Tubular dual-layer MFI zeolite membrane reactor for hydrogen production via the WGS reaction: Experimental and modeling studies

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Abstract

Water-gas shift (WGS) reaction is an important intermediate step in converting fossil fuels to hydrogen (H_2) for chemical production or power generation. Catalytic membrane reactor with a H_2 perm-selective membrane can improve WGS reaction conversion and separate H_2 from carbon dioxide (CO_2) simultaneously. In this work, experimental work and modeling analysis were performed on WGS in a tubular ZSM-5/silicalite bilayer membrane composed of a $3\mu m$ ZSM-5 layer, a $8\mu m$ silicalite base layer and a $2\mu m$ YSZ barrier layer supported on α -alumina substrate. The experimental and modeling studies demonstrated that temperature, H_2O/CO ratio, gas hourly space velocity (GHSV) and feed pressure are key factors that determine the WGS performance in the tubular zeolite membrane reactor. At $500\text{ }^\circ C$ and under 5 atm with the H_2O/CO ratio of 3.0 and GHSV of 72000 h^{-1} , the CO conversion and H_2 recovery reached 89.8% and 28.5%, respectively. Appropriate temperature, pressure, H_2O/CO ratio and GHSV are crucial to obtain high reaction performance. Modeling analysis coupled with experimental data identifies the optimum operation conditions ($550\text{ }^\circ C$, feed pressure of 20 atm, H_2O/CO ratio of 2.0, GHSV of 60000 h^{-1}) under which one can achieve both high CO conversion ($>95\%$) and H_2 recovery ($>90\%$) for WGS in this zeolite membrane reactor.

Keywords: Zeolite membranes; Tubular membranes; Water gas shift; Hydrogen separation; Modeling.

1. Introduction

Water–gas shift (WGS) reaction is a key step in many chemical processes for H₂ production from fossil and biofuels, which allows further conversion of the intermediately formed CO with H₂O to H₂ and CO₂[1]. WGS is a moderately exothermic, reversible and thermodynamic equilibrium limited reaction, especially at high temperature. Commercial WGS is carried out in multiple stage reactors operated at different temperatures. For example, for a two-reactor process, the high-temperature shift reactor is operated at 350-450 °C with an iron-based catalyst, while the low-temperature shift reactor is operated at 190-250 °C using a copper-zinc oxide catalyst [2]. Removing one of the products (i.e. H₂ or CO₂) from the WGS reaction zone can break the equilibrium limitation and significantly enhance the CO conversion. Therefore, numerous studies are focused on catalytic membrane reactors for WGS reaction accompanied by the simultaneous separation of H₂ or CO₂ [3-8].

Majority of the WGS membrane reactors are fabricated based on the H₂ separation membranes [3-5]. The H₂ removal from the reactor facilitates high CO conversion at a given temperature, thus a non-permeate stream comprising mainly CO₂ can be obtained. This arrangement would represent considerable simplification of the process: using a single stage shift reactor to produce high purity H₂ without or with only minimum additional separation/purification efforts. This will reduce the duty of the scrubbing system and deliver CO₂ at high pressure which minimizes the cost of CO₂ capture. However, stability is one of the key issues of WGS membrane reactors. WGS reaction is usually operated at relatively high temperature and pressure. Steam and some corrosive gases are included, such as H₂S. Therefore, high thermal, mechanical and chemical stability of the membranes are required for the WGS membrane reactors. To date, several types of inorganic membranes, such as Pd and Pd-based alloy membranes [9-13], silica membranes [14-16], and zeolite membranes [17-21], have been studied as WGS membrane reactors for H₂ production.

Pd and Pd-based alloy membranes exhibit high H₂ permeability and excellent selectivity. Lee et al.[10] developed a pilot-scale WGS reactor (1 Nm³·h⁻¹ feed gas) using Pd-Cu membranes. The CO₂ concentration of retentate flow reached 80 vol.% and the H₂ concentration of permeate flow was over 99 vol.%. Catalano et al. [11] studied the scaling up of Pd-based WGS membrane reactor with 0.02 m² of effective membrane area. A maximum CO conversion of 98.1% was achieved, with a H₂ recovery of 81.5% and H₂ purity of 99.97% at 440 °C and 20 bar of absolute pressure in the retentate side. The disadvantages of Pd-based membranes lie in their moderate durability and high brittleness which limit their practical applications [22,23].

Amorphous microporous silica membranes synthesized by sol-gel or chemical vapor deposition technologies show good H₂ permeance and selectivity over other gases. Brunetti et al.[14] studied the WGS reaction in a porous stainless steel supported silica membrane reactor. A CO conversion of 95% and H₂/CO₂ selectivity of 40 were achieved at 280 °C and 4 bar. However, the microporous silica membranes are unstable under hydrothermal environment. When exposed to humid gas stream at elevated temperatures, the continuous hydrolysis and condensation of the silica network results in the widening and eventual collapse of the pore structure, and drastically decrease of H₂ separation performance [24,25]. In attempt to address this problem, recent efforts were focused on the development of metal doped silica membranes, such as Ni-, Co- and Nb-doped membranes [15,16,26-28]. Although the doped membranes exhibited an improved hydrothermal stability (up to 300 h) [28], they were still not suitable for long-term industrial applications.

Recent research on crystalline microporous MFI-type zeolite membranes opened up a new direction in developing microporous membranes for high temperature H₂ separation from WGS reaction [17-21]. MFI-type zeolite membranes exhibit good thermal and chemical stability. However, the pore size (around 0.55 nm) is relatively large for selective separation of H₂, resulting in high permeance but low selectivity [29-32]. To reduce the pore size of MFI-type

zeolite, a silane modification strategy was developed by Masuda et al.[33] The precursor molecules of silane were introduced into the zeolitic pores and chemisorbed on the active sites (acid sites and metal cations). After a catalytic cracking process, the mono SiO₂ unit was left on the active sites to reduce the zeolitic pore size. This modification technique has been studied to adjust the effective diameter of mass transport channels in zeolite membranes and to reduce the intercrystalline defects of membranes [30-32,34-37]. A recent improvement in this method was reported by Dong and Lin and their co-workers [32,36] on controlled modification of zeolitic pores of a zeolite membrane to improve hydrogen selectivity with minimum reduction in H₂ permeance.

MFI-type zeolite membranes with improved H₂/CO₂ selectivity were also used for WGS membrane reactors. Tang et al. [17] fabricated a modified MFI zeolite tubular membrane reactor for WGS. At 550 °C with a WHSV of 60,000 h⁻¹ and a H₂O/CO ratio of 1.0, CO conversion of 81.7% was achieved, which was significantly higher than that obtained in the traditional packed-bed reactor. The study examined the effects of reaction conditions such as temperature and space velocity on WGS reaction in the membrane reactor. However, the effect of the pressure, a critical parameter of great importance for practical application, was not studied in this work. Subsequently the effect of pressure on the WGS reaction performance in the zeolite membrane reactor was investigated by both experiment and modeling, but the studies were conducted only on disk zeolite membrane reactor [18,19]. The availability of the stable tubular bilayer zeolite membranes, coupled with the use of a mathematical model, allowed us to study operation of WGS in the zeolite membrane reactor under conditions more close to the practical applications.

Recently, we succeeded in synthesis of disk shaped ZSM-5/silicalite bilayer membranes for H₂ separation and WGS membrane reactor [21,36]. The bilayer structure of the zeolite membranes allowed better control of zeolite membrane modification for improved separation performance.

More excitingly, the bilayer MFI zeolite membranes exhibited unprecedented high thermal and chemical stability under industrial relevant WGS atmospheres even with 400 ppm H₂S at about 500 °C because of the unique properties of MFI-type zeolite and the specific structure design [21]. It was a logic next step for us to synthesize bilayer MFI zeolite membranes in tubular geometry in an effort to explore the use of the stable zeolite membranes for WGS reaction applications.

It should be noted that many experimental and modeling studies on WGS in membrane reactors, mostly of Pd alloy membranes, were reported by other researchers [4,5]. The results of those studies on metal membrane reactors could not be directly used to predict the performance of WGS in the zeolite membrane reactor because of the difference in permeation and separation mechanisms between these membranes. As reviewed above, limited studies on WGS in microporous (e.g. silica) membrane reactors were also reported, but these studies were conducted at low pressures (< 4 atm). In practical applications, WGS zeolite membrane reactor is likely to be operated at high pressures (>20 atm) with high pressure raw syngas from a gasifier as the feed. However, the effect of operation pressure on WGS reaction in a tubular zeolite membrane is not clear. Since it is more difficult to perform WGS in microporous membrane reactor at high pressures, a mathematical model, with values for the parameters obtained from the low pressure experimental data, was set up and used to predict WGS performance of the zeolite membrane reactor at high pressures. The objective of this paper is to report synthesis of the new bilayer MFI zeolite membrane in the tubular geometry, and experimental and modeling study of WGS in the tubular zeolite membrane reactor with focus on examining the effects of the pressure on and optimum conditions for WGS in tubular zeolite membrane reactor.

2. Experimental

2.1 Synthesis of tubular ZSM-5/silicalite bilayer membrane

Porous alumina tubes (PALL Corporation) with the length of 8 cm, inner and outer diameters of 0.7 cm and 1.0 cm, respectively, were used as supports. The average porous size of the inner layer of the alumina support was 200 nm. The inner surface was modified with an yttria-stabilized zirconia (YSZ) intermediate barrier layer to prevent the diffusion of Al^{3+} into zeolite membrane layer [38]. The YSZ suspension was synthesized following the procedure in our previous work [38,39]. YSZ barrier layer was prepared via a dip-coating process and followed by a calcination step at 1000 °C for 3h in air [36]. The outer side of the tube was covered with Teflon tape during the dip-coating to avoid the deposition of YSZ. After YSZ modification, two ends of the alumina tube were coated with glaze and the middle of the support about 1.5 cm in length was left for membrane synthesis.

Silicalite seed was coated onto the surface of YSZ barrier layer by a dip-coating process. The detailed procedure for the preparation of silicalite seed and seed suspension can be found in our previous work [40]. The silicalite layer was then synthesized on the seeded support via a secondary growth process using a precursor with the molar composition of 0.9 NaOH: 0.9 TPABr: 4 SiO_2 : 1000 H_2O : 16 EtOH at 175 °C for 8 h [36]. The as-prepared silicalite membrane was washed and dried, then calcined at 500 °C for 8h in air to remove the organic template. Subsequently, a thin ZSM-5 top layer was fabricated on the silicalite layer via a hydrothermal process at 180 °C for 8 h using a template-free precursor with a composite of 5 g SiO_2 , 60 g H_2O , 1.15 g NaOH, and 0.65 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ [36].

To adjust the zeolitic pore size and improve the H_2 selectivity, the tubular ZSM-5/silicalite bilayer membrane was modified through an in situ catalytic cracking deposition (CCD) process of methyldiethoxysilane (MDES) precursor [21,36]. MDES precursor was carried into the tube side of the bilayer membrane by an equimolar H_2/CO_2 mixture gas. Helium was introduced to another side as sweep gas. The MDES molecules adsorbed onto the active sites (framework Al^{3+} generated acidic sites) on the inner surface of the zeolitic pore channels. At about 450 °C, the

adsorbed MDES molecules decomposed and deposited as SiO₂ units on active sites thereby reduce the zeolitic pore size [33]. The components of permeate stream were continuously analyzed by a gas chromatography (GC, Agilent 6890 N with a column of HayeSep DB 100/120, AllTech).

2.2 Characterization

The crystal structure of the membranes was characterized by X-ray diffraction (XRD, Bruker AXS-D8, Cu K α radiation). Diffraction patterns were collected at room temperature in the range of $5^\circ < 2\theta < 45^\circ$, with a step width of 0.05° and a scan rate of 0.2 s per step. The morphology of the ZSM-5/silicalite bilayer membranes were characterized using a scanning electron microscopy (SEM, Philips, XL 30).

2.3 WGS reaction

About 0.2 g Fe-Cr-Cu catalyst (with the atomic ratio of 10:1:0.25), prepared following the reported procedures [21,41], was packed into the tube side of the ZSM-5/silicalite bilayer membrane for WGS reaction. The catalyst was fixed at the middle of the tube by glass wool at two sides, as shown in **Figure 1a**. The membrane was then assembled into a stainless steel tubular membrane cell using soft graphite for sealing. Before WGS reaction, the catalyst was activated at 400 °C for 4 h using a mixed gas with the composition of 33.3% CO, 25.0% CO₂, 25.0% H₂ and 16.7% steam. The schematic diagram of the set-up for WGS reaction was shown in **Figure 1b**. CO and water were introduced into the tube side of the membrane. The water flow rate was controlled by a precisely calibrated liquid pump (LC-20AD, Shimadzu Corporation). WGS reaction occurred at the catalyst bed. The produced H₂ permeated through the zeolite membrane to the shell side and was swept out by Argon (Ar). The compositions of feed out and sweep out streams were analyzed using GC. The flow rates of the effluents from both feed and sweep gases were measured by a soap film flow meter. The CO conversion and H₂ recovery are calculated by the following equations, respectively.

$$X_{CO} = \frac{F_{CO}^{feed\ in} - F_{CO}^{feed\ out} - F_{CO}^{sweep\ out}}{F_{CO}^{feed\ in}} \quad (1)$$

$$R_{H_2} = \frac{F_{H_2}^{sweep\ out}}{F_{H_2}^{feed\ out} + F_{H_2}^{sweep\ out}} \quad (2)$$

where $F_{CO}^{feed\ in}$, $F_{CO}^{feed\ out}$ and $F_{CO}^{sweep\ out}$ are CO flow rates ($\text{mL} \cdot \text{min}^{-1}$) in feed in, feed out and sweep out streams, respectively; $F_{H_2}^{feed\ out}$ and $F_{H_2}^{sweep\ out}$ are H_2 flow rates ($\text{mL} \cdot \text{min}^{-1}$) in feed out and sweep out streams, respectively.

Figure 1 Schematic diagram of tubular membrane cell (a) and membrane reactor set-up (b) for WGS reaction.

3. Modeling

3.1 Kinetic equation

The empirical power-law equation was widely applied as the WGS reaction rate equation because of its simplicity and effectiveness in correlating the experimental data of WGS reaction over iron-based catalyst [42]. Considering that the Fe-Cr-Cu catalyst was used in our experiments, the following power-law WGS reaction rate equation developed by Hla et al. [42] based on commercial Fe-Cr-Cu catalyst was used to describe the WGS kinetics in this study.

$$r_A = 10^{0.659} \exp\left(\frac{-8.8 \times 10^4}{RT}\right) P_{CO}^{0.9} P_{H_2O}^{0.31} P_{CO_2}^{-0.156} P_{H_2}^{-0.05} \left(1 - \frac{1}{K_{eq}} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}\right) \quad (3)$$

where r_A is the reaction rate ($\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{s}^{-1}$), R is the gas constant, T is the temperature (K), P_i is the partial pressure of component i in the reaction zone (Pa). K_{eq} is the temperature-dependent thermodynamic equilibrium constant for WGS, which can be defined as

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (4)$$

3.2 Permeation equations

The membrane permeance for each gas (H_2O , CO , H_2 , CO_2 and Ar) in the WGS reaction can be expressed as[43]

$$j_i = \frac{\varphi}{\delta} (D_i \beta_i) \quad (5)$$

where j_i is the permeance of component i through the membrane ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$), φ is ratio of membrane porosity (~ 0.25) to tortuosity factor (~ 5), which has the value of 0.05 as reported by Kanezashi and Lin,[44] δ is the thickness of the membrane (m), D_i is the diffusivity of gas i in zeolite ($\text{m}^2 \cdot \text{s}^{-1}$), and β_i is the adsorption equilibrium constant of gas i .

For diffusion of small gases with weak adsorption affinity with zeolites, following gas translational diffusion model was proposed to predict diffusivity in zeolite pores [45]

$$D_i = \frac{\alpha}{\lambda} \left(\frac{8RT}{\pi M_i} \right)^{1/2} \exp \left(\frac{-E_{d,i}}{RT} \right) \quad (6)$$

where α is the diffusion length or distance between two adjacent sites (m), which is about 1 nm for diffusion in MFI-type zeolite [44], λ is the diffusion coordination number (4 for MFI-type zeolite), M_i is the molecular weight of the diffusing gas ($\text{g} \cdot \text{mol}^{-1}$), $E_{d,i}$ is the activation energy for diffusion of the gas i in the micropores ($\text{kJ} \cdot \text{mol}^{-1}$), which is determined by the relative size of diffusing gas molecule to the zeolite pore size. The typical values of $E_{d,i}$ are 13.39, 13.14, 12.55 and $14.97 \text{ kJ} \cdot \text{mol}^{-1}$ for H_2 , CO, CO_2 and Ar, respectively [32].

At elevated temperatures, $\beta_i = 1/RT$ [43], inserting Eq. 6 into Eq. 5 gives

$$j_i = \frac{\varphi}{\delta} \frac{\alpha}{\lambda} \left(\frac{8}{\pi RT M_i} \right)^{1/2} \exp \left(\frac{-E_{d,i}}{RT} \right) \quad (7)$$

From our previous experiment results [21], H_2O vapor permeance through ZSM-5/silicalite bilayer membrane was relatively low and the $\text{H}_2/\text{H}_2\text{O}$ selectivity reached 180 at 500°C . Therefore, the H_2O vapor permeation through the membrane will not be considered in the modeling study.

3.3 Membrane reactor model

Some hypotheses and definitions were made to simplify the calculation: (1) one-dimensional tubular reactor without radial concentration gradients on both the tube and shell sides. (2) No gas film resistance for mass transfer through the membrane walls and negligible mass transfer resistances through the porous support and through catalyst bed. This hypothesis is justified by the relatively low H_2 permeation flux of the modified MFI zeolite membrane and the fact that the pore sizes of the porous support and the catalyst bed are much larger than that of the modified MFI zeolite layer. (3) A steady state, isothermal operation, with a same inlet temperature for the sweep gas and reactant mixture. (4) Ideal gas law is used to describe the gas behaviors of the single component and gas mixture. (1), (3) and (4) are general assumptions and have been widely used for the modeling study of WGS reaction in membrane reactors [46-49].

According to the principle of mass conservation, the design model equations are derived in each region as follows.

$$\frac{dF_i}{dz} = \pi r^2 \rho_B v_i r_A - 2\pi r j_i \Delta P_i \quad (8)$$

where F_i ($i = \text{CO}, \text{CO}_2, \text{H}_2, \text{Ar}$) is the molar flow rate in the tube side ($\text{mol} \cdot \text{s}^{-1}$), v_i the stoichiometry of species i in WGS reaction, $v_{\text{He}}=0$, ΔP_i is the partial pressure difference of specie i between the tube side and the shell side (Pa).

In the shell side:

$$\frac{dQ_i}{dz} = 2\pi r j_i \Delta P_i \quad (9)$$

where Q_i is the molar flow rate in the shell side ($\text{mol} \cdot \text{s}^{-1}$). A one-dimensional reaction model for the traditional fixed-bed reactor for WGS was established by setting $j_i = 0$ in Eqs. 8 and 9.

Eqs. 8 and 9 are eight ordinary differential equations, of which the solutions give profiles of 8 variables ($F_{\text{CO}}, F_{\text{CO}_2}, F_{\text{H}_2}, F_{\text{Ar}}, Q_{\text{CO}}, Q_{\text{CO}_2}, Q_{\text{H}_2}, Q_{\text{Ar}}$) along the longitudinal direction of the membrane reactor. The differential equations, with adequate boundary conditions at $z=0$ and the values of the parameters listed in **Table 1**, were solved using a numerical Rung-Kutta method. The calculation was performed on MATLAB 2012a (MathWorks, Inc., Natick, US).

Table 1 Values for parameters used in the simulation

Parameters	Reference values
Temperature ($^{\circ}\text{C}$)	400–550
Feed side pressure (atm)	1–30
Permeate side pressure (atm)	1
Weight of the catalyst (g)	0.2
Average diameter of the catalyst particles (m)	2.5×10^{-4}
Thickness of the MFI-type zeolite membrane (ZSM-5 layer) (m)	3.0×10^{-6}
Inner radial of the membrane (m)	3.5×10^{-3}
Length of the membrane (m)	1.5×10^{-2}
CO feed flow rate ($\text{mL} \cdot \text{min}^{-1}$)	20–50
Steam to CO ratio	1–3
Ar sweep flow rate ($\text{mL} \cdot \text{min}^{-1}$)	20–50

4. Results and discussion

4.1 Structure and separation performance of tubular ZSM-5/silicalite bilayer membranes

During the preparation of ZSM-5/silicalite bilayer membrane, the crystal structure of each layer of the tubular membrane (on inner surface) was analyzed, as shown in **Figure 2**. Silicalite layer (**Figure 2c**) and the ZSM-5/silicalite bilayer membrane (**Figure 2d**) exhibit typical MFI-type zeolite crystal structure [21,50]. The diffraction peaks of YSZ modified alumina support can also be observed, indicating the relatively small thickness of the zeolite layer. In addition, no obvious impurity phases are found. Therefore, zeolite membrane of pure MFI-type has been successfully fabricated on the tubular support.

Figure 2 XRD patterns of tubular (a) alumina support; (b) YSZ modified alumina support; (c) silicalite membrane on YSZ/alumina support; (d) ZSM-5/silicalite bilayer membrane on YSZ/alumina support.

The morphology of the ZSM-5/silicalite bilayer membranes was further analyzed to evaluate

their quality. Nanosized YSZ particles are deposited on the surface of alumina support, forming the crack-free and uniform YSZ layer (**Figure 3a**). An intergrown silicalite layer composed of sharp grains with the size of about 2 μm is synthesized on the YSZ layer (**Figure 3b**). The surface of the membrane (**Figure 3c**) is covered by continuous and highly intergrowth ZSM-5 grains with the grain size of 1-2 μm . No obvious defect could be observed. The ZSM-5 grains are not as sharp as that of the silicalite because of the template-free synthesis [39,44]. **Figure 3d** shows clear and crack-free alumina, YSZ, silicalite and ZSM-5 layers. These layers are well bonded together. The thicknesses of YSZ, silicalite and ZSM-5 layers are 2 μm , 8 μm and 3 μm , respectively. The cross-section of silicalite layer exhibits typical columnar grains with clear grain boundary [50]. In contrast, the grain boundary on the cross-section of ZSM-5 layer is not obvious.

Figure 3 SEM images of (a) surface of YSZ modified tubular alumina support; (b) surface of

silicalite layer; (c) surface of tubular ZSM-5/silicalite bilayer membrane; (d) cross section of tubular ZSM-5/silicalite bilayer membrane.

An on-stream CCD modification was used to reduce the zeolitic pore size and improve the H₂/CO₂ separation performance of the tubular ZSM-5/silicalite bilayer membrane. At room temperature, this membrane showed a H₂/CO₂ separation factor of 0.31, indicating that the membrane was highly selective to CO₂ at room temperature and the sealing system of the tubular membrane permeation cell worked well at room temperature [34]. The membrane was heated up to 450 °C for CCD modification. **Figure 4** shows CCD modification results. At 450 °C before modification, the membrane shows H₂ and CO₂ permeance of 2.93×10^{-7} and 7.5×10^{-8} mol·m⁻²·s⁻¹·Pa⁻¹ with a H₂/CO₂ separation factor of 3.16 at 450 °C. As the modification started, both H₂ and CO₂ gas permeance decreased significantly. Since the decrease of CO₂ permeance reaches about 87% while the decrease of H₂ permeance is around 34%, the H₂/CO₂ separation factor increases as the modification continued. After the CCD modification, H₂ and CO₂ permeance are 1.94×10^{-7} and 9.8×10^{-9} mol·m⁻²·s⁻¹·Pa⁻¹, respectively, and the H₂/CO₂ separation factor reaches 16.01. Compared with the disk ZSM-5/silicalite bilayer membrane prepared in our previous work (with the H₂ permeance of 1.28×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹ and H₂/CO₂ separation factor of 25.3 after CCD modification at 450 °C) [36], the H₂ permeance of the tubular membrane is higher, however the H₂/CO₂ separation factor is lower. This may be attributed to small amount of intercrystalline defects in the tubular membrane or possible small leak in the graphite seals at the end of the tubes at high temperatures.

Figure 4 Variations of gas permeance and H₂/CO₂ separation factor during CCD modification of the tubular ZSM-5/silicalite bilayer membrane at 450 °C.

4.2 WGS reaction in tubular MFI zeolite membrane reactors under atmospheric pressure

Figure 5 shows the CO conversion and H₂ recovery of the ZSM-5/silicalite bilayer membrane reactor (MR) as a function of reaction temperature. For comparison, the calculated CO conversion of the traditional reactor (TR) without H₂ removal and the CO equilibrium conversion were also added. The CO conversion increases significantly with increasing temperature, while the H₂ recovery shows a slight increase trend. At 550 °C, the CO conversion reaches 88.0%, which is close to the equilibrium conversion and higher than the conversion in TR (84.5%). The H₂ recovery is 16.4% at this temperature. These results indicate that the operation temperature is a key factor to control the reaction. Although the WGS is a weak exothermic reaction, relatively high operation temperature is benefit for obtaining high CO conversion. This is caused by the enhancement of kinetic with temperature [17]. Moreover, the CO conversion is lower than the equilibrium conversion, and therefore the limitation of the thermodynamic equilibrium is not obvious. Below 500 °C, the CO conversion of the MR is very

close to that in TR, indicating that the contribution of membrane to CO conversion is not obvious. In other words, compared with the H₂ production rate, the H₂ removal rate through the membrane is not high enough to shift the reaction equilibrium and promote the CO conversion. Therefore, the further improvement of the H₂ permeation flux is desired.

Figure 5 Effect of temperature on the CO conversion ($Exp-MR-X_{CO}$) and H₂ recovery ($Exp-MR-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor (MR). H₂O/CO ratio is 3.0; GHSV is 72000 h⁻¹ (CO flow rate of 30 ml·min⁻¹); Ar flow rate is 30 ml·min⁻¹; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-MR-X_{CO}$ and $Cal-MR-R_{H_2}$: calculated result of CO conversion and H₂ recovery, respectively; $Exp-TR-X_{CO}$ and $Cal-TR-X_{CO}$: Experimental and calculated results of CO conversion of traditional reactor (TR) under the identical conditions.

Figure 6 shows the experimental and modeling results of the CO conversion and H₂ recovery of the ZSM-5/silicalite bilayer membrane reactor as a function of steam to CO (H₂O/CO) ratio. With increasing the H₂O/CO ratio, the CO conversion increases while the H₂ recovery shows a decrease trend. When the H₂O/CO ratio is 3.0, the CO conversion reaches 82.4% and the H₂

recovery is about 13.0 %. The enhancement of CO conversion is more significant at low H_2O/CO ratio of 1.0-2.0. However, further increase of H_2O/CO results in a relatively slow increase of CO conversion. The CO conversion is lower than the equilibrium conversion even the H_2O/CO ratio reached 3.0. These results are attributed to that high H_2O/CO ratio greatly increases the space velocity since the CO flow rate is fixed at $30 \text{ ml} \cdot \text{min}^{-1}$. As is well known, high space velocity is unfavorable for both CO conversion and H_2 recovery. In addition, excessive steam for the relatively high H_2O/CO ratio reduces the partial pressure of H_2 in the reaction side, resulting in the low H_2 permeation flux and low H_2 recovery.

Figure 6 Effect of H_2O/CO ratio on the CO conversion ($Exp-X_{CO}$) and H_2 recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500°C ; CO flow rate is $30 \text{ ml} \cdot \text{min}^{-1}$; Ar flow rate is $30 \text{ ml} \cdot \text{min}^{-1}$; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion and H_2 recovery, respectively.

The effect of gas hourly space velocity (GHSV) on the WGS performance was also studied based on both experiment and model calculation. The GHSV increased from 48000 h^{-1} to 120000 h^{-1} as

the CO feed flow rate increased from 20 ml·min⁻¹ to 50 ml·min⁻¹. **Figure 7** shows the CO conversion and H₂ recovery of the ZSM-5/silicalite bilayer membrane reactor as a function of GHSV. Both CO conversion and H₂ recovery decrease with increasing GHSV. When the GHSV is 48000 h⁻¹, the CO conversion is 90.3% and close to the equilibrium conversion (91.7%) at 500 °C, and the H₂ recovery is 18.6%. However, the higher GHSV reduces the residence time for WGS reaction and the reaction on the catalyst seems not quick enough to convert so much CO, leading to the decrease of CO conversion. Additionally, the higher GHSV has adverse effect on H₂ removal through the membrane because the H₂ transport rate is not very high under the atmospheric pressure (feed side). Moreover, too much unreacted CO and steam in the feed greatly reduces the H₂ partial pressure, leading to the low H₂ permeation flux and decrease of H₂ recovery. Therefore, the role of zeolite membrane in the membrane reactor is also restrained at high GHSV.

Figure 7 Effect of GHSV on the CO conversion ($Exp-X_{CO}$) and H₂ recovery ($Exp-R_{H2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500 °C; H₂O/CO ratio is 3.0; Ar flow rate is 30 ml·min⁻¹; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H2}$: calculated results of CO conversion and H₂ recovery, respectively.

Figure 8 shows the CO conversion and H₂ recovery of the ZSM-5/silicalite bilayer membrane reactor as a function of sweep gas (Ar) flow rate. In general, the increase of sweep gas flow rate will effectively reduce the partial pressure of H₂ at the permeate side and improve the H₂ permeation flux, resulting in increase of both CO conversion and H₂ recovery. From **Figure 8**, however, both CO conversion and H₂ recovery show a very slight increase with increasing Ar flow rate. A possible explanation is that the high Ar flow rate really reduces the H₂ partial pressure, but also significantly increase the Ar partial pressure at the permeate side, resulting in a permeation of Ar through the membrane in reverse direction. This reverse diffusion of Ar may reduce the H₂ permeation through the zeolite channels. Therefore, the increase of CO conversion and H₂ recovery is not obvious with the increase of Ar flow rate. The model results further confirm that the influence of Ar flow rate on the WGS performance is limited. Tang et al. [17] also stated that the counter-diffusion of sweep gas through the membrane might inhibit the H₂ transfer in the zeolite channels.

Figure 8 Effect of sweep gas (Ar) flow rate on the CO conversion ($Exp-X_{CO}$) and H₂ recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500 °C; H₂O/CO ratio is 3.0; GHSV is 72000 h⁻¹ (CO flow rate of 30 ml·min⁻¹); feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion

and H₂ recovery, respectively.

Table 2 listed the H₂ separation and WGS reaction performance of different MFI-type zeolite membranes. It is really difficult to compare the WGS reaction performance of these membranes in **Table 2** due to the different membrane types, membrane preparations and WGS reaction operating conditions. However, it can be found that the comprehensive performance of our ZSM-5/silicalite bilayer membrane is comparable with other MFI-type zeolite membranes. From **Table 2**, beside the membrane separation performance, the optimum reaction conditions are also crucial to obtain high reaction performance.

Table 2 Hydrogen separation and WGS reaction performance of different MFI-type zeolite membranes.

Membrane Type	Separation Performance		WGS Reaction Performance						Ref.
	Temperature (°C)	H ₂ /CO ₂ Separation Factor	Temperature (°C)	Feed Pressure (atm)	Space Velocity (h ⁻¹)	Steam to CO Ratio	X _{co} (%)	R _{H2} (%)	
disk	450	10.9	550	2	60000	3.5	91.6	32.2	[18]
disk	550	11.3	550	6	60000	3.5	93.6	41	[18]
disk	500	30.7	550	2	60000	3.5	92.7	–	[19]
			550	6	7500	3.5	98.5	73.2	[19]
disk	500	42.6	300	1	1500	1.25	95.4	19.7	[20]
disk	450	25.3	500	1	60000	3.0	84	23.2	[21]
tube	450	43.2	550	1	60000	1.0	81.7	-	[17]
tube	550	45.1	550	1	60000	3.5	94.0	30.4	[17]
			500	1	48000	3.0	90.3	18.6	This work
			500	5	72000	3.0	89.8	34.7	This work
tube	450	16.0	550	1	72000	3.0	88.0	16.4	This work
			500	5	72000	3.0	89.8	34.7	This work

From **Figures 6-8**, it is worth noting that the modeling results agree well with the experimental data, indicating the validity of the values for the parameters used in the model. In other words, our model is highly reliable for the prediction of WGS reaction performance of the ZSM-5/silicalite bilayer membrane reactor.

4.3 High pressure WGS reaction in tubular MFI zeolite membrane reactors

Since there is no change in the volume from reactants to products, the WGS reaction itself will not be affected by pressure. In the ZSM-5/silicalite bilayer membrane reactor, however, high operation pressure at the reaction side (feed side) is beneficial for the transport of the produced H_2 through the membrane, resulting in the shift of the reaction equilibrium toward H_2 production, promoting the CO conversion. Therefore, feed pressure is an important factor for WGS reaction in membrane reactor with H_2 or CO_2 removal [8,18]. The effect of feed pressure on the WGS reaction performance was studied and the results are shown in **Figure 9a**. Considering the safe operation of the experiments in the Lab, the feed pressure increased up to 5 atm. As the pressure increases from 1 to 5 atm, CO conversion increases from 82.4% to 89.8% and the H_2 recovery increases significantly from 11.6% to 28.5%. This result shows the great contribution of the membrane to CO conversion. In addition, high operation pressure promotes the H_2 permeation through the membrane, resulting in high H_2 recovery. Therefore, feed pressure is also a key factor to control the reaction process. In typical practical process, the pressure of WGS reaction is higher than 30 atm [2], such high pressure is very suitable for the application of membrane reactor to obtain high reaction performance.

From **Figure 9a**, the modeling results can well represent the experiment data, further confirming the reliability of our model. Therefore, we predicted the WGS reaction performance in a wide pressure range (from 5 to 30 atm) based on the model calculation. As shown in **Figure 9b**, the CO conversion and H_2 recovery are 93.1% (higher than the equilibrium conversion) and 57.7%, respectively, when the feed pressure is 10 atm. More excitingly, they reach 96.8% and 82.0%, respectively, at 20 atm, and 98.8% and 93.3%, respectively, at 30 atm. From Figure 9b, the high H_2 transport rate caused by the high feed pressure greatly shifts the reaction equilibrium, and a strong enhancement of membrane reactor performance is achieved.

Figure 9 Effect of feed pressure on the CO conversion ($Exp-X_{CO}$) and H₂ recovery ($Exp-R_{H2}$) of the ZSM-5/silicalite bilayer membrane reactor: (a) experiment and modeling results from 1 to 5 atm; (b) modeling results from 5 to 20 atm. Reaction temperature is 500 °C; H₂O/CO ratio is 3.0; GHSV is 72000 h⁻¹ (CO flow rate of 30 ml·min⁻¹); Ar flow rate is 30 ml·min⁻¹. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H2}$: calculated results of CO conversion and H₂ recovery, respectively.

To further evaluate the high pressure WGS performance, the effects of temperature and $\text{H}_2\text{O}/\text{CO}$ ratio on CO conversion was studied at 10, 20 and 30 atm. As shown in **Figure 10a**, the CO conversion increases significantly with temperature before 460 °C, however, further enhancement of CO conversion is difficult by adjusting the temperature. From the WGS reaction kinetic, reaction rate (CO conversion) increases with increasing the temperature [17]. However, the CO conversion is higher than the equilibrium conversion therefore the limitation of CO conversion by the thermodynamic equilibrium is obvious when further increase the temperature. Moreover, the H_2 transport rate has reached a high level under high feed pressure. Further greatly enhancing the H_2 transport rate and strongly shifting the reaction equilibrium by increasing the temperature (from 460 °C to 550 °C) may be difficult. Above 460 °C, the CO conversion increases with increasing $\text{H}_2\text{O}/\text{CO}$ ratio, especially from 1.0 to 2.5. Under the pressure of 20 atm (**Figure 10b**), the CO conversion reaches about 97 % with the $\text{H}_2\text{O}/\text{CO}$ ratio above 2.0 and temperature above 440 °C. In contrast, under the pressure of 30 atm (**Figure 10c**), an extremely high CO conversion (close to 99%) can be obtained at a wider range of temperature and $\text{H}_2\text{O}/\text{CO}$ ratio. Therefore, to achieve a high CO conversion (>95%) is possible under high feed pressure by controlling the temperature and $\text{H}_2\text{O}/\text{CO}$ ratio.

Figure 10 Calculated results of CO conversion as a function of $\text{H}_2\text{O}/\text{CO}$ ratio and temperature in the membrane reactor with the feed pressure of (a) 10 atm; (b) 20 atm; (c) 30 atm. GHSV is 72000 h^{-1} (CO flow rate of $30 \text{ ml} \cdot \text{min}^{-1}$); Ar flow rate is $30 \text{ ml} \cdot \text{min}^{-1}$.

4.4 Optimization of operation condition

The high reliability of the model allows us to further optimize the operation process of the WGS membrane reactor and to achieve both high CO conversion ($>95\%$) and H_2 recovery ($>90\%$). From sections 4.2 and 4.3, temperature, steam to CO ratio, space velocity, and pressure are key factors that affect the WGS reaction performance. Therefore, the optimization was focused mainly on these factors. In addition, the match between the GHSV and the WGS reaction rate, and match between the H_2 production rate from WGS reaction and the H_2 removal rate through the zeolite membrane are also considered.

To obtain a relatively high H_2 recovery, the feed pressure was fixed at 20 and 30 atm, respectively. The $\text{H}_2\text{O}/\text{CO}$ ratio was fixed at 3.0. Then, the effects of temperature and GHSV on the CO conversion and H_2 recovery were analyzed. As shown in **Figure 11a**, above 420°C , the

effect of temperature on the CO conversion (higher than 95%) is not obvious. However, the H₂ recovery increases significantly with temperature. Both CO conversion and H₂ recovery are greatly dependent on the GHSV. At 550 °C, H₂ recovery can reach 90% when the GHSV is relatively low ($\leq 60000 \text{ h}^{-1}$). When the feed pressure and GHSV were fixed at 20 atm and 60000 h⁻¹, respectively, the effects of temperature and H₂O/CO ratio on the CO conversion were further evaluated. As show in **Figure 12a**, a very high CO conversion (close to 98%) is achieved with the temperature above 440 °C and H₂O/CO ratio higher than 2.0.

Figure 11 Calculated results of CO conversion and H₂ recovery as function of temperature and GHSV in the membrane reactor with the feed pressure of (a) 20 atm; (b) 30 atm. H₂O/CO ratio is 3.0; Ar flow rate is 30 ml·min⁻¹; *Eq-X_{CO}*: equilibrium CO conversion.

Further increase of the pressure to 30 atm, similar results can be found, as shown in **Figure 11b**. Although higher GHSV (from 72000 to 96000 h⁻¹) were used, the high CO conversion (>95%) could be obtained. This is attributed to the rapid H₂ removal through the membrane under the high feed pressure, and greatly shifting the reaction equilibrium. At 550 °C, H₂ recovery can reach 90% even with high GHSV of 96000 h⁻¹. When the feed pressure and GHSV were fixed at 30 atm and 84000 h⁻¹, respectively, the effects of temperature and H₂O/CO ratio on the CO conversion were evaluated, as show in **Figure 12b**. Above 440 °C with the H₂O/CO ratio of 2.0-4.0, the change of CO conversion seems not obvious.

Figure 12 Calculated results of CO conversion as a function of H_2O/CO ratio and temperature in the membrane reactor. Ar flow rate is 30 $ml \cdot min^{-1}$. (a) GHSV is 60000 h^{-1} (CO flow rate of 25 $ml \cdot min^{-1}$); feed pressure is 20 atm; (b) GHSV is 84000 h^{-1} (CO flow rate of 35 $ml \cdot min^{-1}$); feed pressure is 30 atm.

From the modeling work, when the feed pressure is higher than 10 atm, the reaction equilibrium

limitation can be easily broken by the rapid removal of H_2 through the membrane. High CO conversion ($>95\%$) could be achieved relatively easily in the membrane reactor operated under high feed pressure (above 20 atm). Considering both CO conversion and H_2 recovery, the H_2O/CO ratio of 2.0~ is appropriate. In contrast, it is rather difficult to achieve high H_2 recovery ($>90\%$). Therefore, a relatively high temperature such as $550^\circ C$ is required. The match between the H_2 production rate from WGS reaction and the H_2 removal rate through the zeolite membrane is crucial. Accordingly, not only suitable feed pressure and temperature, but also appropriate GHSV are required. Considering that only very active catalysts can operate at the GHSV above 40000 h^{-1} [2], the appropriate GHSV of the zeolite membrane may be below 60000 h^{-1} except that the reaction was operated under a high pressure (around 30 atm).

5. Conclusions

MDES modified tubular ZSM-5/silicalite bilayer membrane exhibits high H_2 permeance and moderate H_2/CO_2 separation factor. The experimental and modeling studies demonstrated that this membrane can be used as WGS membrane reactor to effectively improve the WGS reaction performance. Temperature, H_2O/CO ratio, GHSV and feed pressure are proved as key factors that affect the reaction performance in the membrane reactor. To achieve high CO conversion and H_2 recovery, the reactor should be operated at high temperature and under high feed pressure. The high temperature results in the enhanced reaction kinetic. Both high temperature and high pressure are beneficial for the rapid H_2 removal through the membrane, leading to the shift of reaction equilibrium toward H_2 production, resulting in the enhancement of CO conversion and H_2 recovery. Appropriate H_2O/CO ratio (2.0~) and GHSV ($\sim 60000\text{ h}^{-1}$) are also crucial to obtain high reaction performance. Although high H_2O/CO ratio means high CO conversion, it is unfavorable for H_2 recovery. Relatively low GHSV would be advantage to CO conversion. Based on the modeling prediction results, it is possible to achieve both high CO conversion ($>95\%$) and H_2 recovery ($>90\%$) in the zeolite membrane reactor. This work demonstrates that MFI-type zeolite membrane reactors have high potential for practical applications in WGS reaction

process.

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Figure Captions

- Figure 1** Schematic diagram of tubular membrane cell (a) and membrane reactor set-up (b) for WGS reaction.
- Figure 2** XRD patterns of tubular (a) alumina support; (b) YSZ modified alumina support; (c) silicalite membrane on YSZ/alumina support; (d) ZSM-5/silicalite bilayer membrane on YSZ/alumina support.
- Figure 3** SEM images of (a) surface of YSZ modified tubular alumina support; (b) surface of silicalite layer; (c) surface of tubular ZSM-5/silicalite bilayer membrane; (d) cross section of tubular ZSM-5/silicalite bilayer membrane.
- Figure 4** Variations of gas permeance and H_2/CO_2 separation factor during CCD modification of the tubular ZSM-5/silicalite bilayer membrane at 450 °C.
- Figure 5** Effect of temperature on the CO conversion ($Exp-MR-X_{CO}$) and H_2 recovery ($Exp-MR-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor (MR). H_2O/CO ratio is 3.0; GHSV is 72000 h^{-1} (CO flow rate of 30 $ml \cdot min^{-1}$); Ar flow rate is 30 $ml \cdot min^{-1}$; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-MR-X_{CO}$ and $Cal-MR-R_{H_2}$: calculated result of CO conversion and H_2 recovery, respectively; $Exp-TR-X_{CO}$ and $Cal-TR-X_{CO}$: Experimental and calculated results of CO conversion of traditional reactor (TR) under the identical conditions.
- Figure 6** Effect of H_2O/CO ratio on the CO conversion ($Exp-X_{CO}$) and H_2 recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500 °C; CO flow rate is 30 $ml \cdot min^{-1}$; Ar flow rate is 30 $ml \cdot min^{-1}$; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion and H_2 recovery, respectively.
- Figure 7** Effect of GHSV on the CO conversion ($Exp-X_{CO}$) and H_2 recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500 °C; H_2O/CO ratio is 3.0; Ar flow rate is 30 $ml \cdot min^{-1}$; feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion and H_2 recovery, respectively.
- Figure 8** Effect of sweep gas (Ar) flow rate on the CO conversion ($Exp-X_{CO}$) and H_2 recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor. Reaction temperature is 500 °C; H_2O/CO ratio is 3.0; GHSV is 72000 h^{-1} (CO flow rate of 30 $ml \cdot min^{-1}$); feed pressure is 1 atm. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion and H_2 recovery, respectively.

- Figure 9** Effect of feed pressure on the CO conversion ($Exp-X_{CO}$) and H₂ recovery ($Exp-R_{H_2}$) of the ZSM-5/silicalite bilayer membrane reactor: (a) experiment and modeling results from 1 to 5 atm; (b) modeling results from 5 to 20 atm. Reaction temperature is 500 °C; H₂O/CO ratio is 3.0; GHSV is 72000 h⁻¹ (CO flow rate of 30 ml·min⁻¹); Ar flow rate is 30 ml·min⁻¹. $Eq-X_{CO}$: equilibrium CO conversion; $Cal-X_{CO}$ and $Cal-R_{H_2}$: calculated results of CO conversion and H₂ recovery, respectively.
- Figure 10** Calculated results of CO conversion as a function of H₂O/CO ratio and temperature in the membrane reactor with the feed pressure of (a) 10 atm; (b) 20 atm; (c) 30 atm. GHSV is 72000 h⁻¹ (CO flow rate of 30 ml·min⁻¹); Ar flow rate is 30 ml·min⁻¹.
- Figure 11** Calculated results of CO conversion and H₂ recovery as function of temperature and GHSV in the membrane reactor with the feed pressure of (a) 20 atm; (b) 30 atm. H₂O/CO ratio is 3.0; Ar flow rate is 30 ml·min⁻¹; $Eq-X_{CO}$: equilibrium CO conversion.
- Figure 12** Calculated results of CO conversion as a function of H₂O/CO ratio and temperature in the membrane reactor. Ar flow rate is 30 ml·min⁻¹. (a) GHSV is 60000 h⁻¹ (CO flow rate of 25 ml·min⁻¹); feed pressure is 20 atm; (b) GHSV is 84000 h⁻¹ (CO flow rate of 35 ml·min⁻¹); feed pressure is 30 atm.

Graphical Abstract