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, $Na_2WO_4 \cdot 2H_2O$ 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, $H_3PW_{12}O_{40} \cdot nH_2O$ (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 400-1400 cm^{-1} of pure POM and (x%)POM/MCM-41 in various loadings are shown in Figure 4.2.

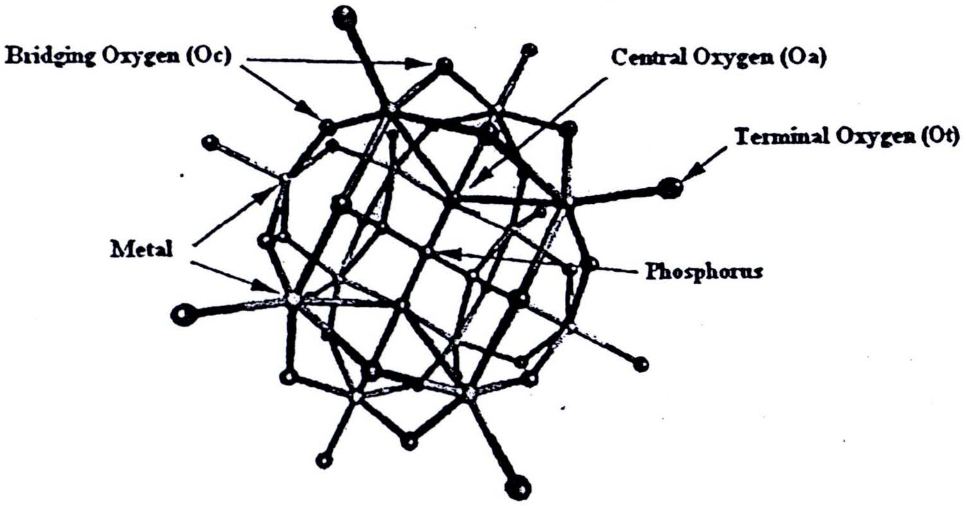


Figure 4.1 The structure of the Keggin polyoxometalate [28].

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})			
	ν_{as} W –O_e-W	ν_{as} W –O_c- W	ν_{as} W =O_t	ν_{as} P-O_a
$[(n\text{-}C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]\cdot 2H_2O$	811	887	965	1084
$[(n\text{-}C_4H_9)_4N]_4[PW_{11}Fe(H_2O)O_{39}]\cdot 2H_2O$	812	890	963	1085
$[(n\text{-}C_4H_9)_4N]_4H\,[PW_{11}CuO_{39}]$	811	888	964	1083

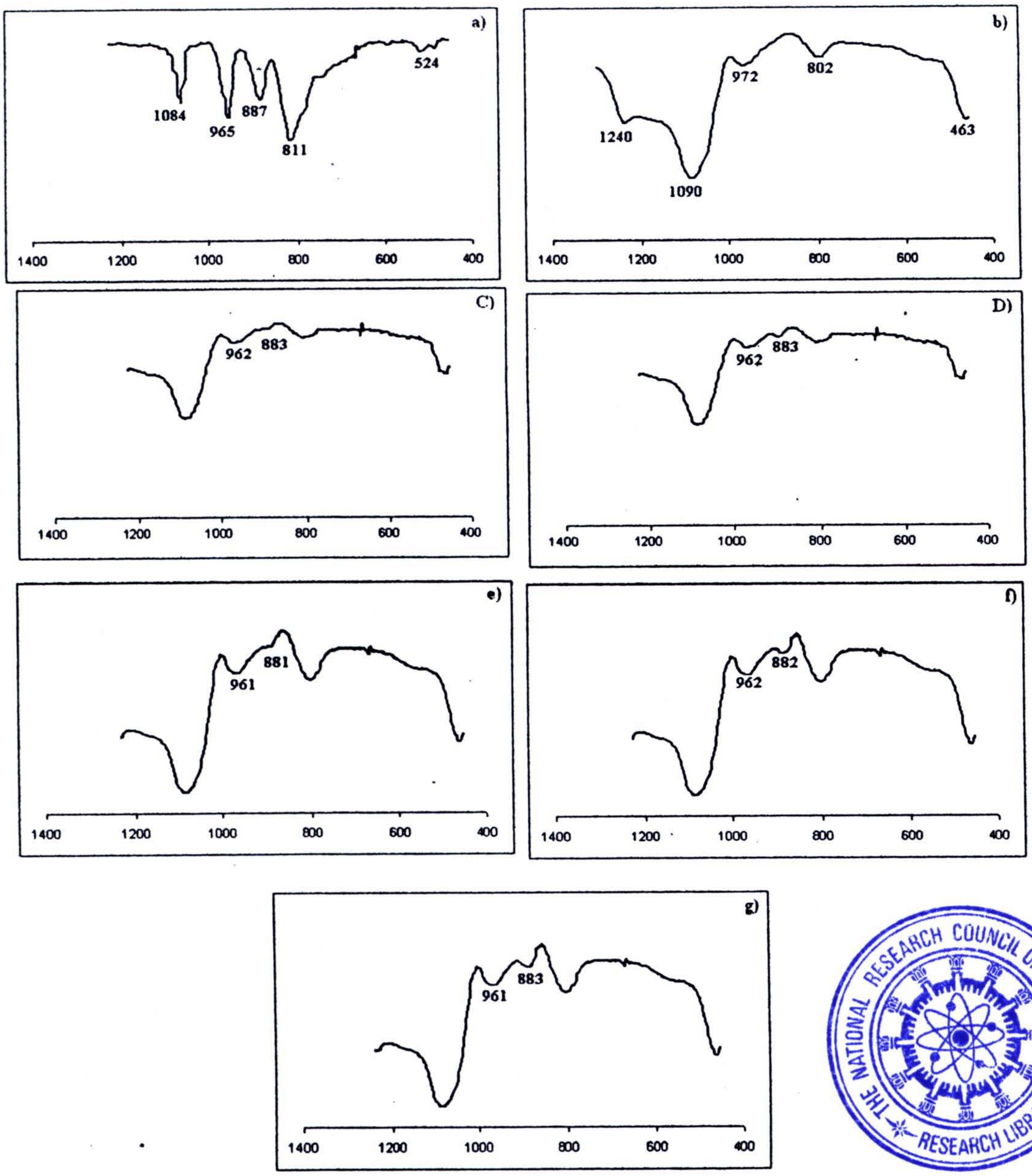


Figure 4.2 FT-IR spectra of (a) Bulk CoPOM (b) MCM-41 (c) 5% CoPOM/MCM-41 (d) 10% CoPOM/MCM-41 (e) 20% CoPOM/MCM-41 (f) 30% CoPOM/MCM-41 (g) 40% CoPOM/MCM-41

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 1240–1090 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 961-962 and 887 to 883-881 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 2θ = 8.3, 9.0, 27.8 and 29.1 [28].

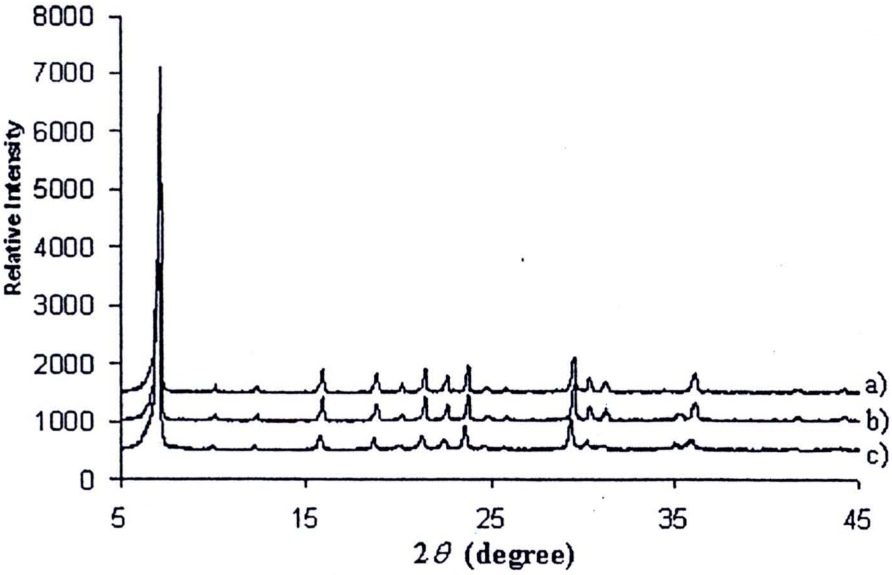


Figure 4.3 XRD patterns of (a) CoPOM (b) FePOM and (c) CuPOM

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

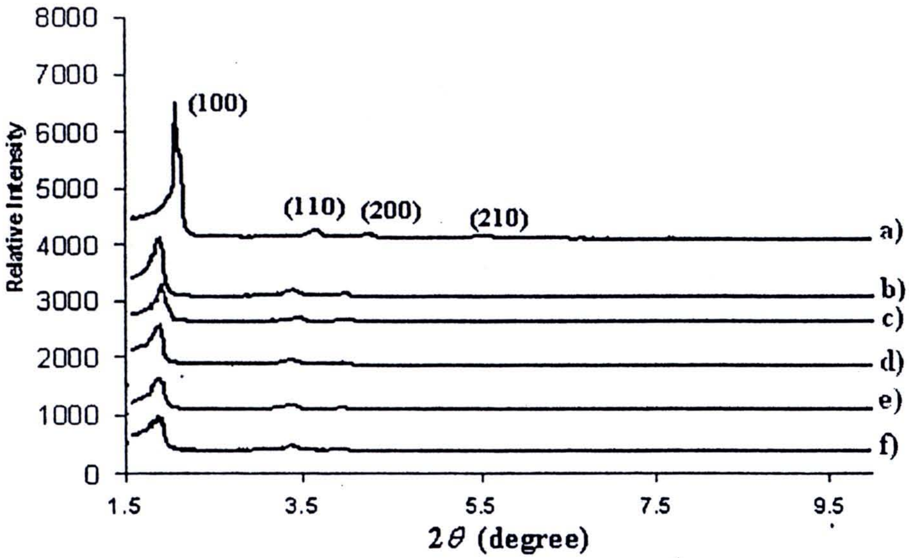


Figure 4.4 XRD patterns of (a) MCM-41 (b) 5% CoPOM-MCM-41 (c) 10% CoPOM-MCM-41 (d) 20% CoPOM-MCM-41 (e) 30% CoPOM-MCM-41 (f) 40% CoPOM-MCM-41

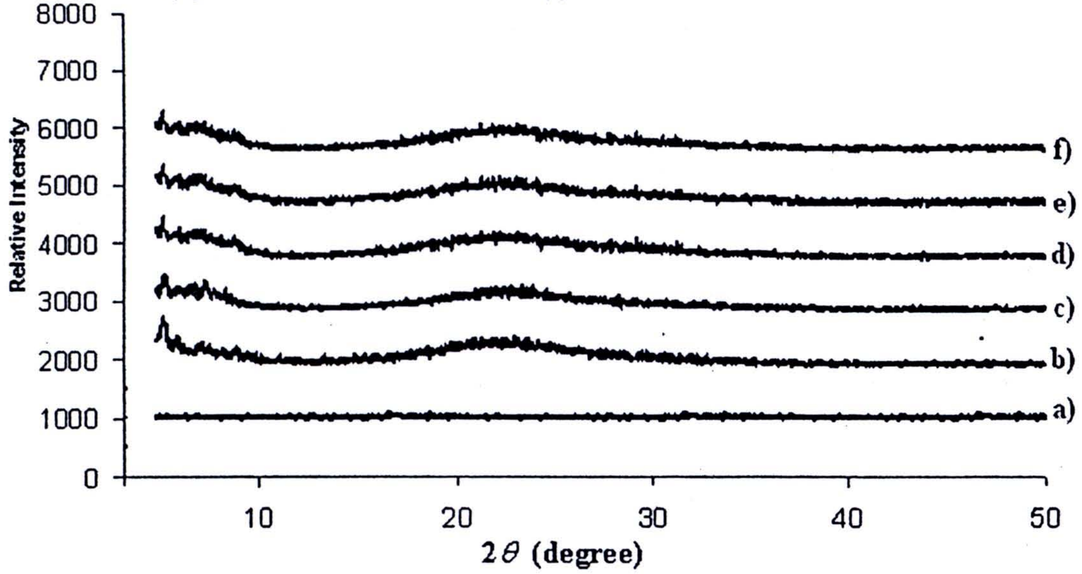


Figure 4.5 XRD patterns at 2θ= 5-50° of (a) MCM-41 (b) 5% CoPOM-MCM-41 (c) 10% CoPOM-MCM-41 (d) 20% CoPOM-MCM-41 (e) 30% CoPOM-MCM-41 (f) 40% CoPOM-MCM-41.

MCM-41 displayed peaks at 2θ = 1.5-10° 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 m^2/g, 0.82 cm^3 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 m^2/g and from 0.82 to 0.30 cm^3/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]

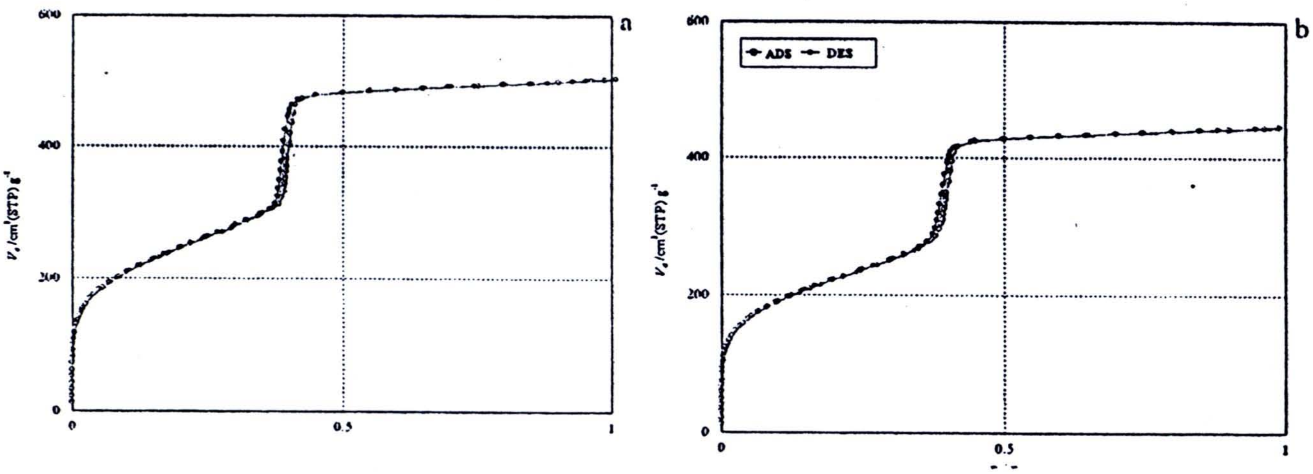


Figure 4.6 Adsorption and desorption isotherm of a) MCM-41 b) 20%CoPOM/MCM-41.

4.6 Thermogravimetric analysis

Typical TGA profiles for bulk CoPOM and supported on MCM-41 are shown in Figure4.7.

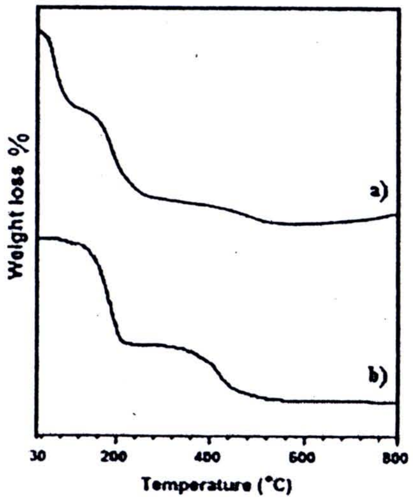


Figure 4.7 TGA profiles of catalysts: (a) bulk CoPOM ; (b) 20%CoPOM/MCM-41

The decomposition temperature analysis of [(n-$C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ 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-$C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ 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 investgated. 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), H_2O_2/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 m^2/g whereas that of the bulk CoPOM was 5 m^2/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.

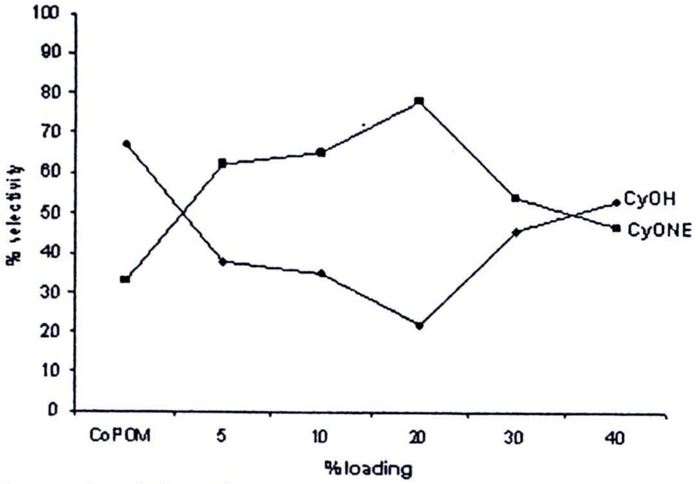


Figure 4.8 Product selectivity of cyclohexane oxidation as a function of POM loading on MCM-41.

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	TON
		CyONE+CyOH	
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), H_2O_2/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.

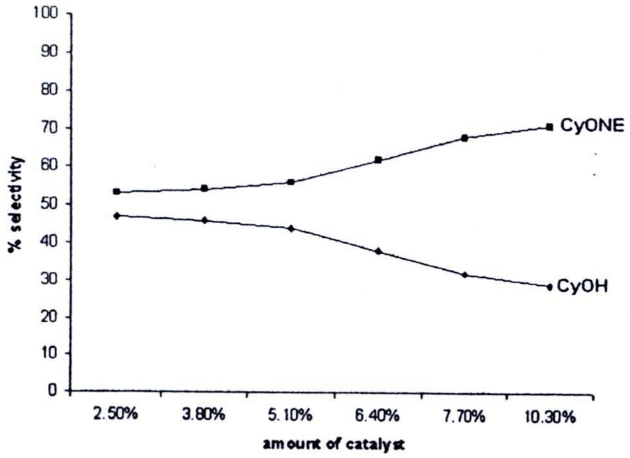


Figure 4.9 Selectivity of cyclohexane oxidation as a function of catalyst amount.

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	Temperture(°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), H_2O_2/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 H_2O_2 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].

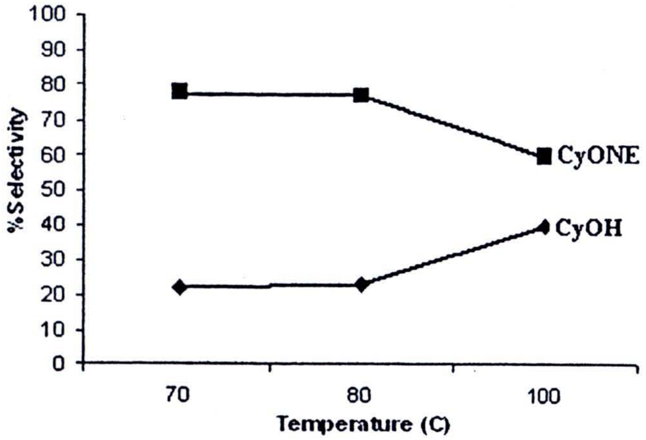


Figure 4.10 Selectivity of cyclohexane oxidation as a function of temperature.

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].

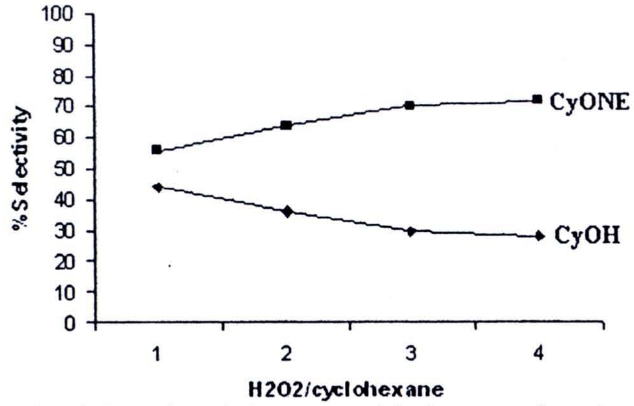


Figure 4.11 Selectivity of cyclohexane oxidation as a function of oxidant amount.

4.7.6 Effect of H_2O_2 and O_2 pressure

From above result, the suitable molar ratio of H_2O_2/cyclohexane was 3. So this ratio was used to study effect of O_2 pressure in participating with H_2O_2 in cyclohexane oxidation. The result is shown in Table 4.8.

Table 4.8 Effect of H_2O_2 and O_2 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), H_2O_2/cyclohexane molar ratio = 3, 80°C. 8 h.

When oxygen was used together with H_2O_2, % 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 (H_2O_2 and O_2).

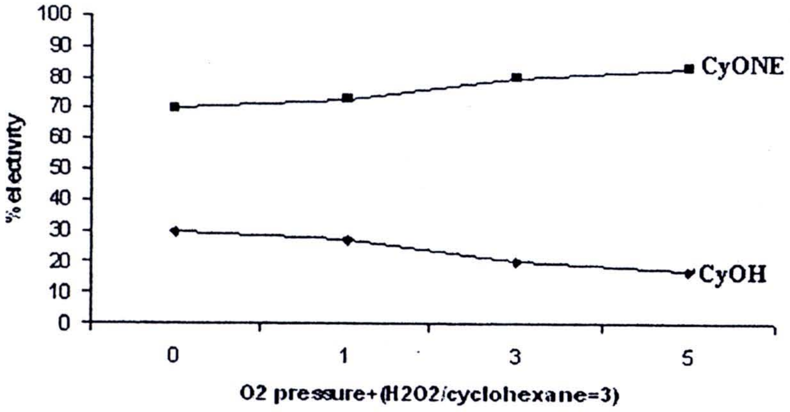


Figure 4.12 Selectivity of cyclohexane oxidation as a function of H_2O_2 and O_2 pressure.

4.7.7 Effect of O_2 pressure

In order to see the effect of only oxygen on the oxidation, experiments were performed using only O_2 with pressure of 1, 3 and 5 atm. The result is shown in Table 4.9.

Table 4.9 Effect of O_2 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 O_2 pressure.

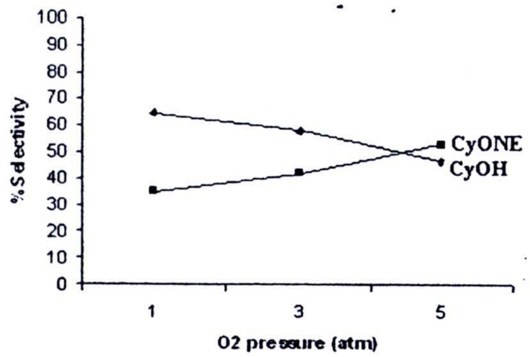


Figure 4.13 Selectivity of cyclohexane oxidation as a function of O_2 pressure

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 5.1wt% , cyclohexane 92 mmol(10ml), H_2O_2/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].

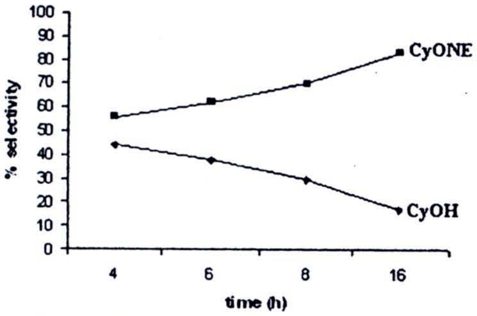


Figure 4.14 Selectivity of cyclohexane oxidation as a function of reaction time.

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), H_2O_2/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].

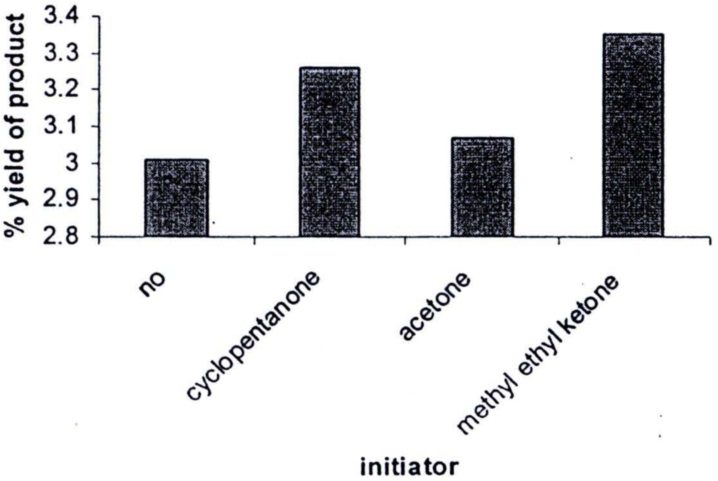


Figure 4.15 Selectivity of cyclohexane oxidation as a function of initiator type.

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_2O_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); H_2O_2/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.

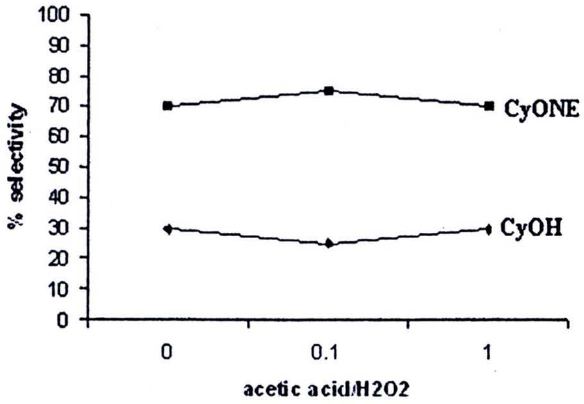


Figure 4.16 Selectivity of cyclohexane oxidation as a function of acetic acid.

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	
		CyOH+CyONE	Acid by-product(%)
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°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]

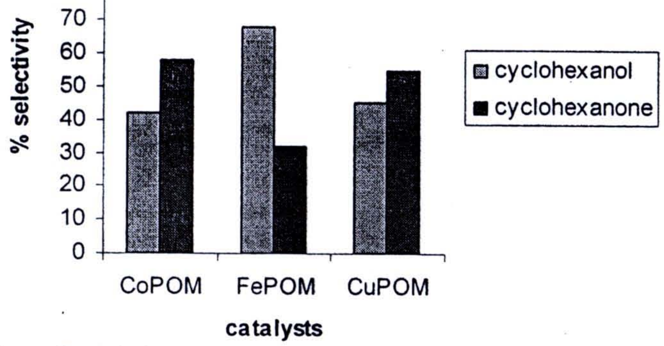


Figure 4.17 Selectivity of cyclohexane oxidation as a function of type of metal.

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.

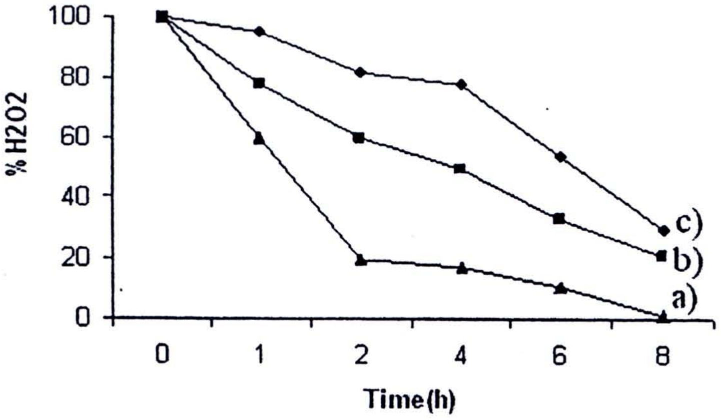


Figure 4.18 Time dependence of the concentration of H_2O_2 in presence of: a) 20%CuPOM/MCM-41, b) 20%CoPOM/MCM-41, c) 20%FePOM/MCM-41.

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°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	CH_3CN(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), H_2O_2/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, H_2O_2/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 CuPOM> CoPOM >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), H_2O_2/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, H_2O_2/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 H_2O_2. As for the selectivity of product, all three methods show only slight increase in cyclohexanol with a decrease in cyclohexanone.

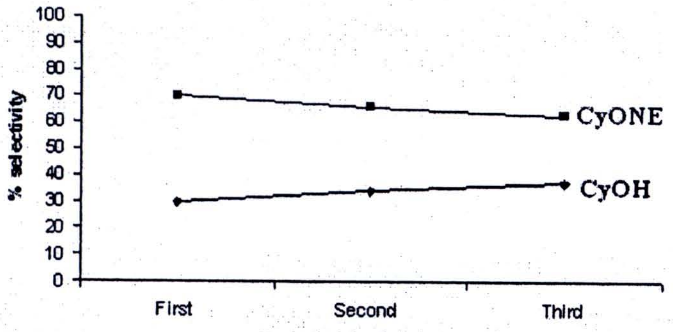


Figure 4.20 Selectivity of cyclohexane oxidation as a function of recycling test 20%CoPOM/MCM-41

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 5.1wt%, 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.

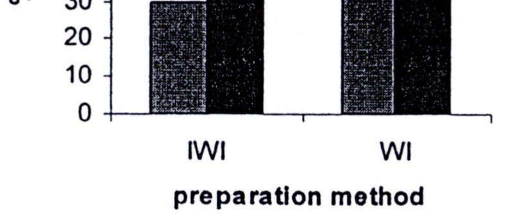


Figure 4.21 Selectivity of cyclohexane oxidation as a function of preparation method

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.

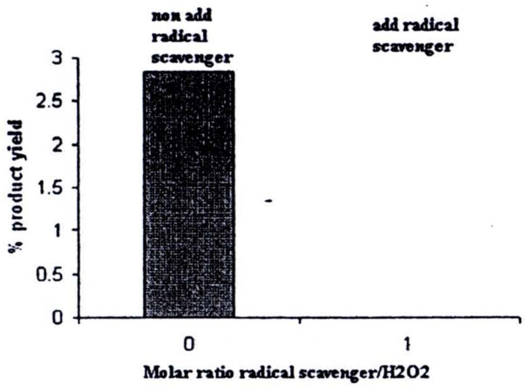


Figure 4.22 The yield of product of cyclohexane oxidation with addition of radical scavenger.

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

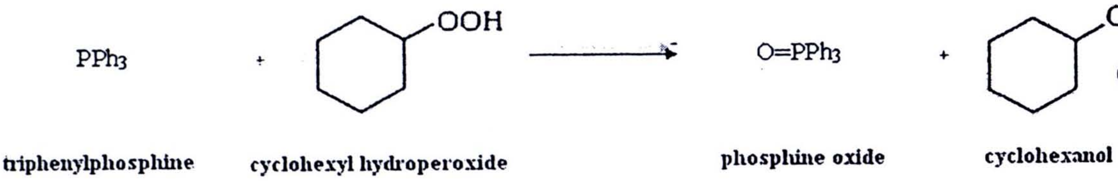
To demonstrate the formation of cyclohexyl hydroperoxide in this oxidation and to estimate its concentration in the course of the reaction, a method by Shulpin was used [45]. An excess of solid PPh_3 was added to the sample before the GC analysis, the cyclohexyl hydroperoxide present was completely reduced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



(2)

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

$$M^{X} + H_2O_2 \rightarrow M^{X+1} + H^{+} + HO\bullet \tag{1}$$

$$HO\bullet + C_6H_{12} \rightarrow H_2O + C_6H_{11}\bullet \tag{2}$$

$$C_6H_{11}\bullet + O_2 \rightarrow C_6H_{11}OO\bullet \tag{3}$$

$$2C_6H_{11}OO\bullet \rightarrow C_6H_{11}OH + C_6H_{11}O + O_2 \tag{4}$$

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