CHAPTER IV

EXPERIMENTS

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into three sections, i.e., catalyst preparation, catalyst characterization and catalytic reaction. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure and surface properties of the catalyst characterized by various techniques are discussed in section 4.2. Finally, the details of the catalytic reaction are illustrated in section 4.3.

4.1 Catalyst preparation

This section of the thesis consists of catalyst preparation step that used in this study. Because the main objective is to modify the Co-TS-1 catalyst, the catalyst preparation is much concerned. The preparation step is the most important because it affects the physical properties, chemical properties and catalytic behavior. Therefore, this research highlights on the preparation of Co-TS-1 catalyst by incorporation method.

The samples of cobalt-titanium silicalite-1 (Co-TS-1) ascribed as Co-TS-1 batch1-batch10 were prepared according to the incorporation method discussed in details below. All chemicals used in the preparation procedure of Co-TS-1 catalysts are shown in Table 4.1.

The preparation procedure of Co-TS-1 by rapid crystallization method (hydrothermal method) is shown in Figure 4.1. This method can advantageously and rapidly prepare the uniform and fine zeolite crystals with the following improvements: (i) the preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals, (ii) the precipitated gel was milled before the hydrothermal treatment, which was essential to obtain the fine crystals, and (iii) the temperature under the hydrothermal treatment was programmed to minimize the time which was necessary for the crystallization.

Table 4.1 The chemicals used in the Co-TS-1 catalyst preparation.

Chemical	Grade	Supplier
Cobalt (II) nitrate Hexahydrate	Analytical	Aldrich
Cobalt (II) chloride Hexahydrate	Analytical	Carlo Erba
Cobalt (II) acetate Tetrahydrate	Analytical	Aldrich
Titanium (IV) butoxide 97%	-	Aldrich
Tetra-n-propyl ammonium bromide 98%	-	Aldrich
Sodium silicate solution	Extra Pure	Merck
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich

Gel preparation   **Decant-solution preparation**

```
┌──────────┬──────────┬──────────┐  ┌──────────┬──────────┬──────────┐
│ A1       │ B1       │ C1       │  │ A2       │ B2       │ C2       │
│ SOLUTION │ SOLUTION │ SOLUTION │  │ SOLUTION │ SOLUTION │ SOLUTION │
└──────────┴──────────┴──────────┘  └──────────┴──────────┴──────────┘
```

HOMOGENIZED MIXING OF
GEL-PREPARATION

HOMOGENIZED MIXING OF
DECANT-SOLUTION

GEL
SOLUTION

GEL
PRECIPITATE

DECANT
GEL

MILLING

DECANT-SOLUTION

HYDROTHERMAL TREATMENT
IN AUTOCLAVE

DECANT AND WASHING
SOLUTION

CRUDE CRYSTALS

DRY

CALCINATION

Co-TS-1

Figure 4.1 The preparation procedure of Co-TS-1 by hydrothermal method.

4.1.1 Preparation of Solutions

The source of metals for the preparation of decantation and gel solutions were $Co(NO_3)_2.6H_2O$, $CoCl_2.6H_2O$ and $Co(C_2H_3O_2)_2.4H_2O$ for Co, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si, respectively. TPABr (Tetra-n-Propyl Ammonium Bromide, $(CH_3CH_2CH_2)_4NBr$) was used as organic template. The solutions were prepared by mixing of prepared gel and decant solution. In the preparation recipe, the atomic ratio of silicon/titanium was set as 50 and silicon/cobalt was set as 150. Various solutions which were involved with preparation of gel and decant solution were listed in Table 4.2 and the amounts of cobalt salts that used to synthesize in each sample were calculated in Appendix B. Also, the types of cobalt salts (cobalt nitrate hexahydrate, cobalt chloride hexahydrate and cobalt acetate tetrahydrate) contained in each solution (A1, B1, C1, A2, B2 and C2), including desired amount of cobalt salts in each sample for synthesizing our desired catalysts were showed in Table 4.3. Because of the insolubility of the cobalt salts ($Co(NO_3)_2.6H_2O$, $CoCl_2.6H_2O$ and $Co(C_2H_3O_2)_2.4H_2O$) into the B1 and B2 solutions, in this work interested in loading cobalt salts only in solution A1, C1, A2 and C2. The addition of cobalt salts in either gel solution or decantation solution in amount of 2X but adding of cobalt salts in both of solutions (A1 and A2) is X. Therefore, the amount of $Co(NO_3)_2.6H_2O$ will be loaded was 1.270g in each solution (ensured from 0.635 g of $Co(NO_3)_2.6H_2O$ into the A1 solution and another 0.635 g into the A2 solution, hence, this work will load 1.270 g of $Co(NO_3)_2.6H_2O$ (0.635 g + 0.635 g) in either gel solution or decantation solution and load 0.635 g of $Co(NO_3)_2.6H_2O$ in both A1 and A2 solutions).

Table 4.2 The reagents used for preparing Co-TS-1 (Si/Ti = 50, Si/Co = 150).

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			**Solution A2**		
Ti[O(CH$_2$)$_3$CH$_3$]$_4$	2.297	g	Ti[O(CH$_2$)$_3$CH$_3$]$_4$	2.297	g
TPABr	5.720	g	TPABr	7.530	g
NaCl	11.930	g	De-ionized water	60.00	ml
De-ionized water	60.00	ml	H$_2$SO$_4$(conc.)	3.40	ml
H$_2$SO$_4$(conc.)	3.40	ml	(Cobalt Salts	X or 2X	g)
(Cobalt Salts	X or 2X	g)			
Solution B1			**Solution B2**		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			**Solution C2**		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104.00	ml
NaOH	2.39	g			
De-ionized water	208.00	ml			
H$_2$SO$_4$ (conc.)	1.55	ml			
(Cobalt Salts	X or 2X	g)			

Table 4.3 The amount of cobalt salts indicated as 'X' for synthesizing various catalyst samples (Si/Ti = 50, Si/Co = 150).

Sample	Type of salts	Loading Solution	Amount of cobalt salts (g)
Co-TS-1 batch1	$Co(NO_3)_2.6H_2O$	A1	$2X = 1.2700$
Co-TS-1 batch2	$Co(NO_3)_2.6H_2O$	A2	$2X = 1.2700$
Co-TS-1 batch3	$Co(NO_3)_2.6H_2O$	C1	$2X = 1.2700$
Co-TS-1 batch4	$Co(NO_3)_2.6H_2O$	A1 and A2	$X = 0.6350$
Co-TS-1 batch5	$CoCl_2.6H_2O$	A1	$2X = 1.0342$
Co-TS-1 batch6	$CoCl_2.6H_2O$	C1	$2X = 1.0342$
Co-TS-1 batch7	$CoCl_2.6H_2O$	A1 and A2	$X = 0.5171$
Co-TS-1 batch8	$Co(C_2H_3O_2)_2.4H_2O$	A1	$2X = 1.0870$
Co-TS-1 batch9	$Co(C_2H_3O_2)_2.4H_2O$	C1	$2X = 1.0870$
Co-TS-1 batch10	$Co(C_2H_3O_2)_2.4H_2O$	A1 and A2	$X = 0.5435$

The detailed procedures are as follows: Firstly, a gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the mixed solution was maintained within 9-11 (H_2SO_4(conc.)) or NaOH solution are used to adjust appropriate pH level if it was necessary). After that, the gel mixture was separated from the supernatant liquid by centrifugal separation and grinded for totally 1 hour before the hydrothermal treatment in order to obtain the uniform, fine crystals. Secondly, a decantation solution was prepared by dropping solution A2 coupling with solution B2 into solution C2, same as for the preparation of gel mixture. Meanwhile the pH value of mixed solutions was also controlled in range of 9-11 during this step. Mixed solutions were stirred and then be centrifuged to derive gel. Then, mixing of prepared gel and decant solution leaded to derive solution for crystallization in the next step.

4.1.2 Crystallization

In the crystallization step, the mixture of solution from the previous step was filled in a Pyrex glass. The glass container was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm^2 gauge. The mixture was heated from room temperature to 160°C with a heating rate of 2°C/min and then heating up from 160°C to 210°C with a heating rate of 2°C/10 min while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave. The product crystals were washed with de-ionized water until the pH of the washing water decreased from about 10 to 7 to remove Cl^{-1} out of the crystals. Then the crystals are dried in an oven at 110°C for at least 24 hours.

4.1.3 Calcination

The dry crystals were calcined in an air stream at 550°C and held at that temperature for 6 h, by heating them from room temperature to 550°C with heating rate 8.6°C/min to burn off the organic templates and leave cavities and channels in the crystals. Then, the calcined crystals were finally cooled down to room temperature and stored in a dessicator for later use. After this step the catalysts formed were called Co-TS-1.

4.2 Catalyst characterization

4.2.1 X-ray fluorescence spectroscopy (XRF)

The qualitative and quantitative elemental analysis in the bulk of the catalyst samples were examined by x-ray fluorescence (XRF) spectrometer of wavelength dispersive type (WDS) with Rh target x-ray tube excited source, max. 3 kW power and detectable elements from B to U. The XRF using ED-XRF model ED-2000 at the Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University.

4.2.2 Scanning electron microscopy (SEM)

The shape and size crystals of the prepared catalyst were observed by using JEOL JSM-35CF scanning electron microscope (SEM) at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The SEM was operated using the back scattering electron (BSE) mode at 10 kV.

4.2.3 X-ray diffraction (XRD)

The crystal structure parameters of the catalyst samples were performed by using X-ray diffractometer (XRD), SIEMENS D5000, using Cu Kα radiation with Ni filter at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The catalyst samples were filled into holder (XRD plate) before placing on the measured position of XRD and the signal during analyzing was reported on a microcomputer. The operating conditions of measurement were shown below :

2θ range of detection :	6-40°
Resolution :	0.02°
Number of scan :	10

4.2.4 BET surface area and pore volume measurement

The specific surface area were measured by BET adsorption isotherm of nitrogen, Micromeritrics ASAP 2020, at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The sample cell which contained 0.3 gram of sample was placed into degas port of BET. After completion of degas step, the degased cell was transfered to the analytical port of that one for processing the analyzing step.

4.2.5 Fourier transform infrared (FT-IR)

The identification of functional groups on the catalyst surface was determined by FT-IR spectroscopy using Nicolet model Impact 6700 at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. . Infrared spectra were recorded between 400 and 1200 cm^{-1} on a microcomputer. The samples were characterized in a diffuse reflectance mode.

4.2.6 Temperature programmed desorption (TPD)

The strong acid and weak acid sites of the catalyst were determined by measuring the amount of adsorbed ammonia on the surface using Micromeritrics Chemisorb 2750 at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University.

The procedure started with placing 0.1 gram catalyst sample into a sample cell before put it to Micromeritrics. Helium gas at flow rate of 15 ml/min was released to flow through the sample. The sample was heated from room temperature to 550 $^{\circ}C$ with a heating rate of 10 $^{\circ}C$/min and hold for 1 hour. Then, the sample was cooled down to 80 $^{\circ}C$ and also held for another hour. In the next step, 15 vol% ammonium gas with a flow rate of 15 ml/min was flowed through the sample instead of helium, and held for 15 minutes. Adsorption of 15 vol% ammonium on the catalyst surface occured in this step. Next, helium gas at the same flow rate flowed through the sample instead of ammonium and also holds for another hour. In the final step which was the desorption step, the sample was heated from 80 $^{\circ}C$ to 550 $^{\circ}C$ with a heating rate of 10 $^{\circ}C$/min. The signal from this step was recorded every 0.1 seconds and reported on a microcomputer.

4.3 The catalytic activity measurements

4.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 4.2. The system consists of a saturator, a microreactor, an automatic temperature controller, an electrical furnace and a gas controlling system. The liquid phase reactant was filled in the saturator. Argon is passed through the evaporator to evaporate the reactant and carried to the microreactor.

The microreactor is made from a stainless steel tube. Three sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

The gas supplying system consists of cylinders of ultra high purity nitrogen or argon and air, each equipped with pressure regulators (0-120 psig), on-off valves and mass flow controller for adjusting the flow rate of these gases.

The composition of oxygenate compounds in the feed and product streams were measured by a Shimadzu GC8A gas chromatograph equipped with flame ionization detector.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and carbon monoxide and a Porapak-Q column to separate CO_2 and water were operated in parallel. The operating conditions are shown in the Table 4.4.

Table 4.4 Operating conditions for gas chromatograph.

Gas chromatograph	Shimadzu GC8A	Shimadzu GC8A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	3% SP-1500
Carrier gas	He (99.999%)	N_2 (99.999%)
Carrier gas flow rate	25 ml/min	25 ml/min
Column temperature		
- Initial	100 °C	70 °C
- Final	100 °C	120 °C
Heating rate	-	4 °C/min
Detector temperature	130 °C	120 °C
Injector temperature	130 °C	120 °C
Analyzed gas	CO, CO_2, H_2O	Oxygenates

4.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

2. The total flow rate was 100 ml/min. Flow rate of 2-propanol, argon and air were adjusted to the required values. The gas mixtures for oxidation reaction were 5 vol% alcohols, 8 vol% oxygen and balance with argon.

3. The reaction temperature was between 100-500 °C. The effluent gases were analyzed by using the FID and TCD gas chromatographs. The chromatograph data

were changed into mole of propylene, 2-propanol, isopropyl ether, acetone and CO_2 by calibration curves in Appendix D.

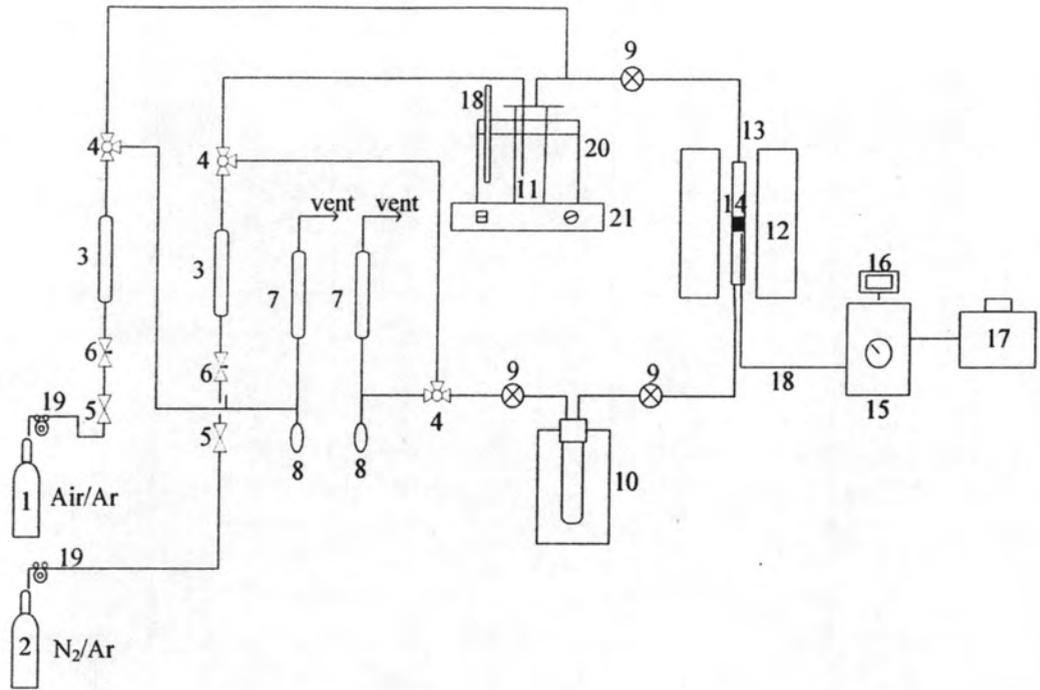4. The result of catalytic test was calculated in the term of

$$\% \text{ A conversion (C)} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

$$\% \text{ Selectivity (S) to B} = \frac{\text{mole of B formed}}{\text{mole of A converted}} \times \frac{\text{no. of C atom of B}}{\text{no. of C atom of A}} \times 100$$

$$\% \text{ Yield (Y) to B} = \frac{\% \text{ A conversion} \times \% \text{ selectivity to B}}{100\%}$$

Where,   A is reactant

B is product

1. Air vessel
2. N_2/Ar vessel
3. Mass Flow controller
4. Three-way-valve
5. Gate valve
6. Needle valve
7. Rotary meter
8. Rubber cock
9. Sampling point
10. Condenser
11. Saturator
12. Furnace
13. Reactor
14. Catalyst bed
15. Temperature controller
16. Digital temperature indicator
17. Variable voltage transformer
18. Thermocouple/Thermometer
19. Pressure regulator
20. Water bath
21. Heating and Stirring controller

Figure 4.2 Flow diagram of the oxidation reaction system.