Full Length Article

La-based catalysts to enhance hydrogen production during supercritical water gasification of glucose

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ABSTRACT

Controlling hydrogen production during supercritical water gasification (SCWG) of biomass is challenging using conventional mono-metallic catalysts. This work examines the role of Lanthanum (La) both as a catalyst and co-catalyst with Nickel (Ni), for enhancing the Water-Gas Shift (WGS) reaction to maximize hydrogen production. A stirred tank batch reactor was used with glucose as feed (model compound for biomass), from T = 400 to 500 °C, residence time = 5–120 min and P = 28 MPa. Compared to non-catalytic gasification, the La_2O_3/Al_2O_3 catalyst enhanced both the H_2 and CO_2 production by 1.9-fold and 2.0-fold respectively. $Ni\text{-}La_2O_3/Al_2O_3$ catalyst increased hydrogen production (3.95 mol/mol feed) to almost thermodynamic equilibrium composition (4.15 mol/mol feed) at 120 min reaction time. By examining the fresh and spent catalysts by various physico-chemical techniques, this enhancement is attributed to the Ni promoting tar cracking, while La promoted the WGS reaction and inhibits the methanation reactions. A parametric study was used to optimize reaction conditions, finding that H_2 production and carbon conversion to gaseous products increased significantly with higher reaction time and temperatures and lower feed concentrations. Almost 98% carbon was gasified at 120 min reaction time using $Ni\text{-}La_2O_3/Al_2O_3$ as catalyst. Using a controlled feedstock of CO and H_2 to further examine the catalytic mechanism, adding La onto the Ni/Al_2O_3 enhanced CO_2 and H_2 production with negligible CH_4 production, showing the importance of the WGS reaction to maximizing H_2 production in SCWG.

1. Introduction

Biomass gasification in supercritical water is a promising alternative for hydrogen production for high water content feedstocks. The energy conversion efficiency of supercritical water gasification (SCWG) has been shown to be higher than thermal gasification, pyrolysis, liquefaction and anaerobic digestion when the moisture content is above 31% [1]. SCWG has an obvious advantage for direct processing of wet biomass from agricultural and industrial residues or sewage sludge as no energy-consuming drying process is required to obtain high energy efficiency [2,3], while allowing production of hydrogen rich syngas and clean liquid effluent to be discharged [4]. Syngas (CO-H₂) produced from SCWG can be used for direct feeding of next generation high efficiency internal combustion engines [5] while hydrogen, a rich energy source with zero carbon emissions, is of great interest for fuel cells. The SCWG process has recently received significant attention as a promising alternative for hydrogen generation [6–12], with a recent expert panel on biomass indicating the promise of SCWG, although noting the need for additional research before large scale investment [13].

Using glucose as a biomass model compound for SCWG, a number of simultaneous reactions have been reported, including [11,14]:

Gasification: $C_6H_{12}O_6 + H_2O \rightarrow 3CO + CO_2 + H_2 + 2CH_4$ (1)

Water-gas shift: $CO + H_2O \leftrightarrows CO_2 + H_2$ (2)

Methanation: $CO + 3H_2 \leftrightarrows CH_4 + H_2O$ (3)

$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$ (4)
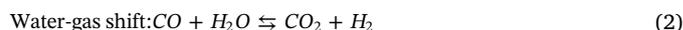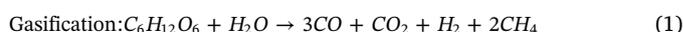
To maximize hydrogen production, the WGS reaction (2) needs to be enhanced while the methanation reactions (3 + 4) need to be decreased, which has been elusive. The WGS reaction is a moderately exothermic, equilibrium-limited reaction. SCWG at moderate temperatures (400–500 °C) generally produces methane rich gases [15], which is a current challenge. This research focused on enhancement of the WGSR and retardation of the methanation reactions at moderate temperatures (400–500 °C) using low cost bicomponent catalysts.

Bicomponent catalysts have recently been found very effective for gasification in SCW with our group reporting almost 98% carbon

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gasification efficiency (CGE) in SCW using Ni-Ru on templated mesoporous alumina supports [16,17]. However, the use of noble metal Ru and template-based synthesis process might be non-attractive. Lu et al. [18] investigated Ni on various supports for SCWG of glucose. They reported that the hydrogen yield is affected by carbon removal efficiency from metallic surfaces by the catalyst support. The yield of hydrogen for different supports decreases in the order: $CeO_2/Al_2O_3 > La_2O_3/Al_2O_3 > MgO/Al_2O_3 > Al_2O_3 > ZrO_2/Al_2O_3$. Sánchez et al. [19] also found that La and Ce prevented coke formation on metallic surfaces. Moreover, La_2O_3 can also act as an adsorbent which selectively adsorbs carbon dioxide [20–22]; indicating that the forward WGS reaction (Eq. (2)) may be enhanced according to Le Chatelier's principle. Furthermore, La_2O_3 is known to increase thermal stability [23] and can avoid metal agglomeration [24–26], which would be important in the aggressive SCW environment. Seri et al. examined the catalytic activity of La for cellulose degradation in water at ambient pressure and 250 °C [27]. However, none of the authors reported the role of La as a catalyst itself or it's role between the two competing reactions in SCWG: i.e. the water gas shift (WGS) and methanation reactions.

In this work we hypothesized that Lanthanum (La) may act as promoter of the WGS reaction, similar to that of cerium (Ce) as Kim et al. [28] found when investigating the removal of CO. The chemical properties of La and Ce with respect to cation charge, ionic radii, and the stability of organic and inorganic complexes are very similar [29]. Hence, Ni, La and Ni-La impregnated on Al_2O_3 catalysts were investigated to investigate the role of La as catalyst and its influence on the WGS and methanation reactions to maximize hydrogen rich syngas production. In addition, a 18 wt% $Ni/\theta\text{-}Al_2O_3$ catalyst was used as a reference catalyst for comparison, which favors CH_4 rich syngas production [30].

2. Experimental

Glucose (reagent grade 99.98%), metallic precursors lanthanum nitrate hexahydrate $[La(NO_3)_3 \cdot 6H_2O]$ and nickel nitrate hexahydrate $[Ni(NO_3)_2 \cdot 6H_2O]$ were obtained from Sigma-Aldrich (Mississauga, Canada), and used as received. $\gamma\text{-}Al_2O_3$ pellets with 3 mm average particle diameter, 198 m^2/g BET surface area and 0.42 cm^3/g pore volume of were received from Aldrich (Mississauga, Canada). To prepare metallic solutions, de-ionized water was obtained from 18.2 MΩ-cm ultrapure system (EASY pure LF, model BDI-D7381, Mandel Scientific Co.).

2.1. Catalyst synthesis

In a typical synthesis via the incipient wetness technique, as received $\gamma\text{-}Al_2O_3$ (198 m^2/g) was transformed into $\theta\text{-}Al_2O_3$ by calcining at 1050 °C to improve its high temperature properties [15,31]. Converting $\gamma\text{-}Al_2O_3$ to $\theta\text{-}Al_2O_3$ also increases pore size [30] for better impregnation of active metals. Large pore size also helps facilitate penetrating bulky intermediate products to the catalyst active sites during SCWG. Metal precursors $(Ni(NO_3)_2 \cdot 6 H_2O$ or $La(NO_3)_3 \cdot 6 H_2O)$ were dissolved in the required amount of deionized water (130 vol% of total pore volume of $\theta\text{-}Al_2O_3$). The metal salt solutions were then introduced to the $\theta\text{-}Al_2O_3$ support with continuous mixing. The impregnated samples were then dried slowly (0.5 °C/min) to 60 °C followed by $NH_3\text{-}H_2O$ vapor treatment to convert the metal salt anion to ammonium salt as described previously [30,31]. The treated sample was further dried by heating to 120 °C at a rate 1 °C/min and then to 250 °C at a rate 1.5 °C/min for one hour. Ammonium salts were removed through sublimation by this thermal treatment. Finally, catalysts were reduced at 600 °C (ramp rate: 5 °C/min and holding time: one hour) based on TPR analysis (Fig. S2) using hydrogen (5 vol% balanced with nitrogen). The actual loading of metal was measured from the weight difference between support alumina and the reduced catalysts.

2.2. Supercritical water gasification process

The synthesized catalysts were evaluated using a 600 ml Hastelloy C-276 autoclave reactor (supplied by Autoclave Engineers, USA) with a 1.5 kW electric furnace for heating. The detailed description of the experimental set-up can be found elsewhere [30]. Lu et al. [18] used a similar 500 ml autoclave reactor while Sinag et al. [32] used a 1 L autoclave reactor for glucose gasification in supercritical water.

In a typical experiment, the reactor was loaded with the required amount of catalyst and then closed. Then, 70 ml of deionized water was injected into the reactor followed by purging with He for 10 min. The reactor was then pressurized to 2.5 MPa with helium. The pressure was then raised to 24 MPa by heating the reactor to 400 °C which is above the critical point of water. The glucose solution (0.25 M) was then injected into the pressurized reactor using a syringe pump (Isco Model 100 DX, USA); providing a final reactor pressure of 28 MPa. The reaction time was calculated from the time of injection of the glucose feed into the reactor.

After a pre-specified period of reaction, the product was cooled down to ambient temperature using a double pipe counter-current heat exchanger. The gaseous products were separated from the liquid effluent using a gas-liquid separator operating by sudden expansion (from 0.635 in. ID of stainless tube to 3 L volume vessel). Total gas flow was then measured by a mass flow meter (OMEGA, FMA 1700/1800, 0–2 L/min, Quebec, Canada) and collected in a Tedlar gas sampling bag for subsequent gas-chromatography (GC) analysis.

2.3. Product analysis and catalyst characterization

The product gases were analyzed by a gas-chromatograph (Shimadzu, GC-2014, 120/80 D Hayesep stainless steel Nickel packed column, and dimensions of 6.2 m × 3.18 mm) equipped with a thermal conductivity detector (TCD) and helium as the carrier gas. Total carbon content in the liquid effluent that did not gasify was analyzed with a TOC-VCPH (Shimadzu Instruments) by sample oxidation in a catalyst-filled combustion tube heated to 680 °C. A non-dispersive infrared detector was used to detect the CO_2 present in the carrier gas. The gas yield and carbon conversion to gas are defined as:

$$Yield = \frac{mol\ of\ gas\ produced}{mol\ of\ glucose\ in\ feed} \tag{5}$$

The carbon conversion to gas is defined by:

$$Carbon\ Conversion = 1 - \frac{mol\ of\ carbon\ in\ gas}{mol\ of\ carbon\ in\ feed} \tag{6}$$

The BET surface area, pore size distribution, and pore volume were determined using a Micromeritics ASAP 2010, with N_2 used as the probe gas at 77 K. The samples were degassed at 250 °C for five hours before analysis.

Powder X-ray diffraction (XRD) was performed utilizing a Rigaku diffractometer employing CuKα1 + Kα2 = 1.54184 Å radiation to estimate the change in crystallinities with time, which may have an effect on the reaction rate. The operating condition of the instrument was set at 45 kV and 160 mA with a scan rate of 10°/min and 2θ angle ranged from 2° to 82°. To collimate X-rays, 1° divergent and scatter slits, a 0.15 mm receiving slit were used.

H_2-pulse chemisorption measurements were conducted to calculate the active particle size, the percent dispersion and the active metal surface area using a Micromeritics Autochem 2920. Ar gas was passed through a bed of pre-reduced catalyst at a rate of 50 ml/min until the flow was stable. Then a series of hydrogen pulses (1.0 ml) were injected into the system at 40 °C. The gases leaving the system were analyzed by a TCD detector. The observed peaks from the TCD are due to hydrogen chemisorption on the active metal sites. As soon as two consecutive peaks showed the same area, the hydrogen pulse was discontinued. The percent metal dispersion was calculated according to: