CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Sodium hydroxide pellets (NaOH) 86.8% purity was obtained from Carlo Erba Reagenti.

Ludox HS-40 colloidal silica, 40 wt% suspension was obtained from Aldrich.

n-Myristyltrimethylammonium bromide (MTAB; $C_{14}H_{29}N(CH_3)_3Br$) was obtained from Acros.

n-Hexadectyltrimethylammonium bromide (CTAB; $C_{16}H_{33}N(CH_3)_3Br$) was obtained from Aldrich.

n-Octane (C_8H_{18}) of min 99% purity was obtained from Lab-Scan (Thailand).

Platinum (II) acetylacetonate ($[CH_3COCH{=}(\text{-}CO\text{-})CH_3]_2Pt$) of 99.99% purity was obtained from Aldrich.

Tetraammineplatinum (II) chloride ($Pt(NH_3)_4Cl_2.H_2O$), Pt 55.89% was obtained from Alfa Aesar.

3.1.2 Gases

High purity (HP) nitrogen

High purity (HP) hydrogen

High purity (HP) helium

3 vol% carbonmonoxide balanced in helium

Air zero grade

All gases were obtained from Thai Industrial Gas Public Co., Ltd. and Praxair (Thailand) Co., Ltd.

3.2 Tools and Equipment

3.2.1 Tools

Glovebox
Magnetic bar
Magnetic stirrer
Mechanical stirrer
Oven
Spatula
Dessicator

3.2.2 Equipment

Continuous flow reactor
Gas chromatograph, GC (Shimadzu, GC-17A)
X-ray diffraction, XRD (Rigaku, RINT-2200)
Transmission electron microscope, TEM (JEOL JEM-2000FX)
Microwave oven, MW (CEM corporation, MARS 5)
Surface area analyzer, BET (Quantachrome, Autosorb-1)
Hydrogen chemisorption apparatus
Temperature programmed oxidation apparatus, TPO
Temperature programmed reduction apparatus, TPR
Fourier transform infrared spectrophotometer, FTIR (Bruker, Equinox 55)

3.3 Synthesis of MCM-41 by using Microwave Hydrothermal Treatment

For this method the procedure was reported by Kim *et al.*, 1998; myristyltrimethylammonium bromide (MTAB; $C_{14}H_{29}N(CH_3)_3Br$) was used as a quaternary ammonium surfactant. A sodium silicate solution was prepared by combining aqueous NaOH solution with Ludox HS-40 (40.0 wt% SiO_2, DuPont). The resultant gel was then heated with stirring at 60°C for 30 min. This solution was slowly added 25 wt% aqueous solution of a MTAB surfactant with vigorous stirring at room temperature for 1 day. The gel composition contained SiO_2: MTAB: NaOH: H_2O= 1.0: 0.167: 0.5: 40.5.

For the next step, the gel mixture was loaded into a Teflon autoclave installed in a microwave oven and heated with two steps; first at 100–150°C for 1 to 30 min under different microwave powers for a nucleation followed by heating at 100°C for 30 min under 300 W of microwave power for crystallization. The pH of the solution mixture was adjusted to 9 by dropwise addition of mineral acid between two steps. The resulting solid product was isolated by filtering, washing with deionized water, and drying in air at 100°C for 10 h. To remove the organic species occluded in the pores of MCM-41, the as-synthesized samples were calcined at 550°C for 6 h in air.

For synthesis of the MCM-41 with bigger pore can be created by increasing the chain length of surfactant template. In this work, *n*-hexadectyltrimethylammonium bromide (CTAB; $C_{16}H_{33}N(CH_3)_3Br$) was used instead of MTAB.

3.4 Characterization of Synthesized MCM-41

Synthesized MCM-41 were identified by X-ray diffraction (XRD). The morphology of as-synthesized MCM-41 were analyzed by using Transmission electron microscope (TEM). And the specific surface area pore volume and pore diameters were measured by Nitrogen adsorption (BET).

3.4.1 X-ray Diffraction (XRD)

X-ray diffraction patterns were recorded on a Rigaku, RINT-2200 using a monochromatic CuK∝ radiation (1.5418 Å) at degree 2-theta from 1.5 to 10 with scan speed 2 degree/ min and step size 0.02.

3.4.2 TEM

The morphology of the MCM-41 were obtained with a JEOL JEM-2000FX TEM. Before preparing the sample, the catalyst was reduced under H_2 flow at 500 °C for 1 h. After that, the reduced catalyst was suspended in 2-propanol and stirred with ultrasound for 15 min. A few drops of the resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis.

3.4.3 Surface Areas and Pore Diameters

The specific surface areas and pore diameters were determined by a Quantachrome surface area analyzer (Autosorb-1). Nitrogen was used as a probe gas. A sample was dried and outgassed in the sample cell at 250 °C over night before adsorption. The specific area and pore diameter were calculated from 25 points adsorption isotherm. The results were analyzed by the Autosorb ANAGAS software version 2.10.

3.5 Catalyst Preparation

All of catalysts were prepared with 1 wt% Pt by two methods; Incipient wetness impregnation (IWI) and Vapor phase impregnation (VPI), whereas Pt/SiO_2 catalyst was only prepared by IWI method.

According to Jongpatiwut *et al.* (2003), VPI method was found to result in the highest Pt dispersion and maximum incorporation of Pt inside the channels of the zeolite compared to any method. Therefore, VPI method was selected to prepare the catalysts. The procedure was described below.

3.5.1 Vapor Phase Impregnation (VPI)

The as-synthesized MCM-41 were calcined in air flow 100 ml/min/g. of the support. Then used 2 h ramp to temperature to 500 °C and held for 5 h. Then the MCM-41 was cooled in air, after that it was removed and quickly transferred to inert atmosphere (used glove box with N_2 flow) in order to avoid any adsorbed moisture.

In the inert atmosphere, the Pt/MCM-41 was prepared by physically mixing with 1% platinum acetylacetonate compound for 30 min. The well mixed solid mixture was transferred into the reactor tube. Flow He (<10 ml/min/g. of catalyst) was performed to make inert atmosphere and then temperature was ramped to 40 °C, held for 3 h. After that temperature was slowly ramped to 60, 80, 90, 100 °C to trace water. Then temperature was ramped to 115 °C and held for 15 min to sublime the platinum acetylacetonate compound.

The next step is to decompose the platinum acetylacetonate. After that the Pt precursor was decomposed by calcining the catalyst in air flow (100ml/min/g. of catalyst) and the temperature was ramped to 350 °C and held for 2 h. The reactor tube was then cooled down to room temperature; the sample was removed and stored in the dessicator.

3.5.2 Incipient Wetness Impregnation (IWI)

As-synthesized MCM-41-C14 and SiO_2 (Hi-Sil 233) were prepared by the incipient wetness impregnation method. To prepare Pt supported on MCM-41 and SiO_2 catalysts, Pt 1.0 wt% was loaded by the incipient wetness impregnation method into the supports using its chloride salt solution. The catalysts were then calcined at 500°C for 6 h in air.

3.6 Characterization of Pt/MCM-41

3.6.1 DRIFTS of Adsorbed CO

The locations of Pt particles were determined by DRIFTS using CO as a probe in a Bruker Equinox 55 spectrometer equipped with a MCT detector. Experiments were performed in a diffuse reflectance cell from Harrick Scientific typed HVC-DR2, with ZnSe windows. For each IR spectrum, a background was collected on the sample reduced in situ under a flow of H_2 at 300°C for 1 h and purged in He for 30 min at ambient temperature. Then, a flow of 5%CO in He was passed through the sample for 30 min, followed by a purge in He flow for 30 min. After such a treatment, the spectrum of adsorbed CO was collected.

3.6.2 Temperature Programmed Reduction (TPR)

TPR-analysis was used for determining the oxidation state of metal, reduction temperature and the interaction of the metal on support. TPR was carried out by flowing 10 ml/min of 5.0% hydrogen in argon. Prior to reduction experiments, 0.03-0.05 g of catalyst was packed to the quartz tube reactor and raising temperature from room temperature to 700°C under heating rate of 10°C/min. The TPR profiles were obtained by passing through the sample. The effluent gas was passed through a moisture trap before the TCD in order to remove water from the exit stream.

3.6.3 Hydrogen Chemisorption

Hydrogen chemisorption was performed at the same apparatus of TPR by using 6 port valves with 10μl of sample loop (see Figure 3.1). H_2 uptake and degree of dispersion were determined by using pulse technique. Prior to pulse chemisorption, the sample was reduced in H_2 atmosphere at 500°C for 1 h. Then the sample was purged with N_2 at 500°C for 30 min and cooled down to 50°C with N_2 flow. H_2-pulse was injected into the sample at room temperature.

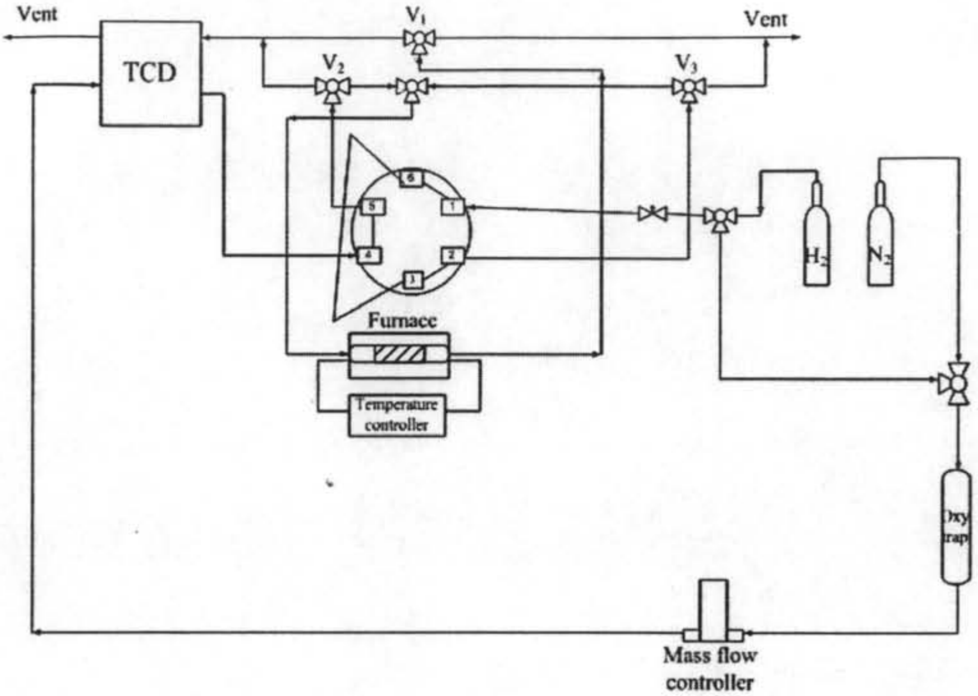

Figure 3.1 Schematic diagram of the hydrogen chemisorption apparatus.

3.6.4 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) was performed to determine the nature and amount of carbonaceous deposition on the spent catalysts. TPO measurement was carried out in a quartz tube reactor. The spent catalyst sample, about 0.01-0.02 g, was loaded in a ¼" quartz tube. Then, the sample was heated at a constant rate (13°C/min) from ambient temperature to 800°C under the continuous flow of $2\%O_2$ in He (40 ml/min). The combustion product, CO_2, was passed to a methanator containing 15 wt% Ni/Al_2O_3 as a catalyst. In this methanator, CO_2 formed from the carbon was completely converted with excess H_2 into methane, to permit precise quantification by FID detector. After the TPO system reached 800°C, where all carbon had been burned off, the FID signal for methane was calibrated by injecting 100 μl of pure CO_2. By integrating the methane signal during the entire TPO run, it was possible to calculate the amount of coke removed from catalyst. Moreover, TPO profile predicted the type of coke formation. Carbonaceous with different morphologies or different locations are burnt at different temperatures.

3.7 *n*-Octane Aromatization Reaction

The catalytic testing was done in a ½" glass tube continuous flow reactor at 500 °C under atmospheric pressure. Prior to test, Pt/MCM-41 catalysts were transferred to the reactor. Then the temperature was slowly ramped in flowing H_2 at the flow rate of 100 ml/min/g of catalyst for 2 h up to 500 °C and held at 500 °C for 1 h.

The reaction took place under atmospheric pressure with continuous flow reactor. The space velocity was fixed at 5 h^{-1}. In each run, the experiments were conducted using 0.1-0.2 g of catalysts and supported on glass wool. The reactor was operated under flowing H_2, and *n*-octane was injected with a syringe pump to the reactor. In all experiments, the molar ratio of H_2 to hydrocarbon molar ratio was kept at 6:1; the reaction was conducted at 500 °C for 9 h.

The products were analyzed in a Shimadzu GC-17A equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column, using a temperature-programmed mode, to obtain optimal product separation, by starting at 40 °C for 10 min, then the temperature was ramped up to 195 °C with a heating rate of 5 °C/min and held for 30 min.

3.8 Apparatus

The experimental apparatus is schematically shown in Figure 3.2.

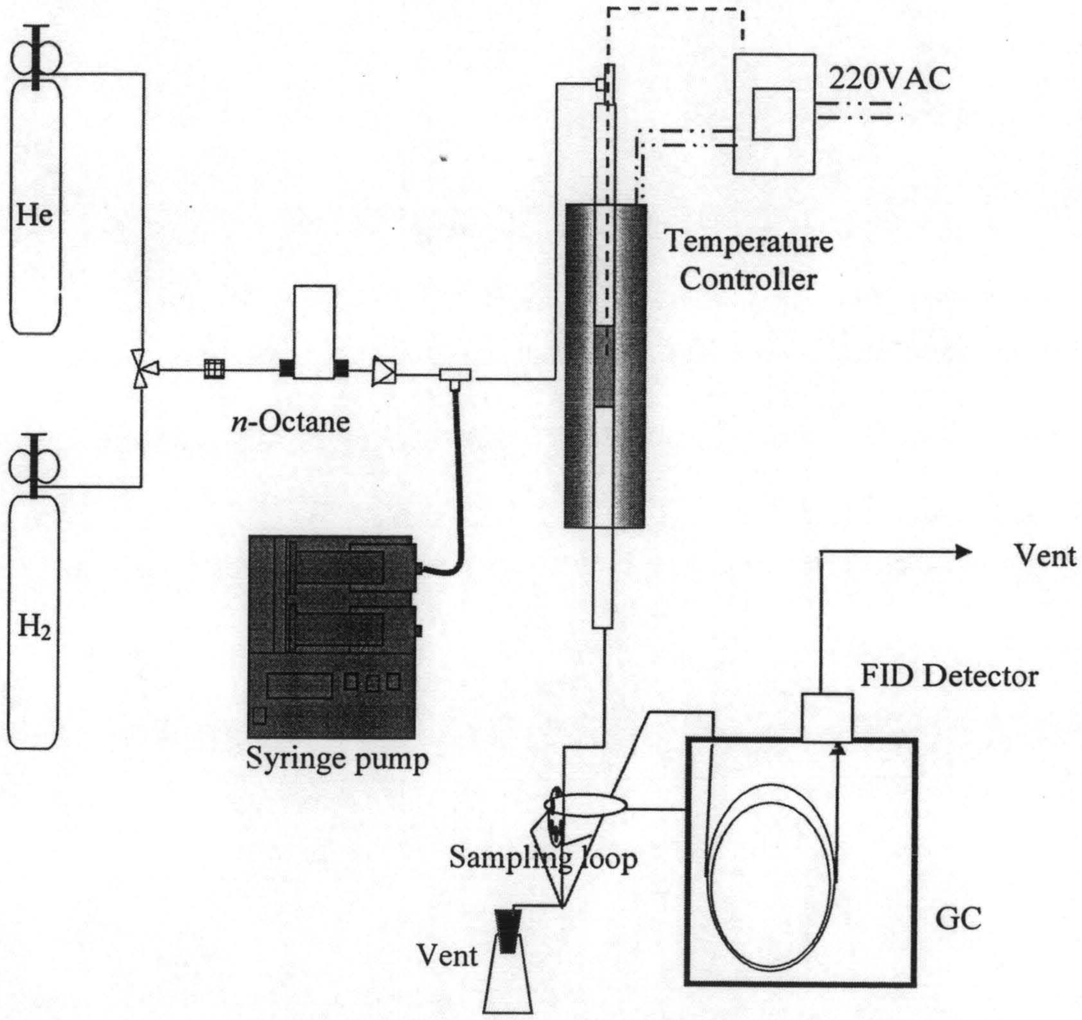

Figure 3.2 Schematic diagram of the experiment setup.