CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Gases

The gases used in this research are:

1. Hydrogen (H_2, 99.99 %purity), PRAXAIR
2. Nitrogen (H_2, 99.99 %purity), PRAXAIR

3.1.2 Chemicals

The chemical reagents used in this research are:

1. Nickel (II) nitrate hexahydrate ($\geq$97 %purity), Sigma-Aldrich
2. Cerium (III) nitrate hexahydrate ($\geq$99 %purity), Sigma-Aldrich
3. Zirconium nitrate hydrate ($\geq$99.5 %purity), Sigma-Aldrich
4. Magnesium nitrate hexahydrate ($\geq$99 %purity), Fluka
5. Hydrazine hydrate (37.5% purity), Right Solution
6. Adiponitrile (99 %purity), Sigma-Aldrich
7. Methanol ($\geq$99.9 %purity), RCI Labscan
8. Aminohexanenitrile ($\geq$98 %purity), Alfa Aesar
9. Hexamethylenediamine ($\geq$98 %purity), Sigma-Aldrich
10. Hexamethyleneimine ($\geq$99 %purity), Sigma-Aldrich

3.2 Equipment

3.2.1 Catalyst Characterization

3.2.1.1 BET Surface Area Measurements

BET surface area was determined by N_2 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 was calculated using Brunauer–Emmett–Teller (BET)

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

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 of the sample was calculated by

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

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)

3.2.1.2 H_2-Temperature Programmed Reduction

Hydrogen temperature programmed reduction (H_2-TPR) experiments were carried out using a TPR analyzer (ThermoFinnigan modeled TPDRO 1100). The sample was pretreated in N_2 atmosphere at 120 °C for 30 min prior to running the TPR experiment, and then cooled down to room temperature in N_2. A 5% H_2/ Ar gas will be used as a reducing gas. The sample temperature was raised at a constant rate of 10 °C/min from room temperature to 900 °C. The amount of H_2 consumption as a function of temperature was determined from a TCD signal.

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3.2.1.3 X-ray Diffraction

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide-angle goniometer using CuK_α radiation (1.5406 Å) and a power of 40 kV×30 mA was used for examination of the crystalline structure. The sample was ground to a fine homogeneous powder and was held on thin-walled glass plate against the X-ray beam. The intensity data was collected at 25 °C over a 2θ range of 20–80° with a scan speed of 5° (2θ)/min and a scan step of 0.02° (2θ).

3.2.1.4 Scanning Electron Microscopy

Supported metal crystallites, morphologies of sample and carbon deposition on the catalysts were investigated using a Hitachi (S-4800) scanning electron microscope operated at 5kV and 10 mA.

3.2.1.5 X-ray Fluorescence Spectroscopy

The composition of materials was determined by the X-ray fluorescence method (XRF) using a PANalytical analysis instrument with AXIOS&SUPERQ version 4.0 systems. IQ+ program was used to measure and analyze the samples. In the analysis procedure, the scans were first searched for peaks. The found peaks were identified and analyzed quantitatively using fundamental parameter.

3.2.1.6 NH₃-Temperature Programmed Desorption

NH_3-Temperature-programmed desorption (NH_3-TPD) was carried out to estimate the amount of acid in the catalysts. NH_3-TPD was carried out in the following; 30 mg of a powder sample was heated at a rate of 10°C/min up to 500°C and kept for 1 hour in the helium atmosphere to remove adsorbed molecules on the catalyst surface. The sample was cooled down to room temperature in the helium atmosphere, then followed by adsorption of NH_3 in pure NH_3 flow for 1 hour. Consecutively, NH_3-TPD was initiated at a heating rate of 10°C/min to 700°C. The rate of NH_3 desorption was determined by using a TCD signal.

3.2.1.7 H₂-Chemisorption

The Ni dispersion was measured by H_2-pulse chemisorption at 25 °C using an N_2 flow and individual pulses of 10 μl (99.99% H_2). For measurements, 50 mg of sample was placed in a quart reactor. Prior to the pulse chemisorption, the sample was reduced at 600 °C under H_2 for 1 h. Then the sample

was purged with N_2 at 300 °C for 1 h and cooled to 25 °C in flowing N_2. The H_2 pulses were continued with an injection interval of 30 sec 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.

3.3 Methodology

3.3.1 Catalyst Preparation

3.3.1.1 Synthesis of $Ce_{0.75}Zr_{0.25}O_2$

$Ce_{0.75}Z_{0.25}O_2$ support was prepared via the co-precipitation method using cerium nitrate hexahydrate (99%), zirconium nitrate hydrate (99.5%) and hydrazine (37.5%). With the volumetric ratio of hydrazine solution to mixed metal salt solution equal to 1.5, a mixed metal salt solution of cerium nitrate (10 g L^{-1}) and zirconium nitrate (10 g L^{-1}) was introduced dropwise into an aqueous solution of hydrazine (5 mol L^{-1}). The resultant mixture then heated under reflux with agitation for 120 h while the pH of 9 or higher was maintained by addition of hydrazine aqueous solution. After being centrifuged and filtered from the mixture, the solid support was dried at 100 °C for 12 h and then calcined in flowing oxygen at 750 °C for 4 h (Ciuparu et al., 2007).

3.3.1.2 Synthesis of $Ce_{0.75}Zr_{0.15}Mg_{0.2}O_2$

$Ce_{0.75}Z_{0.15}Mg_{0.20}O_2$ support (3 %wt. Mg) was prepared via the co-precipitation method from cerium nitrate hexahydrate (99%), zirconium nitrate hydrate (99.5%), magnesium nitrate hexahydrate (99%) and hydrazine (37.5%). The synthesis was carried out in a similar manner as the synthesis of $Ce_{0.75}Z_{0.25}O_2$ support with the additional step of incorporating magnesium aqueous solution (4.16 g L^{-1}) into a mixed metal salt solution.

3.3.1.3 Impregnation of Nickel

Nickel was loaded at 15 %wt. onto support by the incipient wetness method using an aqueous solution of nickel nitrate hexahydrate. The prepared catalyst was dried at 110 °C for 4 h followed by calcination at 500 °C for 4 h prior to the reaction.

3.3.2 Catalytic Activity Testing

The reaction was carried out in 8 mm stainless steel tube reactor at atmospheric pressure. In tube reactor, catalyst was packed between quartz wool layers. In order to ensure eliminating of back filling and channelling in this reactor, a plug flow condition was achieve by providing a catalyst bed length (L) to particle diameter (d_p) ratio at least 50 (L/d_p > 50) and a tube diameter (D) to particle diameter (d_p) ratio at least 10 (D/d_p > 10). The reaction temperature was monitored and controlled by using thermocouples and electrical furnace. Hydrogen and nitrogen flow rate were monitored and controlled by using Brooks Microprocessor Control & Read Out Unit and Brooks Mass Flow Controllers 5850E series. Adiponitrile solution was fed by Eldex HPLC pump. The products were collected by condensation and analyzed by gas chromatograph (GC). Before hydrogenation, the catalyst was reduced in situ with 1 volumetric ratio of hydrogen to nitrogen (total flow rate 50 ml/min) for 2 h (heating rate 10 °C/min). After reduction, the reactor was purged with nitrogen for 10 min.
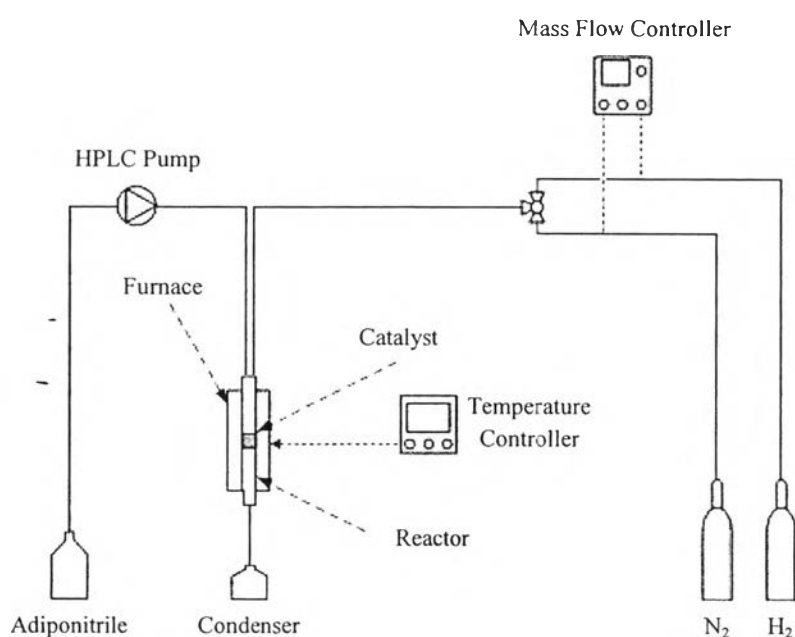

Figure 3.1 Schematic of the experimental setup for adiponitrile hydrogenation.

The ADN conversion (%), selectivity of HMDA, AHN and HMI (%) that reported in this work was calculated using the following expressions:

$$\text{ADN conversion (\%)} = \frac{[ADN]_{in} - [ADN]_{out}}{[ADN]_{in}} \times 100 \qquad (3.3)$$

$$\text{Selectivity}_{HMDA} \ (\%) = \frac{[HMDA]_{produced}}{[ADN]_{use}} \times 100 \qquad (3.4)$$

$$\text{Selectivity}_{AHN} \ (\%) = \frac{[AHN]_{produced}}{[ADN]_{use}} \times 100 \qquad (3.5)$$

$$\text{Selectivity}_{HMI} \ (\%) = \frac{[HMI]_{produced}}{[ADN]_{use}} \times 100 \qquad (3.6)$$

Where

$[ADN]_{in}$	=	molar of ADN in
$[ADN]_{out}$	=	molar of ADN out
$[ADN]_{use}$	=	$[ADN]_{in} - [ADN]_{out}$
$[HMDA]_{produced}$	=	molar of produced HMDA
$[AHN]_{produced}$	=	molar of produced AHN
$[HMI]_{produced}$	=	molar of produced HMI