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Hydrogen generation by direct decomposition of hydrocarbons over molten magnesium

K. Wang, W.S. Li, X.P. Zhou *

Department of Chemical Engineering, Hunan University,
Chang Sha, Hu Nan 410082, China

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Abstract

Methane and higher hydrocarbons were directly decomposed to hydrogen and carbon over molten magnesium. Hydrogen and micrometer size carbon particles were formed as products. The catalyst losses activity because of the evaporation of metal Mg. The activity of the catalyst can be recovered by heating the upper cold section of the reactor to slide Mg back to the reactor bed. Mg_2C_3 was identified as reaction intermediate in the reaction. Compared to the reforming process, the hydrocarbon direct decomposition process produces CO-free hydrogen, does not emit CO_2 to environment, generates useful carbon powder, and is also an energy-saving approach for hydrogen preparation. To form each molar of hydrogen by methane direct decomposition only consumes about 65.1% of the energy as that needed in the steam reforming of methane. The reaction is also proved to be useful in the decomposition of waste polyolefins, such as ploy olefin plastic and rubber.

Keywords: Hydrogen preparation; Molten metal catalyst; Hydrocarbon decomposition; Molten metal catalysis

1. Introduction

As a fuel benign to the environment, hydrogen has attracted much attention in recent years. Currently, hydrogen is commercially produced from the steam reformation of natural gas [1] and coal [2] or from the dehydrogenation processes in petroleum industry [3–5]. There have been other investigations into the processes of hydrogen generation, such as the steam reformation of glucose [6,7] and methanol [8,9], and alcohol partial oxidation [10–11]. These processes, however, were found to be energy consuming and the hydrogen produced usually contains CO, making the direct application of the generated hydrogen in proton exchange membrane fuel cells dissatisfactory. It was also proven that hydrogen could be produced from the photocatalytic decomposition of biomass [12–13] and water [14] as well as the enzyme-catalyzed decomposition of sugar [15,16]. However, the hydrogen production rate is not high enough to meet the commercial requirement. High efficient catalysts or enzyme are needed to bring the arts to industrialization. There are reports on hydrogen generation via methane direct decomposition over solid catalysts [17–19], but the lifetime of the catalysts are usually short. Better technology is required to deal with the hurdles. There are advantages to generating hydrogen via the decomposition of hydrocarbons such as natural gas, polyolefin wastes, and asphaltum, which is shown as follows: (1) these are cheap hydrocarbons easily available, (2) carbon that finds wide industrial applications (such as in smelting industry) is formed as a by-product, and (3) no CO is produced along with hydrogen, thus high-purity hydrogen is obtained as an ideal fuel for fuel cells. In addition, polyolefins as waste are difficult to degrade naturally and so this process can solve two problems simultaneously. Traditional methods such as direct burying and burning are known to be problematic. There have been reports on degradation by means of pyrolysis [20,21], which found the resulting end-products to be difficult to handle and of little value. It is highly desirable, therefore, to find a technology for the direct decomposition of hydrocarbons to high-purity hydrogen and carbon. To achieve such a goal, we have derived a high-temperature homogeneous catalytic system using molten magnesium as catalyst. In this approach, the active metal sites are not poisoned due to the ready diffusion of the liquid metal.

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* Corresponding author. Fax: +86 731/8821017.
E-mail address: hgx2002@hnu.cn (X.P. Zhou).

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2. Experimental

2.1. Methane decomposition over Mg

The stainless steel reactor(s) system is shown in Fig. 1. By means of the system, one can conduct either one-stage or two-stage reaction. In the former, reactant gas was fed in from Port **a** (by shutting Valve 1 and opening Valve 2) and gas samples were taken from Port 2 for analysis. In the two-stage case, reactant gas was fed in from Port **b** (by opening Valve 1 and shutting Valve 2) and gas samples were taken from both Ports 1 and 2 for analysis. The gas samples were analyzed on GC (Agilent 6890N) and GC/MS (Agilent 6890N/5973N).

2.2. Polymers and asphaltum decomposition over Mg

In this method, a two-stage reactor system was designed to carry out the reaction. In the first reactor, 2.0 g of magnesium mixed with 2.0 g of polymers or asphaltum was loaded and another 2.0 g of magnesium was loaded in the second reactor. Before the reaction, inert gas argon (5 ml/min) was used to flush the reactors for 20 min to remove air from the two reactors. An oven with temperature-control program was employed to regulate the heating of the reactors. The second reactor was heated from 20 to 700 °C in 30 min before being kept at 700 °C. The first reactor was heated in stages: (i) from 20 to 250 °C in 30 min, (ii) to 500 °C at a rate of 1 °C min^{-1}, (iii) to 700 °C within 30 min at the same heating rate as stage (ii), and (iv) finally kept at 700 °C for 30 min for complete polymers decomposition.

2.3. In situ FTIR diffusion-reflection

The in situ FTIR diffusion-reflection analysis was performed on a Nicolet NEXUS 670 spectrometer with a Harrick reactor cell HVC-DRP (Harrick Scientific Corporation). The metal Mg powder sample 0.200 g was loaded into the reactor cell. The reactor cell was heated to 400 °C in vaccum (2.5×10^{-4} Pa) for the removal of adsorbed impurities. A background spectrum was first recorded as reference of future spectra. Then the cell was isolated from pumping and CH_4 was passed into the cell at 400 °C to reach a pressure of 1.0 atm; spectra were recorded at different time periods as indicated.

3. Results and discussion

In this work, molten magnesium was employed to catalyze the decomposition of hydrocarbon in stainless steel reactor(s) shown in Fig. 1. By means of the reactor system, one can conduct either one-stage or two-stage reaction (see Section 2). In methane decomposition, the control experiment showed that when without catalyst, methane started to decompose at 500 °C and with the increase of reaction temperature, the methane conversion increased and reached 5.1% at 700 °C (Fig. 2). In the presence of molten Mg, the methane decomposed at 300 °C and methane conversion was much higher than the case without catalyst. However, the equilibrium conversion of methane calculated from thermal dynamics is much higher than the cases of both with and without catalyst. The equilibrium methane conversion is 84.1% at 700 °C. Therefore, it is possible to obtain higher methane conversion by finding high efficient catalyst.

For the one-stage approach, we monitored the decomposition of methane at 700 °C for 123 h. Hydrogen concentration was above 42% in the first 75 h and then declined gradually to around 28% at the 123 h (Fig. 3). In the two-stage approach, higher hydrogen concentration was achieved. As shown in Fig. 3b, a hydrogen concentration higher than 42% (the rest is methane) was obtained after the first reactor, and after the second reactor, hydrogen concentration was above 60%. In ethane decomposition under similar conditions, hydrogen concentration was higher than 70% within a period of 95 h (Fig. 3c) and methane was the only gaseous by-product. In the methane and ethane decomposition reactions, fluffy carbon species was found accu-

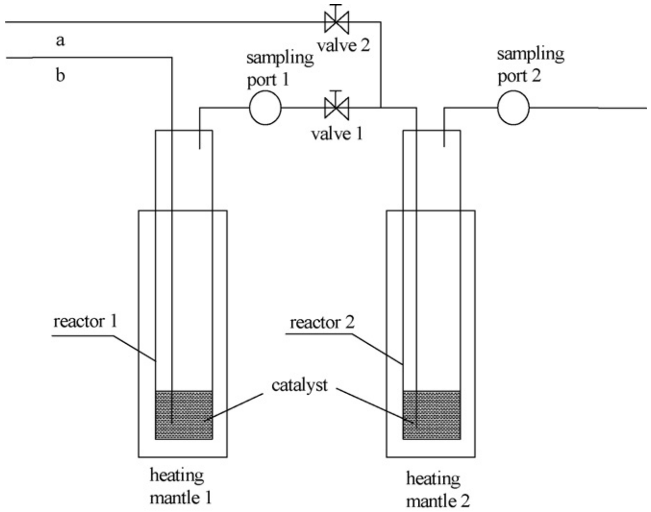

Fig. 1. Reactor system. The stainless steel reactors have i.d. of 16 mm, o.d. of 18 mm, and length of 200 mm and the gas leading tubings have o.d. of 4 mm and i.d. of 3 mm.

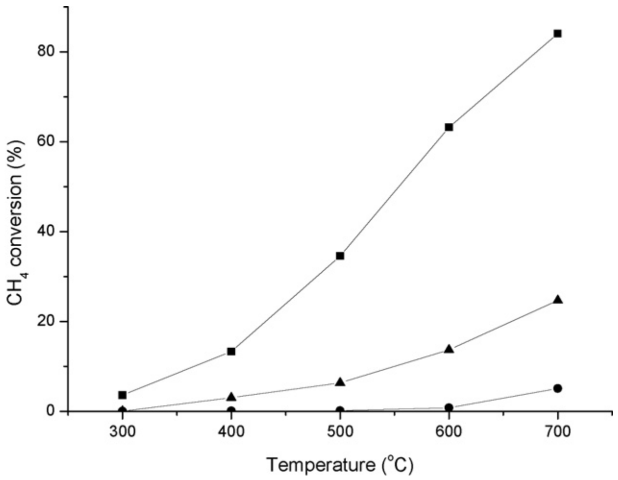

Fig. 2. Methane conversion at different temperature. (●) Without catalyst, (▲) over molten Mg, and (■) the equilibrium conversion of methane according to thermal dynamic calculation.