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Water gas shift reaction over monometallic and bimetallic catalysts supported by mixed oxide materials

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ABSTRACT

In the present work, the water gas shift activities of Cu on ceria and Gd doped ceria were studied for a further enhancement of hydrogen purity after a steam reforming process. The catalytic properties of commercial catalysts were also studied to compare with our as-prepared catalysts. It was found that copper-containing cerium oxide is suitable for the high temperature reaction. Copper-ceria is a stable high-temperature shift catalyst, unlike iron-chrome catalysts which are deactivated severely in CO_2-rich gases. 5%Cu/10%GDC (D) was found to have much higher activity than other copper ceria based catalysts. Finely dispersed CuO species is more favorable due to a higher activity, which explains the activity enhancement of this catalyst. The kinetics of the WGS reaction over Cu catalysts supported by mixed oxide materials were measured in the temperature range 200–400 °C. An independence of the CO conversion rate on CO_2 and H_2 was observed. To improve the catalytic performance of copper catalysts, the behavior of the bimetallic catalysts was compared with that of the monometallic catalysts. It was found that an addition of Re to Cu/GDC significantly improved the activity of copper catalysts. The effect of Re on enhancing the WGS activity of Cu catalysts was due to Re increases the reducibility of the surface ceria, In addition, Re contributes to reduction of Ce^{4+} to Ce^{3+}. The presence of Ce_2O_3 at the ceria surface gives rise to oxygen vacancies which facilitate the electron movement at the surface leading to ease of surface reduction.

1. Introduction

Hydrogen fuel cell is one of the most efficient and environmentally friendly type of an energy conversion device. It has a high potential in mitigating effects of climate change. Recently, there has been a renewed interest in the WGS reaction to supply hydrogen to a fuel-cell power generation [1,2]. Water-gas shift (WGS) reaction is an important step in fuel processors for preliminary CO clean up and generating additional hydrogen. The WGS process is exothermic ($\Delta H = -41.1$ kJ/mol). CO conversion is favoured at low temperature. However, a low temperature reaction is kinetically limited. To attain a good yield of hydrogen at low temperature enough to overcome a thermodynamic limit, two stages WGS catalysts is employed. A WGS process consists of high temperature WGS (HTS) and low temperature WGS (LTS). Conventionally, iron-chromium oxide and copper-zinc oxide catalysts have been used for HTS at 350–500 °C [3,4] and for LTS at 200–250 °C, respectively [5–11]. $Fe_2O_3—Cr_2O_3$ catalyst can effectively reduce CO from several percentage points to the equilibrium CO value dictated. Further reduction of CO takes place at low temperatures over a more active catalyst based on Cu-ZnO. The Cu-ZnO catalyst is very sensitive to temperature excursions, operating in the narrow temperature window of 200–250 °C; requires careful activation in H_2 gas; and is readily deactivated when exposed to air or by water condensation [12].

An optimization of the WGS system for the production of hydrogen for fuel cells is of particular interest among this energy industry. The high-temperature shift (HTS) can be used to increase the hydrogen content of coal gas produced by gasification or of reformate gas. The choice of copper-ceria for HTS contains a nonprecious metal hence, it would be a much more cost-effective catalyst for the intended application. It is also a better choice than nickel-ceria, which catalyzes the methanation reaction [13–15] and it has even better activity than gold-ceria at high temperatures [16,17].

In this work, Cu-containing ceria catalysts were examined as an alternative to the commercial iron-chrome HTS catalysts. Commercial catalyst formulations containing iron oxide were recently found to be deactivated in CO_2-rich gases [18]. The effect of Cu

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and Re monometallic and bimetallic impregnation over ceria-based materials on the WGS reaction performance will be studied with an aim to maximize the yield of hydrogen production from the reforming gas. To understand the catalyst characteristics, the catalyst will be characterized using BET surface area, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray absorption near edge structure (XANES) and Temperature Programmed Reduction (TPR) on top of the catalytic performance study.

2. Experimental procedure

2.1. Catalysts preparation

Cerium oxide and gadolinium doped ceria (GDC) were prepared by a combustion synthesis technique [19] using urea as a fuel. Nitrate salts of cerium ($Ce(NO_3)_3{\cdot}6H_2O$, 99.5%, Alfa Aesar) and gadolinium ($Gd(NO_3)_3{\cdot}6H_2O$, 99.9%, Alfa Aesar) were used as initial chemical reactants. The stoichiometry between metal nitrate and urea was 2.5:1. Nitrate salts of cerium ($Ce(NO_3)_3{\cdot}6H_2O$) and urea were mixed for the preparation of cerium oxide. For the preparation of gadolinium doped ceria (GDC), $Ce(NO_3)_3{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ were mixed with urea as the desired ratio. A minimum amount of deionized water was added to the mixed reactant to obtain a homogenous solution. The crucible containing the mixed reactant was then heated using a Bunsen burner until an autoignition occurred. The catalytic properties of CeO_2 (AlfaAesar), CeO_2 (Nanophase), 10% gadolinia-doped ceria (Daiichi) and 10% gadolinia-doped ceria (FuelCellMaterials), which denoted as A–D, were also studied to compare with the as-prepared catalysts.

Copper (II) nitrate trihydrate; $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich) and ammonium perrhenate; NH_4ReO_4 (Sigma-Aldrich) were prepared by impregnation method. Appropriate amount of metal nitrate was dissolved in a minimal amount of deionized water. The salts solution was added to CeO_2 (Alfa Aesar), CeO_2 (Nanophase), 10% gadolinium doped ceria (FuelCellMaterials), 10% gadolinium doped ceria (Daiichi), CeO_2 (prepared by combustion synthesis method) and 10% gadolinium doped ceria (prepared by combustion synthesis method). All the catalysts were dried at 110 °C for 12 h and then calcined at 650 °C for 8 h.

2.2. Catalyst characterization

2.2.1. Standard characterization

Specific surface areas (m^2/g) and pore size distribution were determined by N_2 adsorption-desorption isotherms at 77.3 K using Quantachrome NOVA 1200e. The specific surface area of the sample was calculated following the Brunauer Emmett Teller (BET) procedure in the range of 0.05–0.3. Prior to the measurements, the samples were outgassed in vacuum at 300 °C for 6 h.

The XRD diffractograms presented in this study were recorded employing nickel-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 40 kV and the current was 40 mA. The analyses were carried out at 0.02° step and 0.5 s per step over a 2θ range of 20–80°. The crystallite sizes of the samples, d_{hkl}, were estimated from Scherrer's equation.

$$d_{hkl} = 0.9\lambda/FWHM\cos\theta \tag{1}$$

where λ is the X-ray wavelength of Cu K_α radiation (1.5406A°), *FWHM* is the broadening (in radians) at half-maximum of the (1 1 1) crystallographic plane which is the most intense peak and θ is the diffraction angle corresponding to the (1 1 1) plane.

2.2.2. Temperature programmed reduction

TPR experiments were performed under a flow of $5\%H_2/95\%Ar$ mixture over 0.05 g of catalyst from 40 °C to 1000 °C using a heating rate of 10 °C/min. Prior to the measurement, the catalysts were treated under high purity helium gas at 120 °C for 30 min. The amount of H_2 uptake during the reduction was measured by using a thermal conductivity detector. The curves in H_2-TPR profile correspond to H_2 consumption.

2.2.3. Scanning electron microscopy (SEM)

SEM images were taken on a FE-SEM (HITACHI SU-8030) with high vacuum mode using secondary electrons and an acceleration of 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer.

2.2.4. CuO dispersion

CuO dispersion in all catalysts was determined by N_2O chemisorption using 10% N_2O/He with a flow rate of 30 mL/min at 50 °C with BELCAT-B instrument. Sample preparation was conducted prior to the measurement as follows: about 50 mg of each catalyst sample was loaded in a quartz tube. The sample was first heated to 120 °C while flowing 100% Ar and held at this temperature for 10 min. Then, the sample was heated up to 300 °C in 5% H_2/He and then kept at this temperature for 30 min. The sample was then purged using 100% He with a flow rate of 30 mL/min at 300 °C for 15 min and cooled to 50 °C for measurement of CuO dispersion.

2.2.5. X-ray absorption near edge structure (XANES)

The oxidation states of copper in each sample were identified using X-ray absorption near-edge structure (XANES) on the beamline 8 of Synchrotron Light Research Institute in Nakhon Ratchasima, Thailand. Cu-K edge was investigated, and bulk CuO, Cu_2O and Cu were used as Cu^{2+}, Cu^+, and Cu^0 standards, respectively. Experimental data were collected in the transmission mode for Ce L_3 and Cu K absorption edge with a Lytle detector. Synchrotron radiation is tunable by fixed-exit Double Crystal Monochromator (DCM) equipped with InSb(111) and Ge(220) crystal for low and high energy ranges, respectively. The samples were deposited over the Kapton window which was placed on the sample frame. Ion chambers were filled with a mixture of argon and helium. These chambers were installed in front of and behind the sample to continuously detect the incident (I_0) and transmitted (I_1) X-ray beams.

2.3. Reaction testing

An amount of 150 mg catalyst was loaded between two layers of quartz wool in a stainless-steel fixed bed flow reactor. The reactor was placed inside a tube furnace. The flow of feed gases was controlled by mass flow controllers (Aalborg). The initial feed gas of CO and N_2 was mixed with water vapour which was controlled by using a syringe pump. Preliminary experiments were conducted to determine suitable conditions from which internal and external mass transfer effects are not predominant. Considering the effect of external mass transfer, the total flow rate was kept constant at 100 mL/min in all testing. In addition, the catalyst particle size diameter was between 100 and 200 μm in all experiments. The mixed feed gas composition of 5% CO, 10% H_2O, balanced in N_2 and of 100 mL/min total flow rate was passed through the catalyst bed in the reactor. The temperature of catalysts was increased from 100 °C up to 500 °C. The column utilized in the chromatograph was a Unibead C, 15 m × 0.53 mm stainless-steel packed column. The outlet gases were analyzed by using an on-line gas chromatography (Shimadzu GC-14B) equipped with a TCD analyzer. The catalytic activities were calculated using equation [2]:

$$\%CO conversion = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \tag{2}$$