

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

The NH₄-ZSM-5 zeolites were purchased from Zeolyst international with the SiO₂/Al₂O₃ ratios 23, 30, 50, 80 and 280. Indium(III)oxide, In₂O₃, was purchased from Aldrich with 99.99 % purity. The benzene feed with 99.7% purity was purchased from Merck. Toluene, *p*-xylene, *o*-xylene and *m*-xylene were purchased from Merck, 99.7% purity.

3.1.2 Gases

The raw material was methane with 99.999% purity which purchased from Praxair (Thailand) Co., Ltd. The treatment gases and carrier gases consisting of oxygen, nitrogen and hydrogen and the utility gases for GC including hydrogen, nitrogen, helium and air zero were high purity grade which 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 $\text{NH}_4\text{-ZSM-5}$ with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios 23, 30, 50, 80 and 280 in furnace at 550 °C in atmospheric pressure for 6 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)oxide, In_2O_3 . Firstly, Indium(III)oxide 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 90 °C before the treatment and reaction testing.

For the treatment, catalyst was packed in quartz tube reactor with the weight of 0.10-0.22 g depended on WHSV. Thermal treatment was performed in hydrogen at 700 °C, oxygen at 350 °C or hydrogen at 700 °C followed by oxygen at 350 °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, oxygen treatment was used 50% oxygen balanced in nitrogen while hydrogen treatment was used 5% hydrogen balanced in nitrogen. Total flow of each treatment was fixed at 40 ml/min.

The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were prepared by using HZSM-5 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios 23, 30, 50, 80 and 280 and then was mixed with In_2O_3 .

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 In_2O_3 before mixing with HZSM-5.

3.2.2 Catalyst characterization

3.2.2.1 *Temperature Program Reduction (TPR)*

The sample was weighed around 0.15 g and placed into a quartz tube that supported with quartz wool. The sample was pre-treated in 20 ml/min nitrogen flow at 120 °C for 30 minutes using heating rate 10 °C/min. The TPR analysis process utilized 30 ml/min of 5% hydrogen balanced in nitrogen and detected the signal by TCD detector from 50 to 800 °C with heating rate 10 °C/min.

3.2.2.2 *Temperature program desorption (TPD)*

The catalyst was weighed approximately 0.04 g and then packed into the quartz tube reactor supported with quartz wool before introduced to the TPD reactor. The sample was treated in helium (80 ml/min) to 150 °C with heating rate 10 °C/min. The sample was then cooled to 30 °C for the isopropylamine adsorption process. Isopropylamine 5 µL was injected to the reactor in continuously helium flow, the injection was done every 10 minutes for 5 times and then flush for 10 minutes before the measurement. In analysis process, the reactor 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 considered. The area of desorbed propylene in TPD profile was integrated to calculate the amount of Brønsted acid by using the calibration factor of propylene.

3.2.2.3 *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.

3.2.2.4 *X-ray Fluorescence Spectroscopy (XRF)*

XRF technique, Philips model PW 2400 was used to examine the quantitative and qualitative elemental analysis of the catalysts. The six gram of boric acid is weighed and then put into the bottom of the pan. The sample was drop over the surface of boric acid. XRF machine analyzes the sample by using X-ray source. An inner shell electron is excited by an incident photon in the X-ray region. If the primary X-ray has sufficient energy, electrons are ejected from the inner shell,

creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and the process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the elemental concentration (quantitative analysis).

3.2.2.5 X-Ray Diffraction (XRD)

X-ray diffraction is an analytical technique which uses for phase identification of a crystalline material and information on unit cell dimensions. This technique has Rigaku X-Ray Diffractometer system (RINT-2200) with copper tube for generating CuK_α radiation (1.5406 Å), and nickel filter. It is also possible to achieve a relative analysis by the intensity of the peak. For the same crystalline substance the higher of the peak indicates the higher content of that phase.

3.2.2.6 Surface area analysis

Surface area analyzer (AS-1-MP) was used to examine the surface area of the catalysts. The glass tube was outgassed at 150 °C for 30 minutes before weighed and used. The sample approximately 0.06-0.10 g was placed into the glass tube. Then the sample was outgassed at 250 °C around 6 to 20 hours depended on the sample. The outgassed 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 catalytic measurement flow diagram is shown in Figure 3.1.

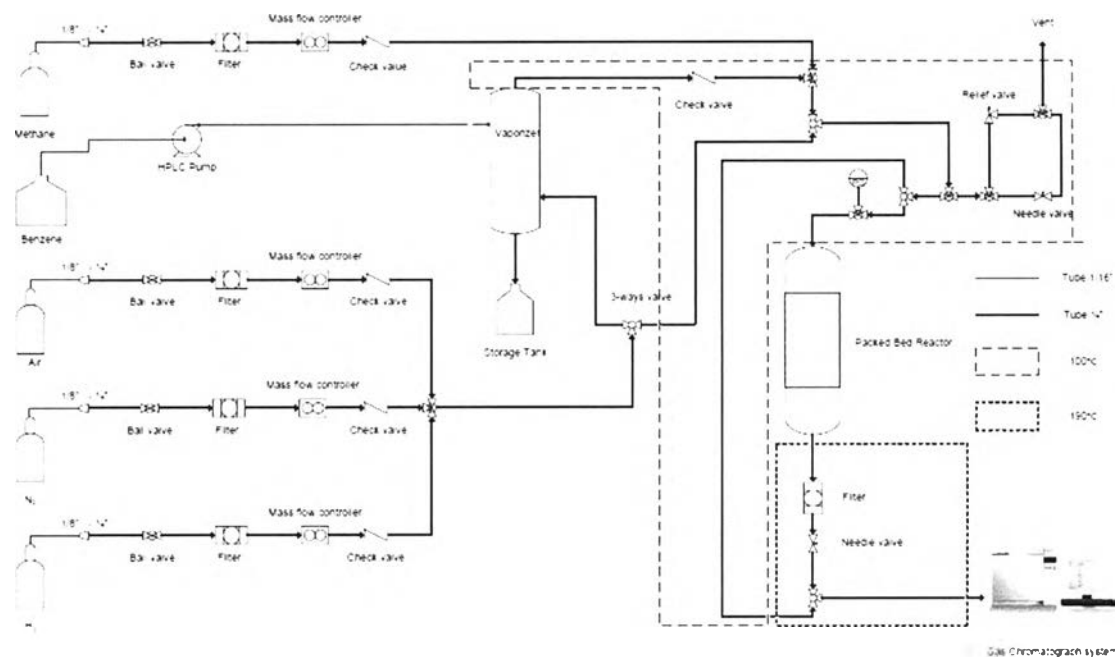


Figure 3.1 The catalytic measurement flow diagram.

The catalytic activity was continuously measured after the treatment process. Firstly, treated catalyst was heated to desired reaction temperature which is 350 °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 40 ml/min and methane to benzene feed ratio varied from 23-104). 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 500 °C, carrier gas or co-feed gas was N₂ and O₂, weight

hourly space velocity (WHSV) was from 2.8 to 12.3 h⁻¹, methane to benzene feed molar ratio was from 23 to 104, and silica to alumina ratios were 23, 30, 50, 80 and 280 in order to find the suitable conditions.