CHAPTER III
EXPERIMENTAL

3.1 Materials

Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt with 1:1 styrenesulfonic acid : maleic acid mole ratio (1:1 PSS-co-MA, M_w ~20000, Sigma-Aldrich, USA), poly(4-styrenesulfonic acid-co-maleic acid) sodium salt with 3:1 styrenesulfonic acid : maleic acid mole ratio (3:1 PSS-co-MA, M_w ~20000, Sigma-Aldrich, USA), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, 99.5%, Acros Organics, USA), silver nitrate ($AgNO_3$, 99.8%, Sigma-Aldrich, USA), gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, 99.9%, Sigma-Aldrich, USA), sodium borohydride ($NaBH_4$, Fisher Scientific, UK) and sodium carbonate anhydrous (Na_2CO_3, 99.5%, Carlo Erba, France) were used without further purification.

3.2 Catalyst Synthesis

3.2.1 Chemical Preparation

De-ionized water was used as solvent for all solutions. A desired amount of $Ce(NO_3)_3.6H_2O$ was dissolved in de-ionized water to obtain a concentration of 10 mM. The solution of 1:1 PSS-co-MA anionic polyelectrolyte at concentration of 0.5, 1, 5, 10, 50 and 100 mM was prepared for use as capping agent. A sodium carbonate aqueous solution at concentration of 0.1 M was used as the precipitating agent.

3.2.2 Synthesis of Ceria Support

Two methods of the support preparation, quick mixing and drop-by-drop, were used in this work to investigate the effect of preparation method on ceria particle size.

3.2.2.1 Quick Mixing

An aqueous solution of 10 mM $Ce(NO_3)_3.6H_2O$ was immediately mix with 0 mM and 10 mM of 1:1 PSS-co-MA solution under gentle

stirring by using a magnetic stirrer.. The mixed aqueous solution was kept at pH 9.0 by adding a sodium carbonate aqueous solution and aging at 60 °C for 1 hour.

3.2.2.2 Drop-by-drop

An aqueous solution of 10 mM $Ce(NO_3)_3.6H_2O$ was poured into burette and then added dropwise to a PSS-co-MA solution at concentration of 0 mM and 10 mM under gentle stirring by using a magnetic stirrer. The mixed aqueous solution was kept at pH 9.0 by adding a sodium carbonate aqueous solution and aging at 60 °C for 1 hour.

To examine the effect of the sonochemical method, an ultrasonic instrument was used as a replacement for the magnetic stirrer. After that, the white precipitate of ceria was filtered and washed by deionized water. The sample was then dried overnight at 100 °C. Moreover, the various concentration of 1:1 PSS-co-MA solution (0, 0.5, 1, 5, 10, 50, and 100 mM) was used to investigate the effect of polyelectrolyte concentrations on the size of ceria support.

3.2.3 Synthesis of Gold/Ceria Catalyst

The prepared ceria was suspended in an aqueous solution of 1 mM $AgNO_3$, followed by $NaBH_4$ reduction. The Ag/CeO_2 catalyst was washed by deionized water to remove excess ions and then dried overnight at 100 °C. The Au/CeO_2 catalyst was further prepared by adding the Ag/CeO_2 powder to an aqueous solution of 1 mM $HAuCl_4$ under gentle stirring at room temperature. The Au/CeO_2 catalyst was washed by deionized water and then dried overnight at 100 °C. For comparison purposes, the Au/CeO_2 catalyst with 3:1 PSS-co-MA also prepared by using the same procedure.

3.3 Materials Characterization

The particle size distribution of ceria support was characterized on a Malvern Mastersizer X Particle Size Analyzer (PSA). The average size of ceria support particles was also calculated. The X-ray diffraction (XRD) of catalysts were recorded on a Rigaku Smartlab® and CuKα source at 40 kV and 30 mA in a range of $2\theta = 20–80°$ with a scanning speed of 2°/min. The Brunauer–Emmet–Teller (BET) method on a Quantasorb Jr. (Autosorb-1) was used to measure the surface area of

Ag/CeO_2 and Au/CeO_2 catalysts. Prior to each analysis, the product was degassed at 200 °C for 12 h. Varian, SpectrAA 300 Atomic absorption spectrophotometer (AAS) was used to determine the silver and gold contents on the ceria support. A Nicolet 6700 Fourier transform infrared spectrometer (FTIR) was used to collect the spectra and the wavenumber range of the functional group of ceria support and catalysts.

3.4 Activity Study

The catalytic activity measurements of Au/CeO_2 catalysts in CO oxidation were followed Sakwarathorn and co-workers' method (Sakwarathorn *et al.*, 2011) by using the packed-bed quartz U-tube reactor with a 0.6 mm inner diameter and a 100 mg sample of each catalyst was packed between two layers of glass wool. The activity was observed at various reaction temperatures over the range of 50 – 190 °C. The feed stream contained 40% H_2, 1% O_2 and 1% CO in helium balance. These measurements were done under atmospheric pressure in a continuous flow with a total flow rate of 50 mL/min. The reactant and product gases were detected by an on-line gas chromatograph. The catalytic activity of Au/CeO_2 catalysts in methanol reforming was also collected at various reaction temperatures over the range of 200 – 400 °C followed Pojanavaraphan and co-workers' method (Pojanavaraphan *et al.*, 2013). A mixture of methanol and distilled water was injected to a vaporizer at a rate of 1.5 mL/h. A vapor of methanol and steam produced from a vaporizer was mixed with helium carrier gas for carrying the reactant gases to mix with oxygen before entering the catalytic reactor. The gas hourly space velocity was kept at 30000 mL/g-cat.h and the total flow rate was 50 mL/min under pressure of 1 atm. The reactant and product gases were detected by an on-line gas chromatograph, as well.