

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Gases

The gases uses in this research are:

- Helium (He 99.99% purity) was obtained from Praxair (Thailand) Co., LTD.
- Air Zero was obtained from Thai Industrial Gas Co., LTD.
- Hydrogen (H₂ 99.99% purity) was obtained from Thai Industrial Gas Co., LTD.
- Methane (CH₄ 99.99% purity) was obtained from Thai Industrial Gas Co., LTD.

3.1.2 Chemicals

The chemical reagents uses in this research are:

- Nickel (II) nitrate hexahydrate ($\geq 97\%$ purity) was obtained from Labscan Asia Co.,Ltd and A.C.S.Xenon Limited Partnership
- Cerium (III) nitrate hexahydrate ($\geq 99\%$ purity) was obtained from A.C.S.Xenon Limited Partnership
- Zirconium oxychloride ($\geq 99\%$ purity) was obtained from A.C.S.Xenon Limited Partnership
- Manganese nitrate tetrahydrate ($\geq 97\%$ purity) will be obtained from A.C.S.Xenon Limited Partnership
- Urea ($\geq 99\%$ purity) was obtained from Fluka Chemie A.G.

3.2 Equipments

3.2.1 Catalyst Characterization

3.2.1.1 *X-ray Diffractometer (XRD)*

An X-ray diffractometer (JEOL) equipped with a JDX-3530 using Cu K α radiation and a power of 40 kV \times 30 mA was used for examination of the crystalline structure. The intensity data was collected at 25°C over a 2θ range of 20 – 90° with a scan speed of 5° (2θ) min⁻¹ and a scan of 0.02° (2θ).

3.2.1.2 *Hydrogen Temperature-Programmed Reduction (H₂-TPR)*

Hydrogen temperature-programmed reduction experiments were carried out with a Micromeritics TPD/TPR 2900 apparatus equipped with a TCD detector. Prior to the reduction experiments, the sample, about 30 mg, was thermally treated under a helium stream at 100°C to remove moisture. TPR profiles were attained by heating the samples under a 10% H₂/Ar flow (50 ml min⁻¹) from 30 to 850°C at a linearly programmed rate of 10°C min⁻¹.

3.2.1.3 *BET Surface Area*

BET surface area was determined by N₂ adsorption at -196°C (a five point Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb-1 MP). Prior to the analysis, the samples were out-gassed to eliminate volatile adsorbents on the surface at 250°C for 4 hours. The quantity of gas adsorbed onto or desorbed from a solid surface was measured at 5 equilibrium vapor pressure (P/P_0) 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:

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

where W = weight of gas adsorbed at relative pressure P_0 (g)
 W_m = weight of adsorbate constituting a monolayer of surface coverage (g)
 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

$$\text{Surface area of sample} = \frac{W_m A_{\text{nitrogen}} (6.02 \times 10^{23})}{Mw_{\text{nitrogen}}} \quad (3.2)$$

where A_{nitrogen} = Crossed-section area of one molecule nitrogen
 = 0.162 nm^2 at -196°C
 Mw_{nitrogen} = molecular weight of nitrogen (g/mol)

3.2.1.4 H_2 -Pulse Chemisorption

The dispersion degree of nickel was measured by H_2 -pulse chemisorption at 50°C using an Ar flow of 50 ml min^{-1} and individual pulses 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 pulse was continued with H_2 with an injection interval of $6 - 8 \text{ min}$ until the areas of successive hydrogen peaks were identical. The nickel dispersion was calculated assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom.

3.2.1.5 Temperature-Programmed Oxidation

The amount of carbon deposited on the spent catalyst was quantitatively determined by temperature-programmed oxidation (TPO) technique, which was carried out in a homemade TPO micro-reactor analyzer coupled with an FID detector. Typically, a 30 mg sample was heated from room temperature in flowing $2\% O_2/He$ at a heating rate $10^\circ\text{C min}^{-1} - 900^\circ\text{C}$.

3.2.1.6 Scanning Electron Microscope

Scanning Electron Microscope (SEM), Hitachi S4800, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. Energy Dispersive X-ray spectrometer (EDX), Oxford Model 6111, was utilized to identify the presence of element (from characteristic x-ray) in the catalyst region being examined. The catalyst sample was placed on stub and coated by platinum in sputtering device before place in the sample holder in SEM.

3.3 Methodology

3.3.1 Catalyst Preparation

Mixed oxide solid solutions of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (CZO) support was prepared via urea hydrolysis. The Ce-Zr mixed oxide sample was 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). Then, the mixed metal salts solution were added with a 0.4 M of urea solution with the salt to urea solution ratio of 2:1 (v/v), and the mixture was kept at 100°C for 50 hours. 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 hours (Pengpanich *et al.*, 2002).

The catalysts were prepared by co-impregnation method using the aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The percentage of Ni loading was fixed at 15 wt% and percentage of Mn loading was varied with 5, 10, and 15 wt% on catalysts. The catalysts were dried at 110°C for 4 hours and calcined at 500°C for 4 hours in air. These catalysts were labeled as 15Ni“a”Mn/CZO “(C)”, where “a” indicates the wt% of Mn and “(C)” stands for “co-impregnation”. For the samples “15Ni5Mn/CZO (C)” was referred to 15%Ni5%Mn/CZO prepared via co-impregnation.

The catalysts were prepared by multi-step incipient wetness impregnation method by using the aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The loading amounts of Mn were varied of 5, 10, and 15 wt% on the supported catalysts. After drying at 110°C for 4 hours and calcined at 550°C for 3 hours in air, the Mn/CZO supports were obtained. The Mn/CZO supports were impregnated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (15 wt%), then drying at 110°C for 4 hours and calcined at 500°C for 4 hours. These catalysts were labeled as 15Ni“a”Mn/CZO “(S)”, where “a” indicates the wt% of Mn and “(S)” stands for “sequential impregnation”. For the samples “15Ni5Mn/CZO (S)” was referred to 15%Ni5%Mn/CZO prepared via sequential impregnation.

3.3.2 Catalytic Activity Testing

Catalytic activity tests for the steam reforming of methane were conducted using the atmospheric flow experimental system shown in Fig. 3.1. A fixed-bed quartz tube micro-reactor (i.d. \varnothing 6 mm) was used. Typically, ca. 100 mg of catalyst sample will be 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 temperature controllers. Before the activity test, the catalyst was reduced at 600°C for 2 h in flowing 50% H₂/Ar. After the reduction, the feed gas (CH₄/H₂O/Ar = 4 mol%/16mol%/balance) was allowed to pass through the catalyst bed at rate of 200 ml min⁻¹ (GSHV = 40,000 h⁻¹). Measurements were performed at various furnace temperatures adjusted sequentially from 600 to 800°C.

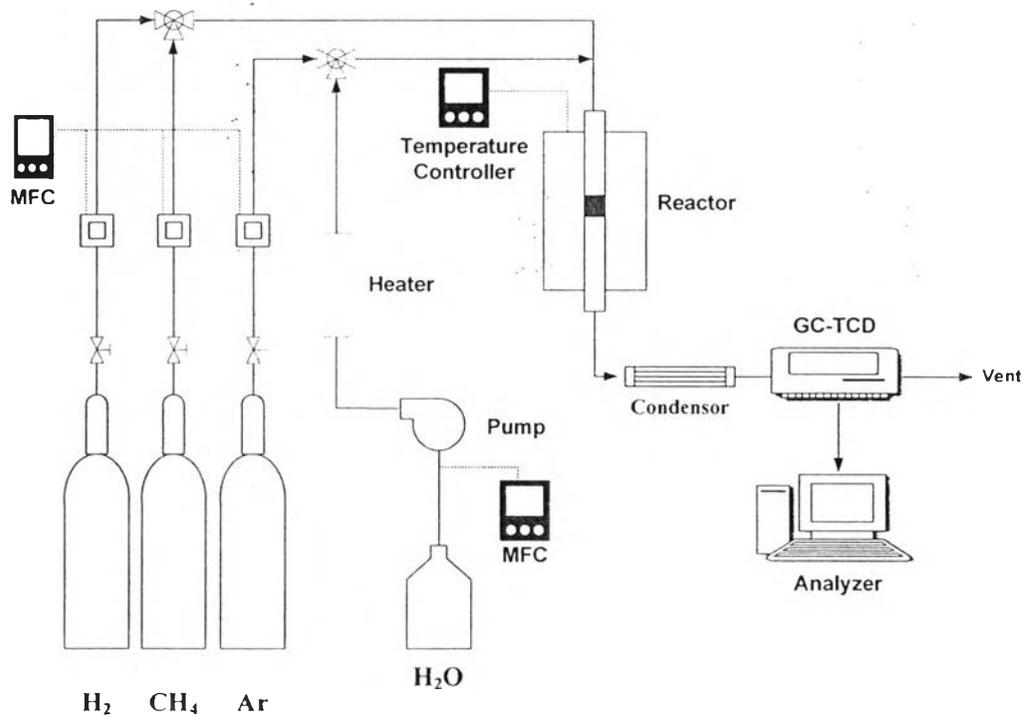


Figure 3.1 Schematic of the experimental setup for methane steam reforming.

The product gases were chromatographically analyzed using a Shimadzu GC 8A equipped with a CTR I (Altech) column and a TCD detector. The methane conversion (X_i), selectivities of carbon containing products and (S_i) in this work will be calculated as follows:

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

$$\%Y_{\text{H}_2} = \frac{\text{H}_2^{\text{out}}}{3\text{CH}_4^{\text{in}}} \times 100 \quad (3.4)$$

$$\%S_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CO}^{\text{out}} + \text{CO}_2^{\text{out}}} \times 100 \quad (3.5)$$

$$\%S_{\text{CO}_2} = \frac{\text{CO}_2^{\text{out}}}{\text{CO}^{\text{out}} + \text{CO}_2^{\text{out}}} \times 100 \quad (3.6)$$

where

CH_4^{in}	=	mole of CH_4 in
CH_4^{out}	=	mole of CH_4 out
CO^{out}	=	mole of CO formed
CO_2^{out}	=	mole of CO_2 formed
H_2^{out}	=	mole of H_2 formed