

CHAPTER III

EXPERIMENTAL

In this chapter, the materials used in this research are described. The various experimental techniques utilized in the catalyst preparation, characterization and reaction studies will be explained. Details of the catalytic activity test system are also given.

3.1 Materials

3.1.1 Gases

The gases used in this research were:

1. Helium (He 99.99%) was obtained from Praxair (Thailand) Co.,LTD.
2. 20% O₂ in Helium was obtained from Thai Industrial Gas Co.,LTD.
3. Air Zero was obtained from Thai Industrial Gas Co.,LTD.
4. Hydrogen (H₂ 99.99%) was obtained from Thai Industrial Gas Co.,LTD.
5. Methane (CH₄ 99.99%) was obtained from Thai Industrial Gas Co.,LTD.

3.1.2 Chemicals

The chemical reagents used in this research were:

1. Nickel (II) nitrate hexahydrate (≥99%) was obtained from Fluka Chemie A.G.
2. Cerous (III) nitrate hexahydrate (≥99%) was obtained from Fluka Chemie A.G.
3. Zirconium oxychloride (≥99%) was obtained from Fluka Chemie A.G.
4. Urea (≥99%) was obtained from Fluka Chemie A.G.
5. iso-Octane (2,2,4 trimethyl pentane ≥99.5%) was obtained from Lab-Scan, Analytical Sciences.

6. Tin (IV) chloride ($\geq 99.5\%$) was obtained from Fluka Chemie A.G.
7. Niobium (V) chloride ($\geq 99.5\%$) was obtained from Fluka Chemie A.G.
8. α -Alumina ($>96\%$) was obtained from Johnson Matthey.
9. β "-Alumina (with Na^+ ion conductor) was obtained from Ionotec (England).

3.2 Experiment

3.2.1 Catalyst Preparation

3.2.1.1 *Ceria-Zirconia Mixed Oxide Solid Solution*

Mixed oxide solid solutions of Ce-Zr metals were prepared as catalyst supports via urea hydrolysis. The Ce-Zr mixed oxide solid solution samples were prepared from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The starting metal salts were dissolved in distilled water to the desired concentration (0.1 M). The ratio between the metal salts was altered depending on the desired solid solution concentration: $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ in which $x = 0, 0.25, \text{ and } 1.0$. Then the mixed metal salt solution was combined with a 0.4 M urea solution with a salt to urea solution ratio of 2 to 1 by volume, and the mixture was kept at 100°C for 50 hr. The sample was then allowed to cool to room temperature prior to being centrifuged to separate the gel product from the solution. The gel product was washed with ethanol, and dried overnight in an oven at 110°C . The product was then calcined at 500°C for 4 hr.

3.2.1.2 *Ni-supported Catalysts*

The catalysts were prepared by the incipient wetness impregnation method. To prepare Ni supported $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts, Ni (5, 10 and 15 wt%) was loaded by the incipient wetness impregnation method into the supports using its nitrate salt solution. The catalysts were then calcined at 500°C for 4 hr in air.

3.2.1.3 *Ni-Sn supported $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ Catalysts*

The catalysts were prepared by co-impregnation method using aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The nominal loading amount

of Ni was kept constant at 5 wt %, and the amount of Sn loadings were varied between 0 and 2 wt%. The catalysts were then calcined at 500°C for 4 hr in air.

3.2.2 Catalyst characterization

3.2.2.1 BET Surface Area

BET surface area was determined by N₂ adsorption at 77 K (a five point Brunauer-Emmett-Teller (BET) method using a Quantachrome Corporation Autosorb. Prior to the analysis, the samples were outgassed to eliminate volatile adsorbents on the surface at 250°C for 4 hr. The quantity of gas adsorbed onto or desorbed from a solid surface was measured at 5 equilibrium vapor pressure (P/P₀) values of 0.1115, 0.1615, 0.2115, 0.2615 and 0.3115 by the static volumetric method. The adsorption data were calculated using Brunauer-Emmett-Teller (BET) equation:

$$\frac{P/P_0}{W(1-P/P_0)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} (P/P_0) \quad (3.1)$$

where W = weight of gas adsorbed at relative pressure P_0
 W_m = weight of adsorbate constituting a monolayer of surface coverage
 C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction

and then the surface area of the sample was calculated by

$$\text{surface area of sample} = \frac{W_m A_{\text{nitrogen}} (6.02 \times 10^{23})}{M_{w, \text{nitrogen}}} \quad (3.2)$$

where A_{nitrogen} = Crossed-section area of one molecule nitrogen
 = 0.162 nm² at 77 K
 $M_{w, \text{nitrogen}}$ = molecular weight of nitrogen

3.2.2.2 H_2 Chemisorption

The amount of H_2 uptake due to the exposed metal was determined by H_2 pulse chemisorption. This technique was carried on the temperature programmed analyzer (ThermoFinnigan modeled TPDRO 1100) using a pulse technique. Prior to pulse chemisorption, 250 mg of sample was reduced in H_2 atmosphere at 500°C for 1 hr. Then the sample was purged with N_2 at 500°C for 30 min and cooled down to 50°C in flowing N_2 . A H_2 pulse (99.99% H_2 with a sample loop volume of 0.4 ml) was injected into the sample at 50°C . The metal dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom.

3.2.2.3 X-ray Diffraction Methods

An X-ray diffractometer (XRD) system (Rigaku) equipped with a RINT 2000 wide-angle goniometer using $\text{CuK}\alpha$ radiation (1.5406 \AA) and a power of 40 kV x 30 mA was used for examination of the crystalline structure. The sample was ground to a fine homogeneous powder and was held on a thin-walled glass plate against the X-ray beam. The intensity data were collected at 25°C over a 2θ range of $20\text{-}90^\circ$ with a scan speed of $5^\circ (2\theta)/\text{min}$ and a scan step of $0.02^\circ (2\theta)$.

3.2.2.4 Transmission Electron Microscope

The size of supported metal crystallites and morphology of carbon deposition on the spent catalysts was observed by transmission electron microscopy (TEM) with a JEOL (JEM-2010) transmission electron microscope operated at 200 kV. The samples were dispersed in absolute ethanol ultrasonically, and the solutions were then dropped on copper grids coated with a lacey carbon film.

3.2.2.5 H_2 and CH_4 Temperature Programmed Reduction

H_2 temperature programmed reduction (H_2 -TPR) experiments were carried out using a TPR analyzer (ThermoFinnigan model TPDRO 1100). The sample was pretreated in N_2 atmosphere at 400°C for 30 min prior to running the TPR experiment, and then cooled down to room temperature in N_2 . A 5% H_2/N_2 gas was used as a reducing gas. The sample temperature was raised at a constant rate of $10^\circ\text{C}/\text{min}$ from room temperature to 950°C . The amount of H_2 consumption as a function of temperature was determined from a TCD signal.

The amount of surface oxygen mobility over the catalysts was determined by CH₄ temperature programmed reduction (CH₄-TPR). The experiments were carried out in a quartz micro-reactor in a similar manner to H₂-TPR experiments but using a 2% CH₄/He as a reducing gas. The effluent gas composition as a function of temperature was measured using a mass spectrometer (Balzer Instruments modeled Thermostar GSD 300T).

3.2.2.6 Temperature Programmed Oxidation

Temperature programmed oxidation was carried out in a TPO micro-reactor coupled to an FID analyser. TPO was used to determine the amount of carbonaceous deposition on the used catalysts. After keeping the catalyst on stream for partial oxidation, the spent catalyst was cooled down to room temperature in He. Then, about 30 mg sample was heated in a 2%O₂ in He (40 ml/min) mixture at a heating rate 10°C/min up to 900°C. The output gas was passed to a methanation reactor containing 15 wt% Ni/Al₂O₃ as a catalyst. In this methanation reactor, CO₂ formed from the carbon was completely converted with excess H₂ into methane, to permit precise quantification in a FID detector. After the TPO system reached 900°C, where all carbon had been burned off, the FID signal for methane was calibrated by injecting 100 µl of CO₂ pulses into the methanation reactor, and sending the methane produced into the FID. By integrating the methane signal during the entire TPO run, it is possible to calculate the amount of coke removed from the catalyst.

3.3.3 Catalytic Activity Tests

3.3.3.1 Catalytic Activity Test for Methane Partial Oxidation

Catalytic activity tests for methane partial oxidation were carried out in a packed-bed quartz microreactor (i.d. Ø 6 mm). Typically, a 100 mg catalyst sample was packed between layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko FCR-13A-S/M temperature controllers. The feed gas mixture containing 4%CH₄, 2%O₂, and balanced with He was used at a gas hourly space velocity (GHSV) maintained at 53,000 hr⁻¹ using Brooks 5850E mass flow controllers. Measurements were carried out at various furnace temperatures adjusted sequentially from 400-800°C with an interval of 50°C.

The carbon formations on the catalysts were further studied using the same system as for MPO at 700-800°C with different conditions (GHSV of 53,000 hr⁻¹ and CH₄/O₂ ratios of 1.6, 2.0 and 2.5). A schematic diagram of the experimental setup is shown in Figure 3.1.

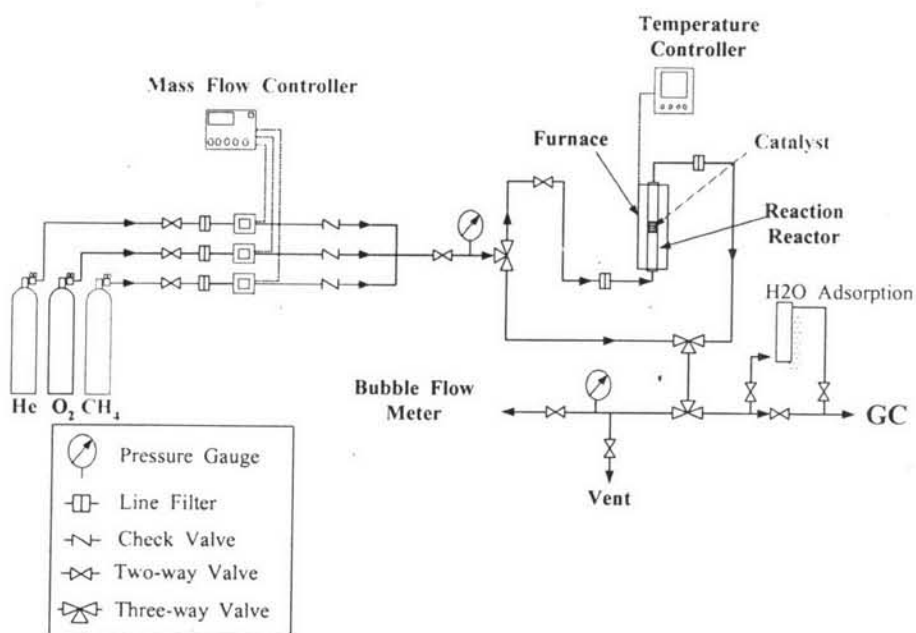


Figure 3.1 Schematic diagram of the experimental setup for methane partial oxidation.

The gaseous products were chromatographically analyzed using a Shimadzu GC 8A fitted with a TCD. A CTR I (Alltech) packed column was used to separate all products at 50 °C except for H₂O which was trapped out prior to entering the column. The CH₄ conversion (X_{CH_4}), O₂ consumption (X_{O_2}) and selectivity (S) that reported in this work were calculated using the following expressions:

$$\% X_{\text{CH}_4} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}} \times 100 \quad (3.3)$$

$$\% X_{O_2} = \frac{O_2^{\text{in}} - O_2^{\text{out}}}{O_2^{\text{in}}} \times 100 \quad (3.4)$$

$$\% S_{CO} = \frac{CO^{\text{out}}}{CO^{\text{out}} + CO_2^{\text{out}}} \times 100 \quad (3.5)$$

$$\% S_{H_2} = \frac{H_2^{\text{out}}}{H_2^{\text{out}} + H_2O^{\text{out}}} \times 100 \quad (3.6)$$

where	CH_4^{in}	=	molar flow rate of CH_4 in
	CH_4^{out}	=	molar flow rate of CH_4 out
	O_2^{in}	=	molar flow rate of O_2 in
	O_2^{out}	=	molar flow rate of O_2 out
	CO^{out}	=	molar flow rate of CO formed
	CO_2^{out}	=	molar flow rate of CO_2 formed
	H_2^{out}	=	molar flow rate of H_2 formed
	H_2O^{out}	=	molar flow rate of H_2O formed

3.3.3.2 Catalytic Activity Test for *iso*-Octane Partial Oxidation

The catalytic activity test for *iso*-octane partial oxidation was carried out in the system operated in a similar manner to that used for methane partial oxidation. A fixed-bed quartz tube microreactor (i.d. \varnothing 6 mm) was used. Typically, ca. 10 mg of catalyst sample diluted in 90 mg of α - Al_2O_3 was packed between the layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko FCR-13A-S/M temperature controllers. *iso*-Octane was vaporized from a saturator set at 10°C using He as carrier gas. The concentration of *iso*-octane was

maintained at 0.8% by mole. Typically, feed composition was altered to obtain C/O ratios in the range between 0.6 and 1.6, balanced with He. The total flow rate of feed gases was kept at 150 ml/min (GHSV = 80,000 h⁻¹) using Aalborg GFC171S mass flow controllers. Measurements were carried out at furnace temperatures adjusted sequentially from 400 - 800°C. The schematic diagram of the experiment setup is shown in Figure 3.2.

The product gases were chromatographically analyzed using a Shimadzu GC 14A equipped with a CTR I (Alltech) column for a TCD detector and Porapak[®] Q (Alltech) column for the FID detector. The selectivities (S) reported in this work were calculated according to the ratio of the moles of a specific product to the total moles of all products based on dry basis. This definition allows selectivities to each sum to unity.

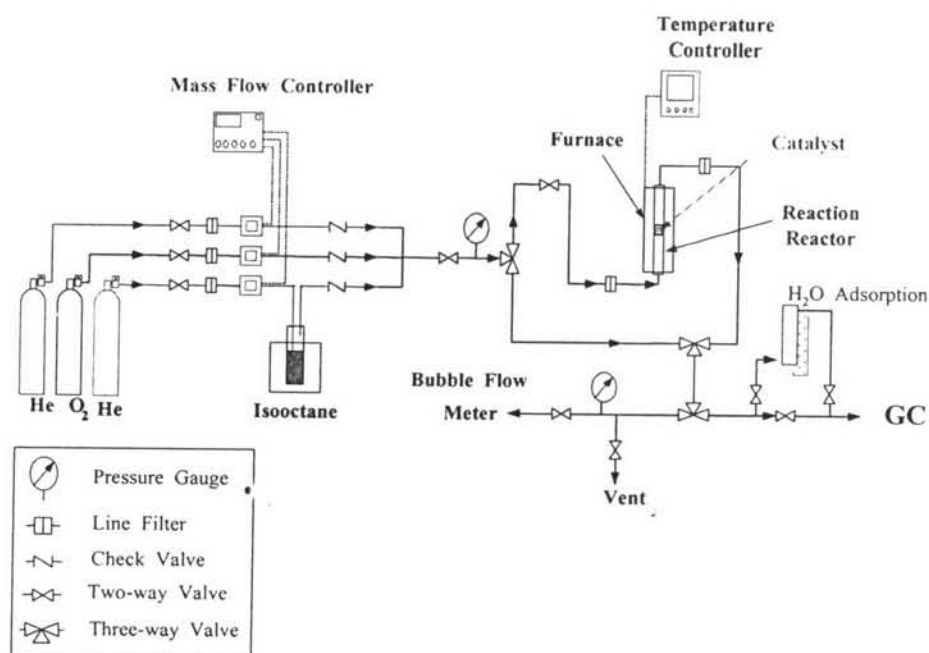


Figure 3.2 Schematic diagram of the experimental setup for *iso*-octane partial oxidation.