CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals (analytical grade) used were obtained as follows:

Table 3.1 Chemical reagent and suppliers

Chemicals	**Suppliers**
Acetic acid	Merck
Acetonitrile	Merck
Ammonia	Merck
Cetyltrimetyllammonium bromide	Fluka Chemies A.G., Switzerland
Cobalt(II) nitrate hexahydrate	Aldrich Chemical Company, Inc., USA
Copper(II) nitrate dihydrate	Aldrich Chemical Company, Inc., USA
Cyclohexane	Fluka Chemies A.G., Switzerland
Cyclohexanol	Fluka Chemies A.G., Switzerland
Cyclohexanone	Fluka Chemies A.G., Switzerland
Di-sodium hydrogen phosphate dihydrate	Fluka Chemies A.G., Switzerland
30% Hydrogen peroxide in water	Merck
Iron(III) nitrate nonahydrate	Aldrich Chemical Company, Inc., USA
Sodium hydrogen carbonate	Aldrich Chemical Company, Inc., USA
Sodium sulfate anhydrous	Merck
Sulfuric acid	Fluka Chemies A.G., Switzerland
Tetrabutylammonium bromide	Fluka Chemies A.G., Switzerland
Tetraethyl orthosilicate	Fluka Chemies A.G., Switzerland

3.2 Equipments

- Pressure reactor (stainless steel, size 50 ml)
- Heater and stirrer
- Magnetic stirrer

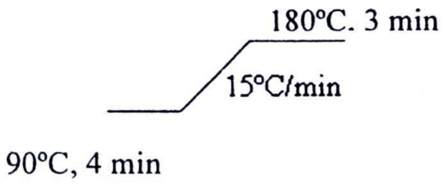
3.3 Analytical measurements

3.3.1 Gas chromatography (GC)

A Varian CP-3800 GC equipped with a flame ionization detector (GC-FID) and CP-Sil (30 m x 0.25 mm) column. The products were analyzed by gas chromatography using internal standard. The GC condition was set as follows:

Column : CP-Sil
Detector : Flame ionization (FID)
Detector temperature : 250°C
Injector temperature : 220°C
Carrier gas : Nitrogen
Pressure : 70 kPa.

Programmed temperature:



3.3.2 X-ray diffraction spectrometer (XRD)

The XRD pattern of catalysts were obtained on Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer equipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA) and angles of 2θ ranged from 2-60 degree at Department of Chemistry, Faculty of Science, Chulalongkorn University.

3.3.3 Nitrogen adsorption (Brunauer-Emmett-Teller method (BET))

BET specific surface area of the catalysts was carried out using a BELSORP-mini. The principle of this method is by adsorption of a particular molecular species from a gas or liquid onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample. The pore size distributions were obtained according to the Barret–Joyner–Halenda (BJH) method from the adsorption branch data.

3.3.4 Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to 4,000 cm^{-1} in transmittance mode.

3.3.5 X-ray fluorescence spectrometry (XRF)

Elemental analysis of MCM-41 included samples was performed by means of X-ray fluorescence spectrometer ARL 8410.

3.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric measurement were performed by using Pyris 1 Thermal gravimetric analyzer. The sample was heated from 20°C to 1000°C with a heating rate of 20°C/min under nitrogen atmosphere. The percentage weight loss at different temperatures was shown in a thermogram.

3.4 Syntheses of catalysts

3.4.1 Tetrabutyl ammonium salts of tungstophosphate
$[(n\text{-}C_4H_9)_4N]_4H_X[PW_{12}M^{X+}(H_2O)O_{39}]$ where M= Co,Fe and Cu [28]

Na_2HPO_4 0.27g (1.52 mmol), $Na_2WO_4{\cdot}2H_2O$ 5.5g (16.67 mmol) were mixed, after that nitrate salt of metal $Co(NO_3)_2{\cdot}6H_2O$ 0.58 g (2 mmol) or $Fe(NO_3)_3{\cdot}9H_2O$ 0.81 g (2 mmol) or $Cu(NO_3)_2{\cdot}2H_2O$ in 30 ml of water and the pH was adjusted to 5 by HNO_3. An aqueous solution (3 ml) of $[(n\text{-}C_4H_9)_4N]Br$ 2.4g (7.5 mmol) was added dropwise, with stirring at 80°C. The precipitated salts were filtered off, washed with water and dried in vacuum at 50°C. The compounds were recrystallized from acetonitrile. The $Co(NO_3)_2 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 2H_2O$ are pink, light yellow and light blue crystals respectively.

3.5 Synthesis of MCM-41 [29]

A composition of SiO_2:CTABr:NH_4OH:H_2O 1.0:0.12:8:114 or 26 ml: 5 g: 57 ml: 235 g. was used. ammonia and CTABr were dissolved in deionized water under electromagnetic stir until homogeneous. TEOS was then added dropwise into the solution. After 2 h stir, a gel was obtained. The gel was transferred into a Teflon bottle that was then heated at 383 K for 96 h. The solid product was recovered by filtration, washed with deionized water until the filtrate was neutral, and finally dried. The removal of template was performed by extracting the as-synthesized product in a refluxing mixed solution of methanol and hydrogen chloride acid. The final product was obtained by centrifugal filtration, washed with ethanol and water, and finally dried.

3.6 Methods of loading POM on MCM-41 support

A. Incipient wetness impregnation [30]

POM was dissolved in CH_3CN 4 ml. This solution was dropped on 1 g MCM-41, containing the desired amount of POM: 5,10, 20, 30 and 40 wt.% based on MCM-41. The supported catalysts were dried to remove solvent at 80°C. These catalysts were designated as X%POM/MCM-41 where X was % of POM loading based on weight of MCM-41.

B. Wetness impregnation [31]

POM 0.2 g was dissolved in 10ml CH_3CN and 1 g MCM-41 was dispersed in this solution, the mixture was stirred overnight. The residue was filtered and washed with CH_3CN in order to remove POM adsorbed on the external surface.

3.7 Direct synthesis [32]

This supported catalyst was prepared as follows: hexadecyltrimethylammonium bromide (surfactant), deionized water, hydrochloric acid and tungstophosphoric acid were mixed at 50 °C and stirred for 30 min. TEOS was added to the above mixture with vigorous stirring to obtain a gel mixture. The molar composition of the gel was 0.0137 CTAB/0.0415 TEOS/0.31 HCl/2.8 H_2O/ 0.00035 HPW. After the mixture was stirred for 24 h at 50 °C, the resultant product was filtered and washed with deionized water, dried at 100 °C for 3 h, and then calcined in air at 550 °C for 6 h.

3.8 Oxidation of cyclohexane

The oxidation of cyclohexane was carried out in a 50 ml Parr reactor using 10 ml (92 mmol) cyclohexane, catalyst 5.1wt%, 30 ml (276 mmol) of oxidizing agent H_2O_2 under solvent free condition at different temperatures (70–100°C), with stir rate of 100 rpm. After a desired time, the reaction mixture was cooled to room temperature. The catalyst was separated by filtration. The liquid mixture was added with 25% H_2SO_4, saturated $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. The oxygenated products in a liquid mixture were quantitatively analyzed by gas chromatography using the cyclooctane as internal standard method.

To determine %products, GC technique was used to detect products from the oxidation of cyclohexane: cyclohexanone, cyclohexanol. The peak area of both were calculated and converted to mole, then to percentage based on initial amount of cyclohexane. The sum of both products led to %yield.

%yield = %cyclohexanol + %cyclohexanone

3.9 Consumption of hydrogen peroxide

At the end of the reaction the organic and aqueous phase were separated. The aqueous phase was pipetted 2 ml to volumetric flask and make volume to 100 ml with deionized water. Pipett 25 ml of this solution to erlenmeyer flask and H_2SO_4

2M 2 ml was added. The aqueous solution of 0.01 M $KMnO_4$ was prepared by dissolving 1.58 g in 100 ml water in a volumetric flask. The consumption of hydrogen peroxide was calculated from equation below (1). At the end point of titration the color of solution was changed from clear to brown solution.

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5\ O_2 + 8H_2O \quad (1)$$

3.10 Determination of cyclohexyl hydroperoxide (CyOOH) [33]

The total concentration of cyclohexyl hydroperoxide in reaction was determined by adding excess PPh_3 into the product mixture. The increase of cyclohexanol in reaction after adding PPh_3 is resulted from cyclohexyl hydroperoxide which was reduced with triphenylphosphine as equation below.

$$PPh_3 + RO_2H \longrightarrow OPPh_3 + ROH$$

The CyOOH present in the final reaction solution is then deoxygenated by PPh_3 to give CyOH (with formation of phosphine oxide), thus eliminating the CyOOH decomposition to CyOH the overall GC detected amounts of cyclohexanol comprise those derived from CyOOH during the reaction and those formed upon decomposition, at the GC operating conditions, of the remaining CyOOH in the final reaction solution.. It was shown the hydroperoxide CyOOH still present in reaction solution.

3.11 Titration of acid in cyclohexane oxidation

The acid in aqueous phase was titrated with 0.01 M NaOH using phynolpthalien as an indicator. At the end point of titration the color of solution was changed from clear to pink.

Various effects in the oxidation reaction of cyclohexane were investigated as follows:

A. Effect of loading

%Loading of POM was varied: 5wt%, 10wt%, 20wt%, 30wt% and 40wt% based on MCM-41.

B. Amounts of catalyst

Amount of supported catalysts was varied: 2.5wt%, 3.8wt%, 5.1wt%, 6.4wt%, 7.7wt% and 10.3wt%. base on cyclohexane.

C. Amounts of H_2O_2

Molar ratio of H_2O_2/cyclohexane was varied: 1, 2, 3 and 4.

D. Effect of O_2 pressure

The O_2 pressure was varied: 1, 3 and 5 atm.

E. Effect of H_2O_2 and O_2 pressure

Molar ratio of H_2O_2/cyclohexane used in reaction was 3 and amount of O_2 was varied: 1, 3 and 5 atm.

F. Effect of temperature

The temperature of reaction was varied: 70, 80 and 100 °C.

G. Effect of reaction time

Effect of reaction time was investigated: 4, 6, 8 and 16.

H. Effect of type and amount of initiator

Different types of initiator were used : cyclopentanone, acetone and methyl ethyl ketone.

3.12 Test of POM leaching

0.4 g of the supported catalyst was suspended in cyclohexane. A 30%H_2O_2 30 ml (294 mmol) was added. The mixture was stirred at 80°C for 8 h. Then the mixture was filtered. The solid was then analyzed to determine leaching amount of POM from the support by X-ray fluorescence (XRF).

3.13 Reusability of POM supported MCM-41 catalysts

After being used in the reaction, the catalyst was removed from the reaction mixture by filtration, washed with diethyl ether and dried at 100°C overnight. Then it was reused for oxidation by adding fresh cyclohexane and 30%H_2O_2 at 80°C for 8 h.