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New catalysts and reactor designs for the hydrogen economy [☆]

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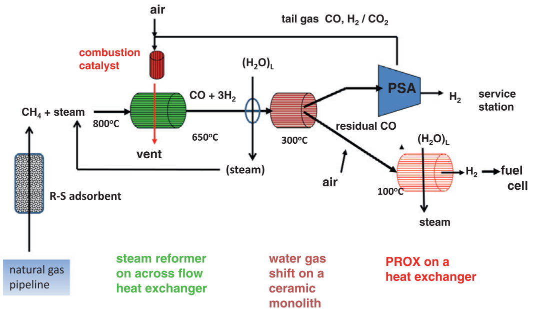
HIGHLIGHTS

- New catalyst and reactor designs for hydrogen generation of fuel cells.
- New precious metal catalysts on monoliths are used for hydrogen generation.
- Precious metals costs are mitigated by savings due to reduced capital cost.
- Applications are for combined heat and power.

GRAPHICAL ABSTRACT



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ABSTRACT

New catalyst and reactor designs are necessary to meet the expanding use of low temperature hydrogen based fuel cells. Residential and commercial power generation requires the reformer integrated to the fuel cell must be sufficiently small given that space is often a premium in many of these applications. Precious metal washcoated monolithic structures, similar to those successfully used since 1975 in automobile catalytic converters [1], provide high activity per unit reactor volume, low pressure drop and greater structural stability than traditional base metal catalysts in packed beds and thus are well suited for distributed hydrogen applications, New precious metal catalysts, with high activity densities, have been formulated for hydrogen generation since traditional base metal oxides have much lower activities per unit mass and thus are not sufficiently active when used in limited amounts as washcoats. The higher cost of precious metals is mitigated by savings due to reduced system size and existing metal recycling operations. Catalytic fuel processing, of infrastructure fuels (e.g. natural gas and LPG), are being reformed for the fuel cell to power homes, commercial and residential buildings, schools, hospitals. Such systems must operate safely and reliably in the user facilities while unattended. This brief review will illustrate the application of automotive washcoating technology to reformers for distributed hydrogen applications.

1. Introduction

The concept of distributed power allows electricity and heat to be generated onsite independent of a central power plant. Fuel cells supply heat and electricity without toxic emissions and are prime candidates for the emerging hydrogen economy. Their high efficiency (not bound by heat engine thermodynamic cycles) compared to traditional combustion technologies results in lower CO_2 emissions. Since low temperature fuel cells require hydrogen-rich gases for the anode, reformers using readily available infrastructure fuels such as natural gas are needed. Designs must be compact given the premium of space available in many applications, have lower pressure drop (natural gas is provided to sites at atmospheric pressure) and greater structural stability to resist attrition. They must also generate H_2 at a rate consistent with varying power demands. Large scale hydrogen plants cannot simply be reduced in size to meet the economic, safety, and frequent duty cycle requirements for fuel cell applications, hydrogen fueling stations, and small scale industrial uses such as hydrogenation reactions, gas

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turbine cooling, metal processing, etc. [2–4]. Consequently, there is a need to completely reassess how hydrogen can be made for distributed applications. This review presents some of the technological advantages of precious metal washcoated monoliths over traditional base metal pellet (or particulate) catalysts and packed bed reformers for reforming hydrocarbons for the generation of distributed hydrogen.

2. Large scale hydrogen generation

Hydrogen is generated in chemical plants by reforming sulfur containing hydrocarbon fuels such as natural gas [5]. Since sulfur is a poison to downstream catalysts it is removed by the catalytic hydrodesulfurization (HDS) shown as reactions (1) and (2). Reaction (1) is catalytic converting sulfur compounds to H_2S using a Co, Mo/Al_2O_3 catalyst at 350 °C, 15 bar at a space velocity (SV) $\sim 1000\ h^{-1}$. Reaction (2) is adsorption of the H_2S in a bed of ZnO at 350 °C.

$$H_2 + R - S \rightarrow H_2S + R - H \tag{1}$$

$$H_2S + ZnO \rightarrow ZnS + H_2O \tag{2}$$

Desulfurization is followed by steam reforming which converts methane (the major component in natural gas) to H_2 and CO by reaction with steam as shown in reaction (3):

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \Delta H^\circ = 201\ \text{kJ/mol} \tag{3}$$

The catalyst is $Ni/\alpha\text{-}Al_2O_3$ in a packed bed tubular reactor operating at 800 °C, 15–20 bar and a space velocity $\sim 3000\ h^{-1}$.

Carbon monoxide (CO) is then reacted in 2 steps (high and low temperature water gas shift) with additional steam to further generate more H_2 while reducing the CO content generating CO_2 (reaction (4)):

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H^\circ = -44\ \text{kJ/mol} \tag{4}$$

The high temperature shift reaction is carried out using an Fe, CrO_x catalyst in a packed bed at 350 °C at reformer pressure and SV $\sim 5000\ h^{-1}$. The low temperature shift reaction uses CuO, ZnO, Al_2O_3 in a packed bed at 180 °C at reformer pressure and a SV $\sim 3000\ h^{-1}$.

The H_2 purification step utilizes pressure swing adsorption (PSA) where all gaseous components, except most of the H_2, are adsorbed in a zeolite. About 90% of the purified H_2 is withdrawn at pressure from the chamber with the 10% remains on the zeolite. A reduction in pressure in the PSA chamber desorbs CO_2, H_2 and residual CO from the zeolite. This "tail gas" is sent to a combustor where the H_2 shown in reaction (5) and traces of CO are oxidized supplying some of the heat required for the endothermic stream reforming reaction.

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad \Delta H^\circ = -243\ \text{kJ/mol} \tag{5}$$

A schematic of the traditional reformer process is shown in Fig. 1.

3. Applicability of traditional hydrogen generation for distributed H_2 applications

The HDS process in large hydrogen plants is carried out at high pressure and temperatures [5]. These conditions are too severe for safe and economic operation (high H_2 compression costs) in commercial buildings, schools and homes. The natural gas is supplied to buildings slightly above atmospheric pressure at ambient temperature.

Steam reforming (SR) of natural gas, catalyzed with Ni pellets operating at atmospheric pressure in multi-tubular reactors is being employed successfully in first generation fuel cells. However issues of pressure drop, heat transfer, system-size, sulfur-containing compounds, such as H_2S always present in natural gas, and air sensitivity exist. The NiO catalyst must be activated by reduction to the metallic state to generate the active sites for SR. One other major design consideration for SR is heat transfer resistance. With tubular reactors, containing packed beds of catalyst, heat transfer from the combustion gas through the outer tube wall through the radial catalyst bed limits the rate of reaction. This can be understood by reference to Fig. 2. Here we see desulfurized CH_4 and steam entering multi-tubular reactors containing packed beds of catalyst. The rate of steam reforming is highest for the catalyst in direct contact with the externally heated tube wall. Moving radially from the tube wall the catalyst bed is cooler due to the endothermic steam reforming reaction and insufficient heat transfer. To minimize this effect H_2 plants operate with small diameter tubular reactors allowing for improved heat transfer to the entire but results in higher pressure drop. These complications can be addressed with a heat exchanger washcoated with a high activity catalyst providing enhanced heat transfer. These designs will be discussed later.

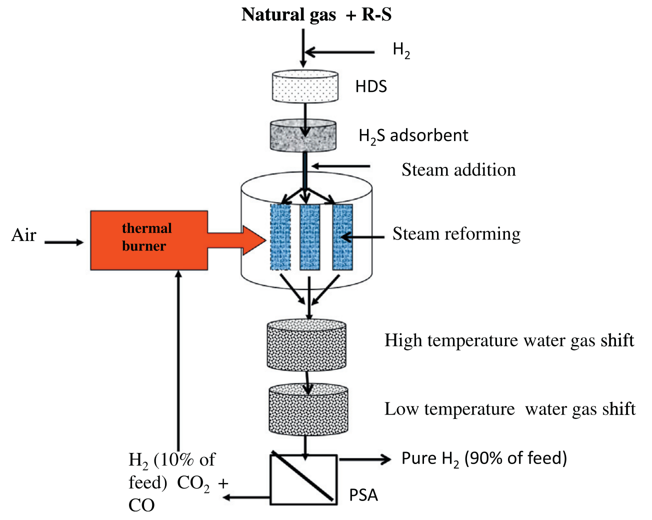

Fig. 1. Traditional packed bed of catalysts for high pressure H_2 generation with HDS, steam reforming, water gas shift, pressure swing adsorption (PSA) and tail gas oxidation.

Water gas shift catalysts, mainly CuO, ZnO, Al_2O_3 in pellet form, are being employed in some first generation fuel processors. They

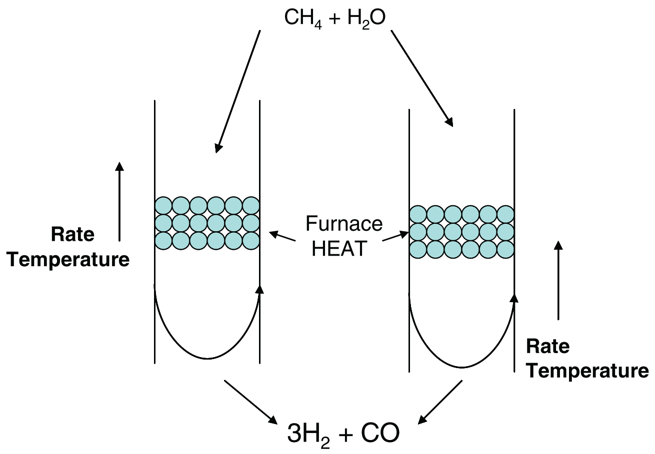

Fig. 2. Schematic demonstrating heat transfer resistance and decreasing SR rate towards the center of the bed.