CHAPTER III

EXPERIMENTS

The chapter is divided into three sections, i.e., catalyst preparation, catalyst characterization and catalytic reaction. The catalyst preparation section consists of preparation of TS-1 catalyst, Cr-TS-1 catalyst preparation using incorporation method and the synthesis methodology of Cr-TS-1 catalyst as shown in section 3.1. The properties of catalyst were characterized by various techniques as shown in section 3.2. Finally, the details of the catalytic reaction are illustrated in section 3.3.

3.1 Catalyst preparation

3.1.1 Preparation of TS-1 catalyst

The synthesis of TS-1 catalyst by hydrothermal method consists of three steps including preparation of solution, crystallization and calcinations. The detail of preparation is performed below.

3.1.1.1 Chemicals

The details of chemicals used in the preparation procedure of TS-1 catalyst are shown in Table 3.1.

Table 3.1 The chemicals used in the catalyst preparation

Chemical	Grade	Supplier
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

3.1.1.2 Preparation of solutions

Solution for crystallization was prepared by mixing a prepared gel and a decant solutions. Various solutions which were involved with the preparation of gel and decant solutions were listed in Table 3.2.

3.1.1.2.1 Gel solution preparation

Gel was prepared by dropping solution A1 coupling with solution B1 into solution C1, meanwhile pH value of the mixed solution was controlled in the range of 9-11 during this step. The mixed solutions were further stirred for 2 hours and then be centrifuged and switched milling to derive gel and clear liquid. This gel will be used for mixing with the decant solution in the next step.

Table 3.2 The compositions of each solution for preparation of gel and decant solution of TS-1 catalyst at Si/Ti = 50

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			**Solution A2**		
$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g	$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
De-ionized water	60	ml	H_2SO_4(conc.)	3.4	ml
H_2SO_4(conc.)	3.4	ml			
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	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

3.1.1.2.2 Decant solution preparation

Decant solution was prepared by dropping solution A2 coupling with solution B2 into solution C2, meanwhile pH value of the mixed solution was controlled in the range of 9-11 during this step. The mixed solutions were further stirred for 2 hours and then centrifuged to derive gel and the clear liquid obtained is called "decant solution".

Mixing of the prepared gel and the decant solutions leads to the derive solution for crystallization in the next step.

3.1.1.3 Crystallization

The mixture of solution from the previous step was filled in a 250 ml 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 was further heated from 160 °C to 210 °C with a heating rate of 2 °C/10 min, 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. Then the crystals were dried in an oven at 110 °C for 24 h.

3.1.1.4 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. The organic templates were burned off leaving cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature and stored in a dessicator for later use.

3.1.2 Cr-TS-1 catalyst preparation using incorporation method

In the past, there were attempts to improve performance of TS-1 catalyst as support of the second metal. Incorporation method is one of interesting methods because this method is the simplest way. Incorporation method is addition of the second metal during the formation of TS-1 crystal. From a former research [Poompichate (2005)], it was found that incorporation method is selected to improve TS-1 catalyst with chromium. The synthesis of chromium titanium silicalite-1 catalyst is the same as the synthesis of TS-1 catalyst as shown in 3.1.1 but it is different in the step of preparation of solution; chromium salt was added in solution A1 of gel solution and solution A2 of decant solution as shown in Table 3.3. The result of chromium titanium silicalite-1 catalyst synthesis using incorporation method found that has some problem concerning about how to control silicon to chromium ratio. Therefore, to solve this problem, synthesis methodology affecting chromium-titanium silicalite-1 catalyst is proposed to study the preparation procedure(s) and factor(s) affecting the chromium-titanium silicalite-1 catalyst synthesis such as kinds of chromium salt, solution for chromium salts to be added.

Table 3.3 The compositions of each solution for preparation of gel and decant solution of Cr-TS-1 catalyst at Si/Ti = 50, Si/Cr = 150

Solution for the gel preparation			**Solution for decant-solution preparation**		
Solution A1			**Solution A2**		
$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g	$Ti[O(CH_2)_3CH_3]_4$ 97%	2.2962	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
De-ionized water	60	ml	H_2SO_4(conc.)	3.4	ml
H_2SO_4(conc.)	3.4	ml	$Cr(NO_3)_3.9H_2O$	0.873	g
$Cr(NO_3)_3.9H_2O$	0.873	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	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

3.1.3 The synthesis methodology of Cr-TS-1 catalyst

Two criteria have been set to specific chromium salts to be use in the incorporation method. Both criteria are:

1. Selected chromium salt can be soluble in water.
2. The anions of the selected chromium salts must be easily to be removed from the obtained catalyst.

From preliminary experiments, it is found that chromium nitrate nanohydrate [$Cr(NO_3)_3.9H_2O$] and chromium oxide [CrO_3] have properties corresponding to criterion above. Therefore, they are selected in this study as shown in Table 3.4.

Table 3.4 The chromium salt used in Cr-TS-1 catalyst preparation

Chemical	Supplier
Chromium nitrate nanohydrate	Aldrich
Chromium oxide	Aldrich

In this study, chromium titanium silicalite-1 catalyst was synthesized using the same procedure as the synthesis of TS-1 described in 3.1.1. The difference is in the step of solution preparation, chromium nitrate nanohydrate and chromium oxide were added in solutions of gel and (or) decant solution with molar ratio of Si/Ti = 50 and Si/Cr = 150. The methodology of adding chromium salt is shown in Table 3.5.

Table 3.5 The various method adding chromium salt into solutions for synthesizing various catalyst samples at Si/Ti = 50 and Si/Cr = 150

Sample	**Chromium salt**	**Solution**
Cr(III)-TS-1-A1	$Cr(NO_3)_3{\cdot}9H_2O$	A1
Cr(III)-TS-1-A1A2	$Cr(NO_3)_3{\cdot}9H_2O$	A1A2
Cr(III)-TS-1-A2	$Cr(NO_3)_3{\cdot}9H_2O$	A2
Cr(III)-TS-1-B1	$Cr(NO_3)_3{\cdot}9H_2O$	B1
Cr(III)-TS-1-C1	$Cr(NO_3)_3{\cdot}9H_2O$	C1
Cr(VI)-TS-1-A1	CrO_3	A1
Cr(VI)-TS-1-A1A2	CrO_3	A1A2
Cr(VI)-TS-1-B1	CrO_3	B1
Cr(VI)-TS-1-C1	CrO_3	C1

According to Table 3.5 mentioned above for convenience of discussion, the Cr-TS-1 catalysts with different in the methodology of adding chromium salt and kinds of chromium salt will be named as Cr(III)-TS-1-A1, Cr(III)-TS-1-A1A2, Cr(III)-TS-1-A2, Cr(III)-TS-1-B1, Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1, Cr(VI)-TS-1-A1A2, Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1. The roman number in the bracket indicates the oxidation number of chromium used and A1, A2, B1 and C1 indicate the solution in which the chromium salt was added. The amount of $Cr(NO_3)_3{\cdot}9H_2O$ used for the preparation Cr-TS-1 catalyst at Si/Cr = 150 is 0.873×2 gram for adding in A1, A2, B1 and C1 solutions (samples Cr(III)-TS-1-A1, Cr(III)-TS-1-A2, Cr(III)-TS-1-B1 and Cr(III)-TS-1-C1). In the preparation of Cr(III)-TS-1-A1A2, that amount of $Cr(NO_3)_3{\cdot}9H_2O$ added in A1 solution is 0.873 gram and 0.873 gram for A2 solution.

Other samples that used CrO_3, the amount of CrO_3 is = 0.218×2 gram and is added in various solutions similarly using $Cr(NO_3)_3\cdot 9H_2O$.

3.2 Catalyst characterization

3.2.1 X-ray fluorescence spectroscopy (XRF)

The composition analysis of elements of catalyst was performed by X-ray fluorescence spectroscopy (XRF). 5 gram of the catalyst sample was examined by XRF using Oxford model ED2000 with energy dispersive X-ray (EDX) technique at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

3.2.2 Scanning electron microscopy (SEM)

The morphology of the catalyst was examined by scanning electron microscopy (SEM). A few amount of the catalyst sample which is coated with gold was examined using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 10 kV.

3.2.3 X-ray diffraction (XRD)

The crystalline structure of the catalysts were analyzed by XRD analysis. The holder filled with the catalyst sample was placed in are X-ray diffractometer, SIEMENS D5000, using Cu Kα radiation with Ni filter, and the signal during the analysis was recorded on a microcomputer. The operating conditions of measurement are shown below.

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

3.2.4 BET surface area and pore volume measurement

Surface area and pore volume were analyzed by BET technique. The sample cell which contained 0.3 gram of sample was placed into a degas port of BET Micromeritrics ASAP 2020. After completion of the degassion step, the degas cell was transfered to the analytical port of that one for processing the analyzing step.

3.2.5 Fourier transform infrared (FT-IR)

To determine the location of titanium incorporated into the MFI crystal lattice, the samples were studied by the FT-IR spectroscopy. The holder filled with the catalyst sample was placed in a FT-IR spectrometer, Nicolet model Impact 6700. Infrared spectra were recorded between 700 and 1200 cm^{-1} on a microcomputer. The samples were characterized in a diffuse reflectance mode.

3.2.6 Electron spin resonance (ESR)

Chromium status in catalyst framework was examined by electron spin resonance (ESR). A tube containing 0.12 gram of the catalyst sample was placed in an ESR spectrometer using JEOSL, model JES – RE2X. X band with 8.8-9.6 GHz were used as microwave unit, and spectra were recorded between 300 and 350 mT on a microcomputer at Science and Technological Research Equipment Centre, Chulalongkorn university.

3.2.7 Temperature programmed desorption (TPD)

Acid site of the catalysts was analyzed by ammonia temperature programmed desorption (TPD) technique (Micromeritrics Chemisorb 2750). Helium gas with flow rate at 15 ml/min was released to flow through the sample. The sample was heated from room temperature to 550 °C with a heating rate of 10 °C/min and hold for 1 hour. Then, the sample was cooled down to 80 °C and hold for another hour. In the next step, 15 vol% ammonium gas with flow rate of 15 ml/min was flowed through the sample instead of helium, and hold for 15 minutes. Adsorption of 15 vol% ammonium on the catalyst surface occured in this step. Consequently, helium gas at the same flow rate flowed through our sample instead of ammonium and also hold for another hour. In the final step which was the desorption step, the sample was heated from 80 °C to 550 °C with a heating rate of 10 °C/min. The signal from this step was recorded every 0.1 seconds and reported on a microcomputer.

3.3 The catalytic activity measurements

3.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 3.1. 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 argon and air, each equipped with pressure regulators (0-120 psig), mass flow and needle valves 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 a 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 3.6.

Table 3.6 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	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
Detector current	80 mA	-
Analyzed gas	CO, CO_2, H_2O	Oxygenates

3.3.2 Reaction conditions

Catalysts : Cr(III)-TS-1-A1, Cr(III)-TS-1-A1A2,
Cr(III)-TS-1-A2, Cr(III)-TS-1-B1,
Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1,
Cr(VI)-TS-1-A1A2, Cr(VI)-TS-1-B1,
Cr(VI)-TS-1-C1
Reactant : 2- Propanol
Feed composition : 2- Propanol 5 vol%
: O_2 8 vol%
: Argon balance
Flow rate of reactant : 100 ml/min
Reaction temperature : 100-500 °C
Pressure : 1 atm

3.3.3 Criteria for test reaction selection

Performance (e.g. Activity, selectivity) of a catalyst can be evaluated by subjecting the suitable test reaction. The criteria for selecting a proper test reaction is discussed below.

1. The homogenous reactions of the reactants should be kept as minimum as possible in order to prevent the interference of the undesired reaction on result interpretation.

2. The reactant should not too inert to cause the tested catalysts behave like an inactive catalyst.

3. The reactant should not extremely reactive in order that the results of performance comparison between different catalysts will be clear.

4. To help in tracing the reaction pathway, the reactant should have only one active functional group and selected reaction should not produce many intermediate agents in the system.

5. The reactant should not cause catalyst deactivation such as poising and coking.

In practice, the reaction corresponding to all the listed criteria above may not available.

For criteria about functional group and reactivity, alcohol is therefore one of the best choice to use as reactant in our study. Alcohol is an organic chemical containing –OH group as its functional group. In addition, alcohol is also reactive for gas phase oxidation which is used as test reaction in this study.

3.3.4 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of the catalyst sample was packed between quartz wools 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 and argon were 62 ml/min, and flow rate of air was 38 ml/min. 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, acetic acid and CO_2 by calibration curves in Appendix D.

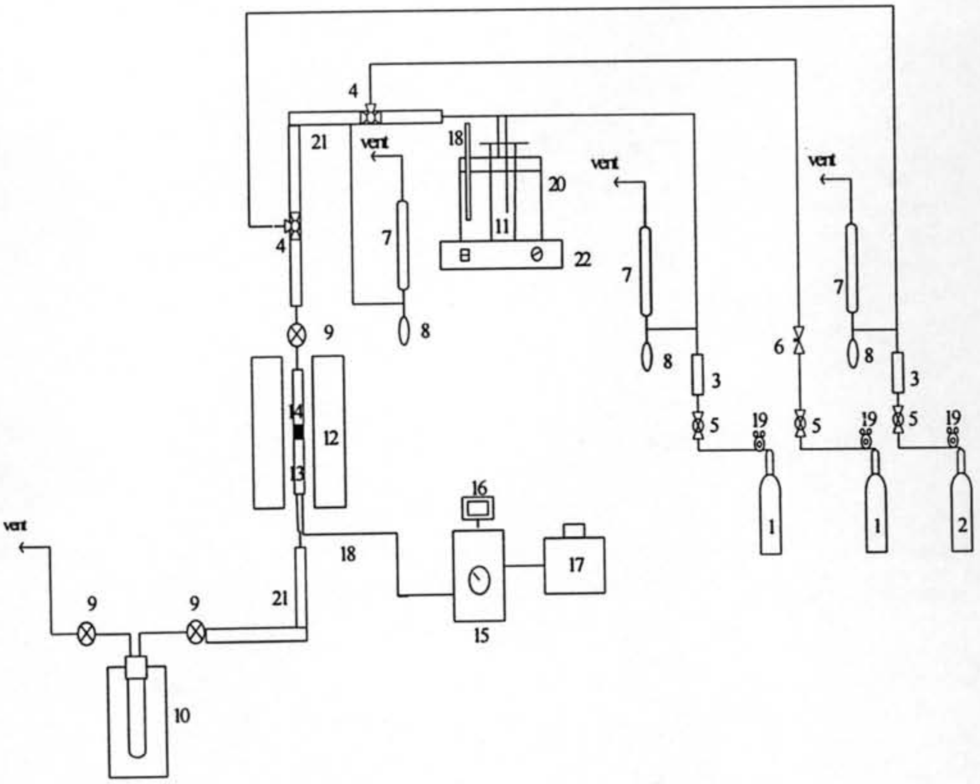
4. The result of catalytic test was calculated in the term of

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

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

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

Where, A is reactant
B is product



1. Ar vessel
2. Air vessel
3. Mass Flow controller
4. Three-way-valve
5. Ball 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 cable
22. Heating and Stirring controller

Figure 3.1 Flow diagram of oxidation reaction system