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. Nitrogen (N_2 99.99%) was obtained from Praxair (Thailand) Co.,LTD.
3. Air Zero was obtained from Thai Industrial Gas Co.,LTD.
4. Hydrogen (H_2 99.99%) was obtained from Praxair (Thailand) Co.,LTD.

3.1.2 Chemicals

The chemical reagents used in this research were:

1. Cerous (III) nitrate hexahydrate ($\geq$99%) was obtained from Fluka Chemie A.G.
2. Zirconium oxychloride ($\geq$99%) was obtained from Fluka Chemie A.G.
3. Chromium (III) nitrate nonahydrate ($\geq$99%) was obtained from Fluka Chemie A.G.
4. Ferric (III) nitrate nonahydrate ($\geq$99%) was obtained from Fluka Chemie A.G.
5. Manganese (II) nitrate tetrahydrate ($\geq$99%) was obtained from Fluka Chemie A.G.

6. Ammonium vanadate was obtained from Fluka Chemie A.G.
7. Oxalic acid was obtained from Fluka Chemie A.G.
8. Urea (≥99%) was obtained from Fluka Chemie A.G.
9. α-Alumina (>96%) was obtained from Johnson Matthey.
10. Nickel (II) nitrate hexahydrate (≥99%) was obtained from Fluka Chemie A.G.
11. Tin (IV) chloride (≥99.5%) was obtained from Fluka Chemie A.G.
12. Benzene (≥99.5%) was obtained from Lab-Scan, Analytical Sciences.
13. Toluene (≥99.5%) was obtained from Lab-Scan, Analytical Sciences.
14. Naphthalene (≥99.5%) was obtained from Fluka Chemie A.G.

3.2 Experiments

3.2.1 Catalyst Preparations

3.2.1.1 Ceria-Zirconia Mixed Oxides

Mixed oxide of ceria-zirconia samples were prepared via urea hydrolysis. The ceria-zirconia mixed oxide samples were prepared from $Ce(NO_3)_3.6H_2O$ (99.0%, Fluka) and $ZrOCl_2.8H_2O$ (99.0%, Fluka). The synthesized procedure has been reported elsewhere (Pengpanich *et al.*, 2002). Briefly, 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 concentration: $Ce_{1-x}Zr_xO_2$ in which x = 0, 0.25, 0.50, 0.75 and 1.0. Then, the mixed metal salt solution was added with a 0.4 M of urea (99.0%, Fluka) solution with the salt to urea solution ratio of 2:1 (v/v), and the mixture was kept at 100 °C for 50 h. The sample was then allowed to cool to room temperature prior to being centrifuged to separate a 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 either 500 °C for 4 h.

3.2.1.2 Transition Metal Oxide-doped Ceria-Zirconia Mixed Oxides

The series of transition metal oxide-doped ceria-zirconia mixed oxide samples, $Ce_{0.75}Zr_{0.15}Me_{0.10}O_2$ (Me = Cr, Fe, Mn and V), were prepared via urea hydrolysis. $Ce(NO_3)_3{\cdot}6H_2O$ (99.0%, Fluka), $ZrOCl_2{\cdot}8H_2O$ (99.0%, Fluka), $Cr(NO_3)_3{\cdot}9H_2O$ (99.0%, Fluka), $Fe(NO_3)_3{\cdot}9H_2O$ (99.0%, Fluka), $Mn(NO_3)_2{\cdot}4H_2O$ (99.0%, Fluka) and NH_4VO_3 (99.0%, Fluka) were used as sources of Ce, Zr,Cr, Fe, Mn and V, respectively. The synthesis procedures of transition metal oxide-doped ceria-zirconia mixed oxides were similar manner as mention in section 3.2.1.1.

3.2.1.3 Ni-supported Catalysts

The catalysts were prepared by the incipient wetness impregnation method. To prepare Ni supported mixed oxide catalysts, 15 wt% Ni was loaded by the incipient wetness impregnation method into the mixed oxide supports using its nitrate salt solution. The catalysts were then calcined at 500°C for 4 h. A Ni/α-Al_2O_3 catalyst was also prepared for comparision purposes.

3.2.2 Catalyst Characterizations

3.2.2.1 X-ray Diffraction

An X-ray diffractometer (XRD) system (Rigaku) equipped with a RINT 2000 wide-angle goniometer using Cu Kα radiation and a power of 40 kV x 100 mA was used for examination of the crystalline structure. The intensity data were collected at 25 °C over a 2θ range of 20-90° with a scan speed of 5° (2θ)/min and a scan step of 0.02° (2θ).

3.2.2.2 BET Surface Area

The specific surface area, the pore volume and the pore size distribution of the samples were determined from adsorption and desorption isotherms of nitrogen at 77 K 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 h.

3.2.2.3 Temperature Programmed Reduction

Temperature programmed reduction (TPR) measurements were carried out to investigate the redox properties over the resultant materials.

About 50 mg of catalyst was placed in a quartz tube and pretreated in a 20 ml/min He atmosphere at 400 °C for 1 h prior to running the TPR experiment, and then cooled down to room temperature in He. The feed of 1% CO in He at a flow rate of 50 ml/min was used as a reducing gas. The temperature of the sample was raised at a constant rate of 10 °C/min. The amount of CO consumption during the increasing temperature period was measured using a mass spectrometer (Balzer Instruments modeled Thermostar GSD 300T).

3.2.2.4 H_2 Chemisorption

The dispersion degree of nickel was measured by H_2-pulse chemisorption at 50 °C using an Ar flow of 50 ml/min and each pulse of 0.1 ml (10% H_2 in Ar). For measurements, about 100 mg of sample was placed in a quartz reactor. Prior to the pulse chemisorption, the sample was reduced at 500 °C under H_2 atmosphere for 1 h. Then the sample was purged with Ar at 500 °C for 30 min and cooled to 50 °C in flowing Ar. The H_2 pulses were carried out with an injection interval of 6-8 min until the areas of successive hydrogen peaks were identical. The nickel dispersion was calculated assuming the adsorption stoichiometry of a hydrogen atom per nickel surface atom.

3.2.2.5 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was carried out in a homemade TPO micro-reactor coupled with an FID detector. TPO was used to determine the amount of carbonaceous deposition on the spent catalysts. Typically, about 30 mg sample was heated in a 2%O_2 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/Al_2O_3 as a catalyst. In this methanation reactor, CO_2 formed form the carbon was completely converted with excess H_2 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 CO_2 pulses into the methanation reactor, and sending the methane produced into the FID. By integrating the methane signal during the entire TPO run, it was possible to calculate the amount of carbon removed from catalyst.

3.2.2.6 Transmission Electron Microscope

The morphology of the fresh catalyst and 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.

3.2.3 Catalytic Activity Tests

3.2.3.1 Catalytic Activity Test for Model Tar Compound Total Oxidation

Catalytic activity tests for model tar compound (benzene, toluene and naphthalene) total oxidation were carried out in a differential fixed-bed quartz tube reactor (i.d. ∅ 6 mm). Typically, 50 mg of a catalyst was packed between the layers of quartz wool. The reactor was placed in an electric furnace equipped with a K-type thermocouple. The catalyst bed temperature was monitored and controlled by a Shinko temperature controller. A total flow rate of 200 ml/min gas mixtures containing 2000 ppmv of benzene (or 2000 ppmv of toluene or 200 ppmv of naphthalene), 10% oxygen and balance of helium was used. Measurements were carried out at various furnace temperatures adjusted sequentially from 200 to 500 °C with an interval of 20 °C. Exit gases were chromatographically analyzed using a Shimadzu GC 8A equipped with a CTR I (Altech) column and a TCD detector and a Shimadzu GC 17A equipped with a HP-1 (Agilent technologies) column and an FID detector. The schematic diagram of the experimental setup was shown in Figure 3.1. The conversions were determined by dividing the moles of reactant consumed by the moles of initial reactant.

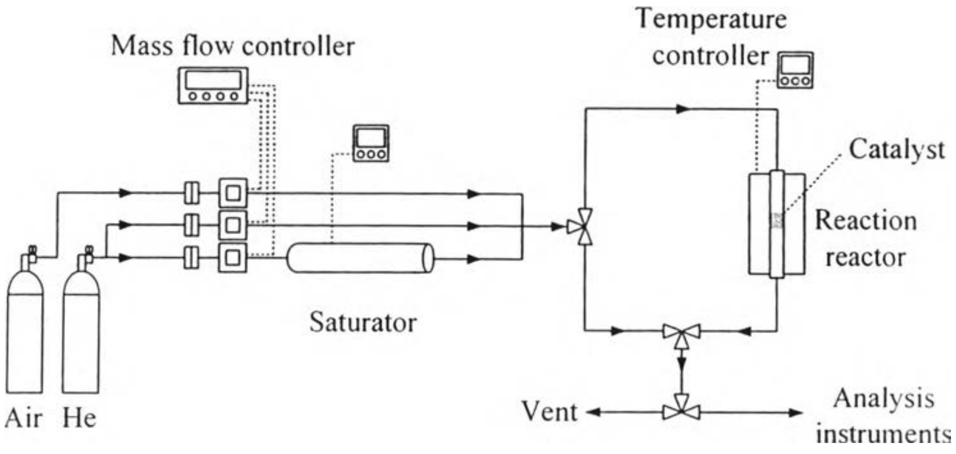

Figure 3.1 Schematic diagram of the experimental setup for model tar compound total oxidation.

3.2.3.2 Catalytic Activity Test for Model Tar Compound Steam Reforming

Catalytic activity tests for the steam reforming of model tar compound (naphthalene and toluene) were conducted by using the atmospheric flow experimental system shown in Figure 3.2. A fixed-bed quartz tube microreactor (i.d. ∅ 6 mm) was used. Typically, ca. 100 mg of 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 temperature controllers.

Naphthalene was vaporized from a saturator at 60 °C using He as carrier gas. The concentration of naphthalene was maintained at ca. 1,500 ppmv. In the case of toluene steam reforming, the toluene concentration was maintained at ca. 2,000 ppmv. Typically, feed composition was altered to obtain H_2O/C ratios in the range between 1.0 and 5.0, balanced with He. The total flow rate of feed gases was kept at 100 ml/min using mass flow controllers. Measurements were carried out at furnace temperatures at 700°C. The product gases were chromatographically analyzed using a a Shimadzu GC 8A equipped with a CTR I

(Altech) column and a TCD detector and a Shimadzu GC 17A equipped with a HP-1 (Agilent technologies) column and an FID detector.

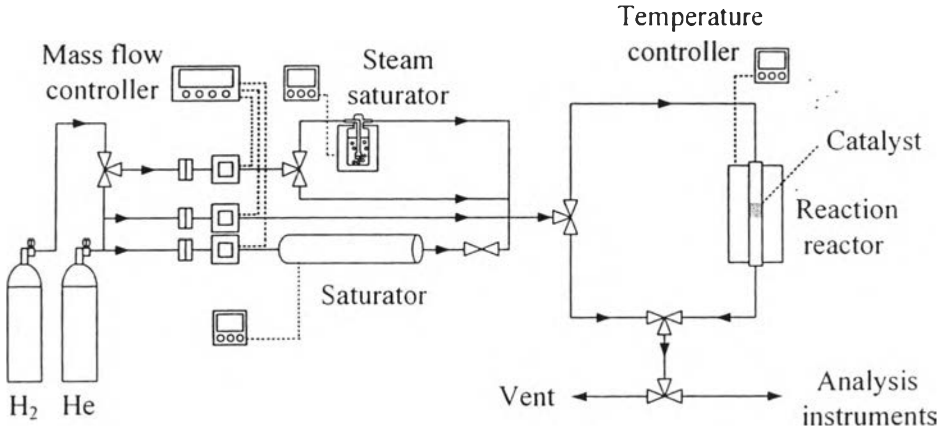

Figure 3.2 Schematic diagram of the experimental setup for model tar compound steam reforming.