

## CHAPTER III EXPERIMENTS

### 3.1 Instruments and apparatus

#### 3.1.1 Oven and furnace

Crystallization of sulfonic functionalized cubic *1a-3d* mesoporous silica (denoted as MCA) and SBA-15 during the synthesis was carried out at a temperature of 100°C for 48 hr. in static condition using UM-500 oven as heater. The calcination was performed on a Carbolite RHF 1600 muffle furnace in air. The organic template and moisture were removed from catalytic channels by calcination for SBA-15. The temperature program used for the calcination of SBA-15 was showed in Figure 3.1.

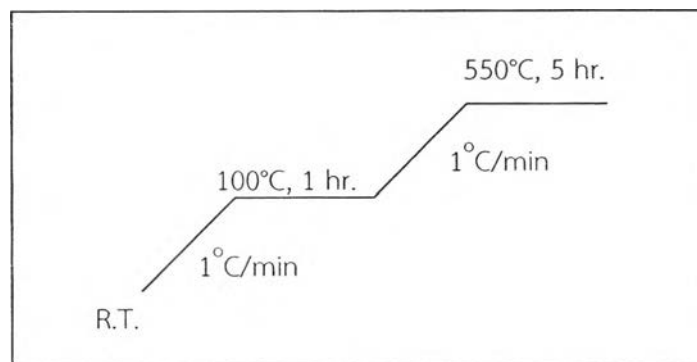


Figure 3.1 The temperature program for the calcination of SBA-15.

#### 3.1.2 X-ray powder diffractometer (XRD)

The XRD patterns and d-spacing of synthesized mesoporous materials (MCA and SBA-15) were determined by a Rigaku D/MAX-2200 Ultima+ X-ray diffractometer equipped with a monochromator and Cu target X-ray tube (40 kV, 30mA) at 2-theta angle between 0.7 to 3.00 degree with a scan speed of 1.00 degree/min and sampling width of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.05 mm, 0.5 degree, and 0.15 mm, respectively. The measured diffractograms were analyzed using MDI software (Jade 6.5).

### 3.1.3 Surface area analyzer

N<sub>2</sub> adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts were carried out using a BEL Japan, BELSORP-mini instrument. The sample weights were nearly 40.0 mg and weighted exactly after pretreatment at 120°C for 4 hr. Glass rods were placed at sample cell and blank cell positions after that the samples were analyzed with BEL-sorp-mini instrument.

### 3.1.4 Scanning electron microscope (SEM)

The morphology and particle sizes of the catalysts were observed using a JEOL JSM-6480 LV scanning electron microscope. All samples were grinded by mortar, which built from agate, and were coated with sputtering gold under vacuum on carbon tape on sample holder because it was less conductivity.

### 3.1.5 Gas chromatograph (GC)

Reaction mixtures from esterification of glycerol mono-, di-, triglycerides were analyzed using a Varian CP 3800 gas chromatograph equipped with a 30 m length, 0.25 mm inner diameter CP-Sil 8 capillary column (equivalent to BP-5 column). Long carbon chain length acids were analyzed by metal column with a 10 m length, 0.32 mm inner diameter. The detector was a flame ionization detector (FID). The reaction mixture weights were 0.05xx-0.10xx g derivatized with (trimethylsilyl)-trifluoroacetamide (MSTFA) 200 µL shook for a minute and waited for 30 minutes. Tetrahydrofuran (THF) was used as solvent for acetic acid reaction but the other was pyridine. Internal standard was dodecane using for calibration of glycerol and triglyceride. The preparation sample injection was shown in **scheme 3.1**. The column oven-heating program was illustrated in **Figure 3.2** for acetic acid and **Figure 3.3** for long hydrocarbon chain acid.

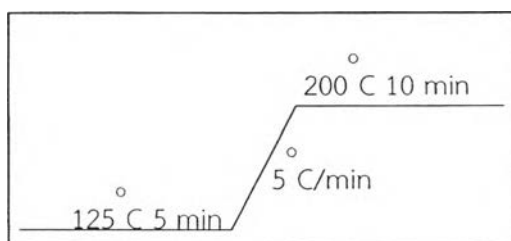


Figure 3.2 The GC heating condition for short fatty acid analysis [15].

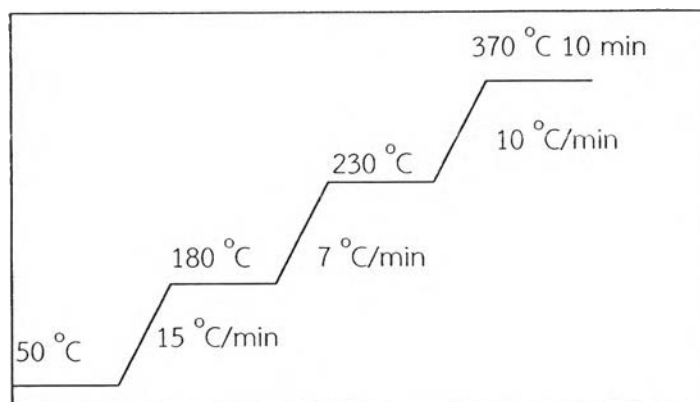
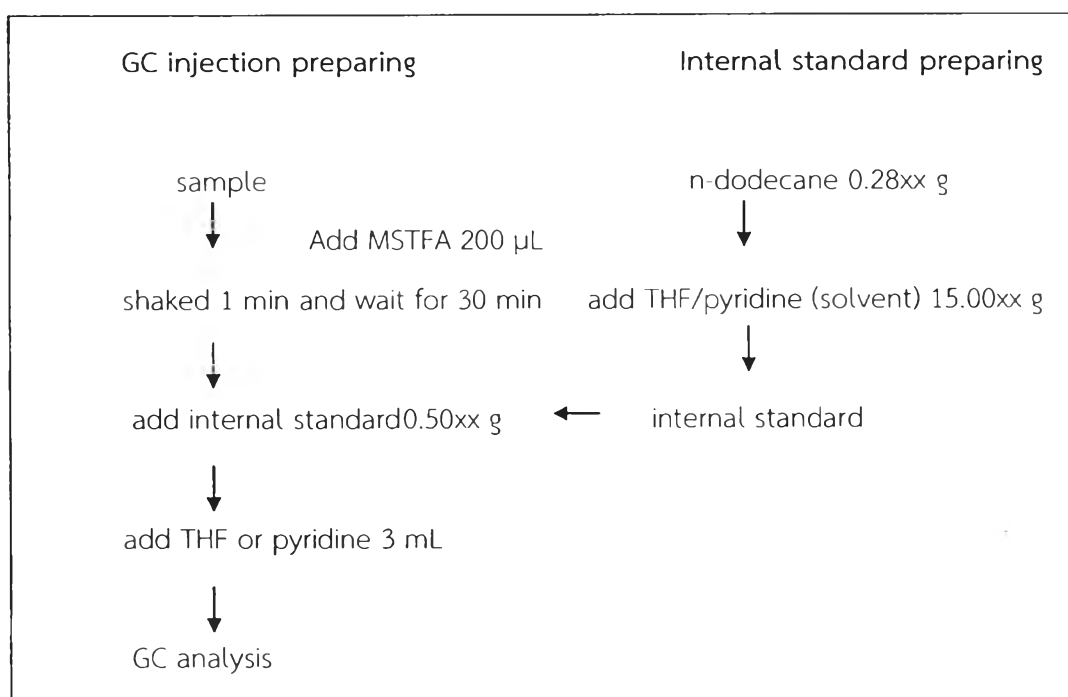


Figure 3.3 The GC heating condition for long fatty acid analysis [54].



Scheme 3.1 Preparation diagram for GC analysis.

### 3.1.6 Ammonia temperature-program desorption (NH<sub>3</sub>-TPD)

Acid strength of catalyst was determined using the BEL-CAT Japan instrument. The pure materials were weighted nearly 80 mg and pretreatment at 400 °C for 20 min. The functionalized materials were pretreatment at 150 °C for 3 hr. before each measurement.

## 3.2 Chemicals

### 3.2.1 Chemicals for synthesis catalysts

1. Triblock copolymer pluronic P123 (PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>, average molecular weight = 5800) (Aldrich)
2. Tetraethyl orthosilicate, TEOS (Fluka, 98 %)
3. Hydrochloric acid, HCl (Fluka, 37 %)
4. (3-Mercaptopropyl)trimethoxysilane, MPTMS (Aldrich, 95 %)
5. Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (Merck, 30 %)
7. Toluene, C<sub>7</sub>H<sub>8</sub> (CARLO ERBA, 99.5%)
8. Sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (Merck, 95-97%)
9. Deionized Water

### 3.2.2 Chemicals for esterification

1. Glycerol, C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>
2. Acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>
3. Caproic acid, C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>
4. Lauric acid, C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>
5. Oleic acid, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>

### 3.2.3 Chemicals for reaction mixture analysis

1. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, C<sub>6</sub>H<sub>12</sub>F<sub>3</sub>NOSi (Derivatization grade, Sigma Aldrich)
2. n-Dodecane
3. Glyceryl trihexanoate
4. 1-monolaurin, C<sub>15</sub>H<sub>30</sub>O<sub>4</sub>
5. Trilaurin, C<sub>39</sub>H<sub>74</sub>O<sub>6</sub>
6. 1-monoolein, C<sub>21</sub>H<sub>40</sub>O<sub>4</sub>
7. 1,3-diolein, C<sub>39</sub>H<sub>72</sub>O<sub>5</sub>
8. Triolein, C<sub>57</sub>H<sub>105</sub>O<sub>6</sub>



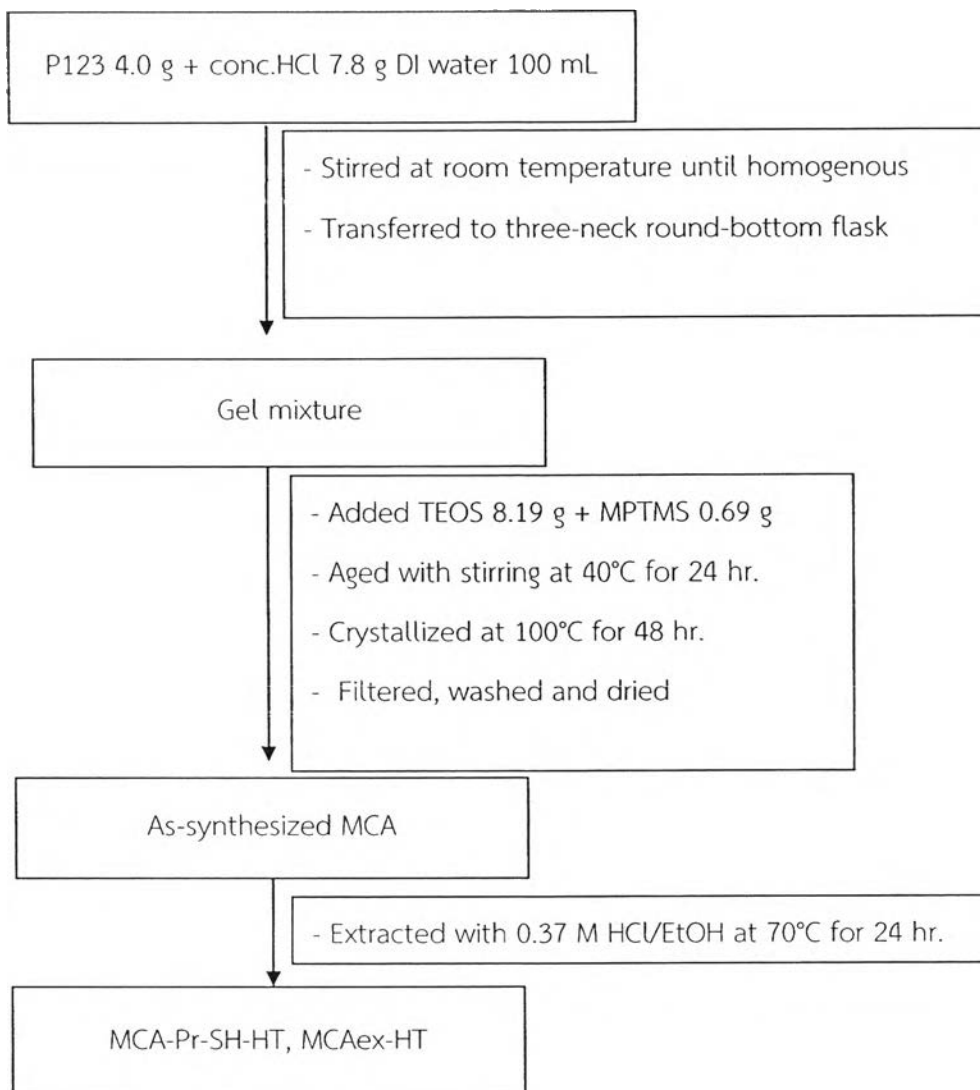
9. Pyridine, C<sub>5</sub>H<sub>5</sub>N
10. Tetrahydrofuran, C<sub>4</sub>H<sub>8</sub>O
11. Octane

### 3.3 Synthesis of cubic *1a-3d* mesoporous silica (MCA)

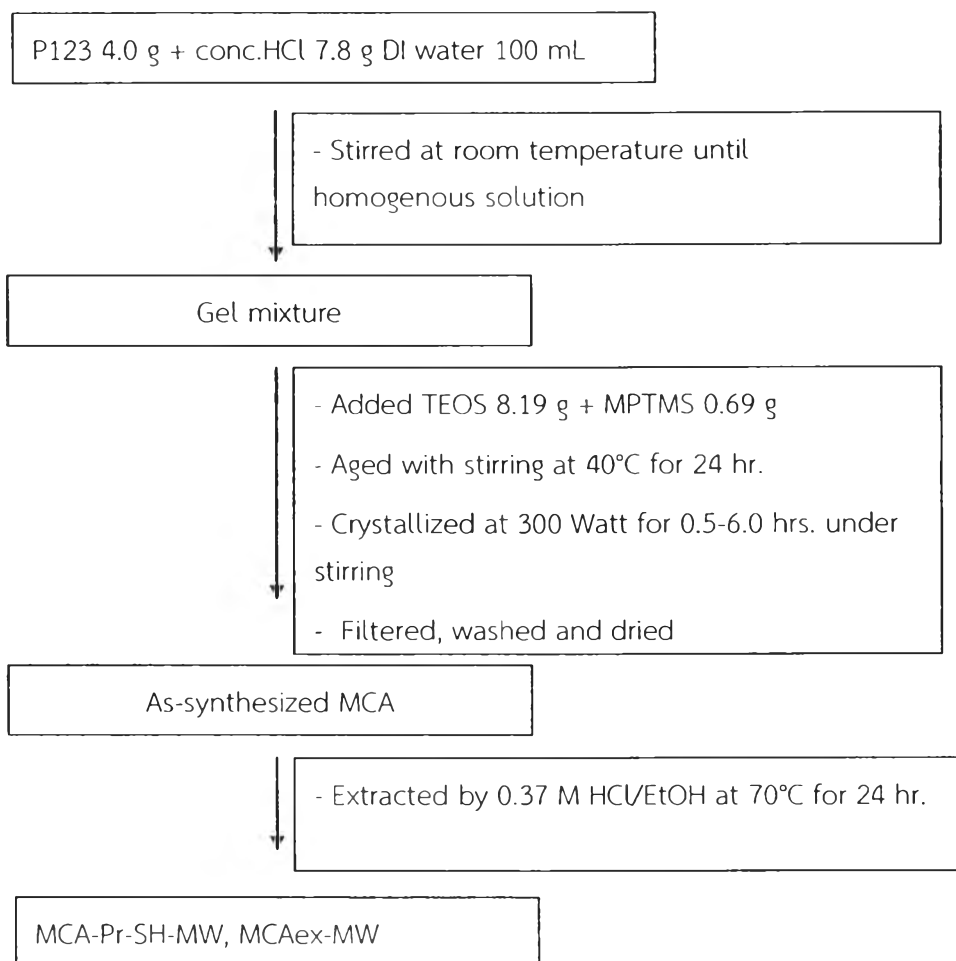
#### 3.3.1 Synthesis MCA by hydrothermal and microwave methods

MCA was synthesized using gel mole composition of 1.0 TEOS: 0.089 MPTMS: 0.018 P123: 2.0 HCl: 148 H<sub>2</sub>O reported by Xing *et al.* [10]. In a typical procedure, 4.0 g of triblock copolymer Pluronic P123 template was dissolved in 7.8 g of conc. HCl and 100 mL of DI water at room temperature under stirring. Subsequently, Transferred the solution to three-neck round-bottom flask and mixtures of TEOS (8.19 g) and MPTMS (0.69 g), were added dropwise and stirred at 40°C for 24 hr. with stirring rate 250 rounds/min. The resulting gel was transferred to a Teflon-lined autoclave for hydrothermal crystallization at 100°C for 48 hr. As-synthesized MCA was separated by filtration, washed with a little deionized water and dried overnight. The template was removed by extracted with 0.37 M HCl/EtOH at 70°C for 24 hr. The extracted sample is denoted as MCAex-HT and the procedure for synthesizing the MCAex-HT was illustrated in Scheme 2.2. For microwave method, the hydrothermal crystallization time was reduced from 2 days to 0.5, 1.0, 2.0, 3.0 and 6.0 hr. at 300 Watt under stirring with mechanical stirrer. The sample is demoted as MCAex-MW<sub>x</sub> where *x* is aging time in hour for microwave method illustrated in Scheme 3.2.





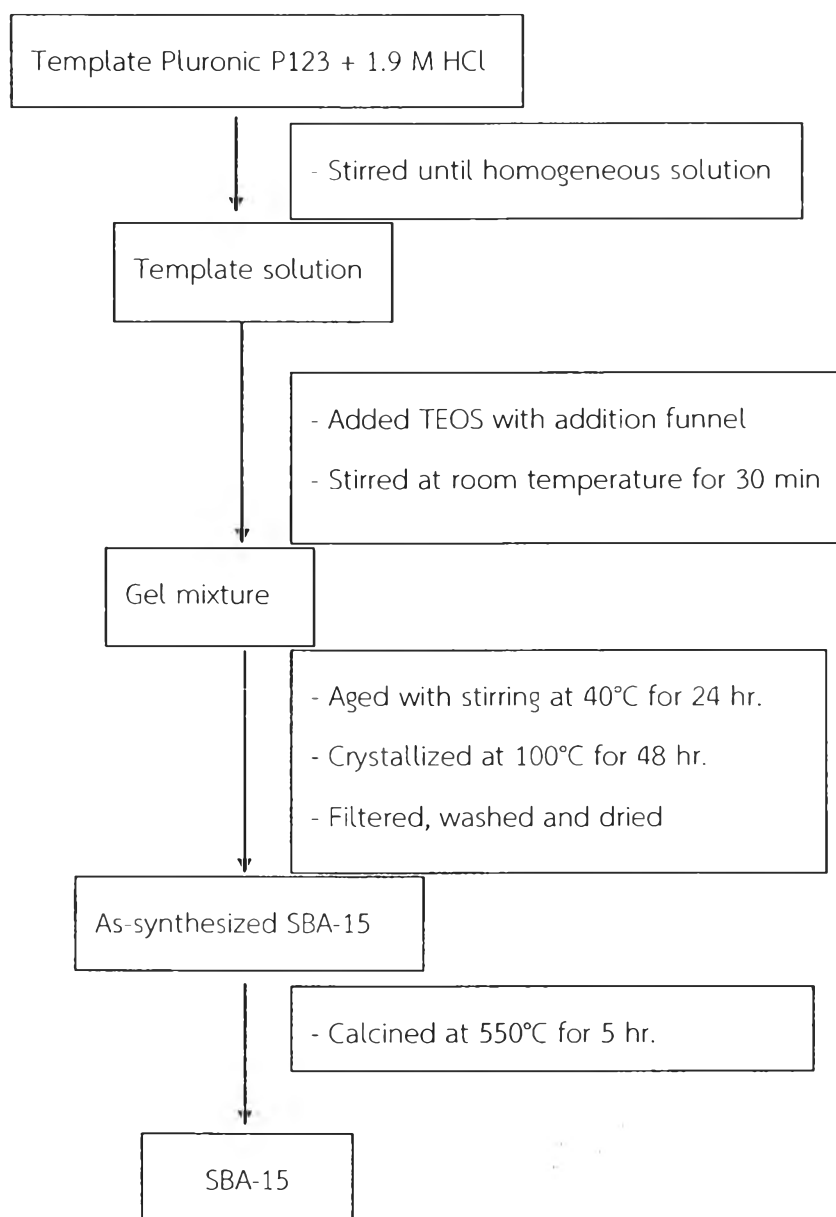
Scheme 3.2 Preparation diagram for MCA by hydrothermal method.



Scheme 3.3 Preparation diagram for MCA by microwave method.

### 3.3.2 Post Synthesis SBA-15 by hydrothermal method

SBA-15 was synthesized using gel mole composition of 1.0 TEOS: 0.0165 P123: 6.95 HCl: 140 H<sub>2</sub>O reported by Zhao *et al.* [32]. In a typical procedure, triblock copolymer Pluronic P123 as template was dissolved in 1.9 M HCl solution at room temperature under stirring. Subsequently, TEOS was added dropwise and stirred for 30 min. Then, it was aged at 40°C for 24 hr. with stirring. The resulting gel was transferred to a Teflon-lined autoclave for hydrothermal crystallization at 100°C for 48 hr. As-synthesized SBA-15 was separated by filtration, washed with deionized water for several times, and dried overnight. The template was removed by calcination at 550°C for 5 hr. The procedure for synthesizing the SBA-15 was illustrated in Scheme 3.4.



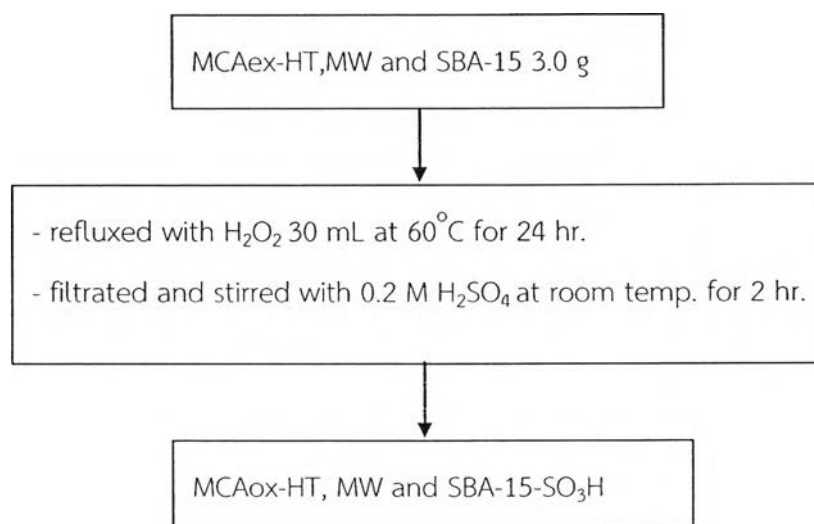
Scheme 3.4 Preparation diagram for SBA-15 by hydrothermal method.

### 3.4 Sulfonic functionalized mesoporous materials

Three grams of calcined SBA-15 mesoporous materials was suspended with 3-mercaptopropyl-tri-methoxysilane (MPTMS), for propyl sulfonic group, 5.301 g and toluene 50 mL, refluxed at 60°C for 6 hr. (SBA-15-Pr-SH). Then the material with thiol groups, MCAex and SBA-15-Pr-SH, were oxidized to sulfonic groups by refluxed at



60°C with H<sub>2</sub>O<sub>2</sub> 30 mL. The wet material was suspended in 0.2 M H<sub>2</sub>SO<sub>4</sub> 50 mL for 2 hr. at room temperature[55]. Finally, the obtained product was filtered and dried in oven for overnight at 60°C. The oxidized samples were denoted MCAox and SBA-Pr-SH. The procedure for synthesizing the oxidized catalyst was illustrated in Scheme 3.5.

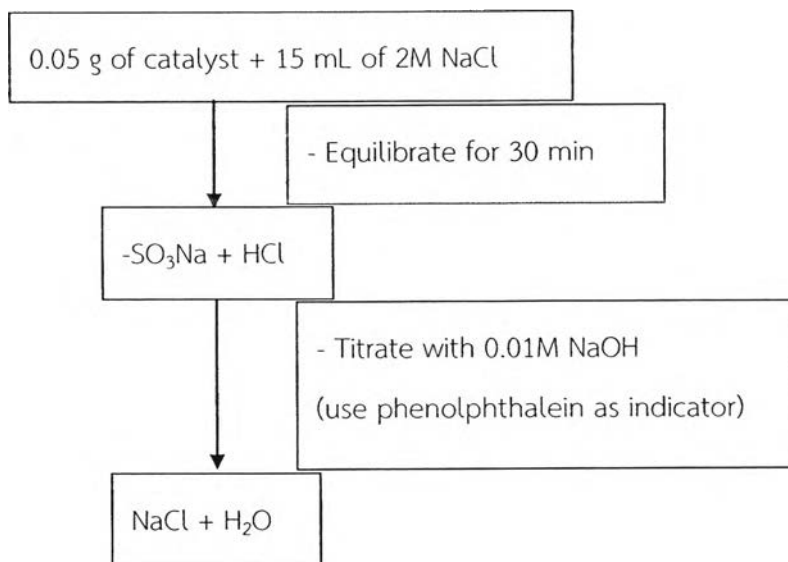


Scheme 3.5 Preparation diagram for oxidized materials.

### 3.5 Acid-base titration

The acid capacities of sulfonic acid groups in the functionalized mesoporous materials were quantified using 2.0 M NaCl solution as the ion-exchange agent (Scheme 3.6). Approximately 0.05xx g of the catalysts was exchanged with 15 ml of NaCl solution for 30 min under constant agitation at room temperature and titration with 0.01 M NaOH by using phenolphthalein as indicator [56].





Scheme 3.6 Diagram for acid-base titration.

### 3.6 Parameters affecting catalytic preparation

#### 3.6.1 Effect of aging time

The reaction was varied in the range 24-48 hr.

#### 3.6.2 Effect of aging temperature

The aging temperature was varied to 40, 60, and 80°C.

#### 3.6.3 Effect of sequence of input material by direct synthesis

1. Add mixture of TEOS and MPTMS
2. Add TEOS prior to MPTMS 15 min.
3. Add TEOS prior to MPTMS 30 min.
4. Add TEOS prior to MPTMS 60 min.
5. Add TEOS prior to MPTMS 120 min.
6. Add MPTMS prior to TEOS 15 min.
7. Add MPTMS prior to TEOS 30 min.



### 3.6.4 Effect of MPTMS and TEOS amount (mol)

The mol ratio of silica sources, TEOS and MPTMS, was varied which the amount of silicon source was 1.089 mol, TEOS = 1.089-X MPTMS = X ( $X = 0.045$ -0.179 mol). Both silica sources were mixed and added into surfactant.

### 3.7 Procedure in esterification of glycerol

Esterification of glycerol with acetic acid was carried out in a round-bottomed flask fitted with a reflux condenser. In each experiment total reaction mixture was 30 g, glycerol, acetic acid and catalyst were added to a round-bottomed flask. Then, the reaction mixture was heated to the desired reaction temperature and kept constant for a period of time. After completion of the reaction, the reaction mixture was cooled down and then catalyst was filtered. The obtained products were confirmed using GC-MS technique and compared to the authentic samples. Likewise, the reaction mixture was quantitatively analyzed by GC-FID.

### 3.8 Parameters affecting esterification of glycerol

#### 3.8.1 Effect of reaction time

The reaction time was varied in range 0.5-4.0 hr.

#### 3.8.2 Effect of temperature

The reaction temperature was varied to 95, 105, 110 and 115°C.

#### 3.8.3 Effect of catalytic amount

The amount of catalyst was varied from 0, 2, 4, 6, and 8 %wt. based on amount of total reaction mixture.

#### 3.8.4 Effect of glycerol to carboxylic acid molar ratio

The mole ratio of glycerol to carboxylic acid was varied in range 1:3, 6, 9, 12...21 and 24.



### 3.8.5 Effect of various catalysts

Catalytic activities of sulfonic functionalized MCA, synthesized by hydrothermal and microwave method, and SBA-15 materials were compared with FSM-16-Pr-SO<sub>3</sub>H and commercial catalysts such as H-ZSM-5, H-beta, Nafion SAC-13, Amberlyst-131, Acidic Clay, MCM-22 and Amberlyst-15.

### 3.8.6 Effect of reused catalyst

After the reaction, the catalyst was separated by filtration and washed with acetone and then reused after drying at 60°C overnight.

### 3.8.7 Effect of chain length of carboxylic acid

Esterification of glycerol with various carboxylic acid chain length e.g. caproic acid (C<sub>6</sub>), lauric acid (C<sub>12</sub>) and oleic acid (C<sub>18</sub>) was carried. .

