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Catalytic hydrogen production from fossil fuels via the water gas shift reaction

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HIGHLIGHTS

- Hydrogen is a clean alternative to hydrocarbon fuels.
- Hydrogen is primarily produced with the water gas shift reaction.
- Development of water gas shift catalysts is essential to the energy industry.
- This work summarizes recent progress in water gas shift catalyst research.

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ABSTRACT

The production of hydrogen is a highly researched topic for many reasons. First of all, it is a clean fuel that can be used instead of hydrocarbons, which produce CO₂, a greenhouse gas emission that is thought to be the reason for climate change in the world. The largest source of hydrogen is the water gas shift (WGS) reaction, where CO and water are mixed over a catalyst to produce the desired hydrogen. Many researchers have focused on development of WGS catalysts with different metals. The most notable of these metals are precious and rare earth metals which, when combined, have unique properties for the WGS reaction. Research in this area is very important to the energy industry and the future of energy around the world. However, the progress made recently has not been reviewed, and this review was designed to fill the gap.

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1. Introduction

The desire for an economic and feasible hydrogen production process can be attributed to climate change. Currently, fossil fuels are burned to create heat and energy. Several technologies are in development to capture CO₂ produced from large point sources [1–6]. There is now a desire to move away from directly burning these hydrocarbons and toward using hydrogen for energy. The question then is where can we get hydrogen?

The answer is also from fossil fuels, such as coal and natural gas. These resources are abundant and domestic products in the United States. Natural gas production has increased in the past decade due to the contribution of advances in hydraulic fracturing and horizontal drilling techniques. These techniques have opened large amounts of natural gas resources that were previously uneconomic to target. These new resource plays such as tight gas and shale gas have a promising future in the energy sector. As of December 31, 2011, the U.S. EIA (Energy Information Administration) estimates 348.8 trillion cubic feet of natural gas and 483 billion short tons of coal reserves in the United States alone [7]. These resources can be further utilized to produce hydrogen instead of being used as a fuel directly. This is due to the fact that hydrogen is clean burning and only produces water. Steam reforming and the water gas shift (WGS) reaction still produce the same amount of CO₂ as if the fuel were simply combusted; the only difference is that the carbon dioxide is at a single point and can then be removed from the product stream and sequestered. Hydrogen can also be utilized in other parts of the world, either from natural gas or coal, depending on location and the resources available. The major production of hydrogen is from steam reforming and coal gasification. The steam reforming and coal gasification reactions create synthesis gas (syngas, a mixture primarily of CO and H₂), and can be further reacted by the WGS reaction to produce more hydrogen.

In recent years, there has been substantial progress made in the WGS reaction. New catalysts have been studied using nanoparticles of a catalytically active metal on a support. There have been studies of many types of WGS catalysts such as iron, copper, cobalt, gold, platinum, and rare earth metals such as cerium, samarium, gadolinium, and lanthanum. The state of the art research in WGS catalysts focuses on rare earth metals to support either previously used metal catalysts or new, more progressive, catalysts such as gold and platinum. The new research targets ceria as a major contributor in the WGS reaction catalyst. This is due to the oxygen storage capacity (OSC) of ceria and its ability to enhance the activity of the supported metals. This review of WGS catalyst development was designed to assist engineers and other energy-field scientists in understanding the progress in this area. Other aspects important to WGS are left for other reviews, such as reactor engineering.

The WGS reaction is expressed as



For clarity, data for CO conversion reported in this review has been recalculated, when necessary, such that CO conversion is defined as

$$X_{\text{CO}} = \frac{y_{\text{CO, in}} - y_{\text{CO, out}}}{y_{\text{CO, in}}} \times 100\% \quad (\text{E1})$$

where $y_{\text{CO, in}}$ and $y_{\text{CO, out}}$ are the mole fractions of CO at the inlet and outlet of the reactor, respectively. Alternatively, CO conversion can be defined as

$$X_{\text{CO}} = \frac{N_{\text{CO, in}} - N_{\text{CO, out}}}{N_{\text{CO, in}}} \times 100\% \quad (\text{E2})$$

where $N_{\text{CO, in}}$ and $N_{\text{CO, out}}$ are the molar flow rates of CO at the inlet and outlet of the reactor, respectively. It is assumed in this paper

that CO conversion is due only to the WGS reaction. Because the WGS reaction has a conservation of moles, the total molar flow rate remains constant throughout the reactor, and E1 and E2 are essentially the same equation. Equilibrium curves in this review are calculated from correlations provided by Callaghan [8], and they are then used to verify equilibrium data provided in original works or to add it for comparison when equilibrium is not provided. Small discrepancies between experimental data and equilibrium data are likely due to experimental error or differing assumptions between Callaghan [8] and the team performing the original research. Catalysts which achieve a conversion higher than the thermodynamic equilibrium may also show some affinity for side reactions, such as methanation or coking, in which the calculated CO conversion is due to more than just WGS.

2. Coal and natural gas based hydrogen production

2.1. Production of syngas

The industrial production of CO and initial amounts of H₂ occurs in two main processes: the first is steam reforming of methane, denoted as R2, and the second method is coal gasification, shown as R3.



The steam gasification reaction, R3, is endothermic ($\Delta H = 131$ kJ/mol) [9,10]. Steam reforming of methane can be described as mixing excess steam with a methane stream to produce CO and hydrogen gas, while steam gasification incorporates coal and steam to produce lesser amounts of hydrogen per carbon gasified. The steam reforming reaction is run at temperatures above 700 °C where the reaction is spontaneous [11]. This method is currently more economical (in the US) to make hydrogen due to the low price of natural gas, while also giving the highest H₂/CO ratio as compared to higher molecular weight hydrocarbons and coal. This is due to the fact that, with coal, the hydrogen is separated from water only, while petroleum-derived fuels have significant hydrogen content. And finally, methane has the highest hydrogen/carbon ratio of petroleum hydrocarbons.

Coal is a mixture of compounds and the composition varies between coal seams and coal types, so a heat of reaction for gasifying coal, R3, is not necessarily useful. Coal rank also affects the gasification, and it is found that reactivity decreases as coal rank increases [12]. Generally, a small portion of coal is burned to heat the reactor to gasification temperatures, while water is fed either with the coal in a slurry or separately. Excess water can also be added if WGS reaction is desired downstream [9].

There are two steps to coal gasification, first is pyrolysis and the second is char gasification. Pyrolysis expels the volatile content of the coals, usually tars and non-condensable gasses [12]. Char gasification is described by R3 and R4, where R4 is the reverse Boudouard reaction.



The reverse Boudouard reaction has a change in enthalpy of 159.7 kJ/mol [12], making it endothermic and requiring heat.

2.2. WGS of syngas

The WGS reaction (R1) is used to reduce the CO content of the gas stream or to adjust the H₂/CO ratio for further chemical production. WGS reactions are slightly exothermic and releases heat ($\Delta H = -41$ kJ/mol) [11], and increases in temperature decrease the equilibrium conversion [9]. Therefore, a compromise between

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