

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Chemicals for Catalyst Preparation

- The idealite ceramic monolith was obtained from the US and also cut in the 2X2X15 mm<sup>3</sup> rod prior to use.
- Gamma alumina [ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>] was obtained from Alfa<sup>®</sup>AESAR<sup>®</sup> (U.S.A).
- Acetic acid [CH<sub>3</sub>COOH], of 99.8% purity, was obtained from Aldrich.
- Palladium (II) nitrate dihydrate [Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O] was obtained from Aldrich.
- Zirconium (IV) chloride [ZrCl<sub>4</sub>] was obtained from Aldrich.
- Titanium (III) chloride [TiCl<sub>3</sub>] was obtained from Carlo Erba.
- Tin (II) nitrate dehydrate [SnCl<sub>2</sub>·2H<sub>2</sub>O] was obtained from Carlo Erba.

#### 3.1.2 Chemicals for Zeolite Preparation

- Diethyl ether was obtained from Aldrich.
- Hydrofluoric acid (HF), of 48% purity, was obtained from Aldrich.
- Tetraethyl orthosilicate was obtained from Fluka Chemical Co., Ltd.
- Germanium (IV) oxide (GeO<sub>2</sub>) was obtained from Aldrich.
- (-)-Sparteinium (C<sub>15</sub>H<sub>26</sub>N<sub>2</sub>) was obtained from Aldrich.
- Aluminium Isopropoxide was obtained from Aldrich.
- Methyl iodide, of 99% purity, was obtained from ACROS.
- Dowes BR resin was obtained from Fluka Chemical Co., Ltd.

### 3.1.3 Gases

- Nitrogen of 99.99% purity, used as purging gas inside the reactor and furnace to avoid the local temperature rise inside the reactor, was supplied from Thai Industrial Gas Public Co., Ltd.
- Hydrogen of 99.99% purity, used for catalyst reduction, was supplied from Thai Industrial Gas Public Co., Ltd.
- Helium of 99.99% purity, used as carrier gas for gas chromatograph, was supplied from Thai Industrial Gas Public Co., Ltd.
- Methane of 99.99% purity, used as a reactant gas, was supplied from Thai Industrial Gas Public Co., Ltd.
- Air, used as a reactant gas, was supplied from Thai Industrial Gases Co., Ltd.

## 3.2 ITQ-21 Zeolite Preparation

ITQ-21 zeolite can be synthesized from the template; N(16)-methylsperineium hydroxide, via sol-gel process.

### 3.2.1 N(16)-methylsperineium hydroxide Preparation

N(16)-methylsperineium hydroxide was prepared by using 9.51 g of (-)-sperine mixed with 47 mL of acetone. While this mixture was stirred at room temperature, 3.7 mL of methyl iodide was added drop by drop, and the stirring was held for 24 hours in darkness until a cream color precipitate appeared. The procedure must be repeated for the case that the cream precipitate did not form. Subsequently, 94 mL of diethyl ether was added to the mixture. The obtained solid was filtered and dried under vacuum. The product is N(16)-methylsperineium iodide with a yield greater than 99.65%. After that, 15.21 g of N(16)-methylsperineium iodide was dissolved into 44 g of water mixture and 41 g of Dowes BR resin to convert iodide ions (I<sup>-</sup>) into hydroxide form (OH<sup>-</sup>). The mixture was continuously stirred overnight. Afterwards, it was filtered and washed with distilled water. The obtained product

was around 60 g of N(16)-methylsarteinium hydroxide ( $C_{16}H_{25}N_2OH$ ), which was used as template for ITQ-21 synthesis.

### 3.2.2 ITQ-21 Synthesis (Arribas *et al.*, 2004)

ITQ-21 zeolite was synthesized using the N(16)-methylsarteinium hydroxide ( $C_{16}H_{25}N_2OH$ ) from the organic directing agent as previously prepared. Synthesis of ITQ-21 in fluoride media was carried out under hydrothermal conditions in a teflon-lined stainless steel autoclave with a gel composition of

0.09GeO<sub>2</sub>: 0.91SiO<sub>2</sub>: 0.02Al<sub>2</sub>O<sub>3</sub>: 0.50C<sub>16</sub>H<sub>29</sub>N<sub>2</sub>OH: 0.50HF: 3H<sub>2</sub>O.

For the synthesis ITQ-21, 0.24 g of germanium oxide (GeO<sub>2</sub>) was dissolved in 19.23 g of N(16)-methylsarteinium hydroxide solution mixed with 5.08 g of tetraethyl orthosilicate (TEOS) and 0.21 g of aluminum isopropoxide as silica and alumina sources, respectively. The mixture was stirred at room temperature until the Si and Al precursors were completely hydrolyzed for 3 days, and the gel concentration was reached. Subsequently, 0.52 g of hydrofluoric acid solution (48.1% wt of HF) was added, and the mixture was homogenized by mechanical stirring in a Teflon-line stainless steel autoclaved at the desired temperature of 175°C for 3 days. Solid ITQ-21 was recovered by filtration, washed with distilled water, and dried at 100°C. Then, it was calcined at 540°C for 3 hours to eliminate organic matter and the fluoride ions occluded in its interior.

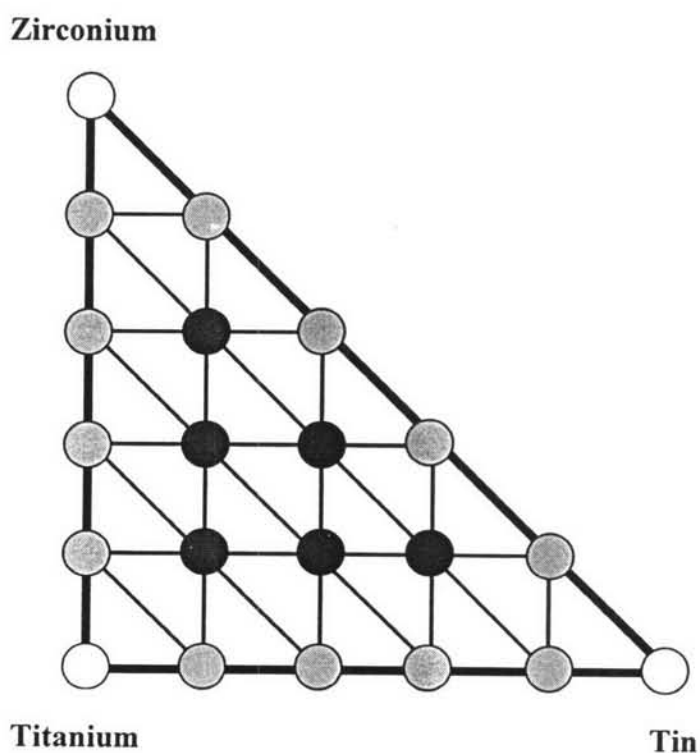
## 3.3 Catalysts Preparation

### 3.3.1 Monolith Washcoating

After drying, the monolith of 2x2x15 mm<sup>3</sup> was dipped into 2.5% (wt) acetic acid solution for about 2 min to increase surface roughness before being rinsed with deionized water to leach the acid from the monolithic surface. After that, the monoliths were dried at 110°C until the weight remained constant before being dipped into the ITQ-21 and/or alumina containing slurry. The monolith was dipped in the prepared washcoat about 2 min, and some of the excess solution plugged in the monolithic channels was sucked out before drying. The whole process was repeated

for 10 times in order to obtain the monolith thickness of about 35 microns. Then, the monolith was dried at 100°C and calcined at 500°C for 3 hours.

Catalysts were prepared by incipient wetness impregnation using a mixed metal solution of active elements. Pd was selected as a base metal, whereas Sn, Ti and Zr were selected as promoters. The composition of Pd on the support was fixed at 4%, while the other elements were mixed to many compositions as represented by the right-angle triangle tertiary diagram in Figure 3.1. The total amount of the promoters was fixed at 1% total for all compositions. All metals must be in a homogeneous solution before being impregnated on the washcoated monolith. After that, the catalysts were dried overnight and calcined at 500°C for 3 hours.



**Figure 3.1** Right-angled triangle tertiary diagram of the catalyst.

### 3.4 Experimental Setup

Activity testing was performed using a multi-flow reactor based on the concept of high-throughput screening. The reactor consists of three parts, which are a

gas mixing section, a catalytic reactor, and an analytical section. After that, the mixed reactant gases were split into eight sub-streams before entering the eight tubular flow reactors. The multi-channel valve then selects only one stream at a time to be sent to the GC for analysis. Activity testing was conducted at 450-650°C under atmospheric pressure.

#### 3.4.1 Gas-Mixing Section

The reactant gas consisted of 2% methane, and air. Methane and air were used as reactant gases to perform the catalytic combustion reaction. These reactants were passed through 7 micron filters to trap particles before entering the mass flow controllers (AALBORG model GFC171S). The mass flow controllers were used to control the flow rate of the reactant gases in order to achieve the desired composition. Check valves with 1 psig cracking pressure were installed after the mass flow controllers to prevent reverse flow. After mixture, the reactant gases were split into 8 sub-streams before entering the eight tubular flow reactors (Figure 3.2). Hydrogen was used as a reducing agent to achieve a metallic state of some active elements before screening for their catalytic activity. Nitrogen was used as a purging gas inside the catalytic reactors and furnace to avoid the local temperature rise on catalysts.

#### 3.4.2 Catalytic Reactor

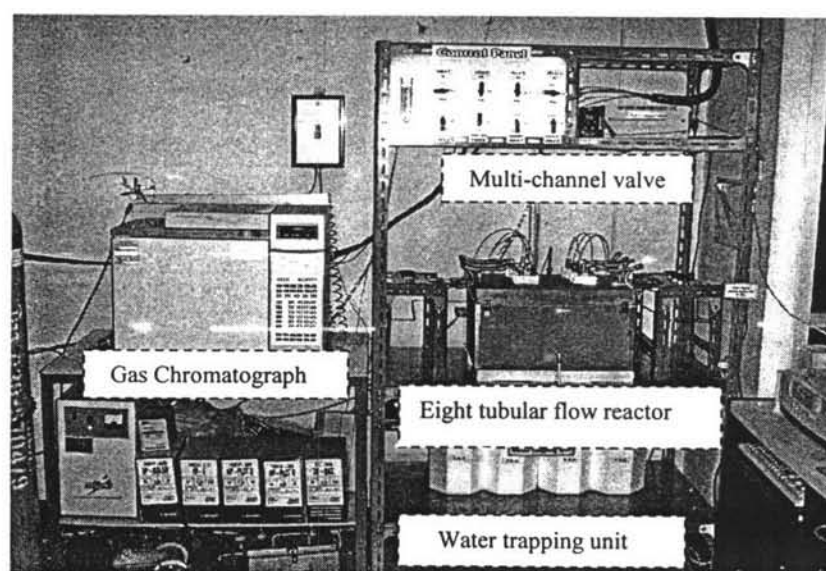
Eight stainless U-tubes with  $\frac{1}{4}$ " outside diameter were used as catalytic reactors in the reactor unit. All eight of the U-tube reactors were placed in a furnace where the temperature of the catalyst bed was monitored and controlled by Maxthermo temperature controller, model MC2438, equipped with K-type thermocouples. The catalysts were packed inside the U-tube reactor between two layers of quartz wool.

#### 3.4.3 Analytical Instrument

Eight streams from the reactors were passed through a multi-channel valve to select only one stream at a time to analyze by GC. Gases from the reactor were analyzed by using gas chromatograph (GC, Agilent Technology, Hewlett

Packard 6890N model) with two capillary columns, HP-PLOTQ and HP-MOLSIV. The selected stream from the multi-channel valve was sent to a HP-PLOTQ column of 20 micrometer coating thickness, 0.32 mm I.D. and 30 m length to separate and analyze CO<sub>2</sub> and CH<sub>4</sub>. Subsequently, other species in the mixture stream were separated and analyzed using a HP-MOLSIV column of 25 micrometer coating thickness, 0.32 mm I.D. and 30 m length to complete the analysis. Each cycle of GC analysis took around 8 min to complete before starting the next injection. The conditions of GC are listed as follows:

Injector Temperature:	100°C
Oven Temperature:	
- Initial time:	63°C
- At 1.00 to 7.17 min:	68°C
- Final Time:	63°C
TCD Conditions:	
- Temperature	200°C
- Reference gas	N <sub>2</sub> (99.99% purity)
Carrier Gas:	He (99.99% purity)
- Flow rate:	2.2 mL/min



**Figure 3.2** Eight Tubular Flow Reactor System and Gas Chromatograph.

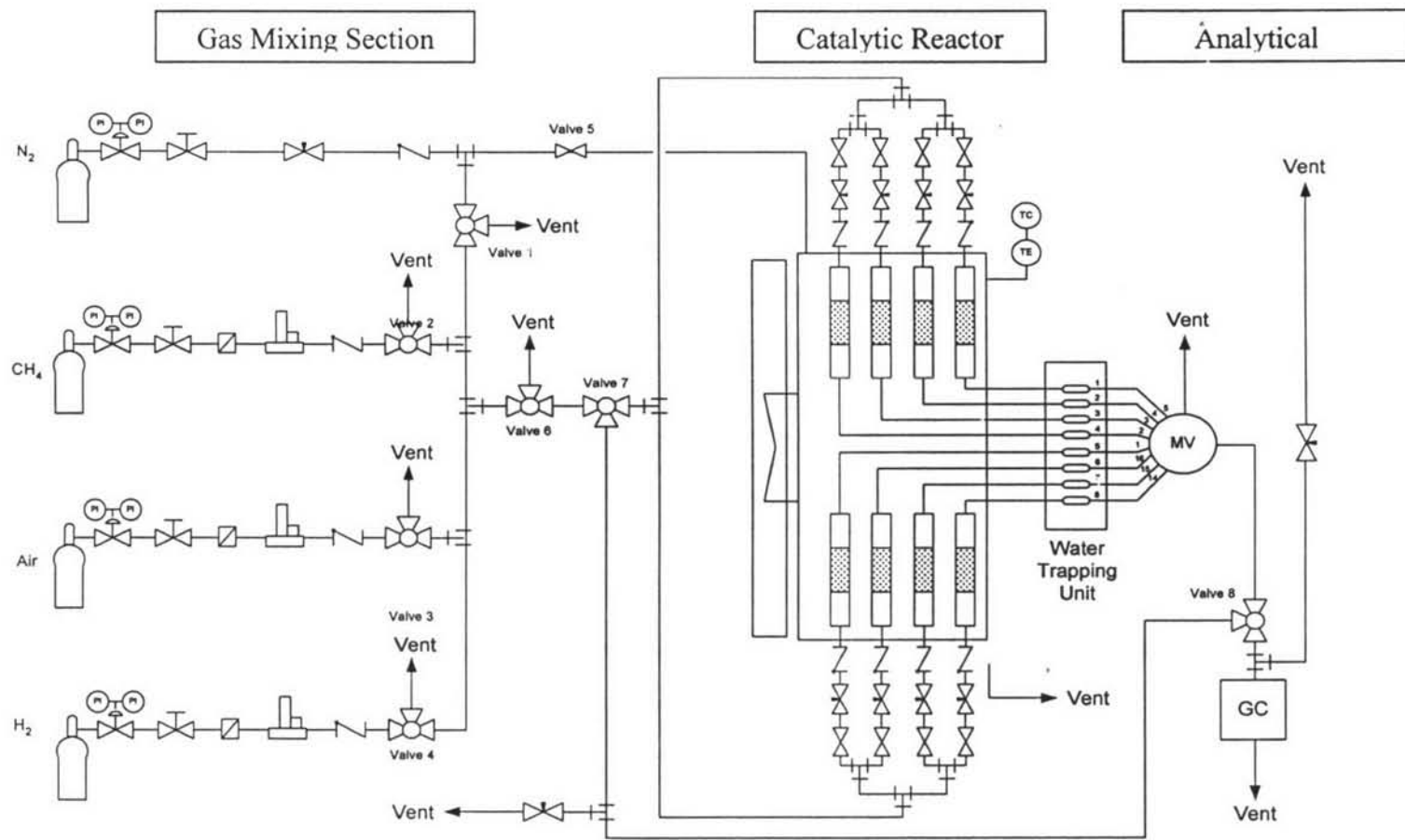


Figure 3.3 Schematic flow diagram of the eight tubular flow reactors equipped with GC (Kraikul *et al.*, 2005).

### 3.6 Catalyst Characterizations

The characterization techniques and equipment applied in this research were X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Temperature Programmed Oxidation (TPO).

#### 3.6.1 X-ray Diffraction (XRD)

The crystalline structure of ITQ-21 catalysts were analyzed by means of a Rigaku X-ray diffractometer system. X-ray Diffraction (XRD) is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns of all catalyst samples were obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered  $\text{CuK}\alpha$  radiation source ( $\lambda = 1.542 \text{ \AA}$ ) of 40 kV and 30mV. A catalyst sample was placed into a hollow of glass holder and held in place by glass window. Then, it was scanned in the range of  $2\theta$  from  $5^\circ$  to  $80^\circ$  in the continuous mode with the rate of  $5^\circ \text{ min}^{-1}$ . The XRD results gave peak parameters, including the centroid  $2\theta$ , the full line width at half the maximum of intensity ( $\beta$ ), d-value and intensity.

#### 3.6.2 Scanning Electron Microscopy (SEM)

The morphology of the catalyst was obtained by using a JEOL 5200-2AE Scanning Electron Microscope (SEM), with a magnification of 35-200,000. SEM was utilized to capture the micrograph of the support morphology. The powder sample was placed on a stub and coated with gold in a sputtering device before taking the micrograph. Moreover, the crystalline size of the zeolite support was roughly estimated.



### 3.6.3 Transmission Electron Microscopy (TEM)

The transmission electron micrographs was employed to investigate the average particle size of metals and to examine the microstructure of prepared catalysts such as the crystalline size of the ITQ-21 catalysts. Catalysts were dispersed in pure water, and a drop of the suspension was then deposited on a copper grid. TEM was carried out using 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.

### 3.6.4 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) patterns were collected using TPDRO machine (Thermo Electron: TPDRO 1100) outfitted with a Quadrupole Mass Spectrometer (QMS) to observe some oxygen desorption behavior from the active elements. Lead formulations were packed in the TPDRO sample cell before being placed in the sample holder of TPDRO machine. Heating rate employed was 10°C/min starting from 100 to 900°C. Thermal conductive detector (TCD), which transferred data online to computer, were employed to detect and plot the oxygen releasing signal versus catalyst temperature.