Behavior of nickel catalysts in supercritical water gasification of glucose: Influence of support

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ABSTRACT

The catalytic performance of Ni-based supercritical water gasification (SCWG) catalysts may be influenced strongly by the nature of support. In this paper, Ni catalysts with the different supports (CeO_2/Al_2O_3, La_2O_3/Al_2O_3, MgO/Al_2O_3, ZrO_2/Al_2O_3) were prepared by two-step impregnation method. The fresh and used catalysts were characterized by X-ray diffraction patterns (XRD), scanning electron microscopy with an Energy Dispersive X-ray (SEM-EDX), Brunauer–Emmett–Teller (BET) specific surface area measurements, X-ray photoelectron spectroscopy (XPS) and Thermo-gravimetric analyses (TGA). The catalyst performance testing was conducted by SCWG of glucose at 673 K and 23.5 MPa with an autoclave reactor, to evaluate the influence of support on the hydrogen production. The results showed that H_2 yield for different supports decreased in order: $CeO_2/Al_2O_3 > La_2O_3/Al_2O_3 > MgO/Al_2O_3 > Al_2O_3 > ZrO_2/Al_2O_3$, and H_2 selectivity decreased in order: $CeO_2/Al_2O_3 > La_2O_3/Al_2O_3 > ZrO_2/Al_2O_3 > Al_2O_3 > MgO/Al_2O_3$. Ni catalysts were deactivated in SCWG reaction because of sintering and coke deposition. Compared with other supports, CeO_2 can be used as the promoter of carbon removal from catalyst surfaces.

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1. Introduction

Biomass is a renewable energy resource, but due to its low energy density, direct use of biomass is not convenient. Thus, it is necessary to convert biomass to liquid, or gas fuel such as hydrogen that can be used cleanly and high-efficiently in fuel cells [1]. Thermo-chemical gasification is likely to be the most cost-effective conversion process. However, a large portion of biomass wastes is wet biomass containing up to 95% water and this wet biomass causes high drying costs if classical gas-phase gasification process is used. With the advantage of avoiding drying process, supercritical water gasification (SCWG) is a promising technology for the utilization of wet biomass [2].

In 1978, Modell [3,4] reported firstly that glucose and maple sawdust could be gasified with a catalyst composition that promotes hydrogenation, reforming and cracking in water in the vicinity of its critical state. Since then, researchers from USA, Japan, EU and other countries conducted a lot of studies on biomass gasification in sub- or supercritical water (SCW) [5–21]. The use of a catalyst can allow low-temperature (~673 K) operation while maintaining useful kinetics. Lower temperature operation allows lower capital costs because of lower pressure operation, requiring less containment structure, and less severe attack on the reactor walls, which allows the use of less costly alloys [22]. Metal catalysts, such as noble metal Pt, Pd, Ru, Rh [5,16,23–25] and Ni [5,10,11,17,23–48], are usually used in SCWG. Among these noble metal catalysts, Ru

is found very active and stable for the gasification of biomass in SCW, but the high cost and limited availability of noble metals prevent their further development. Generally, alkali, such as NaOH, KOH, Na_2CO_3, K_2CO_3 and $Ca(OH)_2$, is used as a catalyst or promoter for SCWG [11,12,14,49,50]. The alkali can catalyze the water-gas shift reactor in SCWG process. However, the alkali such as NaOH, KOH, will react with product gas, eg. CO_2, and recycling alkali from wastewater also requires high energy consumption. Some researchers also use activated charcoal [7–9] and metal oxides as catalysts in SCWG [51,52]. Nickel has been widely used as catalyst in steam reforming, sub or supercritical water gasification reactions because of its high activity and low cost. The Ni catalysts used for sub or supercritical water gasification in literature are summarized in Table 1.

In most cases, carbon deposition, which is one of the serious problems, reduces the activity of Ni-based SCWG catalysts. Adding promoter into the Ni-based catalysts is a common way to prevent carbon deposition. CeO_2, La_2O_3, MgO and ZrO_2 are usually used as the promoter of carbon removal from metallic surfaces [53]. In this paper, Ni catalysts with different supports (CeO_2/Al_2O_3, La_2O_3/Al_2O_3, MgO/Al_2O_3, ZrO_2/Al_2O_3) were prepared by two-step impregnation method. The catalysts were characterized by XRD, SEM-EDX, BET specific surface area measurements, XPS and TGA. The comparison of the Ni catalyst performance was conducted by gasification of glucose as biomass model compound in SCW with an autoclave reactor, to evaluate the influence of catalyst support on hydrogen production.

2. Experimental apparatus and procedure

2.1. Catalyst preparation

Ni catalysts with different supports were prepared by two-step impregnation method. CeO_2/Al_2O_3, La_2O_3/Al_2O_3, MgO/Al_2O_3 and ZrO_2/Al_2O_3 supports were prepared by impregnation of a commercial γAl_2O_3 (China Institute of Daily Chemical Industry, surface area, 140 $m^2.g^{-1}$) with aqueous solutions of metal nitrates (Sinopharm Medicine Holding Company, Sinopharm Chemical Reagent Co.,Ltd). The different solutions were prepared with a mixture of certain amount of metal nitrates and γAl_2O_3. Metal Ce, La, Mg and Zr loading were selected in order to achieve theoretical mass fraction of CeO_2, La_2O_3, MgO and ZrO_2 to 10% in the whole catalysts, respectively. The solution was heated under stirring for about 3.5 h until water evaporation was finished and then the solid residue was grounded into powders. Subsequently, it was calcined into support in air with a 7 K min^{-1} ramp from 300 K to 873 K, holding 5 h at 873 K, and then natural cooling to ambient temperature. The Ni catalysts were prepared by impregnation of each of the above supports with aqueous solutions of $Ni(NO_3)_2$ (Sinopharm Medicine Holding Company, Sinopharm Chemical Reagent Co.,Ltd). The different solutions were prepared with a mixture of certain amount of $Ni(NO_3)_2$ and different supports. Ni-loading was selected in order to achieve theoretical mass fraction of Ni to 10% in the whole catalysts. The solution was heated under stirring for about 3 h until water evaporation was finished and then the solid residue was grounded into powders.

Subsequently, it was calcined in air with a 5 K min^{-1} ramp from 300 K to 823 K, holding 3 h at 773 K, and then natural cooling to ambient temperature.

2.2. Characterization

N_2 adsorption–desorption isotherms of reduced catalysts were conducted at 77 K in a Beckman Coulter SA3100 plus instrument. Samples were degassed at 573 K for 60 min, prior to measurements. Surface area was determined using the BET methods. XRD patterns of the calcined and used catalysts were obtained from a PANalytical X'pert MPD Pro diffractometer using Ni-filtered Cu Kα irradiation (wavelength 1.5406 Å). The composition analyses and properties study of the catalysts were performed using XPS. XPS spectra were obtained by an Axis Ultra, Kratos (UK) using monochromatic Al Kα radiation (150 W, 15 kV, 1486.6 eV). Binding energy was calibrated relative to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of the samples. The morphology and component of the catalysts are characterized by a scanning electron microscopy with an Energy Dispersive X-ray Detector (Shimadzu SSX-550). Thermo-gravimetric analyses (TGA) were carried out using a DSC/DTA-TG (NETZSCH STA449C) with air carrier to determine the amount of coke deposited on catalysts.

2.3. Catalytic testing

Fig. 1 illustrates the schematic diagram of a catalytic testing system (Parr Co.). The reaction system includes an autoclave reactor (Parr 4575A) and a controller (Parr 4857A). The reactor had a volume capacity of 500 mL designed to a maximum temperature and pressure of 773 K (internal temperature) and 35 MPa, respectively. The reactor material was high-temperature alloy C-276. The reactor was externally heated by a 1.5 kW ceramic heater. Two K-type thermocouples were used to measure the internal and wall temperatures of the reactor, respectively. The gauge was uses to measure the internal pressure of the reactor. The reactor was equipped with a pressure release valve, an explosion-proof membrane and a high-temperature alarm, to ensure the reactor safety. The reactor was also equipped with a magnetic stirrer with the speed range of (0–167.6) $rad.s^{-1}$.

A U-type cooling loop was fixed into the reactor, to be used in cooling the reactor fairly rapidly with water, to ambient temperature at the end of an experiment. We can sample online during the reaction by a liquid and gas sampling device. The high-pressure Ar was used to purge the air in the reactor. A certain initial pressure needs to be maintained in the reactor, to prevent boiling during the heating. After reaction, gas volume was measured by a wet gas flow meter.

Analysis of the gaseous products is accomplished by use of Agilent model 7890 gas chromatograph (GC) equipped with a thermal conductivity detector. The carrier gas is Ar and its flow rate is 30 mL min^{-1}. A Carbon-2000 capillary column (Φ0.53 mm × 25 m) is used, operating at 323 K for 8 min. A standard gas mixture with 6 kinds of contents used for calibration is bought from and compounded by Beijing AP Beifen Gases Industry Limited Company.

Feedstock was prepared with glucose loading of 10% by mass. The calcined Ni catalysts were reduced to the catalysts