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High-purity hydrogen gas production by catalytic thermal decomposition using mechanochemical treatment

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ABSTRACT

The objectives of this work, were to produce high-purity hydrogen gas from rice husk by two-step process and to study the effect of nickel hydroxide/nickel acetate/sodium acetate and calcium hydroxide on the concentration of gaseous products. The samples were characterized by X-ray diffraction (XRD) and thermogravimetry-mass spectroscopy (TG/MS). The gaseous products were analyzed by gas chromatography (GC). The results indicated that hydrogen gas was produced from the milled samples by heating at 400–600 °C with the low concentrations of methane, carbon monoxide and carbon dioxide. The highest concentration of hydrogen gas from milled samples with the catalyst, was approximately 95–97 %mol. Furthermore, the milled samples with the carbon dioxide capture agent gave the carbon dioxide concentration, was below 2 %mol.

Introduction

In the case of biomass, the production of hydrogen gas by the process of steam reforming has become an attractive and widespread research due to its inexpensiveness. Because of biomass produces a low net emission of carbon dioxide and the low emissions of NO_x and SO_x. It could help to reduce the effects of global warming and acid rain [1]. However, the steam reforming of biomass in hydrogen gas production has some disadvantages. For example, tar formation and the steam reforming process need high temperature and several techniques of gaseous separation in order to obtain the high purity of hydrogen gas (gaseous concentration is approximately 90–99.9 %mol) [2].

Tongamp W and Zhang Q et al. [3–8] studied on the hydrogen production by employing a reaction in order to avoid those disadvantages. The reaction is similar to the reaction of steam

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reforming (as shown in reaction (1)). It comes from polymer pellet and cellulose (analytical reagent grade), which is using preliminary mechanochemical treatment. Additionally, a solid-state operation was found out by applying the process of mechanochemical treatment. They employed the mechanochemical treatment with catalyst and the carbon dioxide capture agent followed by the thermal decomposition at low temperature.

$$C_nH_m + nH_2O + heat \rightarrow nCO + (n+1/2\ m)H_2 \quad (1)$$

Many catalysts were applied in the reactions of steam reforming for the hydrocarbons decomposition. The catalysts refer to Rh, Ru, Pd, Pt, Ni, zeolite, alumina, zirconia and alkali based compounds. However, the decrease of tar formation, nickel and nickel-based compounds are the most frequently used because of its inexpensiveness and high reactivity [1,4]. Furthermore, carbon dioxide capture agent, such as, calcium/lithium hydroxide and calcium/lithium oxide, could react with carbon dioxide in carbonation to obtain CO_2 free hydrogen [3–9].

Rice husk is the major agricultural biomass in Thailand. In addition, rice husk causes crucial environmental issues such as disposal issue, methane emissions, and breathing issue [10]. In this work, we propose the two-step process for the high-purity of hydrogen gas production from rice husk. The first step of the process is to mill the samples which are rice husk, three catalysts of nickel hydroxide, nickel acetate and sodium acetate. Calcium hydroxide is used as a carbon dioxide capture agent. They are dispersed milling on the rice husk in order to obtain homogeneous mixtures by the process of mechanochemical treatment. The second step is that the milled samples are heated to produce hydrogen by thermal decomposition via steam reforming. Furthermore, the effects of using catalysts and carbon dioxide capture agent on concentration of gaseous products in hydrogen production are evaluated.

Materials and methods

Materials

Rice husk that is agricultural biomass from rice milling in Lampang province, Thailand were dried at 60 °C for 60 min. Rice husk was milled by a grinder and sieve to obtain the fine particles (≤365 μm). This sample was kept in the desiccator until it was used.

Nickel hydroxide ($Ni(OH)_2$) from Kanto chemical co., Inc., nickel acetate ($(CH_3COO)_2Ni$) and sodium acetate (CH_3COONa) from Wako pure chemicals industries Ltd. were used as catalysts. Furthermore, calcium hydroxide ($Ca(OH)_2$) from Wako pure chemicals industries Ltd. was used as a carbon dioxide capture agent.

Methods

Mechanochemical treatment with $Ni(OH)_2$ and $Ca(OH)_2$

Rice husk, $Ni(OH)_2$ and $Ca(OH)_2$ were used as starting materials. The cellulose ($C_6H_{10}O_5$) represents the use of chemical formula and chemical reaction to rice husk. Furthermore, hydroxyl group in nickel/calcium hydroxide represents water in the steam-reforming reaction. According to the ideal reactions that summarized in reactions (2) and (3), the samples were mixed at molar ratios of (1:0.5:6) for ($C_6H_{10}O_5$:$Ni(OH)_2$:$Ca(OH)_2$) and (1:6) for ($C_6H_{10}O_5$:$Ca(OH)_2$). The 4.0 g of the mixtures were milled by planetary ball mill (Pulverisette-7, Fritsch, Germany), which has two mill pots (45 cm^3 inner volume each) made of ZrO_2 with 7 × 15 mm diameter of ZrO_2 balls. According to the researches of William T and Qiwu Z et al. [3–8], they found the proper rate of the optimum milling speed and the milling time were at 700 rpm and 120 min, respectively. Therefore, this work decided to use same proper milling speed and milling time as their results.

$$C_6H_{10}O_5 + 0.5Ni(OH)_2 + 6Ca(OH)_2 \rightarrow 11.5H_2 + 0.5Ni + 6CaCO_3 \quad (2)$$

$$C_6H_{10}O_5 + 6Ca(OH)_2 \rightarrow 11H_2 + 5CaCO_3 + CaO + CO \quad (3)$$

Mechanochemical treatment with $(CH_3COO)_2Ni/CH_3COONa$ and H_2O

Rice husk, $(CH_3COO)_2Ni/CH_3COONa$ and H_2O were used as starting materials. The cellulose ($C_6H_{10}O_5$) also represents rice husk for the use of chemical formula and chemical reaction. According to the unpublished research of Zhang Q, he found that the optimum of starting materials ratio was (1.00:0.02:0.02) for ($C_6H_{10}O_5$: $(CH_3COO)_2Ni$: CH_3COONa). Additionally, he found out the optimum milling speed at 300 rpm and the milling time at 60 min.

In this path, water was used as a precursor for the reaction at different volume (0, 1.5, 4.5 and 6.5 cm^3). The ideal reactions in this path are followed in reaction (4)–(6).

$$C_6H_{10}O_5 + 7H_2O \rightarrow 12H_2 + 6CO_2 \quad (4)$$

$$(CH_3COO)_2Ni + H_2 \rightarrow 2CH_3COOH + Ni \quad (5)$$

$$2CH_3COONa + H_2O + heat \rightarrow 2CH_4 + Na_2CO_3 + CO_2 \quad (6)$$

Thermal decomposition

The mixtures, which were prepared by mechanochemical treatment, were put on a sample tube in a glass tube. The glass tube connected to the source of argon gas and entered in a furnace with discharge line for the collecting gaseous products [3–8]. The sample was heated in the furnace from room temperature to 600 °C for 60 min at heating rate of 20 °C/min. The gaseous products were collected through the discharge line in an aluminum pack.

Characterization method

Ultimate analysis. The percentage of carbon, hydrogen, oxygen, sulfur and nitrogen in rice husk was determined by CHNS/O analyzer (PE 2400 series II, Perkin–Elmer, U.S.A.) for the ultimate analysis. Moreover, the calorific value of rice husk was characterized by bomb calorimeter.