CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

The NH_4-ZSM-5 was purchased from Tosoh corporation with the Si/Al = 20. Indium(III)chloride was obtained from Acros Co.,Ltd, with 99.99% purity and indium(III)oxide was purchased from Aldrich with 99.99% purity. The benzene with 99.7% purity was purchased from Merck. Toluene, p-xylene, o-xylene and m-xylene were purchased from Merck, 99.7% purity. All chemicals were used as received and no future purification unless specified.

3.1.2 Gases

The high purity methane (99.999%) was utilized as raw material. The treatment gases and carrier gases included oxygen, nitrogen and hydrogen. The utility gases for GC are hydrogen, nitrogen, helium and air zero. Each gas is high purity grade supplied by Thai Industrial Gas, Co., Ltd, Thailand.

3.2 Experimental Procedures

3.2.1 Catalyst Preparation

3.2.1.1 Catalyst Preparation of HZSM-5

HZSM-5 was prepared by calcinations of NH_4-ZSM-5 in furnace at 550 °C in atmospheric pressure for 7 hours by using heating rate 2 °C/min.

3.2.1.2 Catalyst Preparation of In/HZSM-5

In/HZSM-5 was prepared by solid-state ion exchange of the HZSM-5 with solid indium(III)chloride ($InCl_3$). Firstly, indium(III)chloride was physically mixed with HZSM-5 using pestle and mortar, the indium to aluminium ratio (In/Al ratio) was in the range of 0.1 to 1.0. The mixed catalyst was then dried in an oven over night at 80 °C before the treatment and reaction testing.

For the treatment, catalyst was packed in quartz tube reactor with the weight of 0.12-0.94 g depended on WHSV. Thermal treatment was performed in nitrogen, oxygen or hydrogen atmosphere at 350-450 °C using heating rate 10 °C/min to desired temperature and then hold for 30 min. The treatment conditions were slightly different in each gas, nitrogen treatment was used 100% nitrogen, oxygen treatment was used 50% oxygen balanced in nitrogen while hydrogen treatment was used 10% hydrogen balanced in nitrogen. Total flow of each treatment was fixed at 45 ml/min.

The effect of indium to aluminum (In/Al) ratio in catalyst was investigated by using In/Al in the range of 0.1-1.0 by vary the weight of $InCl_3$ before mixing with HZSM-5.

3.2.2 Catalyst Characterization

3.2.2.1 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 second prior to observation under SEM. The scanning electron images were investigated by using an acceleration voltage of 5 kV with a magnification in the range 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 using 20 kV with a magnification 6000x.

3.2.2.2 Temperature Programmed Reduction (TPR)

The TPR characterization was separated into two sections, the normal TPR and cyclic reductive/oxidative testing. For the normal TPR, the sample with approximate weight of 0.15 g was placed in a quartz tube and hold to the position by quartz wool. The sample was pre-treated under 20 ml/min nitrogen flow and temperature was increased from room temperature to 120 °C with heating rate 10 °C/min and kept constant at 120 °C for 30 minutes. For TPR analysis, 30 ml/min of 5% hydrogen in nitrogen was used and the temperature was raised from 50 to 800 °C with heating rate 10 °C/min and the detector was a thermal conductivity detector (TCD).

For the reductive/oxidative cyclic testing, the above procedure of pre-treatment and first TPR step was performed. After the reduction step reached to 800 °C, the feed gas was switched to 5% oxygen balanced in helium and then cooled the sample to the room temperature with rate -10 °C/min. Then the next heat with the flow of 5% hydrogen balanced in nitrogen was performed again. This reduction/oxidation step was analyzed for 4 cycles.

3.2.2.3 Temperature Programmed Oxidation (TPO)

The spent catalyst approximately 0.05 g was packed into the quartz tube reactor and supported by quartz wool before TPO analysis. The 2% O_2 in helium as oxidizing agent was fed into the reactor with flow rate of 40 ml/min. The reactor was heated from 30 to 900 °C with heating rate 10 °C/min. The outlet gas was passed to the methanator to convert carbondioxide to methane which subsequently detected by a flame ionization detector (FID).

3.2.2.4 Temperature Programmed Desorption (TPD)

The catalyst with approximate weight of 0.04 g was placed in the quartz tube reactor supported by quartz wool before TPD analysis. The sample was pre-treated under 80 ml/min helium flow and the temperature was increased from room temperature to 150 °C with heating rate 10 °C/min. The sample was then cooled to 30 °C and 5 μL isopropylamine was injected to the reactor in continuously helium flow every 10 minutes for 5 times and then flush for 10 minutes before the measurement. In analysis process, the sample was heated from 30 to 800 °C with heating rate 20 °C/min. The desorbed gas was detected by mass spectrometer, the mass of 41 represented to propylene was followed. The area of desorbed propylene in TPD profile was integrated to calculate the amount of Bronstted acid by using the calibration factor of propylene.

3.2.2.5 UV-Visible Spectroscopy

The powder sample approximately 0.15-0.20 g was pressed into the sample holder and the sample surface was then smoothen. Subsequently, the sample was placed in the UV-Visible Spectrophotometer (UV-2550) and analyzed for the absorbance in the range of 200-900 nm. HZSM-5 was used as a background prior to analysis of the other indium loaded catalysts.

3.2.2.6 Surface Area Analysis

Surface area analyzer (AS-1-MP) 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 identify by the desorbed molecule less than 20 μmol/min. The outgased sample was weighed again to obtain the exact weight before introduce into the analysis station. The measurement was performed at the liquid nitrogen

temperature (-196 °C), using relative pressure (P/P$_0$) in the range of 0.001 to 0.999 with a number of adsorption equal to 21 points and desorption 20 points. The surface area was calculated by using 7 points BET method with P/P$_0$ in the range of 0.05 to 0.3.

3.2.3 Reaction Procedure

The reaction of benzene with methane was carried out in continuous flow reactor under atmospheric pressure. The catalyst testing instrument is shown in Figure 3.1.
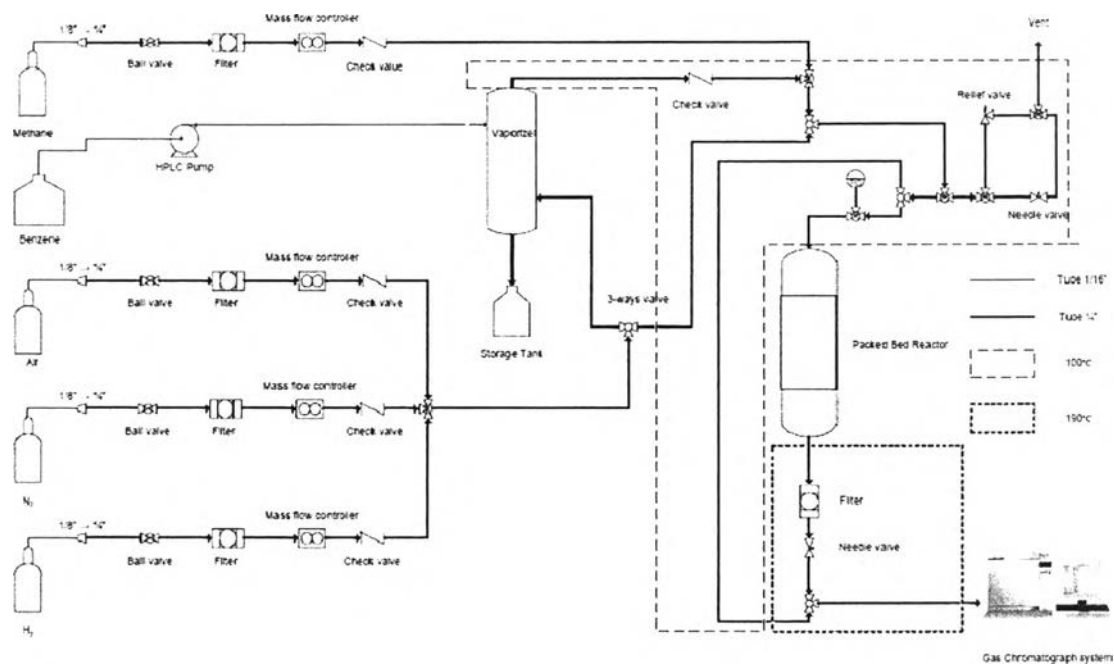

Figure 3.1 The instrumental diagram for catalyst testing.

The catalytic activity was continuously measured after the treatment process. Firstly, treated catalyst was heated to desired reaction temperature which is 300-400 °C. The gas mixture of carrier (nitrogen or oxygen), methane and benzene was checked in by-pass line until the flow and composition was stable (the flow was fixed at 45 ml/min and methane to benzene feed ratio varied from 19-105). After that, valve of the gas mixture was switched into the reaction furnace and continuously fed. Waiting for 10 min and then starting analyzed the products by online gas chromatography. The products was continuously injected every 30 min with the analysis oven temperature in the range of 100-190 °C.

The influence of reaction conditions on conversions of benzene and products selectivity was studied by varying some parameters. Reaction temperature was in the range of 300 to 400 °C, carrier gas or co-feed gas was N_2 and O_2 in different molar ratio from 0 % to 100 % of oxygen, weight hourly space velocity (WHSV) was from 1.8 to 13.2 h^{-1}, and methane to benzene feed molar ratio was from 19 to 105, in order to find the suitable conditions.