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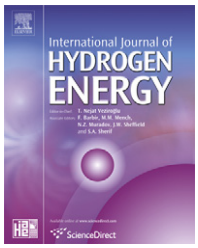

Hydrogen generation from a catalytic water gas shift reaction under microwave irradiation

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ABSTRACT

A new device with microwave irradiation has been developed to trigger hydrogen generation from a water gas shift reaction (WGSR) in this study. In the experiments, the effect of a high-temperature catalyst on the WGSR is investigated. The results indicate that the increase of hydrogen generation tends to slow down once the gas hourly space velocity (GHSV) decreases and approaches 28,000 h^{-1}. When the steam/CO ratio is low, for example, steam/CO = 1, a concave up curve of CO concentration, characterized by conventional heating methods, is not observed a microwave irradiation environment. This comparison shows that the performance of the WGSR with microwave irradiation is better. It is noted, however, that cracks may occur on the catalyst surface as a result of less water to relieve the high thermal gradient, stemming from the microwave radiation on the catalyst bed. With an increase in the reaction temperature or steam/CO ratio, a smoother increase in CO conversion is observed, as opposed to those observed in conventional heating methods. This is attributed to the fact that the energy absorption by steam and the catalyst is more efficient under the effects of microwave radiation. As a whole, this study shows that the microwave reactor heats faster, provides more efficient energy transfer to reactants and minimizes the space needed to achieve the desired results.

1. Introduction

Hydrogen is well known for its clean and high power density characteristics. Public concerns of the rapid consumption of our petroleum reserves (or oil price rise), global warming (or carbon dioxide emissions) and air pollution problems, have made the development of hydrogen as an alternative fuel to fossil fuels more important [1,2]. The role played by hydrogen in the applications of fuel cells is especially remarkable.

Hydrogen generation is the first step to establish a hydrogen economy [3]. In the past, a number of techniques, consisting of the thermochemical, electrochemical, photobiological and photoelectrochemcial methods, have been developed to produce hydrogen [4]. Despite the numerous methods developed so far, the thermochemical technique is still the most common method for hydrogen generation. Conventionally, hydrogen is produced by the process of steam reforming of hydrocarbons such as natural gas (or methane) [5,6], methanol [7], ethanol [4,8] or naphtha oil. The concentration of hydrogen in gas produced from the steam reforming is usually not sufficiently high enough for industrial purposes. For example, the raw product gas from the steam reforming of methanol contains approximately 75% H_2, 20% CO_2 and 5% CO by volume [9]. Therefore, the product gas can't be used in fuel cells yet. The hydrogen within the product gas can be further enriched by means of a water gas shift reaction

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(WGSR) [10–12], followed by using membranes to separate and purify hydrogen [13].

WGSR is a moderate exothermic reaction in nature and it is difficult to be active under normal conditions alone. Because of this, a variety of catalysts have been prepared and used to reduce the activation energy of the WGSR and to trigger hydrogen generation. Commercially, Fe–Cr-based catalysts and Cu–Zn-based catalysts are the most common high-temperature and low-temperature catalysts, respectively. In addition to the aforementioned catalysts, a variety of catalysts such as Co–Mo oxide [14], Au/CeO_2 [15], Pt/CeO_2 [16], Cu- and Cu, Zn–ZSM-5 zeolite catalysts [17], and B, Cu, Ba, Pb, Hg or Ag added in Fe_3O_4/Cr_2O_3 catalysts [18] have also been produced to aid in accomplishing the WGSR. Typically, a reactor with a conventional heating element [12,14,17] is used to carry out the WGSR to analyze the performance of the reaction and the effectiveness of the catalysts.

In the past decade or so, microwaves have been extensively applied in food processing, wood drying, plastic and rubber treating as well as the curing and preheating of ceramics [19–21]. Microwave ovens have also been widely used to heat food at home and they have become an essential household appliance. This arises from the fact that microwaves have the characteristic of providing rapid and energy-efficient heating on materials. Physically, when certain materials contain dielectrics such as water and fat, these materials can be heated rapidly and the temperature rises in a short time, through a process of dielectric heating [20]. In this process, the dipole rotation and ionic conductance of polar substances or ionic species under the microwave irradiation are excited rapidly.

In the past, a number of researchers have used microwave heating methods to study catalytic reactions, such as the production of hydrocarbons [22], CO oxidation [23], selective oxidation of toluene to benzoic acid [24] and methanol–steam reforming [25]. For example, in the study of Perry et al. [23], it was illustrated that microwave heating could significantly increase the rate of CO oxidation, but there was no microwave specific effect on the kinetics of CO oxidation on a 5-wt% Pd/Al_2O_3 catalyst. The study of Liu et al. [24] found that, in the microwave catalytic process, the optimum reactor bed temperature of the selective oxidation of toluene to benzoic acid decreased to 500 K, in contrast to 600 K in the conventional process. A single catalyst pellet model and a two-dimensional packet-bed model were proposed by Perry et al. [25] to investigate the methanol–steam reforming reactions under the effect of a CuO/ZnO catalyst. Their results suggested that the reaction productivity would increase significantly when microwave heating was used in the single catalyst pellet model. The microwaves could also minimize radial heat-transfer effects in a two-dimensional packet bed.

The literature reviewed above has provided some important information relating the effects of microwaves upon catalytic reactions. However, to these authors' knowledge, so far the research of WGSR under the impact of microwave irradiation and heating is still absent. It is known that water is an essential reagent in the WGSR and it is easily heated by microwave irradiation. In addition, the study of Peelamedu et al. [26] has emphasized that iron oxides, which are contained in the presently adopted catalyst, were well-microwave absorbed dielectrics when the reaction temperature was below 600 °C. Because of the double-absorption effect of microwaves by water and the catalyst, it is anticipated that microwave radiation is a very suitable mode to excite the WGSR. For this reason, a study of a new device to trigger WGSR using microwave irradiation has been conducted. Moreover, the results of hydrogen generation with microwave irradiation will be qualitatively compared to that with conventional heating [12] to understand the interaction of microwaves and WGSR. The potential of the microwave reactor for hydrogen generation will be addressed eventually.

2. Experimental

2.1. *Microwave reactor*

A schematic of the entire reaction system is displayed in Fig. 1. The key unit of the reaction system is the microwave reactor (pending for US and ROC patents). In the reactor, the main components consist of a reaction tube, a K-type thermocouple, a mixing layer and a catalyst bed. These components are installed in a chamber, which contains a magnetron to produce microwaves. The microwave frequency was fixed at 2.45 GHz and the maximum power of the microwave source was 800 W. Hence, when a WGSR was performed, the aforementioned components were exposed to an environment with microwave radiation. In a previous study with conventional heating [12], a preheater was used to preheat the mixture of water and CO and to make the reagents mix uniformly. This aided in carrying out the WGSR in the subsequent reactor. Instead, in the conducted microwave reactor, the preheating and reaction processes were integrated by combining the mixing layer and the catalyst bed, in series, in the reaction tube. The mixing layer was a packed bed filled with glass balls (3 mm). These balls provided a space for water residence and for facilitating the dissipation of water in the tube. It is known that water pertains to one of the dielectrics, which can be heated by microwaves rapidly. Therefore, water was transformed into steam in the mixing layer and a mixture of CO and steam was formed therein. This enabled us to decrease the size of the preheating unit in the microwave reactor, greatly reducing the experimental space needed. Following the mixing layer, the WGSR was triggered in the catalyst bed under the effects of microwave irradiation. Another design that should be mentioned in the microwave reactor is that the thermocouple was inserted in the catalyst bed rather than mounted outside the reaction tube as it had been previously [12]. The thermocouple was shielded by an alumina tube to prevent microwaves from being absorbed by any metallic part of the thermocouple [27]. This eliminated the interference in electrical signal due to microwaves in the thermocouple. Seeing that the measured temperature in the catalyst bed represented the exact reaction temperature, a more accurate control in the reaction temperature was achieved. Other than the microwave reactor, the other units