

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Ludox HS-30 (Colloidal silica, SiO₂, 40%) from Sigma-Aldrich
- Aluminium nitrate (Al(NO₃)₃·9H₂O, min.98%) from Ajax Finechem
- Tetrapropylammonium bromide (TPABr, min.98%) from Sigma-Aldrich
- Sodium hydroxide anhydrous pellet (NaOH, min.97%) from Carlo Erba Reagent
- Ammonium nitrate (NH₄NO₃, min.99%) from Ajax Finechem
- Toluene (C₆H₅CH₃, min.99.5%) from Carlo Erba
- Methanol (CH₃OH, min.99.9%) from Carlo Erba

3.1.2 Gases

- High purity N₂ (99.99%)
- High purity H₂ (99.99%)
- High purity He (99.99%)
- Air zero

All the gases were obtained from Praxair (Thailand) Co. Ltd.

3.2 Equipment

- Fixed-bed continuous flow reactor system
- Temperature controller equipped with a K -type thermocouple
- Gas chromatograph (Agilent Technologies model 5890N) with a flame ionization detector and an HP-5 column for detecting the alkylated aromatic hydrocarbons

- Teflon-lined stainless steel autoclave
- Furnace (CARBOLITE/CWE 1100)
- Magnetic stirrer plate (Cole Parmer)
- X-ray diffractometer (XRD, Rigaku/Rint2200 HV)
- X-ray fluorescence spectroscope (XRF, Bruker SRS 3400)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1-MP)
- Field emission scanning electron microscope (FESEM, JEOL 5200-2AE)
- Thermo Finnigan TPD/R/O 1100 equipped with a flame ionization detector

3.3 Methodology

3.3.1 Catalyst Preparation

The reaction mixture compositions (molar basis) to obtain the synthesized HZSM-5 catalyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 90 and 195 are $10\text{Na}_2\text{O}:90\text{SiO}_2:\text{Al}_2\text{O}_3:20\text{TPABr}:4800\text{H}_2\text{O}$ and $9.75\text{Na}_2\text{O}:195\text{SiO}_2:\text{Al}_2\text{O}_3:19.5\text{TPABr}:15600\text{H}_2\text{O}$, respectively. They were prepared by combining the mixture of silica and alumina with clear solutions of TPABr, H_2O , and NaOH. After 0.5 or 12 h of being magnetically stirred, the mixture was transferred to a PTFE cell, placed into a stainless steel autoclave, and heated in an oven at 150 or 180 °C for 24-72 h. The powder was recovered, thoroughly washed with deionized water to reduce its pH from 10.5 to 7. The as-synthesized zeolite ZSM-5 was dried at 120°C for 4 h and a removal of organic template was carried out at 550 °C for 6 h. Ion exchange procedure was carried out for three times with 1 M NH_4NO_3 solution at 80 °C each for 4 h. Subsequently, the resultant product was dried overnight at 120 °C, followed by calcination at 500 °C for 5 h to obtain the H-form catalyst (HZSM-5).

3.3.2 Catalyst Characterization

3.3.2.1 *X-ray Fluorescence Spectroscopy (XRF)*

X-ray fluorescence spectroscopy technique was used to investigate the type and amount of chemical compounds of the catalysts. The X-ray

from a primary X-ray excitation source in X-ray tube is absorbed by the atom, then and the energy created is transferred to an innermost electron. If the primary X-ray has a sufficient energy, vacancies created from electrons are emitted from the inner shells. The vacancies present an unstable condition for the atom. The electrons from the outer shells are transferred to the inner shells while the atom returns to its stable condition. This process brings about a characteristic X-ray that its energy is the difference between the two binding energies of the corresponding shells. Since each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

3.3.2.2 X-ray Diffraction (XRD)

A Rigaku X-ray diffractometer system (RINT-2200) with Cu tube for generating CuK_α radiation (1.5406 Å) and nickel filter, a generator voltage of 40 kV, and a generator current of 30 mA was used to characterize the catalysts as XRD patterns. The scan speed of 5° (2θ)/min with scan step of 0.05 (2θ) was used for the continuous run in 5° to 50° (2θ) range. Due to the specific chemical composition and crystallographic structure of each material which presented on XRD patterns, XRD is an efficient analytical technique used to identify and characterize unknown crystalline materials. Matching of the reference substance's diffraction pattern and sample's diffraction pattern is main principle of the technique. If they have the same pattern, the same crystallite phase will be shown.

3.3.2.3 Field Emission Scanning Electron Microscopy (FESEM)

The sample morphology was observed by a field emission scanning electron microscope (Hitachi S4800). The sample was coated with Au before measurement for improving conductivity of sample. A beam is passed through a series of lenses to form a magnified image of a sample that is inserted in the area of the objective lens. The image from selected area is viewed through projection onto a view of screen.

3.3.2.4 Brunauer-Emmett-Teller (BET) Surface Area Analysis

The surface area of the fresh and spent catalysts was measured using a BET surface area analyzer (Quantachrome/Autosorb 1-MP). The sample was

first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300 °C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data were used to calculate the BET surface area.

3.3.2.5 Temperature Programmed Desorption of Isopropylamine (TPD-IPA)

The acidity of synthesized HZSM-5 catalysts was tested by the amine TPD technique developed by Gorte and co-workers using an in-house TPD system equipped with a (Cirrus MKS) mass spectrometer. First, 50 mg of sample was pretreated at 350 °C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to 100 °C and then 4 µl of isopropylamine was injected over the sample. After removing the excess of isopropylamine by flowing He, the sample was linearly heated to 800 °C at a heating rate of 10 °C/min. Masses 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively.

3.3.2.6 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation was carried out using a Finnigan TPD/R/O 1100 to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O₂/He while the temperature was linearly ramped to 1073 K with a heating rate of 12 K/min. The sample (30 mg) was placed in a 1/4" quartz fixed bed reactor. The CO₂ produced by the oxidation of coke was further converted to methane over 15% Ni/Al₂O₃ catalyst in the presence of hydrogen at 673 K. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100 µl pulses of pure CO₂.

3.3.3 Catalytic Activity Testing

The catalytic activity for the catalysts studied on methylation of toluene with methanol was carried out at atmospheric pressure using a continuous flow packed bed under varied parameters including WHSV, molar ratio of toluene-to-methanol, and reaction temperature.

The Pyrex glass tube with i.d. 6 mm was used as a reactor. The catalyst was packed at the middle of reactor. By preventing the catalyst falling off the reactor, glass wool was placed at bottom and above the bed of catalyst. The reaction temperature was controlled using a PID temperature controller equipped with a type K thermocouple. The reactor was operated under atmospheric pressure and N_2 was used as a carrier gas with a flow rate of 30 ml/min. The mixture of toluene and methanol was injected using a syringe pump and preheated before flowing into the reactor. The products were analyzed using an online gas chromatograph (Agilent 6890) equipped with a capillary HP-5 and an FID every 60 minutes.

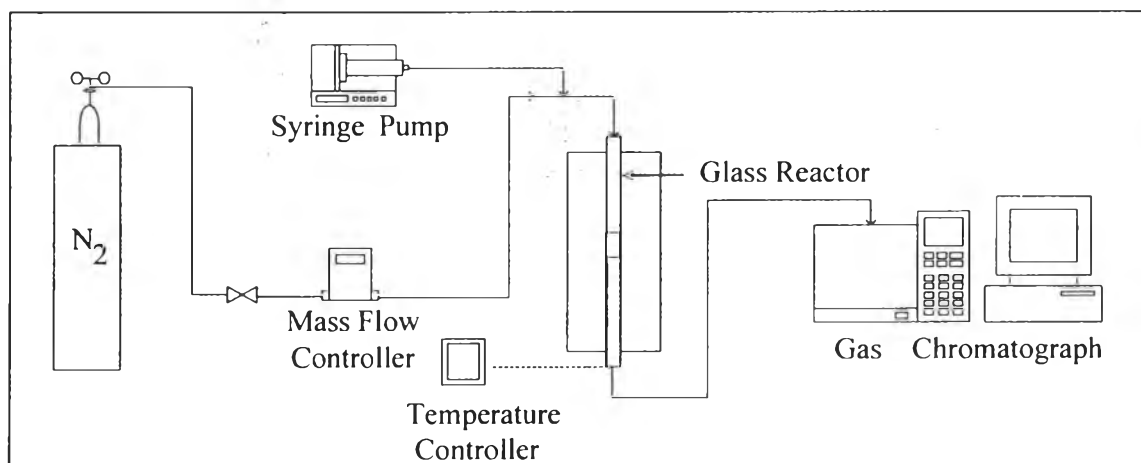


Figure 3.1 Schematic of the catalytic activity testing system.