via WGS reaction

WGS reaction is important reaction for CO conversion and H₂ production from fossil fuel and biomass via gasification and steam reforming [46]. Silica membrane has been integrated to WGS reactor to produce high purity H₂ [47-50]. Generally, WGS reaction membrane reactor is fabricated based on properties of capability to separate H₂ [14, 51, 52]. Therefore, WGS reaction reactor will be to achieve high CO conversion and high hydrogen purity using a single reactor. Thus, membrane used in WGS reaction used should have high H₂ permselectivity, so that it can improve H₂ yield and lower operation costs [42]. Moreover, the membrane should also has good thermal stability because the WGS reaction can be carried out in two condition, which are HT-WGS reaction (high temperature WGS reaction at 350-450°C) and LT-WGS reaction (low temperature WGS reaction at 190-250°C)[53, 54]. Zeolite is suitable for WGS reaction reactor is zeolite because it is hydrothermally stable and intrinsically resistant to sulphur compounds due to their crystalline structure [55, 46, 56, 57]. Scheme of zeolite-based membrane reactor for H₂ production is depicted in figure 1.

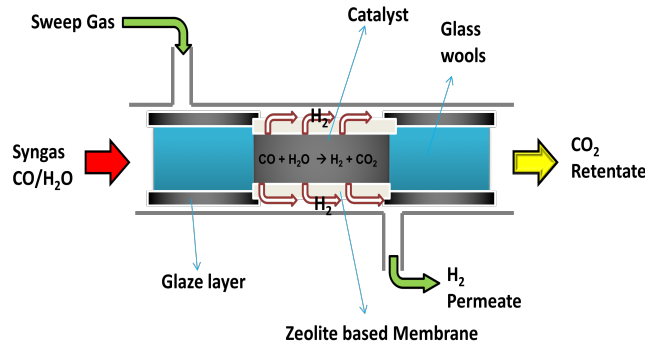


Figure 1. Scheme of zeolite-based membrane reactor for H₂ production

Table 3. Performance of Zeolite based Membrane in Production/Separation H₂ via WGS reaction and Another Reactions

Zeolite Membrane Type	Modification	Catalyst	H ₂ /CO ₂ Separation Factor	CO Conversion (%)	H ₂ Recovery (%)	Ref.
MFI	Synthesized on a porous α -alumina disc	Fe/Ce	31	>99.5	73.2	[58]
ZSM-5	Silicate bilayer	Fe/Cr/Cu	>16	>95	. 90	[16]
ZSM-5/silicate bilayer	Porous α -alumina support coated with an YSZ	N/A	25.3	N/A	>99	[59]
MFI	α -alumina hollow fiber support	Fe/Cr/Al	52	>95	>98.2	[60]
MFI	depositing molecular silica	Ce/Fe	68.3	81.7	40	[61]
ZSM-5 silicate layer	Porous α -alumina support coated with an intermediate YSZ barrier layer	Fe/Ce	23	>80	>20	[42]
MFI	modified by on-stream catalytic cracking deposition (CCD) using methyl diethoxysilane (MDES)	CuO/Zn O/Al ₂ O ₃	42.6	>95.4	18	[10]
A-type	N/A	Pt, Pd, Au	N/A	>99	N/A	[62]
MFI	modified by the on-stream CCD process using MDES	Fe/Ce	45	>99	>60	[46]
MFI	Various high Si/Al	N/A	31	N/A	N/A	[63]

In recent decades, many researchers have developed and used zeolite membrane reactor to improve performance of reactor for H₂ production. Kim et al. [46] have modified MFI zeolite membrane with nanocrystalline Fe/Ce for HT-WGS reaction. The result showed hydrogen permeance of $0.9 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ with selectivity of ~31 and 25 for H₂/CO₂ and H₂/CO selectivity, respectively at above 500°C temperature. Several simulation or modeling experiments of WGS reaction has been studied to know the performance of WGS reactor. Ghasemzadeh et al. [64] studied the modeling of inorganic membrane reactor performance to WGS reaction. The results showed hydrogen recovery and CO

conversion were improved in silica and Pd-Ag membrane by increasing the reaction pressure. Dong et al. [16] modelled the zeolite membrane reactor modified by silica layer to WGS reaction using ZSM-5/silicalite bilayer. The membrane can improve CO conversion and H₂ recovery from 89.8% and 28.5% to > 95% and > 90%, respectively. Tang and coworkers [61] have also modified MFI zeolite membrane by depositing silica and cerium-doped ferrite as catalyst, their research result showed H₂/CO₂ permselectivity at 68.3 with H₂ permeance about 2.94×10^{-7} mol/m²sPa at operating temperature above 550°C. Moreover, the CO conversion is 81.7% which was significantly higher than the CO obtained in the traditional packed-bed reactor i.e. 62.5%. Performance of various zeolite based membrane reactors in production/separation H₂ from WGS reaction and another reaction is shown comprehensively in Table. 3.

6. Optimization of zeolite based membrane in hydrogen production via WGS reaction

The performance of zeolite based membrane should be optimized so that the H₂ production via WGS reaction will increase significantly. Moreover, the product should have high purity and the reaction carried away in milder condition than traditional WGS reaction reactor [58, 65, 34]. At high temperature, transport of small molecules is governed by gaseous diffusion leads to low H₂ selectivity, while the other gases will permeate simultaneously [66-68, 63, 69]. Therefore, many researchers developed studies about the modification of zeolite membrane pores. Accordingly, the pore size of MFI zeolite membranes are reduced by multiform modification such as catalytic cracking of a methyl diethoxysilane (MDES) precursor to deposit mono silica inside the zeolitic channels [70, 59, 10]. By reduction of zeolite membrane pores size, it is expected that the H₂ selectivity will increase [20, 47, 55, 71, 65, 62, 50].

To produce H₂ with high yield, catalyst plays an important role in WGS reaction [11, 72, 73, 70, 2]. Zeolite membrane provides support for catalytically active nano-sized particles so that the catalytic phase may contact reactants directly and reduce by-passing, short contact time, and as centre of reaction is helpful since the temperature of reaction increase can lead to promotion of reverse WGS reaction [74-76]. Hasegawa et al. [73] modified Y-type zeolite membranes by Pt catalyst. Pt catalyst was used to improve the CO conversion and selectivity by dispersing it in the zeolite membrane (ZSM-5) [77, 20, 55, 16, 78, 79]. To further optimize the performance of zeolite membranes, composite membrane was prepared by coating an Rh-loaded C-Al₂O₃ membrane with a defect-free SiO₂ layer hence SiO₂/Rh/C-Al₂O₃ membrane can improve the CO oxidation and the H₂ production will increase rapidly[80, 81].

7. Conclusion

Based on several literatures reviewed, high hydrogen permselectivity material can improve hydrogen yield in WGS reaction thus lower operation cost. One promising material for said purpose is zeolite based membrane. Some profitable properties in zeolite membrane are stability under harsh condition (e.g. harsh chemical, high temperature). Pore size of zeolite membrane needs to be reduced by surface modification with coating materials such as silicate layer, YSZ (Yttria stabilized zirconia), methyl diethoxysilane (MDES), and Si/Al mixture.

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