

CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Catalysts

Fe_2O_3 and CaO .

ITQ-24 was synthesized using these following chemicals: tetraethylorthosilicate (TEOS), Germanium oxide (GeO_2), Hexamethonium dihydroxide, and Amberlite IRN-78.

ITQ-21 was synthesized from tetraethylorthosilicate(TEOS), Germanium oxide (GeO_2), N(16)-methylsparteinium hydroxide, Aluminium isopropoxide (Al_2O_3), and HF.

3.1.3 Tire Tread

A tire tread rubber compound, received from a well-known tire company, was molded and cut into pieces of 1 mm (Boonrudee, 2004).

3.1.4 Gas and Chemical Regents Used for GC Calibration

Standard refinery gas was purchased from Agilent Technologies (Manufactured for Agilent by Scotty Specialty Gases).

3.2 Experimental procedures

3.2.1 The Catalyst Preparation

3.2.1.1 *Preparation of Hexamethonium Dihydroxide*

Hexamethonium dihydroxide was prepared by direct anionic exchange using a resin, Amberlite IRN-78, as the hydroxide source, the resin having been washed with distilled water prior to use until the water was at a pH of 7. The procedure involved dissolving 36.22 g of hexamethonium dibromide in 120 g of Milli-Q water and contacting the resulting solution with 200 g of Amberlite IRN-78 resin for 12 hours under mechanical stirring. After stirring, the mixture was filtered,

and the resin washed with water to yield a solution of hexamethonium dihydroxide. Titration with 0.1 N hydrochloric acid showed the hexamethonium dihydroxide concentration.

3.2.1.2 Synthesis of ITQ-24 (Castañeda et al., 2003)

ITQ-24 had been synthesized from a gel with the following molar composition shown in Table 3.1. The typical gel was prepared by dissolving GeO_2 in a solution of templates. Tetraethyorthosilicate (TEOS) and aluminium triisopropoxide were then hydrolyzed in the solution, and the mixture was stirred gently until the complete evaporation of the alcohols. After crystallization time at 175°C in a microwave, a crystalline solid was obtained by filtration, exhaustively washed with water and acetone and dried at 100°C for 12 hr. The resultant solid was submitted to calcination in air at 580°C for 3hr.

Table 3.1 The conditions and molar compositions of ITQ-24 for synthesis

ITQ-series	Template	Temp. ($^\circ\text{C}$)	Hydrolizing agent	Ratio (on mole basis)		
				Si	Ge	Al
24	Hexamethonium dihydroxide	175	$\text{R}(\text{OH})_2$	5	1	0.15

3.2.1.3 Preparation of N(16)-Methylsparteinium Hydroxide

A 16.23 g of (-)-sparteine was mixed with 80.15 ml of acetone. A 6.29 g of methyl iodide was added drop by drop into the mixture with stirring. After 24 hours, a cream-colored precipitate appears, 160.30 ml of diethyl ether was then added to the reaction mixture. The resulting mixture was filtered, and the solid obtained was vacuum dried. The product was N(16)-methylsparteinium iodide with a yield greater than 99%. The iodide was exchanged for hydroxide form by using an ion exchange resin, according to the following procedure. 25.53 g of N(16)-methylsparteinium iodide was dissolved in 74.88 g of water. To the obtained solution, 68.90 g of Dowes BR resin was added, and stirring was maintained until the following day. It was then filtered and washed with distilled water, and 100.80 g of

N(16)-methylsarteinium hydroxide solution was obtained with concentration of 0.65 mol/kg.

3.2.1.4 Synthesis of ITQ-21 (Arribas et al., 2004)

A 0.24 g of GeO_2 was dissolved in 19.23 g of N(16)-methylsarteinium hydroxide solution with a concentration of 1.48 mol/kg. In the obtained solution, 4.74 g of tetraethylorthosilicate and 0.21 g of aluminum isopropoxide were hydrolyzed, and stirring was maintained allowing all the ethanol formed in the hydrolysis to evaporated for 3 days. Then, 0.52 g of hydrofluoric acid solution was added, and evaporation was continued until the reaction mixture achieved a final composition:

0.91 SiO_2 : 0.09 GeO_2 : 0.5 N(16)-methylsarteinium hydroxide solution : 0.5HF : 3 H_2O .

The gel was heated at 175°C for 48 hours in a steel autoclave with an internal Teflon lining. The obtained solid was filtered, washed with distilled water, and dried at 100°C. The material was calcined at 540°C for 3 hours in airflow in order to eliminate organic matters and the fluoride ions occluded in its interior.

3.2.2 Preparation of Scrap Tires

The tire tread for pyrolysis was cut from tire tread compound to small sizes. The chopped tire tread was sieved in the size of 1 mm. particle size diameter. The chopped material was stored under dry condition.

3.2.3 Pyrolysis Process

Catalytic pyrolysis experiments were performed following these procedures. One gram of chopped tire with 0.5-1.4 mm particle size diameter was mixed with a catalyst, and then loaded into a U-tube reactor. After that, the reactor was positioned in a furnace as shown in Figure 3.1 with a nitrogen flow 30 ml/min for 5 min in order to purge the oxygen from the reactor line. The reactor was heated from room temperature to 500°C with the ramping rate of 10 °C/min. The temperature was held at the final set point for 1 hour. The products from the reactor were classified into three groups: gas, liquid, and solid. The liquid products were trapped in NaCl-ice bath and ice-acetone condensers, which were later, weighed and

analyzed by SIMDIST Gas Chromatograph. And, the gas product was collected in a gas sampling bag and analyzed by Gas Chromatography (GC). The solid residue left in the U-tube reactor was weighed, removed, and washed with tetrahydrofuran. Thus, the gas weight could be calculated by subtracting the oil weight and the residue weight from the total weight of initial tire sample.

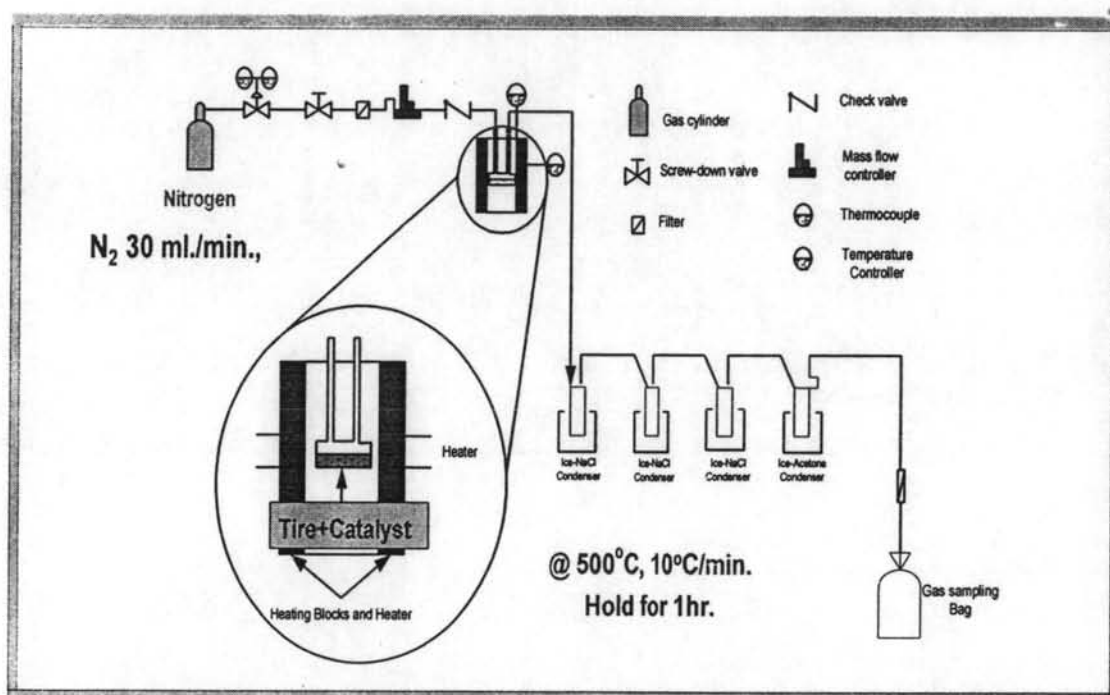


Figure 3.1 Schematic diagram of semi batch reactor for tire pyrolysis experiments.

3.3 Characterization

3.3.1 X-Ray Diffraction (XRD)

XRD patterns were analyzed using a Rigaku X-ray diffractometer system (RINT-2200) with Cu tube for generating $\text{CuK}\alpha$ radiation (1.5406 Å) and nickel filter. X-ray diffraction (XRD) is based upon the fact that the X-ray diffraction pattern is unique for each crystalline substance. The identity of the crystalline phases can be found by matching the pattern of the unknown and standard. RINT-2200 system was used to obtain XRD pattern at a generator voltage of 40 kV and a generator current of 30 mA. The scan speed of $5^\circ (2\theta)/\text{min}$ with scan step of 0.02

(2θ) was used for the continuous run in 5° to 90° (2θ) range. The goniometer parameters were as follows:

divergence slit: 1° (2θ),
 scattering slit : 1° (2θ),
 receiving slit : 0.3 mm.

A sample was ground to fine and homogeneous particles and then packed in glass specimen holder. The signal was sent to an on-line computer to record and analyze.

3.3.2 Surface Area Measurement (BET)

A surface area, total pore volume, and average pore size diameter of all prepared catalyst samples were determined using the Brunauer-Emmer-Teller (BET) method. These characterizations are based on the physical adsorption of nitrogen gas through the Sorptomatic 1990 system (Quantachrome Corporation) at liquid nitrogen temperature of -196°C . Before starting characterization, a catalyst sample was outgassed by heating under vacuum at 300°C for 6 hours in order to remove moisture. A sample cell glass tube with 12 mm diameter was employed, and the sample was weighted for about 0.2 g. The net dried weight of catalysts was the weight after out-gassing. The results were analyzed by Autosorb Anygas Software Version 2.1, which were calculated using the BET equation as shown in Equation 3.2.

$$\frac{1}{W \left(\frac{P}{P_0} - 1 \right)} = \frac{1}{W_m C} + \frac{(C - 1) P}{W_m C P_0} \quad (3.2)$$

where:

W = weight of gas adsorbed at relative pressure P/P_0

W_m = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

P_0 = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be calculated by Equation 3.3.

$$A = \frac{W_m A_{\text{nitrogen}} \times 6.02 \times 10^{23}}{M_{w,\text{nitrogen}}} \quad (3.3)$$

where:

A = Surface area of sample

A_{nitrogen} = Cross-section area of one molecule nitrogen (0.162 nm^2 at -196°C)

$M_{w,\text{nitrogen}}$ = molecular weight of nitrogen (28 g/g-mol).

3.3.3 Scanning Electron Microscopy (SEM)

The scanning electron micrographs (JEOL 5200-2AE) were used to identify the microstructure of the sample. The SEM used the electrons that are back-scattered or emitted from the specimen surface. The powder samples (commercial and synthesized zeolites) were placed on a stub and sputtered with Au metal to render the surface conductive. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattered or emitted as the primary beam bombards each successive point of the metallic specimen surface was measured by an electron detector and used to modulate the intensity of a second electron beam and forms an image on a television screen.

3.3.4 Transmission Electron Microscopy (TEM)

TEM was employed to investigate the average particle size of metals and identify the microstructure of prepared catalysts. Catalysts were prepared in thin form appropriate for TEM, that is, it was dispersed in pure water and a drop of the suspension was deposited on a copper grid. TEM was carried out in a JEM 2010 operating at an accelerating voltage of 200 kV in bright field modes. A beam was

passed through a series of lenses to form a magnified image of a sample that has been inserted in the area of the objective lens. The image from selected area was viewed through projection onto a viewing screen. However, electron beams are easily scattered by air molecules and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam.

3.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis, the Dupont TGA 2590 equipped with a thermal analyzer 2000, measuring weight loss of a sample versus time and temperature, which was employed to study thermal stability of rubber. The chopped tire tread was loaded into platinum pan and pyrolyzed over 30 to 800°C with heating rate of 10°C/min under an inert atmosphere of nitrogen gas.

3.3.5 Gas Chromatography (GC)

Gas phase samples were analyzed by gas chromatography, Agilent Technologied 6890 Network GC system, using HP-PLOT Q column: 30 m 0.32 mm i.d. 20µm film. FID was used as a detector and He as carrier gas. The temperature programs were as follows:

Initial temperature	70°C
Time at initial temperature	8 min.
Heating rate	20°C/min. to 200°C
Hold for	16 min.
Final temperature	220°C
Heating rate	10°C/ min.
Hold for	30 min.

In this study, the gas samples were collected in gas sampling bag and analyzed the component by GC with FID. The GC was calibrated, and the response factors were examined using standard refinery gas containing methane, ethylene, ethane, propylene, propane, C₄, and C₅. A mixture of n-pentane, n-hexane, n-heptane, and iso-octane in 25% volume was used to locate C₆, C₇, and C₈, respectively. The

response factors of gases on FID were calculated on the weight basis by the following equation using methane as the standard.

$$f_i = \frac{A_{std}}{A_i} \times \frac{G_i}{G_{std}} \times f_{std} \quad (3.4)$$

Where G_i is the mass of the component, G_{std} is the mass of methane, A is the area count from GC, i , std replaced each component in the standard. Finally, the mass fraction of any component, m_i can be calculated as the following equation.

$$m_i = \frac{A_i \times f_i}{\sum A_i \times f_i} \quad (3.5)$$

The response factor are listed in Table 3.1

Table 3.2 Response factor of gases

Gas	Response Factor (f_i)
Methane	1
Ethylene	0.94654 ± 0.00217
Ethane	1.00996 ± 0.00247
Propylene	0.97351 ± 0.00324
Propane	0.98920 ± 0.00390
C ₄	0.98242 ± 0.00397
C ₅	0.98411 ± 0.00472
C ₆	0.93943 ± 0.00452
C ₇	0.91804 ± 0.01078
C ₈	0.96873 ± 0.01019

3.3.6 SIMDIST Gas Chromatography (SIMDIST-GC)

The liquid samples from the pyrolysis of used tires were analyzed directly by Varian CP-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC), equipped with FID.