



CHAPTER III EXPERIMENTAL

3.1 Materials

Cerium (IV) hydroxide ($\text{Ce}(\text{OH})_4$, Aldrich), ethylene glycol (EG, J.T. Baker), sodium hydroxide (NaOH, Merck), triethylenetetramine (TETA, Facai Polytech) and acetonitrile (Lab-Scan) were used as received for cerium glycolate synthesis. Cupric acetate monohydrate purum ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 99%) (Fluka), gadolinium (III) nitrate hexahydrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%) (Aldrich), nickel (II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 98%) (Aldrich) and nitric acid (HNO_3 , 65%) (Lab-Scan) were used as received for preparation of gadolinium-doped ceria and metal loaded gadolinium-doped ceria. Methanol (CH_3OH , 99.8%) (Lab-Scan) was used as received for catalytic activity study.

3.2 Equipment

3.2.1 Thermogravimetric/Differential Thermal Analyzer: TG/DTA

TGA thermograms of cerium glycolate, GDC, Ni/GDC and Cu/GDC were monitored by TG/DTA (Perkin-Elmer, Pyris Diamond) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from $30\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$.

3.2.2 Fourier Transform Infrared Spectrometer: FTIR

Functional groups of cerium glycolate was characterized by FTIR (Nicolet, Nexus 670) in a range of $4000\text{--}400\text{ cm}^{-1}$ with 32 scans at the resolution of 4 cm^{-1} . The sample was mixed with KBr and pressed into transparent pellet form.

3.2.3 Surface Area Analyzer: SAA

Surface area of the calcined powder was analyzed on Thermo Finnigan, Sorptomatic 1990 using Brunauer-Emmett-Teller (BET) method. The samples were outgassed to remove moisture adsorbed on the surface at $250\text{ }^\circ\text{C}$ before analysis.

3.2.4 X-ray Diffraction: XRD

The crystalline structure and phase composition of samples were characterized using x-ray diffraction (Rigaku, Rint 2200HV) with Cu-K α radiation at 40 kV and 30 mA. The samples were determined on a glass slide specimen holder in the 2θ range from 20-100° at scanning speed of 5°/min with scan step of 0.02°. The crystallite size was calculated by Scherrer equation.

3.2.5 Scanning Electron Microscope/ Energy dispersive X-ray spectroscopy: SEM/EDX

Morphology of the synthesized products was examined by SEM (Hitachi, S-4800). Energy dispersive X-ray spectroscopy (EDX) was used for observation of element dispersion on the samples.

3.2.6 Temperature Programmed Reduction: TPR

Reduction temperature of the calcined powders was determined by temperature programmed reduction. A measurement was carried out by placing 0.05 g of the sample in a quartz reactor. The sample was subjected to TPR analysis using 5% H₂ in Ar for 30 ml/min. The reduction temperature was raised from 30 to 850 °C at a ramp rate of 10 °C/min. Before reduction, the system was purged while being heated to 150 °C with 4 °C/min for 1 h and cooled to 30 °C in nitrogen with a flow rate of 10 ml/min to eliminate moisture. The thermal conductivity detector (SRI model 110) was used to monitor the difference of hydrogen content before and after the reduction.

3.2.7 Temperature Programmed Oxidation: TPO

The amount of deposited carbon of the spent catalyst was measured by temperature programmed oxidation. The 0.03 g of the spent catalyst was placed in quartz tube reactor and conducted for TPO analysis using 2% O₂ in He for 30 ml/min. The temperature was increased from 30 to 900 °C at a ramp rate of 10 °C/min. Carbon formation was oxidized into carbon dioxide then converted to methane in the methanator. The product gas was analyzed by a gas chromatograph (Shimadzu, GC-17A) equipped with a flame ionized detector (FID). The oven and the detector temperatures were set at 40 ° and 150 °C, respectively

3.2.8 Apparatus of Catalytic Activity

The system for study of steam reforming of methanol (SRM) is shown in Figure 3.1. There are four main parts in this system. Those are:

3.2.8.1 Liquid Feed System

A mixture of distilled water and methanol was filled in a syringe and before injecting by a syringe pump at a rate of 1.5 ml/h to a vaporizer for generating the methanol vapor and steam.

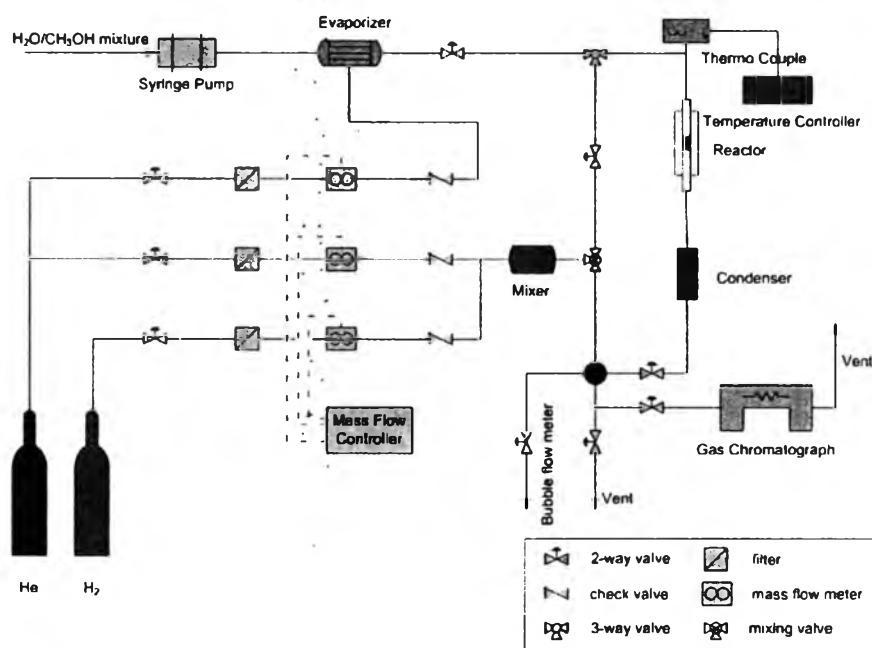


Figure 3.1 Schematic of experimental system for steam reforming of methanol.

3.2.8.2 Gas Blending System

Helium (He) as a purge gas was delivered from the storage tank before passing through a micron filter to remove particles and passing the check valve to prevent reverse flow. The flow rate was controlled by 840 Sierra Instrument model mass flow controller to achieve the desired flow rate. All streams were mixed in a mixing chamber before passing through the catalytic reactor.

3.2.8.3 Catalytic Reactor

The SR of methanol was carried out in a vertical pyrex glass microreactor with an inside diameter of 8 mm. In the middle of the reactor, the catalyst was packed between quartz wool plugs. The reactor was installed and electronically heated in the furnace. The temperature of the catalyst bed was controlled and monitored by a proportional–integral–derivative controller (PID controller) temperature controller equipped with a chromel–alumel thermocouple (Type K).

3.2.8.4 Analytical Instrument

The product gases (e.g. H₂, CO, CO₂, and CH₄) from the reactor were analyzed both qualitatively and quantitative by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in a GC was Carbosphere®, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column. The results were recorded by Agilent Chemstation software. The observed peaks were identified by comparison with the retention time of the standard gas. For quantitative analysis, the peak area was used to determine the concentration of each component, based on the calibration curves obtained from known composition gases.

3.3 Methodology

3.3.1 Preparation of Cerium Glycolate Complex Ce(C₂H₄O₂)₂ Precursor

Cerium glycolate complex was synthesized via oxide one-pot synthesis (OOPS) process (Ksapabutr *et al.*, 2004). The preparation was modified by tripling the scale reported by Ksapabutr *et al.* (2004), i.e. mixing 3.12 g of Ce(OH)₄, 54 mL of EG, and 2.19 g of TETA with NaOH at about 12 mole% equivalent to cerium hydroxide. The mixture was magnetically stirred and heated to the boiling point of EG for 18 h under nitrogen to distill off EG and water liberated from the reaction. The reaction mixture was cooled overnight under nitrogen. The precipitated product was filtered and washed with acetonitrile, followed by drying under vacuum. The reaction for synthesizing cerium glycolate complex was illustrated in Figure 3.2.

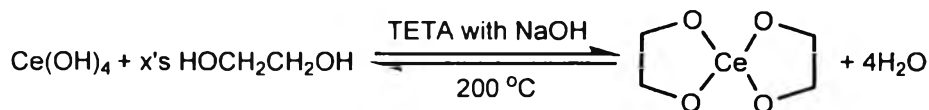


Figure 3.2 Synthesizing reaction of cerium glycolate complex.

3.3.2 Preparation of Gadolinium-doped Ceria and Metal Loaded

Gadolinium-doped Ceria

In this study the amount of gadolinium doped to ceria was fixed at 10 % mole. Gadolinium-doped ceria, nickel loaded gadolinium-doped ceria and copper loaded gadolinium-doped ceria were prepared via sol-gel method by hydrolyzing cerium glycolate precursor with the mixture of metal, nitric acid, and water. In this study, the effects of solvent and acid amounts on the gel formation were investigated. The amounts of starting materials depended on the hydrolysis molar ratio ($h = \text{H}_2\text{O}/\text{Ce}$) and acid molar ratio ($A = \text{acid}/\text{Ce}$) while loaded metals were studied at 10 and 20 mole percent. The gelation reaction was carried out at room temperature with continuously stirring at the suitable mole ratio of acid and solvent.

Soft gel was obtained after aging for 1 h at room temperature. All produced powders were obtained by thermal treatment in a furnace at 500 °C for 7 h. The samples were ground and sieved to 80–120 mesh size. Figure 3.3 presents a flow diagram of the synthesis route.

3.3.3 Catalytic activity

The catalytic test was conducted using a fixed-bed flow reactor at atmospheric pressure and the temperature range of 200–400 °C. A 0.1 g of the catalyst (80–120 mesh size) was packed in the reactor. The methanol vapor and steam were carried by helium with a flow rate of He, being kept at a constant gas space velocity (GHSV) of 14008 ml/g-cat h. Steam to methanol ratio (MeOH:H₂O) was set at 1.5 (Papavasiliou *et al.*, 2007). The product gases were analyzed by GC.

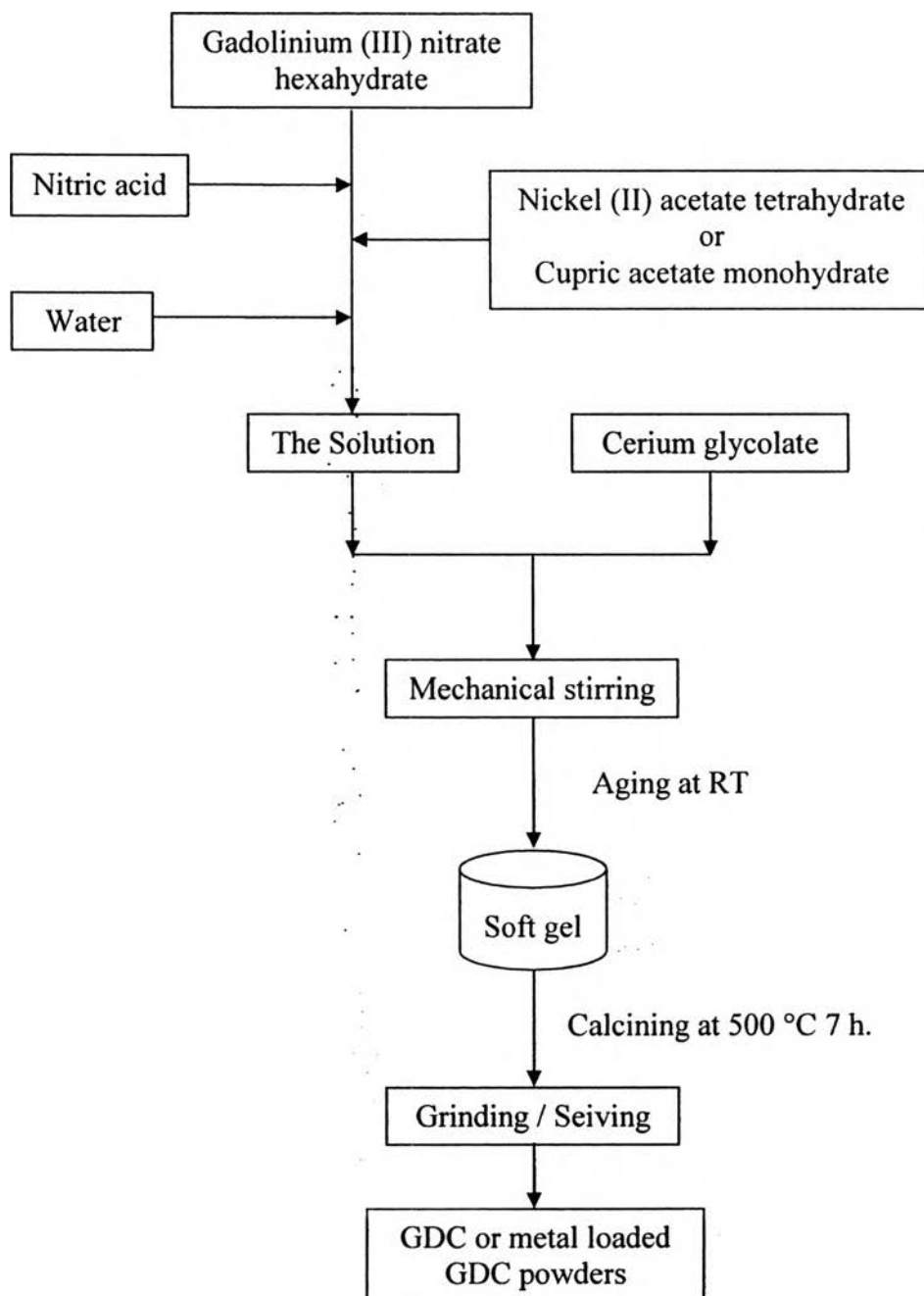


Figure 3.3 Flowchart illustrating the synthesis route to GDC and metal loaded GDC powders via the sol-gel technique.