Effects of system parameters on the performance of CO_2-selective WGS membrane reactor for fuel cells

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Abstract

Performing water gas shift (WGS) reaction efficiently is critical to hydrogen purification for fuel cells. In our earlier work, we proposed a CO_2-selective WGS membrane reactor, developed a one-dimensional non-isothermal model to simulate the simultaneous reaction and transport process and verified the model experimentally under an isothermal condition. Further modeling investigations were made on the effects of several important system parameters, including inlet feed temperature, inlet sweep temperature, feed-side pressure, feed inlet CO concentration, and catalyst activity, on membrane reactor performance. The synthesis gases from both autothermal reforming and steam reforming were used as the feed gas. As the inlet feed temperature increased, the required membrane area reduced because of the higher WGS reaction rate. Increasing the inlet sweep temperature decreased the required membrane area more significantly, even though the required membrane area increased slightly when the inlet sweep temperature exceeded about 160 °C. Higher feed-side pressure decreased the required membrane area as a result of the higher permeation driving force and reaction rate. A potentially more active catalyst could make the membrane reactor more compact because of the enhanced reaction rate. The modeling results have shown that a CO concentration of less than 10 ppm is achievable from syngases containing up to 10% CO.
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1. Introduction

As an efficient and environmentally friendly energy conversion device, fuel cell has attracted worldwide interest for both transportation and stationary power generation in recent years (Acres, 2001; Barnett and Teagan, 1992; Cropper et al., 2004). Hydrogen is the most common fuel for the fuel cell. Due to the lack of large capacity storage systems, hydrogen used in an automotive fuel cell is suggested to be generated by on-site reforming reactions of the commonly available fuels, such as methanol, natural gas, gasoline, diesel, and bio fuel. Steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) are three major reforming processes (Brown, 2001; Ghenciu, 2002).

For transportation fuel cell applications, an important concern is the purity of hydrogen. The platinum electrocatalyst

in polymer electrolyte membrane fuel cells would be poisoned severely and irreversibly by even a very small amount of CO in the hydrogen, e.g., >10 parts per million (ppm) (Ahmed and Krumpelt, 2001). In addition, in order to fit into the restricted space in a vehicle, the whole fuel processor needs to be light and compact. Many studies have been conducted to explore CO-free fuel processing methods. Typically, water gas shift (WGS) reaction is used to convert CO in the synthesis gas from the reformer and generate additional H_2.

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \quad \Delta H_r = -41.1\,kJ/mol \tag{1}$$
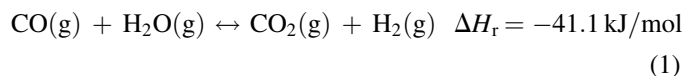
After that, a methanation or CO preferential oxidation step can be used to decrease the CO concentration further to about 10 ppm.

The WGS catalysts have been studied for a long time. A two-stage process is usually used in the industry: Fe_3O_4/Cr_2O_3 catalyst is used for the high-temperature shift (HTS), and Cu/ZnO/Al_2O_3 catalyst is used for the low-temperature shift (LTS). After the development of Cu/ZnO/Al_2O_3 during 1960s, the main industrial application of WGS reaction has been for the generation of H_2 for ammonia production and petroleum

Nomenclature

h	thickness of catalyst layer (cm)
J	permeation flux (mol/cm^2 s)
K_T	reaction equilibrium constant (1/atm^2)
ℓ	membrane active layer thickness (cm)
n	molar flow rate (mol/s)
p	pressure (atm)
P	permeability (Barrer)
r	volumetric reaction rate (mol/cm^3 s)
R	ideal gas constant (atm cm^3/mol K)
T	temperature (°C)
w	width of reactor (cm)
x	feed-side molar fraction
y	sweep-side molar fraction
z	axial position along the length of reactor (cm)

Greek symbols

α	CO_2/H_2 selectivity
ρ_b	catalyst bulk density (g/cm^3)

Subscripts

0	initial
f	feed-side
i	species
s	sweep-side
t	total

refining (Choi and Stenger, 2003; Rhodes *et al.*, 1995). The issues of an automotive application are fundamentally different from those of industrial use. The suitable catalysts should be very active and poison-resistant materials, which would result in a small reactor volume, short start-up time and good stability under transient or steady state conditions.

There are many studies focusing on catalyst preparation and the reaction mechanism in the literature for both classical and novel LT-WGS catalysts. The traditional Cu/ZnO/Al$_2$O$_3$ catalyst has shown good activity at about 180–240 °C as the result of the optimal adsorption heat of CO on Cu (about 80 kJ/mol) (Grenoble *et al.*, 1981). A number of studies on the reaction kinetics have been published (Amadeo and Laborde, 1995; Campbell, 1977; Fiolitakis *et al.*, 1980; Keiski *et al.*, 1993; Moe, 1962; Salmi and Hakkarainen, 1989). The main drawbacks of this catalyst are that it is pyrophoric and highly sensitive to sulfur poisoning. The Novel WGS catalysts active at low temperatures are normally based on platinum or gold. For many years, Pt/CeO$_2$ has been proven to be a very active WGS catalyst especially at high temperatures (Hilaire *et al.*, 2004; Mendelovici and Steinberg, 1985; Swartz *et al.*, 2001). However, the activity and stability of these ceria-supported catalysts need to be improved by optimizing the preparation conditions and formulations. Newly developed Pt-containing catalysts have shown improved durability over a wide range of temperatures (200–500 °C) (Ghenciu, 2002).

Gold-based catalyst for WGS reaction has been a new alternative investigated for the past decade (Andreeva, 2002;

Andreeva *et al.*, 2002; Fu *et al.*, 2001; Tabakova *et al.*, 2004). It has been reported that Au/Fe$_2$O$_3$ has higher activity than Cu/ZnO/Al$_2$O$_3$ starting from 120 °C (Andreeva, 2002). Additionally, improved stability has been obtained from Au/CeO$_2$ (Fu *et al.*, 2001). The activity and stability of these catalysts, however, are sensitive to the preparation techniques, gold particle size and specific gold-support interaction. Recent research by Fu *et al.* has shown that the active sites in these catalysts are gold or platinum ions strongly associated with the surface oxygen of ceria instead of gold or platinum metal nanoparticles (Fu *et al.*, 2003). This finding might significantly decrease the requirement for the precious metal.

In addition to the advancement of the WGS catalyst, a membrane reactor is another promising approach to enhance the CO removal and decrease the reactor size. The general principle of the membrane reactor is to improve the reaction performance with the in situ separation of one or more products. Several studies have been done on H$_2$-selective membrane reactors, mainly based on palladium membranes and using high-temperature WGS catalysts (Armor, 1998; Basile *et al.*, 1996; Criscuoli et al., 2000; Ma and Lund, 2003; Tosti *et al.*, 2003; Uemiya *et al.*, 1991; Xue *et al.*, 1996). By using a novel type of membrane (Huang *et al.*, in press; Ho, 2000; Zou and Ho, 2006; Zou *et al.*, 2007), the CO$_2$-selective WGS membrane reactor is more advantageous than the H$_2$-selective membrane reactor because (1) a H$_2$-rich product is recovered at high pressure (feed gas pressure) and (2) air can be used to sweep the permeate, CO$_2$, on the low-pressure side of the membrane to obtain a high driving force for the separation.

In an earlier paper (Huang *et al.*, 2005), we proposed a CO$_2$-selective membrane reactor and developed a one-dimensional non-isothermal model to simulate the simultaneous reaction and transport process in the countercurrent WGS hollow-fiber membrane reactor. The modeling results have showed that a CO concentration of less than 10 ppm, a H$_2$ recovery of greater than 97%, and a H$_2$ concentration of greater than 54% (on the dry basis) are achievable from autothermal reforming syngas derived from gasoline using air as the oxygen source. If steam reforming syngas is used as the feed gas, H$_2$ concentration can be as high as 99.64% (on the dry basis). The model was later verified experimentally using a rectangular WGS membrane reactor with an autothermal reforming syngas at 150 °C (Zou *et al.*, 2007). For further investigation in this paper, we studied the effects of several important system parameters, including inlet feed temperature, inlet sweep temperature, feed-side pressure, inlet feed CO concentration, and catalyst activity, on the performance of the membrane reactor by using the established model. Both autothermal reforming syngas and steam reforming syngas were used as the feed gases.

2. Calculation description

As described in the earlier paper (Huang *et al.*, 2005), the WGS membrane reactor was configured to be a hollow-fiber membrane module with catalyst particles packed inside the fibers (Fig. 1). The hollow-fiber module was assumed to be composed of CO$_2$-selective facilitated transport membrane.