CHAPTER III

RESULTS AND DISCUSSION

Alcohols are one of the most useful raw materials for industrial usage. Products derived from oxidation reaction are generally ketone, aldehyde and carboxylic acid. This research focused on the oxidation of alcohol using iron complexes including iron complexes on support as catalysts. Cyclohexanol was chosen as a substrate model for reaction condition optimization. The other two alcohols, namely benzyl alcohol and 2-octanol, were selected for regioselectivity study. The major oxidant used in this study was *tert*-butylhydroperoxide (TBHP) and a mixture of pyridine and acetic acid was used as a solvent.

3.1 Synthesis and characterization of iron complexes

3.1.1 Schiff base ligands and Schiff base iron complexes

According to the procedure described in section 2.3.1, eight Schiff base ligands were synthesized. The obtained ligands were confirmed their identities by IR and NMR spectroscopy prior to use for synthesizing interested Schiff base iron complexes. IR spectra of all derived complexes showed a characteristic absorption band in the range of 1613-1630 cm^{-1} for C=N group.[36] For ligands, an azomethine group (C=N) vibration appeared at higher frequencies about 10-15 cm^{-1}. This revealed the occurrence of the bonding between metal and nitrogen of imine while the vibration band of O-H group at 3400-3600 cm^{-1} disappeared. The IR spectra of synthesized complexes showed Fe-O stretching vibration while that vibration disappeared in Schiff base ligands.

3.1.2 1,3-Dicarbonyl ligands and 1,3-dicarbonyl iron complexes

The synthesized $Fe(DMB)_3$ and $Fe(BZA)_3$ were characterized by IR. They were prepared by reacting substituted acetophenones and ethyl benzoate or ethyl benzoate derivatives according to the general procedure cited in section 2.3.4. IR spectra of 1,3-dicarbonyl iron complexes showed a characteristic absorption band in the range of 1580-1600 cm^{-1} for C=O group.[37] Likewise absorption band of 1,3-dicarbonyl ligands appeared at lower frequencies about 10 cm^{-1} revealing the bonding between metal and oxygen from enolate ion occurred.

3.2 Study on the optimum conditions for the oxidation of cyclohexanol

3.2.1 Reaction condition optimization

Variable factors were evaluated to search for optimized conditions for the oxidation of cyclohexanol, a model compound. Those factors included type of ligands, the amount of TBHP, and the amount of substrate, reaction time and type of catalyst used. Table 3.1 illustrates the effect of reaction condition in the oxidation of cyclohexanol.

Table 3.1 The oxidation of cyclohexanol catalysed by various iron salts

Entry	Reaction Conditions	Product (%)		Mass balance
		Cyclohexanone	Recovered cyclohexanol	
1	$FeCl_2 \cdot 4H_2O$	35.17	53.58	88.75
2	$FeSO_4 \cdot 7H_2O$	trace	97.16	97.16
3	$Fe(NO_3)_3 \cdot 9H_2O$	6.76	82.61	89.37
4	$FeCl_3 \cdot 6H_2O$	32.26	57.79	90.05
5	$FeCl_3 \cdot 6H_2O$ without acetic acid	39.85	53.46	93.31
6	$FeCl_3 \cdot 6H_2O$ without TBHP	2.32	107.15	109.47
7	Without Fe salt	4.55	111.18	115.25

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) and TBHP (10 mmol), reaction time 24 hrs at 60°C

Table 3.1 clearly revealed that different iron salts and reaction conditions would provide different amounts of the desired products. $FeCl_3 \cdot 6H_2O$ was found to be prevailed over $Fe(NO_3)_3 \cdot 9H_2O$ and $FeSO_4 \cdot 7H_2O$. Entry 5 showed that acetic acid was not an important composition in this oxidation system. However, in the absence of TBHP or iron salt catalyst, the reaction gave poor yield of cyclohexanone.

3.2.2 Effect of type of catalysts

Two types of catalyst, *i.e.*, iron-Schiff base and iron-1,3-dicarbonyl complexes were examined for their efficiency to convert cyclohexanol into its analogous carbonyl compound, cyclohexanone. The reaction was detected at 3 hours interval to observe how fast the oxidation proceeded, while the reaction monitored at 24 hours would notice how much the desired product was obtained in each reaction. The results are illustrated as shown in Table 3.2 and Fig. 3.1.

Table 3.2 Effect of type of catalysts catalysed in oxidation of cyclohexanol

Catalyst	Cyclohexanone (%)		Recovered Cyclohexanol(%)		Mass balance at 24 hrs
	3 hrs	24 hrs	3 hrs	24 hrs	
11	12.76	40.30	98.89	68.47	108.77
12	23.14	29.97	70.71	53.41	83.38
13	28.97	29.69	96.37	68.73	98.42
14	11.59	39.94	94.84	58.26	98.20
15	9.83	20.08	86.80	78.62	98.70
16	11.29	26.63	83.57	58.04	84.67
17	21.80	28.93	60.23	58.46	87.39
18	16.03	36.40	83.84	67.13	103.53
19	5.23	41.18	90.34	45.12	86.30
20	8.70	47.02	86.85	49.56	96.58
21	11.74	35.06	157.02	39.00	74.06

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) and TBHP (10 mmol) at 60°C

note:

(11) Fe salen

(12) Fe saltn

(13) Fe sal-*o*-phen

(14) Fe-4-nitro sal-*o*-phen

(15) (Fe salen)$_2$O

(16) Fe salen(pyridine)$_4$

(17) Fe sal-*o*-phen(pyridine)$_4$

(18) Fe sal-(4-nitro)-*o*-phen(pyridine)$_4$

(19) Fe(BZA)$_3$

(20) Fe(DMB)$_3$

(21) Fe(acac)$_3$

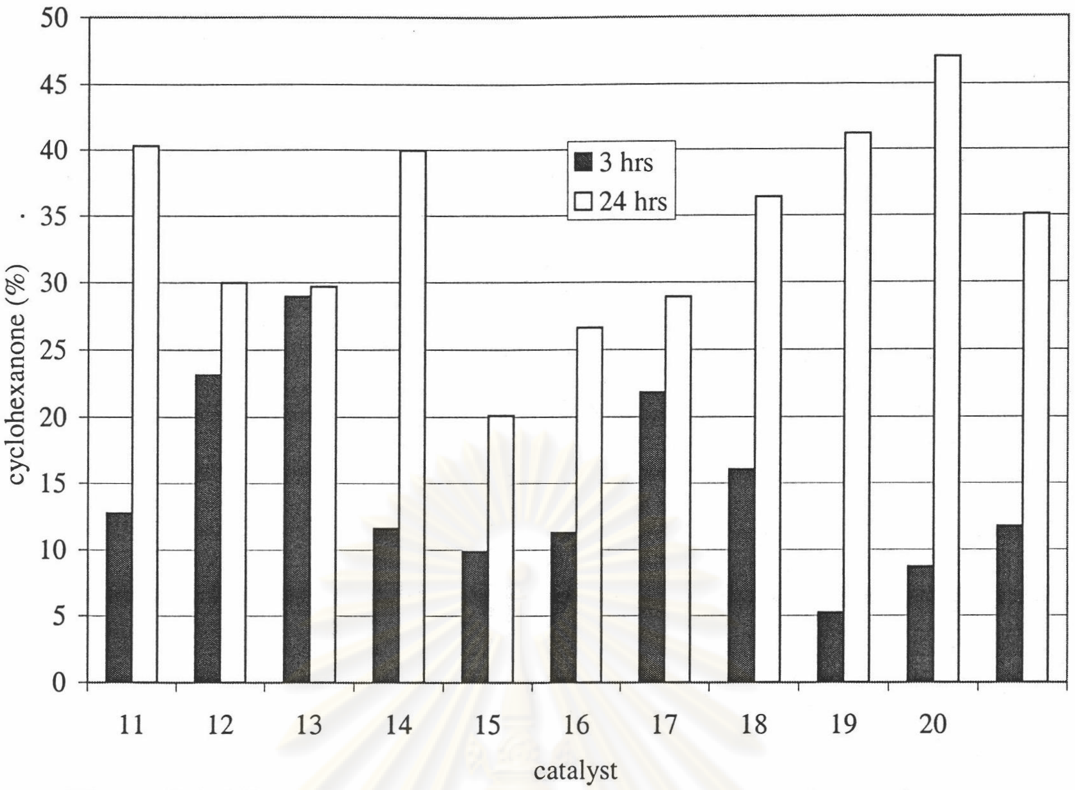


Figure 3.1 Effect of type of catalyst on oxidation of cyclohexanol

The result above revealed that the oxidation reaction in fact could be catalysed by various catalysts; nonetheless, with different level of efficiency. Considering the amount of cyclohexanoe occurred at 3 hours interval, iron Schiff base complexes including Fe sal-*o*-phen(pyridine)$_4$ **(17)**, Fe saltn **(12)** and Fe sal-*o*-phen **(13)** were of a capability in conversion of cyclohexanol to cyclohexanone. Interestingly, Fe sal-*o*-phen **(13)** produced cyclohexanone approximately 29% yield during this period of monitoring time showed the high rate of conversion. Other iron Schiff base complexes, **(11)**, **(14)**, **(15)** and **(16)** gave approximately conversion rate. Different structure of complexes made different reaction rate involving reaction time that ligand complexed with iron. Among iron 1,3-dicarbonyl complexes investigated, Fe(acac)$_3$ **(21)** provided a superior result. However, when two groups of iron catalysts were compared, the rate of the oxidation reaction catalysed by iron Schiff base complexes was found to take place more rapidly than that utilized iron 1,3-dicarbonyl complexes. This may be stemmed from iron 1,3-dicarbonyl complexes had difference structure from iron Schiff base complexes. Taking into the account for the yield observed at 24 hours, iron complexes **(11)**, **(14)**, **(19)** and **(20)** exhibited as promising catalysts.

3.2.3 Effect of temperature on oxidation of cyclohexanol

One crucial parameter in general reaction was temperature. The oxidation reaction was performed at various temperatures to find out the appropriate temperature, *i.e.*, 0°C, RT (28°C), 40°C, 60°C and 100°C. The results are shown in Table 3.3.

Table 3.3 Effect of temperature on cyclohexanol oxidation

Entry	Temperature (°C)	Cyclohexanone (%)	Recovered cyclohexanol (%)	Mass balance
1	0	5.71	89.93	95.64
2	28 (RT)	7.38	86.72	94.10
3	40	12.18	88.93	101.11
4	60	39.26	65.04	104.30
5	100	24.99	66.35	91.34

Reaction conditions: cyclohexanol (10 mmol), Fe salen (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 6 hrs

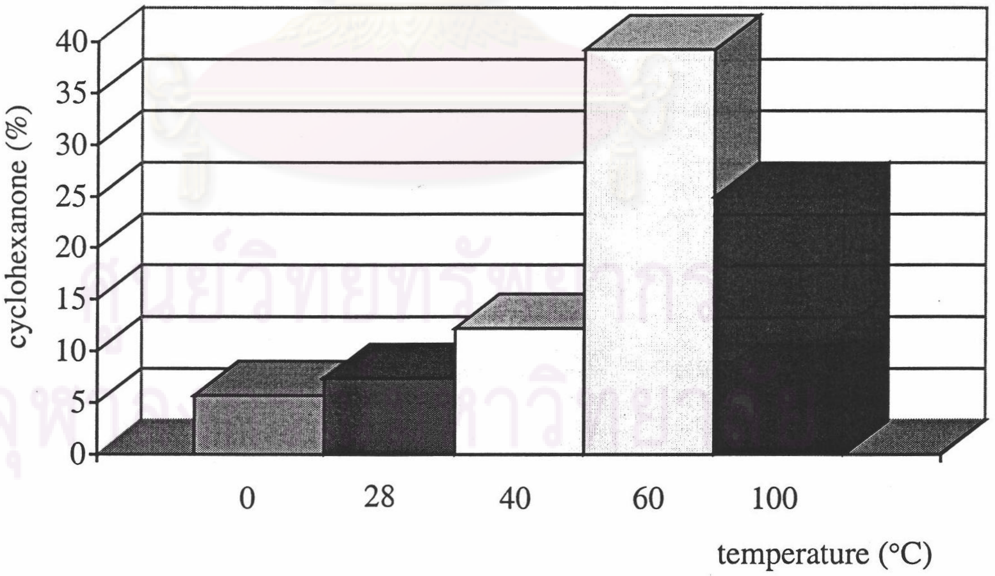


Fig. 3.2 Effect of temperature on cyclohexanol oxidation

Fe(II)salen **(11)** was chosen as a catalyst to study the effect of temperature on cyclohexanol oxidation. From the results shown in Table 3.3 and Fig. 3.4, it was observed that temperature was another important factor affecting the reaction. The highest amount of cyclohexanone was detected with the reaction temperature 60°C. At higher temperature such as 100°C, the over oxidation reaction yielding undesired products may take place.

3.2.4 Effect of type and amount of oxidizing agent

Type of oxidizing agent is another important parameter in oxidation reaction. Various types of oxidizing agents including 30% hydrogen peroxide (H_2O_2), $KMnO_4$, O_2/2-ethylbutyraldehyde and TBHP were chosen. The results are presented as shown in Table 3.4.

Table 3.4 Effect of type of oxidizing agent on the oxidation of cyclohexanol

Oxidizing agent	Cyclohexanone (%)	Recovered cyclohexanol (%)	Mass balance at 24 hrs
30% H_2O_2	trace	104.56	104.56
$KMnO_4$	29.80	41.84	71.64
O_2/2-ethylbutyraldehyde	trace	105.86	105.86
TBHP	35.49	59.43	94.92

Reaction conditions: cyclohexanol (10 mmol), Fe salen (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), oxidizing agent (10 mmol), reaction time 24 hrs at 60°C

Among various oxidizing agents studied, TBHP was found to be the most appropriate oxidizing agent based on its efficiency towards the transformation of cyclohexanol to cyclohexanone. Thus, the amount of TBHP affected the oxidation reaction was the next influent parameter to be examined. The results are accumulated as presented in Table 3.5 and Fig 3.3.

Table 3.5 Effect of the amount of TBHP on the oxidation of cyclohexanol

Entry	TBHP (mmol)	Cyclohexanone (%)	Recovered cyclohexanol (%)	Mass balance
1	0	4.71	103.58	108.29
2	1	7.02	108.08	115.10
3	3	12.75	102.58	115.33
4	5	16.53	75.68	92.21
5	10	35.49	59.43	94.92
6	20	28.58	61.95	90.53

Reaction conditions: cyclohexanol (10 mmol), Fe salen (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) reaction time 6 hrs at 60°C

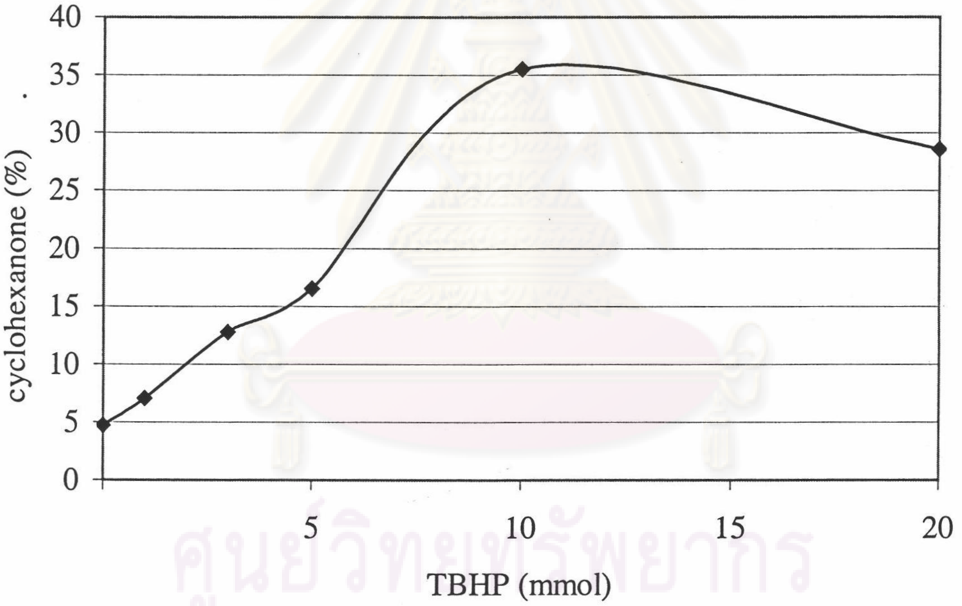


Figure 3.3 Effect of the amount of TBHP on oxidation of cyclohexanol

From data shown above, focusing on the reaction in the absence of TBHP, it was found that cyclohexanone was detected in a small quantity (4.71%). This was probably derived from the air oxidation. Efficiency of reaction based on TBHP indicated the ability of TBHP in conversion of cyclohexanol to cyclohexanone. Fig. 3.3 illustrates that the reaction utilizing TBHP 10 mmol provided the highest amount of the desired product, cyclohexanone. The use of TBHP 20 mmol gave less cyclohexanone and the mass balance of the reaction was only 91%. This might be because the over oxidation of cyclohexanone was taken place. Therefore, for all reaction optimization study, the amount of the oxidizing agent, TBHP 10 mmol was kept constant.

3.2.5 Effect of the amount of substrate

Another significant feature that also needs to study was the effect of the amount of the substrate. The amount of cyclohexanol was varied and the results are shown in Table 3.6.

Table 3.6 Effect of the amount of cyclohexanol on the oxidation reaction

Entry	Cyclohexanol (mmol)	Cyclohexanone (%)	Recovered cyclohexanol (%)	Mass balance
1	2	24.11	67.84	91.95
2	5	21.99	90.92	112.91
3	10	35.49	59.43	94.92
4	20	20.70	55.28	75.98

Reaction conditions: cyclohexanol (varied), Fe salen (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol), reaction time 6 hrs at 60 °C

From Table 3.6, it could clearly observe that the more substrate, cyclohexanol used, the more product, cyclohexanone was attained. The amount of cyclohexanol had a strong influence on the obtained yield. The maximum yield was obtained when cyclohexanol 10 mmol was employed. The use of cyclohexanol 20 mmol gave the yield less than 10 mmol. Excess quantity of substrate cause of over oxidation and cyclohexanol 10 mmol was sufficient amount for this reaction conditions.

3.2.6 Kinetic study on the reaction rate of cyclohexanol oxidation

The kinetic study on the rate of cyclohexanol oxidation was conducted utilizing two iron catalysts: $FeCl_3 \cdot 6H_2O$ and Fe salen **(11)**. Their kinetic analysis results are shown in Table 3.7 and Fig. 3.4.

Table 3.7 Effect of reaction time on cyclohexanol oxidation

Time (hrs)	Cyclohexanone (%)	
	$FeCl_3{\cdot}6H_2O$	Fe salen
2	20.65	11.82
4	30.46	15.91
6	39.26	21.08
24	32.26	41.13
48	24.70	44.35

Reaction conditions: cyclohexanol (10 mmol), iron catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60 °C

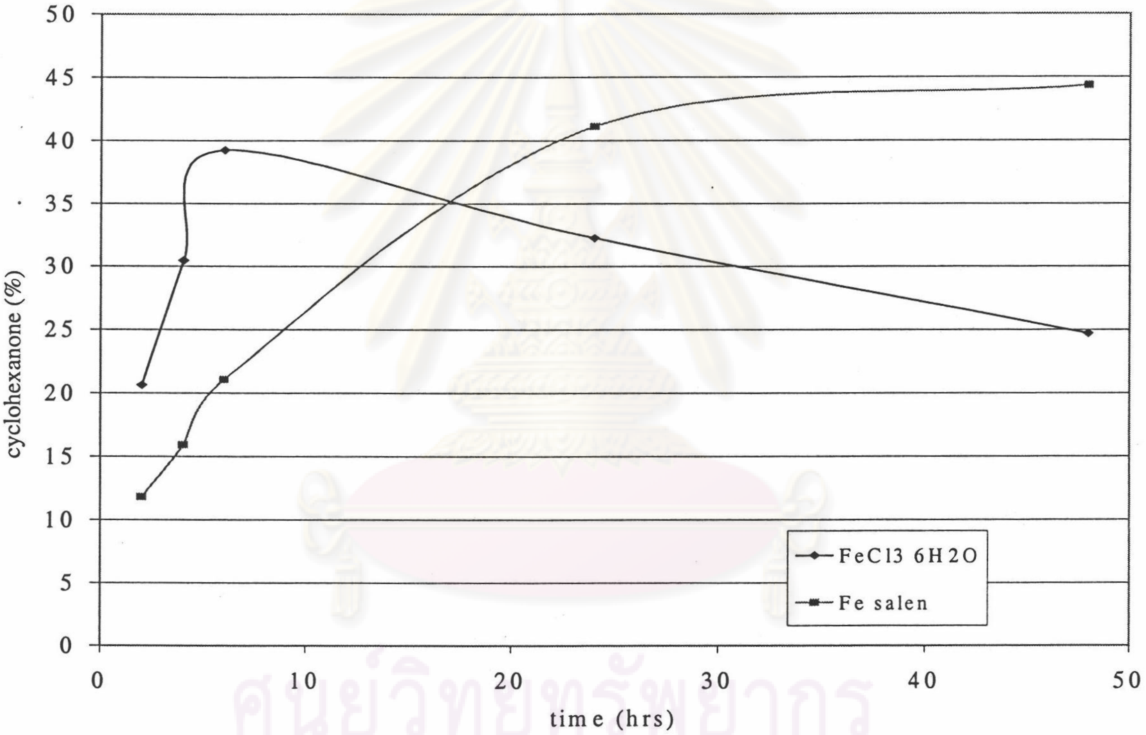


Fig.3.4 Kinetic analysis for oxidation of cyclohexanol

From the results shown above, it was found that the reaction time was also the significant factor to affect the reaction rate. Considering the results exhibited in Table 3.7, it was noticed that the oxidation using different catalysts proceeded with different rates. The oxidation reaction using $FeCl_3{\cdot}6H_2O$ as a catalyst gave interesting results since the reaction could take place rapidly. The highest yield reached within 6 hours. Nevertheless, under the conditions studied $FeCl_3{\cdot}6H_2O$ could catalyze further oxidation of the desired product to unwanted compound(s). The amount of cyclohexanone was thus lessen. In contrast to the system utilized Fe salen **(11)** catalysts, even the reaction took place not as rapidly as that of $FeCl_3 \cdot 6H_2O$, the oxidation could proceed smoothly and produced more desired product than other systems examined.

3.2.7 Comparative study on cyclohexanol oxidation caalyzed by iron complexes and iron complexes on support

The cyclohexanol oxidation catalysed by iron salts: $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot H_2O$: iron complex: $Fe(acac)_3$ and iron catalyst on support was conducted. Supporting material chosen were silica gel and celite. The comparative oxidation results are addressed as shown in Table 3.8.

Table 3.8 Cyclohexanol oxidation catalysed by iron complexes and iron catalyst on support

Entry	Catalyst	Percentage		Mass balance
		Cyclohexanone	Recovered cyclohexanol	
1	$Fe(acac)_3$	35.06	58.72	93.78
2	$Fe(acac)_3$ on silica gel	39.97	56.40	96.37
3	$Fe(acac)_3$ on celite	15.85	87.89	103.74
4	$Fe(NO_3)_3 \cdot 9H_2O$	10.52	105.79	116.31
5	$Fe(NO_3)_3 \cdot 9H_2O$ on silica gel	5.38	86.98	92.36
6	$Fe(NO_3)_3 \cdot 9H_2O$ on celite	13.55	106.51	120.06
7	$FeCl_3 \cdot 6H_2O$	31.05	55.62	86.67
8	$FeCl_3 \cdot 6H_2O$ on silica gel	5.38	86.90	92.28

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) reaction time 24 hrs at 60°C

As presented in Table 3.8, the oxidation employing Fe(acac)$_3$ and Fe(acac)$_3$ on silica gel gave similar results. However, the oxidation using Fe(acac)$_3$ on celite, on the other hand, produced less amount of the desired product. The reactions carried out utilizing $Fe(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ on celite gave comparable results, while the reaction using $Fe(NO_3)_3 \cdot 9H_2O$ on silica gel provided very poor yield of cyclohexanone. Entries 7 and 8 manifestly displayed the distinct feature of homogeneous and heterogeneous catalysts. To illustrate this, the former $FeCl_3 \cdot 6H_2O$ produced cyclohexanone over 30% yields, whereas the latter catalyst provided significantly less amount of the desired product. This may be from low efficiency in impregnation was occurred.

3.2.8 Kinetic study employing Fe(acac)$_3$ and Fe(acac)$_3$ on support

The kinetic study of cyclohexanol oxidation employing Fe(acac)$_3$ and Fe(acac)$_3$ on support was carried out. The results are tabulated in Table 3.9.

Table 3.9 Kinetic study on cyclohexanol oxidation catalysed by Fe(acac)$_3$ and Fe(acac)$_3$ on support

Entry	Time (hrs)	% Cyclohexanone		
		Fe(acac)$_3$	Fe(acac)$_3$ on silica gel	Fe(acac)$_3$ on celite
1	3	11.74	6.04	0
2	24	35.06	39.97	15.85
3	48	37.95	34.13	39.96
4	72	37.86	35.41	48.27

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) and TBHP (10 mmol) at 60°C

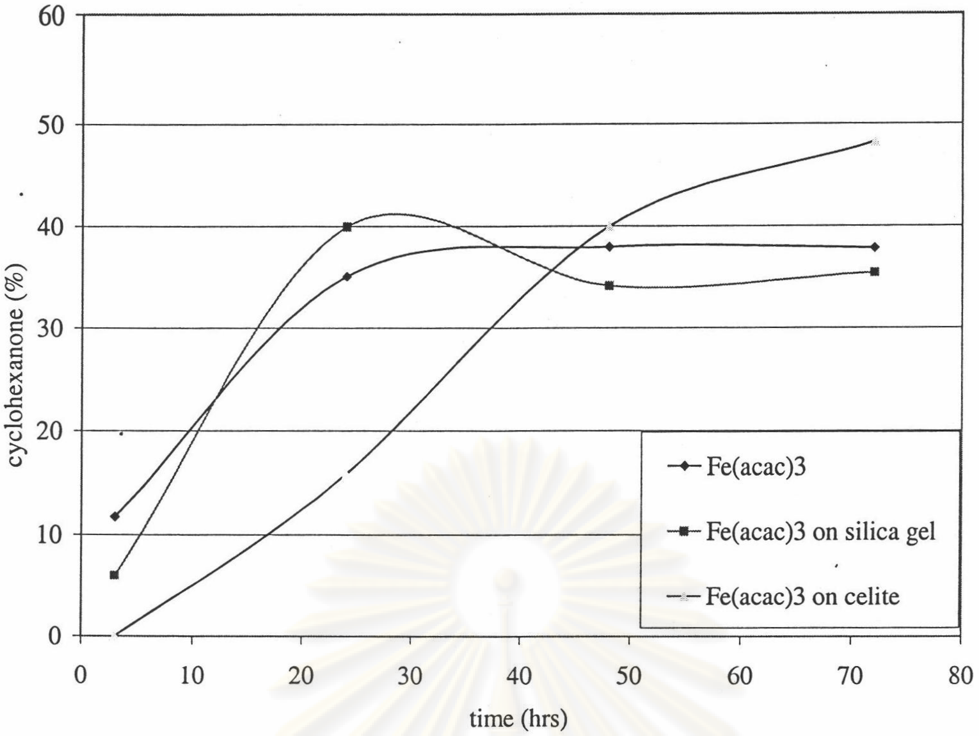


Fig.3.5 Comparative study on cyclohexanol oxidation catalysed by Fe(acac)$_3$, Fe(acac)$_3$ on silica gel and Fe(acac)$_3$ on celite

The results addressed in Table 3.9 and Fig 3.5 revealed that Fe(acac)$_3$ and Fe(acac)$_3$ on silica gel provided similar results. The use of Fe(acac)$_3$ on celite as a catalyst gave interesting result. In the initial step, the rate seemed to be slower than those systems using the other two catalysts. However, the yield of the desired product was reached approximately 50% yield after the reaction time was carried out for three days.

3.2.9 Effect of the second addition of TBHP on cyclohexanol oxidation

In order to improve the yield of cyclohexanone, the attempt to add the second portion of TBHP (10 mmol) was conducted. The progress of the oxidation reactions catalysed by both Fe(acac)$_3$ and Fe(acac)$_3$ on silica gel were monitored at 3 and 24 hours intervals. The results are presented as illustrated in Table 3.10.

Table 3.10 Effect of the second addition of TBHP on cyclohexanol oxidation

Entry	Time (hrs)	Cyclohexanone (%)	
		$Fe(acac)_3$	$Fe(acac)_3$ on silica gel
	1st addition		
1	3	17.40	6.00
2	24	48.60	61.30
	2nd addition		
3	24+3	60.20	58.30
4	24+24	69.10	67.60

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

The attempt of the addition of the second portion of TBHP gave good results. The cyclohexanone was produced almost twice upon the addition of the oxidant utilizing either $Fe(acac)_3$ or $Fe(acac)_3$ on silica gel.

3.2.10 Further study on $Fe(acac)_3$ on silica gel catalysed cyclohexanol oxidation

Based upon the observation that the solution of the oxidation catalysed by $Fe(acac)_3$ on silica gel turned to be brown during the reaction proceeded, the assumption that iron complex may not impregnate on silica gel was conceivable. To prove this assumption, the cyclohexanol oxidation was performed as described in the general procedure. The catalyst was then filtered off to yield the solid part, designated as portion **A**. The brown filtrate was named as portion **B**. These two fractions were then put back to the oxidation reaction of cyclohexanol. The results are shown as presented in Table 3.11.

Table 3.11 The cyclohexanol oxidation catalysed by $Fe(acac)_3$ on silica gel

Entry	Reaction conditions	Cyclohexanone (%)	Mass balance
1	$Fe(acac)_3$ on silica gel, Without TBHP, 3 hrs	4.10	115.78
2	Portion **A**, 3 hrs	3.28	95.71
3	Portion **A**, 24 hrs	30.82	118.17
4	Portion **B**, 3 hrs	4.29	79.25
5	Portion **B** , 24 hrs	9.03	113.04

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

It was clearly visualized from Table 3.11 that $Fe(acac)_3$ was still stuck on the support, silica gel. The oxidation employing in filtered solid portion **A** could still be used as a catalyst in the reaction. The filtrate **B** could also assist the cyclohexanol oxidation, but in a lesser extent. Thus, $Fe(acac)_3$ on silica gel could be utilized as a good iron catalyst on support.

3.2.11 Effect of doped silica gel on cyclohexanol oxidation

Another type of iron catalyst on support, doped silica gel was investigated. Sal-*o*-phen on doped silica gel complexed with Fe(II) was utilized as a catalyst. The comparative results of cyclohexanol oxidation using Fe sal-*o*-phen **(11)** and Fe sal-*o*-phen on doped silica gel **(22)** are illustrated as presented in Table 3.12.

Table 3.12 Comparative study between Fe sal-*o*-phen and Fe sal-*o*-phen on doped silica gel catalysed cyclohexanol oxidation

Entry	Catalyst	Cyclohexanone (%)						
		2 hrs	4 hrs	6 hrs	8 hrs	24 hrs	48 hrs	72 hrs
1	**(11)**	trace	trace	trace	trace	trace	trace	9.16
2	**(22)**	trace	8.61	10.73	12.04	25.19	31.65	36.87

Reaction conditions: cyclohexanol (10 mmol), catalyst (0.025 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

(11) Fe sal-*o*-phen
(22) Fe sal-*o*-phen on doped silica gel

From Table 3.12, it was clearly revealed that the reaction catalysed by **(22)** provided superior results. The reaction took place more rapidly than that without support. This interesting results are still called for further thorough investigation.

3.3 Oxidation of benzyl alcohol

Benzyl alcohol could be oxidized to its corresponding carbonyl compound, benzaldehyde, by suitable conditions. There are many reports involving the oxidation reaction of benzyl alcohol. In general, product derived from the oxidation of benzyl alcohol was mainly benzaldehyde. Other products may include benzoic acid, carbon dioxide, benzene and toluene in small amount.[38] From previous literature, it was reported that hydrogen peroxide (H_2O_2) was investigated in the alcohol oxidation using heteropolyacid in conjunction with phase transfer catalysts in oxidation of benzyl alcohol yielding benzaldehyde.[39] Moreover, oxygen molecule was also widely used under this particular reaction. It was reported that the oxidation of benzyl alcohol occurred over pumice supported bimetallic and monometallic Pd and Ag catalysts.

3.3.1 Effect of reaction time on benzyl alcohol oxidation

The effect of reaction time on benzyl alcohol oxidation was investigated. The results are illustrated in Table 3.13.

Table 3.13 Kinetic study on benzyl alcohol oxidation

Entry	Time (hrs)	Product (%)		Mass balance
		Benzaldehyde	Recovered Benzyl alcohol	
1	2	27.51	60.16	87.67
2	4	33.54	53.78	87.32
3	6	37.24	48.18	85.42
4	10	34.68	49.28	83.96

Reaction conditions: Benzyl alcohol (10 mmol), $FeCl_3\cdot 6H_2O$ (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

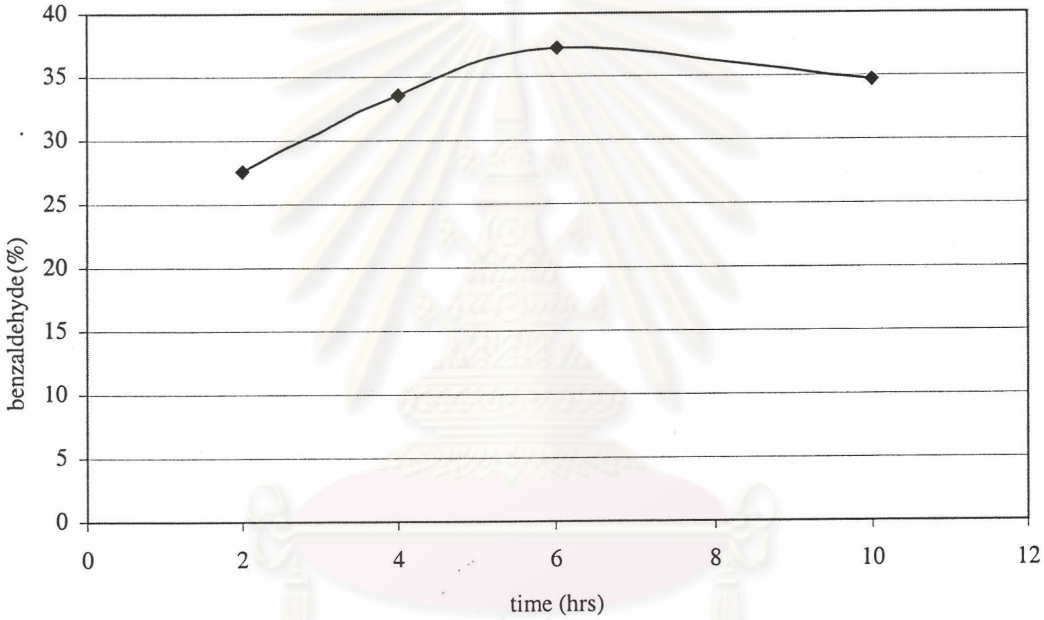


Figure 3.6 Kinetic results on benzyl alcohol oxidation

From Table 3.13 and Fig. 3.6, the major product attained from the reaction was benzaldehyde. The oxidation reaction proceeded quite rapidly. However, the mass balance of the reaction was approximately 85%. This implied that perhaps another oxidized product, benzoic acid which derived from the further oxidation of benzaldehyde was taken place.

3.3.2 Effect of type of catalyst on benzyl alcohol oxidation

Some iron complexes were emploted as catalyst in oxidation of benzyl alcohol. The results are illustrated as shown in Table 3.14.

Table 3.14 Effect of type of catalyst on benzyl alcohol oxidation

Catalyst	Benzaldehyde		Recovered benzyl alcohol		Mass balance
	3 hrs	24 hrs	3 hrs	24 hrs	
Fe sal-*o*-phen	27.72	29.16	62.84	55.87	85.03
Fe sal-*o*-phen (pyridine)$_4$	29.19	30.03	66.23	68.35	98.38
Fe salen(pyridine)$_4$	26.92	27.28	61.39	55.60	82.88
$FeCl_3 \cdot 6H_2O$	22.86	27.81	49.90	53.96	81.77

Reaction conditions: Benzyl alcohol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL) at 60°C

Four different iron complexes were used as a catalyst in the oxidation of benzyl alcohol. It was observed that the reaction took place rapidly: however, the amount of benzaldehyde attained was not different.

3.3.3 Effect of supported catalyst on benzyl alcohol oxidation

The comparative study on the oxidation of benzyl alcohol using iron complexes and iron catalyst on support was carried out. The results are illustrated as shown in Table 3.15.

Table 3.15 Oxidation of benzyl alcohol catalysed by supported catalyst

Catalyst	Benzaldehyde		Recovered benzyl alcohol	
	3 hrs	24 hrs	3 hrs	24 hrs
$FeCl_3 \cdot 6H_2O$ on silica gel	28.44	28.66	62.14	48.97
$Fe(NO_3)_3 \cdot 9H_2O$ on silica gel	trace	28.91	110.81	55.29

Reaction conditions: Benzyl alcohol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

From the results presented in Table 3.15, it was noticed that $FeCl_3{\cdot}6H_2O$ on silica gel could catalyze the oxidation reaction much more efficient than $Fe(NO_3)_3{\cdot}9H_2O$ on silica gel.

To ensure that silica gel was a good support for $FeCl_3{\cdot}6H_2O$, a set of experiments was carried out. The oxidation reaction was performed in the presence of $FeCl_3{\cdot}6H_2O$, but in the absence of TBHP for 6 hrs. Only trace amount of oxidized product was obtained from this reaction. The catalyst was then filtered and resubmitted to the oxidation reaction with the addition of TBHP 10 mmol. Benzaldehyde was still observed as small amount. On the contrary, the filtrate from the previous reaction could catalyze the oxidation of benzyl alcohol. Benzaldehyde was detected in the amount comparable with the normal oxidation reaction performed. Consequently, it could be concluded that $FeCl_3{\cdot}6H_2O$ did not impregnate on silica gel well compared with $Fe(acac)_3$ as previous discussed (section 3.2.10).

3.4 Oxidation of 2-octanol

The product derived from the oxidation of 2-octanol is 2-octanone. Different conditions such as temperature, the amount of substrate, and the amount of catalyst, type of solvent or stirring speed affected on the product yield. The oxidation of 2-octanol was reported employing molecular oxygen and *N*-hydroxyphthalimide in the presence of a Co species. The reaction proceeded with high efficiency at 70°C yielding 2-octanone in high yield.[40] Various catalysts were utilizing in the oxidation of 2-octanol, *i.e.,* silica supported NiO_2, MnO_2, Fe_2O_3, ZnO, titanium dioxide supported on silica gel and 0.5 %wt palladium/alumina catalysed in the reaction at 80-140°C and 75-125 bar of oxygen.[41] In this study, various iron complexes were screened to search for a potential catalyst for the oxidation reaction of 2-octanol. The results are presented as shown in Table 3.16.

Table 3.16 Effect of type of catalysts on 2-octanol oxidation

Catalyst	2-Octanone (%)		Recovered 2-Octanol (%)		Mass balance at 24 hrs
	3 hrs	24 hrs	3 hrs	24 hrs	
Fe saltn	21.32	36.68	73.49	74.28	110.96
Fe sal-*o*-phen(pyridine)$_4$	20.71	28.04	72.12	79.35	107.39
Fe salen(pyridine)$_4$	13.08	25.25	69.04	70.93	96.18
Fe sal-*o*-phen	13.72	30.53	62.11	67.03	97.56
Fe(BZA)$_3$	18.06	45.13	94.36	72.11	117.24

Reaction conditions: 2-octanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

Among iron complexes investigated, Fe(BZA)$_3$ **(19)** was clearly revealed as a good candidate catalyst for 2-octanol oxidation. Fe saltn **(12)** and Fe sal-*o*-phen(pyridine)$_4$ **(17)** were also found to catalyze this oxidation reaction with a good extent.

3.4.1 Effect of iron catalyst on support on 2-octanol oxidation

The comparative examination of the effect of iron complexes and iron catalyst on support on 2-octanol oxidation was carried out. The results are tabulated as shown in Table 3.17.

Table 3.17 Effect of supported catalysts on 2-octanol oxidation

Catalyst	2-Octanone (%)		Recovered 2-Octanol (%)		Mass balance at 24 hrs
	3 hrs	24 hrs	3 hrs	24 hrs	
$FeCl_3{\cdot}6H_2O$	15.26	29.55	69.90	51.26	80.81
$FeCl_3{\cdot}6H_2O$ on silica gel	25.61	36.01	78.04	70.62	106.63
$Fe(NO_3)_3{\cdot}9H_2O$ on silica gel	10.41	30.90	85.42	51.78	82.68

Reaction conditions: 2-octanol (10 mmol), catalyst (0.25 mmol), pyridine (28 mL), acetic acid (2.3 mL), TBHP (10 mmol) at 60°C

The results shown above provided intriguing points. $FeCl_3{\cdot}6H_2O$ on silica gel could catalyze the oxidation reaction of 2-octanol very efficiently. The yield was superior to that attained from the other two oxidation systems ($FeCl_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ on silica gel). This finding may be due to the effect of support, silica gel assisted the reaction with $FeCl_3{\cdot}6H_2O$.

3.5 Comparative efficiency of the oxidation reaction catalysed by iron salen supported on doped silica gel

The comparative study on the oxidation of three model alcohols: cyclohexanol, benzyl alcohol and 2-octanol catalysed by iron on doped silica gel was examined. The results are collected in Table 3.18.

Table 3.18 Comparative result from the oxidation of model alcohols catalysed by Fe salen on doped silica gel

Time (hrs)	Product (%)		
	Cyclohexanone	Benzaldehyde	2-octanone
2	trace	trace	4.56
4	trace	trace	4.57
6	trace	trace	5.03
8	trace	trace	3.75
24	trace	trace	4.90
48	trace	9.48	8.38

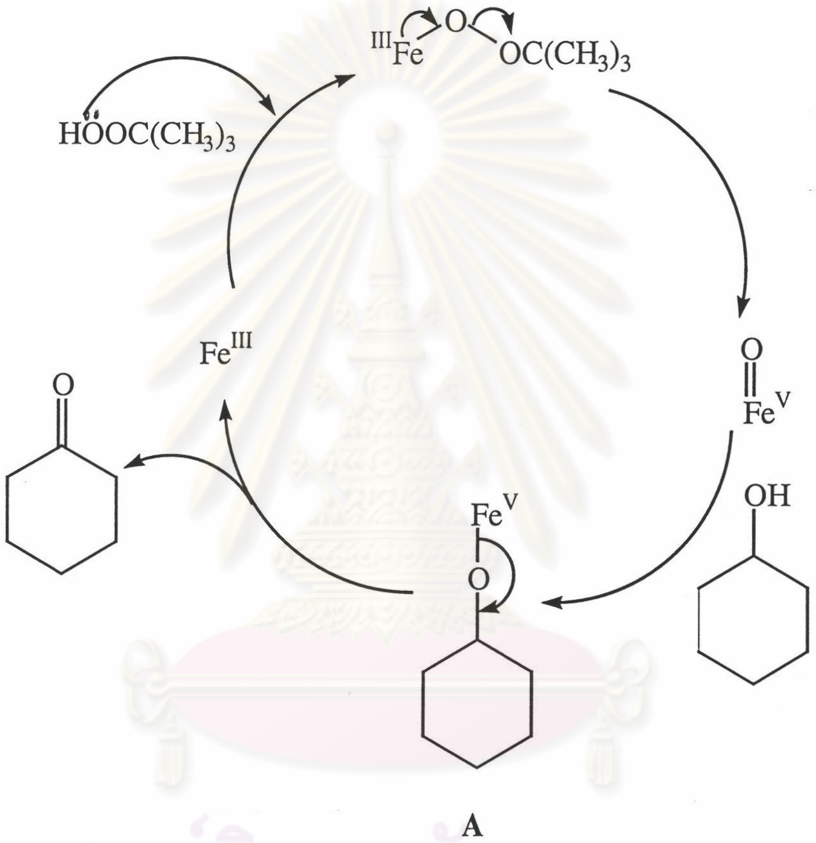
Reaction conditions: substrate (10 mmol), Fe salen on doped silica gel (0.025 mmol), pyridine (28 mL), acetic acid (2.3 mL) and TBHP (10 mmol) at 60°C

The results displayed in Table 3.18 revealed crucial points. Comparison with the results obtained when utilizing Fe sal-*o*-phen on doped silica gel, it was observed that the oxidation reaction proceeded more rapidly than that using Fe salen on doped silica gel. Considering the rat of the oxidation reactions with three model alcohols, it was clearly seen that 2-octanol could be easily oxidized under this particular condition. However, the rate of the reaction was far slower than the soluble iron catalysts.

For further application, the use of iron catalysts on support may be of advantages. The ease of separation of catalysts and desired products should be the attractive feature for this developed system.

3.6 Proposed mechanism for iron catalysed oxidation of alcohols

The mechanism of the iron catalysed oxidation of alcohols using TBHP as an oxidant was proposed as depicted in Scheme 3.1. The high valent iron species (formally $Fe^{V}=O$)[42] was formed in the first step and responsible as a real oxidant for the oxidation of alcohol. The interaction between alcohol and high valent iron species would produce intermediate like **A** which would then be collapsed to the final product.



Scheme 3.1 The proposed mechanism for the iron catalysed oxidation of alcohol using TBHP as an oxidizing agent