


ออกฤทธิ์ของไซโคลเฮกเซนเร่งปฏิกิริยาด้วยพอลิออกไซเมทาเลตบนตัวรองรับเอ็มซีเอ็ม-41



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OXIDATION OF CYCLOHEXANE CATALYZED BY POLYOXOMETALATES SUPPORTED ON MCM-41



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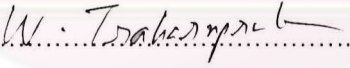
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ได้สังเคราะห์และพิสูจน์เอกลักษณ์ตัวเร่งปฏิกิริยาพอลิออกซิเมทาเลตและได้บรรจุตัวเร่งปฏิกิริยาบนตัวรองรับเอ็มซีเอ็ม-41โดยใช้วิธีการบรรจุที่แตกต่างกัน ได้แก่ วิธีการ incipient wetness impregnation (10% 20% 30% และ 40% เทียบกับน้ำหนักของเอ็มซีเอ็ม-41) และวิธีการ impregnation (11% เทียบกับน้ำหนักของเอ็มซีเอ็ม-41) ได้พิสูจน์เอกลักษณ์ตัวเร่งปฏิกิริยาที่บรรจุอยู่บนวัสดุรองรับด้วยเทคนิคหลายอย่าง ได้แก่ XRD, XRF, FT-IR, N₂-adsorption และ TGA หลังจากนั้นใช้ศึกษาหาความสามารถในการเร่งปฏิกิริยาออกซิเดชันของไซโคลเฮกเซนโดยใช้ไฮโดรเจนเปอร์ออกไซด์ 30% ในน้ำหรือแก๊สออกซิเจนเป็นสารออกซิไดซ์ ผลิตภัณฑ์หลักจากปฏิกิริยาออกซิเดชันที่ได้จากการวิเคราะห์ด้วยเทคนิค GC คือ ไซโคลเฮกซานอลและไซโคลเฮกซาโนนศึกษาตัวแปรต่างๆที่มีผลต่อปฏิกิริยาออกซิเดชัน พบว่าการทำปฏิกิริยาที่เหมาะสมคือทำปฏิกิริยาที่อุณหภูมิ 80 องศาเซลเซียสเป็นเวลา 8 ชั่วโมงโดยใช้ ไฮโดรเจนเปอร์ออกไซด์ 30% ในน้ำเป็นสารออกซิไดซ์ โดยที่ปริมาณการเติมที่เหมาะสมคือ สัดส่วนโดยโมลของไฮโดรเจนเปอร์ออกไซด์ต่อไซโคลเฮกเซนเท่ากับ 3 ผลการทดลองแสดงว่า 20wt%CoPOM/MCM-41 เป็น ตัวเร่งปฏิกิริยามีประสิทธิภาพสูงสุด ผ่านกลไกของปฏิกิริยาออกซิเดชันไซโคลเฮกเซนด้วยไฮโดรเจนเปอร์ออกไซด์เกิดผ่านอนุมูลอิสระ นอกจากนี้ตัวเร่งปฏิกิริยาสามารถนำกลับมาใช้ใหม่ได้ถึง 3 ครั้งโดยที่ความสามารถในการเร่งปฏิกิริยาลดลงเพียงเล็กน้อย

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อ... จิรวโรจน์ จากพิศาลพงศ์

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Polyoxometalates (POMs) were synthesized and characterized. The POMs were then supported on MCM-41 using different loading methods: incipient wetness impregnation method (10% 20% 30% and 40% based on weight of MCM-41) and impregnation method (11% based on weight of MCM-41). The supported catalysts were characterized by several techniques: XRD, XRF, FT-IR N_2 -adsorption and TGA. They were used as a catalyst for cyclohexane oxidation with 30% aqueous hydrogen peroxide or oxygen as oxidant. The oxidation products detected by GC were mainly cyclohexanol and cyclohexanone. Parameters affecting the oxidation reaction were studied. The optimum condition found was at 80°C, 8 h reaction time and the H_2O_2 /cyclohexane molar ratio of 3. The result showed that the 20wt%CoPOM/MCM-41 was the most active catalyst. The mechanism of the cyclohexane oxidation with H_2O_2 was proposed to occur via radical pathway. In addition, the catalysts can be reused for 3 times with slight drop of activity.

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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LIST OF ABBREVIATIONS

atm	atmosphere
sec	second
min	minute
h	hour (s)
GC	gas chromatography
cm ⁻¹	unit of wavenumber
ml	milliliter (s)
g	gram (s)
°C	degree Celsius
XRD	X-ray diffraction
deg	degree
BET	Brunauer-Emmett-Teller method
FT-IR	Fourier transform infrared spectroscopy
mmol	millimole
Nd	Not determined
XRF	X-ray fluorescence



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CHAPTER I

INTRODUCTION

Selective oxidation reactions using heterogeneous catalysts are of growing importance for modern chemical industry. The oxidation products of cyclohexane, viz., cyclohexanol and cyclohexanone, are important intermediates in the production of adipic acid and caprolactam, which are used in the manufacture of nylon-6 and nylon-6,6 polymers. In addition, they are also used as solvents for lacquers, shellacs, and varnishes as well as stabilizers and homogenizers for soaps and synthetic detergent emulsions. Other uses of cyclohexanone are as starting material in the synthesis of insecticides, herbicides, and pharmaceuticals. In general, both cyclohexanol and cyclohexanone are produced on an industrial scale by the oxidation of cyclohexane. In the early 1940s, Du Pont developed a process in which cyclohexane was oxidized in the presence of air to cyclohexanol and cyclohexanone using cobalt naphthenate or cobalt acetate as catalyst. In this process, several by-products, viz., mono- and dicarboxylic acids, esters, aldehydes, ketones, and other oxygenated materials, were generated. Later, in the 1950s, Scientific Design (now Halcon International) developed a new process where anhydrous meta-boric acid was added as a slurry in the oxidation vessel. This led to the formation of cyclohexyl ester which is subsequently hydrolyzed to cyclohexanol. In comparison to the former, the latter process showed good yield of cyclohexanol, which, however, requires high investment and a high operating cost to recover and recycle the boric acid.

On the other hand for the laboratory-scale reaction extensive literatures are available on the selective oxidation of cyclohexane using a variety of transition metal compounds in stoichiometric amounts or as homogeneous catalysts. In the cases of the latter, the use of initiators, e.g., cyclohexanone, cyclohexyl peroxide, methyl ethyl ketone, and acetaldehyde reduced the induction period as well as enhances the catalytic activity. However, owing to the limitations of these soluble (homogeneous) catalysts, viz., catalyst separation from the product and the disposal of solid/liquid wastes, which pose serious problems to the environment, in recent years attention has been focused on the development of transition metal-based heterogeneous catalysts

with oxygen or peroxides as nonpolluting oxidants. However in most cases, extreme reaction conditions such as high pressure (2 MPa) and high temperature (450 K) in conjunction with low activity make the process less attractive. In addition, leaching of active metal ions has often been observed under the reaction conditions. Hence, the oxidation of cyclohexane over heterogeneous catalysts under mild/moderate conditions is a topic of great interest.

Transition-metal-substituted polyoxometalates (M-POM for short) have attracted much attention as oxidation catalysts because of their unique ensemble of properties, including metal oxide-like structure, thermal and hydrolytic stability, tunable acidities and redox potentials, and alterable solubilities in various media, etc. It has been established that cobalt compounds, including Co-POM, are among the best catalysts for homogeneous aerobic aldehyde oxidation and cooxidation of alkenes with aldehydes [1]. Tetraalkylammonium salts have been prepared to ensure the solubility in the organic solvents. M-POM have small surface area ($1-5 \text{ m}^2\text{g}^{-1}$) Dispersion M-POM on support, such as silica, alumina, resin, active carbon, clays and microporous zeolites, to enlarge the surface area, which increases the number of acidic sites on the surface and enhances catalytic activity was performed [2]. MCM-41s materials have very large surface area (typically $1000 \text{ m}^2/\text{g}$) and a uniform large pore size (20 \AA), the MCM-41s materials can act as an excellent supports. This is because such mesoporous materials, which have relatively small diffusion hindrance, can aid the easy diffusion of bulky organic molecules in and out of their mesopores [3].

1.1 Objectives of the thesis

To synthesize supported polyoxometalates catalysts containing transition metal Co, Fe and Cu.

To study catalytic activities of the synthesized catalysts in the oxidation reaction of cyclohexane.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Cyclohexane oxidation [4]

The selective oxidation of cyclohexane produces an important KA-oil (a mixture of cyclohexanone and cyclohexanol) intermediate in the petroleum industrial chemistry. Such oil can be used for the production of adipic acid and caprolactam, which are key materials for manufacturing 6,6-nylon and 6-nylon, respectively. Modern industrial methods usually require high pressure and temperature when using soluble cobalt as catalyst, which has led to the realization of high selectivity (about 80%) for the sum of cyclohexanone and cyclohexanol only at a low conversion (1–4 mol%), since the cyclohexanone and cyclohexanol are substantially more reactive than the cyclohexane reactant. Thus, it is difficult to receive high conversion and selectivity simultaneously under mild conditions.

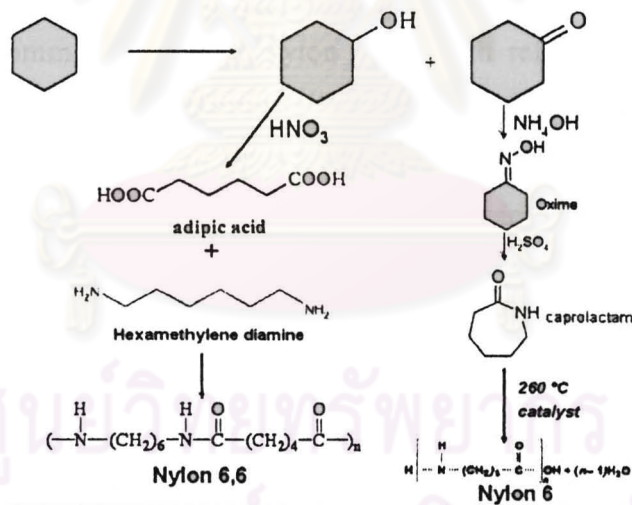


Figure 2.1 Cyclohexane to nylon 6,6 and nylon 6.

2.2 Adipic acid [5]

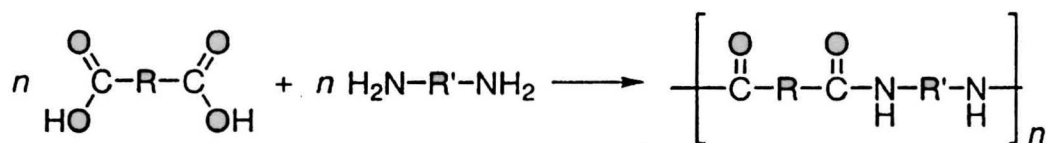
Adipic acid (also called hexanedioic acid) is a white, crystalline compound of C6 straight-chain dicarboxylic acid; slightly soluble in water and soluble in alcohol and acetone. Almost all of the commercial adipic acid is produced from cyclohexane through two sequent oxidation processes. The first oxidation is the reacting of

cyclohexane with oxygen in the presence of cobalt or manganese catalysts at a temperature of 150 - 160 °C, which produce cyclohexanol and cyclohexanone. Then, the intermediates are further reacted with nitric acid and air with a catalyst (copper or vanadium) or without nitric acid. Adipic acid consumption is linked almost 90% to nylon production by the polycondensation with hexamethylenediamine. Adipic acid is also used in manufacturing plasticizers and lubricants components. Its derivatives, acyl halides, anhydrides, esters, amides and nitriles, are used in making target products such as flavoring agents, pesticides, dyes, textile treatment agents, fungicides, and pharmaceuticals.

2.3 Nylons [6]

Nylons are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid, so that peptide bonds form at both ends of each monomer in a process analogous to polypeptide biopolymers. Chemical elements included are carbon, hydrogen, nitrogen, and oxygen. The numerical suffix specifies the numbers of carbons donated by the monomers; the diamine first and the diacid second. The most common variant is nylon 6-6 which refers to the fact that the diamine (hexamethylene diamine) and the diacid (adipic acid) each donate 6 carbons to the polymer chain. As with other regular copolymers like polyesters and polyurethanes, the "repeating unit" consists of one of each monomer, so that they alternate in the chain. Since each monomer in this copolymer has the same reactive group on both ends, the direction of the amide bond reverses between each monomer, unlike natural polyamide proteins which have overall directionality: DuPont patented nylon 6,6, so in order to compete, other companies (particularly the German BASF) developed the homopolymer nylon 6, a condensation polymer, but formed by a ring-opening polymerization (alternatively made by polymerizing aminocaproic acid). The peptide bond within the caprolactam is broken with the exposed active groups on each side being incorporated into two new bonds as the monomer becomes part of the polymer backbone. In this case, all amide bonds lie in the same direction, but the properties of nylon 6 are sometimes indistinguishable from those of nylon 6,6 except for melt temperature (N6 is lower) and some fiber properties in products like carpets and textiles.

The general reaction is:



Scheme 2.1 Synthesis of Nylon.

2.4 Homogeneous and heterogeneous catalysts

Homogeneous catalysts are often more selective, more active, and more reproducible, but are generally more difficult to remove after the reaction. In this case, complicated processes such as distillation, liquid-liquid extraction and ion exchange must often be used.

Heterogeneous catalysts can be easily separated from the reaction mixture without any solvent, and show easy regeneration and have a less corrosive character, leading to safer, cheaper and more environment-friendly operation.

Table 2.1 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Diffusion problems	practically absent	present
Reaction condition	mild (50-200°C)	severe (often > 250°C)
Application	limited	wide
Activity loss	irreversible reaction with products (cluster formation); poisoning	sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high

Table 2.1 Comparison of homogeneous and heterogeneous catalysts(Cont.)

	Homogeneous	Heterogeneous
Catalyst separation	sometimes laborious (chemical decomposition, distillation, extraction)	fixed-bed: unnecessary suspension: filtration
Catalyst recycling	possible	unnecessary
Cost of catalyst losses	high	low

2.4.1 Polyoxometalate [7]

Among the solid acid catalysts, polyoxometalates (POMs) are more efficient catalyst and have many advantages over conventional acid catalysts. The applications of polyoxometalates are based on their unique properties, including size, mass, electron and proton transfer/storage abilities, thermal stability, liability of lattice oxygen and high Brønsted acidity of the corresponding acids. They have long been used in analytical chemistry, in many pharmaceuticals and in medicinal chemistry. The catalytic function of polyoxometalates is used in solution as well as in the solid state, as acid and oxidation catalysts.

The strong acidity of POMs is caused by two main factors: 1) The dispersion of the negative charge over many atoms of the polyanions and 2) The negative charge is less distributed over the outer surface of the polyanions owing to the double-bond character of the M=O bond, which polarizes the negative charge of O to M.

There are a large number of different POMs, but the most well known and studied are the Keggin type due to their easy preparation, relatively high redox and acid properties, and thermal stability. The basic structural unit of these compounds is the Keggin anion $[X^{n+}M_{12}O^{40}]^{n-8}$ (Fig. 2.1), which consists of a central tetrahedron (X: B³⁺, Si⁴⁺, P⁵⁺, etc.) surrounded by twelve edge-sharing metal-oxygen (M: Mo⁶⁺, W⁶⁺) octahedron.

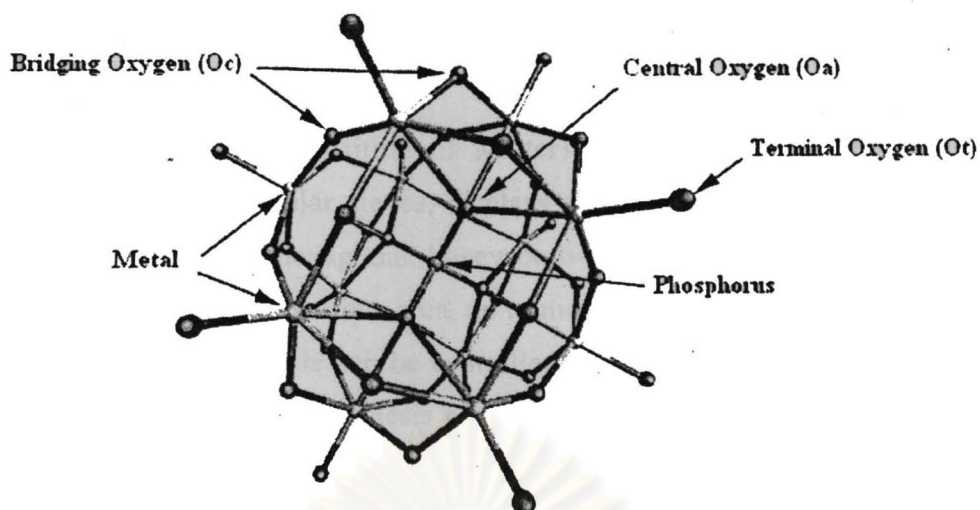


Figure 2.2 Primary structure of the polyoxometalate (Keggin structure).

2.5 Mesoporous materials

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures. The templating agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially. Three different mesophases in this family have been identified, i.e., lamellar hexagonal, and cubic phase. MCM-41[8] has a hexagonally packed array of cylindrical pores. The structure of MCM-48[9] has a three-dimensional, cubic-ordered pore structure and MCM-50[10] contain a lamellar structure as illustrated in Figure 2.3.

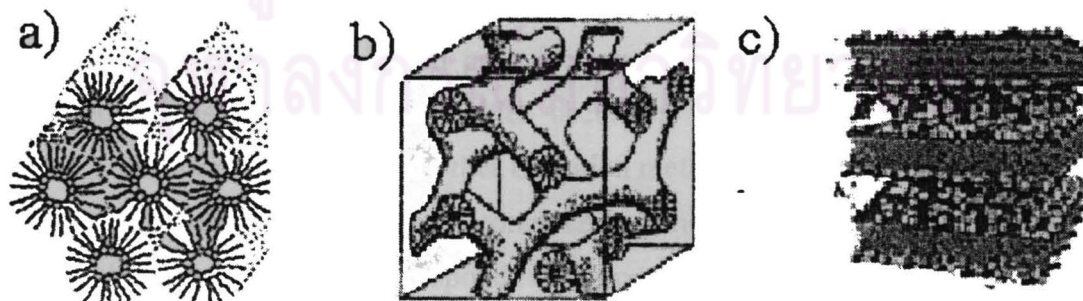


Figure 2.3 A presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

2.5.1 MCM-41[11]

MCM-41 (Mobil Composition of Matter)-41, a member of the extensive family of mesoporous molecular sieves, displays an ordered structure with uniform mesoporous arranged into a hexagonal, honeycomb-like lattice as show in Figure2.4. These materials possess large surface area, up to more than $1000 \text{ m}^2\text{g}^{-1}$ Moreover, the pore diameter of these materials can be controlled within mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions and/or by employing surfactants with different chain lengths in their preparation. The high thermal and hydrothermal stability, uniform size and shape of the pores, large surface areas and, hydrophobicity and acidity of these materials make them of interest as sorbents and solid support in catalysis.

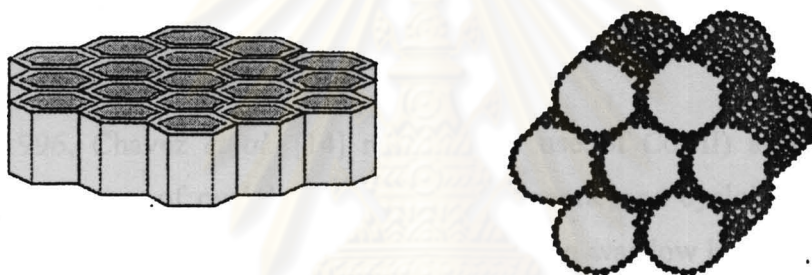


Figure 2.4 Hexagonal packing of uni-dimensional cylindrical pores.

2.6 Hydrogen peroxide, H_2O_2

Hydrogen peroxide is an effective oxidant that could be used in many industrial processes because the only by-product of oxidation using hydrogen peroxide is water. It is commercially available in aqueous solutions of 30% or 90% concentration. The 30% hydrogen peroxide is a colorless liquid (d 1.110) and it is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminum, platinum, and other transition metals. The 30% hydrogen peroxide does not mix with nonpolar organic compounds. When formic or acetic acid is used, the reacting species is the corresponding peroxy acid. Under such conditions, the products of oxidation by hydrogen peroxide resemble those obtained with peroxy acid.

2.7 Literature reviews

2.7.1 Homogeneous catalysis

In 1992 Barton *et al.* [12] reported the use of $\text{Cu}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst in GoChAgg system. GoChAgg system is the homogeneous oxidation by $\text{Cu}(\text{II})\text{-H}_2\text{O}_2$ in pyridine-acetic acid. Reactivity, selectivity and mechanistic study of system by using various cycloalkanes such as cyclohexane, cycloheptane, adamantane as substrate were thoroughly examined. The mechanism proposed was involved non-radical pathway.

In 1995 Craig L *et al.* [13] studied the redox characteristics of the polyoxometalates. The redox potentials depend on negative charge density and elemental composition. The polyoxometalate ions in order of decreasing redox potentials are $\text{V}(\text{V})$ (most oxidizing) > $\text{Mo}(\text{VI})$ > $\text{W}(\text{VI})$ (least oxidizing).

In 1996, Chavez *et al.* [14] reported the use of $\text{Co}(\text{III})$ alkyl peroxide to catalyze in oxidation of cyclohexane to cyclohexanone and cyclohexanol by using tert-BuOOH as oxidant. The selectivity of the reaction was low but the time required for reaction was short.

In 1997 Noritaka *et al.* [15] studied oxidation of cyclohexane to the corresponding alcohols and ketones with molecular oxygen catalyzed by the $\text{Fe}_{3-x}\text{Ni}_x$ -substituted Keggin-type heteropolyanion, $[\text{PW}_9\text{O}_{37}(\text{Fe}_{3-x}\text{Ni}_x(\text{OAc}))]^{(9+x)-}$ ($x = 1$). Its catalytic activities of $[\text{PW}_9\text{O}_{37}\{\text{Fe}_{3-x}\text{Ni}_x(\text{OAc})_3\}]^{(9+x)-}$ was compared with mono-transition-metal substituted heteropolytungstates and other compounds having oxo-bridged tri-transition-metal sites. The reaction was carried out without any solvent, air 1 atm, at 82°C for 48 h. The result showed that $[\text{PW}_9\text{O}_{37}\{\text{Fe}_2\text{Ni}_1(\text{OAc})_3\}]^{(10)-}$ gave 0.36% conversion and 83% selectivity of cyclohexanone.

In 2001 Suss-Fink *et al.* [16] studied oxidation of alkanes (cyclooctane, *n*-octane, adamantane, ethane) by hydrogen peroxide in acetonitrile using tetra-*n*-butylammonium salts of the vanadium-containing polyphosphomolybdates $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ and $[\text{PMo}_6\text{V}_5\text{O}_{39}]^{12-}$ catalysts. The oxidation of alkanes gave rise to the corresponding alkyl hydroperoxides as the main products, which slowly

decomposed to produce the corresponding ketones (aldehydes) and alcohols. The reaction in acetic acid and water is much less efficient. The oxidation of cyclooctane at 60°C in acetonitrile gives within 9 h oxygenates with turnover numbers >1000 and yields >30%. Pyrazine-2-carboxylic acid added as co-catalyst accelerates the reaction but does not enhance the product yield.

In 2001 Mizumo *et al.* [17] compared the catalytic activity of tetrabutylammonium salts of mono-, di- and tri-iron-substituted. Best results were obtained with the diiron species and the main products were cyclohexanone and cyclohexanol. Keggin-type heteropolytungstates $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{M}(\text{L})\text{O}_{39}]^{(7-m)-}$ (where $\text{M}^{m+} = \text{Co}, \text{Mn}$ or Ni and $\text{L} = \text{H}_2\text{O}$ or CH_3CN) as catalysts in cyclohexane oxidation with H_2O_2 . The polyanions $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$ showed higher catalytic activity. With iron species, a conversion of 76%.

In 2004 Saletе *et al.* [18] synthesized tetrabutylammonium salts of the Keggin-type polyoxotungstates $[\text{XW}_{12}\text{O}_{40}]^{n-}$, $[\text{XW}_{11}\text{O}_{39}]^{(n+4)-}$, $[\text{XW}_{11}\text{VO}_{40}]^{m-}$ and $[\text{XW}_{11}\text{M}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]^{p-}$, $\text{X} = \text{P}$ or Si and $\text{M} = \text{Fe}$ or Mn . These were used for the oxidation of cyclooctane with hydrogen peroxide in acetonitrile. High turnover numbers and selectivity for cyclooctyl hydroperoxide were obtained. They got 13-96% cyclooctane conversion after 9 h. The tungstosilicates were less active than tungstophosphates but presented higher selectivity for cyclooctyl hydroperoxide. Excess of hydrogen peroxide afforded higher selectivity for cyclooctyl hydroperoxide.

In 2004 Kholdeeva *et al.* [1] reported the aerobic oxidation of isobutyraldehyde with $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{CoO}_{39}]$, and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{PW}_{11}\text{CoO}_{39}]$. The reaction was carried in acetonitrile, air 1 atm at 20°C for 6 h. The results found that $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{CoO}_{39}]$ gave higher activity than $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{PW}_{11}\text{CoO}_{39}]$ (94 and 71% conversion) with 54% selectivity of isobutyric acid. From the result indicated that the presence of proton is important for the activity of Co-POMs in isobutyraldehyde oxidation.

In 2008, Mirkhani, *et al.* [19] published the oxidation of alkanes (cyclohexane, cyclooctane and ethylbenzene) with H_2O_2 using $\text{Fe}^{3+}(\text{salen})\text{Cl}$ and $\text{M}(\text{salen})\text{-C}$, where $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ and Mn at 80°C for 5 h in CH_3CN . It was found that $\text{Fe}^{3+}(\text{salen})\text{-POM}$ gave the highest activity. Its activity is much higher than the $\text{Fe}^{3+}(\text{salen})\text{Cl}$. The conversion for all substrates is $>50\%$ with $>90\%$ selectivity of ketone.

2.7.2 Heterogeneous catalysis

In 1999 Alexander M. *et al.* [20] studied the impregnation of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ onto MCM-41 and amino-modified MCM-41 materials. They were used for aerobic hydrocarbon oxidation using isobutyraldehyde as a reducing agent. The oxidation of alkenes and alkanes gave product selectivities similar to those observed in the corresponding homogeneous reaction although catalytic activity was lower. Under appropriate experimental conditions there was no leaching and the solid catalyst could be reused.

In 1999, Carvalho, *et al.* [21] synthesized and characterized $\text{M}(\text{NC}_3)\text{Si-MCM-41}$ ($\text{M} = \text{Cu(II)}$ and Fe(III)) and M-MCM-41 catalysts. These catalysts were employed in the oxidation reaction of cyclohexane with aqueous H_2O_2 (reaction temperature 100°C , 12 h). They found that $\text{M}(\text{NC}_3)\text{Si-MCM-41}$ were more active than M-MCM-41 . The activity of catalysts decreased in the following order: $\text{Fe}(\text{NC}_3)\text{Si-MCM-41} > \text{Fe-MCM-41} > \text{Cu}(\text{NC}_3)\text{Si-MCM-41} > \text{Cu-MCM-41}$. However, when the catalysts were recycled, leaching of the metal was observed.

In 2004 S.E. Dapurkar *et al.* [22] studied oxidation of cyclohexane over mesoporous VMCM-41 molecular sieve catalyst using aqueous hydrogen peroxide as oxidant, acetic acid as solvent, and methyl ethyl ketone as initiator. The activity of catalyst slightly decreased after first recycle (from 99 to 93 %conversion), owing to leaching of small amount of non-framework vanadium ion. At the optimized condition cyclohexanol was obtained as the major product with 94.5% selectivity. The use of strong oxidizing agent, TBHP resulted in the formation of cyclohexanone as the major product 82.4% selectivity.

In 2006 Yuan *et al.* [23] studied oxidation of cyclohexane by molecular oxygen over metal-containing ZSM-5 catalysts in a solvent-free system. Among those M-ZSM-5 and M/ZSM-5 catalysts tested, Co-containing ZSM-5 catalysts including Co/ZSM-5 (prepared by ion-exchange and calcination) and Co-ZSM-5 (prepared by ion-exchange and drying) showed the best activity for the oxidation of cyclohexane to cyclohexanone and cyclohexanol. Co/ZSM-5 had almost the same activity as Co-ZSM-5 for the cyclohexane oxidation; however, the leaching of cobalt from Co-ZSM-5 readily occurred. Co/ZSM-5 (calcined) catalyst could achieve about 10 mol% conversion of cyclohexane and 97% selectivity of KA-oil (the mixture of cyclohexanone and cyclohexanol) at 393 K under the pressure of 1.0 MPa O₂.

In 2007 Dharmesh *et al.* [24] studied on the immobilization of the polyoxometalate [PV₂Mo₁₀O₄₀]⁵⁻ on modified mesoporous MCM-41. The MCM-41 host material was made by functionalization of the surface with [(MeO)₃-Si(CH₂)₃N⁺(CH₃)₃]Cl. POM is deprotonated and could be easily immobilized by wet impregnation of the modified silica using CH₃OH as the solvent. These techniques indicated that the POM is intact on the surface after impregnation. High loadings of POM caused a decrease in the surface area and pore volume of solid, presumably due to both pore blockage and restructuring of the silica during wet impregnation.

In 2008 Shahram *et al.* [25] synthesized vanadium polyoxometalate (PVMo) supported on MCM-41 and MCM-41-NH₂ for hydrocarbon oxidation with hydrogen peroxide. PVMo-MCM was prepared by introduction of PVMo into the mesoporous molecule sieves of MCM-41 by impregnation and adsorption techniques. Oxidation of the alkenes and alkanes gave product selectivities, similar to those observed for corresponding homogeneous catalyst. Ultrasonic irradiation has a particular effect on MCM-41 structural uniformity and reduced the reaction times and improved the product yields. In addition, the solid catalysts could be recovered and reused several times without loss of activity.

In 2008 Jiquan *et al.* [26] synthesized secondary amino group modified MCM-41 and used as a support for the immobilization of a salen oxovanadium complex via a multi-grafting method. The immobilized complex was an effective catalyst for oxidation of cyclohexane using H₂O₂ under mild conditions. A conversion

of 45% of cyclohexane was obtained with a selectivity of 100% of the cyclohexanone/cyclohexanol mixture when the reaction was run at 60 °C for 12 h in acetonitrile.

In 2009 Sreevardhan *et al.* [27] synthesized Co-SBA-15 catalysts by direct synthesis and post-synthetic impregnation methods at two different loadings of Co viz., 1.2 and 2 wt%. The structure of SBA-15 was found to remain intact even after the incorporation of Co. The encapsulation of Co in SBA-15 was found to be highly advantageous in yielding significant amounts of the desired products (cyclohexanone and cyclohexanol) in the oxidation of cyclohexane without using any solvent under moderate pressure of O₂ at 433 K. 2 wt% Co-SBA-15 catalyst showed 9.4% conversion of cyclohexane and 78% selectivity of cyclohexanone.



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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
Cetyltrimethylammonium 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

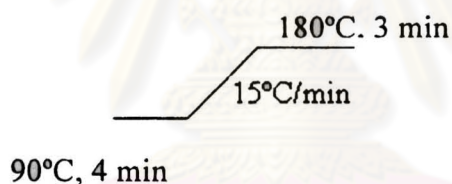
3.3 Analytical measurements

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 $4,000\text{ cm}^{-1}$ 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 $20^\circ\text{C}/\text{min}$ 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

$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}_x[\text{PW}_{12}\text{M}^{\text{X}+}(\text{H}_2\text{O})\text{O}_{39}]$ where $\text{M} = \text{Co, Fe and Cu}$ [28]

Na_2HPO_4 0.27g (1.52 mmol), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 5.5g (16.67 mmol) were mixed, after that nitrate salt of metal $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 0.58 g (2 mmol) or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 0.81 g (2 mmol) or $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of water and the pH was adjusted to 5 by HNO_3 . An aqueous solution (3 ml) of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ 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 $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ are pink, light yellow and light blue crystals respectively.

3.5 Synthesis of MCM-41 [29]

A composition of $\text{SiO}_2:\text{CTABr}:\text{NH}_4\text{OH}:\text{H}_2\text{O}$ 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 H₂O/ 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 H₂O₂ 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% H₂SO₄, saturated NaHCO₃ solution and dried over anhydrous Na₂SO₄. 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 H₂SO₄

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.



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.



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 phenolphthalein 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 H₂O₂

Molar ratio of H₂O₂/cyclohexane was varied: 1, 2, 3 and 4.

D. Effect of O₂ pressure

The O₂ pressure was varied: 1, 3 and 5 atm.

E. Effect of H₂O₂ and O₂ pressure

Molar ratio of H₂O₂/cyclohexane used in reaction was 3 and amount of O₂ 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% H₂O₂ 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% H₂O₂ at 80°C for 8 h.

CHAPTER IV

RESULTS AND DISCUSSION

The synthesis and characterization of polyoxometalates, MCM-41 and supported catalysts were described. The oxidations of cyclohexane with hydrogen peroxide and oxygen catalyzed by these synthesized supported catalysts were studied.

4.1 Preparation and characterization of catalysts

Tetrabutylammonium salts of polyoxometalates were synthesized by reaction of Na_2HPO_4 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and the metal nitrate in water at pH 5. Tetrabutyl ammonium bromide was then added.

MCM-41 was synthesized by reaction of cetyltrimethyl ammonium bromide (CTAB), ammonia and tetraethyl orthosilicate in water at 110°C for 96 h. The as-synthesized MCM-41 was refluxed in acidified HCl to remove the template (CTAB).

4.2 Polyoxometalate supported on MCM-41

Polyoxometalate supported on MCM-41 were prepared by two different methods:

- (1) incipient wetness impregnation method
- (2) wetness impregnation method

In addition, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (acidic POM) was also immobilized on the MCM-41 by direct synthesis method in order to reduce leaching of POM from the support.

The synthesized catalysts were characterized by following techniques: Fourier transform infrared techniques (FT-IR), X-ray diffraction spectrometry (XRD) surface characteristics and thermal properties were measured by BET and TGA. The details of each technique were described and discussed as follows.

4.3 Fourier transform infrared spectroscopy (FTIR)

The FT-IR technique was used to characterize functional group of catalysts. The structure of the Keggin polyoxometalate shown in Figure 4.1. Assignment of Peaks in FTIR spectra of Keggin-polyoxometalates is shown in Table 4.1. FT-IR spectra in the range of $400\text{-}1400\text{ cm}^{-1}$ of pure POM and (x%)POM/MCM-41 in various loadings are shown in Figure 4.2.

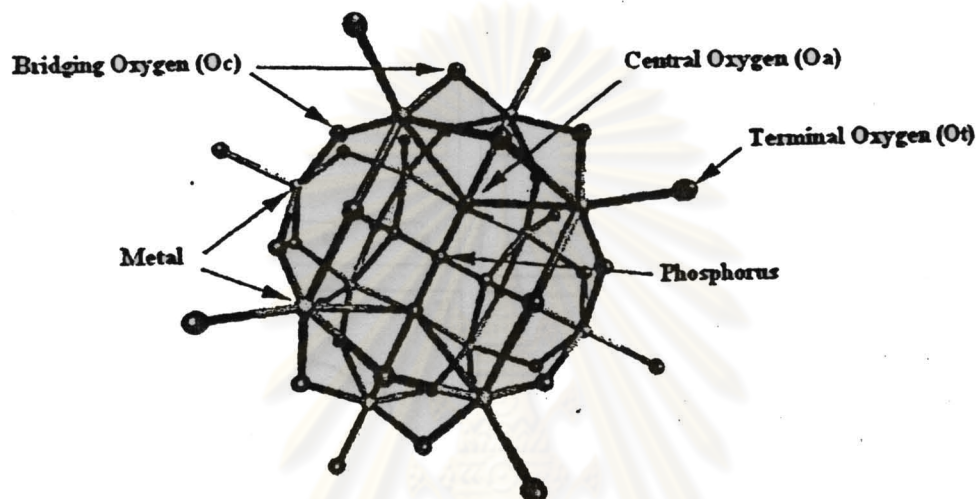


Figure 4.1 The structure of the Keggin polyoxometalate [28].

The O_a is the tetrahedrally-coordinated phosphorous atom in the center of the structure, O_c is the octahedral corner-sharing bridging oxygen atoms between two trimetallic groups, O_e is the octahedral edge-sharing bridging oxygen atoms and terminal oxygen atoms is O_t .

Table 4.1 FTIR spectra of transition metal substituted polyoxotungstates

Catalyst	Wavenumber (cm^{-1})			
	$\nu_{as} W - O_e - W$	$\nu_{as} W - O_c - W$	$\nu_{as} W = O_t$	$\nu_{as} P - O_a$
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot 2\text{H}_2\text{O}$	811	887	965	1084
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}] \cdot 2\text{H}_2\text{O}$	812	890	963	1085
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{CuO}_{39}]$	811	888	964	1083

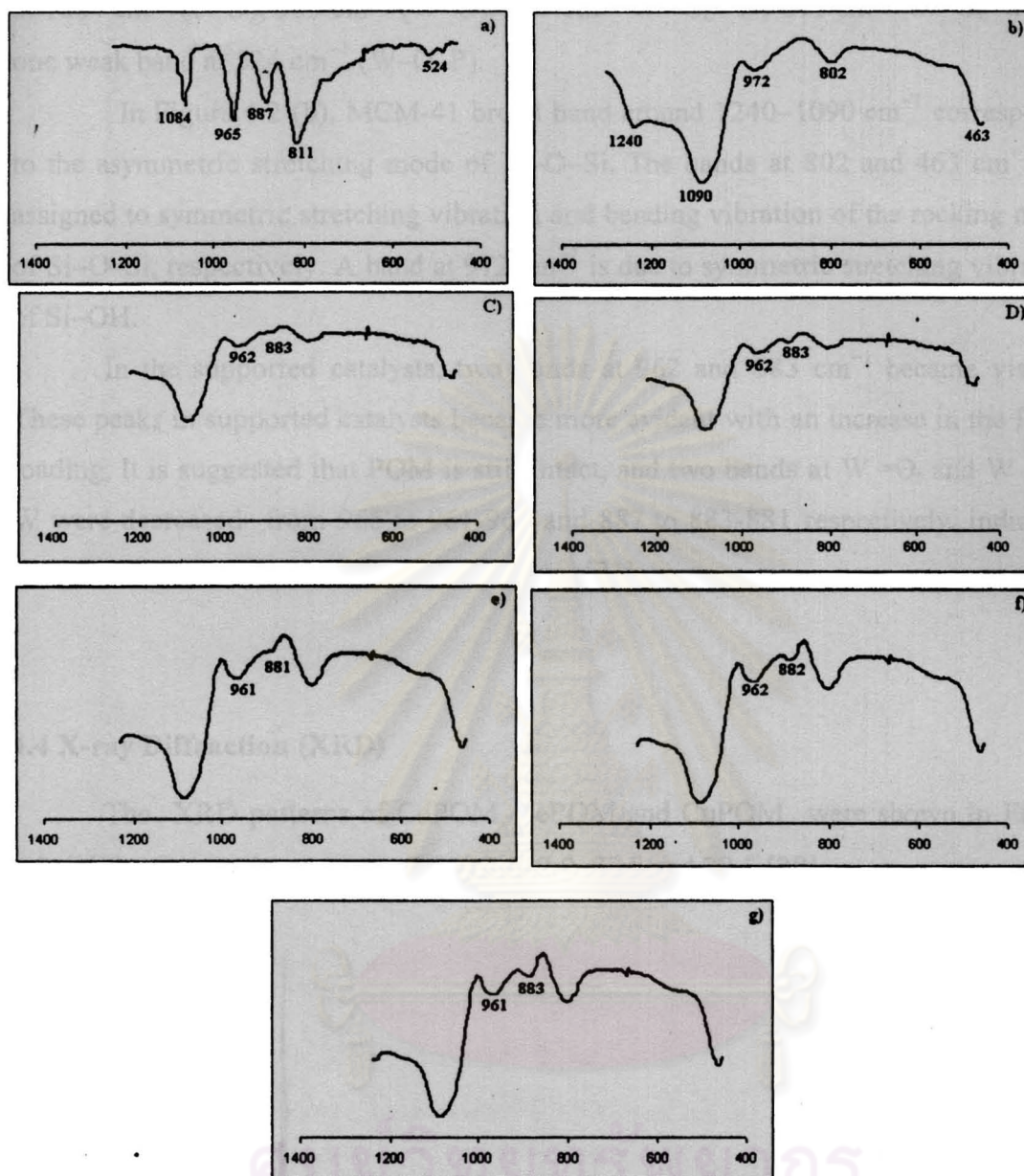


Figure 4.2 FT-IR spectra of (a) Bulk CoPOM (b) MCM-41 (c) 5% CoPOM/MCM-41 (d) 10% CoPOM/MCM-41 (e) 20% CoPOM/MCM-41 (f) 30% CoPOM/MCM-41 (g) 40% CoPOM/MCM-41

In Figure.4.2 (a), bulk POM with a Keggin structure shows four strong bands at 1084 cm^{-1} (P–O), 965 cm^{-1} (W=O), 887 cm^{-1} W –O_c- W, 811 cm^{-1} W –O_e-W and one weak band at 524 cm^{-1} (W–O–P).

In Figure.4.2 (b), MCM-41 broad band around $1240\text{--}1090\text{ cm}^{-1}$ corresponds to the asymmetric stretching mode of Si–O–Si. The bands at 802 and 463 cm^{-1} are assigned to symmetric stretching vibration and bending vibration of the rocking mode of Si–O–Si, respectively. A band at 972 cm^{-1} is due to symmetric stretching vibration of Si–OH.

In the supported catalysts, two bands at 962 and 883 cm^{-1} became visible. These peaks in supported catalysts became more evident with an increase in the POM loading, It is suggested that POM is still intact, and two bands at W =O_t and W –O_c-W were decreased from 965 to $961\text{--}962$ and 887 to $883\text{--}881$ respectively, indicated the POM have chemical bond with MCM-41. [31].

4.4 X-ray Diffraction (XRD)

The XRD patterns of CoPOM, FePOM and CuPOM were shown in Figure 4.3. Diffraction peaks appear at $2\theta = 8.3, 9.0, 27.8$ and 29.1 [28].

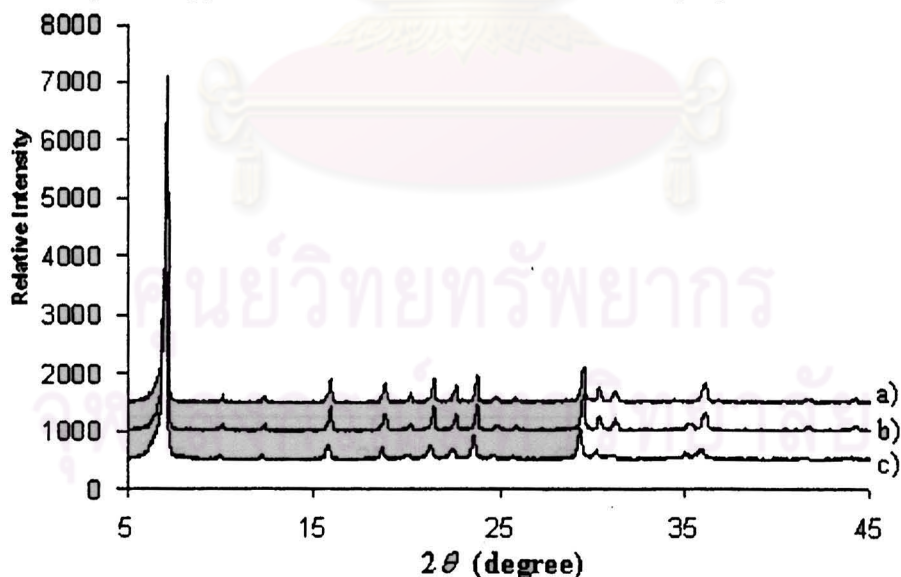


Figure 4.3 XRD patterns of (a) CoPOM (b) FePOM and (c) CuPOM

The XRD patterns of MCM-41 and (X%)CoPOM/MCM-41 in various loadings whereas the diffraction peaks at high angle $2\theta = 5-50^\circ$ are displayed in Figure 4.5.

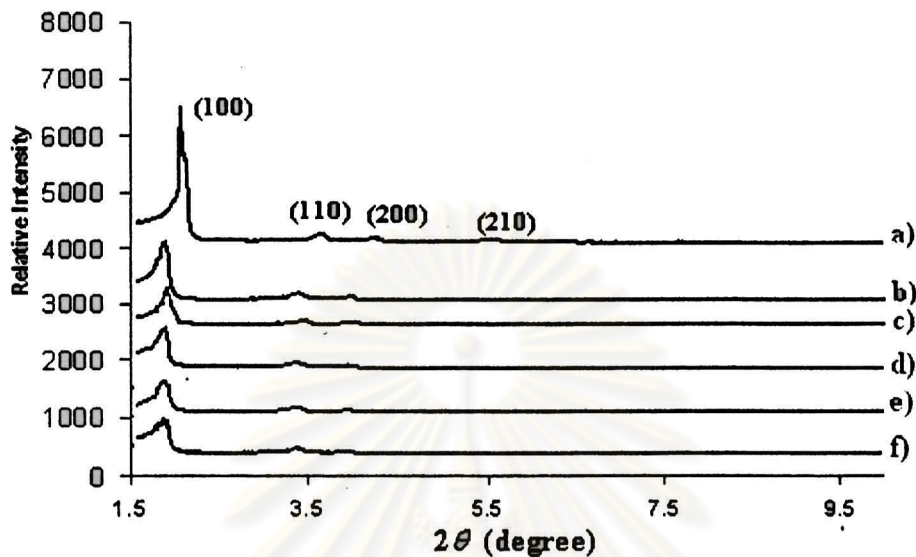


Figure 4.4 XRD patterns of (a) MCM-41 (b) 5% CoPOM-MCM-41 (c) 10% CoPOM-MCM-41 (d) 20% CoPOM-MCM-41 (e) 30% CoPOM-MCM-41 (f) 40% CoPOM-MCM-41

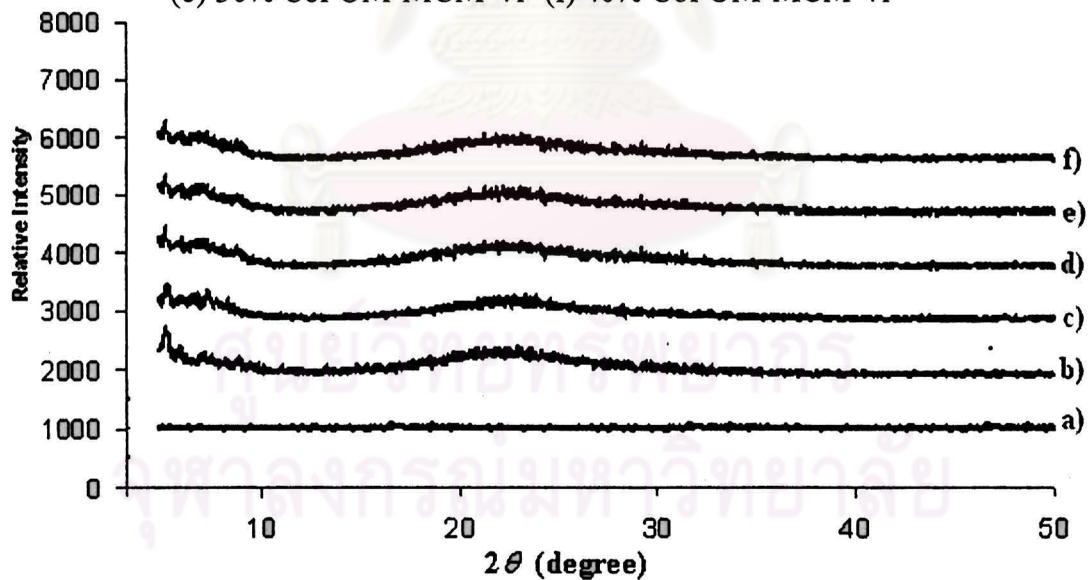


Figure 4.5 XRD patterns at $2\theta = 5-50^\circ$ of (a) MCM-41 (b) 5% CoPOM-MCM-41 (c) 10% CoPOM-MCM-41 (d) 20% CoPOM-MCM-41 (e) 30% CoPOM-MCM-41 (f) 40% CoPOM-MCM-41.

MCM-41 displayed peaks at $2\theta = 1.5-10^\circ$ in Figure 4.4 corresponding to (100), (110), (200), and (210) planes, respectively. The increase amount of CoPOM on MCM-41 resulted in a decrease in the intensity of (100). No peaks of CoPOM are observed in for the supported catalysts. These results indicate that the POM was well dispersed on the MCM-41 support [2].

The XRD patterns of other metal-POMs are similar to that of the CoPOM/MCM-41 (as shown in Appendix A)

4.5 Surface analysis by nitrogen adsorption

The surface of supported catalysts were observed by the nitrogen adsorption technique. The result has been collected in Table 4.2.

Table 4.2 Surface analysis of supported catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (nm)
MCM-41	1084	0.82	2.97
Bulk CoPOM	5	0.12	1.12
Direct synthesis	938	0.43	1.86
20% CoPOM-41 (WI)	830	0.42	2.64
5% CoPOM-MCM-41	1047	0.53	2.83
10% CoPOM-MCM-41	927	0.49	2.80
20% CoPOM-MCM-41	704	0.41	2.75
20% FePOM-MCM-41	715	0.42	2.68
30% CoPOM-MCM-41	556	0.36	2.57
40% CoPOM-MCM-41	420	0.30	2.51

Table 4.2 shows surface area, pore volume and mean pore diameter of MCM-41: 1084 m²/g, 0.82 cm³ and 2.97 nm, respectively. When loading CoPOM on MCM-41 the surface area, pore volume and mean pore diameter were decreased. The BET surface area and the pore volume of the POM/MCM-41 samples decrease from 1084 to 420 m²/g and from 0.82 to 0.30 cm³/g, for pore volume respectively. The pore size of the POM/MCM-41 samples is smaller than that of MCM-41. These facts lead us to assume that POM is located inside the pore.

(monolayer coverage). Sharp inflections at 0.4-0.3 for MCM-41 and supported catalyst are related to the capillary condensation and confirm the existence of uniform pores. In addition, the inflection heights of 20%CoPOM in nitrogen adsorption isotherm plots are smaller than that of MCM-41. It is attributed to the reduced pore volume, which reflects the surface area decreasing. This effect can be attributed to the CoPOM inclusions into the MCM-41 pores. [34]

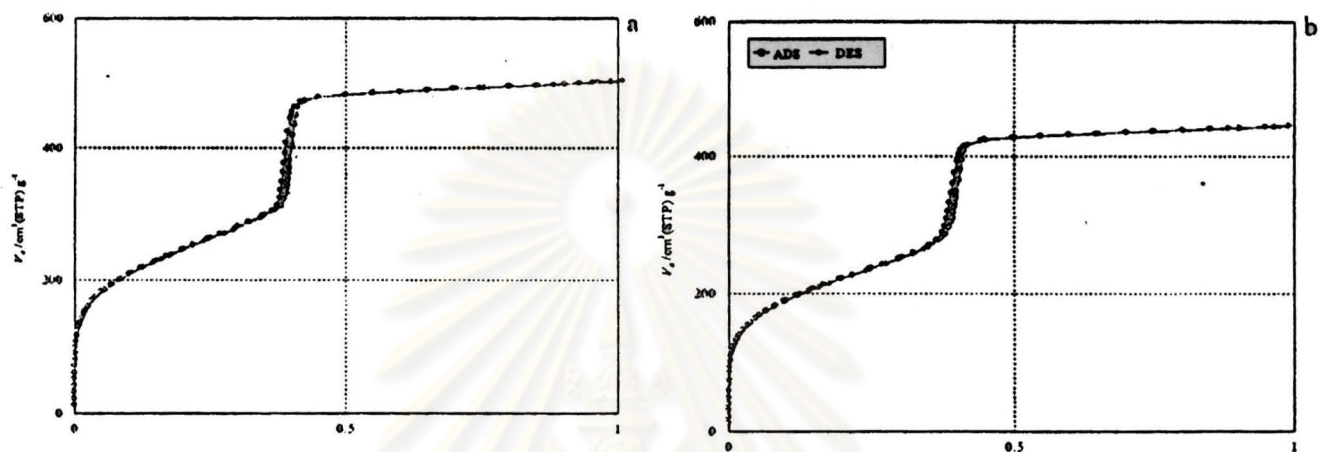


Figure 4.6 Adsorption and desorption isotherm of a) MCM-41 b) 20%CoPOM/MCM-41.

4.6 Thermogravimetric analysis

Typical TGA profiles for bulk CoPOM and supported on MCM-41 are shown in Figure 4.7.

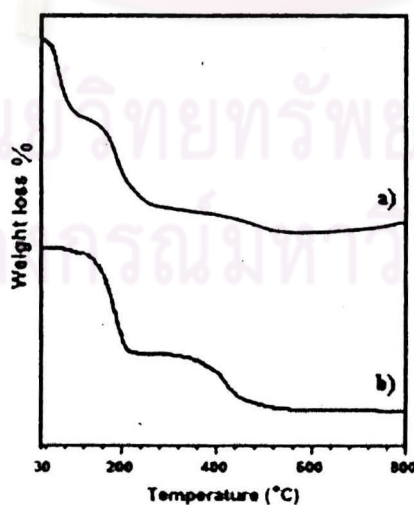
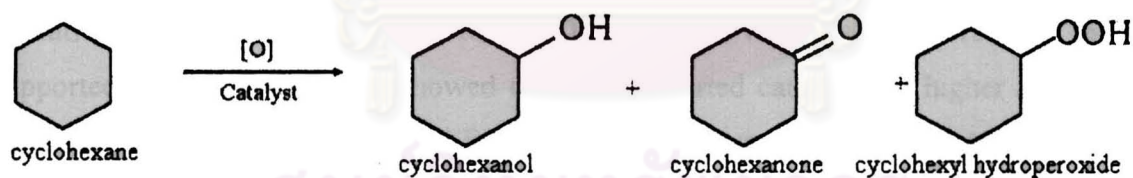


Figure 4.7 TGA profiles of catalysts: (a) bulk CoPOM ; (b) 20%CoPOM/MCM-41

The decomposition temperature analysis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}]$ catalyst exhibits three main ranges of weight loss as seen in Figure 4.7. The first region at 100-250°C is due to the loss of physisorbed water and the second region at 250-450°C corresponds to the loss of water of hydration and due to the decomposition of the organic part. At temperature above 450°C, it was the decomposition of polyoxometalate to corresponding metal oxide, this is in good agreement with the reported data [35]. After impregnation of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}]$ on MCM-41, the increasing of the decomposition temperature from 100 to 250°C was observed. The higher temperature weight losses are due to the difficulty in the elimination of the water contained in CoPOM molecules inside the channels of MCM-41. This demonstrated stabilization of CoPOM molecules in the channels of MCM-41 [36].

4.7 Oxidation of cyclohexane

Oxidation of cyclohexane was performed to compare the catalytic efficiency of various synthesized supported catalysts. Oxidized products detected with GC are as shown in Scheme 4.1. The percentage yield of product is based on initial cyclohexane. Reaction parameters influencing the oxidation were studied and the results are described in details below.



Scheme 4.1 Oxidation reaction of cyclohexane.

4.7.1 Effect of CoPOM loading on MCM-41.

Variable loading of catalysts on MCM-41: 5%, 10%, 20%, 30% and 40% were investigated. The results are presented in the Table 4.3.

Table 4.3 Effect of CoPOM loading on MCM-41.

Entry	Catalyst	% yied of products
		CyOH+CyONE
1	CoPOM ^a	0.53
2	5	0.46
3	10	0.68
4	20	0.79
5	30	0.61
6	40	0.50

Condition: Catalyst 2.5wt%, cyclohexane 92 mmol (10ml), H₂O₂/cyclohexane molar ratio = 1, 8h, 80°C.

^a bulk catalyst 0.03 g (0.38wt%).

From table 4.3 when comparing the activity between bulk catalyst (Entry 1, which was heterogeneous catalyst) and supported catalyst (Entry 2), of which both had the same amount of CoPOM, 20%, it was found that the yield of product in oxidation reaction from bulk CoPOM was 0.53% which was less than 0.79% of the supported catalyst. This result showed that the supported catalyst has higher activity due to high surface area resulted from the porous nature of the MCM-41 support. The surface area of the 20%CoPOM/MCM-41 was 704 m²/g whereas that of the bulk CoPOM was 5 m²/g.

For the catalysts with CoPOM loadings from 5 to 20 wt%, the catalytic activity was found to increase with the percentage of loading due to higher amount of active sites on supported catalyst.

However, when the loading was higher, 30-40 wt%, the product yields dropped. One explanation for this result can be due to the diffusional constraint for the reactants to access the active sites (POM) on the support. Since the support was covered with high amount of POM, some POM on the surface of the MCM-41 obstructed cyclohexane to enter the pore of the MCM-41 to react with the POM active

sites inside. The similar result was reported [33]. In their work, they compared activity of acidic POM supported on zeolite and on MCM-41 in acetalization of carbonyl compounds and found that pore size and surface area had affected on diffusion of reactant and products in reaction.

As for the selectivity, the results obtained (in Figure. 4.8) show that in case of the unsupported catalyst, cyclohexanol (67% selectivity) was a major product. For the supported catalyst, 5 wt%, 10wt%, 20wt% and 30wt% cyclohexanone were major products with 62, 65, 78 and 54 %selectivity, respectively.

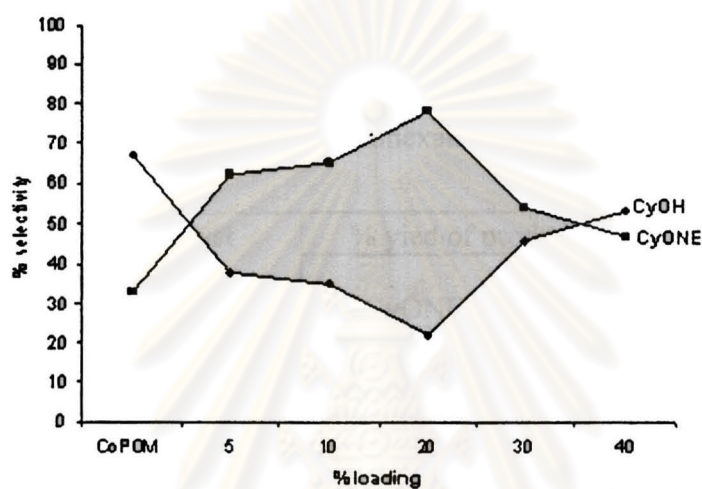


Figure 4.8 Product selectivity of cyclohexane oxidation as a function of POM loading on MCM-41.

4.7.2 Test of leaching

The CoPOM/MCM-41, CoPOM/MCM-41 and CoPOM/MCM-41 (with 10-30% loadings) were studied the effect of leaching after use in cyclohexane oxidation reaction. The amount of POM remained on the MCM-41 after reaction was analyzed by XRF technique.

Table 4.4 Leaching of POM from MCM-41

Entry	% loading (actual), based on MCM-41	% POM loading (analyzed by XRF)	% POM after used (analyzed by XRF)	%leaching of POM
1	10	9.87	9.43	0.44
2	20	19.00	17.68	1.32
3	30	29.78	18.54	11.24

Condition: Catalyst 2.5wt%, cyclohexane 92 mmol (10ml), H_2O_2 /cyclohexane molar ratio = 1, 8h, 80°C.

From Table 4.4 the 30%CoPOM/MCM-41 showed higher POM leaching than the 10% and 20% supported catalysts. Therefore for next experiments, the 20%CoPOM/MCM-41 was used in the cyclohexane oxidation.

4.7.3 Catalyst amount

Cyclohexane oxidation was performed using 20%CoPOM/MCM-41 catalyst in various weights based on cyclohexane (2.5wt%– 10.3wt%). Results is shown in Table 4.5.

Table 4.5 Effect of catalyst amount in cyclohexane oxidation.

Entry	Amount of catalyst (wt.% based on cyclohexane)	% yied of product	
		CyONE+CyOH	TON
1	2.5	0.79	91
2	3.8	1.18	100
3	5.1	2.11	113
4	6.4	2.16	94
5	7.7	2.23	82
6	10.3	2.28	65

Condition: 20%CoPOM/MCM-41, cyclohexane 92 mmol(10ml), H₂O₂/cyclohexane molar ratio = 1, 8h, 80°C.

TON (turnover number) = mol. of (cyclohexanol + cyclohexanone)/mol. of catalyst

The increasing of the amount of the supported catalyst led to an increase of the product yield. It can be seen that the 5.1%wt catalyst showed the highest TON. Beyond 5.1 wt% the TON was decreased.

The selectivity of cyclohexanone increased with increasing the catalyst amount but selectivity of cyclohexanol decreased. This might be explained that cyclohexanol was converted to cyclohexanone.

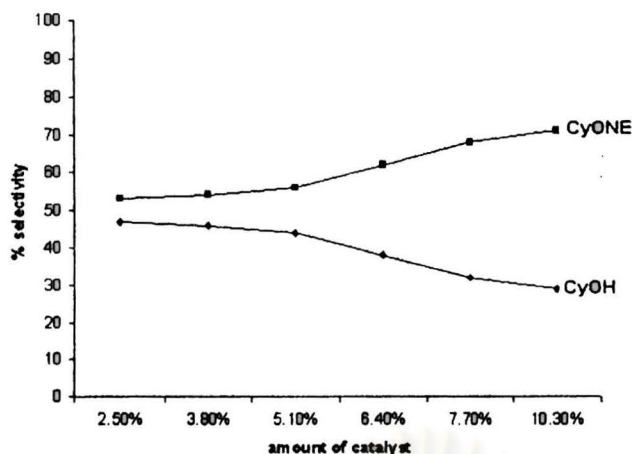


Figure 4.9 Selectivity of cyclohexane oxidation as a function of catalyst amount.

4.7.4 Effect of temperature

Reaction temperature could influence the reaction rate. In this work, the reaction temperature was varied: 70, 80 and 100 °C. The result is shown in Table 4.6.

Table 4.6 Effect of temperature

Entry	Temperature(°C)	% yield of product
		CyOH+CyONE
1	70	1.78
2	80	2.11
3	100	1.73

Condition: 20%CoPOM-MCM-41 5.1wt% , cyclohexane 92 mmol(10ml),
H₂O₂/cyclohexane molar ratio = 1, 8 h.

In Table 4.6, the yield of product increased with temperature: 1.78% at 70 °C and 2.11% at 80 °C. The H₂O₂ was able to form reactive intermediate which then oxidized cyclohexane at 80 °C better than 70 °C, so the %yield increased.

However, when the temperature was increased to 100 °C, yield of product decreased to 1.73%. The results agreed with the previous report [24]. At high temperature, cyclohexyl hydroperoxide was easily decomposed to cyclohexanol, therefore the content of cyclohexanol was increased. However, too high reaction temperature(100 °C) led to formation of by products such as 2-butanone, 5-oxohexanoic acid, 4-hydroxycyclohexanone and 1,4-cyclohexadione which were detected by GC-MS (in Appendix D). A similar result was previously reported [37].

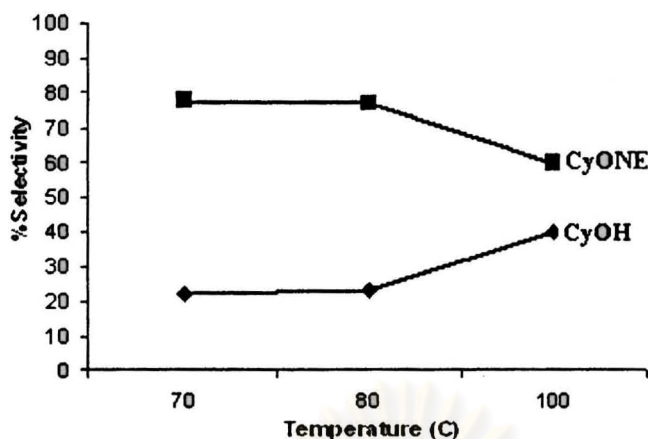


Figure 4.10 Selectivity of cyclohexane oxidation as a function of temperature.

4.7.5 Effect of oxidant/cyclohexane molar ratio

The amount of oxidant in the reaction was varied from 1-4 (H_2O_2 /cyclohexane mmol ratio) in order to find the most appropriate amount of H_2O_2 that provided the highest yield of the desired product. The results are presented in Table 4.7.

Table 4.7 Effect of oxidant amount

Entry	H_2O_2 /cyclohexane (mmol ratio)	% yied of product	TON
		CyOH+CyONE	
1	1	2.11	113
2	2	2.73	147
3	3	3.01	162
4	4	2.53	136

Condition: 20%CoPOM-MCM-41 5.1wt%, cyclohexane 92 mmol(10ml), 8h, 80 C.

When the amount of H_2O_2 was increased, the yield of product increased. Increase in the amount of H_2O_2 helps generating more radicals and thereby increasing the yield of product. However, it was found that the yield of product decreased for H_2O_2 /cyclohexane = 4. This may be due to the distinct phase separation between the aqueous oxidant and the organic substrate (cyclohexane), limiting the substrate interaction with the active catalyst sites. For the product selectivity, selectivity of cyclohexanone increased but selectivity of cyclohexanol decreased with increasing H_2O_2 amount [38].

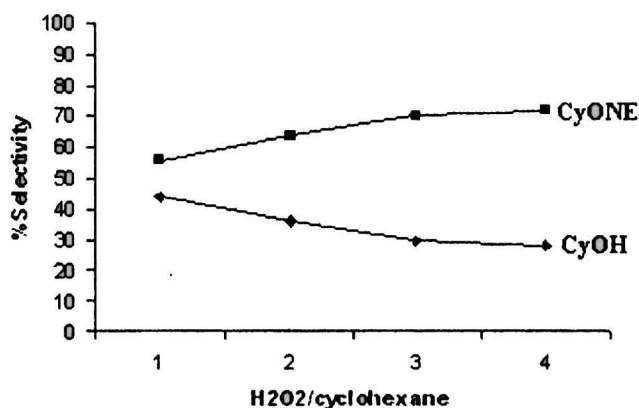


Figure 4.11 Selectivity of cyclohexane oxidation as a function of oxidant amount.

4.7.6 Effect of H₂O₂ and O₂ pressure

From above result, the suitable molar ratio of H₂O₂/cyclohexane was 3. So this ratio was used to study effect of O₂ pressure in participating with H₂O₂ in cyclohexane oxidation. The result is shown in Table 4.8.

Table 4.8 Effect of H₂O₂ and O₂ pressure

Entry	O ₂ (psig)	% yied of product
		CyOH+CyONE
1	0	3.01
2	15	3.12
3	45	3.25
4	75	3.32

Condition: 20%CoPOM-MCM-41 5.1wt%, cyclohexane 92 mmol (10ml),
H₂O₂/cyclohexane molar ratio = 3, 80°C. 8 h.

When oxygen was used together with H₂O₂, % yield of products increased. Selectivity of cyclohexanone also increased, as seen in Figure 4.12. This result agrees with previous work [39]. They reported on the oxidation of cyclohexane using Ce-doped MCM-48 catalyst with a combined oxidant (H₂O₂ and O₂).

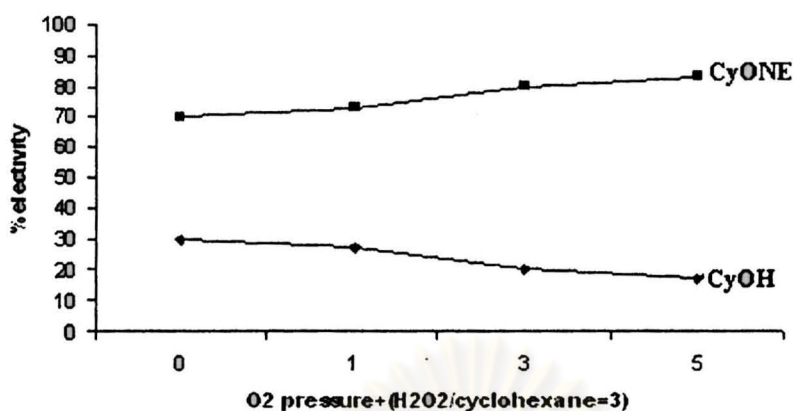


Figure 4.12 Selectivity of cyclohexane oxidation as a function of H₂O₂ and O₂ pressure.

4.7.7 Effect of O₂ pressure

In order to see the effect of only oxygen on the oxidation, experiments were performed using only O₂ with pressure of 1, 3 and 5 atm. The result is shown in Table 4.9.

Table 4.9 Effect of O₂ pressure

Entry	O ₂ (psig)	% yied of product
		CyOH+CyONE
1	0	0.15
2	15	0.80
3	45	1.30
4	75	1.70

Condition: 20%CoPOM/MCM-41 5.1wt% , cyclohexane 92 mmol (10 ml), 80°C, 8h.

It was clear that the % product yield increased with increasing oxygen pressure. The higher the oxygen pressure, the higher the oxygen solubility in the liquid phase. In Figure 4.13 the selectivity towards cyclohexanone also increased with O₂ pressure.

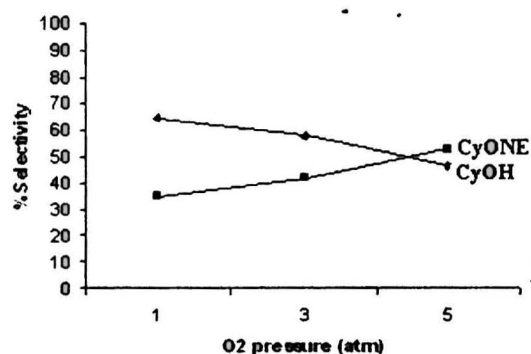


Figure 4.13 Selectivity of cyclohexane oxidation as a function of O₂ pressure

4.7.8 Effect of time

Oxidation of cyclohexane was monitored with time, the results are shown in Table 4.10.

Table 4.10 Effect of time for cyclohexane oxidation

Entry	Time (h)	% yied of product
		CyOH+CyONE
1	4	1.86
2	6	2.54
3	8	3.01
4	16	3.08

Condition: 20% CoPOM/MCM-41 5.1 wt% , cyclohexane 92 mmol(10ml),
H₂O₂/cyclohexane molar ratio = 3, 80°C 8h.

From Table 4.10 the yield of product increased with time. In Figure 4.14, it can be seen that the selectivity to cyclohexanol decreased with time but with the concomitant formation of cyclohexanone. These results suggest that the primary product formed is cyclohexanol and that the decrease of cyclohexanol at longer time is due to further oxidation to cyclohexanone. This result agrees with previous report [40].

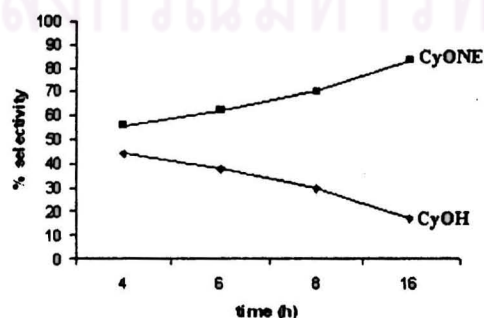


Figure 4.14 Selectivity of cyclohexane oxidation as a function of reaction time.

4.7.9 Effect of initiator type

Effect of initiator type was investigated. Initiator used are cyclopentanone, acetone and methyl ethyl ketone (MEK). The results were shown in Table 4.11.

Table 4.11 Effect of initiator type

Entry	Initiator	% yied of product
		CyOH+CyONE
1	-	3.01
2	cyclopentanone	3.26
3	acetone	3.07
4	methyl ethyl ketone	3.35

Condition: 20%CoPOM-MCM-41 5.1wt%, initiator 25 mmol, cyclohexane 92 mmol(10ml), H₂O₂/cyclohexane molar ratio = 3, 80°C, 8h.

Among various types of initiator tested, the results show that methyl ethyl ketone or MEK is the most suitable initiator because it gave highest yield (entry 4). MEK is an unsymmetric ketone so it may easily be cleaved into a free radical capable of initiating chain transfer by hydrogen abstraction with cyclohexane. On the other hand, the symmetric ketones such as cyclopentanone and acetone can be used but they produced lower yield [41].

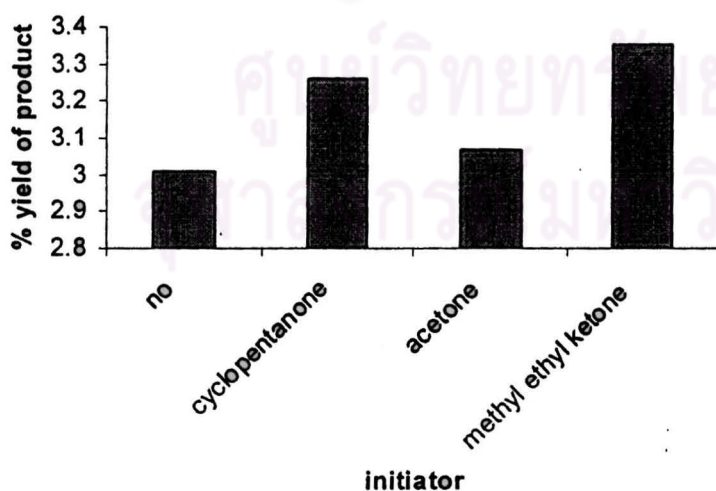


Figure 4.15 Selectivity of cyclohexane oxidation as a function of initiator type.

4.7.10 Effect of acetic acid

Effect of acetic acid was collected in Table 4.13.

Table 4.12 Effect of acetic acid

Entry	Acetic acid/H ₂ O ₂ (mmol ratio)	% yied of product
		CyOH+CyONE
1	0	3.01
2	0.1	3.16
3	1	3.84

Condition: 20%CoPOM-MCM-41 5.1wt%, cyclohexane 92 mmol(10ml);
H₂O₂/cyclohexane molar ratio = 3, 8 h, 80°C.

Acetic acid acts as a good oxidizing agent. This is because of the formation of the peracetic acid when it reacts with hydrogen peroxide. The peracetic acid is relatively more stable than hydrogen peroxide and can still serve as the oxidizing agent at high temperatures. That the %yield of product was enhanced with increasing amount of acid. This result agrees with the previous report [42] in which oxidation of cyclohexane was conducted using Co doped mesoporous titania catalyst at 100°C for 12 h. The oxidation products increased when increasing acetic acid.

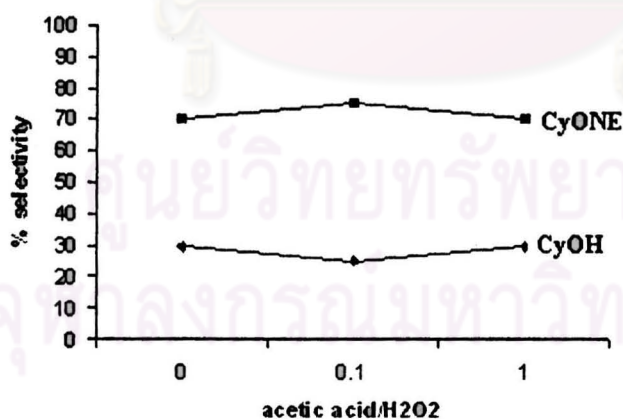


Figure 4.16 Selectivity of cyclohexane oxidation as a function of acetic acid.

4.7.11 Effect of type of metal in catalyst

The catalytic activity of the supported containing different types of metal were compared under the same reaction conditions. The result is shown in Table 4.13.

Table 4.13 Effect of type of metal in POM

Entry	Catalyst	% yied of product	Acid by-product(%)
		CyOH+CyONE	
1	CoPOM	3.32	0.020
2	FePOM	3.26	0.051
3	CuPOM	3.52	0.034

Condition: 20% POM supported catalyst 5.1wt% , cyclohexane 92 mmol(10ml), $O_2 = 5$ atm, H_2O_2 /cyclohexane molar ratio = 3, $80^\circ C$, 8 h.

From the table the activity order of catalysts is: CuPOM > CoPOM > FePOM. The activity order of the supported catalyst (POM on MCM-41) is in good agreement with those obtained from the same series of the homogeneous catalysts in cyclohexane oxidation [18].

In Table 4.13, the amount of acid by-product produced in cyclohexane oxidation was also determined. This acid amount was obtained by titration of the acid with NaOH. The result shows the order of acid amount as FePOM > CuPOM > CoPOM. Figure 4.17 shows the CoPOM and CuPOM selective with cyclohexanone product but FePOM selective with cyclohexanol product this result agree with previous reported [18]

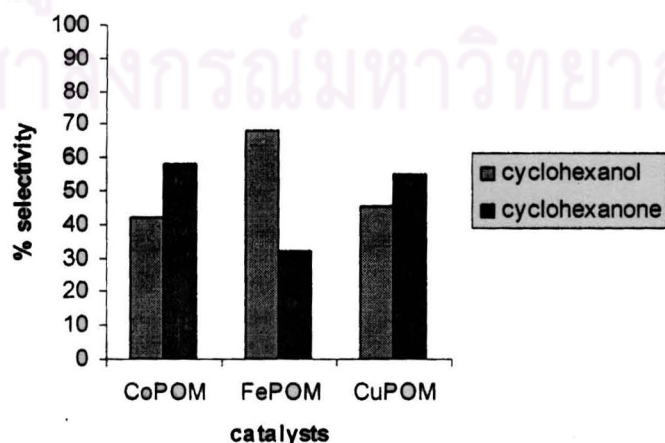


Figure 4.17 Selectivity of cyclohexane oxidation as a function of type of metal.

4.7.12 Decomposition of H_2O_2

The decomposition of H_2O_2 by 20%CoPOM/MCM-41, 20%FePOM/MCM-41 and, 20%CuPOM/MCM-41 was investigated under the same reaction conditions. The results are shown in Figure 4.18.

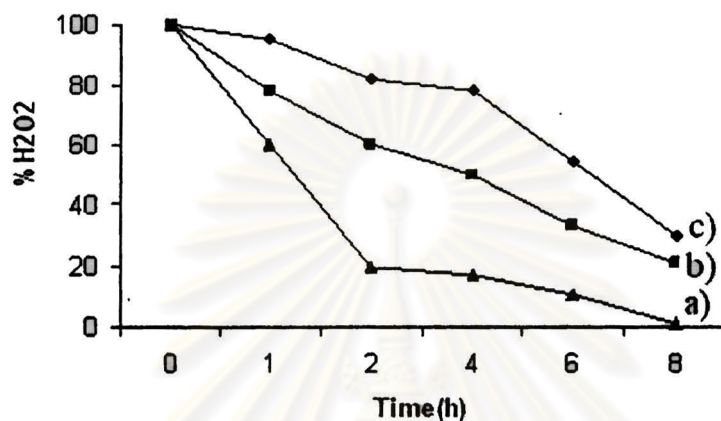


Figure 4.18 Time dependence of the concentration of H_2O_2 in presence of:
 a) 20%CuPOM/MCM-41, b) 20%CoPOM/MCM-41, c) 20%FePOM/MCM-41.

Figure 4.18 shows the decomposition of H_2O_2 (oxidant) in cyclohexane oxidation reaction by using 20%CuPOM/MCM-41, 20%CoPOM/MCM-41 and 20%FePOM/MCM-41. The order of H_2O_2 decomposition is: CuPOM/MCM-41 > CoPOM/MCM-41 > FePOM/MCM-41. The fastest H_2O_2 decomposition was achieved by the CuPOM/MCM-41. Higher yield of product in cyclohexane oxidation can be obtained in accordance with the faster rate of H_2O_2 decomposition [18]. It was reported that in homogeneous oxidation of cyclohexane using CuPOM, CoPOM and FePOM catalysts, CH_3CN as solvent and H_2O_2 as oxidant at $80^\circ C$ for 12 h, the CuPOM has highest activity due to high decomposition of H_2O_2 .

4.7.13 Effect of solvent

Effect of solvent (CH_3CN) was collected in Table 4.14.

Table 4.14 Effect of solvent

Entry	$\text{CH}_3\text{CN}(\text{ml})$	% yied of product
		CyOH+CyONE
1	No	3.01
2	10	3.34

Condition: 20% CoPOM/MCM-41 5.1wt% , cyclohexane 92 mmol(10ml), $\text{H}_2\text{O}_2/\text{cyclohexane}$ molar ratio = 3, 80°C 8h.

From Table 4.14, the % yield of product in entry 1 (without CH_3CN) was lower than entry 2 (with CH_3CN), this is due to phase separation between cyclohexane and oxidant (H_2O_2 in water). The solvent (CH_3CN) in reaction acted as a 'medium' serving homogeneity for the liquid phase. Cyclohexane and hydrogen peroxide are mutually dissolved in CH_3CN thus promoting mass transportation in reaction.

4.7.14 Cyclooctane oxidation

The optimal reaction conditions were applied to the oxidation of cyclooctane. The results are listed in Table 4.15.

Table 4.15 Cyclooctane oxidation

Entry	Catalyst	% yied of product
		CyOH+CyONE
1	CoPOM	3.82
2	FePOM	3.65
3	CuPOM	4.35

Condition: 20% supported catalyst 5.1wt%, cyclooctane 92 mmol, $\text{H}_2\text{O}_2/\text{cyclooctane}$ molar ratio = 3, 80°C 8h.

The order of % yield of product in cyclooctane oxidation is similar to that in the cyclohexane oxidation, that is $\text{CuPOM} > \text{CoPOM} > \text{FePOM}$. % Yield of product in

cyclooctane oxidation was higher than cyclohexane oxidation as cyclooctane can form cycloalkyl radical more easily. This radical was the intermediate which was converted to the cyclooctanol and cyclooctanone.

4.7.15 Homogeneous catalysts

The catalytic activity between supported catalyst and homogeneous catalyst with the same amount of CoPOM: 20%CoPOM/MCM-41 (5.1 wt%) and homogeneous CoPOM catalyst (0.067 g) were compared under the reaction conditions: 20%CoPOM/MCM-41 5.1wt%, cyclohexane 92 mmol(10ml), H₂O₂/cyclohexane molar ratio = 3, 80°C, 8h. The result was indicated in Table 4.16.

Table 4.16 Comparison between homogeneous and heterogeneous catalysts in cyclohexane oxidation

Entry	Catalysts	Condition	% yied of product
			CyOH+CyONE
1	Bulk CoPOM	Homogeneous	4.64
2	CoPOM/MCM-41	Heterogeneous	3.01

Table 4.16 shows the cyclohexane oxidation by homogeneous and heterogeneous catalysts at the similar reaction condition, exception that for the homogeneous catalysis, solvent was used to dissolve the catalyst. The homogeneous catalyst showed higher activity than heterogeneous catalyst with 4.64 and 3.01 % yield of product , respectively.

As for the selectivity, Figure 4.19 shows that the heterogeneous catalyst produced higher percentage of cyclohexanone than homogeneous catalyst. This demonstrated that the supported catalyst can control product selectivity.

4.7.16 Recycling of catalyst

Recycling tests with repeated use of the catalysts in three consecutive reactions were carried out. The catalysts were removed from the reaction mixture and subjected to the next catalytic run under the same conditions, and the results were listed in Table 4.17. In recycling tests, the % product yield changed slightly.

Table 4.17 Reusability of catalyst

Entry	Method	Run		
		first	second	third
1	Incipient wetness impregnation	3.01%	2.98%	2.95%
2	Wetness impregnation	2.53%	2.48%	2.42%
3	Direct synthesis	1.24%	0.94%	0.68%

Condition: 20%CoPOM-MCM-41 5.1wt%, cyclohexane 92 mmol, H₂O₂/cyclohexane molar ratio = 3, 80°C 8h.

In Table 4.17, entries 1 and 2 showed reusability of the supported catalysts prepared by three methods: incipient wetness impregnation and wetness impregnation and direct synthesis methods. It was found that in both incipient wetness impregnation and wetness impregnation method, the activity decreased a little but in direct synthesis method a significant decrease was observed. This can be due to the leaching of the acidic HPW from MCM-41 in the presence of H₂O₂. As for the selectivity of product, all three methods show only slight increase in cyclohexanol with a decrease in cyclohexanone.

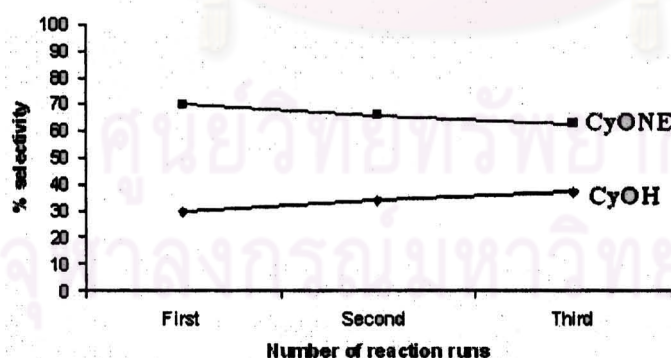


Figure 4.20 Selectivity of cyclohexane oxidation as a function of recycling test 20%CoPOM/MCM-41

4.7.17 Method of supporting POM on the MCM-41

Two different methods to prepare supported catalysts in this work are: incipient wetness impregnation and wetness impregnation methods. Amount of POM loading, leaching and activity of supported catalyst are compared and shown in Table 4.18.

Table 4.18 Methods of POM loading

Method	% loading before use (analyzed by XRF)	%POM on MCM-41 after use	%leaching of POM	%yield of product CyONE+CyOH
Incipient wetness impregnation	19.00	17.68	1.32	3.01
Wetness impregnation	11.00	10.18	0.82	2.53

Condition: 20%CoPOM-MCM-41 5.1 wt%, cyclohexane 92 mmol(10ml), H_2O_2 /cyclohexane molar ratio = 3, 80°C 8h.

Table 4.18 show results on oxidation of cyclohexane with the catalysts prepared by different methods: incipient wetness impregnation and wetness impregnation. As the incipient wetness impregnation method gave higher amount of POM on the support, therefore it showed higher product yield. However the leaching of POM was higher (1.32%) than that of the catalyst prepared by wetness impregnation (0.82%). The selectivity of the desired product in Figure 4.21 between incipient wetness impregnation and wetness impregnation methods were similar.

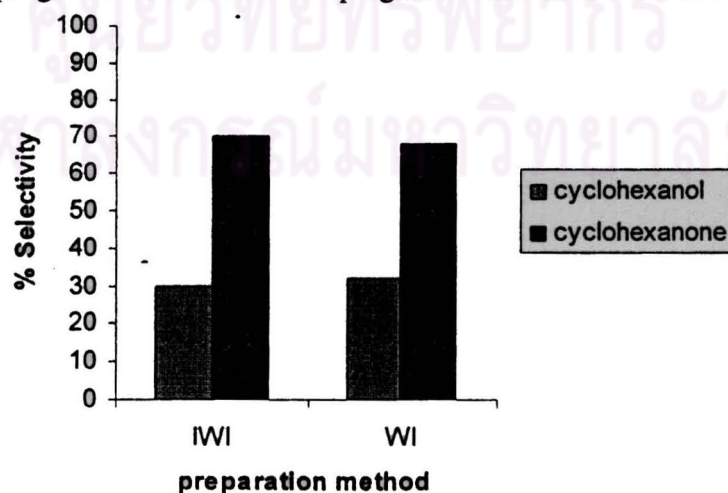


Figure 4.21 Selectivity of cyclohexane oxidation as a function of preparation method

4.7.18 Direct synthesis

The direct synthesis method was used in order to reduce metal leaching from the support that occurred in the case of impregnation methods. The result is shown in Table 4.19.

Table 4.19 Direct synthesis method

% loaded before used (analyzed by XRF)	%POM on MCM-41 after used	%leached	CyONE+CyOH (%yield)
5.83	5.81	0.02	1.24

Condition: 20%CoPOM-MCM-41 5.1wt%, Cyclohexane 92 mmol(10ml), H_2O_2 /cyclohexane molar ratio = 3, 80°C 8h.

Table 4.19 shows that the POM leaching from the support was very low (only 0.02%). However when comparing this method with the incipient wetness impregnation and wetness impregnation method, the activity of supported catalysts prepared by the direct synthesis method was the lowest. This can be due to low amount of POM on the support.

4.7.19 Effect of radical scavenger

To test whether the oxidation reaction occurs via radical pathway or not, in this work radical scavenger (2,6-di-*tert*-butyl-4-methylphenol) was added in the reaction mixture. The result is shown in Figure 4.22.

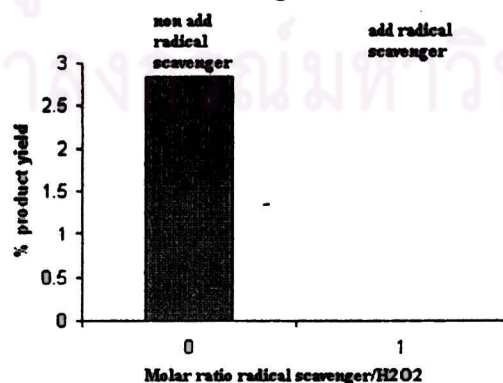


Figure 4.22 The yield of product of cyclohexane oxidation with addition of radical scavenger.

The result in Figure 4.22 shows no traces of cyclohexanol or cyclohexanone produced in the presence of radical scavenger. This reveals that the reaction occurred via a radical mechanism [44].

4.7.20 Cyclohexyl hydroperoxide

To demonstrate the formation of cyclohexyl hydroperoxide in this oxidation and to estimate its concentration in the course of the reaction, a method by Shulpin was used [45]. An excess of solid PPh_3 was added to the sample before the GC analysis, the cyclohexyl hydroperoxide present was completely reduced to the corresponding cyclohexanol. The results were shown in Table 4.20.

Table 4.20 Amount of cyclohexyl hydroperoxide by adding PPh_3 .

Catalysts	Cyclohexanol before addition PPh_3	Cyclohexanol after addition PPh_3	Cyclohexyl hydroperoxide(%)
CoPOM	0.82	0.90	0.08
FePOM	0.61	0.75	0.14
CuPOM	1.18	1.24	0.06

Condition: 20%MPOM-MCM-41 5.1wt% , cyclohexane 92 mmol (10ml), H_2O_2 /cyclohexane molar ratio = 3, 8h, 80°C .

From Table 4.20, the cyclohexanol was increased when PPh_3 had been added. The CyOOH still present in the final reaction solution is then deoxygenated by PPh_3 to give CyOH (with formation of phosphine oxide), Therefore CyOH amount in the gas chromatograph, was increased indicated that the oxidation reaction produced cyclohexyl hydroperoxide in this reaction [45].

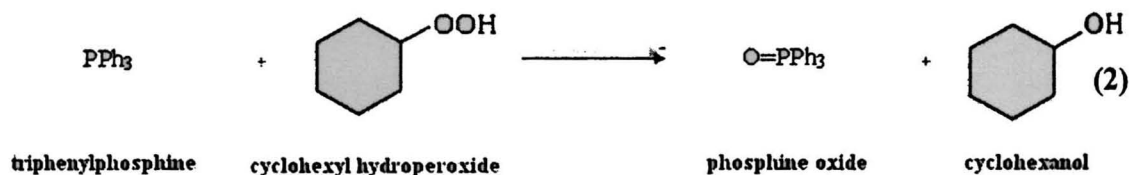
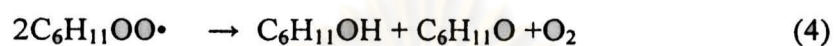
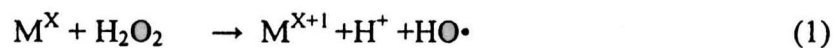


Figure 4.23 The formation of the cyclohexanol deoxygenated by PPh_3 .

4.8 Proposed mechanism

In this work mechanism for oxidation of cyclohexane by hydrogenperoxide oxidant was proposed to occur via free radical pathway, as shown in Equations 1-4



The metal in polyoxometalate was transformed to high valent M^{X+1} species and $HO\cdot$ initiator radical was formed. In the next step, hydrogen was transferred between $HO\cdot$ and cyclohexane, forming $C_6H_{11}\cdot$ radical. Then oxygen from the decomposition of H_2O_2 or from air reacted with $C_6H_{11}\cdot$ radical and produced cyclohexyl hydroperoxide radical ($C_6H_{11}OO\cdot$) that was then converted to cyclohexanone and cyclohexanol in the next step.

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CHAPTER V

CONCLUSION AND SUGGESTIONS

The polyoxometalate, $[(n-C_4H_9)_4N]_4H[PW_{11}M^{X+}(H_2O)O_{39}]$ $M = Co, Cu$ and Fe were synthesized and impregnated on mesoporous material, MCM-41, to prepare supported catalysts with variable loading amounts of 5-40wt% using incipient wetness impregnation method. All catalysts were characterized by FT-IR, XRD, TGA, XRF and N_2 adsorption techniques.

The prepared catalysts were used for cyclohexane oxidation. Parameters affecting the reaction were studied. The results showed that % product (cyclohexanol and cyclohexanone) yield increased with increasing amount of oxidant and reaction time. High catalytic activity was found when the reaction was performed at 20% loading, 5.1 wt%, $80^\circ C$, for 8 h and used 30% H_2O_2 (in water) molar ratio $H_2O_2/cyclohexane = 3$ as oxidant. The maximum % yield of product obtained using 20%CoPOM/MCM-41 was 3.32%. The selectivities of cyclohexanol and cyclohexanone were 30% and 70% respectively.

For 20%CuPOM/MCM-41, even if higher % product yield than 20%CoPOM/MCM-41, a lot of acid by-product was also produced.

In the case of different initiator used in reaction, the result indicated that the methyl ethyl ketone was highest % yield of product.

For the comparison of the preparation method of the supported catalysts was found the incipient wetness impregnation method could immobilize POM on MCM-41 more than the wetness impregnation.

For the reusability of the catalyst, after three cycles, its activity slightly dropped which might be caused by the leaching of POM from the support.

Comparison between the supported and homogeneous catalysts for cyclohexane oxidation, it could be seen that the supported catalysts showed

comparable catalytic activity to the homogeneous CoPOM. The main advantages of the supported system were the reusability and the ease of separation from the reaction. Moreover, the supported catalyst remained effective in the absence of solvent, this was a good benefit for the environment in view of the solvent contamination. The mechanism of the oxidation reaction is via radical pathway.

Suggestion for the future work

Future work for the improvement of the system should be focused on the study of other transition metals, e.g. V or Ni.



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Appendices

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APPENDIX A

Gas chromatography analyzer was used to determine products of cyclohexane oxidation. Cyclohexanone and cyclohexanol products were identified using standard addition method.

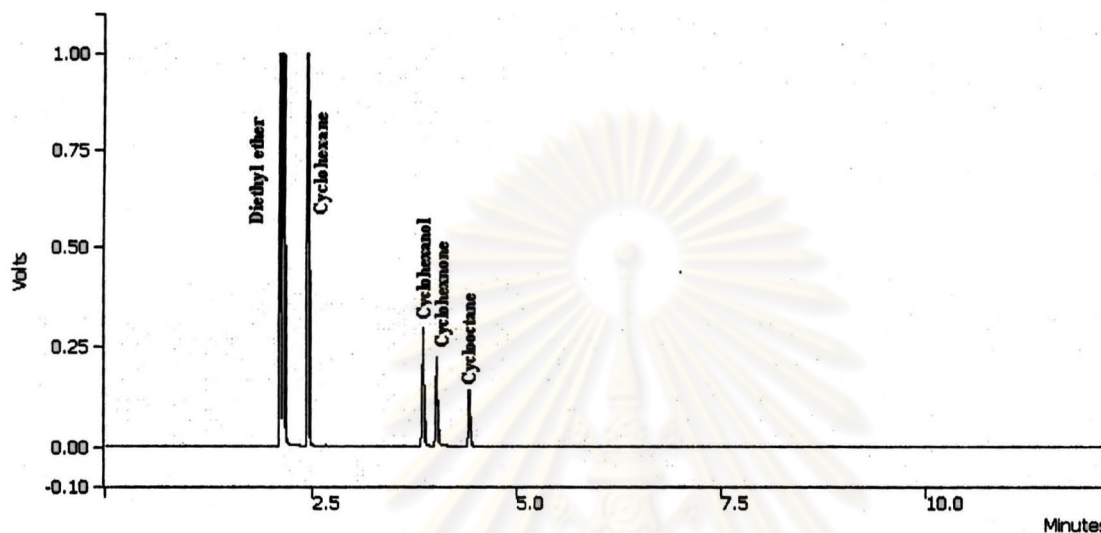


Figure A-1 A gas chromatogram of liquid products from oxidation of cyclohexane.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatographic analysis (see also the experimental section). Cyclooctane was used as an internal standard.

Example:

- A: exact amount of desired product prepared (mmol)
- B: total volume of the reaction (ml)
- C: peak area of the desired product
- D: peak area of the internal standard
- E: exact amount of substrate (mmol)
- F: exact amount of internal standard was added (mmol)

The calculation of the correction factor can be described as follows:

The amount of the product from the reaction mixture

$$= (F \times C/D) = G$$

The amount of the product in B ml (total volume of the reaction)

$$= G \times B = H$$

Thus, the correction factor of the product can be calculated as:

$$= A/H = I$$

The % product can be calculated as:

$$\% \text{Yield of product} = (H \times I / E) \times 100$$

The correction factors of chemicals are listed as follows:

$$\text{Cyclohexane} = 3.2$$

$$\text{Cyclohexanone} = 5.4$$

$$\text{Cyclohexanol} = 4.2$$

Calculation of %selectivity of cyclohexanone and cyclohexanol

Using peak areas obtained from GC analysis

% Selectivity of cyclohexanone

$$= (\% \text{yield of cyclohexane} / \% \text{yield of product}) \times 100$$

%Selectivity of cyclohexanol

$$= (\% \text{yield of cyclohexanol} / \% \text{yield of product}) \times 100$$

Determination of cyclohexyl hydroperoxide

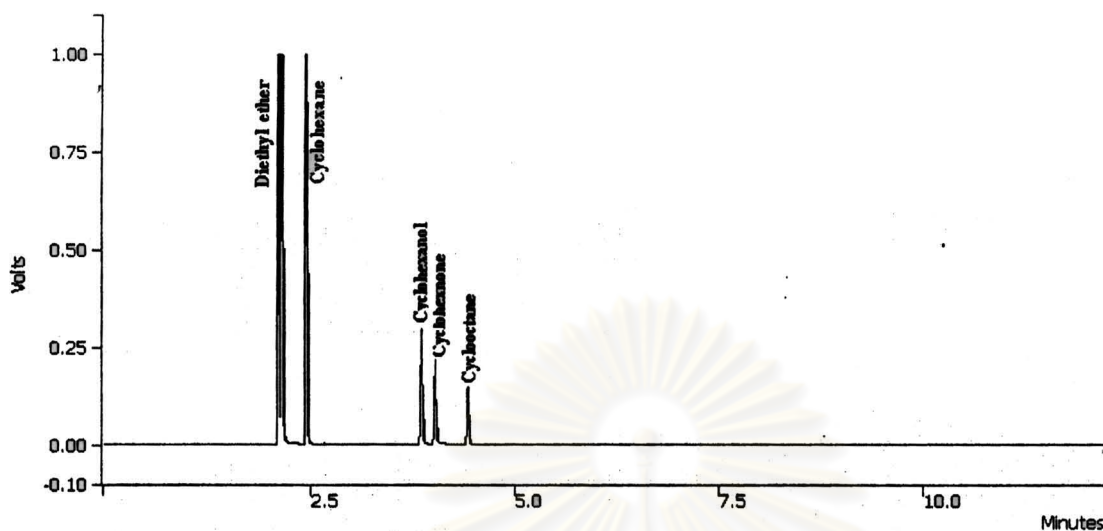


Figure A-2 GC diagram of cyclohexane oxidation and their oxygenated products using FePOM-MCM-41

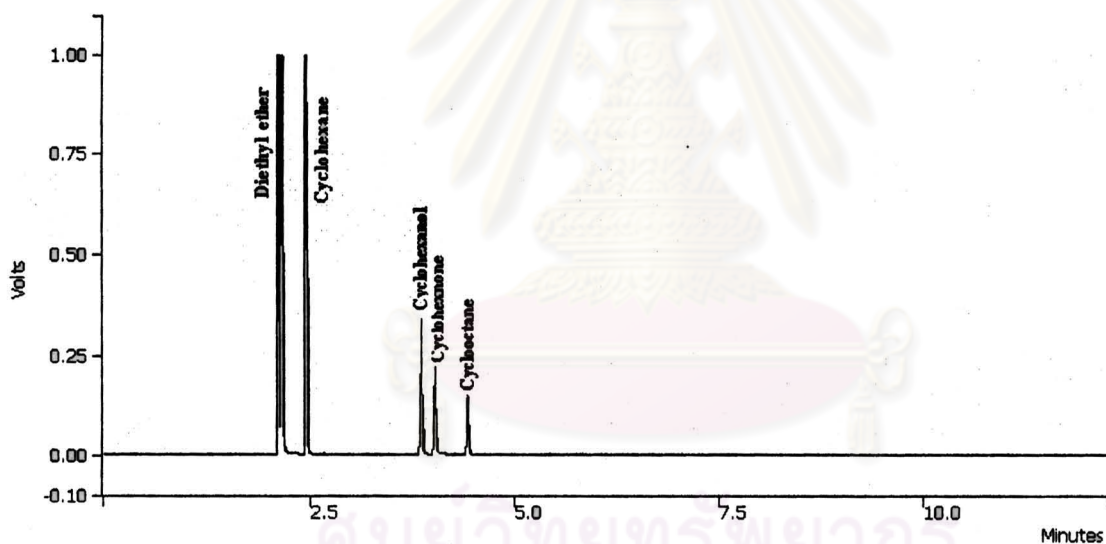


Figure A-3 GC diagram of cyclohexane oxidation and their oxygenated products using FePOM-MCM-41 after adding PPh_3 .

APPENDIX B

Adsorption and desorption isotherms of 20%CoPOM/MCM41,
20%FePOM/MCM-41 and 20%CuPOM/MCM-41.

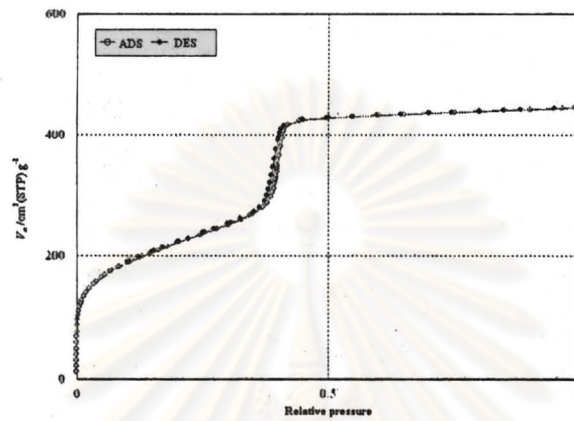


Figure B-1 Adsorption and desorption isotherm of the 20%CoPOM/MCM-41.

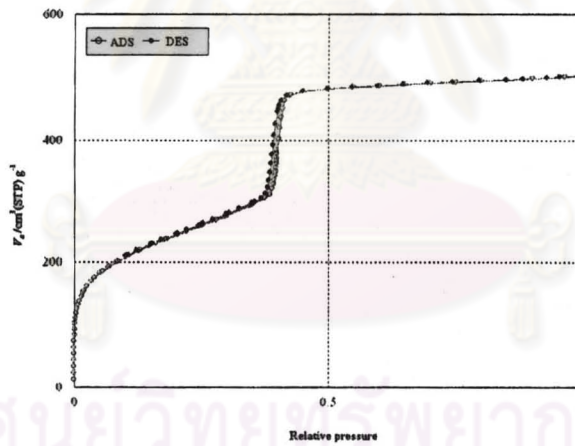


Figure B-2 Adsorption and desorption isotherm of the 20%FePOM/MCM-41

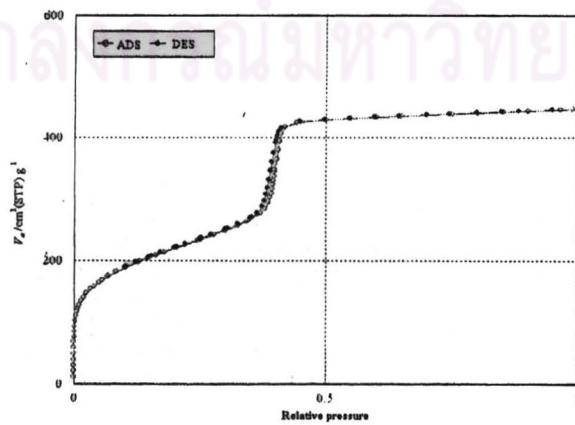


Figure B-3 Adsorption and desorption isotherm of the 20%CuPOM/MCM-41

APPENDIX C
Thermo gravimetry analysis (TGA)

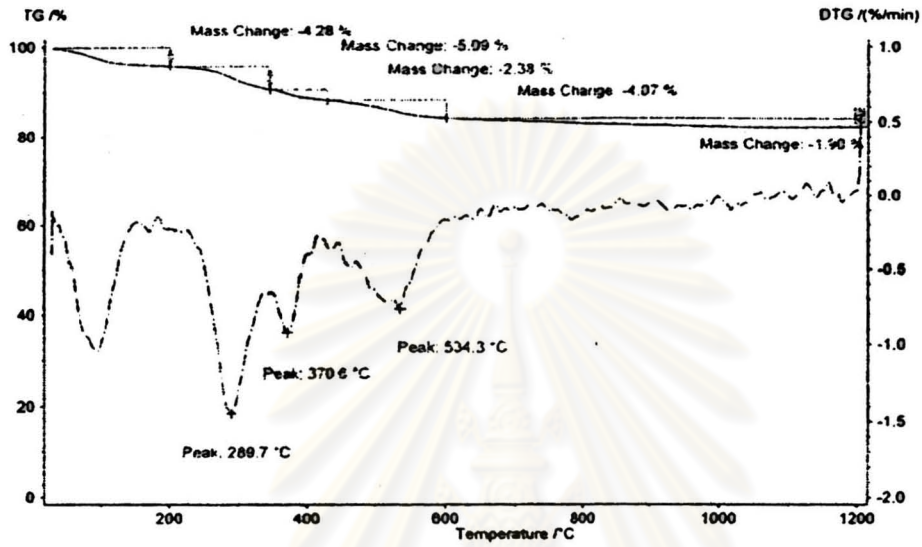


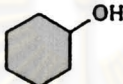
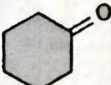


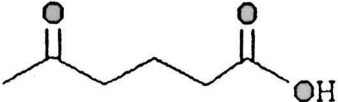
Figure C-1 TGA profile of the 20%CoPOMMCM-41

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APPENDIX D
GC-MS

Table D-1 GC-MS of cyclohexane oxidation reaction

Condition: 20%CoPOM-MCM-41 5.1wt% , cyclohexane 92 mmol(10ml),
H₂O₂/cyclohexane molar ratio = 1, 100°C, 8 h.

Formula	Structure	% Selectivity
cyclohexanol		35.71
cyclohexanone		52.55
1,4 cyclohexadione		4.08
4-hydroxy cyclohexanone		1.53
Hexanoic acid		6.12

File : E:\CIF2010\CIFSA065\CYCHER4.D
 Operator : SK
 Acquired : 12 Jan 2010 9:45 using AcqMethod CIF065-2
 Instrument : Instrumen
 Sample Name : CYCLOHEXANE EX
 Misc Info : CYCLOHEXANE EXTRACT
 Vial Number: 1



Area Percent Report

Data File : E:\CIF2010\CIFSA065\CYCHER4.D
 Acq On : 12 Jan 2010 9:45
 Sample : CYCLOHEXANE EX
 Misc : CYCLOHEXANE EXTRACT

Vial: 1
 Operator: SK
 Inst : Instrumen
 Multiplr: 1.00
 Sample Amount: 0.00

MS Integration Params: autoint1.e

Method : C:\MSDCHEM\1\METHODS\CIF065-2553.M (Chemstation Integrator)
 Title :

Signal : TIC

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.149	5	24	138	BV	15534	1253585	5.74%	2.291%
2	3.658	168	207	324	VB 4	46793	2198711	10.07%	4.019%
3	4.777	539	609	655	BB 7	6269	284044	1.30%	0.519%
4	5.166	677	749	825	BV 3	379542	21839725	100.00%	39.918%
5	5.436	825	846	959	VV	383216	20803407	95.25%	38.024%
6	6.415	1163	1198	1253	BB 5	5380	324566	1.49%	0.593%
7	8.797	2031	2054	2092	BV 5	5716	243491	1.11%	0.445%
8	8.945	2092	2107	2158	VV 4	33176	1021706	4.68%	1.867%
9	9.376	2158	2262	2321	PV 4	20173	1728770	7.92%	3.160%
10	9.587	2321	2338	2414	VV 4	11084	962053	4.41%	1.758%
11	9.863	2414	2437	2516	VB 3	31930	1224678	5.61%	2.238%
12	10.650	2691	2720	2780	BV 3	12749	507051	2.32%	0.927%
13	11.173	2857	2908	3014	BB 4	28900	1922590	8.80%	3.514%
14	13.471	3691	3734	3791	BB 6	8737	396608	1.82%	0.725%

Sum of corrected areas: 54710985

Figure D-1 GC diagram of cyclohexane oxidation and their oxygenated products using 20%CoPOM/MCM-41 at 100°C.

APPENDIX E

X-ray fluorescence spectrometry (XRF)

Table E-1 X-ray fluorescence spectrometry of 20%CoPOM/MCM-41

Sample	(% by wt.)				
	SiO ₂	P ₂ O ₅	Cl	CoO	WO ₂
20%CoPOM/MCM-41	84.20	0.33	1.24	0.38	13.85

Calculation of %POM on MCM-41

From Table E-1 CoO = 0.38% so Co = 0.29%

From theory 20%CoPOM/MCM-41 have Co = 0.32%

If 20%CoPOM/MCM-41 has Co 0.32%

So X%CoPOM/MCM-41 has Co 0.29%

$$X = (0.29 \times 20) / 0.32$$

$$X = 18.12\%$$

So the amount of CoPOM on the supported MCM-41 calculated by XRF technique was 18.12 % based on MCM-41.

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VITAE

Mr. Jiraroj Jatupisarnpong was born on Mach 16, 1986 in Maehongson Thailand. He received a Bachelor Degree of Engineering, major in Petrochemicals and Polymeric Materials from Silpakorn University in 2008. Since 2008 he has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2010.

International conference presentation

1. ISAMAP at Chulalongkorn University 17-18 September 2009
2. PACCON 2010 at Ubonratchathani 21-23 January 2010.

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