Renewable Energy 41 (2012) 23–28

Contents lists available at SciVerse ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Hydrogen production by catalytic cracking of rice husk over Fe_2O_3/γ-Al_2O_3 catalyst

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ARTICLE INFO

Article history:
Received 4 January 2011
Accepted 7 September 2011
Available online 4 November 2011

Keywords:
Hydrogen
Catalyst characterization
Continuous pyrolysis
The secondary catalyst cracking
Hercynite

ABSTRACT

$Fe_2O_3/\gamma-Al_2O_3$ catalyst is prepared by incipient wetness impregnation. The catalyst is characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The catalytic activity of $Fe_2O_3/\gamma-Al_2O_3$ catalysts is evaluated via the experimental study on the catalytic cracking of rice husk to produce hydrogen in a self made biomass continuous pyrolysis system. The results show that the reaction activities of the catalysts are greatly influenced by the calcinations temperature for catalyst, the secondary catalytic pyrolysis temperature and the mass ratio of Fe to Al. When the calcinations temperature is 550 °C, the pyrolysis temperature is 500 °C, the secondary catalytic pyrolysis temperature is 700 °C, and the Fe to Al mass ratio is 0.07, the experimental results indicate that $Fe_2O_3/\gamma-Al_2O_3$ catalyst could fully convert the volatile matters from biomass pyrolysis into small molecular gases such as H_2, CH_4, CO, CO_2, C_2H_4 and C_2H_6. Meanwhile, the catalyst has shown fine catalytic activity and stability as well as good resistance to coke deposition.

1. Introduction

At present, there is a growing interest in the use of hydrogen as a clean energy vector, especially for power generation in fuel cells. In this respect, hydrogen production from renewable biomass is particularly suitable for sustainable development concerns [1]. The methods of hydrogen production from biomass energy at home and abroad are mainly thermochemical conversion, microbial conversion and chemical reforming. Biomass thermochemical conversion for hydrogen production includes gasification, supercritical conversion, high temperature decomposition and methane, methanol, ethanol conversion and so on [2,3]; the microbial conversion includes direct biological photolysis, indirect biological photolysis, light fermentation, dark fermentation, and microbial fuel cell technology; and the chemical reforming process can also convert methane, methanol, ethanol and other simple compounds into hydrogen [4–7].

To obtain hydrogen from biomass, pyrolysis and gasification are two main effective thermochemical conversion methods. In the process of traditional pyrolysis, with air introduced in the over all process, the energy density of gas product is decreased due to the appearance of N_2 and CO_2 dilution, resulting in increased difficulty in gas separation [8]. More important, there is always large content of tar that is a serious threat to the downstream fuel cell system, both for the electrodes and for the pipelines in the traditional gas producing process [9–13]. The method of continue pyrolysis was adopted in order to avoid air being introduced, and to improve the purity of hydrogen. Moreover, the tar content in the pyrolysis gas was decomposed through the second catalytic cracking. At present, due to the advantages of converting tar into useful gases and adjusting the compositions of producer gases, the method of catalytic cracking for producing hydrogen-rich gas has been more interested since the middle 1980s. In the biomass catalytic cracking process, the dolomite and the Nickel-based catalysts are two kinds of the most common catalysts. The calcined dolomite is a highly efficient catalyst for removing tar, however, the conversion rate of tar catalyzed by dolomite was difficult to reach or exceed the range of 90–95%. Although dolomite could reduce the tar in the producer gas and change the distribution of tar compositions, it was difficult to convert the heavy tars [14]; as described by Zhang [15], Nickel supported on silica was active for tar catalytic cracking at relatively low temperature(550 °C), however, these catalysts could only maintain their activities for a short time because of large amounts of coke accumulation on their surfaces [16,17]. Merete Hellner Nilsen et al observed that Fe–Al-MCM-41 material could altered the quality of the bio-oil, especially significantly decreasing amount of phenols, acids, phenol compounds in comparison to the non-

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0960-1481/$ – see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.renene.2011.09.004

catalytic runs [18]. Moreover, the characteristics of $Fe_2O_3/\gamma-Al_2O_3$ could be satisfied with the criteria for catalyst.

2. Experiment

2.1. Reagents and instruments

The rice husk in the experiment was purchased from a rice processing plant in Zengcheng, Guangzhou. The distribution of rice husk particle size and approximate analysis result were shown in Table 1. The compositions of volatile matters are some small molecular gases (such as H_2, CO, CO_2, CH_4 and etc.) and some organic substances (such as acids, phenols and etc.).

$Fe(NO_3)_3 \cdot 9H_2O$ ($\geq$98.50% in purity) was purchased from Fuchen Chemical Reagent Co., Ltd. in Tianjin. And γ-Al_2O_3 carrier was purchased from Xinyu Chemical Packing Co., Ltd, whose composition is as follows: $SiO_2 + Al_2O_3 \leq 5\%$, $Fe_2O_3 \leq 1\%$, γ-$Al_2O_3 \geq 93\%$, $D = 3.6–4.7$ mm. The H_2 ($\geq$99.99% in purity) and N_2($\geq$99.99% in purity) are from Wugang Gas Co., Ltd in Shanghai.

The temperature programmed reduction (TPR) of catalyst was carried out on the AutoChemII-2920 instrument from Micromeritics Co., Ltd. The 0.05 g of catalyst sample was pretreated by heating in Argon flow to a temperature of 600 °C and keeping the temperature for 2 h in order to remove the adsorbed water and other contaminants and then cooling to 40 °C. Subsequently, the sample was heated up to 800 °C at a heating rate of 10 °C/min while the 10%H_2/N_2 mixture flowed over it at a flow rate of 20 ml/min. The effluent gas passed through a cold trap for removing the water content before the amount of hydrogen consumed during the reduction process being measured by the TCD detector. The scanning electron microscopic analysis on the catalyst was performed by FEI-XL30 environmental scanning electron microscope (SEM) with the accelerating voltage of 20 kV. The X-ray powder diffractograms were recorded following the step-scanning procedure (step size = 0.028, two theta degree scanning from 0 to 80) by using a computerised D/max-Ra diffractometer (Cu Ka radiation, $l = 0.15418$ nm). At a heating rate of 10 °C/min and a nitrogen flow rate of 50 cm^3/min, the thermal analysis (TG and DSC) on the catalyst was carried out on a STA449CJupiter® Simultaneous produced in NETZSCH Co., Ltd of German. A Pt crucible was used to contain about 0.89 mg of sample for the thermal analysis. The Fourier transmission infrared (FT–IR) spectra of the catalyst powders (as pellets in KBr) were recorded by using a Fourier transmission infrared spectrometer (Spectrum One FT-IR Spectrometer, Brucker VERTEX70, Germany) within the range of 4000–400 cm^{-1}.

For the pyrolysis producer gas, the GC analysis was performed by Agilent 6820 Gas Chromatograph (for H_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6) with N_2 as carrier gas. The GC is equipped with a HP-PLOT-Q column which is 30 m in length and 30 °C in temperature. The thermal conductivity detector (TCD) temperature was 250 °C.

2.2. Catalyst preparation

The Fe_2O_3/γ-Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 with $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solutions of different concentrations, and stirring for 2 h at room temperature, followed by drying at 70 °C overnight. The material was then calcined in air for 8 h at a desired value among 500 °C and 700 °C. By changing the concentration of Fe $(NO_3)_3 \cdot 9H_2O$ solution, the Fe dosages in the catalyst were controlled according to the ratios of Fe to Al, which are 0.02, 0.05 and 0.07 respectively.

2.3. Testing and analysis on the catalytic activity

Catalytic tests were conducted by using the biomass continuous pyrolysis system, which was made by us and shown in Fig. 1. The screw conveyer is made of mild steel, which length and diameter were 1000 mm and 26 mm, respectively. The number of revolution of the conveyer center axis was set at 18 r/min.

Rice husk was continuously transported to the pyrolysis reactor from the hopper by the screw feeder. The feeding rate was controlled by the rotary speed of the screw. The rice husk feeding rate was 390–410 g/h. The temperature in the pyrolysis reactor was set at 500 °C. The volatile pyrolysis constituents were piped into the catalytic cracking furnace through heat-insulated pipelines. Around 200 g of catalyst was placed in the catalyst bed in a quartz tube reactor fixed by two quartz brackets in the cracking furnace. The catalyst bed temperature was monitored by the central thermocouple in catalytic cracking furnace. For the catalytic test, all the catalysts had been reduced in H_2/N_2 (10/90 in vol.%) mixture at 800 °C for 120 min with the heating rate of 10 °C/min. After reduction of the catalyst, the catalytic cracking experiment was conducted. The charcoal yielded from rice husk pyrolysis, which is 32–35% of the total weight of rice husk, was pushed into the char box by the screw.

The gas flow rate was measured by a gas flowmeter. The pyrolysis gas, which was collected every 5 min with collecting bag, was analyzed by GC (Agilent GC6820).

For the same experiment, it was run for two times. And the data of the experimental was similar. Therefore, one of them was chosen to finish the Figs. 7–9.

T_0:Calcinations temperature, T_1: Pyrolysis temperature , T_2:Secondary catalyst cracking temperature, Fe/Al: Fe/Al mass ratio, W_{H_2}:Concentration of H_2, $W_{H_2} = V_{H_2}/V_{gases}$.

3. Results and discussion

3.1. Characterization of catalyst

The TG/DTG/DSC curves were presented in Fig. 2. From the figure, the TG and DTG curves showed the mass losses due to thermal decomposition at a N_2 atmosphere that occurred in two distinct regions. The Region 1 was observed that was from the ambient temperature to 127 °C with a peak at 92 °C. The mass loss in this region was characterized of released hydroscopic water. The Region 2, which was from 127 to 480 °C, was characterized by a two-steps decomposition process of Nitrate hydrate. It was concluded from the TG curves that the catalyst calcinations temperature must be higher than 480 °C in order to enable Nitrate hydrate to completely decompose. Between the ambient temperature and 693 °C, the DSC curves showed three well defined exothermic peaks due to the three effects of mass losses. Over 693 °C, the DTG curve was smooth. But there was an obvious peak appearing in DSC curve attributed to the hercynite formation by melting Fe_2O_3 into γ-Al_2O_3, which was in accordance with XRD pattern. In XRD pattern, the special peaks of hercynite were found in catalyst that was calcined at 700 °C.

Table 1
Granularity distributing and industrial analysis of rice husk.

Distribution of particle size/%					Industrial analysis/(wt) %			
>350 μm	350–245 μm	245–198 μm	198–165 μm	<165 μm	Moisture	Ash	Volatile material	Carbon fixation
0.89	26.70	41.06	12.61	18.75	2.47	12.67	67.57	17.30