

## CHAPTER IV EXPERIMENTAL

### 4.1 Materials

#### 4.1.1 Chemicals

First, for methylation work in Thailand,  $\text{NH}_4\text{-ZSM-5}$  with Si/Al molar ratio of 20 was purchased from Tosoh corporation. Silver nitrate with 99.99% purity for making Ag/HZSM-5 catalyst was purchased from Merck. Ammonia heptamolybdate ( $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ ) for making Mo/HZSM-5 catalyst was purchased from Carlo Erba reagent. Benzene, toluene, *p*-xylene, *o*-xylene, and *m*-xylene with 99.7% purity were purchased from Merck. All chemicals were used as received with no future purification unless specified. Second, for Fischer-Tropsch synthesis work in USA, Sasol Catalox-150  $\gamma\text{-Al}_2\text{O}_3$  was used as a catalyst support, while cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) from Alfa Aesar served as the Co precursor in the loading solution for preparing Co/ $\text{Al}_2\text{O}_3$  catalysts. Metal promoter precursors, including tetra-amine platinum (II) nitrate solution (Alfa Aesar), silver (I) nitrate (Alfa Aesar), ruthenium nitrosyl nitrate (Alfa Aesar), rhenium (VII) oxide (Alfa Aesar), gold (III) chloride trihydrate (Sigma Aldrich), rhodium (III) chloride hydrate (Sigma Aldrich), and iridium (III) chloride hydrate (Sigma Aldrich), were employed in this study.

#### 4.1.2 Gases

First, for methylation work in Thailand, high purity methane (99.999% purity) was utilized as a raw material. The treatment gases and carrier gases used consist of oxygen, nitrogen, and hydrogen. The utility gases for GC are hydrogen, nitrogen, helium, and air (zero grade). Each gas is ultra-high purity grade and all were supplied by Thai Industrial Gas, Co., Ltd, Thailand. Second, for Fischer-Tropsch synthesis work in USA, pure hydrogen and carbon monoxide were utilized as reactant gases. 25% hydrogen in helium was used as standard calcination gas. 1% oxygen in nitrogen was used as passivation gas in oxidation-reduction experiments.

## 4.2 Experimental Procedures

### 4.2.1 Catalyst Preparation

#### 4.2.1.1 *Preparation of HZSM-5 Catalyst*

HZSM-5 was prepared by calcination of NH<sub>4</sub>-ZSM-5 in a muffle furnace at 550 °C at atmospheric pressure for 7 hours using a ramp rate of 2 °C/min.

#### 4.2.1.2 *Preparation of Ag/HZSM-5 Catalyst*

Ag/HZSM-5 was prepared by using a conventional liquid ion-exchange technique with aqueous AgNO<sub>3</sub> solution as an Ag precursor. In detail, HZSM-5 and Ag solution were mixed together in a flask with magnetic stirring at ambient conditions for 24 h. Ag exchanged HZSM-5 was subsequently washed with deionized water using a vacuum pump, and dried at 120 °C for 12 h. Then, dried Ag/HZSM-5 catalyst was treated in-situ under different conditions in order to introduce Ag species with different forms in a catalyst. For the treatment, catalyst was packed in a quartz tube reactor with a weight range of 0.10-0.90 g depending on the WHSV of the reaction test. Thermal treatment was performed in either nitrogen, oxygen or 5%hydrogen/nitrogen atmosphere at 350-550 °C with a ramp rate of 10 °C/min and held for 30 min. Total flow of each treatment was fixed at 45 ml/min.

#### 4.2.1.3 *Preparation of Mo/HZSM-5 Catalyst*

Mo/HZSM-5 was prepared by using incipient wetness impregnation. 5 grams of HZSM-5 were impregnated with molybdenum aqueous solution prepared by using ammonia heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>]·4H<sub>2</sub>O) as a Mo precursor. Different molybdenum loadings in HZSM-5 were prepared by adding the solutions drop wise with different Mo concentrations. The catalyst was then dried at 120 °C for 12 h and calcined at 500 °C for 6 h under static air. For the treatment, catalyst was packed in a quartz tube reactor with a weight of 0.10-0.90 g depending on WHSV and conducting an in-situ treatment within a reactor. Thermal treatment was performed in nitrogen, oxygen, or hydrogen atmosphere at 450-750 °C using a heating rate of 10 °C/min and held for 1 h. The treatment conditions were slightly different in each gas (nitrogen treatment uses 100% nitrogen, oxygen treatment uses

100% oxygen, while hydrogen treatment uses 100% hydrogen). The total flow of each treatment was fixed at 45 ml/min.

#### *4.2.1.4 Preparation of Metal-promoted Co/Al<sub>2</sub>O<sub>3</sub> Catalyst*

The catalyst support used was Sasol Catalox-150  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. To achieve 25%Co loading, a slurry impregnation method was applied. Cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) (Alfa Aesar) was employed to make the Co precursor solution. The ratio of the volume of loading solution used to the weight of alumina was 1:1, such that approximately 2.5 times the pore volume of solution was used. Two impregnation steps of cobalt nitrate were applied. Between each step the catalyst was dried under vacuum in a rotary evaporator. After the last step of cobalt addition, metal promoter (e.g., Pt, Re, Ru, Ag, Au, Rh, Ir) precursor solution was added to the Co/Al<sub>2</sub>O<sub>3</sub> catalyst by incipient wetness impregnation. Only after the final step were catalysts calcined under air flow at 350 °C for 4 h.

### 4.2.2 Catalyst Characterization

#### *4.2.2.1 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX)*

Field-Emission Scanning Electron Microscope (Hitachi, S4800) was used to examine the morphological structure of the catalysts. The samples were placed on the holder with an adhesive tape and coated with a thin layer of platinum using a Hitachi E-1010 ion sputtering device for 180 seconds prior to performing SEM. The scanning electron images were investigated by using an acceleration voltage of 5 kV with a magnification in the ranges of 1500x-10000x. Energy dispersive x-ray spectroscopy was used to identify the elemental composition in the catalyst and also examine the elemental distribution. The sample preparation was the same as SEM, the acceleration voltage was 20 kV with a magnification of 6000x.

#### *4.2.2.2 Powder X-ray Diffraction (XRD)*

First, for methylation work in Thailand, powder x-ray diffraction (XRD); X'Pert Pro MPD PW3040/60 using Cu K $\alpha$  radiation, was utilized to verify the crystallinity of ZSM-5 and the crystal phases of Ag and Mo. The diffractograms of the catalysts were recorded the  $2\theta$  in range of 5-65° with scanning

speed of  $5^\circ \text{ min}^{-1}$ . Second, for Fischer-Tropsch synthesis work in USA, powder diffractograms on calcined catalysts were recorded using a Philips X'Pert diffractometer. Two different tests were performed for each sample – a short time scan over a long range and a long time scan over a short range. The objective of the short time scan was to assess the crystalline phases present using the following conditions: scan rate of  $0.02^\circ/\text{step}$  and scan time of  $5 \text{ s/step}$  over a  $2\theta$  range of  $15\text{--}80^\circ$ . The long time scan was conducted to quantify average  $\text{Co}_3\text{O}_4$  domain sizes using line broadening analysis for the peak at  $2\theta = 37^\circ$  representing (311). The latter conditions employed were a scan rate of  $0.01^\circ/\text{step}$  and a scan time of  $30 \text{ s/step}$  over a  $2\theta$  range of  $30\text{--}45^\circ$ .

#### *4.2.2.3 Temperature Programmed Reduction (TPR)*

First, for methylation work in Thailand, the sample with approximate weight of  $0.15 \text{ g}$  was placed in a quartz tube and held in position by quartz wool. The sample was pre-treated under  $20 \text{ ml/min}$  nitrogen flow and temperature was increased from room temperature to  $120^\circ \text{C}$  with a heating rate of  $10^\circ \text{C/min}$  and kept constant at  $120^\circ \text{C}$  for 30 minutes. For TPR analysis,  $30 \text{ ml/min}$  of 5% hydrogen in nitrogen was used and the temperature was raised from  $50$  to  $800^\circ \text{C}$  with heating rate  $10^\circ \text{C/min}$  and the detector was a thermal conductivity detector (TCD). Second, for Fischer-Tropsch synthesis work in USA, temperature programmed reduction (TPR) profiles of calcined catalysts were recorded using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD). Samples were pretreated by purging with argon flow at  $350^\circ \text{C}$  to remove traces of water. The TPR was performed using a 10%  $\text{H}_2/\text{Ar}$  gas mixture and referenced to argon at a flow rate of  $30 \text{ cm}^3/\text{min}$ . The sample was heated from  $50$  to  $800^\circ \text{C}$  using a heating ramp of  $10^\circ \text{C/min}$ .

#### *4.2.2.4 Temperature Programmed Oxidation (TPO)*

The spent catalyst (approximately  $0.05 \text{ g}$ ) was packed into the quartz tube reactor and supported by quartz wool before TPO analysis. The 2%  $\text{O}_2$  in helium (oxidizing agent) was fed into the reactor with a flow rate of  $40 \text{ ml/min}$ . The reactor was heated from  $30$  to  $900^\circ \text{C}$  with a heating rate of  $10^\circ \text{C/min}$ . The outlet gas was passed to the methanator to convert carbon dioxide to methane which was subsequently detected by a flame ionization detector (FID).

#### 4.2.2.5 *UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)*

The powder sample of approximately 0.15-0.20 g was pressed into the sample holder and the sample surface was then smoothed. Subsequently, the sample was placed in the UV-Visible Spectrophotometer (SHIMADZU UV-2550) and analyzed for the absorbance in the range of 200-800 nm. HZSM-5 was used as a background prior to analysis.

#### 4.2.2.6 *Surface Area and Porosity Measurement*

First, for methylation work in Thailand, a surface area analyzer (Quantachrome Autosorb-1MP) was used to examine the surface area of the catalysts. The sample (approximately 0.06-0.10 g) was placed into the dried glass tube, and then outgased at 250 °C until the moisture completely desorbed which can be identified by the desorbed molecule being less than 20  $\mu\text{mol}/\text{min}$ . The outgased sample was weighed again to obtain the exact weight before introduction into the analysis station. The measurement was performed at liquid nitrogen temperature (-196 °C) using relative pressures ( $P/P_0$ ) in the range of 0.001 to 0.999 with a number of adsorption steps equal to 21 points and desorption 20 points. The surface area was calculated by using a 7 point BET method with  $P/P_0$  in the range of 0.05 to 0.3. Second, for Fischer-Tropsch synthesis work in USA, the measurements of BET surface area and porosity of the calcined catalysts were conducted using a Micromeritics Tri-Star system. Before performing the test, the temperature was gradually ramped to 160 °C and the sample was evacuated at least 12 h to approximately 50 mTorr. The BET surface area, pore volume (single point), and average pore radius (single point and BJH adsorption) were obtained for each sample.

#### 4.2.2.7 *Elemental Measurements*

An x-ray fluorescence spectrometer, XRF (AXIOS PW4400) was used to determine elemental composition of the catalyst (Ag/HZSM-5). And, inductively coupled plasma optical emission spectrometry, ICP-OES (Varian 720-ES ICP) was applied to analyze the metal promoter content in metal-promoted  $\text{Co}/\text{Al}_2\text{O}_3$  catalyst before and after undergoing oxidation-reduction for 3 cycles. The weighed samples were digested using an aqua regia solution, a mixture of concentrated nitric and hydrochloric acids optimally in a volume ratio of 1:3 and, consequently, diluted

using a volumetric flask. The sample solutions were aspirated into the spectrometer for analysis.

#### 4.2.2.8 *H<sub>2</sub> Chemisorption and Percentage Reduction by Pulse Reoxidation*

Hydrogen chemisorption was conducted at using temperature programmed desorption (TPD), also measured with the Zeton-Altamira AMI-200 instrument. The sample weight was typically ~0.220 g. Catalysts were activated in a flow of 10 cm<sup>3</sup>/min of H<sub>2</sub> mixed with 20 cm<sup>3</sup>/min of argon at 350 °C for 10 h. and then cooled under flowing H<sub>2</sub> to 100 °C. The sample was held at 100 °C under flowing argon to remove and/or prevent adsorption of weakly bound species prior to increasing the temperature slowly to 350 °C, the reduction temperature of the catalyst. The catalyst was held under flowing argon to desorb remaining chemisorbed hydrogen until the TCD signal returned to baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing its area to the areas of calibrated hydrogen pulses. The loop volume was first determined by establishing a calibration curve with syringe injections of hydrogen in helium flow. Dispersion calculations were based on the assumption of a 1:1 H:Co stoichiometric ratio and a spherical cobalt cluster morphology. After TPD of hydrogen, the sample was reoxidized at 350 °C using pulses of oxygen. The percentage of reduction was calculated by assuming that metal reoxidized to Co<sub>3</sub>O<sub>4</sub>.

#### 4.2.2.9 *Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge (XANES) Spectroscopies*

In situ H<sub>2</sub>-TPR XAFS studies were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline, 10BM, at Argonne National Laboratory's Advanced Photon Source. A water-cooled Si(111) monochromator selected the incident energy and was detuned to 50% of the peak intensity to reduce higher-order harmonics of the fundamental beam energy.

In detail, a stainless steel multi-sample holder (3.5 mm i.d. channels) was used to monitor the in situ reduction of 6 samples during a single TPR run. For the Pt series, approximately 10 mg of each sample was loaded as a self-supporting wafer in each channel. The charge was about 7 mg for the Ag series. The holder was placed in the center of a quartz tube, equipped with gas and thermocouple

ports and Kapton windows. The amount of samples used was optimized for the Pt L<sub>III</sub>-edge and Ag-K edge, considering the absorption by Al of the support. The quartz tube was placed in a clamshell furnace mounted on positioning table. Each sample cell was positioned relative to the beam by finely adjusting the position of the table to an accuracy of 20 μm (for repeat scans). Once the sample positions were fine-tuned, the reactor was purged with helium for more than 5 min at 30 ml/min then the reactant gas (H<sub>2</sub>/He, 4%) was flowed through the samples (30 ml/min) and a temperature ramp of 0.78°C/min (starting from ~50 °C after a more rapid startup) was initiated for the furnace

For cobalt, XANES/EXAFS spectra were recorded at the cobalt K-edge (7.709 keV) in transmission mode and a Co metallic foil spectrum was measured simultaneously with each sample spectrum for the purpose of energy calibration. The Pt L<sub>III</sub>-edge spectra were recorded in transmission mode and a Pt metallic foil spectrum was measured simultaneously with each sample spectrum for energy calibration. X-ray absorption spectra for each sample were collected from 11632 – 12108 eV. The Ag K-edge spectra were also recorded in transmission mode and a Ag metallic foil spectrum was employed for energy calibration. X-ray absorption spectra were collected from 25266 – 26157 eV.

XANES spectra were processed using the WinXAS program. For cobalt, a simultaneous pre- and post-edge background removal step was carried out using 2 polynomials (degree 2) over the ranges 7.63-7.67 and 7.79-8.68 keV, respectively, and the resulting spectra were normalized by dividing by the height of the absorption edge. For the case of Pt promoted catalysts, simultaneous pre and post-edge background removal was carried out using degree 2 polynomials over the ranges 11.413-11.498 and 11.662-12.076 keV, respectively, and normalization by division of the height of the absorption edge. For Ag promoted catalysts, XANES spectra were processed in the same manner but over the pre-edge range of 25.342-25.444 keV and the post-edge range of 25.615-25.122 keV with normalization. Once the spectra were processed, they were compared with reference compounds. For Pt-25%Co/Al<sub>2</sub>O<sub>3</sub>, all of the beginning spectra closely resemble the bulk PtO<sub>2</sub> reference compound. Therefore, the initial spectrum for each catalyst was used as the reference for PtO<sub>2</sub> in the sample. As the temperature trajectory was followed, it was clearly

observed that a PtO<sub>2</sub> to PtO transition took place for all the samples, considering the white line intensities and the line shapes. Further following the temperature trajectory, the conversion from PtO to Pt<sup>0</sup> occurred. The catalyst spectra at 350 °C resemble the spectrum of Pt<sup>0</sup>, so they were used as a Pt<sup>0</sup> reference. To specify the spectrum of PtO in the catalyst samples, which has a line shape similar to PtO<sub>2</sub> but with an attenuated intensity, a linear combination fitting was performed using PtO<sub>2</sub> and Pt<sup>0</sup> in samples as references. The spectrum composed of 50% PtO<sub>2</sub>-50%Pt<sup>0</sup> was empirically selected as a PtO sample reference. This is in agreement with the white line intensity of PtO as compared to PtO<sub>2</sub> in the work of Christensen et al. Finally, a linear combination fitting was performed by using those 3 Pt reference compounds for analyzing spectra along the temperature trajectory. For Ag-25%Co/Al<sub>2</sub>O<sub>3</sub> catalyst, the starting spectra of all samples did not resemble any bulk Ag compound references (i.e., AgO, Ag<sub>2</sub>O). However, it has been previously suggested that Ag<sub>2</sub>O was more likely to be a Ag species in calcined samples. Along with the temperature trajectory, it was obvious that Ag<sub>2</sub>O converted to Ag<sup>0</sup>. Thus, a linear combination fitting was performed using Ag<sub>2</sub>O and Ag<sup>0</sup> in the samples as references.

Data reduction of EXAFS spectra was also performed using WinXAS. For cobalt, following the normalization procedure previously described, spectra were converted to k-space and a k weighting of 1 was used. An advanced cubic weighted spline over 3 sections of the 2-14 Å<sup>-1</sup> range was used to remove the background of the  $\chi(k)$  function. Finally, the k<sup>1</sup>-weighted results were Fourier transformed to R-space using a Bessel window. To quantify the changes in Co-O and Co-Co coordination number, fitting of the spectra in k space was carried out using FEFFIT. The k-range used was from 2 to 14 Å<sup>-1</sup>. Theoretical EXAFS were generated using FEFF for model cobalt metal and CoO crystal parameters generated by ATOMS. For platinum and silver, simultaneous pre and post-edge background removal was carried out with two polynomial degree 2 functions over the ranges 11.413-11.498 and 11.662-12.076 keV, respectively, for Pt promoted catalysts and over the ranges 25.342-25.444 and 25.615-25.122 keV, respectively, for Ag promoted catalyst. The spectra were normalized by dividing by the height of the edge jump. Spectra were then calibrated versus the Pt<sup>0</sup> or Ag<sup>0</sup> reference spectrum, and then converted to k-space. A cubic weighted degree 7 spline was used to remove the



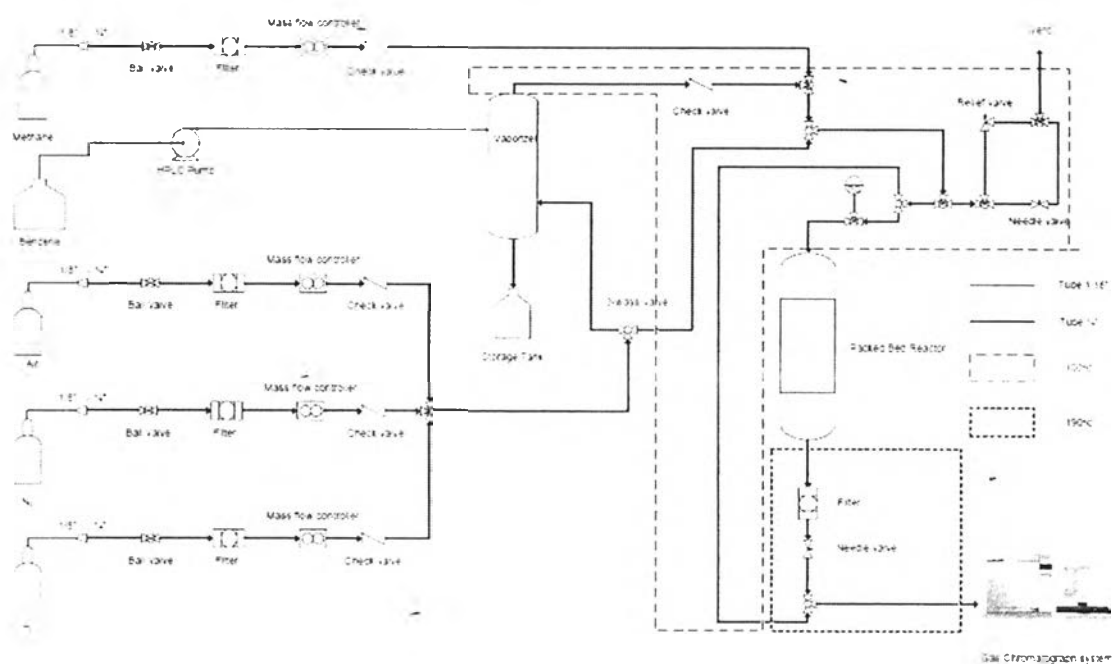
background of the  $\chi(k)$  function. Finally, the data in k-space were Fourier transformed to R-space using a Bessel window (using a  $k^3$ -weighting for Pt promoted catalysts and  $k^1$ -weighting for Ag promoted catalysts). EXAFS fittings were carried out using the catalysts in their final state following TPR and cooling. All catalysts displayed high quality data over the k-range of 2-12  $\text{\AA}^{-1}$  range. In R-space for Pt promoted catalysts, the first Pt-Co coordination shell was isolated by employing a Bessel window and then taking the back-Fourier Transform. After converting to  $\chi(k)$ , fitting of the spectra was carried out in k-space using FEFFIT. The k-range employed was 3-12  $\text{\AA}^{-1}$ . The FEFF program was used to construct a model of Pt-Co FCC to be used in fitting, and the atomic coordinates of Pt FCC (with lattice parameters) were inputted to the FEFF program with the aid of the program Atoms. In order to use coordination number as a fitting parameter, the amplitude reduction factor  $S_0^2$  must be fixed for all scattering paths in the solid, and it was assumed to be 0.9 by the zeroth order approximation. For Ag promoted catalysts, the first Ag-Co and Ag-Ag coordination shells in R-space were identified and also isolated by using a Bessel window and then back Fourier transformed to k-space. Fitting was performed over the k-range of 2-10  $\text{\AA}^{-1}$ . The model for Ag consisted of Ag-Co and Ag-Ag bonds generated by the FEFF and Atoms programs. The amplitude reduction factor  $S_0^2$  of 0.9 was also applied.

#### 4.2.3 Catalyst Activity Test

##### 4.2.3.1 *Methylation Reaction*

The reaction between benzene and methane was carried out in a fixed-bed flow reactor, made of quartz (8.4 mm inside diameter and 40 cm length), under non-oxidizing conditions at atmospheric pressure. Catalysts were packed into a quartz tube reactor at the middle of the reactor with bounding at each side (top and bottom) by quartz wool. An inserted quartz tube was used to support the catalyst bed and also help to reduce reactor volume, thus increasing the product flow. Prior to the catalytic measurements, the packed catalyst was heated (10°C/min) to 120°C under  $N_2$  flow (30 ml/min) and held for 30 min in order to remove humidity. Subsequently, it was calcined at 350 °C for 30 minute under different atmospheres, and then flushed with  $N_2$ . The reactant feed stream was prepared by feeding liquid benzene

into a vaporizer operated at 40 °C. Saturated benzene at 40 °C was then carried by N<sub>2</sub> into a mixer, where benzene, methane and nitrogen carrier were mixed prior to feed to the reactor. The feed stream was first checked by online-GC via a by-pass line before sending to the reactor. The reaction products were analyzed by GC (Agilent 7820A), equipped with an Innowax capillary column and a flame ionization detector (FID), and with a Porapack packed column combined with a valve configuration and a thermal conductivity detector (TCD). The first data point was collected at TOS of 10 min and every 30 min.



**Figure 4.1** The schematic flow diagram of catalyst testing instrument for methylation reaction.

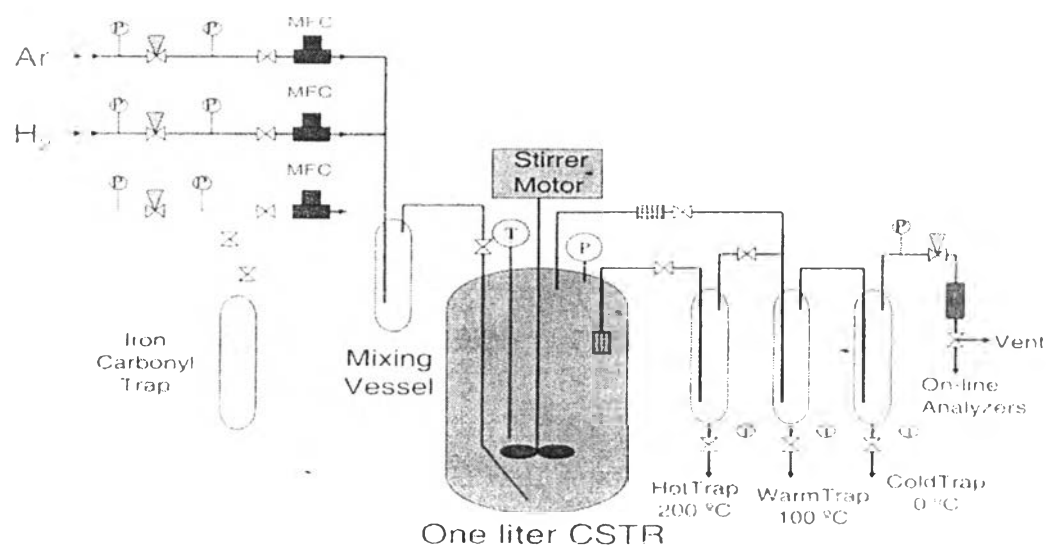
#### 4.2.3.2 Fischer-Tropsch Reaction

Fischer-Tropsch synthesis (FTS) reaction tests were conducted using a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter (7  $\mu$ m) placed external to the reactor. A tube fitted with a SS fritted filter (2  $\mu$ m opening) extends below the liquid level of the reactor for withdrawing reactor wax to

maintain a nearly constant liquid level in the reactor. Separate mass flow controllers were used to control the flow of hydrogen and carbon monoxide at the desired flow rate. The reactant gases were premixed in a vessel before entering the reactor. Carbon monoxide was passed through a vessel containing lead oxide-alumina to remove traces of iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. The reactor slurry temperature was maintained constant by a temperature controller.

Prior to performing the reaction test, the catalyst (~13.0 g) was ground and sieved to 45-90  $\mu\text{m}$ , and then loaded into a fixed-bed reactor for ex-situ reduction at 350  $^{\circ}\text{C}$  under atmospheric pressure for 15 h using a gas mixture of  $\text{H}_2/\text{He}$  (60 NL/h) with a molar ratio of 1:3. The reduced catalyst was then transferred to a 1 L continuously stirred tank reactor (CSTR) containing 315 g of melted Polywax 3000, by pneumatic transfer under the protection of a  $\text{N}_2$  inert gas. Weighing the reactor before and after the transfer of catalyst was done to ensure that all catalyst powder was successfully transferred to the reactor. The transferred catalyst was further reduced in-situ at 230  $^{\circ}\text{C}$  at atmospheric pressure using pure hydrogen (30 NL/h) for another 10 h before starting the Fischer-Tropsch synthesis (FTS) reaction. In this study, the FTS conditions used were 220  $^{\circ}\text{C}$ , 2.2 MPa,  $\text{H}_2/\text{CO} = 2.1$ . The reactant gas mixture was analyzed prior to sending to the reactor to ensure the composition. The reaction products were continuously removed from the vapor space of the reactor and passed through two traps, a warm trap maintained at 100  $^{\circ}\text{C}$  and a cold trap held at 0  $^{\circ}\text{C}$ . The uncondensed vapor stream was reduced to atmospheric pressure. The gas flow was measured using a wet test meter and analyzed by online GC. The accumulated reactor liquid products were removed every 24 h by passing through a 2  $\mu\text{m}$  sintered metal filter located below the liquid level in the CSTR. Conversions of CO were obtained by gas-chromatography analysis (micro-GC equipped with thermal conductivity detectors) of the outlet gas product. The reaction products were collected in three traps maintained at different temperatures; a hot trap (200  $^{\circ}\text{C}$ ), a warm trap (100  $^{\circ}\text{C}$ ), and a cold trap (0  $^{\circ}\text{C}$ ). The products were separated into different fractions (rewax, wax, oil, and aqueous) for quantification. However, the oil and wax fractions were mixed prior to GC analysis. To investigate the effect of Pt and Ag on the activity and selectivity, a reference CO

conversion of about 50% was used and achieved by adjusting the space velocity in all cases. Activities were compared by adjusting space velocity and measuring the space velocity used to achieve 50%CO conversion, while selectivities were directly compared at the same level of conversion.



**Figure 4.2** The schematic flow diagram of catalyst testing instrument for Fischer-Tropsch reaction.