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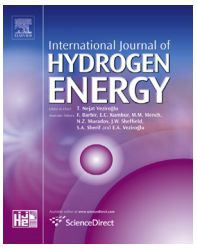

Supercritical water synthesis of bimetallic catalyst and its application in hydrogen production by furfural gasification in supercritical water

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ABSTRACT

Supercritical water not only provides good solvent of biomass gasification but also causes catalyst agglomeration. Therefore, the supercritical water synthesis method was utilized to guarantee the stability of the catalyst. In order to take into account the advantages of different metal catalysts, bimetallic catalysts were prepared based on Ni, Co, Zn and Cu, with TiO_2 as carrier. Hydrogen production by furfural gasification in supercritical water was conducted with different catalysts. The experimental results turned out that all combinations showed remarkable stability except for the combination Co + Ni. Zn + Ni and Cu + Zn showed better selectivity on hydrogen, and Co + Ni showed better carbon gasification efficiency. Spherical coke particles were obtained after the reaction with bimetallic catalysts, while the coke particles were amorphous after the reaction with K_2CO_3.

Introduction

While the consumption of traditional fossil fuels becomes more and more fast, it is notoriously necessary to lay the foundation for the future renewable energy. Due to the vast amount and its renewable property, biomass has been a hot issue for researchers over the recent years [1–5]. However, there are many disadvantages of biomass, such as low energy density, high moisture content and low energy conversion efficiency [6–10]. Depolymerisation is a favourable method for the high efficiency and clean utilization of biomass for liquid fuel. Meanwhile, the waste depolymerisation liquid was produced as by products with furfurals as one of the main components. Moreover, the liquid fuel can be upgraded by subsequent hydrogenation [11–13]. Therefore, hydrogen production by the waste depolymerisation liquid makes the whole conversion system more complete and independent, which also consumes the waste liquid. Nevertheless, the concentration of the organic content is low, and the cost for conversion is extremely high due to the expensive drying process during the traditional thermochemical conversion [14–17].

Supercritical water (SCW) gasification is a promising method to produce hydrogen from biomass in water phase [18–22] and the system economy will be greatly improved owing to the omitting of drying process. The key to a more efficient system is a proper catalyst with great performance in SCW environment. Recent years, many researchers [1,23–29] have paid great attention to catalysts in SCW to improve the

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Nomenclature

CE	(total carbon in the gaseous products)/(total carbon in furfural) × 100%
GE	(mass of the gaseous products)/(mass of furfural) × 100%
HE	(total hydrogen in the gaseous products)/(total hydrogen in furfural) × 100%
YH_2 (yield of H_2)	molar amount of H_2 after reaction/ mass of furfural, mol/kg

whole system. Kruse [30] studied the effect of KOH on the gasification of biomass in SCW. It turned out that the yield of hydrogen increased threefold. Ott [31] used zinc sulfate for acrolein production in sub- and supercritical water.

Heterogeneous catalysts in SCW tend to sintering and carbonize, so that catalysts are easily inactivated [25,32]. As a result, a proper method to prepare catalyst is of great importance. Masaru used ZrO_2 for catalytic hydrogen generation from glucose and cellulose [33]. Byrd [34]conducted hydrogen production from glycerol by reforming in supercritical water over Ru/Al_2O_3 catalyst. In their experiment, feed concentration of glycerol was up to 40 wt%. "Many researchers synthesized catalyst in supercritical water environment because supercritical water has high performance in micro- or nanoparticle formation" [35]. Sue [36] used micro reactor to prepare ZnO nano crystals and conducted rapid hydrothermal synthesis without organics [37]. Kojima [38] used sodium borohydride for hydrogen generation accelerated by applying metal metal oxide catalysts such as Pt/TiO_2, Pt/CoO and $Pt/LiCoO_2$. Kawasaki [39] synthesized NiO nano-particles using a T-shaped mixer with a continuous supercritical hydrothermal method. The relation between particle diameter and the heating rate was investigated.

The aim of this paper is firstly to enlarge the supercritical water synthesis method for the preparation for bimetallic catalyst to ensure the hydrothermal stability of the heterogeneous catalyst. The combination effect of inexpensive Zn, Ni, Cu and Co was test to evaluation the synergetic catalytic effect. Multiple analysis methods such as SEM, XRD and EDS were conducted to reveal the catalytic mechanism. Furfural was selected to be the model reactant for the waste depolymerisation liquid, in order that a novel catalyst preparation was obtained for biomass advanced utilization.

Experimental section

Apparatus and procedure

A high-throughput batch reactor system with 6 subsystems was used for the synthesis and gasification processes. The reactor was fabricated from Inconel 625 and designed with a maximum temperature and pressure of 750 °C and 30 MPa, respectively. A subsystem consists of batch reactor, electric furnace, and data acquisition station of temperature and pressure. The electric furnace operates at a certain temperature for experiment with a temperature controller. The DAS can monitor and record the temperature and pressure inside the reactor using an inserted thermocouple. The operating condition for the gasification is within the following range: residence time 20 min, pressure 23–25 MPa, temperature 200–400 °C.

To acquire the combination of different metal elements, metal salt solution of two different elements were mixed with enough time to be distributed uniformly. Afterwards, measured TiO_2 particles were added into the reactor and deionized water was injected into the reactor with a syringe. Then, a purging process was conducted to replace the air to prevent the undesired effect of air. As for metal catalysts, after being dried in an oven, they were analysed by multiple methods to obtain the properties. Gasification characteristics were used to analyse the catalytic effects and make a comparison. The operating condition for the synthesis process is within the following range: residence time 20 min, pressure 23–25 MPa, temperature 400 °C.

Materials

Reagents are commercial products bought from special companies and their content information is listed in Table 1. It can be seen that acetate was applied in the work, and suppose metal M is positive 1, the reaction pathway is showed as Eqs. (1)–(3): Acetate was used because it can be gasified in supercritical to omit the unwanted effect of anion. Moreover, it can prevent the severe acid cession caused by chlorate or sulphate.

$$MCH_2COOH + H_2O \rightarrow MOH + CH_3COOH \quad (1)$$

$$CH_3COOH + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

$$2MOH \rightarrow M_2O + H_2O \quad (3)$$

Characterization and analytical methods

All the characterizations were obtained on freeze-dried powders. The samples were characterized by X-ray diffraction (XRD) using a PANalytical X'pert MPD Pro X automatic diffractometer. The volt and current is 40 kV and 40 mA, respectively. Powders were all observed by scanning electron microscopy (SEM). These experiments were conducted on a JEOL JSM-7800F electron microscope coupled with an energy dispersive spectroscope. The composition of the gaseous products was analyzed by gas chromatography (Agilent

Table 1 – Reagents involved in this paper.

Chemicals	Company	Content no less than
Furfural	Sigma–Aldrich	98.0%
Zinc acetate	Tianjin Shengao Reagents	99.0%
Nickel acetate	Tianjin Yongsheng Fine Chemicals	98.0%
Copper acetate	Tianjin Shengmiao Fine Chemicals	99.0%
Cobalt acetate	Tianjin Fuchen Chemicals	99.5%

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