

Activity of GDC and YDC Synthesize by Co-Precipitation Method toward Water Gas Shift Reaction

Eumporn Buarod¹, Navadol Laosiripojana¹⁺, Sumittra Charojrochkul²

¹ The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

² National Metal and Material Technology Center, Thailand Science Park, Pathumthani 12120, Thailand

Abstract. Doped ceria have been widely used as water gas shift catalyst to increase the number of hydrogen production. Gadolinia-doped ceria (GDC) and yttria-doped ceria (YDC) powders have been studied. The supports have calcined at 260 °C and monometallic catalysts have calcined at 650 °C. The cubic phase of ceria was present in the powder for every condition as investigated by XRD. And the water gas shift activity test found the approximate percentage of CO conversion is 30%.

Keywords: water-gas shift reaction, GDC, YDC, co-precipitation.

1. Introduction

In the last few decades, there are many kind of technology that uses biomass as raw materials to produce energy and chemicals. We can classified process that convert biomass into gasification, pyrolysis and hydrolysis. One of the useful products from gasification process is syngas. Syngas or synthesis gas is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide and very often some carbon dioxide. With synthesis gas is widely used to produce many products, such as hydrogen, methanol, ethanol and etc.

For clean energy production, pure hydrogen is required as a feed gas for electricity generation in fuel cell. Hydrogen is generally produced by steam reforming of hydrocarbons and reformat including a small amount of some gases such as CO, CO₂, H₂O and CH₄. Among the impurities, CO is poisonous to the Pt electrode in the fuel cell and its concentration must be reduced before entering the fuel cell system. So far, the most technologically feasible purification trend is water-gas shift reaction. It was repeated to be able to reduce CO from 8% to 1% [1].

Water gas shift (WGS) is an important step in fuel processors for preliminary CO cleans up and additional hydrogen generations prior to the final CO clean up stage. The WGS reaction is used to convert carbon monoxide to carbon dioxide and hydrogen through a reaction with water [2].

Since the water gas shift reaction is an exothermic reaction, it is favoured at low temperatures. And the current water gas shift catalysts are kinetically limited at low temperature since they are not active enough to attain equilibrium. Iron oxide – chromium oxide catalyst were develop for the high temperature catalyst. It can operate in the temperature range of 310 °C to 450 °C and are called ferrochromochrome catalysts because of their composition. And copper based catalyst were developed to operate at lower temperature in the range of 200 °C to 250 °C [3].

Cerium (IV) oxide, also known as ceria, cerium oxide or cerium dioxide, is an oxide of the rare earth metal cerium. It is a pale yellow-white powder with the chemical formula CeO₂. Cerium (IV) oxide is formed by the calcination of cerium oxalate or cerium hydroxide. CeO₂ has the fluorite type crystal structure with space group Fm3m. Cerium oxide is highly promising support for water gas shift catalysts because of its ability to undergo rapid reduction and oxidation cycle [4], [5]. Ceria can also serve as a stabilizer for alumina and other metal oxide supports, maintaining a high dispersion of the catalyst component [6]. The

⁺ Corresponding author. Tel: + 662-4708309; fax: + 662-4279634.
E-mail address: navadol_1@jgsee.kmutt.ac.th.

association of other rare earth element into ceria is reported to improve the structural stability of ceria toward sintering and also enhance water gas shift activity [7]. Rare earth oxide dopants such as Y_2O_3 and Gd_2O_3 from solid solution with ceria and demonstrate a significant improvement in electrical property [8].

Recently, literature has become available on several methods to prepare gadolinia-doped ceria (GDC) and yttria-doped ceria (YDC) powders such as solid state method [9], hydrothermal synthesis [10], combustion [8], sol-gel [11] and cation complexation method [12]. A solid state synthesis has been generally employed to make GDC and YDC [9]. However, this method requires a high calcination temperature. To overcome these problems, solution phase method like co-precipitation has been adopted for this synthesis.

2. Experimental Procedure

2.1. Support preparation

Mixed oxide supports are prepared by co-precipitation method. Nitrate salts of cerium and two dopant concentrations (10 mol% and 20 mol% of Gd_2O_3 and Y_2O_3) are used. Stoichiometric quantities of $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%) and $Gd(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%) were dissolved separately in deionized water for GDC synthesis. In case of YDC, $Y(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%) was used instead of $Gd(NO_3)_3 \cdot 6H_2O$. The solutions were mixed and sodium hydroxide (NaOH) was added to make the solution pH equal to 10. Then filtered and washed twice with boiling deionized water. The filtered ceria precipitate was dried overnight at 110 °C and then calcined at 260 °C for 10 hours.

2.2. Catalysts preparation

Monometallic based catalysts are prepared by impregnation method. $Ni(NO_3)_2 \cdot 6H_2O$ is dissolved in minimal amount of deionized water. The salts solution is added to Ce-M-O mixed oxide support. The catalyst are dried overnight at 110 °C and then calcined in an oven at 650 °C for 8 hours.

2.3. Characterization and activity test

The phase of synthesized powder and crystalline size were determined using X-ray Diffraction (XRD, JEOL, JDX-3530).

Catalyst activity measurement will be carried out over a wide range temperature, increased from 100 °C to 500 °C. Normally in the flow reactor, a flow of gas mixture of 5% CO, 10% H_2O and balanced N_2 which total flow rate 100 ml/min was controlled by mass flow controllers. The input gases are then passed into the tube reactor which is loaded with catalyst. The reactor is situated inside the tube furnace which controls the temperature of reactor. Reaction occurs in the reactor and the outlet gasses are analyzed by on-line gas chromatograph equipped with TCD analyzer.

3. Results and Discussion

3.1. Phase structure and particle size of powders

Figure 1 showed the XRD patterns of support powders synthesized at 260 °C, including 10%GDC, 20%GDC, 10%YDC, and 20%YDC. Peak identification were made with reference to the JCPDS file Nos. 46-0507, 46-0507, 09-0286, and 09-0286, respectively. All main reflections of a typical cubic fluorite structure, corresponding to (111), (200), (220), (311), (222), (400), (331), and (420) planes in the 2θ scanning range 20-80 ° were found in every prepared powders.

Figure 2 also showed the XRD patterns of catalyst powders which impregnated by 5% Nickel and calcined at 650 °C, including 5%Ni/10GDC, 5%Ni/20GDC, 5%Ni/10YDC, and 5%Ni/20YDC. For commercial CeO_2 was used to determine the lattice parameter. As you see in the figure that peaks of catalyst were shift into the left hand side, it can concluded that addition of Ni can be modification.

The average crystallite size in the table 1 was calculated from the (111) plane reflection, based on the full width at half maximum (FWHM) method using Scherrer equation:

$$D = 0.9\lambda / \beta \cos \theta \quad (1)$$

Where D is the crystallite size in nm, λ is the radiation wavelength (0.15056 nm in this case for Cu target), θ is the diffraction angle, and β is the corrected line width at half peak intensity in radian. β can be calculate using the formula:

$$\beta^2 = \beta_m^2 - \beta_s^2 \quad (2)$$

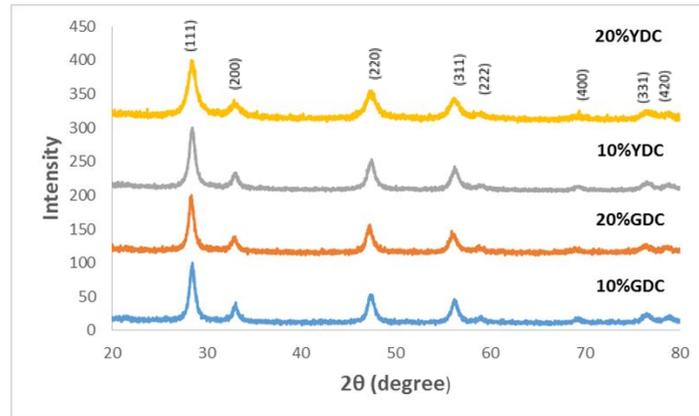


Fig. 1: XRD patterns of support powders synthesized at 260 °C.

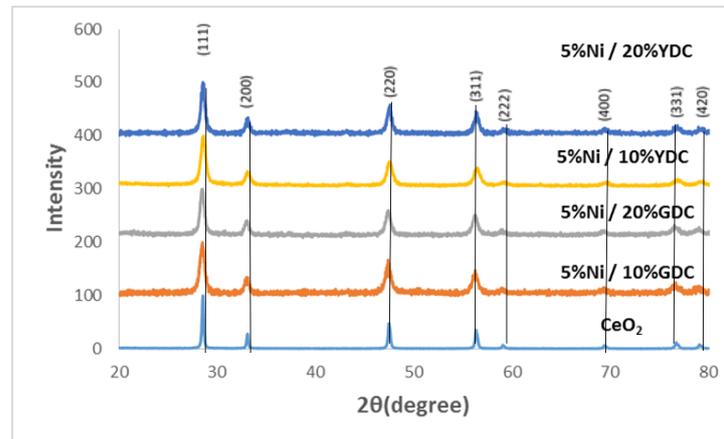


Fig. 2: XRD patterns of monometallic catalyst powders.

Table 1: variation of the crystallite size of synthesized GDC and YDC powders determined by XRD peak broadening.

Powders	Crystallite size (nm)
10% GDC	11.667
20% GDC	12.003
10% YDC	11.036
20% YDC	7.929
5%Ni / 10%GDC	14.361
5%Ni / 20%GDC	16.465
5%Ni / 10%YDC	14.044
5%Ni / 20%YDC	16.669

Where β_m is the measured FWHM and β_s is the FWHM of a standard silicon sample.

3.2. Water gas shift catalytic activity test

The water gas shift (WGS) catalytic activity test for all powders were carried out in a flow reactor in the temperature range of 100 - 500 °C which the results were showed in figure 3. All of them have nearly percentage of CO conversion.

4. Conclusions

Support powders of GDC and YDC with 10 mol% and 20 mol% dopant concentrations were successfully synthesized under low temperature (260 °C). The cubic phase of ceria was present in the powder for every condition as investigated by XRD. But the percentage of CO conversion still quite low, so the water gas shift activity test of monometallic must be test to compare the different of support and monometallic catalyst.

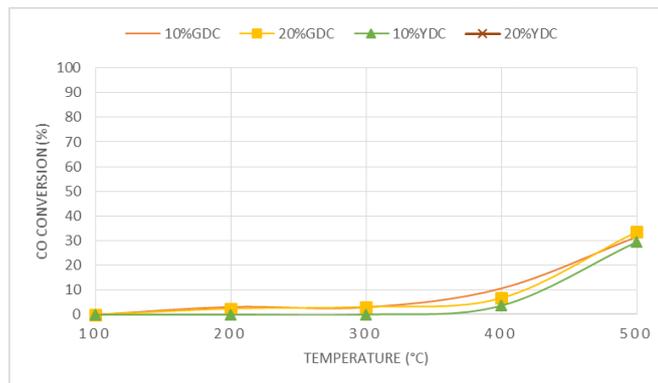


Fig. 3: water-gas shift activity of 10%GDC, 20%GDC, 10%YDC, and 20%YDC.

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6. References

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