

CHAPTER III

METHODOLOGY

A typical study on catalysis usually consists of three primary steps: catalyst preparation, characterization and catalytic performance test. The catalyst preparation procedure will be stated in the next section. The following characterization techniques were used extensively:

- Neutron Activation Analysis(NAA) for the exact Pt and Ce amounts.
- BET Surface Area measurement for catalyst physical surface area.
- Powder X-ray Diffraction Analysis(XRD) for the mean particle sizes of ceria.

Finally, the reactor system, experimental concept and working procedure are thoroughly explained.

3.1 Materials

3.1.1 Chemicals

The chemicals used as standards for catalyst characterization were:

- Standard platinum solution which was delivered from Merck with a platinum concentration of 1,000 ppm.
- Standard cerium oxide(CeO_2) in the fine powder form obtained from Johnson&Matthey company, 99.99%purity.

The other chemicals involved in the catalyst preparation step as the platinum and ceria precursors were:

- γ -alumina from Merck (70-230 mesh ASTM) of active and neutral type was used as the catalyst support.
- Hydrogen hexachloroplatinate (IV) hydrate [$\text{H}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$] from Aldrich Chemical Company. This chemical was kept under vacuum until being used.
- Cerous nitrate hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] of 99.0% purity from Fluka. It was also kept under vacuum and was used immediately after being unsealed.

3.1.2 Gases

All gases used in this study were obtained from Thai Industrial Gases Public Company(TIG). Their specifications are as follows:

- Ultra high purity helium (99.999% purity, major contaminants: $\text{O}_2 < 3$ ppm, $\text{H}_2\text{O} < 3$ ppm and

Hydrocarbon < 1 ppm). This gas was used as the carrier gas in the reactor system.

- High purity helium (99.9% purity) used as the thermal conductivity detector (TCD) reference gas.
- High purity oxygen (99.8% purity) used in the catalyst oxidation step.
- Carbon monoxide (5.28 +/- 0.11% mole balance with helium)

3.2 Catalyst Preparation

As mentioned in the first chapter, the model used for study was Pt/CeO₂/Al₂O₃. Both platinum and ceria were impregnated into alumina by the incipient wetness method. The platinum loading was fixed at 0.7%wt. for all catalysts while the ceria loading was varied, i.e. 0, 7.5, 10, 15, 20 and 23 %wt. nominal.

Alumina(γ -Al₂O₃) was sieved and the portion between 80 and 200 mesh was selected to be the support. The CeO₂/Al₂O₃ samples were prepared by wetting the alumina with sufficient amounts of cerous nitrate Ce(NO₃)₃ aqueous solution prepared by dissolving cerous nitrate hexahydrate crystal in warm distilled water to the desired concentrations. The wet samples were dried at 60 °C for 6 hours and at 150 °C for 3 hours prior to calcination process. The dried samples were then calcined in air by Carborite furnace at

600 °C for 15 hours with a heating ramp rate of 10 °C/min from room temperature to 600 °C. The calcined samples were rinsed by distilled water (conductivity is 2 μ s./cm.) at 70 °C. Sample rinsings were repeated until there was no significant change in the rinsed water conductivity. After rinsing, the catalyst were dried again at 120 °C for 15 hours. The platinum precursor [H₂PtCl₆] solution of desired concentration and having volume just only to incipiently wet the CeO₂/Al₂O₃ was poured onto the catalyst precursor with stirring. The wet samples were dried at 60 °C for 15 hours ,and subsequently were calcined at 600 °C for 6 hours with a heating ramp rate of 10 °C/min. The dried samples were rinsed again and then were dried at 120 °C or 15 hours. Finally, the catalysts were sieved for the portion between 80 and 200 mesh to be used as catalysts. The prepared catalysts were stored in a desiccator until being used.

3.3 Catalyst Characterization

Three characterization techniques were used on the prepared catalysts. However, the catalysts should be able to keep their initial structures till the end of runs due to higher temperature and much longer time used in the calcinations compared to those used during each run.

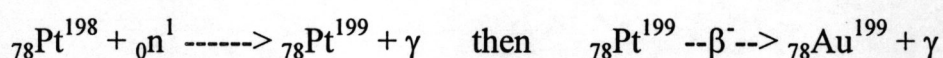
3.3.1 Neutron Activation Analysis(NAA)

NAA was used to determine the exact amounts of platinum and cerium. The analysis was based on a non-destructive method typically called instrumental neutron activation analysis(INAA). All catalysts were separately

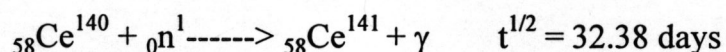
analyzed for platinum and cerium because the half life of the isotope of cerium was much longer than that of platinum.

In both platinum and cerium analysis, each sample was put in two plastic vials to recheck the results against each other. Each vial contained about 0.05 g of sample. The conditions used distinctively between platinum and cerium are shown below.

For platinum, the samples were activated by means of the thermal neutrons for a day. This irradiation time was enough to activate platinum according to:



Cerium was analyzed by using 4 days of irradiation time. The activation process was based on:



The irradiated samples were measured for their γ -ray activities. The loadings were obtained from Equation 3.1 which neglected the time variable because of the small measuring time compared to the half-life.

$$\%M = (A/W) * (W_{\text{std}}/A_{\text{std}}) * (\%M_{\text{std}}) \quad (3.1)$$

where

- $\%M$ = % of metal in sample by wt.
- A = Activity of sample
- A_{std} = Activity of standard

W = Weight of sample(g)

W_{std} = Weight of standard(g)

3.3.2 BET Surface Area Measurement

The catalyst physical surface areas were estimated by Quantachrome Corporation Autosorb I. The 0.5 g nominal weight of samples were outgassed to clean out the surface at 120 °C for at least 6 hours. Their weights were evaluated after outgassing. The measurements were done under nitrogen gas having 16.2 Å² in cross-sectional area. The surface area was estimated by BET equation fitted to five adsorption points.

3.3.3 X-ray Diffraction Analysis

This analysis was done to determine the ceria-crystallite size. Well-mixed catalyst powder was scattered on the 25.4x76.2 mm glass slide without further grinding. The Phillips PW3710 diffractometer was equipped with a Cu anode X-ray tube and a monochromator which initiate K α -ray with the wavelengths of 1.54060(α 1) and 1.54439(α 2) Å. Each sample was scanned two times: Once to perform qualitative peak location and the second time for quantitative data gathering.

The ceria crystallite sizes were estimated from the XRD patterns using the CeO₂-peak approximately at α 1 position of 28.6 degrees scattering angle. The mean particle sizes of ceria crystallites were calculated by the Scherrer equation(Equation 3.2) explained extensively by Baiker (1985), which relates the peak broadening to crystallite size.

$$d_{\text{avg}} = K\lambda/(\beta\cos\theta) \quad (3.2)$$

- where
- d_{avg} = the mean ceria particle size(\AA)
 - K = a constant postulated to be about 0.9 (spherical shape was assumed and peak width was measured at its half height)
 - λ = the wavelength of the monochromatic X-ray radiation(\AA)
 - β = the particle-size dependent line broadening (radian)
 - θ = the scattering angle(radian)

3.4 The Oxygen Storage Capacity Test

This topic is separated into 2 parts. The first part describes the reactor system built up particularly for the OSC test. The second one deals with OSC measurements based on a pulsing technique.

3.4.1 *Experimental Apparatus*

The reactor system is shown in Figure 3.1. Three gases, the carrier and the two reactants, passed through the inlet-gas control box before going to the reactor system.

In the inlet-gas control box, the gases were filtered by 7 micron filters. The flow rates of gases were controlled at the desired values by a SIERRA Instrument mass flow controller. The check valves were installed on

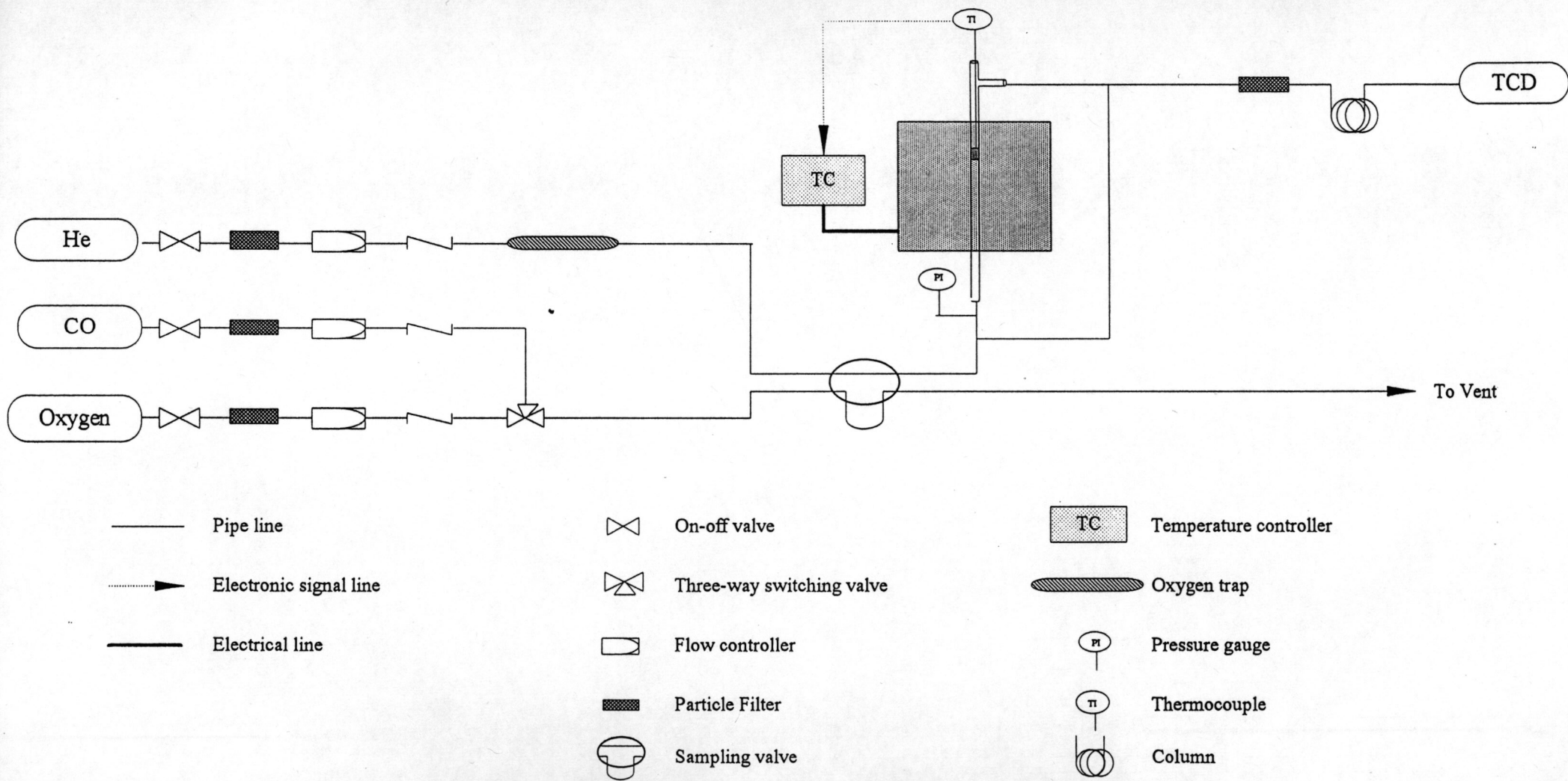


Figure 3.1 The reactor system for OSC testing

the lines to prevent the mass flow transducers from back pressure. Helium (99.999 %purity), which acted as a purging gas, was further treated by an oxygen scrubber which was capable of reducing oxygen impurity to less than 3 ppm. Purified helium passed directly to the sampling valve before proceeding continuously through the tubular reactor. The reactants were selected by a three-way switching valve. The selected gas filled up the sampling loop having a volume of 0.32 cm^3 .

The catalyst was precisely positioned at the hottest point determined by varying the position of the thermocouple with $20 \text{ cm}^3/\text{min}$ helium flowrate and in the upflow direction. A type-K thermocouple obtained from Cole-Palmer was placed on the catalyst bed. Its signal went to the Yokogawa PID controller which controlled the heater. The temperature variations during the experiment (450°C) never fell outside the precision of $\pm 0.1^\circ\text{C}$.

Gases coming out of the reactor were screened by the other 7 micron particle filter before entering the Altech washed molecular sieve 5A 80/100 mesh gas chromatography column. The column was connected to a thermal conductivity detector(TCD). Indeed, this column and the TCD were originally the parts of a HP5890 Series II gas chromatograph from Hewlett Packard with an on-line computer. It was modified simply by disconnecting the column end from the injection port and connecting it to the reactor outlet gas line instead. In this machine, the TCD was a single wire type. The reactant gas and reference gas(helium 99.99 %purity) were selectively switched into the detector by the switching frequency of 10 Hz. The detector output was fed to a computer running HP Chemstation to automatically interpret the data and report the results.

3.4.2 *Experimental Procedure*

3.4.2.1 General Strategy

The catalyst was mixed with non-calcined alumina as a diluent before being packed into the tubular reactor. Prior to the OSC testing, the catalyst was oxidized. After the catalyst was oxidized for a period of time, which was enough to change all ceria to its oxidized form, the oxygen was purged out. First, two carbon monoxide pulses were injected through the reactor by-pass line to the GC column directly to find the carbon monoxide inlet amount, this was followed another pulse of carbon monoxide was fed to the reactor. The difference between the carbon monoxide inlet and outlet was taken as the amount of carbon monoxide oxidized by the stored oxygen in the catalyst due to the absence of the oxygen in gas phase.

As explained in the catalyst preparation section, both of 0.7%wt. Pt/Al₂O₃ and 0.7 %wt.Pt/ X%wt.CeO₂/ Al₂O₃ were prepared. The amount of carbon monoxide oxidized by 0.7%wt.Pt/Al₂O₃ was subtracted from that oxidized by 0.7%wt.Pt/ X%wt.CeO₂/ Al₂O₃. The resulting value was the carbon monoxide oxidized by additional oxygen coming from ceria only. This value was taken as the OSC of 0.7 wt.Pt/ X%wt.CeO₂ /Al₂O₃. Because the OSC was defined as the amount of the oxygen stored by ceria, the OSC of 0.7%wt.Pt/Al₂O₃ was subtracted out.

Since the flowrate during the OSC testing was 20 cm³/min, the amount sampled by the injection loop of 0.32 cm³ represents a contact time of about 1 sec. Therefore the amount of oxygen given can be

representative of the maximum amount of oxygen available in a 1 Hz frequency A/F ratio oscillations.

3.4.2.2 The Oxidation Time

Theoretically, if the oxidizing time is prolonged at the proper temperature, all metals can be fully oxidized at one point. The amount of carbon monoxide was used as the indicator of the degree of catalyst oxidation.

The 0.7 %wt.Pt/ 23 %wt.CeO₂/ Al₂O₃ sample was first studied for testing because it has the highest ceria loading. This catalyst was diluted by alumina using the smallest dilution ratio. This way, the amount of oxygen found adequate for oxidizing this catalyst would also be adequate for the rest of the study.

The catalyst diluted 40 times was oxidized by various oxidation times ranging from 0.5 to 4.5 hours. The resulting carbon monoxide removals were plotted versus the oxidizing times. The time that the graph levels off was taken as the one at which maximum oxidation was reached.

3.4.2.3 The Dilution Ratio

The other factor to be optimized is the dilution ratio. The dilution ratios were altered from 50 to 600 g.catalyst/g.bed. Because we were looking for the ultimate values of catalyst OSC, the amount of catalyst was reduced until the catalyst OSC reached a constant value. This meant that no more oxygen atom can be removed within 1 hour of contacting.

As a first test, the 0.7%wt.Pt /23%wt.CeO₂ /Al₂O₃ sample was selected because it had the highest ceria loading.

3.4.2.4 Catalyst OSC Testing Procedure

As the oxidation time and the dilution ratio were kept constant through out the study, each catalyst was tested in turn. The testing procedure is described below in detail.

All catalysts were diluted with non-calcined alumina to the desired ratio. The diluted catalysts were kept in a desiccator until being used, and just before use 0.0500 g of a diluted catalyst was packed into the tubular reactor.

Initially helium at 90 cm³/min was directed to the reactor for purging out the air for 15 minutes. Then the catalyst was heated up to 450 °C with a heating ramp rate of 20 °C/min. After the catalyst bed reached 450 °C, it was kept at this temperature for another 15 minutes to desorb surface contaminants. After the desorption time, the catalyst was oxidized for 1 hour, as indicated from the oxidation time variation result, under helium flow rate of 20 cm³/min. The gaseous oxygen was purged again by helium. The purging time of 1 hour was consistently used. After 1 hour of purging, the TCD baseline was constant at very low attenuation confirming that all oxygen was cleaned out.

A pulse of carbon monoxide was injected by means of bypass line to TCD. The carbon monoxide amount was recorded. A second bypass carbon monoxide pulse was followed the first one in order to recheck the

carbon monoxide amount by leaving seven minutes in between. The difference between the first and the second pulses never went over 1 percent. Finally the last carbon monoxide pulse was fed to the reactor to measure how much carbon monoxide could be oxidized by catalyst.