

# HYDROXYLATION OF 2-METHYLNAPHTHALENE TO 2-METHYLNAPHTHOQUINONE OVER TI-SUBSTITUTED CATALYSTS

*by*

**Jamey Rose**

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**Supervised by**

Dr L.H. Callanan

**STELLENBOSCH**

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## DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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## SYNOPSIS

Partially oxygenated aromatic compounds, e.g. quinones, hydroquinones and cresols, play a vital role in the fine chemical industry and were initially prepared by stoichiometric oxidation processes that produce toxic products that are hazardous towards the environment. As a result, it was important to investigate environmentally friendly processes for the hydroxylation of aromatic compounds. This resulted in newer methods using Ti-substituted microporous zeolites as catalysts with hydrogen peroxide as oxidant in the presence of a solvent.

However, the methods were found to be ineffective for large, bulky substrates due to the small pore structure. This led to using Ti-mesoporous materials as catalysts but suffered from two drawbacks; the hydrophilic nature and low hydrothermal stability of the catalyst structure. Ti-microporous and Ti-mesoporous materials acting as catalysts for the oxidation of bulky substrates achieved environmentally friendly processes but obtained low conversions and quinone yields. Therefore, the challenge has been to develop a process that is environmentally friendly, achieves high conversions, where the catalyst acts truly heterogeneous and obtains high quinone yields for the hydroxylation of bulky substrates. Recently, micropores/mesopores catalysts incorporating advantages of both micropores and mesopores materials were synthesised and seemed promising for the hydroxylation of bulky substrates.

This study focuses on synthesising and evaluating the feasibility of various Ti-substituted catalysts for improving the hydroxylation of the bulky substrate, 2-methylnaphthalene (2MN) with hydrogen peroxide as oxidant in the presence of a solvent, acetonitrile. The oxidation of 2MN produces 2-methyl-1,4-naphthoquinone (2MNQ). 2MNQ is also known as menadione or Vitamin K<sub>3</sub> and acts as a blood coagulating agent. The catalysts synthesised for this study were mesoporous catalysts, Ti-MCM-41 and Ti-MMM-2 and microporous/mesoporous catalysts, Ti-MMM-2(P123) and a highly ordered mesoporous material. The main objective of this study was to design an efficient process that is environmentally friendly and achieves high 2MN conversions and 2MNQ yields. This was achieved by evaluating the various catalysts synthesised, reaction conditions, testing if the catalyst was truly heterogeneous and identifying the products formed from the process.

The designed process was proved to be environmentally friendly because the system did not produce products that were harmful towards the environment. The products identified in this study were 2MNQ, 2-methyl-1-naphthol, 2-naphthaldehyde, 3-ethoxy-4-methoxybenzaldehyde and menadione epoxide. An investigation was conducted to determine which catalyst synthesised favoured this process by quantifying the effect reaction conditions have on the various catalysts. The reaction conditions were defined in terms of the hydrogen peroxide volume, catalyst amount, solvent volume, substrate amount, reaction time and reaction temperature. The desired catalyst for this study obtained the highest 2MN conversions in comparison with the other catalysts and favoured the formation of 2MNQ. The catalyst achieving the highest conversions and favouring 2MNQ in most cases for this investigation was the highly ordered mesoporous material.

Improving operating conditions to obtain high 2MNQ yields for the oxidation of 2MN to 2MNQ over the highly ordered mesoporous material was determined by varying the reaction conditions with the one factor at a time approach and a factorial design. The one factor at a time approach showed that best 2MNQ yields were obtained at 1 g substrate when investigating a change in substrate amount between 0.5 g and 2 g. Best 2MNQ yields were obtained at 10 ml solvent when investigating a change of solvent volume between 5 ml and 20 ml. The 2MNQ yield increased with increasing the catalyst amount (50 mg to 200 mg), hydrogen peroxide volume (1 ml to 6 ml) and increasing the reaction times (2 hour to 6 hours) at reaction temperatures, 120°C and 150°C. The yield decreased with increasing the reaction time (2 hours to 6 hours) at reaction temperature, 180°C. A preliminary 2 level factorial design was prepared to observe if there were any important interactions affecting the 2MNQ yield. The results from the factorial design indicated that the hydrogen peroxide volume had the most influence on the 2MNQ yield followed by the reaction time-reaction temperature interaction and reaction temperature. From the factorial design, the yield increased by increasing the hydrogen peroxide volume and reaction temperature whilst decreasing the reaction temperature-reaction time interaction. The highest 2MNQ yields and 2MN conversions obtained for the hydroxylation of 2MN to 2MNQ over the highly ordered mesoporous material in this study were in the ranges 48-50 % and 97-99 %, respectively.

This study indicates that the process system, reaction conditions and catalyst type have an impact on the products formed, 2MN conversion, 2MNQ selectivity and 2MNQ yield. The highly ordered mesoporous material was found to be truly heterogeneous because no leaching occurred and the catalyst could be recycled without losing its catalytic activity and selectivity for at least two catalyst cycles. It can be concluded that the highly ordered mesoporous material is therefore a promising catalyst for the selective oxidation of bulky substrates with aqueous H<sub>2</sub>O<sub>2</sub> because it produces an environmentally friendly process, achieves high conversions, obtains high quinone yields and the catalyst truly acts heterogeneous.

## OPSOMMING

Gedeeltelik geoksideerde aromatiese verbindings (bv. kinone, hidrokinone en kresole) speel 'n belangrike rol in die fynchemiebedryf. Hierdie verbindings is aanvanklik voorberei deur stoïchiometriese oksidasie prosesse wat giftowwe nadelig vir die omgewing veroorsaak. Daarom is dit belangrik om omgewingsvriendelike prosesse vir die hidroksilering van aromatiese verbindings te ondersoek. Hierdie ondersoek het gelei tot nuwe metodes wat Ti-vervangende mikroporeuse seoliete as katalisator met waterstofperoksied as oksideermiddel in die teenwoordigheid van 'n oplosmiddel benut.

Dit is egter gevind dat hierdie metodes oneffektief is vir groot, lywige substrate weens die fyn poriestruktuur van die katalisator. Dit lei tot die gebruik van Ti-mesoporeuse materiale as katalisators, maar toon twee tekortkominge, naamlik die hidrofiliese aard en lae hidrotermiese stabiliteit van die katalisatorstruktuur. Ti-mikroporeuse en Ti-mesoporeuse materiale benut as katalisators vir die oksidasie van lywige substrate lewer omgewingsvriendelike prosesse, maar vermag lae omsetting en kinaonopbrengs. 'n Uitdaging is dus om 'n omgewingsvriendelike proses te ontwikkel met hoë omsetting, waar die katalisator werklik heterogeen optree en hoë kinaonopbrengs lewer vir die hidroksilering van lywige substrate. Katalisators vir die hidroksilering van lywige substrate wat die voordele van beide mikroporieë/mesoporieë ten toon stel is onlangs gesintetiseer, met belowende resultate.

Hierdie studie is ingestel op die sintetisering en evaluering van uitvoerbaarheid van verskeie Ti-vervangende katalisators vir die optimering van die hidroksilering van die lywige substraat, 2-metielnaftaleen (2MN), met waterstofperoksied as oksideermiddel met asetonitriël as oplosmiddel. Die oksidering van 2MN produseer 2-metiel-1,4-naftokinoon (2MNK), ook bekend as vitamien K<sub>3</sub>, 'n bloedstollingsmiddel. Die katalisators vervaardig vir hierdie studie was die mesoporeuse katalisators, Ti-MCM-41 en Ti-MMM-2, en die mikroporeuse/mesoporeuse katalisator Ti-MMM-2(P123), sowel as 'n hoogs geordende mesoporeuse materiaal. Die hoofdoel van hierdie studie was om 'n doeltreffende, omgewingsvriendelike proses met hoë 2MN omsetting en 2MNK opbrengs te ontwerp. Voorgenoemde is vermag deur verskeie gesintetiseerde katalisators en reaksiekondisies te evalueer, om te toets of katalisators werklik heterogeen is, en om die prosesprodukte te identifiseer.

Die ontwerpde proses kan beskou word as omgewingsvriendelik, aangesien die stelsel geen produkte lewer wat skade aan die natuur kan veroorsaak nie. 2MNK, 2-metiel-1-naftol, 2-naftaldehyd, 3-etoksi-4-metoksibensaldehyd en menadioonepoksied is in hierdie studie geïdentifiseer as prosesprodukte. Om te bepaal watter gesintetiseerde katalisators hierdie proses begunstig, is 'n ondersoek geloods om die effek van reaksiekondisies op die verskeie katalisators te kwantifiseer. Die reaksiekondisies is omskryf in terme van waterstofperoksiedkonsentrasie, katalisatorhoeveelheid, oplosmiddelvolume, substraathoeveelheid, reaksietyd en reaksietemperatuur. Die gewenste katalisator vir hierdie proses was die katalisator wat die hoogste 2MN omsetting lewer en die vorming

van 2MNK bevorder. Die hoogs geordende mesoporeuse materiaal was in hierdie ondersoek die katalisator met die hoogste omsetting wat ook 2MNK-vorming bevorder het in die meeste gevalle.

Om die beste bedryfstoestand vir hoë 2MNK opbrengs vanaf die oksidering van 2MN oor hoogs geordende mesoporeuse materiaal te bepaal, is die reaksiekondisies verander deur met een faktor op 'n slag te verander, sowel as faktorverandering volgens 'n faktoriaalontwerp. Die een-faktor-op-'n-slag benadering het getoon dat die 2MNK opbrengs 'n maksimum bereik waar die substraathoeveelheid tussen 0.5 g en 2 g wissel, met die oplosmiddelvolume tussen 5 ml en 20 ml. Die opbrengs het ietwat verbeter met 'n groter hoeveelheid katalisatorhoeveelheid (van 50 mg na 200 mg), terwyl die opbrengs drasties verbeter het waar die waterstofperoksiedvolume van 3 ml tot 6 ml verhoog is. Die opbrengs het ook verbeter met 'n styging in reaksietemperatuur (van 120°C tot 180°C) met reaksietydintervalle van 1 tot 6 ure. Die opbrengs het egter gedaal by 180°C waar reaksietye langer as 2 ure.

Volgens die resultate van die een-faktor-op-'n-slag benadering blyk dit dat reaksietemperatuur, waterstofperoksiedvolume, katalisatorhoeveelheid en reaksietyd faktore is wat verhoogde 2MNK opbrengs bevorder. Hierdie reaksiekondisies is geselekteer vir die faktoriaalontwerp. 'n Voorlopige 2-vlak faktoriaalontwerp is voorberei om te bepaal of daar enige belangrike interaksies is wat die 2MNK opbrengs beïnvloed. Die resultate van die faktoriaalontwerp het aangetoon dat waterstofperoksiedvolume die grootste invloed op 2MNK opbrengs het, gevolg deur die interaksie van reaksietyd en reaksietemperatuur, en dan reaksietemperatuur. Die faktoriaalontwerp resultate toon verder dat opbrengs verhoog met toenemende waterstofperoksiedvolume en reaksietemperatuur, terwyl die opbrengs verlaag soos wat die reaksietyd-reaksietemperatuur interaksie toeneem. Hierdie studie het hoogste 2MNK opbrengs van 48-50% en 2MN omsetting van 97-99% vir die hidrosilering van 2MN na 2MNK oor hoogs geordende mesoporeuse materiale behaal.

Hierdie studie bevestig bevindinge van die literatuur dat die prosesstelsel, reaksiekondisies en katalisatortipe 'n groot impak het op prosesprodukte, 2MN omsetting, 2MNK selektiwiteit en 2MNK opbrengs. In hierdie navorsingstudie is bevind dat hoë 2MN omsetting en 2MNK opbrengs behaal word by hoë reaksietemperature met kort reaksietye en hoë waterstofperoksiedvolumes. Dit is gevind dat die hoogs geordende mesoporeuse materiaal werklik heterogeen is, aangesien geen loging plaasgevind het nie, en aangesien die katalisator hergebruik kon word sonder verlies aan katalisatoraktiwiteit en -selektiwiteit, vir ten minste twee katalisatorsiklusse. 'n Gevolgtrekking kan gemaak word dat die hoogs geordende mesoporeuse materiaal 'n belowende katalisator vir die selektiewe oksidering van lywige substrate met waterige  $H_2O_2$  is, aangesien dit 'n omgewingsvriendelike proses lewer met hoë omsetting, hoë kinoonopbrengs en katalisatorgedrag wat waarlik heterogeen is.

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## NOMENCLATURE

### *Symbols*

A	Pre-exponential factor	[-]
$A_i$	Absolute area of species i	[a/u]
$C_i$	Concentration of species i	[gmol/ml]
E	Activation energy	[J/mol]
$k_i$	Specific reaction rate constant	[(ml) <sup>3</sup> /gmol.h]
$M_r$	Molecular mass	[g/gmol]
$n_i$	Moles of species i	[mol]
R	Gas constant	[J/mol.K]
$r_i$	Rate of formation/consumption of compound i	[gmol/h.ml <sup>2</sup> ]
$RF_i$	Response Factor of species i	[-]
T	Absolute Temperature	[K or °C]
t	Time	[h, min or s]
$V_i$	Volume of compound i	[ml]
$X_i$	Conversion of species i	[mol]

### *Greek*

$\Delta$	Difference	[-]
$\Theta_{H2O2}$	Molar ratio of hydrogen to 2-methylnaphthalene at t=0	[-]
$\lambda$	Wavelength	[nm]

## **Abbreviations**

2MN	2-Methylnaphthalene
2MNL	2-Methyl-1-naphthol
1,4DOH-2MN	2-Methynaphthalene-1,4-dihydroxy
2MNQ	2-Methyl-1,4-naphthoquinone
6MNQ	6-Methyl-1,4-naphthoquinone
AcOH	Acetone
BET	Brunauer-Emmett-Teller Isotherm
DRS-UV	Ultraviolet Diffuse Reflectance Spectroscopy
E	E-factor
EDX	Energy Dispersive X-ray spectroscopy
EXAFS	Edge X-ray Absorption Fine Structure
FT-IR	Fourier Transform Infra-red
FWHM	Full Width at Half Maximum
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
ICP/AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IR	Infra-Red
MeCN	Acetonitrile
MeOH	Methanol
PBQ	Para-benzoquinone
PTFE	Polytetrafluoroethylene (Teflon)
Q	Environmental Quotient
SDA	Structure-Directing Agent
SEM	Scanning Electron Microscopy
TBHP	Tert-butylhydroperoxide
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV-VIS	Ultraviolet-Visible
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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# 1 INTRODUCTION

Oxidation of organic substances is of great consequence since numerous base and fine chemicals are produced from these oxidative processes (Herrmann, *et al.*, 1997). Selective oxidation plays an important role for the manufacture of many fine chemicals, agrochemicals and pharmaceutical intermediates (Li, *et al.*, 2006). Hydroxylation of organic compounds has for decades been a research focus from an academic as well as an industrial perspective. However, there is always room for improvement, e.g., formulating alternative or new catalysts, limiting the number of process steps, reducing waste by-products and optimising the process (Bjorsvik, *et al.*, 2005; Eimer, *et al.*, 2006).

Fine chemicals are usually complex, multifunctional molecules with high boiling points. This allows reactions to be conducted in the liquid phase at moderate temperatures (Ziolek, 2004). The fine chemical industry normally conducts reactions with archaic stoichiometric oxidation technologies. These reactions result in unacceptable environmentally detrimental processes, exhibiting high E-factors. Generally, the fine chemical industry processes were not noticed in previous decades because reactions were generally conducted on a small production scale (Sheldon, *et al.*, 1994).

In this era, with strict environmental laws and regulations, the effect that global warming, CO<sub>2</sub> emissions, pollution, etc. have on the environment, it is becoming less possible to implement archaic technologies in the fine chemical industry that are toxic and hazardous towards the environment. It is therefore necessary to develop cleaner and economically efficient processes. This has become known as 'Green Chemistry', which is defined as follows:

*"Green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products."* (Sheldon, 2000)

Green chemistry can be achieved through better use of catalysis by:

- Alternative synthesis routes that excludes the use of toxic solvents and/or feedstocks
- Reducing the number of synthesis steps
- Preventing the need to store or transport toxic intermediates or reagents
- Novel energy efficient methods (Clark, *et al.*, 2000).

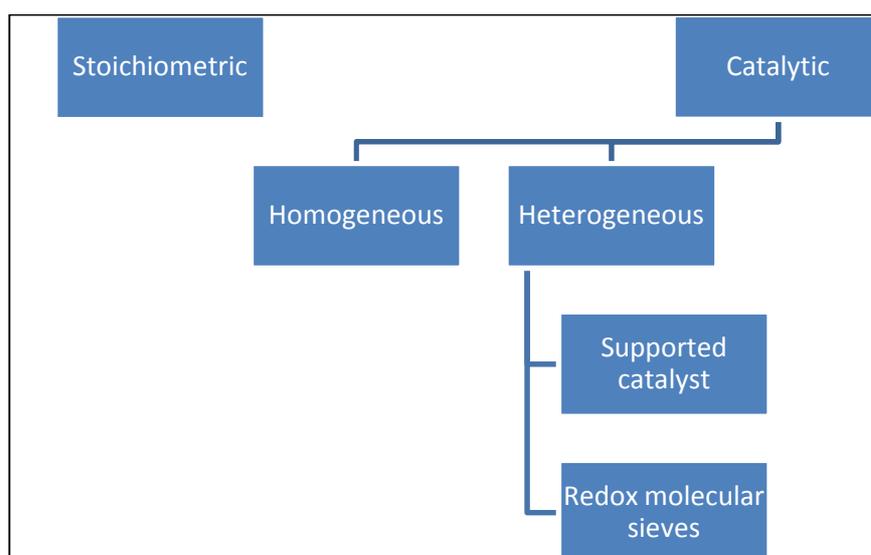
The most technically and economically feasible process to achieve 'Green chemistry' is by substituting a catalytic process for the traditional stoichiometric process (Sheldon, *et al.*, 1999). As a result, the catalysis market is increasing exponentially due to the rapid growth in use of catalysis; to control the pollution prevention and waste minimisation through the introduction of catalysts to processes where catalysis had not previously been implemented and through the introduction of improved catalysts which gives better product quality or process efficiency and reduces waste (Clark, *et al.*, 2000).

The two main measurements to determine the impact a process has on the environment are the E-factor and the atom utilisation efficiency. The E-factor is defined as the mass ratio of waste to the desired product. The atom utilisation is calculated by dividing the molecular weight of the desired product by the molecular weights of all the products produced in the reaction (Sheldon, 2000). The atom utilisation efficiency is an estimation of the waste that could be produced if the reaction took place, whereas the E-factor is the actual waste produced from the reaction. When determining the actual waste of a reaction, the E-factor is not the only factor that should be taken into consideration but also the environmental quotient (Q). The environmental quotient is determined by the nature of the waste; how severe its impact on the environment and the cost of recycling using state of the art technology. Therefore, the actual waste of a reaction is determined by EQ: (Sheldon, *et al.*, 1994)

$$EQ = E \left( \frac{\text{kg waste}}{\text{kg product}} \right) \times Q(\text{environmental quotient})$$

**Equation 1-1**

Figure 1-1 illustrates the various options that can be taken to oxidize a substrate in the liquid phase. Stoichiometric oxidation is not the most appropriate pathway to take because literature has proven the negative impact it has on the environment (Kholdeeva, *et al.*, 2007). It is therefore suggested that oxidation processes should follow the catalyst pathway. Between a homogeneous or heterogeneous catalyst, a heterogeneous catalyst is favoured because of the ease of recovery and recyclability of the catalyst (Sheldon, *et al.*, 1999). Separating of substrates and products from the catalyst is also easy and inexpensive, whereas for homogeneous catalysts it can result in contamination of the target product with hazardous transition metal compounds leaching from the catalyst (Kholdeeva, *et al.*, 2002).



**Figure 1-1 Catalyst options in the liquid phase [Redrawn from (Sheldon, *et al.*, 1994)]**

A heterogeneous catalyst can be divided into supported metal catalysts or redox molecular sieves. Supported metal catalysts lead to rapid catalyst deactivation because organic ligands surrounding the metal can influence the activity, selectivity and stability of the catalyst (Sheldon, *et al.*, 1994). The problem with organic ligands is that they are thermodynamically unstable in oxidizing media and as a result, presents two limitations: The tendency of some oxometallic species to oligomerize, forming  $\mu$ -oxocomplexes that are catalytically inactive and the other limitation is the destruction of the catalyst due to the oxidative destruction of the ligands (Sheldon, 1993; Corma, 2003). These limitations can be resolved by isolating redox metal ions in stable inorganic matrices. The isolating redox metal ions can be incorporated via isomorphous substitution into the framework of the inorganic matrices (molecular sieves) forming redox molecular sieves (Sheldon, *et al.*, 1994).

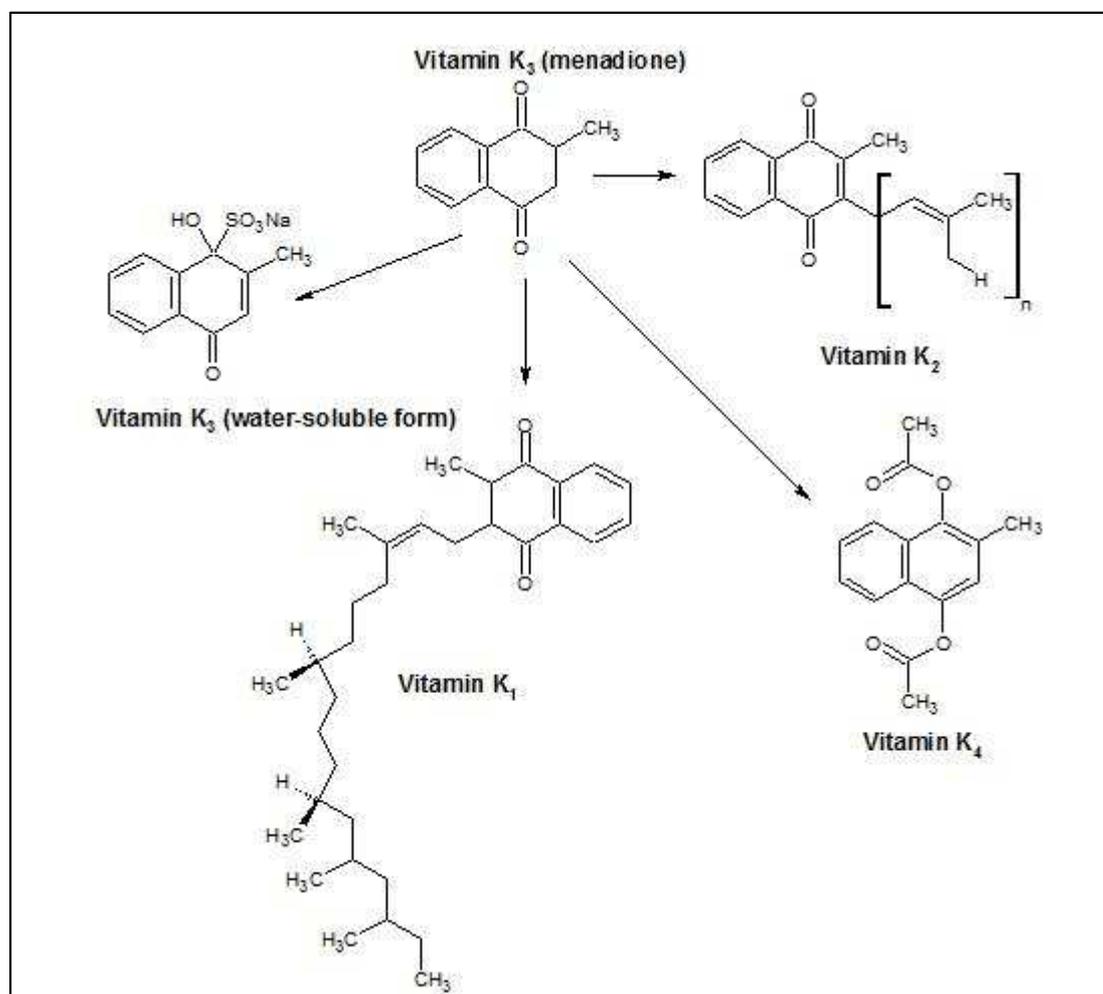
The advantages of redox molecular sieves oxidizing a process in comparison with the supported catalyst system are:

- They possess a regular microenvironment with homogeneous internal structures consisting of uniform, well defined cavities and channels
- The site-isolation of the redox metal centres prevents deactivation of the active species
- The catalyst structure is more stable, which diminishes leaching of the metal
- Shape-selective catalysis could occur
- The molecular sieve can be considered as a second solvent that extracts the substrate out of the bulk solvent
- Generally acts as heterogeneous catalysts, preventing contamination of the effluent (Sheldon, *et al.*, 1994; Carvalho, *et al.*, 1997).

## 1.1 Vitamin K<sub>3</sub>

One particular example of selective oxidation, which is pivotal for the fine chemical industry, is the hydroxylation of aromatic compounds to quinones or biaryl (Sorokin, *et al.*, 2002). Quinones are very useful compounds because they possess biological activity resulting in medical implications and can occur within the molecular frameworks of natural products (Zalomaeva, *et al.*, 2006). Among the various quinones that play an important role in the fine chemical industry, the most common quinones are the biologically active Vitamins K<sub>3</sub> and E, fragrances like 1,4-butanedione, cresols, hydroquinones and plastic fibre precursors like 1,2-epoxy-3,4-butene (Anunziata, *et al.*, 2004). Quinones were initially prepared by archaic stoichiometric oxidation processes. These processes produced reasonable yields but E-factors in the range of 10-20 (Zalomaeva, *et al.*, 2006). Over the past years, it has been challenging to produce an efficient environmentally friendly process for the hydroxylation of bulky substrates to quinones.

Natural naphthoquinones form an intrinsic part of microorganisms, plants and mammals but the most important compounds are vitamins from the K-group (Schmid, *et al.*, 1999). As illustrate in Figure 1-2, the precursor molecule of all vitamins in the K-group is Vitamin K<sub>3</sub> (Kholdeeva, *et al.*, 2007).



**Figure 1-2 Vitamins of group K [Redrawn from (Kholdeeva, *et al.*, 2007)]**

Vitamin K<sub>3</sub> is widely used as a blood coagulating agent (Kholdeeva, *et al.*, 2007). It is significant to the fine chemical industry because it has about twice the antibleeding activity of the natural vitamin K<sub>2</sub> and thrice the activity of the natural vitamin K<sub>1</sub> (Anunziata, *et al.*, 1999). The vitamins derived from Vitamin K<sub>3</sub> are Vitamin K<sub>1</sub> (2-Methyl-3-phytnaphtho-1,4-quinone, phyloquinone), Vitamin K<sub>2</sub> (2-Methyl-3-(isoprenyl) naphtho-1,4-quinone, menaquinone), Vitamin K<sub>4</sub>, sodium bisulphate and dimethylpyrimidinol bisulphate adduct of Vitamin K<sub>3</sub> (Matsumoto, *et al.*, 1997).

Vitamin K<sub>3</sub> is also known as menadione or 2-methyl-1,4-naphthoquinone (2MNQ) (Matsumoto, *et al.*, 1997). It is an almost odourless, light sensitive bright yellow crystalline powder

with an empirical formula of  $C_{11}H_8O_2$ . 2MNQ is insoluble in water but soluble in vegetable oils, acetone and benzene and slightly soluble in alcohol and chloroform (Anunziata, *et al.*, 1999).

## 1.2 Synthesis of Menadione from 2-Methyl Naphthalene

Traditionally, about 1500 ton/year 2MNQ was produced on an industrial scale from the outdated stoichiometric oxidation of 2-methylnaphthalene (2MN) with chromium trioxide in sulphuric acid. The process produced 30-60% yield of 2MNQ with a high E- factor of 18 and 6-Methyl-1,4-naphthoquinone(6MNQ) and 2-Naphthoic acid as the by-products (Narayanan, *et al.*, 2002; Kholdeeva, *et al.*, 2007).

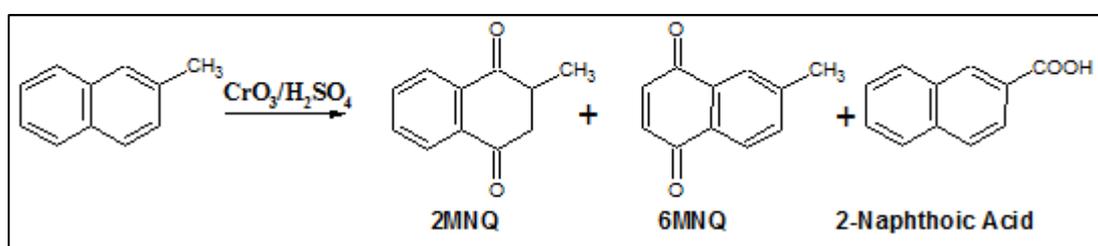


Figure 1-3 Oxidation of 2-methylnaphthalene over  $CrO_3/H_2SO_4$  (Kholdeeva, *et al.*, 2007)

This reaction process is regarded an example of a “dirty” fine chemical industry process, caused by the chromium compounds (Matsumoto, *et al.*, 1997). Other stoichiometric and catalytic methods for the oxidation of 2MN to 2MNQ have been proposed but still have limitations due to their high E-factors. Over the past decade, the development of cleaner catalytic methods has received some attention (Yamazaki, 2001).

In recent years, various methods were conducted to obtain a more efficient and environmentally friendly process for the selective oxidation of bulky aromatic rings, particularly, the production of 2MNQ from the selective oxidation of 2MN but it is still a challenging goal (Shi, *et al.*, 2007). Yamaguchi, *et al.*, (1985) proposed that a more efficient reaction system would result by using a solid catalyst such as redox molecular sieves with a suitable oxidant and solvent (Anunziata, *et al.*, 1999). A major concern for this type of reaction system is the use of oxidants and solvents that are toxic and hazardous to the environment and the nature of oxidants, redox molecular sieves and solvents has shown to have large influence on the process system (Sheldon, 2000; Corma, *et al.*, 1996).

This research study focuses on the development of an environmentally friendly and efficient process for the hydroxylation of 2MN to 2MNQ. This is done by replacing the archaic stoichiometric oxidation process with a suitable oxidant, solvent and redox molecular sieve as a catalyst. The aim of

this study is to produce an environmentally friendly process that achieves high 2MN conversion and 2MNQ yields. This is done by synthesising and investigating various redox molecular sieves for the hydroxylation of 2MN to 2MNQ to determine which catalyst favours high 2MN conversions and 2MNQ yields.

## 2 LITERATURE REVIEW

### 2.1 Oxidants

Redox molecular sieves acting as catalysts for the selective oxidation of substrates require a clean oxidant for oxidation to occur in an environmentally friendly manner (Li, *et al.*, 2006). Successful, clean oxidants for the hydroxylation of organic substrates should possess a high percentage of active oxygen and produce a co-product that is non-toxic and/or simple to recycle (Arends, *et al.*, 1997). It is important that the choice of oxidant is cost efficient, simple to handle and favours the practicability and efficiency of the process (Shi, *et al.*, 2007; Sheldon, 1993).

Table 2-1 indicates some of the popular oxidants used for the selective oxidation of organic substrates in the fine chemical industry. The problem with using inorganic oxygen donors and acids such as nitric acid is that they are detrimental toward the environment because of their co-products (Sheldon, *et al.*, 1994). The most common oxidants that contain the properties of clean oxidants are molecular oxygen, ozone, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and alkyl hydroperoxides such as tert-butylhydroperoxide (TBHP) (Arends, *et al.*, 1997). Ozone obtains high selectivities but is very expensive to maintain because it requires specialised equipment to generate (Sheldon, *et al.*, 1994). The oxidant that is cheaper and exhibits more active oxygen than ozone is hydrogen peroxide. Although hydrogen peroxide is more expensive per kilo than molecular oxygen, hydrogen peroxide is the oxidant of choice in most cases because of its simplicity of operation (Kuznetsova, *et al.*, 2007; Sheldon, 1993).

Table 2-1 Oxygen donors (Sheldon, 1993)

Donor	%Active oxygen	Co-product
Hydrogen Peroxide, H <sub>2</sub> O <sub>2</sub>	47.0	H <sub>2</sub> O
Ozone, O <sub>3</sub>	33.3	O <sub>2</sub>
CH <sub>3</sub> CO <sub>3</sub> H	26.6	CH <sub>3</sub> CO <sub>2</sub> H
Tert-butylhydroperoxide, t-BuO <sub>2</sub> H	17.8	t-BuOH
Sodium Chlorite, NaClO	21.6	NaCl
Sodium Chlorite, NaClO <sub>2</sub>	19.9	NaCl
Sodium Bromate, NaBrO	13.4	NaBr
Nitric acid, HNO <sub>3</sub>	25.4	NO <sub>x</sub>
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> <sup>a</sup>	13.7	C <sub>5</sub> H <sub>11</sub> NO
Potassium sulphate, KHSO <sub>5</sub>	10.5	KHSO <sub>4</sub>
NaIO <sub>4</sub>	7.0	NaI
PhIO	7.3	PhI

<sup>a</sup>N-Methylmorpholine-N-oxide (NMO)

Hydrogen peroxide is known as the “green oxidant” in the fine chemical industry because of the co-product nature and percentage of available oxygen. It has become a favourable oxidant over the years in both homogeneous and heterogeneous catalysts because of its ease to obtain (Clerici, *et al.*, 1998). Alkyl hydroperoxides also produce water as a co-product by the addition of an extra step; reacting the alcohol formed with hydrogen peroxide to reform the hydroperoxide (Sheldon, 1993).

## 2.2 Catalyst

The activity and selectivity of catalysts are influenced by the solvent nature, oxidant type and hydrophobic/hydrophilic characteristic of the substrate (Corma, *et al.*, 1996). The main factors influencing the framework of a catalyst to ensure good activity and selectivity are:

- i. The accessibility of a substrate to the active sites inside the pores: the size of the pores should not limit the accessibility of the substrates
- ii. The surface acidity: presence of acidic impurities such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  cations as well as high concentration of hydroxyl groups present on the pore surface, are responsible for undesired secondary reactions
- iii. The surface hydrophobicity: The surface polarity of the catalyst is very important because if the surface is hydrophilic, water will strongly be adsorbed on the surface. This prevents the substrates access to the active sites. While, if the surface is hydrophobic it does not adsorb water
- iv. Recyclability of catalyst and stability towards leaching of metal ions
- v. Surface area, pore volume, size distribution and method used to synthesize the catalyst (Hulea, *et al.*, 2004; Ziolk, 2004; Clark, *et al.*, 2000; Sheldon, *et al.*, 1998).

The pore size is important because the substrate molecules penetrates through the channels of the pores to reach the internal region containing the bulk of the active sites where the substrate is oxidized and the product molecules must diffuse out of the pore network (Clark, *et al.*, 2000).

The pore size of porous solids can be divided into three categories, namely, microporous, mesoporous and macroporous (Clark, *et al.*, 2000). Table 2-2 illustrates the classification of the various pore-size regimes. Micropores and mesopores are the two pore-size regimes used extensively as heterogeneous catalysts in the fine chemical industry (Beck, *et al.*, 1992).

**Table 2-2 Pore-size regimes and representative porous inorganic materials (Ying, et al., 1999)**

<b>Pore-size regimes</b>	<b>Definition</b>	<b>Examples</b>	<b>Actual size range</b>
Microporous	<20 Å	Zeolite, zeotypes	<14.2 Å
		Activated carbon	6 Å
Mesoporous	20-500 Å	Aerogels	>100 Å
		Pillared layered clays	10 Å, 100 Å
		M41S	16 Å -100 Å
Macroporous	>500 Å	Glasses	>500 Å

*a) Redox molecular sieves*

The incorporation of redox metal ions into molecular sieves creates versatile heterogeneous oxidation catalysts because they have the ability to control which molecule has access to the active sites based on their size and/or their hydrophobic/hydrophilic character (Sheldon, et al., 1998). Redox molecular sieves are synthesised from aqueous gels containing a source of framework building elements (Al, Si, P), a mineralizer (OH<sup>-</sup>, F<sup>-</sup>) that regulates the dissolution and condensation processes during crystallization and a structure-directing agent (SDA), usually referred to as a template (generally an organic amine or ammonium salt) (Arends, et al., 1997). Metal ions are isomorphously substituted into the framework positions of molecular sieves via hydrothermal synthesis or post synthesis modification (Sheldon, et al., 1998). Different types of redox molecular sieves and their properties are illustrated in Figure 2-1.

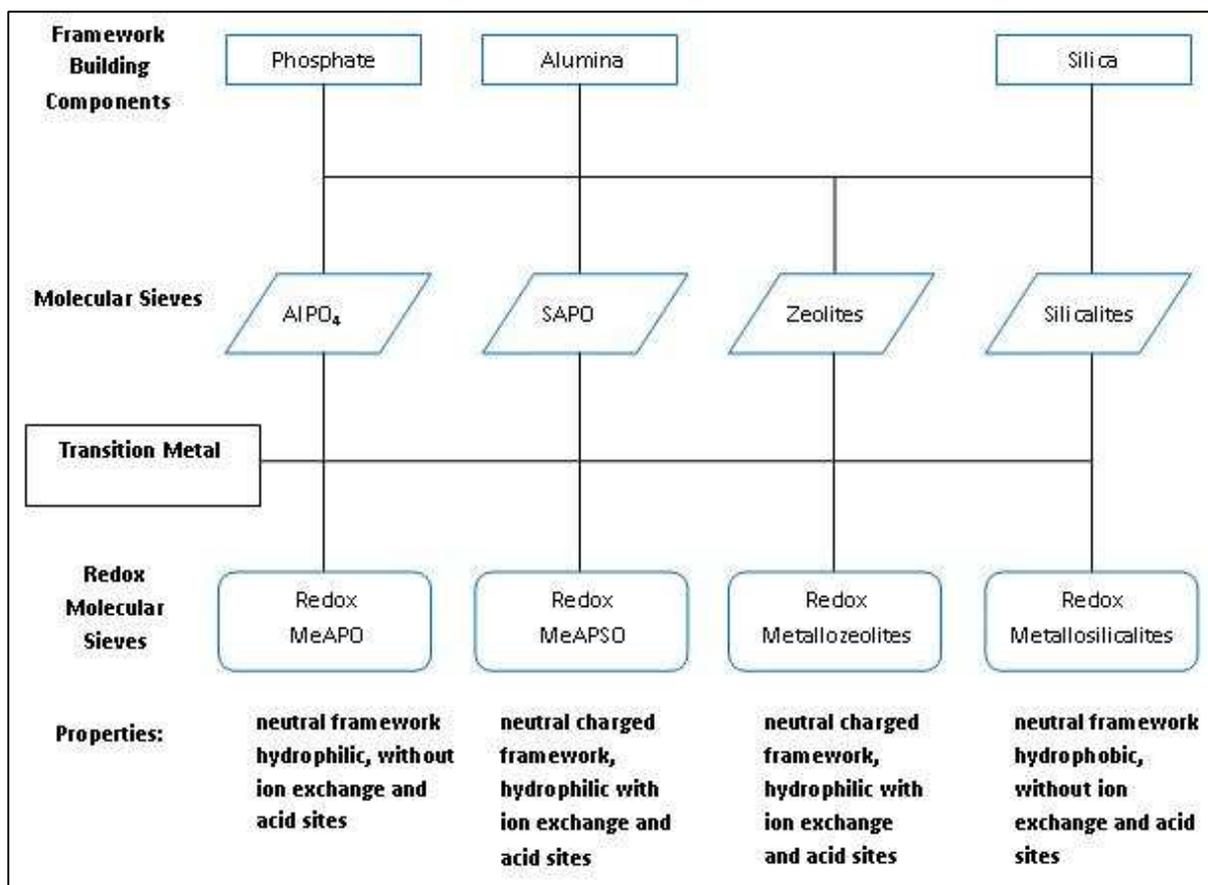


Figure 2-1 Types and properties of redox molecular sieves (Sheldon, *et al.*, 1998)

The most common molecular sieves are zeolites or zeotypes. Zeolites are defined as crystalline structures which are constructed from TO<sub>4</sub> tetrahedra, where T is either Si or Al and consists of a regular pore system with diameters of molecular dimensions. The different valence of Si (tetravalent) and Al (trivalent) produces an overall negative charge for each incorporated aluminium atom and can be neutralised by protons or other cations. The framework is neutralised in some cases when the trivalent atoms in the zeolites framework (Al) are substituted by tetravalent atoms such as Si or Ti, producing metallosilicalites (Sheldon, *et al.*, 1998).

Zeotypes are tetrahedra framework structures containing aluminium and phosphorus coordinated by oxygen. Aluminophosphates (AIPO's) and its derivatives have the same structural form as some of the zeolites. Metal-aluminium phosphates (MeAIPOs) can be formed by metals such as Li, Be, Mg, Mn, Fe and Zn by replacing some of the aluminium in the AIPO framework. Silicoaluminophosphates (SAPOs) and metal-silica aluminium phosphates (MeSAPOs) are AIPOs and MeAIPOs, respectively with the exception of containing silicon in the structure. Zeolites are better heterogeneity catalysts than zeotypes because they lack the acid strength and stability of zeolites (Clark, *et al.*, 2000). Examples and chemical composition of metallozeolites, metallosilicalites and metal-silica aluminium phosphates can be found in Table 2-3.

**Table 2-3 Examples and chemical composition of redox molecular sieves (Arends, *et al.*, 1997)**

Redox molecular sieves	Chemical composition	Examples
Metallozeolites	$(\text{Si}^{\text{IV}}\text{-O-Al}^{\text{III}}\text{-O-Si}^{\text{IV}})^-$ $\text{H}^+$ or $\text{M}^+$	Ti-ZSM-5 Ti- $\beta$ Ti-MCM-41
Metallosilicalites	$\text{Si}^{\text{IV}}\text{-O-Si}^{\text{IV}}\text{-O-Si}^{\text{IV}}$	TS-1 TS-2 VS-1
MeAPO	$\text{Al}^{\text{III}}\text{-O-P}^{\text{V}}\text{-O-Al}^{\text{III}}$ $\text{H}^+$ or $\text{M}^+$	VAPO CrAPO

Zeolites containing charges generally possess a hydrophilic surface depending on the extra-framework cations and Si/Al framework ratio. Whereas, pure silica zeolites with no positive charges are highly hydrophobic materials provided that the numbers of internal silanol defects are low (Corma, 2003).

Usually, redox silicates containing tetravalent metal ions in the active sites (e.g.  $\text{Ti}^{\text{IV}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{Zr}^{\text{IV}}$  and  $\text{Sn}^{\text{IV}}$ ) are hydrophobic, whereas bi- or trivalent cations as active sites (e.g.  $\text{Cr}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Al}^{\text{III}}$  and  $\text{Cu}^{\text{II}}$ ) are hydrophilic and contain Bronsted acid sites that catalyze undesirable side reactions (Arends, *et al.*, 1997).

Redox molecular sieves are divided by pore size and the pore system may be one, two or three-dimensional (Sheldon, *et al.*, 1998). The dimension of the pore system influences catalyst deactivation. One dimensional pore systems are limited because molecules can only travel in one direction which restricts the activity of the catalyst, whereas for two and three dimensional pore systems, alternative pathways are available (Arends, *et al.*, 1997).

Redox molecular sieves, in particular zeolites, are the most favoured catalyst in modern chemistry for the selective oxidation of hydrocarbons because of their remarkable activity and selectivity. The main drawback in heterogeneous catalyst is the possibility that leaching can occur (Sheldon, *et al.*, 1998).

#### *b) Leaching*

Leaching occurs due to the solvolysis of the metal-oxygen bonds attached to the framework of the catalyst causing the metal ions to break from the framework and leach into the liquid solution (Arends, *et al.*, 1997). The small amounts of leached metal have a negative impact on the catalytic

results because the conclusions drawn from the physico-chemical characterisation are invalid and the products from the reaction are contaminated (Ziolek, 2004).

Redox molecular sieves prevent leaching from occurring due to the internal surface of the sieve containing stable metal oxygen bonds but some redox molecular sieves lose this stability and leaching occurs (Arends, *et al.*, 1997) (Ziolek, 2004).

The main factors influencing whether or not leaching occurs are:

- i. Nature of the transition metal
- ii. Nature of the solvent
- iii. Nature of the oxidant
- iv. Reaction temperature
- v. Matrix structure (Ziolek, 2004)

Leaching often occurs in oxidizing catalysis due to polar molecules because of their strong complexing and solvolytic properties (Arends, *et al.*, 2001). Since polar molecules are involved in the oxidation of reactions either as oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{RO}_2\text{H}$ , etc.) and/or products ( $\text{H}_2\text{O}$ ,  $\text{ROH}$ ,  $\text{RCO}_2\text{H}$ , etc.), leaching is bound to be a problem (Sheldon, *et al.*, 1998).

There are three scenarios for heterogeneous catalyst in the liquid phase:

- 1) The metal does not leach and the observed catalysis is truly heterogeneous in nature
- 2) The metal does leach but is not an active catalyst, the observed catalysis is (predominantly) heterogeneous
- 3) The metal does leach to form an active catalyst (the metal ion exhibits high catalytic activity in liquid solution), the observed catalysis is theoretically heterogeneous but actually homogeneous in nature (Sheldon, *et al.*, 1998).

Leaching of the metal ion can be avoided or reduced by a suitable metal ion choice and an appropriate reaction medium (e.g. aprotic solvent). Heterogeneous titanium-based (ep)oxidation catalysts fall under scenario 1 or 2 because titanium(IV) is known to be a mediocre homogeneous catalyst and a truly heterogeneous catalyst in nature, while chromium and vanadium-based catalysts belong to scenario 3 (Ziolek, 2004). Polar molecules like  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and alcohols promote titanium leaching by interacting with the tetrahedral framework titanium species to form octahedral coordinated titanium peroxide species. This allows the possibility of titanium species to break from the framework and move into the solution (Chen, *et al.*, 1998).

c) *Catalyst mechanism*

The oxidation mechanism for redox molecular sieves as catalysts with H<sub>2</sub>O<sub>2</sub> or RO<sub>2</sub>H as oxidant can occur in two ways, either by oxygen transfer or one-electron oxidant reactions. The type of oxidation mechanism is generally determined by the metal ion used in the catalyst (Arends, *et al.*, 2001).

One-electron oxidant reactions, e.g., Co<sup>III</sup>, Mn<sup>III</sup>, Ce<sup>VI</sup>, Fe<sup>III</sup>, Cu<sup>II</sup>, etc., involves free radical autoxidation processes by promoting the decomposition of alkyl hydroperoxides into chains, forming alkoxy and alkyl peroxy radicals (Reaction 2-1 and Reaction 2-2) (Arends, *et al.*, 2001).



Oxygen transfer reactions can be divided into two types of pathways, namely, peroxometal or oxometal. Peroxometal pathways involves transition elements with d<sup>0</sup> configuration and weakly oxidizing metal ions e.g., V<sup>V</sup>, W<sup>VI</sup>, Ti<sup>IV</sup> etc. The metal ion does not change in the oxidation state for the peroxometal pathway. Strong oxidizing agents promotes oxometal pathways, e.g. Cr<sup>VI</sup>, Mn<sup>V</sup>, Ru<sup>VI</sup> etc. and the two-electron redox reaction occurs in the oxidation state. The main difference between the pathways is illustrated in Figure 2-2 (Arends, *et al.*, 2001; Arends, *et al.*, 1997). The peroxometal pathway is favoured because the metal species does not change its oxidation state and therefore the reducibility of the metal species does not play an important role (Ziolek, 2004).

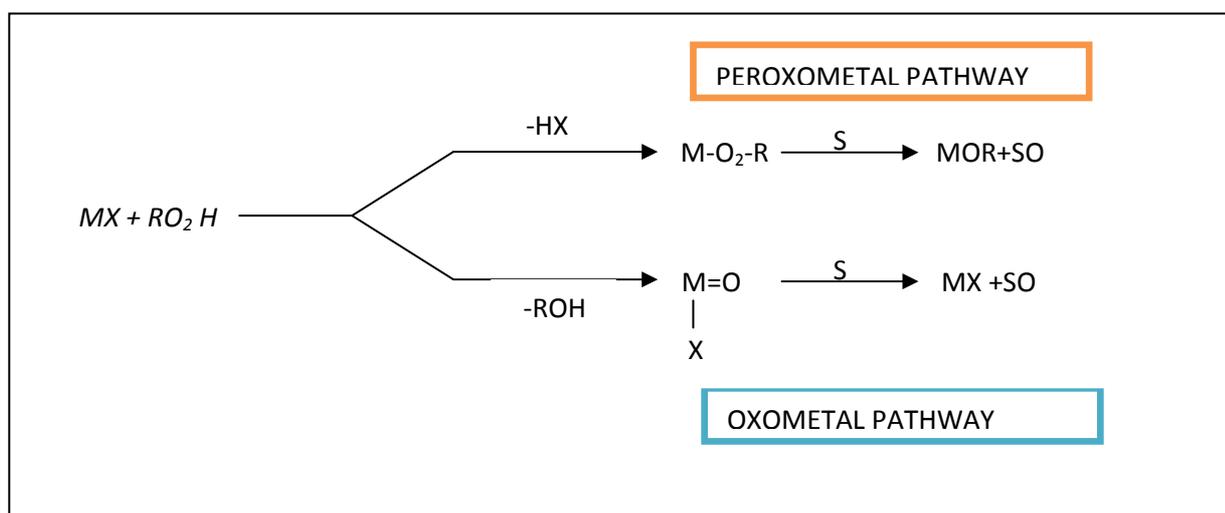


Figure 2-2 Peroxometal vs oxometal pathways (Arends, *et al.*, 2001)

Both chromium and vanadium can isomorphously substitute  $\text{Si}^{\text{IV}}$  or  $\text{Al}^{\text{III}}$  in the silicate, AlPO or SAPO framework. In as-synthesis, they are present as  $\text{Cr}^{\text{III}}$  and  $\text{V}^{\text{V}}$  but after calcination, chromium and vanadium oxidizes to  $\text{Cr}^{\text{VI}}$  and  $\text{V}^{\text{V}}$ , respectively. Chromium(VI) contains only two extra-framework  $\text{Cr}=\text{O}$  bonds and can only be secured to the framework at defect sites. As a result, it is not surprising that leaching occurs because chromium(VI) is attached to the surface by only two metal-oxygen bonds and it was found that for stability of the framework to prevent leaching from occurring, at least three metal-oxygen bonds should be attached to the framework (Arends, *et al.*, 2001). Abbenhuis, *et al.*, (1997) showed that when titanium(IV) acts as the metal incorporated into the silica matrix, at least three metal-oxygen bonds are attached to the structure.

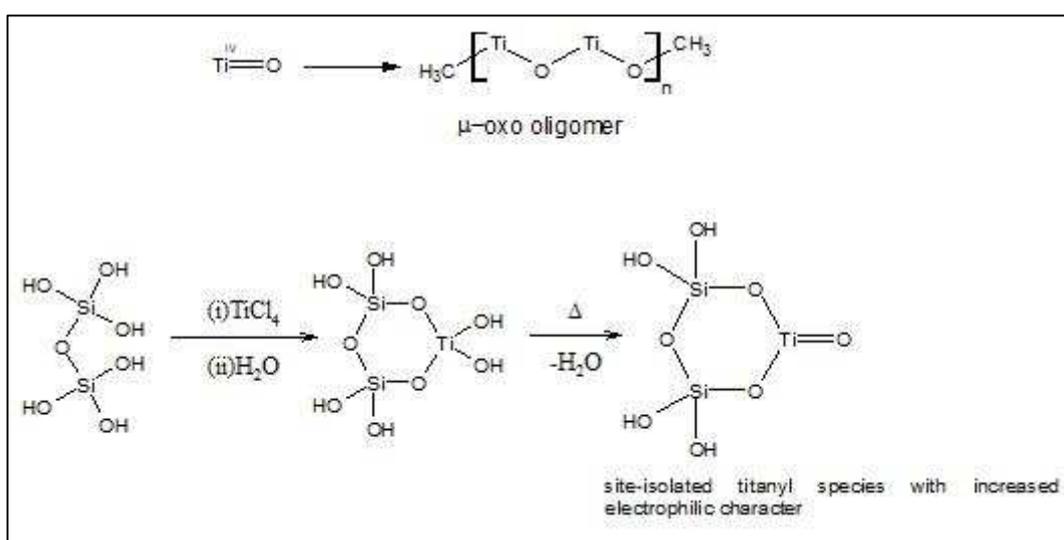


Figure 2-3 Site isolation of  $\text{Ti}^{\text{IV}}$  species [Redrawn from (Sheldon, *et al.*, 1994)]

Literature illustrates that  $\text{Ti}^{\text{IV}}$  is not a very good homogeneous catalyst for selective oxidation of hydrocarbons with  $\text{RO}_2\text{H}$  as oxidants. This is due to the facile oligomerization of oxotitanium(VI) species forming unreactive  $\mu$ -oxotitanium(IV) oligomers (Sheldon, *et al.*, 1994). The  $\mu$ -oxo oligomers ( $\text{Ti}^{\text{IV}}$  with silica) produce a very stable heterogeneous catalyst which prevents leaching from occurring. Other transition metal ions, e.g.,  $\text{Mo}^{\text{VI}}$ ,  $\text{W}^{\text{VI}}$ ,  $\text{V}^{\text{V}}$ , etc. with silica allow rapid leaching of the metal ion to occur (Arends, *et al.*, 2001).  $\text{Ti}^{\text{IV}}$  is the most favourable redox metal ion incorporated into molecular sieves because it follows the peroxometal pathway, prevents leaching from occurring due to its strong stability characteristic and contains isolated titanium atoms that are responsible for the formation of titanium peroxo-species. These species promote direct insertion of oxygen onto the organic substrate (Anunziata, *et al.*, 2004).

Great interest has been shown in Ti-silicate molecular sieves for the hydroxylation of aromatic rings, alkanes and alkenes with hydrogen peroxide as oxidant (Anunziata, *et al.*, 1999). The advantage of using Ti-containing molecular sieves as catalysts with  $\text{H}_2\text{O}_2$  as oxidant for the selective oxidation of

organic compounds enables the production of environmentally friendly systems (Bjorsvik, *et al.*, 2005). These systems are favoured because:

- High activity and selectivity can be achieved
- Catalyst is heterogeneous and can be separated by filtration
- No toxic/hazardous reactants and solvents are involved
- Leaching rarely occurs, resulting in high purity of the product
- No corrosive problems (Kholdeeva, *et al.*, 2002)

Titanium molecular sieves are characterized by isolated titanium incorporated into the silica framework and sometimes extra-framework TiO<sub>2</sub> are found on the surface of the catalyst. This results in a negative impact on the selectivity of the desired product by producing undesired by-products. Other impurities such as Al<sup>3+</sup> may also be present in redox molecular sieves. These impurities possess acidic properties causing leaching and the formation of undesired by-products (Notari, 1996).

### 2.2.1 Microporous Materials

The subject of porous titanium molecular sieves is one of the fastest developing areas of porous materials (Mrak, *et al.*, 2006). Crystalline microporous zeolite materials have become pivotal catalysts for oil refining, petrochemistry, and organic synthesis in the production of fine and special chemicals (Corma, 1997). The term zeolite comes from the Greek meaning “boiling stone” and was named in 1756 by the Swedish mineralogist Cronstedt, who observed that mineral salts frothed and gave off steam when heated. There are various types of microporous zeolites as illustrated in Table 2-4 and they are defined in terms of structure types, how the tetrahedral are linked together and each structure is given a unique framework code (Clark, *et al.*, 2000).

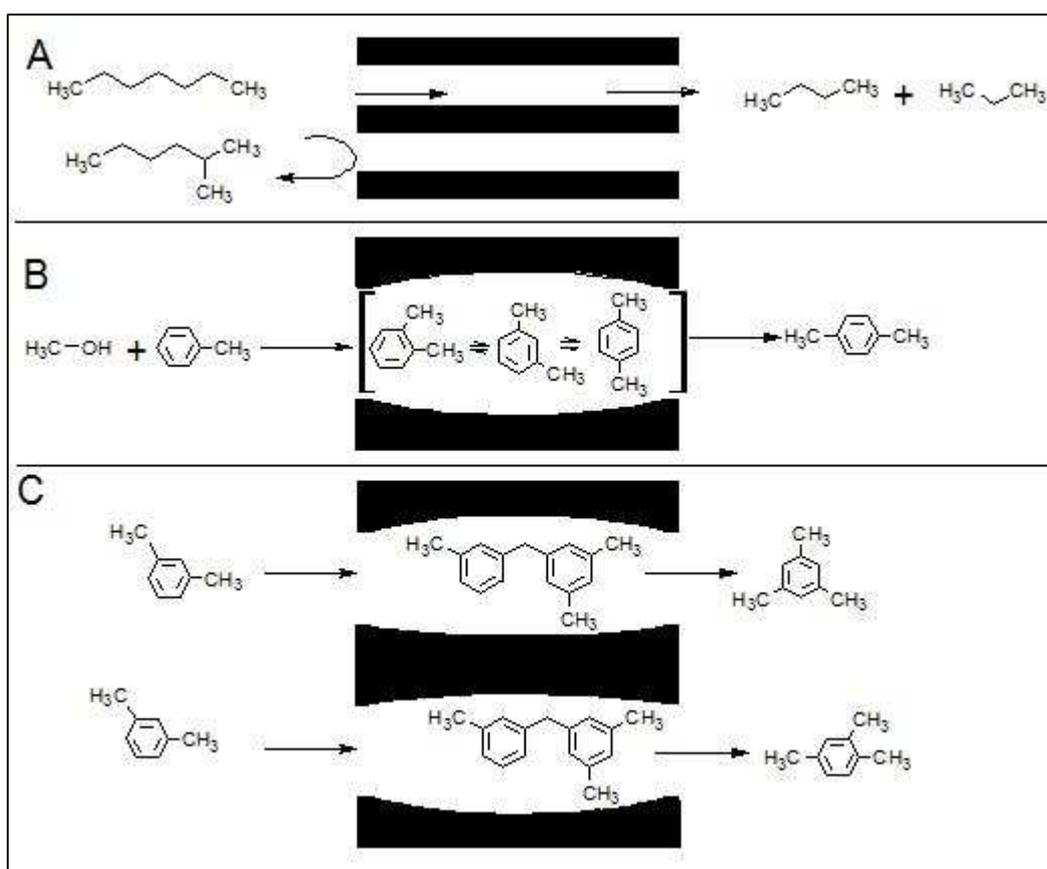
**Table 2-4 Zeolite codes and ring sites (Clark, *et al.*, 2000)**

Zeolite	Framework code	Number of tetrahedral in ring
Sodalite	SOD	4
Zeolite A	LTA	8
Erionite-A	ERI	8
ZSM-5	MFI	10
Faujasite	FAU	12
Mordenite	MOR	12 and 8
Zeolite-L	LTL	12

The presence of strong electric fields and controllable adsorption properties within the pores makes zeolites a unique catalyst (Corma, 2003). Features that make microporous zeolites special and ideal for catalysis are:

- High surface areas and adsorption capacities
- Active acid sites: Can be generated in the pores, on channels of different dimensions and on the external surface of the microcrystals in the catalytic bed.
- The ability to implement shape selectivity by differences in diffusivity through a given pore channel system (Corma, 1997; Schoonheydt, 2008; Corma, 2003).

Shape selectivity occurs in three ways as illustrated in Figure 2-4: (A) reactant selectivity, (B) product selectivity and (C) transition selectivity. Reactant selectivity is the ability of allowing only certain molecules to be absorbed into the zeolite cavities to reach the active acid sites. Product selectivity occurs when certain products of the correct dimensions can escape the zeolite. Transition selectivity relies on certain intermediates that are formed during the reaction at the active sites and not able to fit in the cavities (Clark, *et al.*, 2000).



**Figure 2-4** Shape selectivity governed by zeolites: (A) reactant selectivity; (B) product selectivity; (C) transition-state shape selectivity [Redrawn from (Arends, *et al.*, 1997)]

### 2.2.1.1 TS-1

Titanium silicalite-1 (TS-1) developed by Enichem in 1983, was the first successful titanium-silica redox molecular sieve for the selective oxidation of organic compounds (Sheldon, *et al.*, 1994). TS-1 has attracted much attention for its unique catalytic properties and has become a highly-efficient heterogeneous catalyst for the selective oxidation of organic compounds using hydrogen peroxide as an oxidant (Tamura, *et al.*, 2007). It is remarkably active for olefin (ep)oxidation, phenol hydroxylation, cyclohexanone ammoximation, conversion of ammonia to hydroxylamine, secondary alcohols to ketones and secondary amines to dialkylhydroxylamines (Bordiga, *et al.*, 2002).

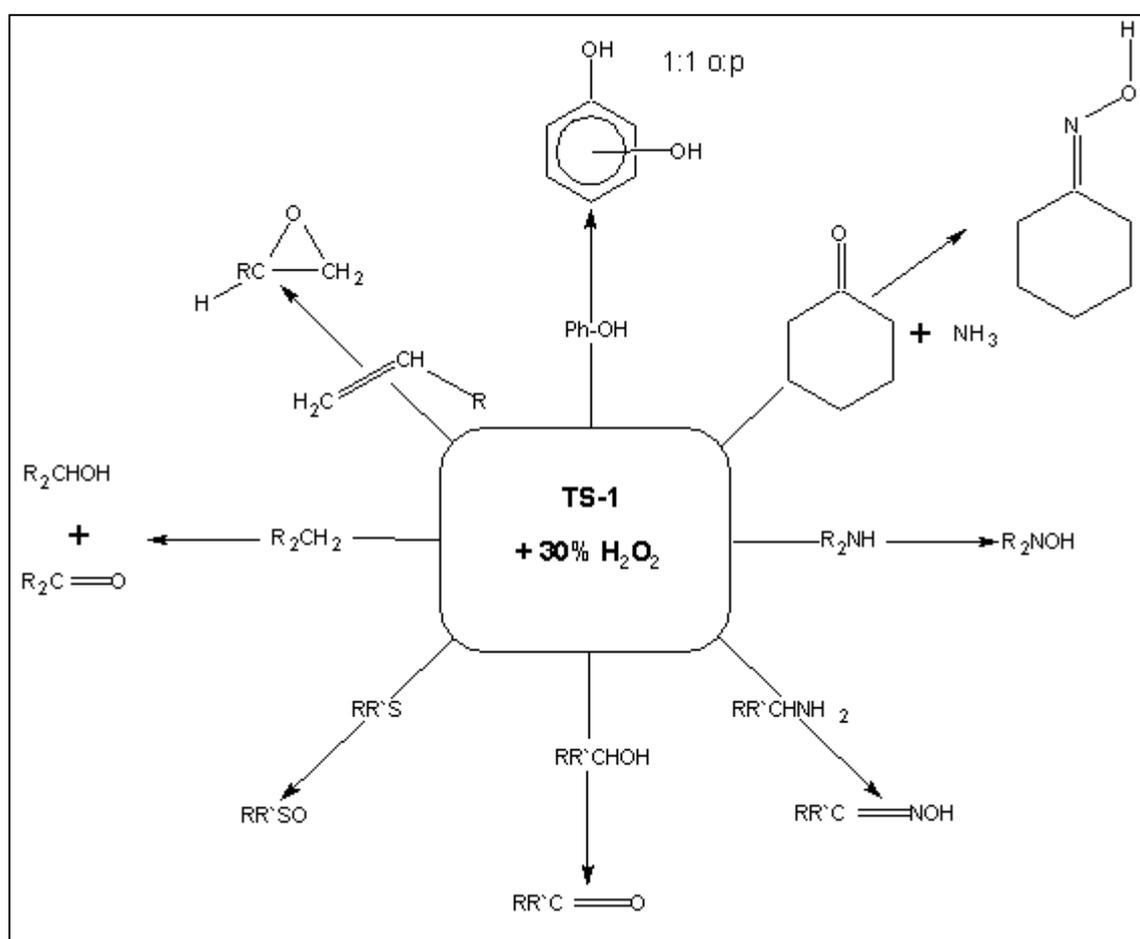


Figure 2-5 Schematic representation of the most relevant oxidation reaction catalyzed by TS-1 [Redrawn from (Sheldon, *et al.*, 1998)]

- *Characteristic and Framework structure*

TS-1 has an MFI structure with molecular diameter channels of 5.1-5.6 Å (Corma, 2003). It is a titanium-substituted aluminium-free silicalite, with a hydrophobic molecular sieve possessing a three-dimensional system of intersecting elliptical pores of  $\text{Ti}^{\text{IV}}$  atoms as active sites and  $[\text{SiO}_4]$  isomorphically inserted into the framework (Sanderson, 2000; Sheldon, *et al.*, 1998). The

hydrophobic character of the catalyst is very important because during the selective oxidation process, the abilities of the reactants and products to penetrate through the zeolite channels are strongly influenced by the polar character of the zeolite (Blasco, *et al.*, 1998).

Its remarkable activity for the selective oxidation of organic substrates is due to the site isolation of  $Ti^{IV}$  centres in the hydrophobic pore silicalite. It allows coinciding adsorption of the substrate and oxidant and confinement of the adsorbed molecules to the active sites which are located in cavities of molecular dimensions. This means that the solvent and substrate molecules do not compete for the active sites containing the active peroxotitanium(IV) oxidant (Sheldon, *et al.*, 1998 ; Sheldon, *et al.*, 1994).

The catalytic activity of TS-1 strongly depends on the content of Ti in the zeolite framework. It was found that only small amounts of Ti (1-2 wt%) can be incorporated into the framework (Tamura, *et al.*, 2007). The incorporation of Ti into the zeolite framework has been illustrated by various spectroscopic techniques such as XRD, UV-VIS, DRS-UV, XPS and EXAFS-XANES. In a well-prepared TS-1 catalyst, Ti is present in tetrahedral coordination, preferably as isolated  $Ti^{IV}$  atoms (Corma, 2003). According to literature, catalysts containing isolated Ti atoms as active sites typically show a DRS-UV band in the range of 208-230 nm depending on the coordination number of  $Ti^{IV}$  (Kholdeeva, *et al.*, 2009). The X-ray patterns indicated the change from the monoclinic structure of silicate-1 to orthorhombic when  $Ti^{IV}$  was introduced into the framework (Notari, 1996). The X-ray microprobe examination demonstrated that titanium distribution within the crystals were perfectly uniform. This verifies that titanium substitutes the silicon in the silicalite structure and not present in other forms. The adsorption isotherm determined by the BET method with  $O_2$  showed that TS-1 possessed typical behaviour of molecular sieves with a pore volume saturation capacity of  $0.16-0.18 \text{ cm}^3 \text{ g}^{-1}$ . These properties make TS-1 a suitable adsorbent with hydrophobic characteristics (Taramasso, *et al.*, 1983).

- *Previous Work*

Based on its relevance in industrial applications, TS-1 has become one of the most studied materials in heterogeneous catalysis in the 20<sup>th</sup> and 21<sup>st</sup> centuries. The most commercialised process, in which TS-1 acts as the heterogeneous catalyst, is the hydroxylation of phenol to hydroquinone and catechol by Enichem, Italy (Thangaraj, *et al.*, 1991). Tuel, *et al.*, (1991) proved that catechol is produced primarily on the surface of the MFI-Ti silicalite crystals and hydroquinone in the channels.

The selective oxidation of phenol has often been used as a test reaction to characterize the presence/absence of  $Ti^{IV}$  atoms in the framework of TS-1. Thangaraj, *et al.*, (1991) investigated the effect pure silicalite-1,  $TiO_2$  (both amorphous and crystalline) and TS-1, as catalysts, has on the oxidation of phenol with  $H_2O_2$  as oxidant. The results indicated that pure silicalite-1 and  $TiO_2$  were inactive for the reaction but TS-1 was active due to the titanium atoms incorporated into the MFI framework structure.

Table 2-5 shows the influences of titanium content, catalyst amount, reaction time and phenol:H<sub>2</sub>O<sub>2</sub> ratio for the selective oxidation of phenol. The phenol conversion increased with increasing titanium content, whereas the selectivity of hydroquinone was not influenced by the content. The hydroquinone selectivity and phenol conversion increased with increasing catalyst amount, hydrogen peroxide volume and reaction time. It was found that if H<sub>2</sub>O<sub>2</sub> did not completely decompose to H<sub>2</sub>O + ½ O<sub>2</sub> during the reaction, then another product, para-benzoquinone(PBQ) was formed (Thangaraj, *et al.*, 1991).

**Table 2-5 Hydroxylation of Phenol with hydrogen peroxide over TS-1 zeolites (Thangaraj, *et al.*, 1991)**

	Reaction conditions											
	Catalyst concentration [g cat/ g phenol]			[Phenol/H <sub>2</sub> O <sub>2</sub> ] mole			Reaction time [hours]			Ti/(Ti+Si)		
	2	5	10	1	3	4	1	3	6	2.1	4.2	5.6
Phenol Conversion %	42	84	87	36	82	92	21	87	96	78	87	90
Hydroquinone Selectivity %	17	40	47	5	43	47	0	33	47	47	47	46

Kumar, *et al.*, (1998) evaluated what had been absorbed by TS-1 after an experiment for the hydroxylation of anisole (C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>) with H<sub>2</sub>O<sub>2</sub> as the oxidant, by varying the solvent between MeCN and water. The adsorption of the catalyst was measured by thermogravimetric analyses. The results illustrated in Table 2-6 indicate the solvent (acetonitrile) and substrate (anisole) are responsible for the weight loss between 40-90°C and 90-250°C, respectively.

**Table 2-6 Thermogravimetric analyses of various adsorbed components in TS-1 after competitive adsorption (Kumar, *et al.*, 1998)**

System	Temperature range (°C)	Weight loss (%)	Total weight loss (%)
TS-1/MeCN	40-90	3.9	12.0
	90-250	8.1	
TS-1/MeCN/C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	40-90	3.7	11.5
	90-250	7.8	
TS-1/C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	90-300	11.7	11.7
TS-1/H <sub>2</sub> O/C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	90-300	12.1	12.1
TS-1/H <sub>2</sub> O	40-423	2.0	2.0

Marchel, *et al.*, (1993) investigated the effect the nature of the oxidant has on the hydroxylation of phenol and toluene with TS-1 as catalyst. Hydrogen peroxide as oxidant was successful for oxidizing phenol to catechol and hydroquinone and toluene to para and ortho cresols. However, for TBHP as oxidant, no products were observed for phenol whereas for toluene, oxidation only occurred on the methyl group, i.e., formation of benzyl alcohol, benzaldehyde and/or benzoic acid. The undesired products formed on the surface of the catalyst because the oxidant (TBHP) size it is too large to penetrate through the channels of TS-1. Therefore, hydrogen peroxide is the only single successful stable peroxide able to enter the channels of TS-1.

- *Limitations*

A serious drawback of TS-1 is its limitation towards substrates with kinetic diameters  $\leq 5.5$  Å because it cannot accommodate the transition state for oxygen transfer from the peroxotitanium (IV) species to the double bonds of larger substrates (Sheldon, *et al.*, 1998). TS-1 is the preferred catalyst for the (ep)oxidation of short linear alkenes chains but the channels of TS-1 will not accommodate o- or m-distributed aromatics, alicyclic terpenes or tertiary aliphatic compounds and simple alicyclics or branched aliphatics (van der Waal, *et al.*, 1998; Sanderson, 2000). For instance, TS-1 easily (ep)oxidizes 1-hexene with aqueous  $\text{H}_2\text{O}_2$  but was unreactive for cyclohexene (ep)oxidation due to the substrate's large dimensions (4.7 x 6.2 Å) (van der Waal, *et al.*, 1998).

### **2.2.1.2 Ti-Beta**

Due to the limitations of TS-1, a larger microporous pore diameter zeolite, Ti-Beta (Ti- $\beta$ ) was investigated for the selective oxidation of bulky organic substrates (Arends, *et al.*, 2001). Ti- $\beta$  has a BEA structure and is an excellent catalyst for the hydroxylation of bulky olefins, such as norbornene, limonene and  $\alpha$ -terpineol (van der Waal, *et al.*, 1997).

The MFI and BEA structures possess both multidirectional channel systems. The main differences between MFI and BEA zeolites is that BEA zeolites have bigger pore diameters than MFI zeolites and MFI exhibits a 10-membered ring channel system, while BEA has a 12-membered ring channel system (Perez-Ramirez, *et al.*, 2005). Ti- $\beta$  is less hydrophobic than TS-1 and therefore intrinsically less active than TS-1 towards substrates that can be accommodated easily in both pore structures (Carati, *et al.*, 1999). The intrinsic activity of Ti- $\beta$  is less due to the presence of aluminium in the Ti- $\beta$  structure and since Ti- $\beta$  is not as hydrophobic as TS-1, the solvent and substrate compete for the same active sites (Corma, *et al.*, 1994; Sanderson, 2000).

- *Characteristic and Framework structure*

Ti- $\beta$  has a three-dimensional structure with pore dimensions of 7.6 x 6.4 Å (van der Waal, *et al.*, 1997). It is a disordered intergrowth of several hypothetical polymorphs consisting of 12-membered

ring channels running in the *a* and *b* directions and a more complex 12-membered ring system parallel to the *c* direction (Serrano, *et al.*, 2001).

Ti-β was introduced in 1992 as titanium incorporated into a zeolite aluminium framework (van der Waal, *et al.*, 1998). The preparation for Ti-β used tetraethylammonium cation as a SDA and required the presence of aluminium for framework stability (Carati, *et al.*, 1999). The problem with aluminium present in the framework causes the formation of acid sites with a hydrophilic interior. This produces acid-catalyzed ring openings during the selective oxidation of substrates with aqueous H<sub>2</sub>O<sub>2</sub> (Arends, *et al.*, 2001). The acid-catalyzed ring opening causes unwanted acid-catalyzed side reactions and diminishes the stability of the structure. (Saxton, 1999). It was then proposed to synthesise an aluminium-free Ti-β. This was achieved by using di(cyclohexylmethyl)dimethylammonium (DCDMA) as the SDA (van der Waal, *et al.*, 1997).

Analytical and physical characterization indicated that the environment surrounding the titanium in Ti-β is very similar to TS-1 (Saxton, 1999). The characterization of Ti-β was performed by XRD, ICP/AES, UV-VIS, SEM and FT-IR. The incorporation of Ti in the framework was confirmed by a continuous increase in the interplaner d-spacing (XRD), presence of strong adsorption maximum at 47000-50000 cm<sup>-1</sup> with the UV-VIS spectra and an intensity of 960 cm<sup>-1</sup> IR band was obtained (van der Waal, *et al.*, 1997). The XRD indicated the presence of Ti with the intergrowth of at least two polymorphs (Blasco, *et al.*, 1998). The SEM revealed very homogeneous, rounded shaped crystals (Corma, *et al.*, 1994).

- *Previous Work*

Corma, *et al.*, (1994) studied the catalyst activity of Ti-β and TS-1 for the (ep)oxidation of 1-hexene, cyclohexene, 1-dodecene and cyclododecene with H<sub>2</sub>O<sub>2</sub> as oxidant. This study is shown in Table 2-7.

**Table 2-7 Selective oxidation of Different Olefins over Ti-β and TS-1 catalysts (Corma, *et al.*, 1994)**

Substrate	Catalyst	Conversion %	Product Selectivity%		
			Epoxide	Glycol	Glyolethers
1-hexene	TS-1	98	96	-	4
	Ti-β	80	12	8	80
Cyclohexene	TS-1	-	100	-	-
	Ti-β	80	-	-	100
1-dodecene	TS-1	83	77	23	-
	Ti-β	80	-	100	-
Cyclododecene	TS-1	26	66	34	-
	Ti-β	42	80	20	-

1-Hexene easily diffused through the channels of the MFI and BEA structure. TS-1 was more active than Ti- $\beta$  because of its strong hydrophobic framework. For cyclohexene, Ti- $\beta$  obtained a higher substrate conversion than TS-1 because the substrate had difficulty penetrating through the channels of the MFI structure (Corma, *et al.*, 1994). The oxidation of cyclohexene occurred 14 to 80 times faster with Ti- $\beta$  than with TS-1 as catalyst (van der Waal, *et al.*, 1998). 1-Dodecene could penetrate the BEA structure and the linear channels of the MFI structure but not the complex channels of the MFI structure, this meant that not all Ti sites of TS-1 were accessible to the substrate. For cyclododecene, the substrate could not diffuse through the channels of Ti- $\beta$  but by the external surface of the catalyst, whereas cyclododecene could not be accommodated by the MFI structure. The product selectivity indicated TS-1 obtained high epoxide selectivity with small amounts of epoxide ring opening products called glycols. Whilst for Ti- $\beta$ , the opening of the epoxide ring occurred more frequently, resulting in high glycol selectivity (Corma, *et al.*, 1994).

Corma, *et al.*, (1995) investigated the (ep)oxidation of olefins with Ti- $\beta$  as catalyst by comparing the oxidants; H<sub>2</sub>O<sub>2</sub> and TBHP. TBHP showed less activity and slower reaction rates than H<sub>2</sub>O<sub>2</sub>. The lower activity is due to the fact that H<sub>2</sub>O<sub>2</sub> has a higher oxygen activity than TBHP. Slower reaction rates can be explained by the complex electrophilic character, Ti-OOR (R=C-(CH<sub>3</sub>)<sub>3</sub>) species formed with TBHP and not the simpler character, Ti-OOH formed with H<sub>2</sub>O<sub>2</sub>.

- *Limitations*

The drawback of Ti- $\beta$  is that it generally requires Al<sup>3+</sup> in order to crystallize and enhance the stability of the framework. Aluminium in the framework causes secondary acid-catalyzed reactions and leaching. Newer methods have been implemented to synthesis Ti- $\beta$  free of aluminium but these methods still produce secondary acid-catalyzed reactions (Notari, 1996). Due to the larger pore diameter, Ti- $\beta$  can accommodate substrates: cycloalkanes, cyclohexenes and cycloalcohols for oxidation and use TBHP as an oxidant but is limited to substrates smaller than 7 Å. As a result, it will have difficulty to accommodate some of the substrates illustrated in Table 2-8, which are of interest to the fine chemical industry (Blasco, *et al.*, 1995).

**Table 2-8 Molecular diameters of some aromatic rings (Ruthven, *et al.*, 1991)**

Aromatic Ring	Diameter [Å]
Benzene	6.9
Toluene	6.9
p-Xylene	6.9
o-Xylene	7.3
Naphthalene	7.3
2-6,2-7 Dimethylnaphthalene	7.3
1-2,1-5,1-6 Dimethylnaphthalene	7.9
1-3 Dimethylnaphthalene	8.6
1-4 Dimethylnaphthalene	9.1
Mesitylene	8.4
Tri-isopropylbenzene	9.3

For this reason, there is still scope to develop titanium molecular sieves with larger pore diameters to accommodate bulkier organic substrates in the fine chemical industry (Blasco, *et al.*, 1995).

### 2.2.2 Mesoporous Materials

Microporous titanium silicate catalysts are hindered due to their small pores for the selective oxidation of bulky substrates that are of interest to the fine chemical and pharmaceutical industries. It was therefore urged to create frameworks with pore diameters falling in the mesopore category (Beck, *et al.*, 1992). The new family of porous materials are promising in catalysis, adsorption, electronics, optics and many other developing applications (Fenelonov, *et al.*, 1999). Mesoporous molecular sieves as catalyst are applied in industrial processes such as the selective oxidation of olefins, unsaturated alcohols, vegetable oils and hydroxylation of aromatic rings (Eimer, *et al.*, 2006). Compared to microporous materials, mesoporous materials possess several advantages for the selective oxidation of bulky organic substrates:

- Have larger pore sizes
- Higher internal surface areas ( $>1000 \text{ m}^2 \cdot \text{g}^{-1}$ )
- Large number of surface hydroxyl groups (Li, *et al.*, 2006).

Mesoporous materials are either amorphous or paracrystalline solids (Beck, *et al.*, 1992). The presence of mesopores in the crystallites of redox molecular sieves increases the external surface and in the process creates larger pore diameters available for the substrates (Corma, 1997). Mesoporous molecules sieves are amorphous silica with regular pore structures and well-defined channel systems (Notari, 1996). The mesopore size is influenced by the size of the surfactant molecules used to synthesize the redox molecular sieve and the pore diameter is generally varied in

the range from 20-500 Å (Fenelonov, *et al.*, 1999). It was found that no diffusion limitations occurs for bulky substrates with mesopores larger than 25 Å (Kholdeeva, *et al.*, 2009).

### 2.2.2.1 *Ti-MCM-41*

In 1992, a new family of mesoporous molecular sieves designated as M41S were discovered (Beck, *et al.*, 1992). MCM(Mobil Crystalline Materials)-41 is one of the members of this extensive family of mesoporous molecular sieves and possess properties between those of amorphous SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and microporous sieves (Sheldon, *et al.*, 1998). Titanium incorporated into the framework of siliceous MCM-41 forms the redox molecular sieve Ti-MCM-41, which is formed via a Liquid Crystal Templating (LCT) mechanism. Ti-MCM-41 has a regular array of one dimensional pores and is a promising catalyst for the selective oxidation of bulky substrates (Chen, *et al.*, 1998). The type of surfactant, silicon/surfactant ratio, synthesis method, alkyl chain length of surfactant, pH value, hydrothermal synthesis time and temperature are the main factors affecting the pore diameter, wall thickness and framework structure of the catalyst (Blin, *et al.*, 2001). Ti-MCM-41 as catalyst, favours the hydroxylation of bulky aromatic compounds, oxidation of primary and secondary alcohols, long linear alkane and alkene chains (Li, *et al.*, 2006).

The advantages of Ti-MCM-41 as catalyst for the selective oxidation of bulky organic substrates are:

- No diffusion limitation occurs if the metal is located in the framework
- Reasonably easy isomorphous substitution of metal into the skeleton of MCM-41
- Isolation of metals is more easily achieved than in microporous zeolites
- Ability to (ep)oxidize large substrates and use organic hydroperoxides as oxidants (Ziolek, 2004; Corma, 1997).

The catalytic activity and selectivity for Ti-containing mesoporous materials is not as high as for Ti-containing microporous materials for the (ep)oxidation of organic substrates (C<sub>3</sub>-C<sub>8</sub>). The main reasons for the low activity are the poor hydrothermal stability (the substitution of Ti for Si in the silica framework of MCM-41 reduces the stability of the structure), titanium's ability to easily leach out of the silicalite framework and the low hydrophobic framework (Li, *et al.*, 2006).

- *Characteristic and Framework structure*

Ti-MCM-41 is an amorphous silicate containing highly ordered hexagonal array of uniform one-dimensional mesopores varying between 20-100 Å with a very narrow pore-size distribution (Li, *et al.*, 2006). The uniform one-dimensional mesopores are cylindrical/hexagon in shape with thin small walls between them in a honeycomb shape structure (Fenelonov, *et al.*, 2001). The titanium mesoporous molecular sieve possesses a surface area above 700 m<sup>2</sup>/g and hydrocarbon sorption capacity of 0.7 cc/g or greater (Beck, *et al.*, 1992). The narrow pore-size distribution and high internal surface indicates that Ti-MCM-41 has similar properties to microporous sieves. However,

unlike microporous molecular sieves, the pore walls do not possess an ordered structure. This indicates similar properties to amorphous SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Arends, *et al.*, 1997). The surface area and pore diameter decreases with increasing the titanium content, while higher Ti content enhances catalytic activity (Chen, *et al.*, 1998; Tamura, *et al.*, 2007).

Ti-MCM-41 was characterized by infrared spectroscopy (IR), powder X-ray diffraction (XRD), N<sub>2</sub> and Ar adsorption, thermal analysis, diffuse reflectance ultraviolet absorption spectra (DRS-UV) and extended X-ray absorption fine (Near Edge) structure (EXAFS and XANES) (Li, *et al.*, 2006). The N<sub>2</sub> and Ar adsorption indicates that Ti-MCM-41 illustrates a type IV isotherm with a sharp inflection at a relative pressure around P/P<sub>0</sub>=0.2-0.3. The pore size distribution curve illustrates a narrow and strong band. This is a characteristic of well ordered mesoporous materials with a narrow and uniform pore size distribution (Eimer, *et al.*, 2006). There are six basic adsorption isotherm types as illustrated in APPENDIX A. Type I is characteristic of adsorbents with extremely small pores (micropores) and Types II illustrate isotherms of nonporous adsorbents. Type IV is characteristic of adsorbents with relatively large pores (mesoporous materials), whereas Types III and V represent adsorptive molecules that have greater affinity for one another than they do for the solid. Type VI is a rare isotherm and indicates a nonporous solid with an almost completely uniform surface. (Lowell, *et al.*, 1984). Porous materials can represent a combination of these adsorption isotherms types. Mesoporous materials often possess adsorption isotherms that have a shape in-between isotherm types IV and I. There are methods used to determine if these mesoporous materials possess micropores and mesopores or only mesopores. The methods are the t-plot method, α<sub>s</sub>-plot method or Dubinin-Radushkevitch isotherm (Schneider, 1995).

XRD analysis illustrates that Ti-MCM-41 possess three peak patterns, a very strong feature at a low angle (100 reflection line) and two other peaks with weaker intensities at higher angles. The weaker peaks indicate that the channels are hexagonally organized and a highly ordered MCM-41 structure is formed (Blin, *et al.*, 2001). The sharp diffraction peak at the low angle confirms that the material is mesoporous (Chen, *et al.*, 1998). X-ray diffraction calculates the d<sub>100</sub> spacing and the hexagonal unit cell can be determined by Equation 2-1. Knowing the hexagonal unit cell, the wall thickness can be calculated as illustrated in

Table 2-9. The wall thickness is the difference between the unit cell and pore diameter determined by the BJH method (Blin, *et al.*, 2001).

$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

**Equation 2-1 Unit cell (Blin, *et al.*, 2001)**

**Table 2-9 Volume determined by Ar physisorption, Pore diameter, BET area,  $d_{100}$  peak and hexagonal unit cell parameter  $a_0$  (Blasco, *et al.*, 1995)**

Sample	$V_p$ [cm <sup>3</sup> /g]	Pore size [Å]	BET surface area [m <sup>2</sup> /g]	$d_{100}$ [Å]	$a_0$ [Å]	Wall thickness [Å]
TiO <sub>2</sub> (soild wt%) 2.4	0.45	31	884	33	38	7
TiO <sub>2</sub> (soild wt%) 2.0	0.70	35	1102	38	44	9

Mesoporous silica materials are generally prepared by synergistic self-assemblies between surfactants acting as organic templates and silica species forming mesoscopically ordered composites (Kim, *et al.*, 2000). Ti-MCM-41 involves the direct interaction between an ionic bond between a cationic charged surfactant with silica and an anionic inorganic species (Meynen, *et al.*, 2007). The cationic surfactant interacts electrostatically with the inorganic species (Kim, *et al.*, 2000). The surfactant plays a pivotal role in the synthesis to form the self-assembly of the mesoporous materials (Corma, *et al.*, 1997). For the synthesis of Ti-MCM-41, various alkyl chain lengths from C<sub>6</sub> to C<sub>16</sub> were used as surfactants. When alkyl chain lengths C<sub>6</sub> to C<sub>8</sub> acted as the surfactant, Ti-MCM-41 was not formed but formed with longer chains (Corma, 1997). Usually, quaternary ammonium salts, C<sub>n</sub>H<sub>2n+1</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, such as alkyltrimethylammonium bromide (CTAB) acts as the surfactant for the synthesis of Ti-MCM-41 (Blin, *et al.*, 2001).

- *Previous Work*

A comparison was conducted with TS-1, Ti-β and Ti-MCM-41 as catalyst for the selective oxidation of 1-hexene with H<sub>2</sub>O<sub>2</sub>. Although the coordination of Ti is similar in the three cases: the Ti atoms incorporated into the Si framework, redox potential and adsorption characteristics are different, resulting in a difference between activity and selectivity. The substrate in this case can penetrate easily through all the structures and the results are illustrated in Table 2-10. The intrinsic activity is as follows, TS-1 >Ti-β> Ti-MCM-41. This is explained as a result of hydrophobicity (Blasco, *et al.*, 1995; Ziolk, 2004). TS-1 has the highest hydrophobicity among the titanium catalysts, while Ti-β has a lower hydrophobicity than TS-1 due to acidic sites and Ti-MCM-41 is more hydrophilic than Ti-β because the internal surface consists mainly of Si-OH groups (van der Waal, *et al.*, 1998). Another reason for the low activity of Ti-MCM-41 for small substrates is the pore diameters (31 Å) are too large to show any shape selectivity (Chen, *et al.*, 1998). TS-1 and Ti-MCM-41 are more selective towards the formation of (ep)oxide, whereas Ti-β favours acid-catalyzed ring openings (Blasco, *et al.*, 1995).

**Table 2-10 Activity of Ti-molecular sieves for oxidation of 1-hexene with H<sub>2</sub>O<sub>2</sub> (Blasco, *et al.*, 1995)**

Catalyst	Alkene conversion (mol%)	Epoxide selectivity (mol%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)
TS-1	49	96	99
Ti-β	38	7	94
Ti-MCM-41	9	96	65

For the (ep)oxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub> as oxidant and Ti-MCM-41 as catalyst, 10% of cyclohexene was converted with 5% epoxide selectivity. When anhydrous TBHP acted as the oxidant, the conversion was 67% with epoxide selectivity of 92%. Higher conversions and selectivity were obtained with TBHP than H<sub>2</sub>O<sub>2</sub> because of Ti-MCM-41 hydrophilic framework (Hagen, *et al.*, 2002). Due to the catalyst hydrophilic structure with H<sub>2</sub>O<sub>2</sub> as oxidant, the adsorption of the hydrophobic substrate and desorption of the polar oxidation products are hindered. Whereas when TBHP acted as the oxidant, deactivation by adsorbed products molecules do not occur (Carvalho, *et al.*, 1997).

- *Limitations*

Ti-MCM-41 has the potential of oxidizing bulky substrates for the fine chemical industry but is hindered by two obstacles. The first limitation is the hydrophilic surface due to the large population of defect silanol groups (Ungureanu, *et al.*, 2003). This hydrophilic framework decreases the catalyst activity and selectivity in reactions with aqueous H<sub>2</sub>O<sub>2</sub> as oxidant because silanol strongly absorbs water molecules. This causes problems for organic substrates to enter and products to leave the active sites (Ziolek, 2004). The second drawback is the low hydrothermal stability in comparison to TS-1 and Ti-β (Mrak, *et al.*, 2006). The hydrothermal instability is due to the amorphous silica nature of the pore walls in Ti-MCM-41 (Solberg, *et al.*, 2005). These drawbacks allow the structure to collapse during the oxidation process, causing titanium to leach and disable the discovery of the catalyst (Sheldon, *et al.*, 1998).

With regards to scenarios for heterogeneous catalyst in a liquid phase as discussed in section 2.2b), TS-1 belongs to scenario 1 while Ti-MCM-41 with H<sub>2</sub>O<sub>2</sub> as oxidant belongs to scenario 2 (Arends, *et al.*, 2001). Both microporous and mesoporous materials have drawbacks causing to limit the hydroxylation of substrates. It is therefore urged to create a material that compensates the disadvantages of microporous materials and mesoporous materials by creating a microporous/mesoporous material (Solberg, *et al.*, 2005).

### 2.2.3 Microporous/Mesoporous Materials

It was proposed to combine the advantages of microporous and mesoporous materials to synthesise microporous/mesoporous catalysts (Mrak, et al., 2006). Microporous/mesoporous catalysts are built up of large pore sizes with high mass transfer rates to ensure good absorption of bulky substrates similar to mesoporous materials but at the same time, displays similar characteristics to microporous materials with regards to good hydrothermal stability and strong hydrophobic structures (Meynen, et al., 2007).

One of the procedures for producing microporous/mesoporous materials is implementing a non-ionic triblock amphiphilic copolymer surfactant as a SDA and synthesising under strongly acidic hydrothermal conditions (Li, et al., 2006). There are generally two types of surfactants used for the synthesis of mesoporous silica redox molecular sieves, namely, ionic and non-ionic. Alkyltrimethyl ammonium bromide is used in most cases as the cationic surfactant and triblock amphiphilic copolymers as the non-ionic surfactant. Ionic surfactants interact electrostatically with inorganic species, while non-ionic surfactants react through hydrogen bonding or van der Waals interactions (Kim, et al., 2000).

The most common amphiphilic block copolymers are poly(alkylene oxide)triblock copolymers poly(ethylene oxide)-poly(propylene oxide)-(poly(ethylene oxide)) (PEO-PPO-PEO) because of their mesostructural ordering properties, amphiphilic character, low-cost commercial availability, nontoxic and biodegradability (Kim, et al., 2000). The most popular PEO-PPO-PEO material is Pluronic P123. It is a difunctional block copolymer surfactant terminating in primary hydroxyl groups and is 100% active (BASF, 2004). Under acidic conditions, the PPO block acts as the hydrophobic segments, the EO block contains the hydrophilic head group and the pore size and thickness of the silica walls are manipulated by varying the temperature (Zhao, et al., 1998).

#### 2.2.3.1 Ti-MMM-2

Ti-MMM-2 is a highly active, hydrothermally stable mesoporous titanium-silicate synthesised under moderate acidic conditions (Kholdeeva, et al., 2004). It is a two dimensional hexagonal ordered mesoporous with a narrow pore size distribution (Maksimchuk, et al., 2005).

The main advantage of the Ti-MMM-2 system for the hydroxylation of bulky substrates with hydrogen peroxide as oxidant is that it behaves as a true heterogeneous catalyst. This results in recyclability of the catalyst and high purity products (Kholdeeva, et al., 2007).

- *Characteristic and Framework structure*

This catalyst is synthesised with hydrochloric acid and Kholdeeva, et al., (2004) prepared Ti-MMM-2 with two methods. The first method used only CTAB as a surfactant, while the second method used a mixture of P123 and CTAB (95% non-ionic template P123 and 5% ionic CTAB,). It was found that

the catalyst with only CTAB as surfactant possessed only mesopores and no micropores. The catalyst with the surfactant mixture possessed mesopores and micropores (Kholdeeva, *et al.*, 2005).

Ti-MMM-2 was characterised by XRD diffraction, N<sub>2</sub> adsorption/desorption, TEM analysis and DR UV-VIS spectroscopy (Zalomaeva, *et al.*, 2006). The XRD (100) reflection was of symmetric shape with full-width-at-half-maximum (FWHM) values in the 0.2-0.8°2 $\theta$ . The N<sub>2</sub> adsorption isotherms indicated a type IV with a narrow interval of relative pressure  $\Delta(P/P_0)$  (Kholdeeva, *et al.*, 2005). The TEM images indicated that the mesopores of the catalyst were not very ordered (Kholdeeva, *et al.*, 2004).

The XRD measurements and N<sub>2</sub> adsorption for Ti-MMM-2 with only CTAB as surfactant possessed an ordered hexagonal arrangement of uniform mesopores with a diameter of 32 Å, surface area between 900-1400 m<sup>2</sup>/g and silicate wall thickness of 10 Å. The catalyst with the surfactant mixture, exhibited 60-70 Å mesopore diameters, 500 m<sup>2</sup>/g surface area and 40 Å silicate wall thickness (Kholdeeva, *et al.*, 2004). The DR-UV spectrum indicates that titanium is mostly in a site-isolated form, likely tetrahedral-coordinated because it has a narrow band with a maximum of 211 nm (Maksimchuk, *et al.*, 2005). The physiochemical characterization and catalytic properties indicates that Ti-MMM-2 allows an ease of access and high dispersion of titanium. This promotes high catalytic activity and selectivity (Li, *et al.*, 2006).

The catalyst with the mixture surfactant obtained optimum results and is a novel mesoporous titanium silicate that should be studied in more detail (Kholdeeva, *et al.*, 2005). Ti-MMM-2 as catalyst has only been studied for the selective oxidation of bulky aromatic rings bearing hydroxyl functions to form quinones. This resulted in high conversions and product selectivity. Ti-MMM-2 is therefore a promising catalyst for bulky aromatic rings exhibiting hydroxyl functions but further studies should be conducted for the selective oxidation of bulky aromatic rings not possessing hydroxyl functions (Zalomaeva, *et al.*, 2006).

### **2.2.3.2 Highly ordered mesoporous material**

Kim, *et al.*, (2000) found that catalysts possessed irregular structures with low surface areas when synthesised with sodium metasilicate, hydrochloric acid and non-ionic amphiphilic blocopolymers as SDA. A highly ordered molecular sieve was synthesised using sodium silicate, sulphuric acid and non-ionic blocopolymer surfactant as SDA. Highly ordered mesoporous material sieves possess uniform pore sizes (30-65 Å), high surface areas, thick mesopore walls and hexagonal/cubic structures (Fortier, *et al.*, 2006).

The charge of the acid anion and strength plays an important role in the structure of the catalyst, since the formation of the mesophase occurs through counter ion mediated interactions (hydrogen bonds or van der Waals interactions). The bonds/interactions are between (S<sup>0</sup>H<sup>+</sup>) and (X<sup>-</sup>I<sup>+</sup>) where S<sup>0</sup> is the non-ionic surfactant, H<sup>+</sup> the proton, X<sup>-</sup> the acid anion, (e.g., Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and I<sup>+</sup> is the

protonated silicic acid. With sulphuric acid, the anion  $\text{SO}_4^{2-}$  is directly synchronised to the silicon atom at the surfactant-silica interface. While for hydrochloric acid, the anion  $\text{Cl}^-$  is not directly attached to the silicon atom as illustrated in Figure 2-6. This directly coordinated assembly ensures sufficient electrostatic shielding and effective hydrogen bonding. This results in highly ordered structures (Fortier, *et al.*, 2006).

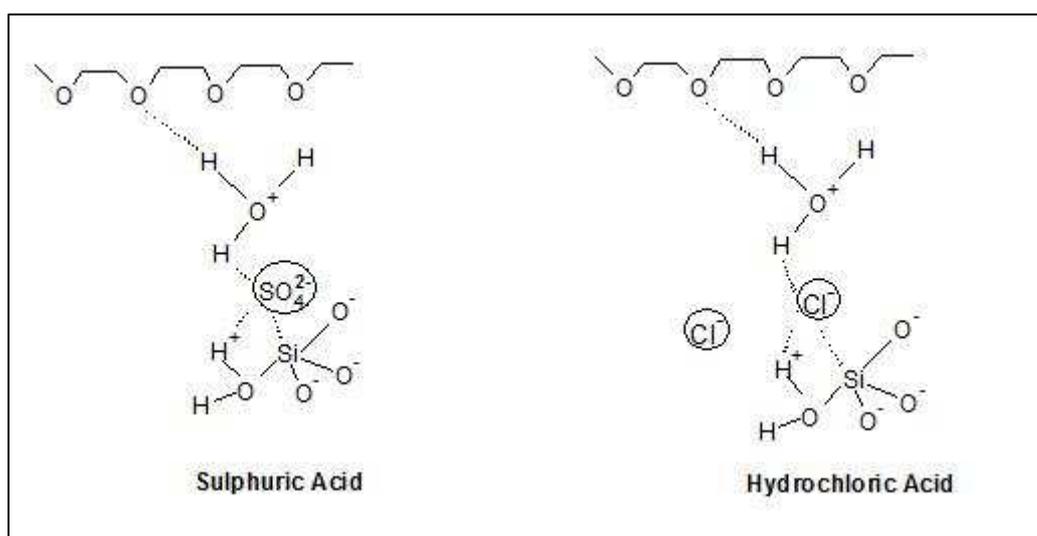


Figure 2-6 Surfactant surface interface [Redrawn from (Fortier, *et al.*, 2006)]

- *Characteristic and Framework structure*

The highly ordered catalysts were characterized by X-ray diffraction, TEM and  $\text{N}_2$  adsorption/desorption isotherms. The X-ray diffraction illustrates a very intense diffraction peak with two or more weaker peaks. This indicates a characteristic of a hexagonal structure. The TEM images indicate well-ordered structures and the FTIR spectra show a titanium framework with a  $960\text{ cm}^{-1}$  band. The  $\text{N}_2$  isotherm is a typical IV type adsorption isotherm with an irreversible  $\text{H}_1$  hysteresis loop as a result of large pores. The isotherm illustrates  $P/P_0$  is in the 0.4-0.7 range, a BJH diameter of  $72\text{ \AA}$  and BET surface area of  $840\text{ m}^2\text{g}^{-1}$  (Fortier, *et al.*, 2006). Little work has been done for the investigation of the highly ordered mesoporous material as a catalyst. Nevertheless, it seems promising for the selective oxidation of bulky substrates.

## 2.2.4 Reusability of catalyst

One aspect that should be taken in consideration to ensure process efficiency and economical feasibility is to test whether the catalyst truly acts as a heterogeneous catalyst (Maksimchuk, *et al.*, 2005).

The instability of Ti species resulting in leaching is directly influenced by the lifespan and reusability of the catalyst (Li, *et al.*, 2006). The common test to observe if the catalyst truly acts heterogeneous is by recycling the catalyst and conducting the experiment under the same conditions without any loss in activity or selectivity (Arends, *et al.*, 2001). The catalyst could lose activity due to damage of the porous structure and partial oligomerization of titanium (Maksimchuk, *et al.*, 2005).

The catalytic activity decreased when the catalyst was reused for the selective oxidation of organic compounds with H<sub>2</sub>O<sub>2</sub> and Ti-MCM-41 as catalyst. This was the result of titanium leaching (Chen, *et al.*, 1998). The cyclohexene conversion decreased 2-3 times compared to a fresh catalyst because the catalyst structure was destroyed when H<sub>2</sub>O<sub>2</sub> acted as the oxidant (Rhee, *et al.*, 1996). When TBHP was used as the oxidant under the same conditions. The catalyst possessed good stability and could be regenerated without a retard in activity (Hagen, *et al.*, 2002). For this process with TBHP as oxidant, TBHP interacted reversibly upon heating with titanium in Ti-MCM-41. Whereas H<sub>2</sub>O<sub>2</sub> interacted irreversibly, this led to the transformation of isolating oligomerix and oxide-like titanium species. Although no leaching occurred with TBHP as oxidant, the process still reports to be less active than using H<sub>2</sub>O<sub>2</sub> (Kholdeeva, *et al.*, 2000). Therefore, the interaction of the oxidants with the titanium species is also a factor affecting the catalyst activity and selectivity (Hagen, *et al.*, 2002).

For the selective oxidation of 2-methyl-1-naphthol, Ti-MMM-2 behaved as a true heterogeneous catalyst because it did not suffer titanium leaching and could be recycled without loss in catalytic activity and selectivity (Kholdeeva, *et al.*, 2007). The catalyst was recycled by separating the catalyst from the reaction mixture via filtration, washed with methanol, dried in air at 100°C and then reused (Kholdeeva, *et al.*, 2005). This proves that Ti-MMM-2 is a promising catalyst for the selective oxidation of bulky substrates with aqueous H<sub>2</sub>O<sub>2</sub> (Kholdeeva, *et al.*, 2004).

## 2.3 Solvents

The role played by the solvent is not simple. The nature of the solvent for the selective oxidation of organic compounds has a pivotal impact on the activity, product selectivity and reaction kinetics (van der Waal, *et al.*, 1997). The main purpose of a solvent in a reaction process is to homogenize the reaction solution in the liquid phase in order to prevent mass-transfer problems. The solvent has an effect on the reaction pathway; the pathway plays a role in the interaction between the substrate, catalyst and oxidant (Fan, *et al.*, 2008). The interaction between the catalyst and solvent influences the ability of the substrate to be accommodated by the active sites. The catalyst is regarded as a second solvent that selects the substrate from the solvent. The substrate extracted is resolved by the size and hydrophobicity of the catalyst pores and substrate (Arends, *et al.*, 1997). Factors affecting the solvent are: the aprotic/protic nature, polarity of the solvent, diffusion/counterdiffusion and the solubility of the substrate and products in the solvent (Fan, *et al.*, 2008).

The polarity of solvents is divided into two categories, namely, polar and non-polar. Polarity of solvents is measured by the dielectric constant. Solvents with a dielectric constant of less than 15 are generally considered to be non-polar and dielectric constants higher than 15 are regarded as polar solvents. Usually, polar compounds dissolve best in polar compounds and non-polar compounds dissolve best in non-polar compounds. Best results will be obtained with polar solvents because organic compounds and hydrogen peroxide are considered as polar compounds (McMurry, 2000).

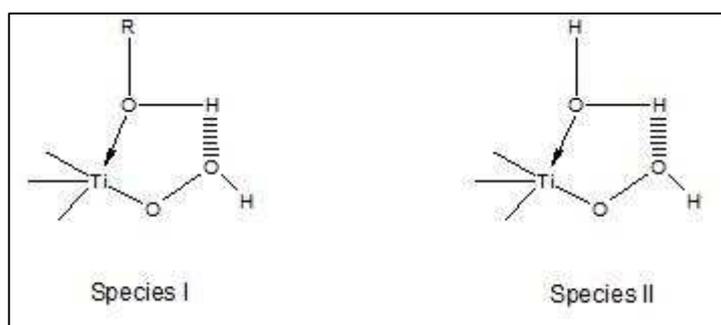
The nature of solvents is divided into two types, namely, protic and aprotic. Protic solvents contain –OH or –NH groups while aprotic does not. Protic solvents favour  $S_N1$  reactions whereas aprotic solvents are suitable for  $S_N2$  reactions.  $S_N1$  is a nucleophilic substitution reaction with a rate-determining step that is unimolecular, while  $S_N2$  reaction is a rate-determining step that is bimolecular. It is bimolecular because in the reaction a lone pair from a nucleophile attacks an electron deficient electrophilic centre and bonds to it. Protic solvents are the worst solvent for  $S_N2$  reactions because they slow down the reaction by clustering around the reactant nucleophile. Aprotic solvents slow down the  $S_N1$  reactions (McMurry, 2000).

Table 2-11 illustrates the most common aprotic/protic solvents used for the selective oxidation of organic substrates with hydrogen peroxide as oxidant because they prevent mass transfer problems by forming a single phase with the reaction solution due to their polarity (Corma, *et al.*, 1996). From literature, the dielectric constant is directly proportional to the conversion of the substrate with the respective solvents (Hulea, *et al.*, 1996). As a result, the higher the solvent polarity, the more concentration of substrate is available in the active sites area. This results in higher reaction rates (Corma, *et al.*, 1996). Therefore, either acetonitrile or methanol would achieve the highest activity and selectivity for the selective oxidation of organic compounds.

**Table 2-11 Characteristics of the most common solvents used in the oxidation of organic substrates (Corma, *et al.*, 1996)**

Solvent	Protic (P) or Aprotic (A)	Dielectric constant	Boiling point (°C)
Methanol	P	32.7	64.7
Ethanol	P	24.5	78.3
t-Butyl alcohol	P	10.9	82.2
Acetonitrile	A	37.5	81.6
Acetone	A	20.7	56.3
Methyl ethyl ketone	A	18.5	79.6

Figure 2-7 illustrates the active intermediate sites formed for the hydroxylation of organic substrates when Ti-containing molecular sieves and hydrogen peroxide as catalyst and oxidant, respectively. The active intermediate consists of a stable five-membered cyclic structure that is formed by the coordination of the solvent to the Ti centres and hydrogen bonding to the Ti-peroxo complex (Ziolek, 2004). In this complex, Ti increases the electrophilicity of the peroxo complex. This makes the nucleophilic attack of organic substrates and the coordination of a solvent to the active site easier, leading to the stabilization of the intermediate (Hulea, *et al.*, 1996). Species I present the complex for protic solvents because alcohol is a ligand of Ti, while Species II presents aprotic solvents with a water molecule instead of alcohol as a ligand of Ti. Species I are complexes with a very strong hydrophobic character because they readily favour an alcohol molecule instead of a water molecule. Species II is slightly hydrophilic because it attracts a water molecule instead of the alcohol molecule. Water has a lower donor property than alcohol. This results in a higher electrophilic character and therefore Species II will have a higher intrinsic oxidation activity than Species I (Corma, *et al.*, 1996).



**Figure 2-7 Structural scheme of proposed intermediate Ti species [Redrawn from (Hulea, *et al.*, 2004)]**

Disregarding the type of titanosilicates used in the process, protic solvents generally give lower (ep)oxide selectivity in comparison to aprotic solvents due to the stronger nucleophilicity of alcohol than water (Fan, *et al.*, 2008). Protic solvents favour very strong hydrophobic catalysts while aprotic solvents favour less hydrophobic catalysts (Hulea, *et al.*, 2004). The obvious Ti-containing molecular sieves favouring protic solvents over aprotic solvents is TS-1 because it has a very strong hydrophobic character, while most other Ti-molecular sieves will be favoured by aprotic solvents (Fan, *et al.*, 2008).

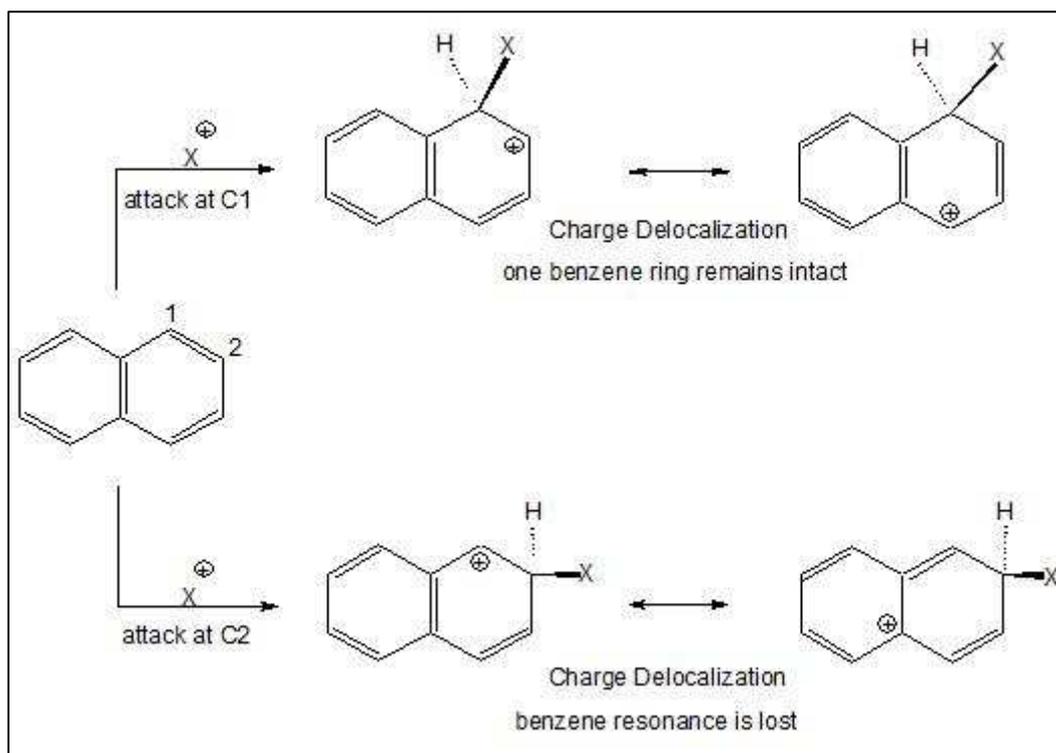
For Ti-molecular sieves, if the titanium-site is slightly acidic, the interaction of alcohol solvents will increase the acidity causing to deactivate the catalyst. This will result in the formation of acid-catalyzed by-products (van der Waal, *et al.*, 1997). Aprotic solvents reduce acid-catalyzed by-products, particularly MeCN because it diminishes the acidity of the catalyst surface because of its slightly basic character (Sheldon, *et al.*, 1998).

MeCN is regarded to be one of the best solvents for the hydroxylation of organic substrates with Ti-molecular sieves and hydrogen peroxide because of its slightly basic character and promotes (ep)oxide selectivity (Carati, *et al.*, 1999). The additional reaction formed between hydrogen peroxide and MeCN molecules activated by the electrophilicity of Ti, results to peroxyimide acid [R-C(=NH)-O-O-H]. This is known to be an active oxidant agent towards certain organic substrates (Hulea, *et al.*, 1996).

## 2.4 Substrates

The environmentally friendly selective oxidation process for producing Vitamin K<sub>3</sub> is generally produced via two routes: (i) the hydroxylation of 2-methylnaphthalene (2MN) (ii) the oxidation of 2-methyl-1-naphthol (2MNL) (Kulkarni, *et al.*, 1998).

2MN and 2MNL are obtained from naphthalene, which is two benzene rings fused together. Naphthalene has a cyclic conjugated 10- $\pi$ -electron system and stabilized by resonance. It has three resonance forms and the only difference is the placement of the  $\pi$  and nonbonding valence electrons. Naphthalene is more reactive than benzene, both in substitution and addition reactions. Electrophilic substitution reactions for naphthalene occur mostly on the C1 and C2 as illustrated in Figure 2-8. Electrophilic substitution reactions take place more rapidly at C1. The kinetically favoured C1 creates a cationic intermediate while keeping one benzene ring intact, whereas if C2 is favoured, the resonance is lost because both benzene rings are affected (McMurry, 2000; <http://www.cem.msu.edu/~reusch/VirtualText/benzrx2.htm>, 2010).



**Figure 2-8** The two naphthenonium intermediates created by attack at C1 and C2 (<http://www.cem.msu.edu/~reusch/VitualText/benzrx2.htm>, 2010)

2MN and 2MNL are naphthalene with substituents. The influence of a substituent present on an aromatic ring has two effects:

- 1) A substituent affects the reactivity of the aromatic ring. Some substituents activate the ring, making it more reactive than benzene whereas some substituents deactivate the ring, making it less reactive than benzene. Activating groups donate electrons to the ring and thus, stabilize the carbocation intermediate from electrophilic addition and cause it to form fast. Deactivating groups withdraw electrons from the ring and as a result, destabilize the carbocation intermediate and cause it to form slowly.
- 2) A Substituent affects the orientation of the reaction. The nature of the substituent already present on the benzene ring determines the site at which the electrophilic substitution occurs. The three possible sites are ortho, meta and para positions (McMurry, 2000).

Reactivity and orientation in electrophilic substitution are controlled by inductive and resonance effects. The inductive effect is the withdrawal or donation of electrons through a  $\sigma$  bond due to electronegativity and polarity of bonds in functions groups. The resonance effect is the withdrawal or donation of electrons through a  $\pi$  bond due to the overlap of a p orbital on the substituent with a

p orbital on the aromatic ring. Alkyl groups are activating because of their electron-donating inductive effect, whereas hydroxyl groups are activating due to their strong electron-donating resonance effect. Both groups are more reactive towards ortho- and para-directing positions (McMurry, 2000; <http://www.cem.msu.edu/~reusch/VirtualText/benzrx2.htm>, 2010).

### 2.4.1 Hydroxylation of 2-Methyl Naphthalene

Figure 2-9 illustrates possible products that are formed from the oxidation of 2MN. The oxidation mainly occurs either on the methyl group or the aromatic rings. Oxidation on the methyl group forms 2-naphthaldehyde, 2-naphthol or 2-naphthoic acid while on the aromatic rings, the desired product 2MNQ, intermediate 2MNL or the undesired isomeric 6-methyl-1,4-naphthoquinone can be formed. Products of radical coupling and over-oxidation can also be produced (Kholdeeva, *et al.*, 2007; Sorokin, *et al.*, 2002). With all the possible products for the oxidation of 2MN, it is always challenging to obtain high yields of 2MNQ in a reaction system (Zalomaeva, *et al.*, 2006).

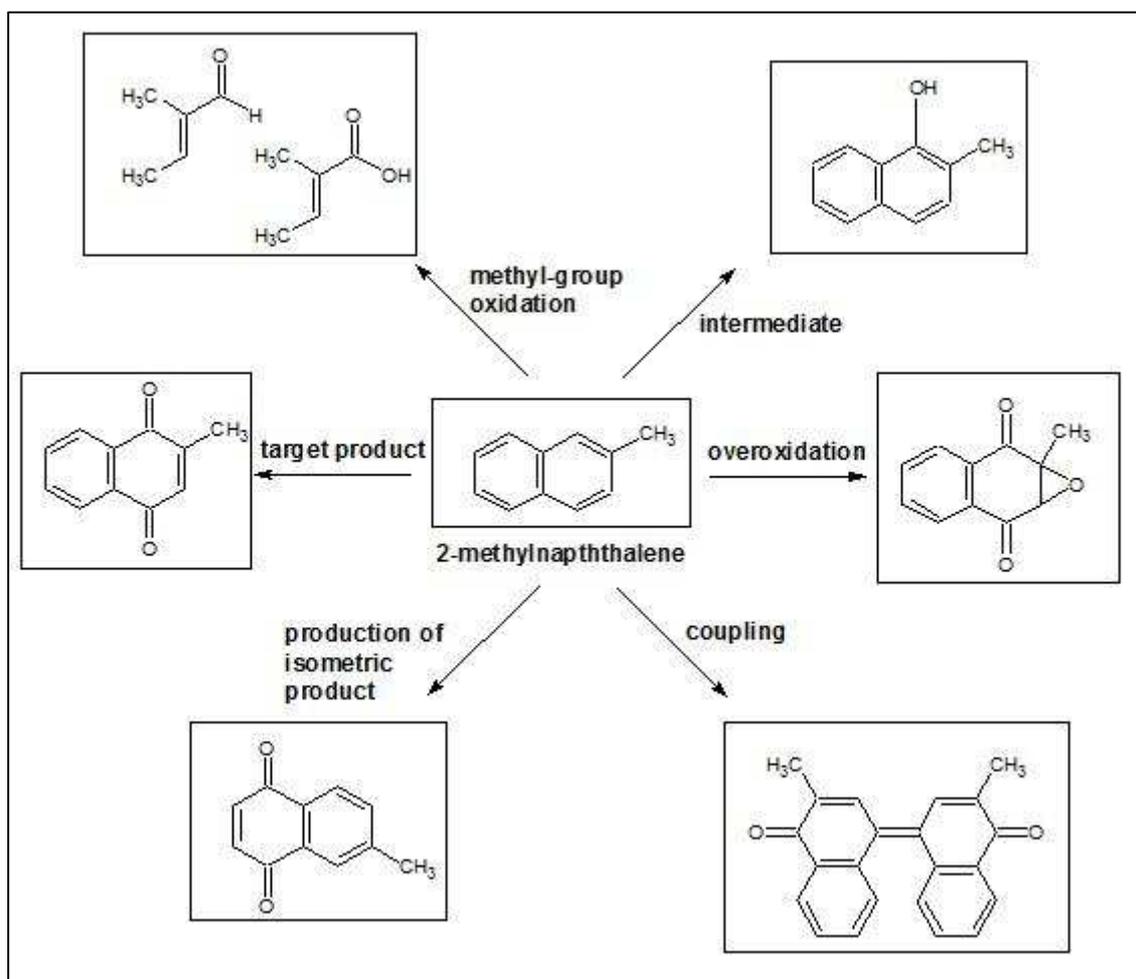


Figure 2-9 By-products in 2MN oxidation [Redrawn from (Kholdeeva, *et al.*, 2007)]

Anunziata, *et al.*, (1999) investigated the oxidation of 2MN to 2MNQ with hydrogen peroxide as oxidant and zeolites/Ti-MCM-41 as catalysts in a 150ml Teflon batch reactor (autoclave). The major products as shown in Figure 2-10 were 2-methyl-1,4-naphthoquinone(2MNQ), 2-methyl-1-naphthol (2MNL), 1,4-dihydroxy-2-methyl naphthalene(1,4DOH-2MN) and the minor products were unidentified.

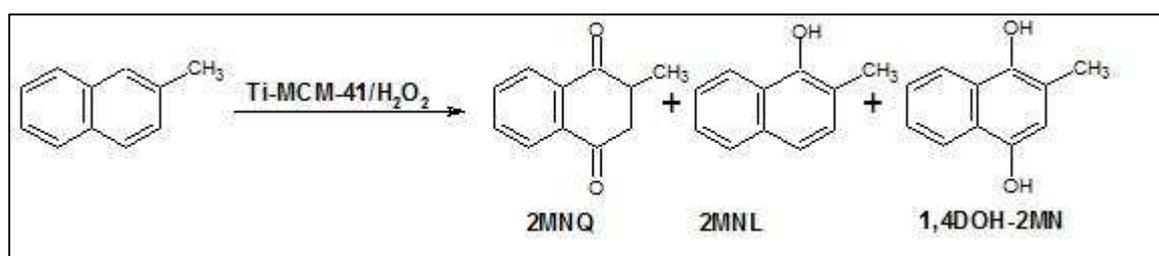


Figure 2-10 Oxidation of 2-methyl naphthalene over zeolites/Ti-MCM-41 (Anunziata, *et al.*, 1999)

The following zeolites: TS-1, Ti-beta, Fe-beta and Ti-MCM-41 were synthesised from the sol-gel method.

Table 2-12 illustrates the results obtained from Anunziata, *et al.*, (1999) and indicates that Ti-MCM-41 and Fe-beta obtained the highest 2MN conversion. Fe-Beta was the favoured catalyst for this study because 2MNQ was the dominant product, whereas Ti-MCM-41 favoured 2MNL.

Table 2-12 Conversion and product selectivity over different redox molecular sieve catalysts, Reaction conditions: 100 mg Catalyst; 100°C; 6 ml 30 wt % aqueous  $\text{H}_2\text{O}_2$ ; 1 g 2MN; 4 hours; 10 ml Solvent (Anunziata, *et al.*, 1999)

Catalyst	Ti,Fe (mol%)	2MN conversion (mol%)	Product selectivity (mol%)		
			2MNL	1,4DOH-2MN	2MNQ
TS-1	1.81	10	34	11	55
Ti-Beta	1.80	11	34	3	63
Fe-Beta	1.32	22	45	1	54
Ti-MCM-41	1.82	28	55	10	35

Anunziata, *et al.*, (2004) then prepared Ti-MCM-41 from two different synthesis methods and found that the hydrothermal procedure obtained a higher selectivity of 2MNQ and MN conversion than the sol-gel procedure as illustrated in Table 2-13

**Table 2-13 Conversion and product selectivity, using Ti-MCM-41 synthesized by different techniques, Reaction Conditions: 100 mg Catalyst; 10 ml Solvent; 6 ml 30 wt% aqueous H<sub>2</sub>O<sub>2</sub> ; 1 g 2MN; 120°C;4 hours (Anunziata, *et al.*, 2004)**

Catalyst	Ti (mol%)	2MN conversion (mol%)	Product selectivity (mol%)		
			2MNL	1,4DOH-2MN	2MNQ
Ti-MCM-41 (sol-gel procedure)	1.82	25	57	11	32
Ti-MCM-41 (hydrothermal procedure)	1.80	34	31	15	54

These processes exhibit low E-factors but with low 2MN conversions and 2MNQ selectivities due to the small pore openings of the microporous materials and the strong hydrophilic character of the mesoporous material.

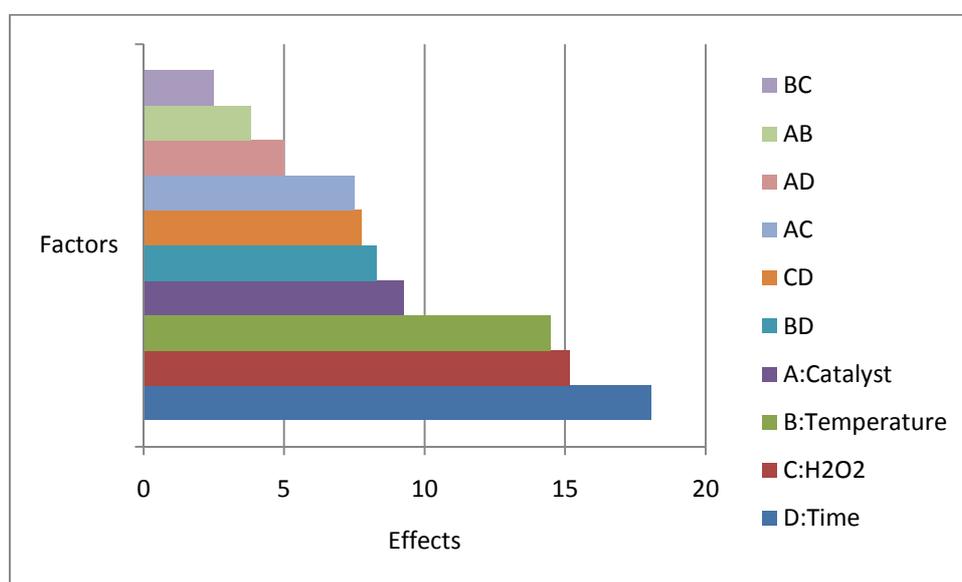
#### **2.4.1.1 Reaction Conditions**

Anunziata, *et al.*, (1999) suggested that the most important reaction conditions in this process are the catalyst amount, hydrogen peroxide volume, reaction time and reaction temperature. These reaction conditions were important because 2MNQ selectivity and 2MN conversion increased when these reactions conditions were increased. Anunziata, *et al.*, (1999) illustrated that the catalyst amount and hydrogen peroxide concentration were regarded as first order dependence because the initial reaction rate increased almost linearly with these parameters for the hydroxylation of 2MN over microporous zeolites. While, the 2MN conversion increased directly proportionally to the hydrogen peroxide volume and reaction temperature for Ti-MCM-41. It is pivotal to mention that to a certain point in both cases, the selectivity for 2MNQ increased while the naphthol derivatives decreased as the conversion increased (Anunziata, *et al.*, 1999; Anunziata, *et al.*, 2004).

Since the catalyst amount and hydrogen peroxide volume resulted in first order dependence for microporous zeolites, the overall reaction rate equation could be deduced to a first-order rate equation. The first-order rate constant was calculated to derive an Arrhenius plot of the first-order constant. The Arrhenius plot determined the activation energy for this process, 31 kJ/mol (Anunziata, *et al.*, 1999).

Anunziata, *et al.*, (1999) studied the effect the nature of the solvent had on the oxidation of 2MN to 2MNQ with Ti-MCM-41 as catalyst and found that the highest 2MNQ yields were obtained for polar aprotic solvents such as acetone and acetonitrile. Anunziata, *et al.*, (2004) optimised the hydroxylation of 2MN to 2MNQ process with Ti-MCM-41 as catalyst, hydrogen peroxide as oxidant and acetonitrile as solvent. Twenty-seven experimental runs were conducted with a Box-Behnken

statistical design to determine the influence the parameters and interactions have on 2MNQ yield. The results from Box-Behnken design is illustrate in Figure 2-11. The Box and Behnken design is used to replace full factorial designs. It is favoured when all levels are evenly spaced and there is no interest in the corner points. The advantage of a Box and Behnken design is that is reduces the number of experimental runs in comparison to a full factorial design and the disadvantage is that it is unable to predict the response at the corners. A full factorial design test all possible explanations, main effects and interaction effects and its disadvantage is the large number of experimental runs because it increases exponentially (Rekab, *et al.*, 2005).



**Figure 2-11 Pareto chart for the estimated effects for 2MNQ yield (Anunziata, *et al.*, 2004)**

The results indicated that all the main factors have a major effect on the 2MNQ yield and the interaction between temperature-time, hydrogen peroxide-time and catalyst-time illustrated similar effects. These factors and interactions were then used to optimise the process and the following results were obtained as shown in Table 2-14 (Anunziata, *et al.*, 2004).

**Table 2-14 Catalytic activity of Ti-MCM-41 in the optimal conditions of reaction (Anunziata, *et al.*, 2004)**

Temperature [°C]	Amount of catalyst [mg]	H <sub>2</sub> O <sub>2</sub> [ml]	Time [hours]	Conversion 2MN [mol%]	2MNQ selectivity [%]	2MNQ yield [%]
200	230	21	2	64	90	59
220	250	23	3	66	91	60
220	230	23	3	66	90	60

Table 2-14 illustrates that best 2MN conversions and 2MNQ yields are achieved at high reaction temperatures with low reaction times, high hydrogen peroxide volumes and large amounts of catalyst.

#### 2.4.2 Hydroxylation of 2-Methyl-1-naphthol

The hydroxylation of 2MNL to 2MNQ was considered because 2MNL is an intermediate between 2MN and 2MNQ. This results in an increase in the 2MNQ selectivity and prevents the oxidation on the methyl group (Kholdeeva, *et al.*, 2007). For the hydroxylation of 2MNL to 2MNQ with aqueous  $H_2O_2$  and Ti-MMM-2 as indicated in Figure 2-12, the main products were 2MNQ, 4,4-di(2-methyl-1-naphthol) (4,4-di(2MNL)), 4,4-di(2MNQ), 2-methyl-2,3-epoxy-1,4-naphthoquinone(2MNQ epoxide) and unidentified tars (Kholdeeva, *et al.*, 2007; Kholdeeva, *et al.*, 2005).

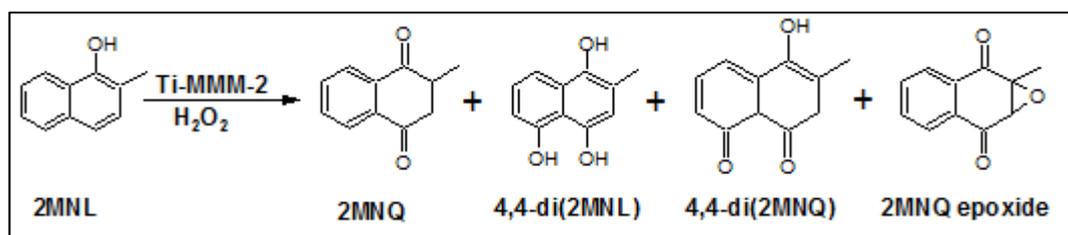


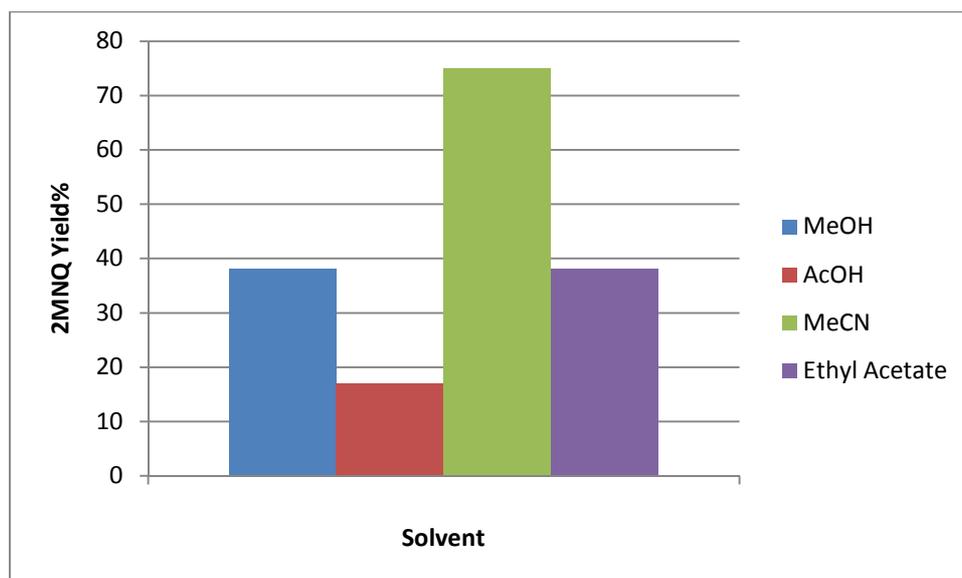
Figure 2-12 Hydroxylation of 2-methyl-1-naphthol over Ti-MMM-2 (Kholdeeva, *et al.*, 2007)

This process is environmentally friendly because the E-factor is about 0.3 and experiments were conducted under vigorous stirring in a thermostated glass vessel (Kholdeeva, *et al.*, 2007).

##### 2.4.2.1 Reaction Conditions

Ti-MMM-2 was synthesised at different conditions for the hydroxylation of 2MNL to 2MNQ with  $H_2O_2$  as oxidant. Three samples with CTAB as the surfactant were prepared with different Ti ratios and another sample was synthesised with a surfactant consisting of P123 and CTAB. For the three samples with only CTAB as surfactant, the sample with highest Ti ratio, obtained the highest 2MNQ yield and the sample with the surfactant mixture obtained the highest 2MNQ yield out of all the samples (Kholdeeva, *et al.*, 2005).

Kholdeeva, *et al.*, (2007) optimised the process and found that the reaction temperature, solvent nature,  $H_2O_2$  volume and catalyst amount had a significant effect on the 2MNQ yield. MeCN was the solvent choice as illustrated in Figure 2-13. The 2MNQ selectivity increased with increasing reaction temperature,  $H_2O_2$  volume and catalyst amount. At optimal reaction conditions, 100% 2MNL conversion and 75-78% 2MNQ yield was obtained.



**Figure 2-13** The effect of solvent on the 2MNL oxidation over Ti-MMM-2, Reaction conditions: 0.025 M 2MNL; 0.125 M aqueous 30 wt% aqueous H<sub>2</sub>O<sub>2</sub>; 3.8 mg Ti-MMM-2; 80°C; 1 ml solvent; 30 min (Kholdeeva, *et al.*, 2007)

This process seems promising for the formation of 2MNQ but from an economical aspect, it is not feasible because 1 g of 2MNL costs R 1857.57, whereas 1 kg 2MN is R 1235.18 (Zalomaeva, *et al.*, 2006; <http://www.sigmaaldrich.com>, 2010). Therefore, an efficient process for the hydroxylation of 2MN to 2MNQ should still be considered.

## 2.5 Conclusions from Literature

It is challenging to achieve an efficient process for the hydroxylation of bulky organic substrates to quinones, particularly, the selective oxidation of 2MN to 2MNQ. It is a problem because it is difficult to achieve an environmentally friendly process with high 2MN conversions and 2MNQ yields. An environmentally friendly process is achieved with redox molecular sieves as a catalysts, clean oxidants and solvents. The clean oxidant and solvent favourable for the hydroxylation of 2MN to 2MNQ is hydrogen peroxide and acetonitrile, respectively.

From literature, the studies conducted for the hydroxylation of 2MN to 2MNQ achieved an environmentally friendly process with microporous and mesoporous redox molecular sieves but obtained low 2MN conversions and 2MNQ yields. It was suggested that the reaction temperature, reaction time, catalyst amount and hydrogen peroxide volume had a significant effect on the 2MN conversion and 2MNQ yield. It was found that the structure and synthesis procedure of the catalyst, diffusion of substrate molecules, oxidant and solvent influenced the catalytic performance, substrate

conversion and quinone selectivity. The process from literature that achieved the highest 2MN conversion and 2MNQ yield was with a Ti-MCM-41, H<sub>2</sub>O<sub>2</sub> and MeCN system. This process was optimised by evaluating the reaction conditions with a Box and Behnken design.

The process systems conducted for the selective oxidation of 2MN to 2MNQ produced different results based on their reaction conditions, process system, redox molecular sieve, oxidant and solvent. The by-products produced from the hydroxylation of 2MN to 2MNQ are unclear because each study conducted in literature identified different by-products.

Efficient processes were achieved for the hydroxylation of bulky organic substrates possessing hydroxyl functions with redox molecular sieves containing microporous/mesoporous materials. These processes were environmentally friendly and achieved high conversions and product yields.

### 3 HYPOTHESIS & PROJECT OBJECTIVES

Based on the findings in literature the following hypothesis is proposed:

“Improved 2-Methylnaphthalene conversions and 2-Methyl-1,4-naphthoquinone yields will be obtained for the hydroxylation of 2-Methylnaphthalene to 2-Methyl-1,4-naphthoquinone with microporous/mesoporous redox molecular sieves as catalyst, hydrogen peroxide as oxidant and acetonitrile as the solvent.”

To prove the hypothesis, the following objectives will be implemented:

- Design an efficient process that is environmentally friendly, achieves high 2MN conversion and high 2MNQ yield
  - This is done by obtaining low E-factors by producing by-products that are not toxic and harmful to the environment.
  - Synthesise catalysts Ti-MCM-41, Ti-MMM-2, Ti-MMM-2 (P123) and the highly ordered mesoporous material to determine which catalyst will obtain the best results for the hydroxylation of 2MN to 2MNQ with hydrogen peroxide as oxidant and acetonitrile as solvent
  - Evaluate the process system and reaction conditions, namely, the reaction temperature, reaction time, hydrogen peroxide volume, substrate amount, solvent volume and catalyst amount.
  - Determine if the catalyst is truly heterogeneous and model the process to determine the reaction rate.

## 4 RESEARCH DESIGN AND EXPERIMENTAL METHODOLOGY

This section encompasses a description of the experimental apparatus and setup, experimental conditions and procedure and analysis techniques that were conducted in this work.

### 4.1 Catalyst Synthesis and Preparatory Treatment

The procedure used to synthesize a catalyst is important because the structure, pore size and surface area are controlled by the synthesis conditions and surfactant choice (Fortier, *et al.*, 2006).

A list of the chemical purity and supplier of the chemicals used can be found in APPENDIX C.

#### 4.1.1 Synthesis of mesoporous Ti-MCM-41

Ti-MCM-41 was synthesised according to the method described by Blasco, *et al.*, (1995). In a typical synthesis, 29 wt% surfactant solution was gently mixed under magnetic stirring in a polypropylene beaker to form a clear solution. The surfactant solution was prepared by adding 24 g distilled water to 9.7 g cetyltrimethyl ammonium bromide (CTAB). 6.54 g, 25 wt% aqueous solution of tetramethylammonium hydroxide (TMAOH) was slowly added dropwise under continuous stirring to this solution to obtain a milky solution. The milky solution indicated that a homogenised mixture was attained. To this mixture, 4 g silica (*Aerosol Degussa 200*) as the silicon source and 0.34 g titanium isopropoxide as titanium source was added respectively to form a paste/gel.

The thick paste was then transferred to a 125 ml Parr PTFE-lined stainless steel autoclave and aged for 24 hours at room temperature while magnetic stirring occurred to ensure full incorporation. The paste was then heated under static autogeneous pressure at 125°C for a crystallisation period of 14 hours without stirring.

After the crystallisation time, the autoclave was quenched in cold water at room temperature and the material was then washed three times and filtered under a vacuum. Finally, the solid was dried at 80°C for 14 hours and then calcined.

#### 4.1.2 Synthesis of highly mesoporous Ti-MMM-2

Ti-MMM-2 was synthesised from two different procedures demonstrated by Kholdeeva, *et al.* (2004). The first procedure used only cetyltrimethyl ammonium bromide (CTAB) as the surfactant, while the second procedure used a mixture surfactant, consisting of 95% of neutral triblock copolymer Pluronic EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (P-123) and 5% CTAB. The catalyst synthesised from the first procedure was known as Ti-MMM-2 and the catalyst from second procedure was Ti-MMM-2 (P123)

for this study. Ti-MMM-2 and Ti-MMM-2 (P123) was generally synthesised by mixing three solutions. The first solution was a mixture of 6.5 g surfactant dissolved in 108 g of distilled water and the second solution was 2.7 g of 0.5 M  $\text{TiOSO}_4$ . The third solution from literature consisted of sodium disilicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ) as the silicate source with 133 g of distilled water, while in this study, sodium trisilicate ( $\text{Na}_2\text{Si}_3\text{O}_7$ ) was used as the silicate source with the same relative amount of silicate found in literature. Each solution was inserted in a polypropylene beaker and vigorous magnetic stirring was employed until a clear and transparent solution was attained.

The three solutions were mixed together under vigorously stirring conditions and the pH of the solution was adjusted to 3 by using 4 M hydrochloric acid ( $\text{HCl}$ ). The mixture was then kept overnight under ambient conditions with gentle stirring and then hydrothermally treated at 50°C for 24 hours without any agitation. The mixture was then filtered off, washed and dried in static air at 120°C before calcination.

#### **4.1.3 Highly ordered mesoporous material**

The catalyst was prepared by the method followed by Fortier, *et al.* (2006). The highly ordered mesoporous material was prepared by dissolving 16 g of Pluronic P123 in 320 g distilled water. This solution was vigorously stirred and heated at 35-40°C for 2 hours in order to obtain a clear aqueous solution. To this solution, 34.3 g of sodium silicate solution (28.7 %  $\text{SiO}_2$ , 8.9 %  $\text{Na}_2\text{O}$ ) and a clear solution of 1.93 g tetraethoxide titanium dissolved in 50 g of distilled water was added respectively under room temperature. Vigorous stirring for 1-2 hours occurred for this solution to obtain a homogenous solution. Once the homogenous solution was attained, 48 g of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was quickly added with vigorous stirring.

The resulting mixture was stirred for 18 hours at room temperature and subsequently heated for 24 hours at 80°C in an oven without any stirring. No stirring occurred in order to form a solid precipitate and to increase the degree of silanol group condensation. The precipitate was recovered by filtration and washed with distilled water and filtered again. The residual surfactant template was removed by treating the precipitate in 380 g of distilled water at 80°C for 24 hours. Finally, the product was filtered, washed in distilled water and dried in an oven before calcination.

#### **4.1.4 Calcination**

Calcination of the catalyst was performed in order to remove moisture and the organic surfactant from the catalyst. Calcination for all the catalysts was conducted in a furnace ramping from 25°C to 550°C at a heating rate of 0.1°/50 s and holding it at this temperature for 6 hours.

## 4.2 Catalyst Characterisation

### 4.2.1 Catalyst Structure and Morphology

The crystal morphology, impurities and physiochemical properties of catalysts are important factors that play a vital role in the interior structure of redox molecular sieves and the ability of the substrate to reach the active sites (Schoonheydt, 2008). These factors were studied by determining the specific surface area, pore size distribution and average pore size of the calcined redox molecular sieves (Vannice, 2005).

#### 4.2.1.1 Adsorption Measurements

The surface areas of the calcined catalysts were determined by the BET method on the basis of the N<sub>2</sub>-BET adsorption isotherms by using a Micromeritics ASAP 2010 (Accelerated Surface Area and Porosimetry System) adsorption apparatus equipped with a Micromeritics VacPrep 061 Sample Degas System.

Prior to N<sub>2</sub> adsorption, 0.5 g of the catalyst sample was first dried at 90°C for 1 hour and then 300°C under vacuum for 20 hours. The sample was degassed at 77K overnight and the nitrogen was adsorbed at liquid nitrogen temperature until ambient pressure was reached.

The method used to determine if the mesoporous materials possess micropores and mesopores or only mesopores was based on the t-plot method introduced by de Boer. A t-plot is constructed by plotting the volume absorbed with the statistical thickness (t) determined by the Harkins and Jura equation.

$$t = \left[ \frac{13.99}{0.034 - \log \frac{P}{P_0}} \right]^{1/2} (\text{\AA})$$

Equation 4-1

Where

P= Adsorbate pressure

P<sub>0</sub>= Saturation pressure of the gas

A t-plot compares a standard isotherm to the analysed porous isotherm. A standard isotherm is a nonporous solid having the same chemistry character as the analysed porous sample, e.g., silica. A straight line is drawn through the points where the standard isotherm is equal to the analysed porous isotherm. Micropores are present if the straight line extrapolates to a positive y-intercept and absent if the y-intercept is not positive. The y-intercept gives the micropore volume and the slope is proportional to the external + mesoporous surface (Lowell, *et al.*, 1984).

#### **4.2.1.2 Particle Size Distribution**

Samples of the calcined catalysts were analysed for particle size distributions by using a Satorius Digsizer 5200. The samples were suspended in Tetra Sodium Pyrophosphate (TSPP) using ultrasound prior to analysis.

#### **4.2.1.3 X-ray Powder Diffraction(XRD)**

X-ray Powder Diffraction (XRD) was used to determine the crystallographic structure, crystalline size (grain size) and chemical composition with the aid of X-ray intensities. A diffraction pattern recorded the X-ray intensity as a function of 2- $\theta$  angle. The X-ray Powder diffraction spectra of the calcined catalysts were conducted in air at room temperature on a Bruker D8 Advance Powder Diffractometer. The instrument generated monochromatic Cu-K $\alpha$  radiation ( $\lambda=0.1542$  nm), generated at 40 kV and 25 mA. Scanning was prepared in the range of 1 to 10 with 30 s counting time for 15 minutes and a step size of 0.05° 2 $\theta$ . A slit divergence of 3° was used.

#### **4.2.1.4 Scanning Electron Microscopy & Energy-dispersive X-ray spectroscopy**

The crystal morphology and structure size were identified by using a Leo 1430VP Scanning Electron Microscope (SEM). To prevent surface charging and thermal damage from the electron beam, the samples were mounted on aluminium stubs and coated with a thin gold film before scanning. The instrument was operated at an accelerating voltage of 20 keV, a tilt angle of 0° and an aperture size of 30  $\mu$ m with a working distance of 17 mm. Energy Dispersive X-ray spectroscopy (EDX) was used to determine the chemical characterisation of the calcined catalyst by determining the weight percentage of the elements that compose the catalyst.

#### **4.2.1.5 Thermogravimetric Analysis (TGA)**

Spent catalyst samples from the experiments were investigated by Thermogravimetric Analysis (TGA) to determine if any contents left from the experiment were on the catalyst that would have an impact on the performance on the recyclability of the catalyst. The TGA measured the change in the recovered catalyst weight as a function of change in temperature. It was determined by using a Shimadzu TGA-50H thermogravimetric analyser equipped with a TA-60WS thermal analyser (TGA/DTA).

At first, a sample of  $\leq 12$  mg recovered catalyst was heated in a thermal analyser in nitrogen at 5°C/min to 100°C, holding at this temperature for 60 minutes to desorb water and light components with an initial carrier gas flow rate of 60 ml (NTP)/min. The carrier gas was then changed to a mixture containing air (80 ml(NTP)/min) and nitrogen (15 ml(NTP)/min). The sample was heated further at 5°C/min to 600°C and kept at this temperature for 6 hours.

## 4.3 Experimental Reactions

### 4.3.1 Apparatus and Setup

Figure 4-1 illustrates the experimental setup for the hydroxylation of 2-methyl naphthalene for this study. The experimental setup was comprised of a 45 ml Parr PTFE-lined stainless steel autoclave immersed in an oil bath. A magnetic stirrer/heater unit used to heat the oil to the required reaction temperature and the oil bath settings were calibrated using a thermometer. In addition, the stirrer/heater unit provided continuous stirring in the reactor. Prior to experimental reactions, the temperature was calibrated but could have varied as a result of the change in ambient temperature.

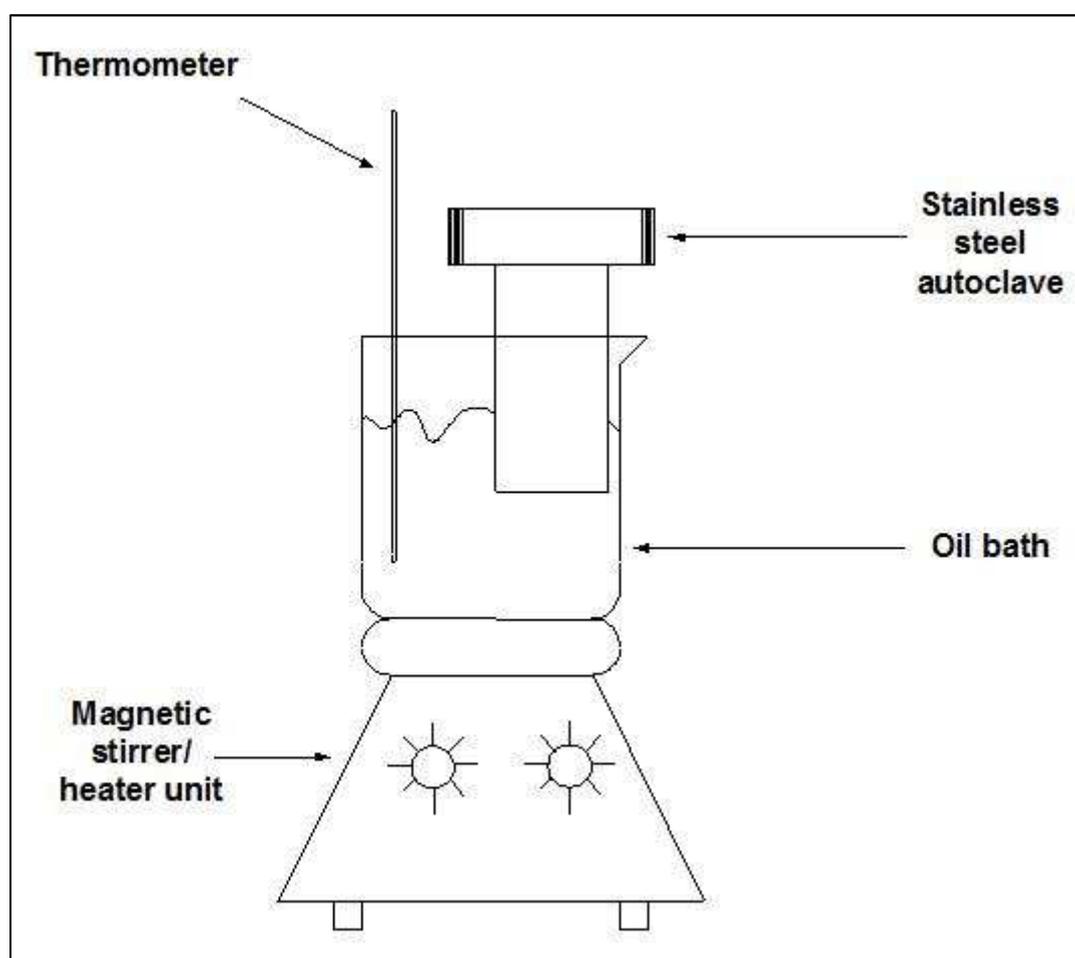


Figure 4-1 Experimental setup used for the hydroxylation of 2-methylnaphthalene

### 4.3.2 Experimental Design

All experiments for the hydroxylation of 2-methylnaphthalene were conducted in a batch system under continuous magnetic stirring. The experiments were initially conducted at the same reaction conditions as literature. It was based on the study by Anunziata, *et al.* (2004) for the selective

oxidation of 2MN to 2MNQ with Ti-MCM-41 as catalyst. The conditions were: reaction temperature 120°C; reaction time 4 hours; solvent 10 ml; 2MN 1 g; catalyst 100 mg; 6 ml 30 wt% aqueous H<sub>2</sub>O<sub>2</sub>. Experiments conducted for this study are illustrated in Table 4-1.

The purpose of this study was to provide an efficient and environmentally friendly process for the hydroxylation of 2MN to 2MNQ with hydrogen peroxide as oxidant and acetonitrile as the solvent. This was done by identifying the products formed from this process. The process system was investigated by varying the size of the oil bath and oil type for this process. Initially, the Parr PTFE-lined autoclave was submerged in polyethylene glycol in a stainless steel pot with a 120 mm diameter and depth of 60 mm. While later experiments were carried out with silicon oil in a stainless steel pot with a 120 mm diameter and depth of 150 mm. The best catalyst for this study was determined by comparing the effect that reactions conditions have on the various catalysts synthesised for this study in terms of 2MN conversion and 2MNQ selectivity. The reaction conditions were the substrate amount, catalyst amount, hydrogen peroxide volume, solvent volume, reaction time and reaction temperature. The catalyst that was favoured for this study obtained the highest 2MN conversion in comparison to the other catalysts and favoured the formation of 2MNQ. Once the best catalyst was identified, the system was improved by evaluating the reaction conditions. The reaction conditions were evaluated by the one factor at a time approach in order to determine the affect the reaction conditions have on the 2MN conversion and 2MNQ yield. The one factor at a time approach means that one factor is varied at a time while the other factors are kept constant. This design grasps the effect the reaction condition has on the 2MN conversion and 2MNQ yield but do not explain if the interactions between the reaction conditions play a significant role in the process. To get an understanding of the interactions between the reaction conditions on the 2MNQ yield, a simple full factorial design was investigated. The catalyst was recycled and conducted under the same reaction conditions as the original catalyst to test if the catalyst truly acted heterogeneous in the study.

**Table 4-1 Overview of experiments conducted in this study**

Same reaction conditions as literature (Anunziata, <i>et al.</i> ,(2004))						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Ti-MCM-41	1	100	120	4	10	6
Identify products						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Ti-MCM-41	1	100	150	2	10	6
				4		

Investigate process system						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Ti-MCM-41	1	100	150	2	10	6
				4		
				6		
Ti-MMM-2	1	100	150	2	10	6
				4		
				6		
Examine the various catalysts						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
-Ti-MCM-41,	1	100	120	2	10	6
				4		
				6		
-Ti-MMM-2	1	100	150	2	10	6
				4		
				6		
-Ti-MMM-2 (P123)	1	100	180	2	10	6
				4		
				6		
-Highly ordered mesoporous material	1	100	150	4	10	3
						9
(all experiments on right performed on each catalyst)	0.5	100	150	4	10	6
	2					
	1	50	150	4	10	6
		200				
	1	100	150	4	5	6
					15	

Improve system with highly ordered mesoporous material (One factor approach)						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Highly ordered mesoporous material	1	100	150	1	10	6
				5		
	1	100	180	1	10	6
	1	100	150	1	10	1
				2		
				3		
				4		
				5		
				1		
				2		
				3		
	5					
	1	70	150	4	10	6
	1	150	150	4	20	6
		100				
0.75	100	150	4	10	6	
1.5						
Improve system with highly ordered mesoporous material (Factorial design)						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Highly ordered mesoporous material	1	50	180	2	10	6
				4		
		50	150	2		3
				100		
		100	180	4		
		100	150	2		
		100	150	4		
		50	180	2		
				4		
			150	2		
				4		

Arrhenius plot						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Highly ordered mesoporous material	1	100	4	135	10	6
				160		
Reusability						
Catalyst	2MN [g]	Catalyst amount [mg]	Reaction Temperature [°C]	Reaction time [hours]	MeCN [ml]	H <sub>2</sub> O <sub>2</sub> [ml]
Highly ordered mesoporous material	1	100	150	2	10	6
				4		

### 4.3.3 Experimental Procedure

The following steps were taken to conduct the experiments. Firstly, the required amount of 2MN was added to a 30 ml glass vial containing the required amount of MeCN to ensure that the substrate completely dissolved in the solvent. The desired amount of catalyst was prepared in a 4 ml glass vial and then transferred to the Parr PTFE-liner after which was then weighed. The vial containing the substrate/solvent mixture was then added to the Parr PTFE-liner and weighed before and after the magnet was added. The liner was then placed on a magnetic unit so that the mixture could be stirred vigorously in order for the catalyst to fully incorporate with the substrate and solvent. This was done for about 3 hours before the required amount of H<sub>2</sub>O<sub>2</sub> was added to the Parr PTFE-liner and then weighted again before being inserted into the stainless steel autoclave. The autoclave was then placed in the oil bath for the experiment to occur at the required reaction temperature and time.

When the experiment occurred to its required reaction temperature and time, the autoclave was removed from the oil bath and immersed in cold water to cool down the autoclave and prevent the reaction from proceeding further. Once the autoclave was cooled, the PTFE liner was removed from the stainless steel autoclave and 1 ml of reaction sample was removed with a surgical syringe and injected into a 30 ml glass vial. The reaction sample was diluted by 3 ml MeCN in the 30 ml vial. The diluted sample was then filtered through a sterile 45 µm Millipore filter (Millex-GV) into a 4 ml glass vial and stored in a freezer to prevent any further reactions occurring.

The catalyst was recovered by filtering and washing the remaining reaction sample with acetone. The recovered catalyst was then air dried at 100°C.

## 4.4 Products and Sample Analysis

The samples to be analysed were prepared by removing 1 ml from the stored vial in the freezer and placed into a 3 ml vial containing a known amount of internal standard, Biphenyl. The samples were analysed using Gas Chromatography (GC) and Gas Chromatography-Mass Spectroscopy (GC-MS).

### 4.4.1 Gas Chromatography (GC) & Gas Chromatography-Mass Spectroscopy (GC-MS)

The gas chromatography (GC) conducted in this study was performed on a GC-Varian 3400 connected to a flame ionization detector (FID), equipped with a 50 m x 0.25 mm bounded phase SGE capillary column made of fused silica.

Prior to analysing the experiments, blank samples were injected in the GC to clean the column of residue from previous analyses to ensure accuracy.

A specific GC method (APPENDIX B) was designed for this process to allow the separation of all components. The various components of the mixture will display a specific spectral peak at different retention times because the transition from liquid to gas phase occurs at different times for the components. The area of the specific spectral peak of each component was used to determine the number of moles for the component in the reaction sample with the following equation:

$$RF_i = \left( \frac{A_i}{n_i} \right) \left( \frac{n_{BPH}}{A_{BPH}} \right)$$

Equation 4-2

Where	$RF_i$	=	Response Factor of species i
	$A_i$	=	Absolute area of species i
	$n_i$	=	Moles of species i [gmol]
	$n_{BPH}$	=	Moles of biphenyl [gmol]
	$A_{BPH}$	=	Absolute area of biphenyl

The response factor of each component was determined by preparing a standard solution. The standard solution consisted of a known amount of the substrate, internal standard and the possible products of the reaction. The standard solution was then injected onto the GC to obtain the specific spectral peak of each component and as a result, the response factor for each component could be calculated as shown in APPENDIX B.

A Gas Chromatography-Mass Spectroscopy (GC-MS) was used to identify the products formed from this reaction system. The purpose of a GC-MS is to determine the molecular weight and elemental

compositions of unknown compounds in complex mixtures. The GC-MS is designed in such way that it gives the molecular weight break down of a component so that it is easy to identify the compound and determine the structure of the compound by matching their spectra with reference spectra.

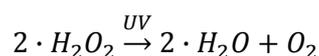
## 4.5 Kinetic Modelling

The chemical kinetics were evaluated by constructing concentration-time profiles from the experiments and using initial reaction rates to calculate the rate constants. The ideal reaction for the hydroxylation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone with hydrogen peroxide as oxidant can be expressed as:



**Reaction 4-1**

Other by-products were also formed but will be discussed later. It was found that hydrogen peroxide also undergoes a non-selective decay/decomposition due to the presence of light according to the following equation:



**Reaction 4-2**

For the purpose of modelling this data, it was assumed that hydrogen peroxide was only reacting with 2-methylnaphthalene to form 2-methyl-1,4-naphthoquinone and by-products because experiments were conducted in a closed vessel. The conversion of the 2-methylnaphthalene was determined by the generic equation:

$$X_{2MN} = \frac{C_{2MN,0} - C_{2MN,t}}{C_{2MN,0}}$$

**Equation 4-3**

The selectivity for each product was calculated with the following expression:

$$Selectivity_i = \frac{C_{i,t}}{\text{sum of products formed}}$$

**Equation 4-4**

Where	$X_{2MN}$	=	2-Methylnaphthalene conversion
	$C_{2MN,0}$	=	Initial concentration of 2-methylnaphthalene [gmol/ml]
	$C_{2MN,t}$	=	Concentration of 2-methylnaphthalene at time (t) [gmol/ml]

$C_{i,t}$  = Concentration of species i at time (t)[gmol/ml]

The yield of 2-methyl-1,4-naphthoquinone was defined with the total concentration yield equation:

$$Yield_{2MNQ} = \frac{C_{2MNQ,t}}{\sum C_{All\ compounds}}$$

Equation 4-5

The differential form of the mole balance in terms of 2-methylnaphthalene conversion for a batch reactor can be expressed as:

$$N_{2MN,0} \cdot \frac{dX_{2MN}}{dt} = -r_{2MN} \cdot V$$

Equation 4-6

The reaction volume remains constant and as a result, the mole balance can be changed to the following equation in terms of concentration:

$$-r_{2MN} = C_{2MN,0} \cdot \frac{dX_{2MN}}{dt}$$

Equation 4-7

Since, this is an irreversible reaction; the basic power rate law for this system can be defined as:

$$-r_{2MN} = k_{2MN} \cdot C_{2MN,t}^{\alpha} \cdot C_{H_2O_2,t}^{\beta}$$

Equation 4-8

$k_{2MN}$  = specific reaction rate constant [(ml)<sup>3</sup>/gmol.h]

$C_{H_2O_2,t}$ , is the concentration of hydrogen peroxide at time (t),  $\alpha$  refers to the reaction order of 2-methylnaphthalene while  $\beta$  refers to the reaction order of hydrogen peroxide. Assuming that for this study, the reaction order for both 2-methylnaphthalene and hydrogen peroxide was one. This assumption was based on similar oxidation processes conducted in literature and resulted in a second order overall reaction (Burton, 2006):

$$-r_{2MN} = k_{2MN} \cdot C_{2MN,t} \cdot C_{H_2O_2,t}$$

Equation 4-9

The time (t) concentration of 2-methylnaphthalene and hydrogen peroxide can be expressed in terms of 2-methylnaphthalene conversion, initial 2-methylnaphthalene concentration and  $\theta_{H_2O_2}$  (the molar ratio of hydrogen peroxide to 2-methylnaphthalene fed into the reactor):

$$C_{2MN,t} = C_{2MN,0} \cdot (1 - X_{2MN})$$

**Equation 4-10**

$$C_{H_2O_2,t} = C_{2MN,0} \cdot (\theta_{H_2O_2} - 3X_{2MN})$$

**Equation 4-11**

Substituting Equation 4-11 and Equation 4-10 into the rate law Equation 4-9, the following equation was derived.

$$-r_{2MN} = k_{2MN} \cdot C_{2MN,0}^2 \cdot (1 - X_{2MN}) \cdot (\theta_{H_2O_2} - 3X_{2MN})$$

**Equation 4-12**

Substituting (Equation 4-12) into the differential form mole balance for a constant batch reactor (Equation 4-7), the equation can be expressed as:

$$\frac{dX_{2MN}}{dt} = k_{2MN} \cdot C_{2MN,0} \cdot (1 - X_{2MN}) \cdot (\theta_{2MN} - 3X_{2MN})$$

**Equation 4-13**

Rearranging gives:

$$\frac{dX}{(1 - X_{2MN})(\theta_{H_2O_2} - 3X_{2MN})} = k_{2MN} \cdot C_{2MN,0} \cdot dt$$

**Equation 4-14**

Integrating over the boundaries  $t_1$  and  $t_2$ , the equation can be expressed as:

$$\frac{1}{3(\theta_{H_2O_2} - 1)} \cdot \left| \ln \frac{\theta_{H_2O_2} - 3X_{2MN}}{\theta_{H_2O_2} \cdot (1 - X_{2MN})} \right|_{X_{t1}}^{X_{t2}} = k_{2MN} \cdot C_{2MN,0} \cdot (t_2 - t_1)$$

**Equation 4-15**

The following equation is derived by raising the exponent:

$$\frac{\theta_{H_2O_2} - 3X_{2MN}}{\theta_{H_2O_2} \cdot (1 - X_{2MN})} = \exp[k_{2MN} \cdot C_{2MN,0} \cdot \Delta t \cdot 3(\theta_{H_2O_2} - 1)]$$

**Equation 4-16**

Simplifying the equation and making  $X_{2MN}$  the subject of the expression, gives the following:

$$X_{2MN} = \frac{\theta_{H_2O_2} \cdot (1 - \exp[k_{2MN} \cdot C_{2MN,0} \cdot \Delta t \cdot 3(\theta_{H_2O_2} - 1)])}{3 - \theta_{H_2O_2} \cdot \exp[k_{2MN} \cdot C_{2MN,0} \cdot \Delta t \cdot 3(\theta_{H_2O_2} - 1)]}$$

**Equation 4-17**

It is possible to determine the theoretical 2-methnaphthalene concentration at time (t) using (Equation 4-10) and (Equation 4-17). Knowing the theoretical concentrations, the specific rate constants could be calculated. The specific rate constant could be determined by using nonlinear least squares regression, by minimising the sum of squares of the difference between the 2MN conversion calculated from experimental data and the theoretical conversion by changing the rate constant. The regression was analysed with Solver® in Microsoft Excel with the rate constant constrained to be greater than zero.

The Arrhenius equation suggested that the temperature dependence of the specific reaction rate can be expressed in the following equation:

$$k_{2MN} = Ae^{-\frac{E}{RT}}$$

**Equation 4-18**

Where	A	=	pre-exponential factor
	E	=	activation energy, J/mol
	R	=	gas constant, 8.314 J/mol.K
	T	=	absolute temperature, K

The activation energy of the process could be calculated by taking the logarithm of Equation 4-18 by determining the specific rate constant at several reaction temperatures:

$$\ln k_{2MN} = \ln A - \frac{E}{R} \left( \frac{1}{T} \right)$$

**Equation 4-19**

## 5 RESULTS AND DISCUSSIONS

### 5.1 Physical and Chemical Catalyst Characterisation

The crystal morphology, impurities and physiochemical of catalysts are all important factors that can be manipulated by changing the framework composition (Thangaraj, *et al.*, 1991). To understand the crystal morphology and physiochemical of the catalyst, it is important to measure and determine the surface area, metal dispersion and crystallite size of the catalyst (Vannice, 2005). The particle size distribution is an important characteristic because it influences the transport and equilibrium of substrates being adsorbed in the structure (Kowalczyk, *et al.*, 2003).  $N_2$ -isotherms, particles size distributions and t-plots were used to determine the surface areas and whether the catalyst exhibits micropores, mesopores or micropores and mesopores. The crystallite sizes and chemical composition for the various catalysts were determined by SEM and EDX analysis, respectively.

#### 5.1.1 Adsorption Measurements

The  $N_2$ -adsorption isotherm for Ti-MCM-41 is illustrated in Figure 5-1 and the other catalysts'  $N_2$ -adsorption isotherms for this study can be found in APPENDIX D.

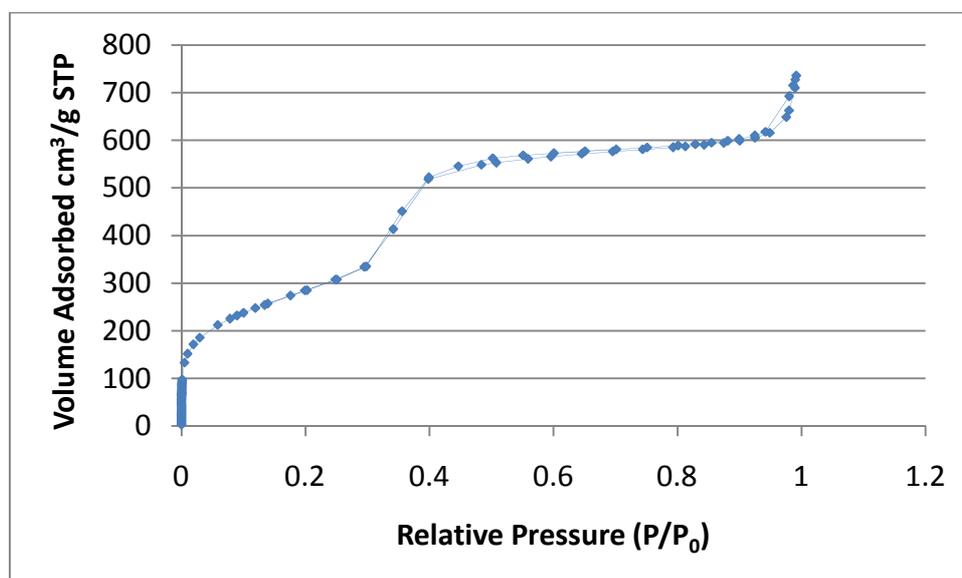


Figure 5-1 Nitrogen adsorption-desorption isotherms for hydrothermally synthesised calcined Ti-MCM-41 at 408K after 14 hours

Based on the  $N_2$ -adsorption isotherms, it is suggested that Ti-MCM-41, Ti-MMM-2, Ti-MMM-2 (P123) and the highly ordered mesoporous material illustrate isotherms similar to type IV and type I as indicated in APPENDIX A. The catalysts exhibit defined hysteresis loops but further tests should be conducted to determine if the catalysts illustrate a type I adsorption isotherm at the low relative

pressure region. This test is conducted with the t-plot introduced by de Boer (discussed in section 4.2.1.1). The four catalysts exhibit large pores due to the mesoporous structures and the inflection point indicating mesopore filling occurs between  $0.2 < P/P_0 < 0.4$  for Ti-MCM-41, while between  $0.5 < P/P_0 < 0.7$  for the other catalysts. The t-plots for the various catalysts can be found in APPENDIX F. The fitted points on the t-plots indicate the points that the standard isotherm is equal to the analysed porous isotherms. The t-plots indicate that the highly ordered mesoporous material is the only catalyst with a positive y-intercept. Therefore, it is suggested that the highly ordered mesoporous material is the only catalyst that possess both micropores and mesopores, whereas the other catalysts only possess mesopores. As a result, the highly ordered mesoporous material demonstrates isotherms similar to type IV and type I, while the other catalysts shows isotherms similar to type IV only. Therefore, the rise of sorption at  $P/P_0 < 0.05$  for the highly ordered mesoporous material is the volume filling of micropores. It is suggested that the rise of sorption at  $P/P_0 < 0.05$  for the other catalysts may perhaps be the monolayer adsorption of  $N_2$  on the walls of the mesopores as illustrated in literature (Kruk, *et al.*, 2001).

The pore size distributions were calculated based on the desorption branch of the nitrogen sorption isotherms using the Barrett, Joyner and Halenda (BJH) method. The pore size distributions for the various catalysts are shown in APPENDIX E. The pore size distribution curves for Ti-MCM-41 (Figure 12-1) and the highly ordered mesoporous material appear ordered with very narrow and symmetric peaks. The peak for Ti-MMM-2 (Figure 12-2) seems disordered, irregular and broad, whereas Ti-MMM-2(P123)(Figure 12-3) appears more ordered with a narrower peak. Ti-MMM-2 (P123) appears to be less ordered and symmetric than the highly ordered mesoporous material. This may well be due to the different acids used for synthesising the catalysts as illustrated in Figure 2-6. The highly ordered mesoporous material is synthesised with sulphuric acid and Ti-MMM-2 with hydrochloric acid. The anion  $SO_4^{2-}$  is directly attached to silicon-surfactant assembly, whereas the  $Cl^-$  is not directly attached to the assembly. This directly coordinated assembly for the highly ordered mesoporous material ensures a highly ordered structure as indicated in section 2.2.3.2.

### 5.1.2 XRD

The XRD analysis for Ti-MCM-41 (Figure 5-2) and the highly ordered mesoporous material (Figure 5-5) agrees well with the XRD analysis obtained by Blasco, *et al.*, (1995) and Fortier, *et al.*, (2006), respectively. Ti-MMM-2 (Figure 5-3) and Ti-MMM-2 (P123) (Figure 5-4) do not correspond with the results obtained from literature for the XRD analysis for Ti-MMM-2 and Ti-MMM-2 (P123), respectively (Kholdeeva, *et al.*, 2005). Ti-MMM-2 and Ti-MMM-2 (P123) from this study differs from literature because it does not present a sharp feature ( $d_{100}$ ) of symmetric shape at a low angle as mentioned in section 2.2.3.1. Ti-MCM-41 and the highly ordered mesoporous material show three peaks. A strong peak  $d_{100}(100)$  and two other weaker peaks  $d_{110}(110)$  and  $d_{200}(200)$ . These three peaks occur at low angles which suggest that the catalysts exhibit a hexagonal symmetry and highly ordered pore system with a high porosity.

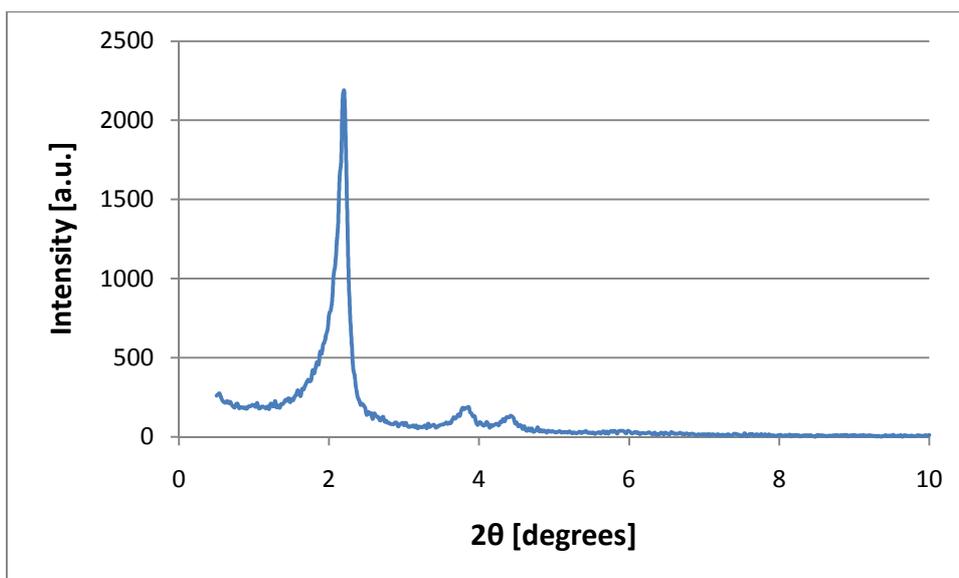


Figure 5-2 XRD diffraction pattern of Ti-MCM-41

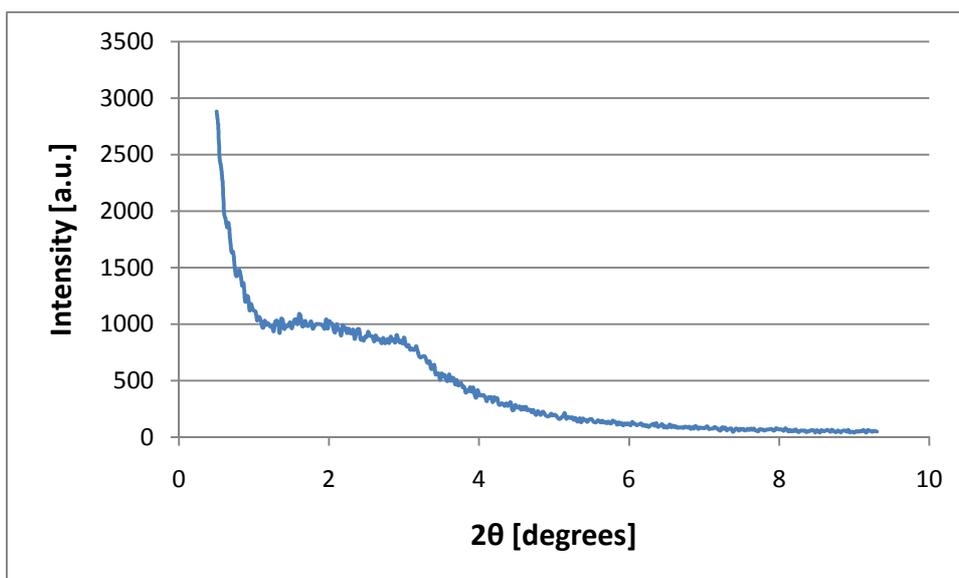


Figure 5-3 XRD diffraction pattern of Ti-MMM-2

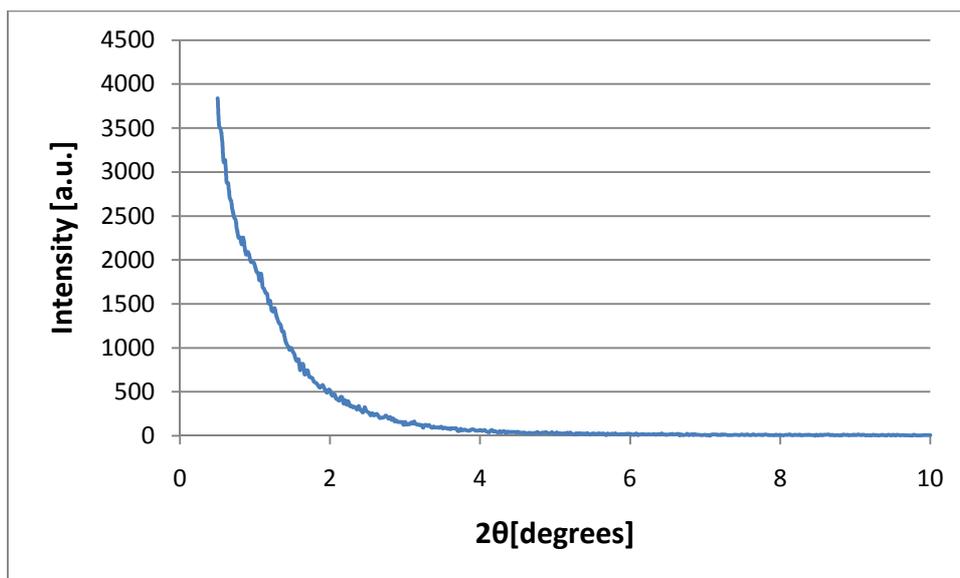


Figure 5-4 XRD diffraction pattern of Ti-MMM-2 (P123)

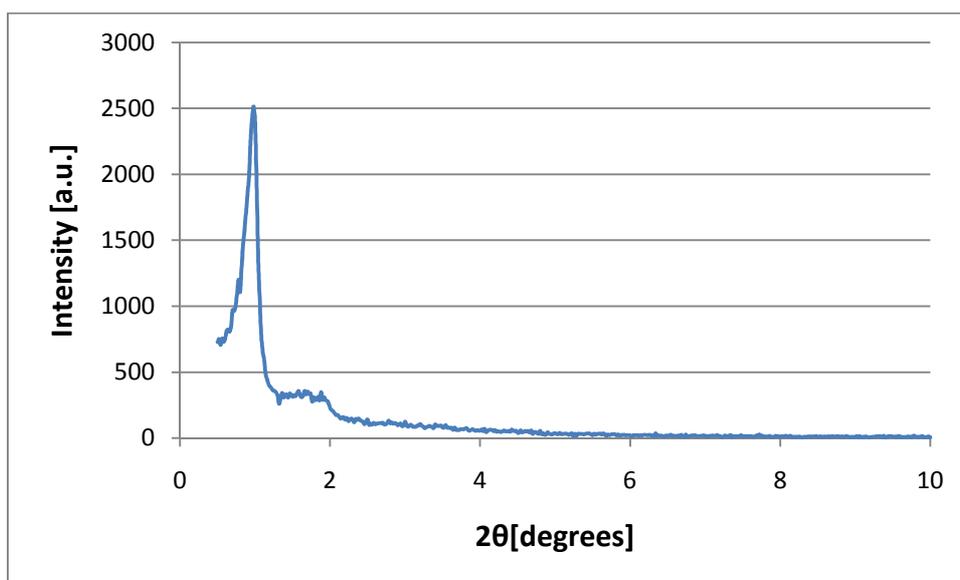


Figure 5-5 XRD diffraction pattern of Highly ordered mesoporous material

### 5.1.3 SEM & EDX Analysis

It is difficult to determine the particle size because particles have a tendency to form aggregates. Normally particles are irregular and clustered together in aggregates and these aggregates may be broken down by grinding. The aggregates itself can be regarded as secondary particles and contain some internal surface often larger than the external surface. These aggregates could exhibit a pore structure (Clark, *et al.*, 2000).

The SEM images for Ti-MCM-41(Figure 5-6) seem to present uniform particles in a spherical shape with some of the particles fusing together forming worm-like shapes. SEM analysis for Ti-MMM-2 is given in Figure 5-7, the particles appear to be shaped in a triangular pyramid form. The particles look as if they are irregular and spherical in shape for the SEM images for Ti-MMM-2(P123) in Figure 5-8. Figure 5-9 presents the SEM images for the highly ordered mesoporous material and the particles appear to look irregular cubic/spherical shaped.

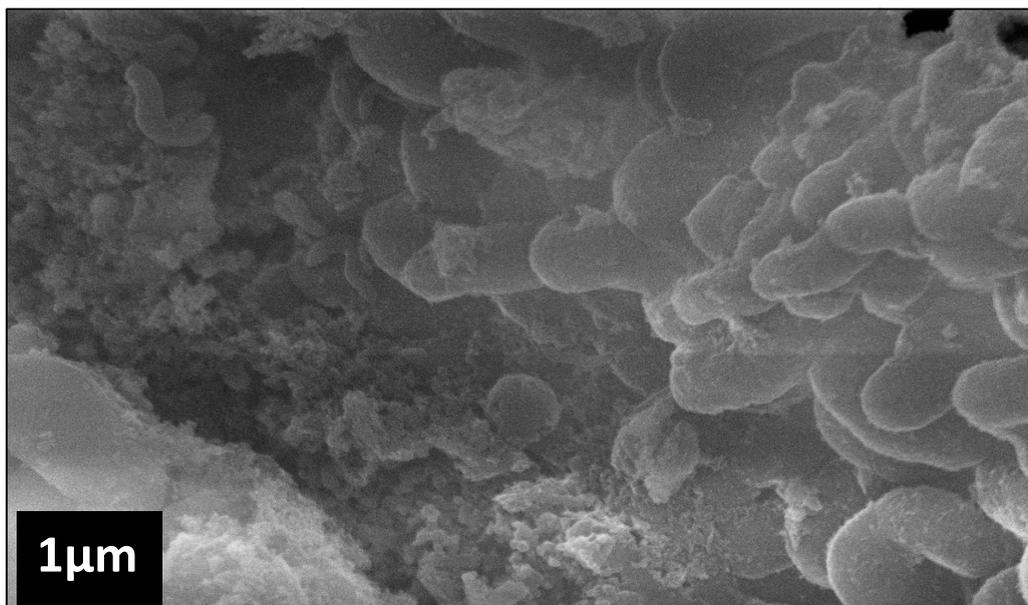


Figure 5-6 SEM micrograph of Ti-MCM-41

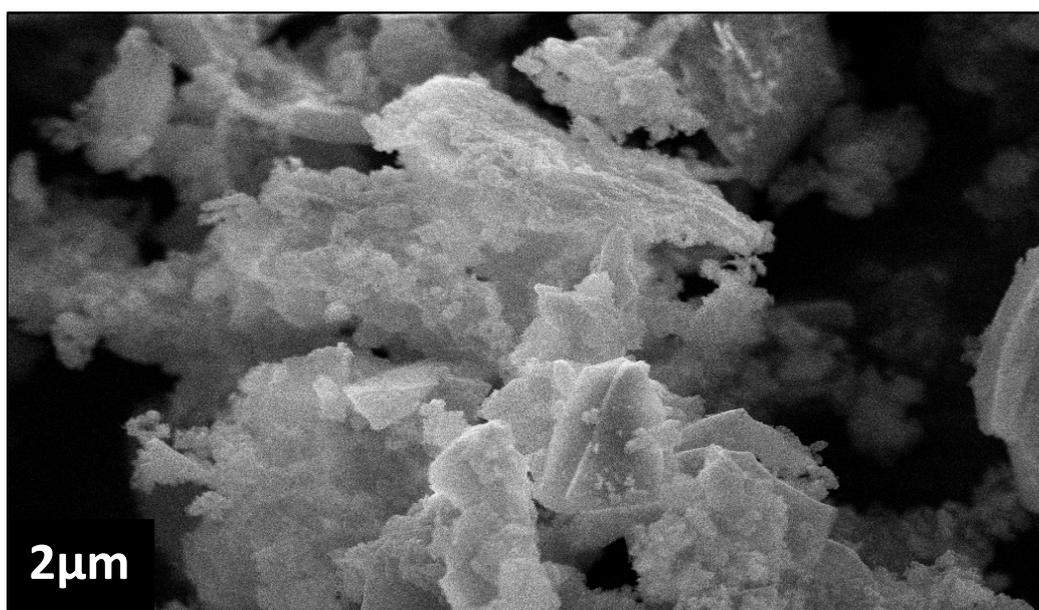


Figure 5-7 SEM micrograph of Ti-MMM-2

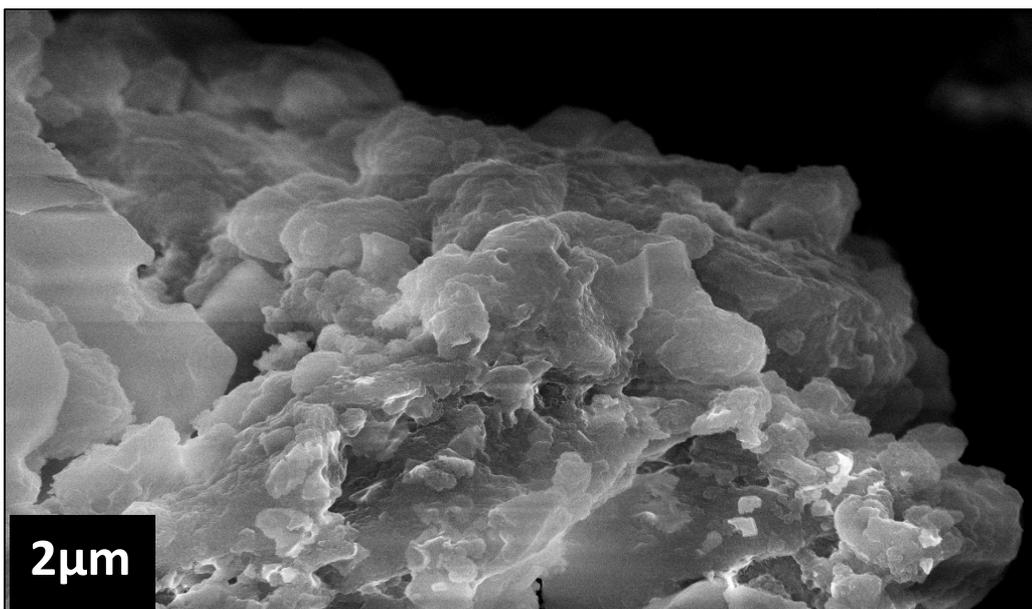


Figure 5-8 SEM micrograph of Ti-MMM-2(P123)

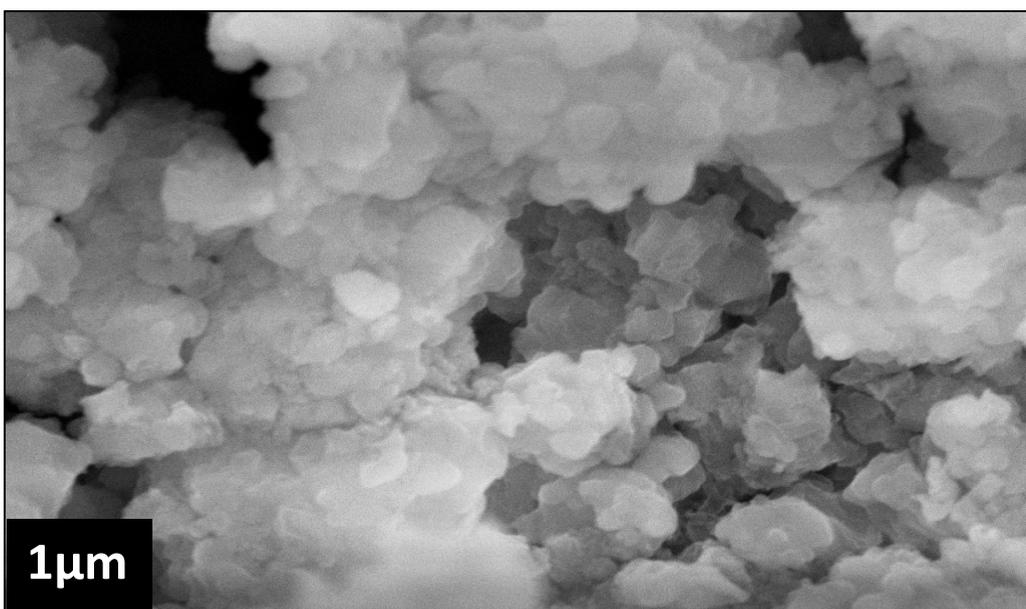


Figure 5-9 SEM micrograph of Highly ordered mesoporous material

Table 5-1 illustrates the results obtained from the EDX for the various catalysts. The chemical composition for all the catalysts composed of oxygen, silicon and titanium. Ti-MMM-2, Ti-MMM-2(P123) and the highly ordered mesoporous material also possessed sodium because the silicate source used for the synthesis was sodium trisilicate and a sodium silicate solution,

respectively. It appears that the Ti weight% for the highly ordered mesoporous material is much lower than Ti weight% for the other catalysts. The silicon/titanium (Si/Ti) ratio for the various catalysts corresponds well with the results obtained from literature (mentioned in section 2.2). The Si/Ti ratios for Ti-MCM-41, Ti-MMM-2 and Ti-MMM-2(P123) are in the same range (25-32) and the highly ordered mesoporous material has a ratio of 229.

**Table 5-1 Elemental analysis performed using an EDX on calcined catalysts**

Catalyst	Weight %				Si/Ti
	O	Na	Si	Ti	
Ti-MCM-41	65.7	0.0	33.2	1.1	31.6
Ti-MMM-2	66.1	0.2	32.4	1.3	25.5
Ti-MMM-2 (P123)	64.8	3.9	30.2	1.1	26.7
Highly ordered mesoporous material	62.8	0.1	37.0	0.2	229

Table 5-2 illustrates the characterisation of the various catalysts from this study in comparison with literature. The results from this study may vary to literature due to the possibility that different Ti (wt%) percentages was used for this study. It was found that catalysts are more active towards oxidation of reactions at a higher Ti content because more Ti-O-Ti entities connectivity's are formed (Chen, *et al.*, 1998). The wall thickness of the various catalysts is calculated with Equation 2-1.

**Table 5-2 Surface area, average pore diameter and wall thickness for the various catalysts obtained from this study in comparison with literature**

Catalyst	Particle Size [μm]	BET Surface Area [m <sup>2</sup> /g]	Average Pore Diameter [Å]	d <sub>100</sub> [Å]	a <sub>0</sub> [Å]	Wall Thickness [Å]	Author
Ti-MCM-41	12	1034	40	40	46	7	
Ti-MMM-2	13	1018	25	65	75	50	
Ti-MMM-2 (P123)	24	382	83	82	94	11	
Highly ordered mesoporous material	8	572	44	90	104	60	
Ti-MCM-41 ( 2wt% Ti)	-	1102	35	-	-	9	Blasco, <i>et al.</i> , (1995)
Ti-MMM-2 (1.67 wt% Ti)	-	1147	32	-	-	10	Kholdeeva, <i>et al.</i> , (2004)
Ti-MMM-2 (P123) (1.82 wt% Ti)	-	492	67	-	-	40	Kholdeeva, <i>et al.</i> , (2005)
Highly ordered mesoporous material (1.5 wt% Ti)	-	925	65	-	-	-	Fortier, <i>et al.</i> , (2006)

From

Table 5-2 the catalyst with the smallest particle size is the highly ordered mesoporous material and Ti-MMM-2(P123) possesses the largest particle size. The large particle size possessed by Ti-MMM-2 (P123) in this study might be because the particles clustered together forming large agglomerates. These agglomerates possessed a hard texture and could not be crushed or ground into smaller particles. A possible explanation for agglomerates forming and dissimilarities from literature for Ti-MMM-2 and Ti-MMM-2 (P123) is due to the synthesis procedure of the catalysts. These catalysts used a different silicon source as in literature. Igarashi, *et al.*, (2003) found that the use of different Si sources for synthesising a catalyst can alter the crystal morphology due to the difference in degree of condensation of the silica source.

## 5.2 Hydroxylation of 2-Methylnaphthalene

### 5.2.1 Preliminary reaction testing

Before investigating an environmentally friendly process for the hydroxylation of 2MN to 2MNQ, it is imperative to take the following parameters into consideration to ensure accurate results:

- Conduct a catalyst-screening test to ensure that all catalysts synthesised for this study successfully oxidize 2MN to 2MNQ.
- Evaluate the reproducibility of the process system. This implies that experiments conducted under the same reaction conditions and same samples analysed with the GC should produce identical results.
- Identify all possible products produced from this system

#### 5.2.1.1 Catalyst-screening test

Since catalysts Ti-MMM-2 and Ti-MMM-2(P123) do not correspond with findings found in literature, it is important to observe if the catalysts will oxidize 2MN to 2MNQ. Based on previous studies, Ti-MMM-2 and Ti-MMM-2(P123) have only been successful for the selective oxidation of bulky organic substrates containing hydroxyl functions (Kholdeeva, *et al.*, 2005). There is little work in literature with regards to the hydroxylation of bulky substrates with the highly ordered mesoporous material as the catalyst. Therefore, it is important to perceive if Ti-MMM-2 will oxidize bulky substrates not possessing hydroxyl groups and if the highly ordered mesoporous material is successful in oxidizing bulky substrates. Ti-MCM-41 has already acted as catalyst for the hydroxylation of 2MN to 2MNQ from previous studies (discussed in section 2.4.1).

A preliminary catalyst-screening test for this process was conducted in order to see if the catalysts synthesised for this study obtains a substrate conversion. Figure 5-10 illustrates the preliminary test for this process and shows that the highly ordered mesoporous material, Ti-MMM-2 and Ti-MCM-41 obtain a substrate conversion. Therefore, it is suggested that these catalysts successfully oxidizes the hydroxylation of 2-methylnaphthalene to 2-methy-1,4-naphthoquinone.

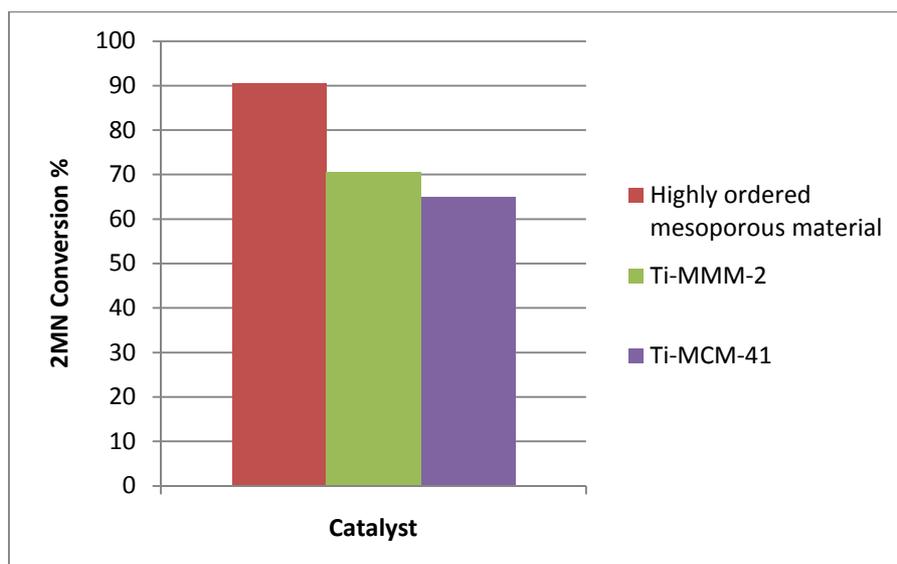


Figure 5-10 Preliminary test at 150°C, 6 hours, 1 g 2MN, 100 mg catalyst, 10 ml MeCN, 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

Since Ti-MMM-2 obtains a conversion for this process and Ti-MMM-2(P123) is a similar catalyst with the exception of a different surfactant, it is assumed that Ti-MMM-2(P123) would also be an appropriate catalyst for this process. Therefore, it can be concluded that all catalysts synthesised for this study would be a suitable candidate for improving the hydroxylation of 2MN to 2MNQ process.

### 5.2.1.2 Reproducibility

The reproducibility for the reactor system is studied by conducting three experiments at 150°C with Ti-MMM-2 as the catalyst. The experiments were conducted under the same reaction conditions and the reproducibility was expressed in terms of 2MN conversion, 2MNQ yield and 2MNQ selectivity.

Table 5-3 Reproducibility of 2MN conversion%, 2MNQ yield% and 2MNQ selectivity for the reaction system at 150°C, 100 mg Ti-MMM-2, 10 ml MeCN, 6 ml H<sub>2</sub>O<sub>2</sub>, 3.5 hours

	Experiment 1	Experiment 2	Experiment 3	Standard deviation	95 % Confidence
2MN Conversion %	73.49	74.37	73.60	0.39	0.44
2MNQ Yield %	23.25	23.63	23.50	0.16	0.18
2MNQ Selectivity %	62.31	60.49	61.45	0.74	0.84

Based on Table 5-3 the mean value for 2MN conversion was calculated as  $73.82 \pm 0.39$ . A 95% confidence level for the reproducibility of conversion, yield and selectivity for the reaction system was calculated using MS Excel. The confidence interval if 2MN conversion was reproducible would have been  $73.82 \pm 0.44$ . The mean value for 2MNQ yield was calculated as  $23.46 \pm 0.16$ . The confidence interval if 2MNQ yield conversion was reproducible would be  $23.46 \pm 0.18$ . The mean value for 2MNQ selectivity was calculated as  $61.42 \pm 0.74$  for a 95% confidence level. The confidence interval if 2MNQ selectivity was reproducible would be  $61.42 \pm 0.84$ . Based on the results it is suggested that the reaction system for this study produces good reproducible results. The repeatability for the GC analysis is determined by injecting a sample thrice on the GC. The repeatability is expressed in terms of 2MN conversion, 2MNQ yield and 2MNq selectivity.

**Table 5-4 Repeatability of 2MN conversion%, 2MNQ yield% and 2MNQ selectivity for the analysis system at 150°C, 100 mg Ti-MMM-2, 10 ml MeCN, 6 ml H<sub>2</sub>O<sub>2</sub>, 4.5 hours**

	Analysis 1	Analysis 2	Analysis 3	Standard deviation	95 % Confidence
<b>2MN Conversion %</b>	76.49	76.93	76.66	0.18	0.20
<b>2MNQ Yield %</b>	25.02	25.35	25.48	0.20	0.22
<b>2MNQ Selectivity %</b>	74.97	74.53	74.63	0.19	0.21

**Based on**

Table 5-4 the mean value for 2MN conversion was calculated as  $76.70 \pm 0.18$ . A 95% confidence level for the repeatability of conversion, yield and selectivity for the analysis system was calculated using MS Excel. The confidence interval if 2MN conversion was repeatable would be  $76.70 \pm 0.20$ . The mean value for 2MNQ yield was calculated as  $25.28 \pm 0.20$ . The confidence interval if 2MNQ yield conversion was repeatable would be  $25.28 \pm 0.22$ . The mean value for 2MNQ selectivity was calculated as  $74.71 \pm 0.19$  for a 95% confidence level. The confidence interval if 2MNQ selectivity was repeatable would be  $74.71 \pm 0.21$ . Based on the results it is suggested that the analysis system for this study produces good repeatable results.

### **5.2.1.3 Identifying products**

Figure 2-9 illustrates possible products that could be formed for the oxidation of 2MN. The products formed for the hydroxylation of 2MN with the exception of 2MNQ are uncertain because various studies conducted in literature identified different by-products for this process. It is suggested that

difference in by-products with these studies are due to reactions conducted under different reaction conditions and process systems.

To identify the products formed from this process and compare them to literature, an experiment under the same reaction conditions and catalyst as Anunziata, *et al.*, (2004) (as discussed in section 2.4.1) was conducted and analysed with the GC-MS. The GC-MS identified 2MNQ, 2-naphthaldehyde and 3-ethoxy-4-methoxybenzaldehyde as the products for this study, whereas Anunziata, *et al.*, (2004) identified 2MNQ, 2MNL and 1,4DOH-2MN as the products. A possible difference in by-products for this study and Anunziata, *et al.*, (2004) is due to a difference in the process system. The process system implies to the reactor type/size, heating unit, heating bath. Reactions are performed in a 45 ml autoclave for this study, whereas Anunziata, *et al.*, (2004) used a 150 ml autoclave. In this study, 2MNL and menadione epoxide were also identified as by-products. Kholdeeva, *et al.*, (2005) also detected menadione epoxide as a product for the hydroxylation of 2MNL to 2MNQ over Ti-MMM-2. The products identified for this study are illustrated in Figure 5-11.

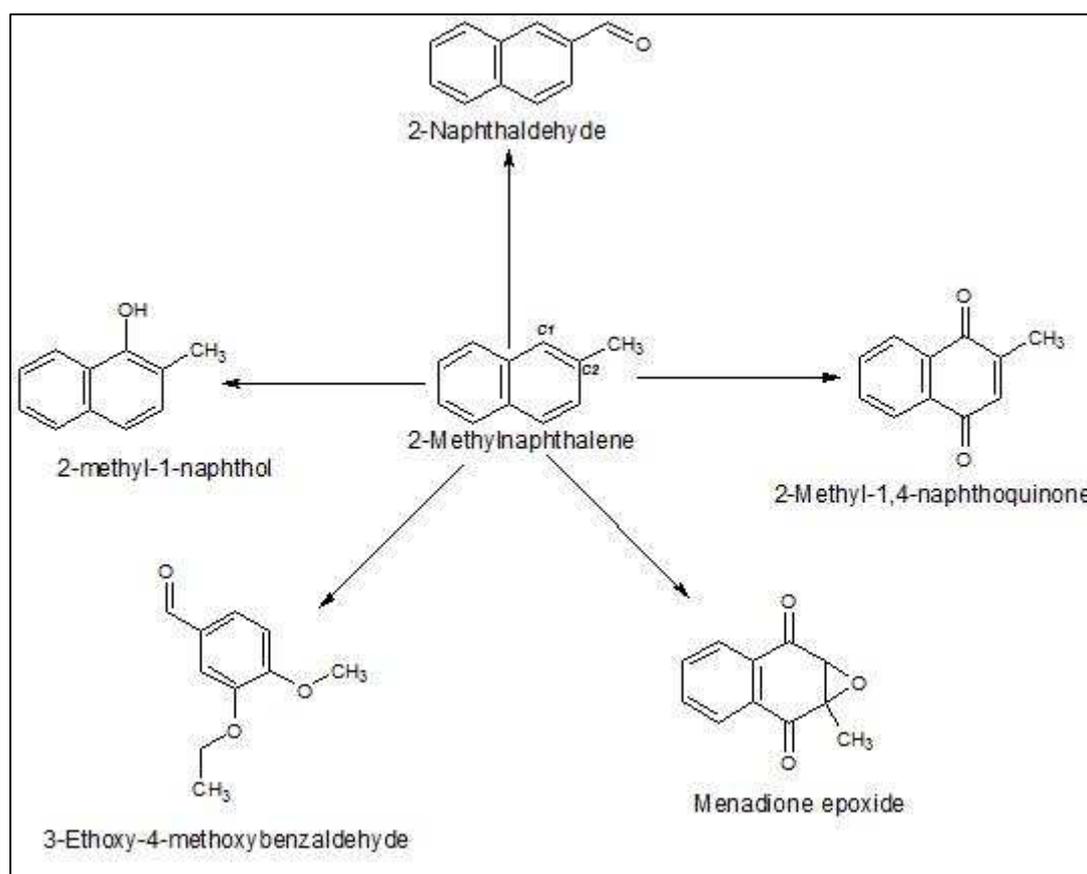


Figure 5-11 Products identified for this study

The products identified from the GC-MS for this study are all possible products that can be formed from the hydroxylation of 2-methylnaphthalene based on literature (see Figure 2-9). The formation of 2MNQ, menadione epoxide and 2MNL is based on the C1 attack in Figure 2-8. These products are favoured because the resonance is not lost. This keeps one benzene ring intact and alkyl groups as substituents for benzene rings favours ortho- and para- directing positions.

2-Naphthaldehyde and 3-ethoxy-4-methoxybenzaldehyde are formed based on the C2 attack in Figure 2-8. The reaction oxidizes C2 by forming an aldehyde and in the process, resonance is lost and both benzene rings are affected causing them to destabilize and break one ring to form 3-ethoxy-4-methoxybenzaldehyde.

Therefore, it implies that the reaction mechanism for this study can occur in two ways. A reaction can either follow one pathway or both pathways. It is suggested that multiple series reactions occurs in this study for the two pathways. The reaction pathway is based on the C1 attack and produces 2MNL, 2MNQ and menadione epoxide. 2MNL is an intermediate between 2MN and 2MNQ, whereas 2MNQ is an intermediate between 2MN and menadione epoxide. Menadione epoxide occurs when the reaction is over-oxidized between 2MN and 2MNQ. For the reaction pathway based on the C2 attack, 2-naphthaldehyde is an intermediate between 2MN and 3-ethoxy-4-methoxybenzaldehyde.

2-Naphthaldehyde is used as an intermediate for the synthesis of pharmaceuticals, photochemicals, dyes and other organic compounds (<http://chemicaland21.com/specialtychem/finechem/2-naphthaldehyde.htm>,2009). 2MNL acts as an intermediate between 2MN and 2MNQ, whereas 1,4DOH-2MN is used as a drug for the treatment of hypoprothrombinaemia haemostatic agent antioxidant (<http://www.extc.cn/products/1-4-dihydroxy-2-methylnaphthalene-1541-4571.htm>,2009). 3-Ethoxy-4-methoxybenzaldehyde is used as a pharmaceutical intermediate and menadione epoxide is the main metabolic reaction produced from the Vitamin K family (<http://www.fags.org/rulings/rulings2005NYL88199.html>,2009;<http://ethesis.helsinki.fi/julkaisut/ma/a/skemi/vk/koivu-tikkanen/ch2.html>,2009). Therefore, it is suggested that all the products produced from this study are environmentally friendly because they are not harmful or hazardous towards the environment. This implies that this process is environmentally friendly.

## 5.2.2 Process system

Figure 5-12 to Figure 5-15 illustrates the choice of heat transfer medium on the reaction behaviour.

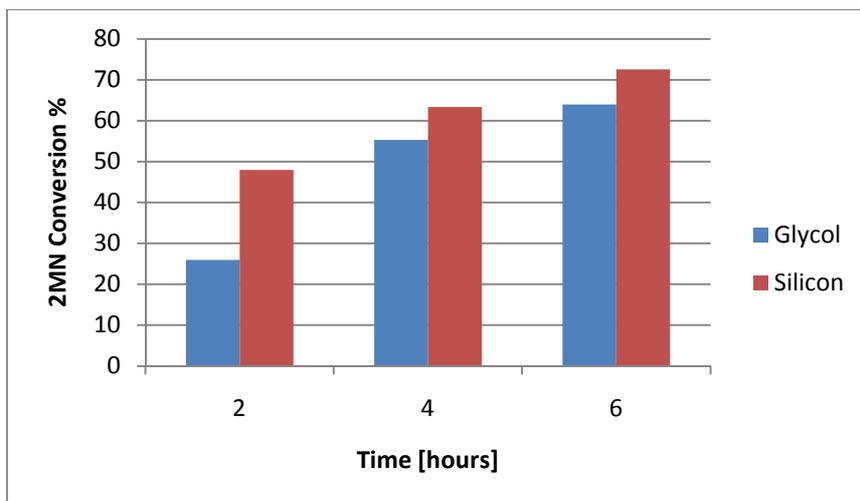


Figure 5-12 Effect of different oil bath at 150°C, 1 g 2MN, 100 mg Ti-MCM-41, 10 ml MeCN, 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

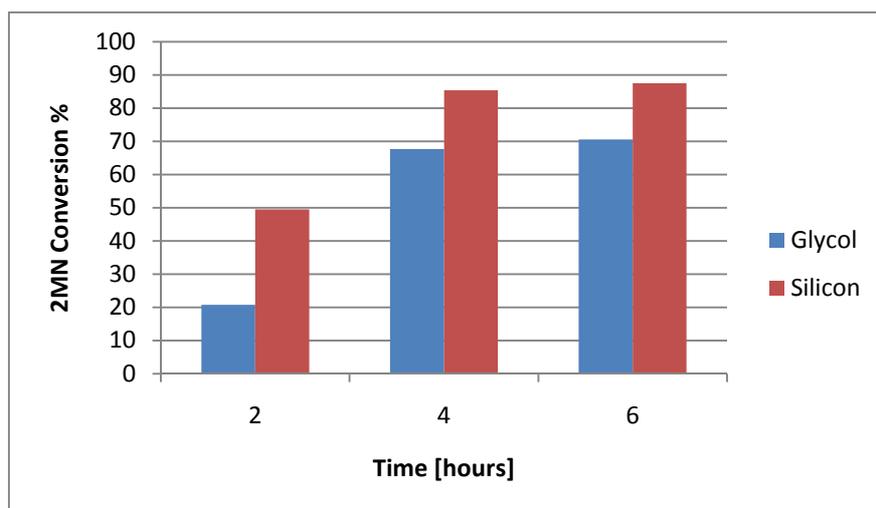


Figure 5-13 Effect of different oil bath at 150°C; 1 g 2MN; 100 mg Ti-MMM-2; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

From Figure 5-12 and Figure 5-13 it appears higher 2MN conversions in all cases are obtained with the silicon oil system instead of the glycol system. The highest 2MNQ yields for all cases are also acquired with the silicon system as illustrated in Figure 5-14 and Figure 5-15.

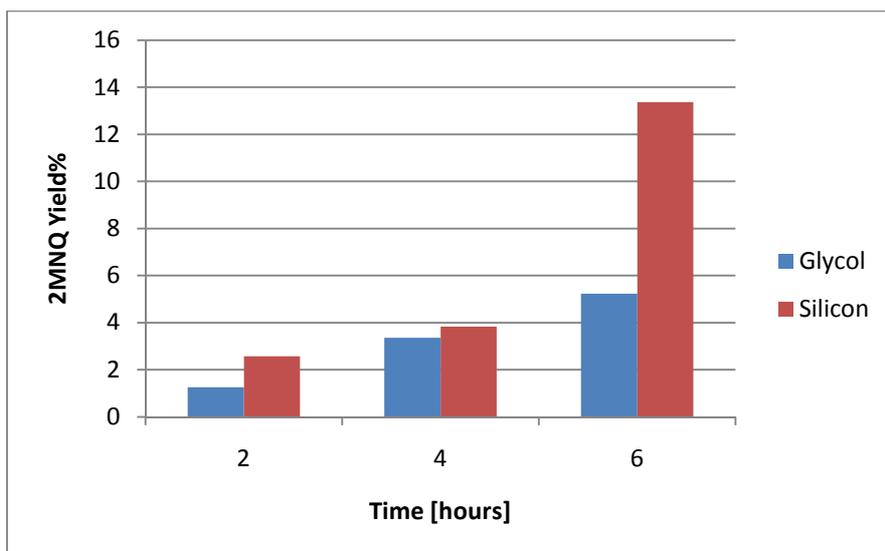


Figure 5-14 Effect of different oil bath at 150°C, 1 g 2MN, 100 mg Ti-MCM-41, 10 ml MeCN, 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

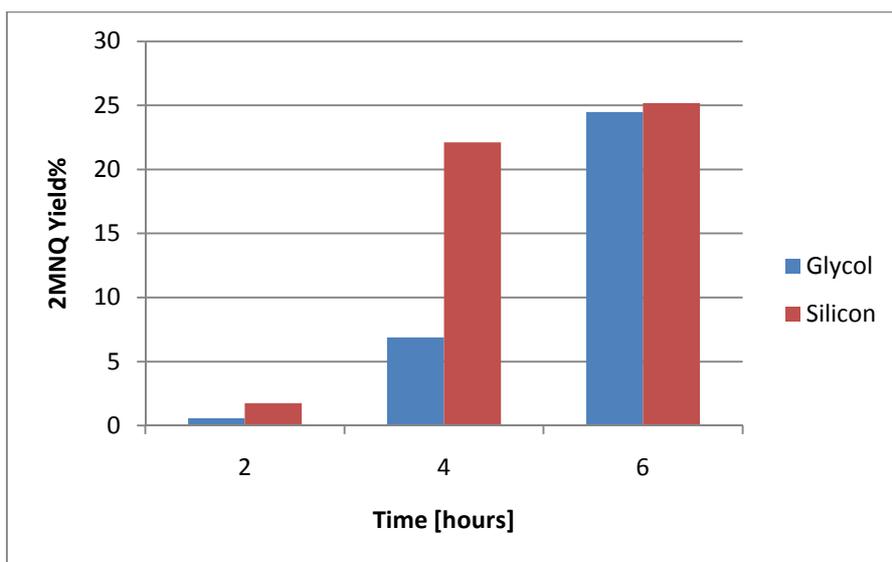


Figure 5-15 Effect of different oil bath at 150°C; 1 g 2MN; 100 mg Ti-MMM-2; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

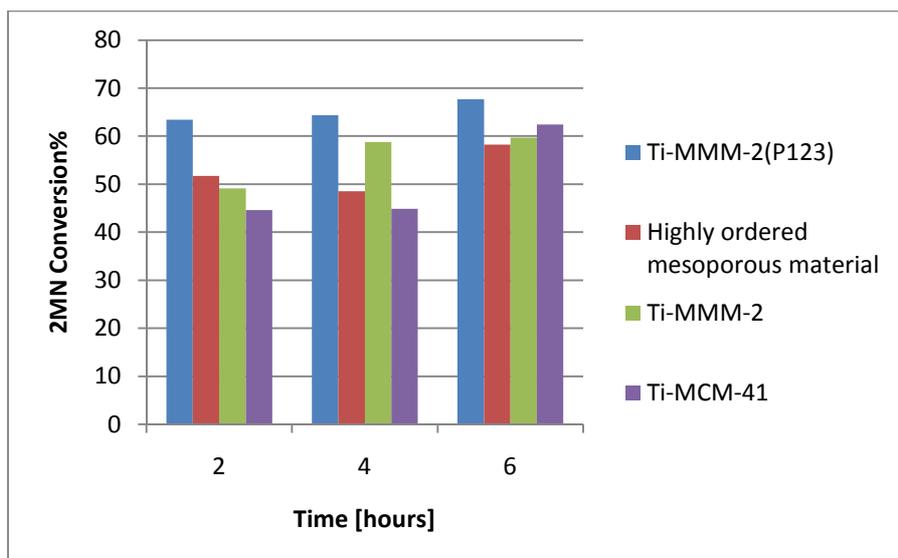
It is suggested that these results are not based on the oil type but purely on the fact that the autoclave is submerged deeper in the silicon system due to a bigger oil bath. This allows a more efficient thermal contact between the autoclave and the oil. It is not the oil type because the heat capacity for glycol (2.36 kJ/kg.K) is higher than silicon (1.80 kJ/kg.K). This implies that the glycol is a better medium to store thermal energy than silicon oil but a problem occurred with the glycol system (<http://www.engineeringtoolbox.com,2010>). The glycol started to react at the reaction

temperatures causing to burn and form carbon deposits on the autoclave. The products formed by the two systems also differ as illustrated in APPENDIX G; the glycol system produces only 2MNQ and 2-naphthaldehyde as products, whereas the silicon system forms 2MNQ, 2-naphthaldehyde and 3-ethoxy-4-methoxybenzaldehyde. Therefore, it is proposed that these results confirm that the process system has an impact on the substrate conversion, products formed, product yield and product selectivity. The disadvantage of the silicon system is that the oil bath takes a while to reach its desired reaction temperature in comparison with the glycol system because the thermal conductivity of silicon oil (0.1W/mK) is lower than glycol oil (0.26 W/mK) (<http://www.engineeringtoolbox.com>,2010). Based on these findings, it is suggested that the silicon system is favoured for this process. Therefore, all experiments are conducted with the silicon system.

### 5.2.3 Identify suitable catalyst

All catalysts synthesised for this study are investigated in order to determine which catalyst performs best for this study. This is done by observing the effect reaction conditions have on the various catalysts. The reaction conditions are the reaction temperature, reaction time, hydrogen peroxide volume, catalyst amount, substrate amount and solvent volume. The investigation occurs by conducting experiments with the various catalysts under the same reaction conditions and the catalyst acquiring the highest 2MN conversion and favouring the formation of 2MNQ, is the desired catalyst for this process.

The different catalysts were initially studied under the same reaction conditions conducted by Anunziata, *et al.*, (2004): 120°C; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 10 ml MeCN; 1 g 2MN; 100 mg catalyst at different reaction times intervals: 2 hours, 4 hours and 6 hours. The results for the various catalysts at 120°C are illustrated in Figure 5-16. It appears that catalyst Ti-MMM-2 (P123) obtains the highest conversions in comparison with the other catalysts for the various time intervals at 120°C. The second highest 2MN conversion achieved at 120°C fluctuates because for 2 hours the highly ordered mesoporous material is favoured, whereas Ti-MMM-2 at 4 hours and Ti-MCM-41 at 6 hours.

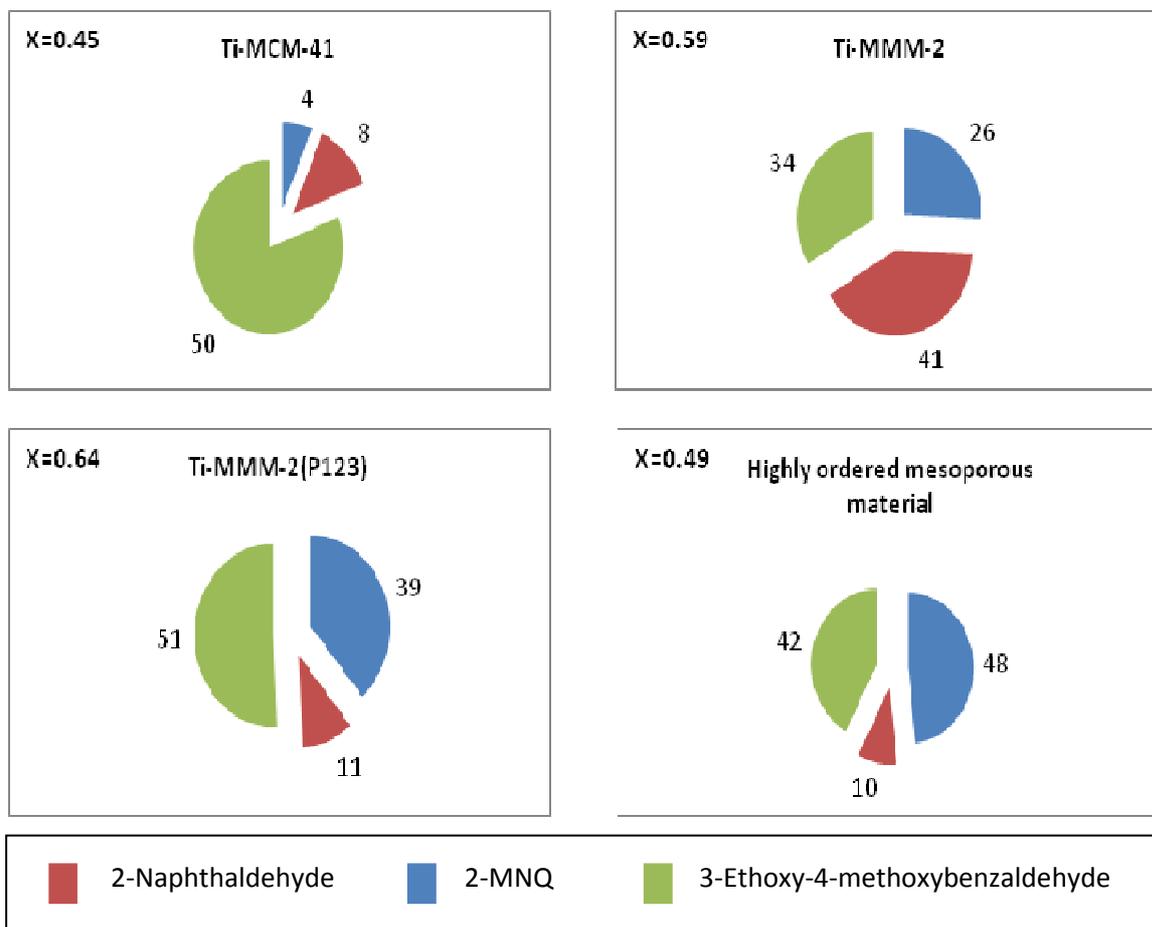


**Figure 5-16 Effect of reaction time on the various catalysts at 120°C; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

Based on Figure 5-16 it seems the conversions for the various catalysts increase with increasing reaction time except for the highly ordered mesoporous material at 4 hours. Similar results were obtained in literature for conversion increasing with reaction time. Therefore, it is suggested that the conversion obtained for the highly ordered mesoporous material at 4 hours might be an experimental error. The experimental error might have occurred due to a variation in the reaction condition.

It is found that the conversions obtained in this study are higher than the conversions obtained by Anunziata, *et al.*, (2004) under the same reaction conditions (Table 2-14). Dissimilarity of conversions between Ti-MCM-41 catalyst from this study and Anunziata, *et al.*, (2004) is not due the difference in titanium content (1.2%) for this study and titanium content (1.8%) for Anunziata, *et al.*, (2004). If this is the case then Anunziata, *et al.*, (2004) should obtain a higher substrate conversion based on studies in literature. Increasing the titanium content in redox molecular sieves enhances the catalytic activity of a catalyst and increases the substrate conversion (Chen, *et al.*, 1998; Thangaraj, *et al.*, 1991). A possible explanation for a higher conversion in this study could be due to the process system used in this study in comparison with the system by Anunziata, *et al.*, (1998) because the process system affects the activity and selectivity of a process (discussed in section 0).

It is important to determine the selectivity of the products formed from the experiments to ensure 2MNQ is the favoured product. Figure 5-17 presents the selectivity of the products for the various catalysts at 120°C with a reaction time of 4 hours. The results for the other time intervals at 120°C can be found in Figure 15-1 and Figure 15-2 (APPENDIX H).

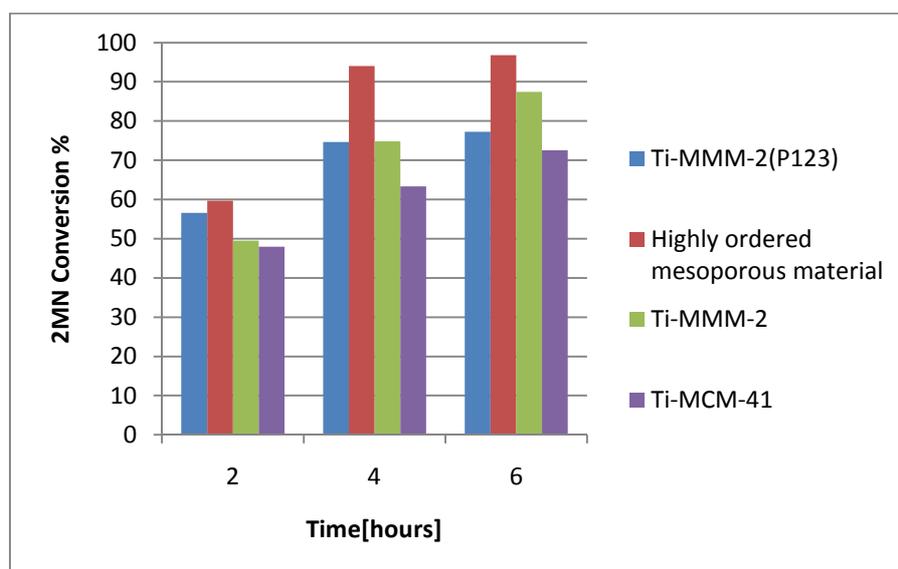


**Figure 5-17 Selectivity for various catalysts at 120°C; 4 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

It appears the only catalyst favouring the formation 2MNQ for all time intervals at 120°C is the highly ordered mesoporous material. The highly ordered mesoporous material produces 44% 2MNQ selectivity at 2 hours, 48% 2MNQ selectivity for 4 hours and 55% 2MNQ selectivity at 6 hours. This implies that the highly ordered mesoporous material favours 2MNQ production as the reaction time increases at 120°C. Ti-MCM-41 and Ti-MMM-2 favours 2-naphthaldehyde at 2 hours and 4 hours and 3-ethoxy-4-methoxybenzaldehyde at 6 hours. This implies that Ti-MCM-41 and Ti-MMM-2 favours the oxidation on the C2 and not on the benzene ring as discussed in section 5.2.1.3. Ti-MMM-2 (P123) favours the production of 3-ethoxy-4-methoxybenzaldehyde at 2 hours and 4 hours and 2MNQ at 6 hours. Ti-MMM-2 (P123) favours 2MNQ at 6 hours but the highly ordered mesoporous material still produces more 2MNQ in terms of yield.

Therefore, even though catalyst Ti-MMM-2 (P123) obtains the highest 2MN conversions at 120°C for all time intervals, it does not come forth as the most suitable catalyst under these reaction conditions because it favours the formation of 3-ethoxy-4-methoxybenzaldehyde at 2 hours and 4 hours and produces less 2MNQ at 6 hours than the highly ordered mesoporous material. Based on these results, it appears the highly ordered mesoporous material is the favoured catalyst under these reaction conditions because it is the only catalyst promoting the formation of 2MNQ for all time intervals. The downside of the highly ordered mesoporous material under these conditions is that it acquires a low 2MN conversion. Based on literature and kinetic modelling, the substrate conversion can be increased by increasing the reaction temperature (Fogler, 1999). Therefore, the reaction temperature is raised to 150°C.

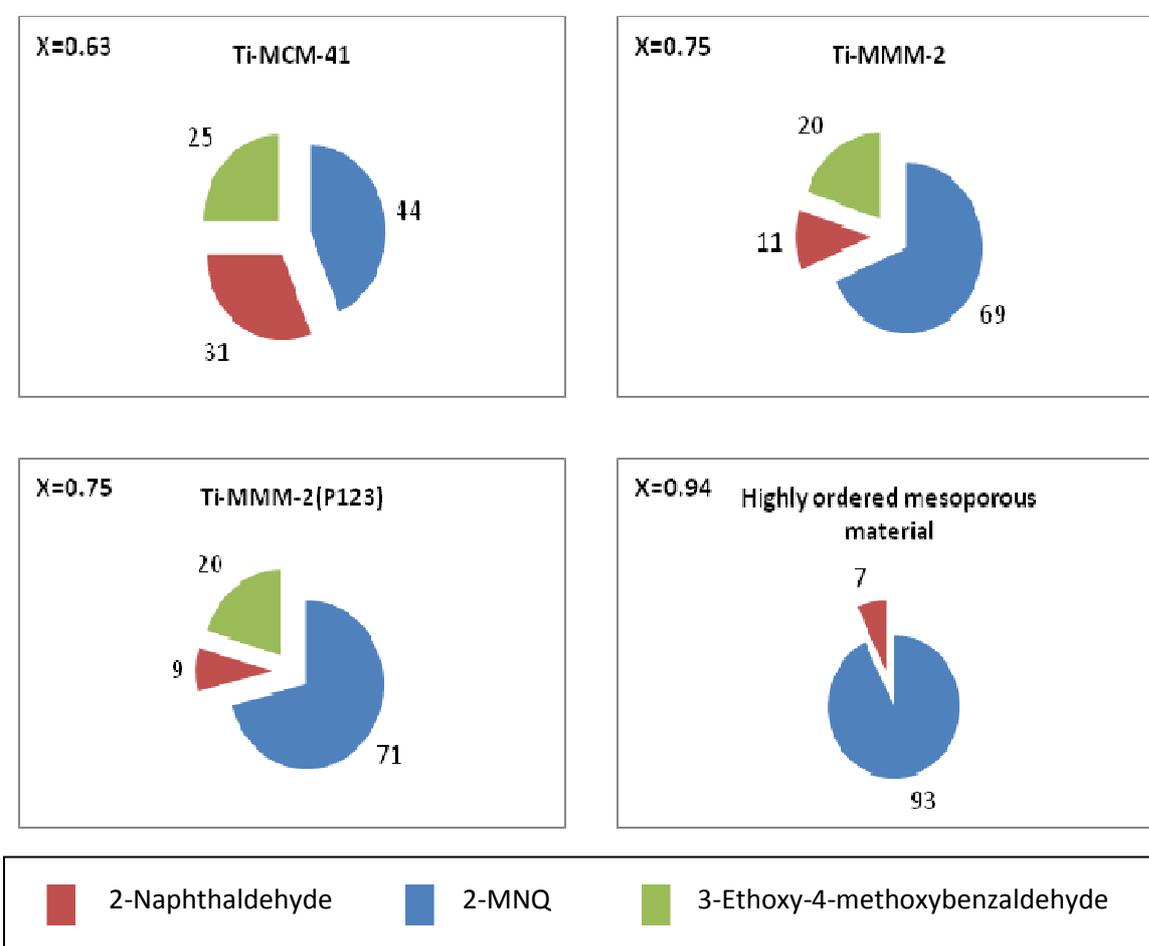
Figure 5-18 demonstrates the results for the various catalysts under the same reaction conditions as Figure 5-16 with the exception that the reaction temperature is raised to 150°C.



**Figure 5-18 Effect of reaction time on the various catalysts at 150°C; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

From the results in Figure 5-18 it appears the highly ordered mesoporous material obtains the highest 2MNQ conversions for all time intervals at 150°C. The conversions for the various catalysts increase as the reaction time increases. This corresponds to kinetic modelling and studies conducted in literature (Fogler, 1999). The highly ordered mesoporous material obtains 60%, 94% and 97% 2MN conversions for the time intervals, 2 hours, 4 hours and 6 hours, respectively. Ti-MMM-2 (P123) obtains the second highest conversion at reaction times 4 hours and 6 hours, whereas Ti-MMM-2 achieves the same conversion as Ti-MMM-2 (P123) for 4 hours and the second highest conversion at 2 hours. Ti-MCM-41 attains the lowest 2MN conversion for all time intervals under these reaction conditions. It is suggested that low conversions are achieved due to the poor hydrothermal stability

and hydrophilic framework structure of Ti-MCM-41 as discussed in section 2.2.2.1. Figure 5-19 illustrates the product selectivity at 150°C for 4 hours, while the other time intervals can be found in Figure 15-3 and Figure 15-4 (APPENDIX H).

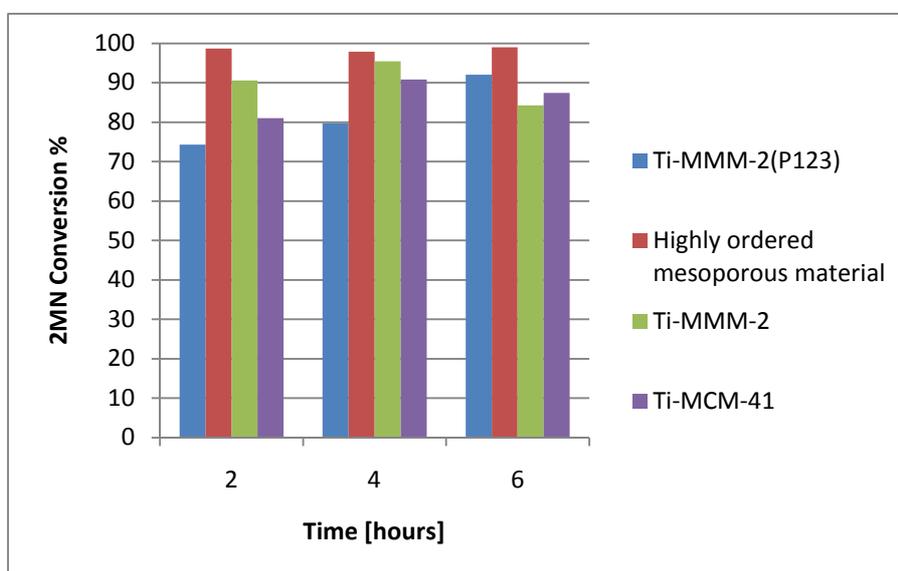


**Figure 5-19 Selectivity for various catalysts at 150°C ; 4 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

Based on the product selectivity figures for the various catalysts at 150°C, Ti-MCM-41, Ti-MMM-2 and Ti-MMM-2(P123) produced 2MNQ, 2-naphthaldehyde and 3-ethoxy-4-methoxybenzaldehyde as products, whereas the highly ordered mesoporous material produced 2MNQ, 2-naphthaldehyde, 3-ethoxy-4-methoxybenzaldehyde and menadione epoxide. It appears the product selectivity of 2MNQ is the highest in comparison to other products for catalysts Ti-MCM-41, Ti-MMM-2 (P123) and the highly ordered mesoporous material at all reaction times. Ti-MMM-2 favours 2MNQ at 4 hours and 6 hours but 3-ethoxy-4-methoxybenzaldehyde at 2 hours. It is found that the 2MNQ selectivity for the various catalysts increases as the reaction time increases except for the highly ordered mesoporous material. The 2MNQ selectivity for the highly ordered mesoporous material is 43%, 93% and 77% for 2 hours, 4 hours and 6 hours, respectively. It is proposed that the selectivity decreases from 4 hours

to 6 hours because the reaction between 2MN and 2MNQ starts over-oxidizing, favouring menadione epoxide (as discussed in section 5.2.1.3) as the reaction time increases. If this is the case, it is suggested that reactions should not be conducted at longer reaction times than 6 hours at 150°C in order to favour 2MNQ formation. Even though the selectivity for 2MNQ decreased for the highly ordered mesoporous material, the highly ordered mesoporous material still produced higher 2MNQ product than the other catalysts. Therefore, the highly ordered mesoporous material is the favoured catalyst because it obtains the highest 2MN conversions and favours 2MNQ formation for these reaction conditions.

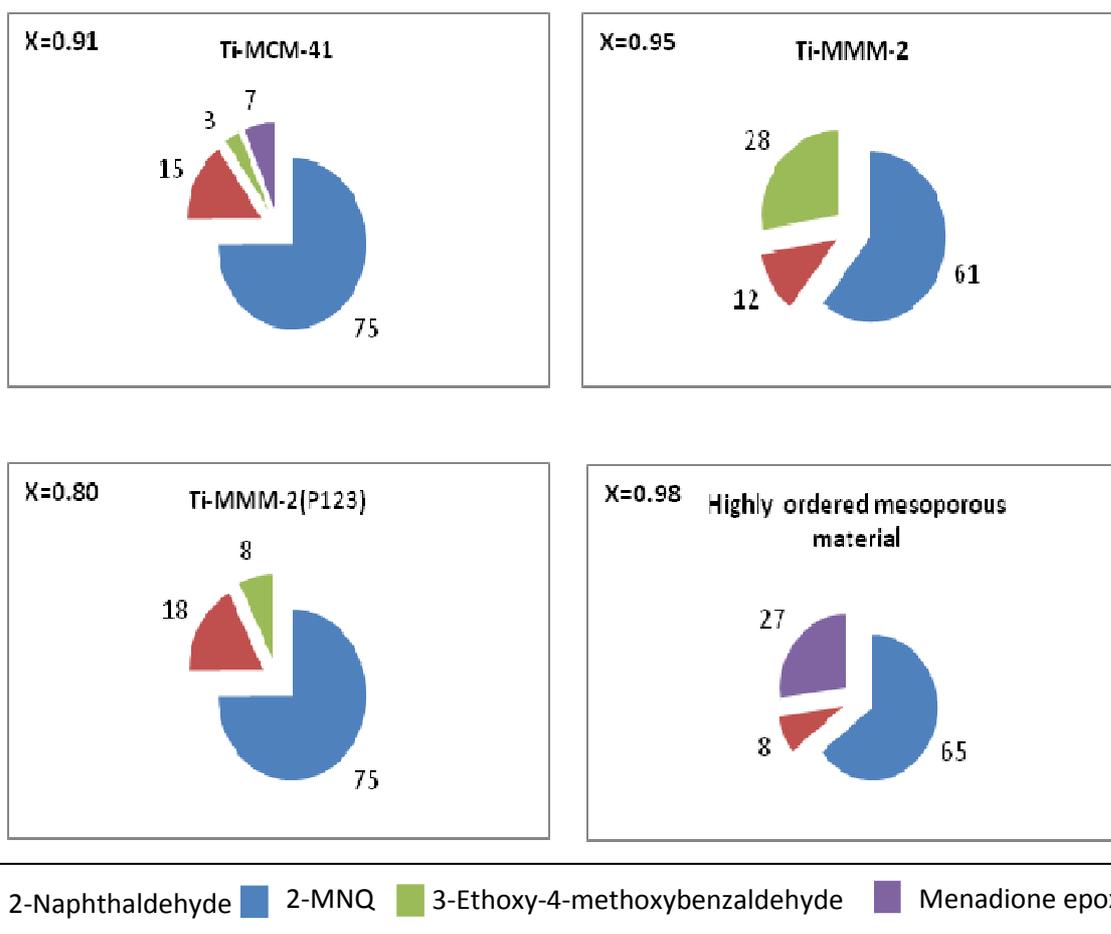
Due to the 2MN conversion and 2MNQ selectivity increase as a result of increasing reaction temperature, the temperature is increased to the heating bath maximum, 180°C. Figure 5-20 illustrates the 2MN conversion for the various catalysts at 180°C as previous reaction time intervals.



**Figure 5-20 Effect of reaction time on the various catalysts at 180°C; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

From Figure 5-20, the highly ordered mesoporous material achieves the highest conversion for all the reaction times at 180°C. It appears that the highly ordered mesoporous material obtains almost complete conversion for the various reaction times. The conversion for the highly ordered mesoporous material is 99%, 98% and 99% for 2 hours, 4 hours and 6 hours, respectively. Ti-MMM-2 obtains the second highest conversion at 2 hours and 4 hours and Ti-MMM-2 (P123) at 6 hours.

Figure 5-21 shows the product selectivity for the various catalysts at 180°C for 4 hours, while the other time intervals can be found in Figure 15-5 and Figure 15-6 (APPENDIX H).



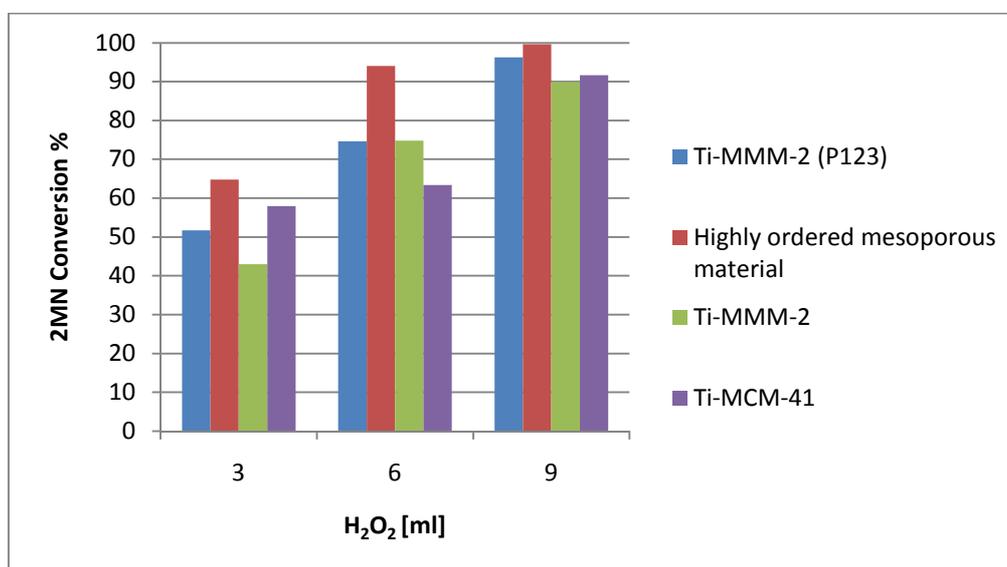
**Figure 5-21 Selectivity for various catalysts at 180°C ; 4 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

It appears from the product selectivity figures for the various catalysts at 180°C that Ti-MCM-41, Ti-MMM-2 and Ti-MMM-2 (P123) favour the formation of 2MNQ at all reaction time intervals. The highly ordered mesoporous material favours 2MNQ formation at 2 hours and 4 hours but not at 6 hours. The highly ordered mesoporous material favours menadione epoxide at 6 hours. The product selectivity for the highly ordered mesoporous material obtains 100% 2MNQ at 2 hours, 65% 2MNQ, 8% naphthaldehyde and 27% menadione epoxide at 4 hours and 27% 2MNQ and 73% menadione epoxide at 6 hours. It is suggested that the reaction with highly ordered mesoporous material favours the over-oxidation reaction of 2MN to 2MNQ (as discussed in section 5.2.1.3) as the reaction time increases at 180°C because 100% 2MNQ selectivity was achieved at 2 hours. The 2MNQ selectivity starts decreasing at 4 hours and 6 hours, while the menadione epoxide selectivity increases. Therefore, the reaction time should not be lower than 4 hours when the highly ordered mesoporous material acts as the catalyst at 180°C.

Although the highly ordered mesoporous material does not favour 2MNQ at 6 hours, it is still suggested as the favourable catalyst for these reaction conditions because it obtains the highest conversion at all time intervals and favours 2MNQ formation at the other time intervals.

Based on the results, the catalyst appearing to perform the best for the reaction temperature and reaction time profile for this study is the highly ordered mesoporous material because it achieves the highest 2MN conversion in comparison to the other catalysts in most cases and favours 2MNQ formation.

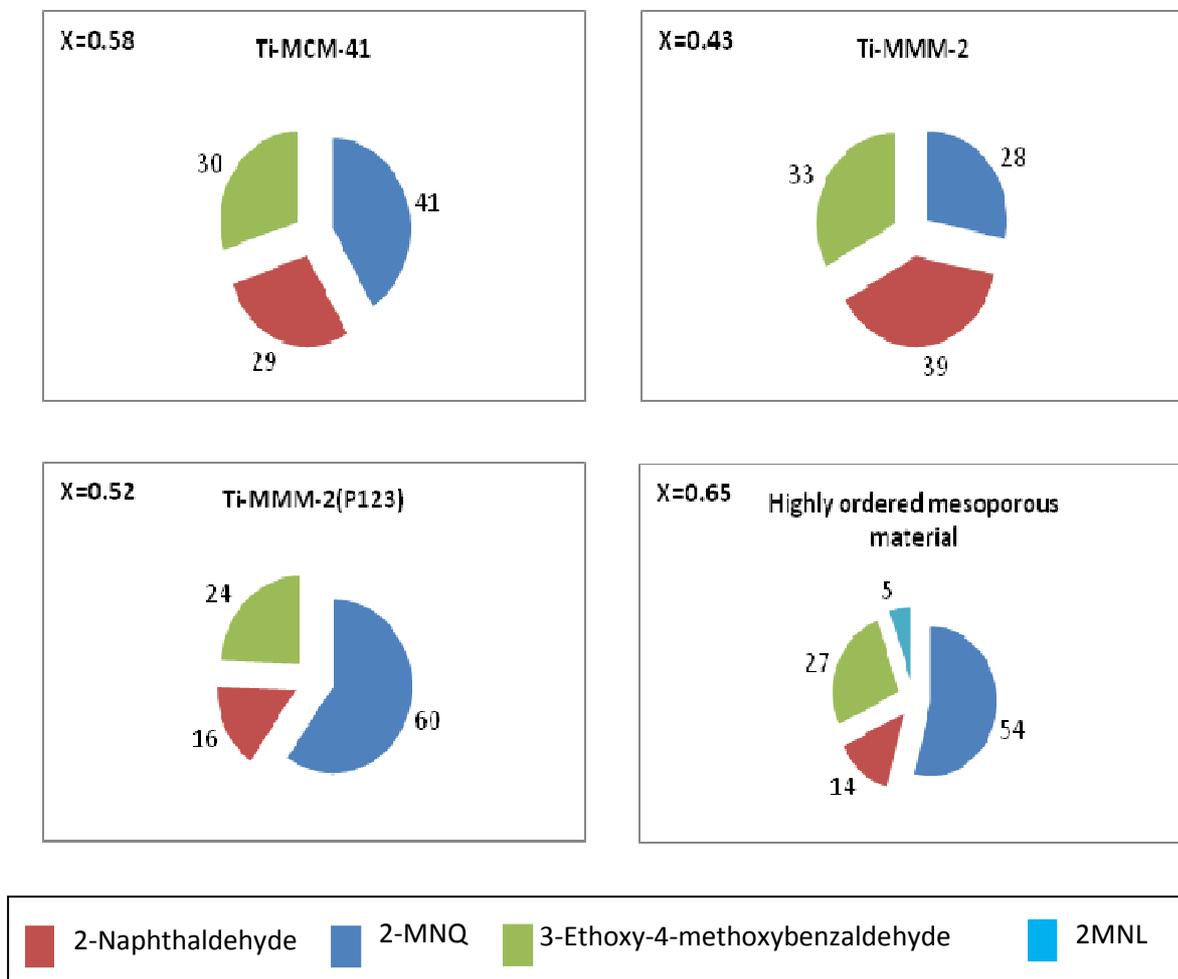
The investigation for the rest of the reaction conditions were conducted at a reaction temperature of 150°C with a reaction time of 4 hours. The effect hydrogen peroxide has on the various catalysts is studied by changing the hydrogen peroxide volume between 3 ml and 9 ml. Figure 5-22 shows the results for the various catalysts investigated for the effect of the hydrogen peroxide volume.



**Figure 5-22 Effect of hydrogen peroxide volume on the various catalysts at 150°C ; 4 hours ; 100 mg catalyst; 10 ml MeCN**

Figure 5-22 illustrates that the highly ordered mesoporous material obtains the highest 2MN conversions at the different hydrogen peroxide volumes. The 2MN conversions for the highly ordered mesoporous material are 65%, 94% and 100% for the 3 ml, 6 ml and 9 ml, respectively. The second highest conversion at 3 ml is Ti-MCM-41, Ti-MMM-2 at 6 ml and Ti-MMM-2 (P123) at 9 ml. In all cases, the conversion increases with increasing the hydrogen peroxide volume and this is similar to the results obtained in literature as mentioned in section 2.4.1.1. For this system, the hydrogen peroxide volume could not be increased to a higher peroxide volume than 9 ml because the autoclave could not withstand the pressure, causing the reactor to explode.

Figure 5-23 illustrates the selectivity for the various catalysts with 3 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub>. The selectivity for the various catalysts with 9 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> is presented in Figure 15-7 (APPENDIX H) and the 6 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> in Figure 5-19.

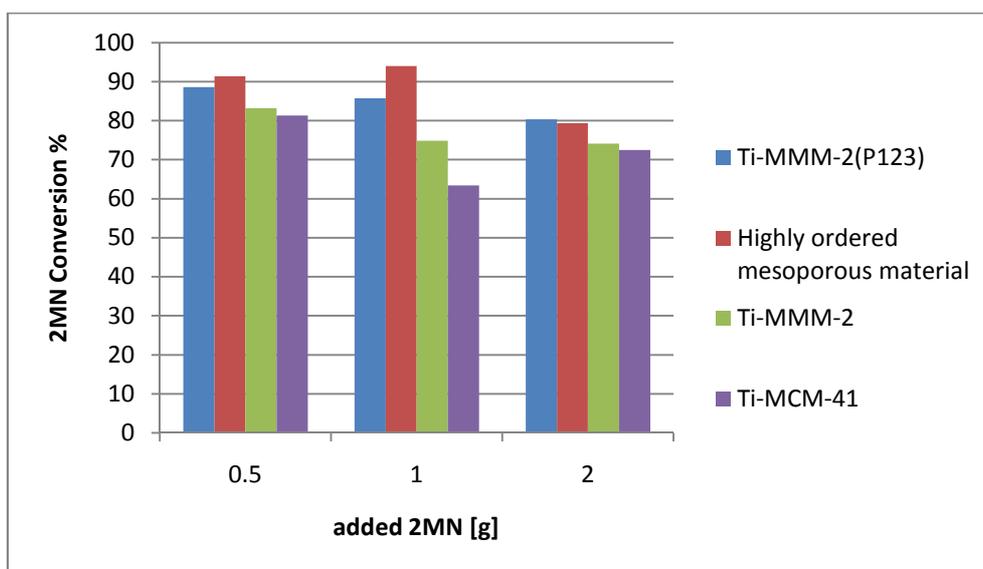


**Figure 5-23 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 3 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

2MNQ is the product with the highest selectivity for all cases except for the highly ordered mesoporous material at 9 ml 30 wt% aqueous H<sub>2</sub>O<sub>2</sub> favouring menadione epoxide and Ti-MMM-2 at 3 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> favouring 2-naphthaldehyde. An explanation for this is that Ti-MMM-2 favours reaction pathway based on the C2 attack at 3 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> and the highly ordered mesoporous material favours the over-oxidation of 2MNQ at 9 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub> (as discussed in section 5.2.1.3). The highly ordered mesoporous material appears to be the only catalyst producing 2MNL. This is the intermediate between 2MN and 2MNQ (as mentioned in section 5.2.1.3) and occurs at the 3 ml 30 wt% aqueous H<sub>2</sub>O<sub>2</sub>. Therefore, it is proposed that the highly ordered mesoporous material favours menadione epoxide at hydrogen peroxide volumes higher than 9 ml for these reaction conditions and forms 2MNL at hydrogen peroxide volume lower

than 3 ml. Even though the highly ordered mesoporous material does not favour 2MNQ at 9 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub>, it is suggested as the favourable catalyst for these reaction conditions because it obtains the highest conversion at all hydrogen peroxide volumes and favours 2MNQ formation at the other time volumes.

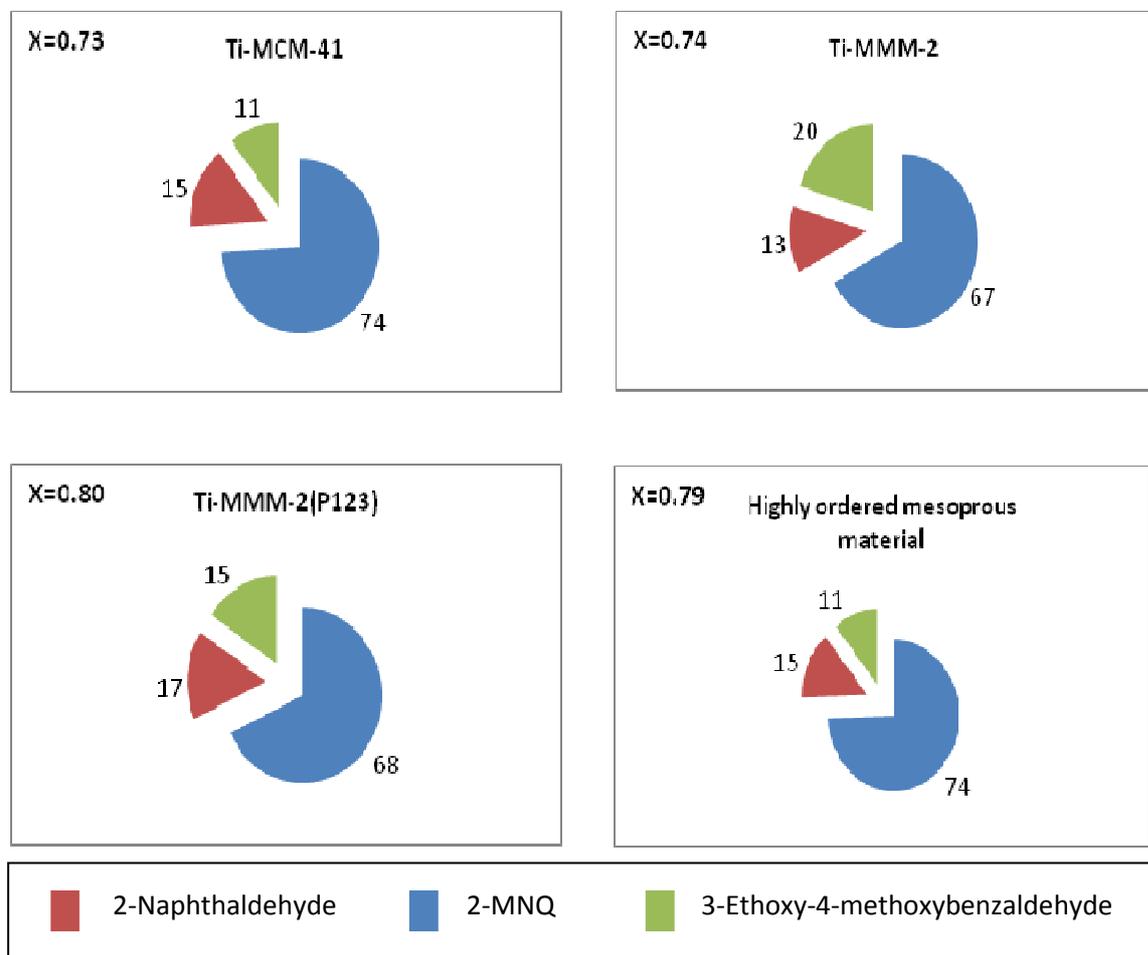
Figure 5-24 shows the investigation for the change in substrate amount on the various catalysts.



**Figure 5-24 Effect of Substrate (2MN) amount on the various catalysts at 150°C ; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 100 mg catalyst; 4 hours; 10 ml MeCN**

The catalyst achieving the highest conversion for 0.5 g 2MN and 1 g 2MN is the highly ordered mesoporous material followed by Ti-MMM-2(P123), Ti-MMM-2 and Ti-MCM-41. The highly ordered mesoporous material conversion is 91% and 94% for 0.5 g and 1 g, respectively. Ti-MMM-2(P123) achieves the highest conversion at 2 g 2MN with 80% conversion, whereas the highly ordered mesoporous material obtains 79%. It appears in some cases, the conversion decreases as the substrate amount increases. This could be as a result of too much substrate absorbed on the catalyst and not able to accommodate all the substrate successfully, therefore, obtaining lower conversions.

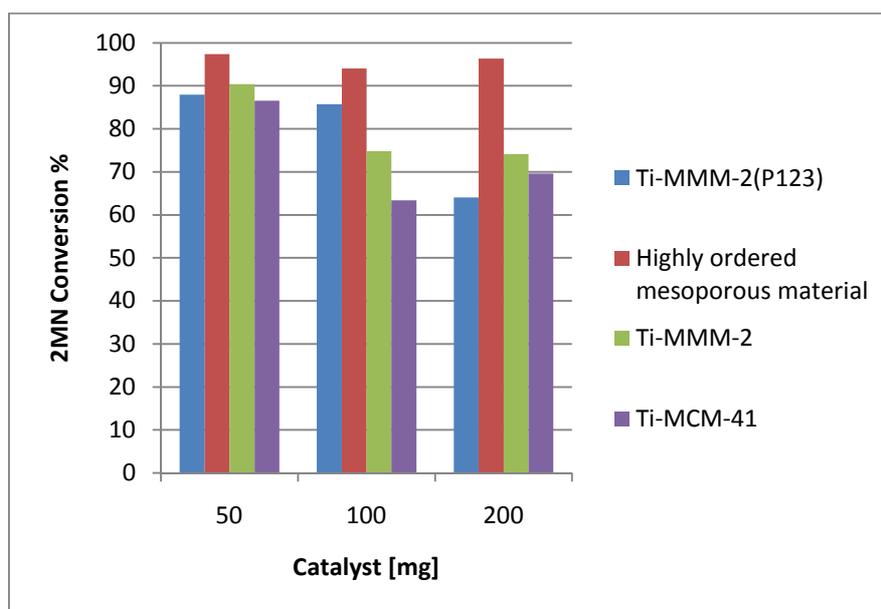
Figure 5-25 demonstrates the selectivity for the various catalysts with 2 g substrate. The results for the 1 g substrate selectivity are shown in Figure 5-19 and the 0.5 g in Figure 15-8 (APPENDIX H).



**Figure 5-25 Selectivity for various catalysts at 150°C; 4 hours; 2 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

The results show that in all cases, the product attaining the highest selectivity is 2MNQ. The highly ordered mesoporous material obtains the highest 2MNQ selectivity for all substrate amounts. The 2MNQ selectivity is 100%, 93% and 74% for 0.5 g, 1 g and 2 g, respectively. Therefore, it is suggested that the highly ordered mesoporous material is the favoured catalyst for these reaction conditions because it achieved the highest conversions in most cases and the highest 2MNQ selectivity in comparison to the other catalysts.

The effect the amount of catalyst has on the conversion for the various catalysts is shown in Figure 5-26.



**Figure 5-26** Effect of catalyst amount on the various catalysts at 150°C; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 1 g 2MN; 4 hours; 10 ml MeCN

The catalyst attaining the highest 2MN conversions in all cases is the highly ordered mesoporous material with conversions in the range between 94-97%. The conversions for the highly ordered mesoporous material appear to be constant for this investigation, whereas the substrate conversion decreases as the catalyst amount increases for the other catalysts. Based on reaction kinetics, increasing the catalyst amount should increase the conversion because more active sites will be available for oxidation (Fogler, 1999). A possible explanation for the conversion decreasing with increasing the catalyst amount is that more active sites are available and this could lead to competitive interaction between the sites for the substrate and hydrogen peroxide. If this occurs, it could retard the catalyst in the process. It is suggested that further studies be conducted because this is beyond the scope of this work.

The product selectivity for the various catalysts conducted with 200 mg catalyst is shown in Figure 5-27. The selectivity for the various catalysts with 100 mg and 50 mg can be found in Figure 5-19 and Figure 15-9 (APPENDIX H), respectively.

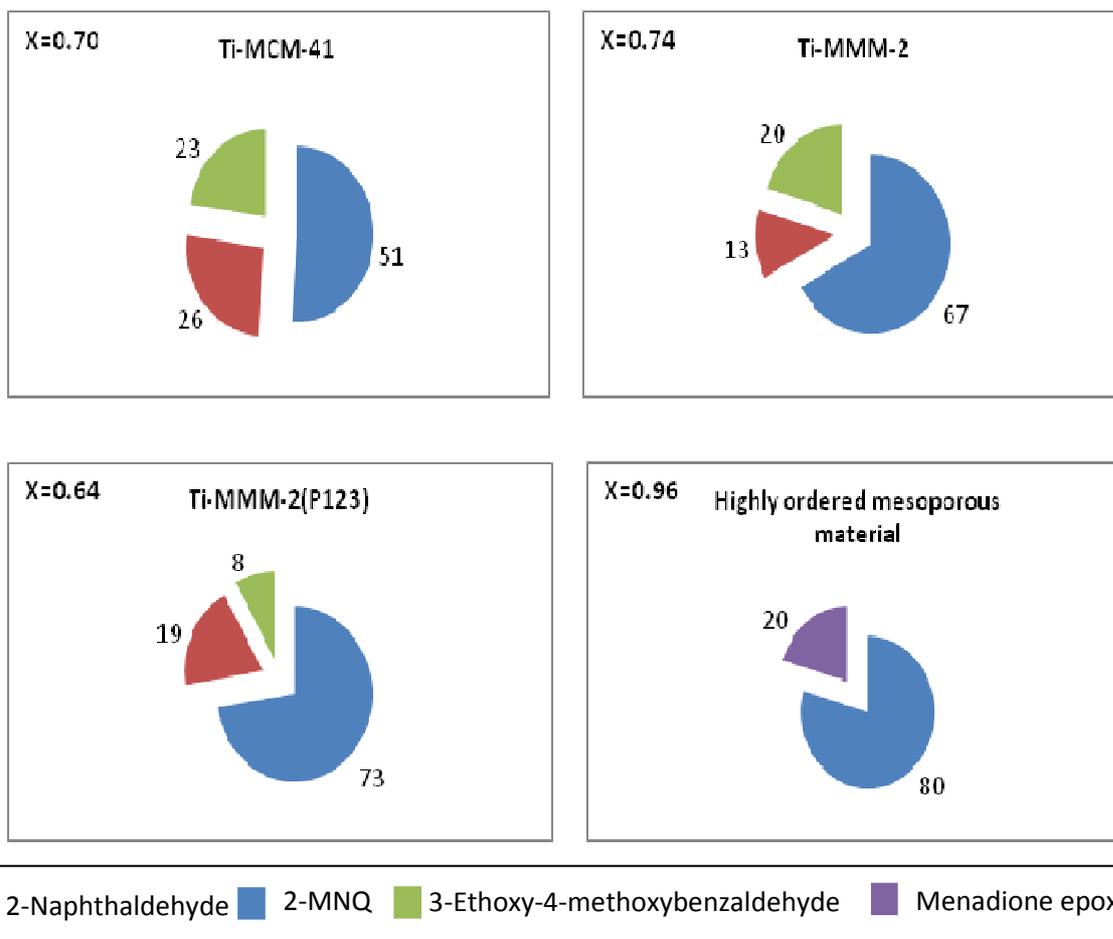
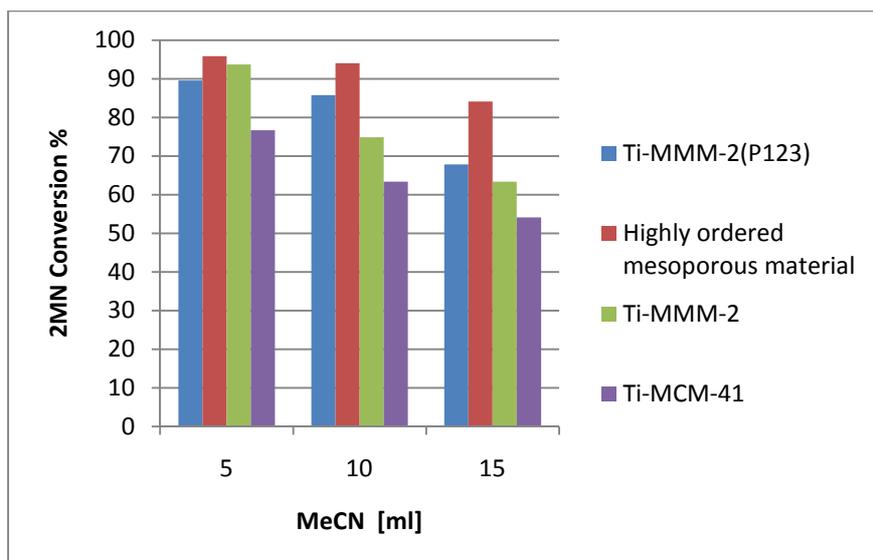


Figure 5-27 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 200 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

All the catalysts favour 2MNQ as the product for the investigation of change in catalyst amount. Therefore, it appears that the highly ordered mesoporous material is the favoured catalyst for these reaction conditions because it obtains the highest 2MN conversion in all cases and favours 2MNQ formation.

Investigating the effect solvent volume has on the 2MN conversion for the various catalysts is illustrated in Figure 5-28.

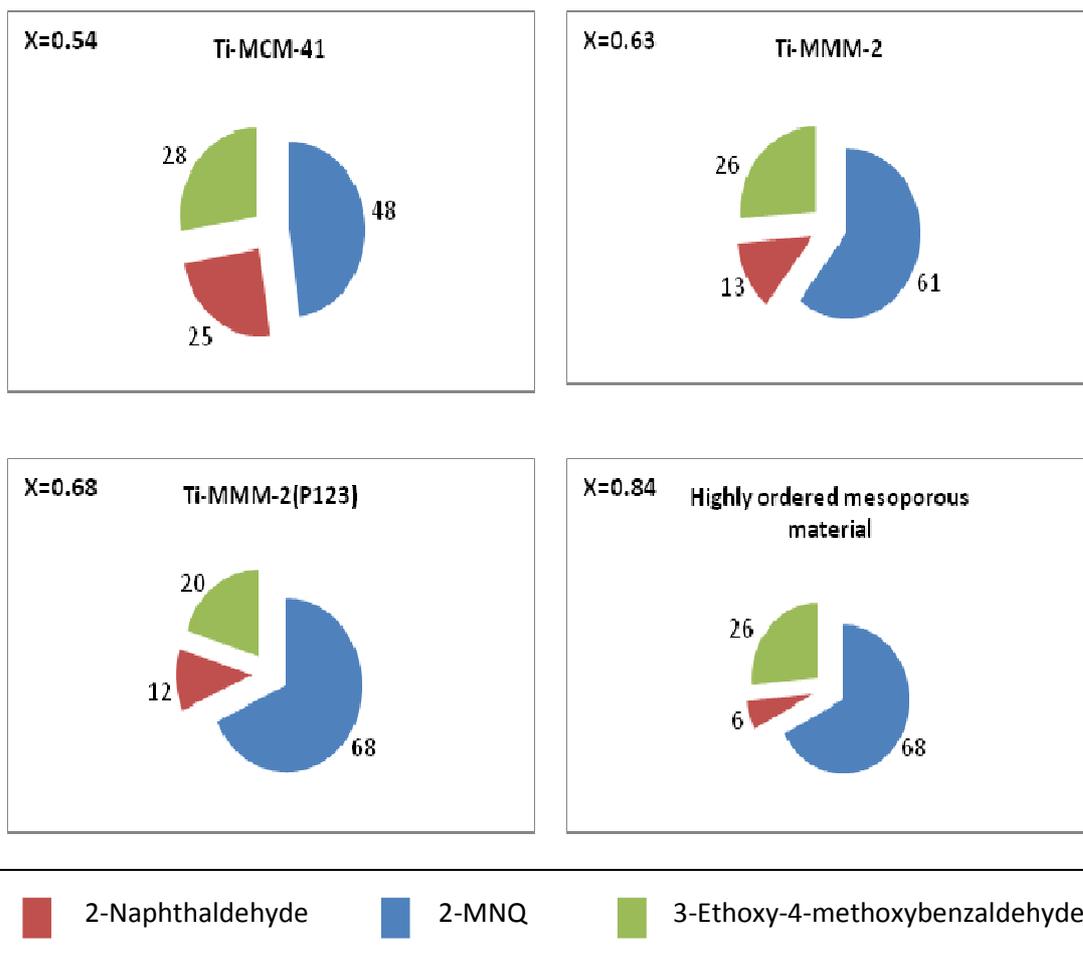


**Figure 5-28 Effect of solvent (MeCN) volume on the various catalysts at 150°C ; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 1 g 2MN; 4 hours; 100 mg catalyst**

The catalyst achieving the highest 2MN conversions for all solvent volumes is the highly ordered mesoporous material followed by Ti-MMM-2 at 5 ml and Ti-MMM-2(P123) at 10 ml and 15 ml. Ti-MCM-41 obtains the lowest conversion for all cases. The results indicate that the conversion decreases as the solvent volume increases. This could be as a result of excess solvent hindering the substrate absorption on the catalyst.

Figure 5-29 shows the product selectivity for the various catalysts with the effect of 15 ml solvent.

Figure 15-10 (APPENDIX H) and Figure 5-19 demonstrates the results for the 5 ml and 10 ml solvent, respectively.



**Figure 5-29 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 100 mg catalyst; 15 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

In all cases, 2MNQ achieves the highest product selectivity for the various catalysts except for the highly ordered mesoporous material at 5 ml. Menadione epoxide is the favoured product and a possible explanation is that the reaction is not diluted enough and as a result, promotes over-oxidation of 2MNQ (as discussed in section 5.2.1.3). Although the highly ordered mesoporous material does not favour 2MNQ at 5 ml solvent, it is still suggested as the favourable catalyst for these reaction conditions because it obtains the highest conversion at all solvent volumes and favours 2MNQ formation at 10 ml and 15 ml solvent.

From the results above it appears the highly ordered mesoporous material is the catalyst achieving the best results in comparison with the other catalysts because it achieves the highest 2MN conversions and favours the formation of 2MNQ in most cases. A possible reason for favouring 2MN conversion and high 2MNQ selectivity is as a result of the highly ordered mesoporous material

porous structure. The highly ordered mesoporous material is the only catalyst in this study that posses both micropores and mesopores. As mentioned in section 2.2.1, microporous materials have the ability to promote shape selectivity and possess a high surface area. This results in high reaction rates. Therefore, it is suggested that the highly ordered mesoporous material is the chosen catalyst to improve the environmentally friendly process for the hydroxylation of 2MN to 2MNQ.

#### 5.2.4 Improvement of process system

In order to determine the best operating conditions for the oxidation of 2MN to 2MNQ over the highly ordered mesoporous material as catalyst, a one factor at a time approach and a factorial design are implemented.

##### 5.2.4.1 One factor approach

The one factor approach is conducted by varying the reaction temperature, reaction time, hydrogen peroxide volume, catalyst amount, substrate amount and solvent volume.

- *Reaction temperature*

The reaction temperature and reaction time profile for the hydroxylation of 2MN to 2MNQ over the highly ordered mesoporous material with 30 wt% aqueous H<sub>2</sub>O<sub>2</sub> as oxidant is illustrated in Figure 5-30.

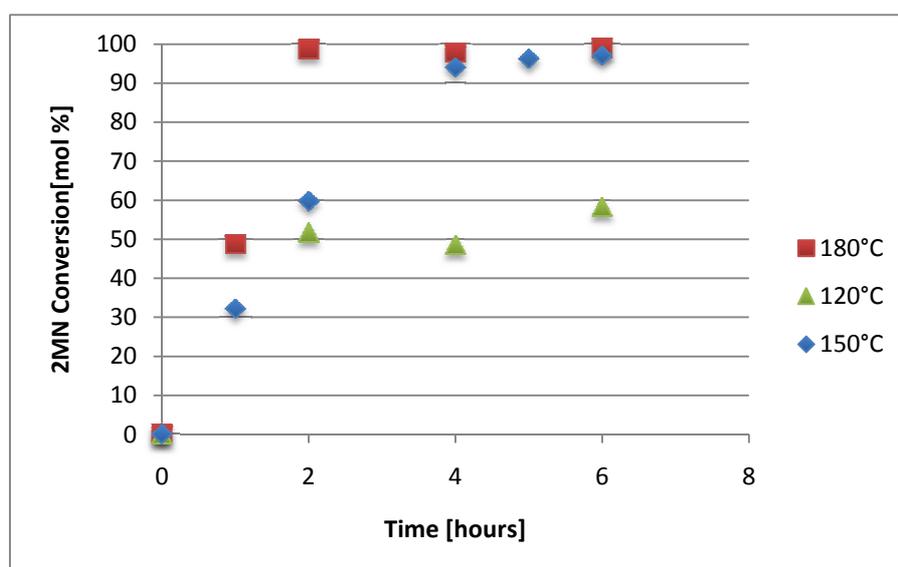
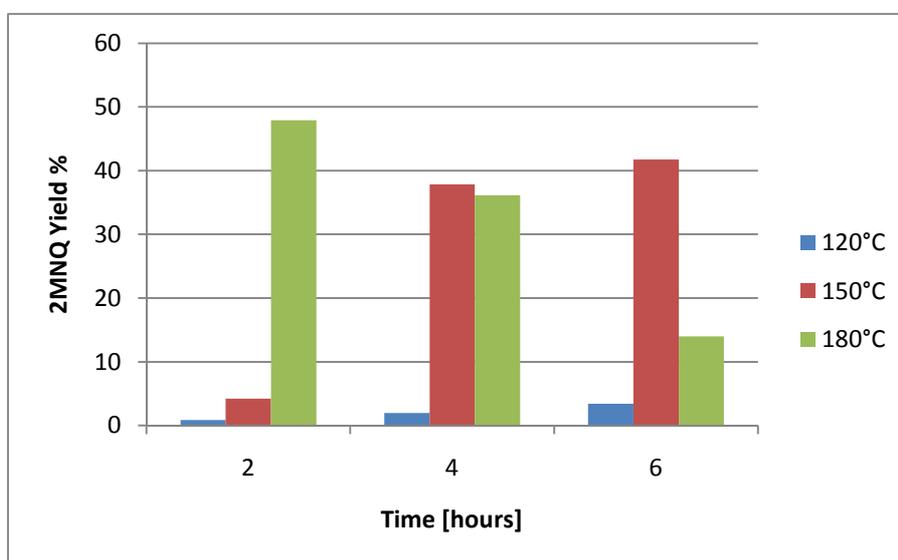


Figure 5-30 Reaction temperature profile at 1 g 2MN; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 100 mg Highly ordered mesoporous material

From Figure 5-30 it appears the substrate conversion increases by increasing the reaction temperature and time. These results correspond with studies conducted in literature as mentioned in section 2.4. A possible explanation for substrate conversion increasing with increasing the reaction temperature is based on reaction kinetics. The rate of reaction increases because the specific rate constant has a directly proportional relationship with the reaction temperature (Equation 4-19). A possible explanation for conversion increasing with increasing reaction time is that longer reaction times allow the substrate to interact longer with the active sites.

The 2MNQ yield obtained for the reaction temperature and reaction time profile is presented in Figure 5-31.

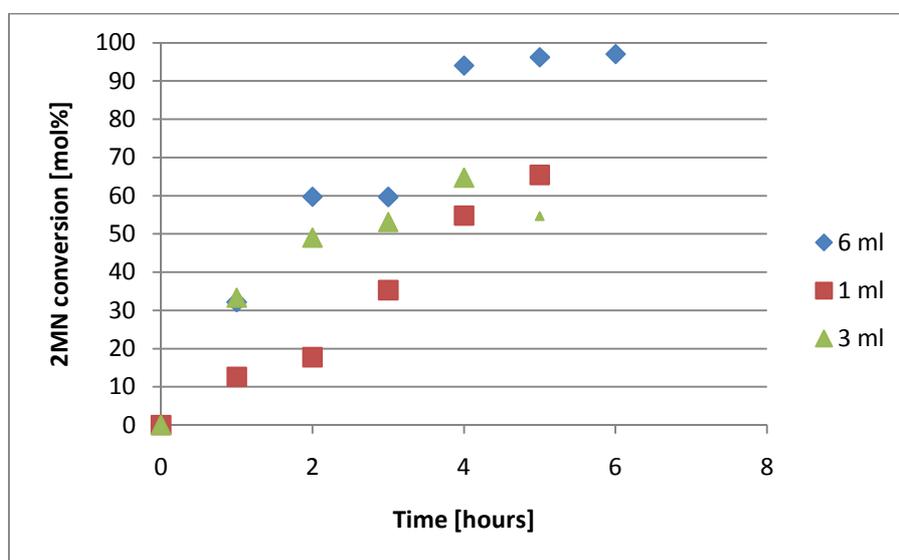


**Figure 5-31 2MNQ Yield for temperature and time profile at 1 g 2MN; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 100 mg Highly ordered mesoporous material**

Based on Figure 5-31 it appears the 2MNQ yield increases as the reaction time increases for the reaction temperature 120°C and 150°C but decreases for reaction temperature 180°C. From literature it was found that the 2MNQ yield increases with raising the reaction temperature and time (as mentioned in section 2.4.1.1), as in the case for the 120°C and 150°C. A possible explanation for 2MNQ yield decreasing with increasing reaction time at 180°C is that the reaction mechanism favours menadione epoxide, the over-oxidation of 2MNQ (as mentioned in section 5.2.1.3). Therefore, to obtain high 2MNQ yields at 180°C, it is suggested that the reaction times be lower than 4 hours.

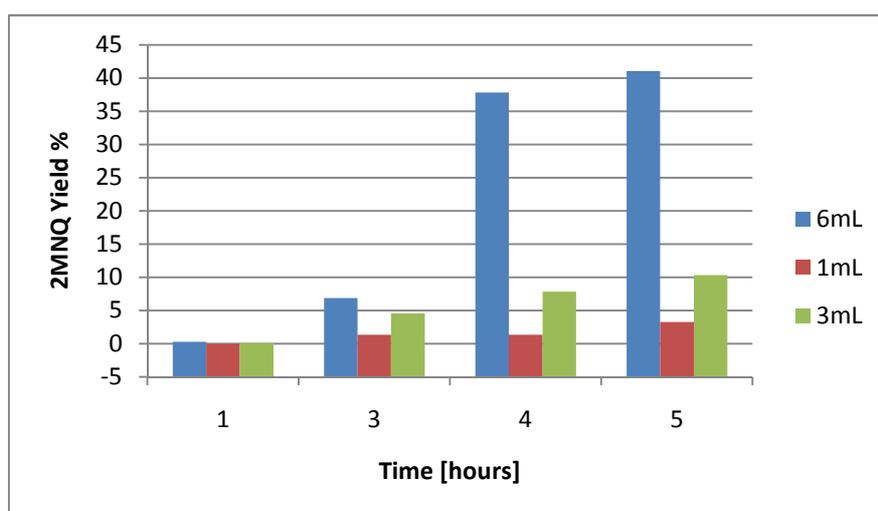
- *Hydrogen peroxide volume*

The effect hydrogen peroxide volume has on the hydroxylation of 2MN to 2MNQ with highly ordered mesoporous material as catalyst is illustrated in Figure 5-32.



**Figure 5-32 Peroxide profile at 150°C; 1 g 2MN;10 ml MeCN;100 mg Highly ordered mesoporous material**

Figure 5-32 shows that 2MN conversion increases with increasing the hydrogen peroxide volume and corresponds with results found in literature (mentioned in section 2.2.1.1 and 2.4). It is suggested that this occurs because by increasing the oxidant volume, the peroxide interaction with the titanium sites gives more Ti-hydroperoxo active sites available for oxidation. The 2MNQ yield obtained for the hydrogen peroxide volume profile is presented in Figure 5-33.

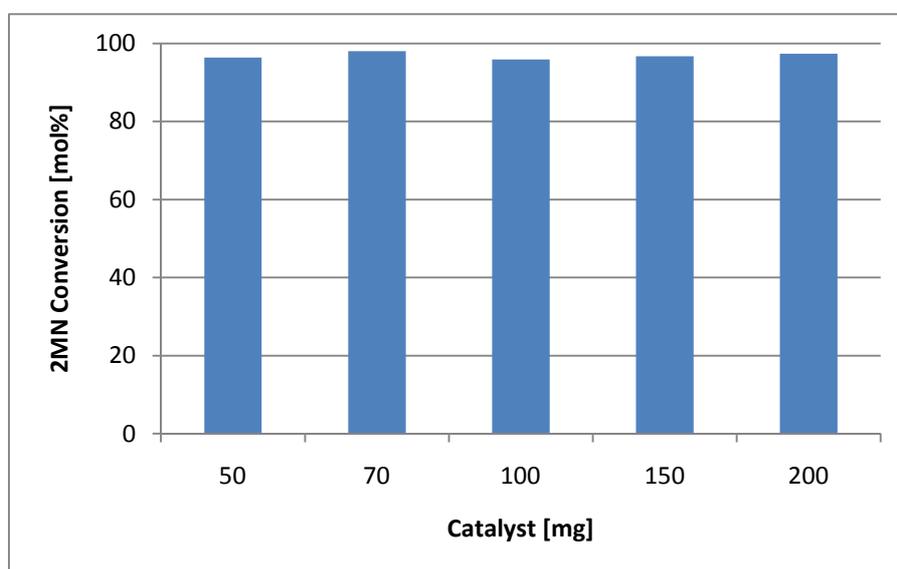


**Figure 5-33 2MNQ Yield for peroxide profile at 150°C;1 g 2MN;10 ml MeCN;100 mg Highly ordered mesoporous material**

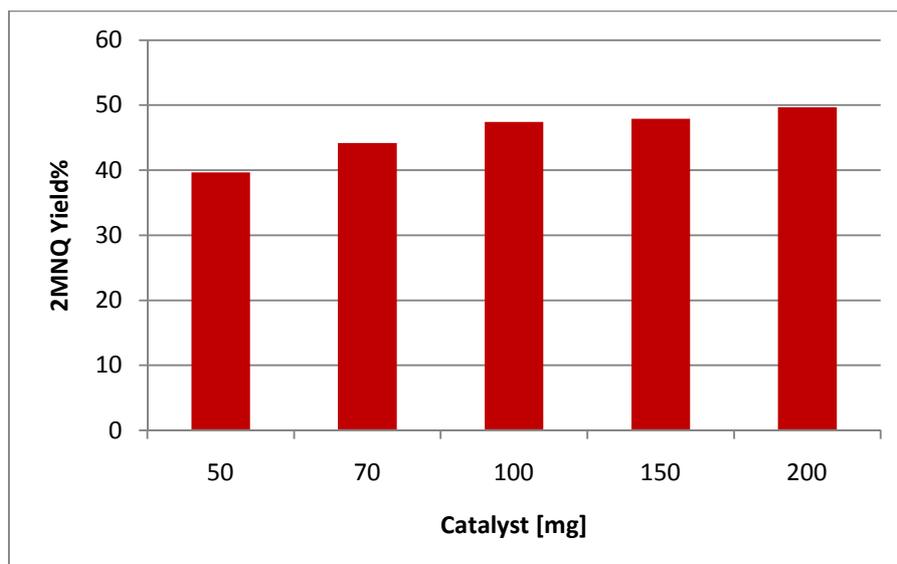
It is apparent that the 2MNQ yield increases with increasing the hydrogen peroxide volume. It is suggested that the hydrogen peroxide volume has a major effect on the 2MNQ yield as the reaction times increases, the 2MNQ yields at 5 hours are 1%, 10% and 41% for 1 ml, 3 ml and 6 ml aqueous 30 wt% H<sub>2</sub>O<sub>2</sub>, respectively. Shi, *et al.*, (2007) stated that a high volume of hydrogen peroxide is needed in order to get acceptable yields of 2MNQ but very high peroxide volumes may lead to explosive mixtures and cause severe safety problems.

- *Catalyst amount*

The effect catalyst amount has on the conversion and 2MNQ yield for the hydroxylation of 2MN with highly ordered mesoporous material as catalyst is illustrated in Figure 5-34 and Figure 5-35, respectively.



**Figure 5-34 Effect of catalyst amount on 2MNQ conversion at 150°C; 1 g 2MN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 10 ml MeCN; Highly ordered mesoporous material**

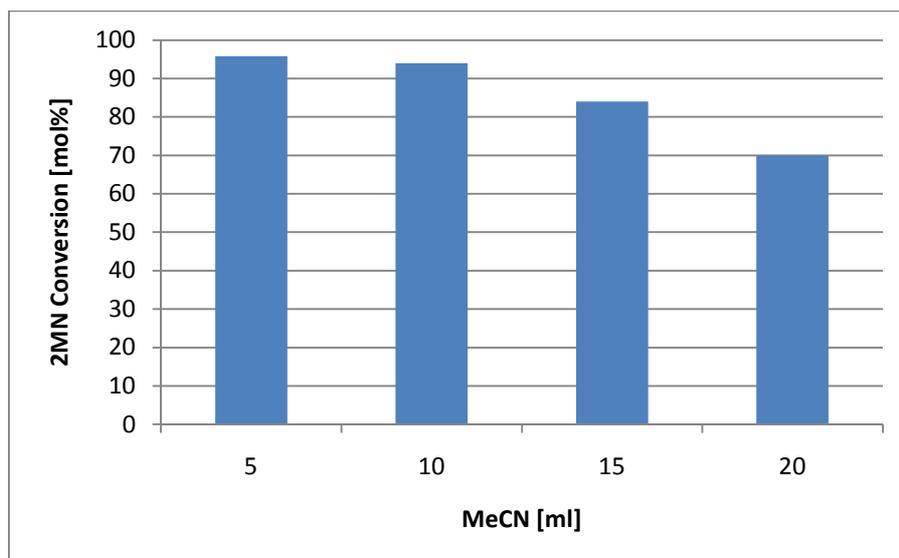


**Figure 5-35 Effect of catalyst amount on 2MNQ yield at 150°C; 1 g 2MN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 10 ml MeCN; Highly ordered mesoporous material**

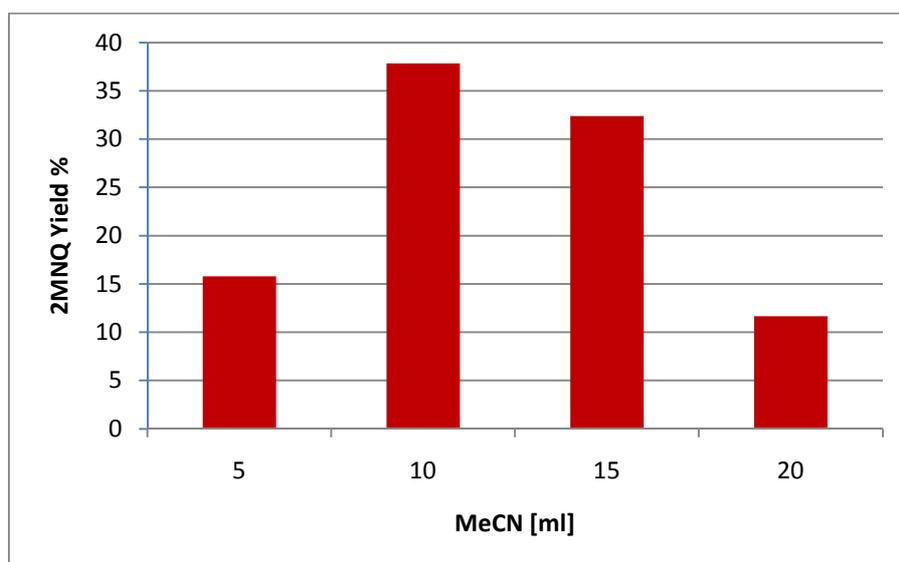
From Figure 5-34 it appears that complete conversion almost occurs in all catalyst amounts. It is suggested that this occurs because the catalyst amount in each case possess sufficient active sites to absorb and interact with substrate for oxidation to occur. Figure 5-35 illustrates the 2MNQ yield increases as the catalyst amount increases. The 2MNQ yield is 40%, 44%, 47%, 48 and 50% for 50 mg, 70 mg, 100 mg, 150 mg and 200 mg, respectively. These observations are consistent with previous findings, Kholdeeva, *et al.*, (2005) and Kholdeeva, *et al.*, (2007). Therefore, it is proposed to increase the amount of catalyst in order to achieve higher 2MNQ yields.

- *Solvent volume*

The influence of solvent volume on the conversion and 2MNQ yield for the hydroxylation of 2MN to 2MNQ with highly ordered mesoporous material as catalyst is shown in Figure 5-36 and Figure 5-37, respectively.



**Figure 5-36** Effect of solvent (MeCN) volume on 2MN conversion at 150°C; 1 g 2MN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 100 mg Highly ordered mesoporous material



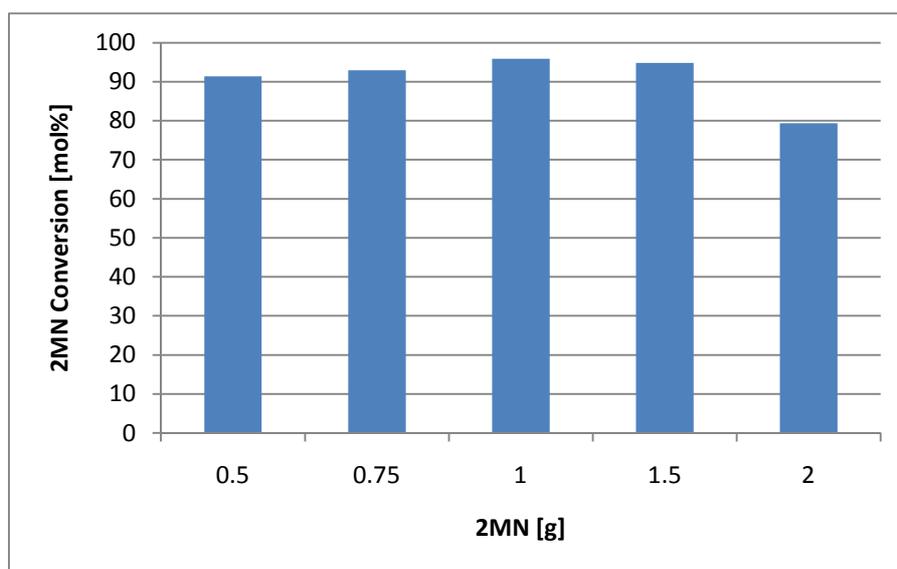
**Figure 5-37** Effect of solvent (MeCN) volume on 2MNQ yield at 150°C; 1 g 2MN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 100 mg Highly ordered mesoporous material

Based on Figure 5-36 it appears the substrate conversion decreases with increasing the solvent volume. From literature, two explanations were deduced for a possible decrease in the substrate conversion due to the presence of excess solvent (i) the solvent become a barrier hindering the diffusion of substrate and products while also decreasing the amount of adsorbed substrate, thereby decreasing the reaction rates (ii) the solvent also competes with hydrogen peroxide for the second coordination at the titanium site (Kumar, *et al.*, (1998); van der Waal, *et al.*, (1997)). Therefore it is proposed that experiments should not be diluted with excess solvent based from findings found in literature and this study due to the competitive adsorption between the solvent and hydrogen

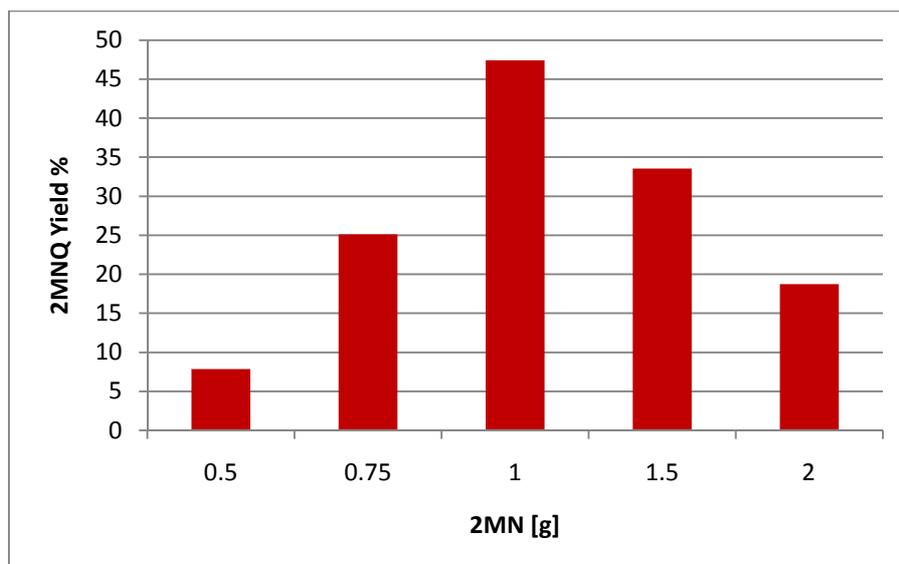
peroxide. Figure 5-37 illustrates that best 2MNQ yields are obtained with 10 ml solvent for these reaction conditions.

- *Substrate amount*

The effect substrate amount has on conversion and 2MNQ yield for the hydroxylation of 2MN to 2MNQ with highly ordered mesoporous material as catalyst is illustrated in Figure 5-38 and Figure 5-39, respectively.



**Figure 5-38 Effect of Substrate (2MN) amount on 2MN conversion at 150°C; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 10 ml MeCN; 100 mg Highly ordered mesoporous material**



**Figure 5-39 Effect of Substrate (2MN) amount on 2MNQ Yield at 150°C; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 4 hours; 10 ml MeCN; 100 mg Highly ordered mesoporous material**

Figure 5-38 indicates that the 2MN conversion increases as the substrate amount increases between 0.5 g and 1 g. The conversion then starts decreasing as the substrate amount increase between 1 g and 2 g. From Figure 5-39 it seems as if a bell-shape pattern is observed and the yield obtains a maximum at 1 g 2MN.

The results obtained from the one factor approach for the hydroxylation of 2MN to 2MNQ over highly ordered mesoporous material confirms that reaction conditions have a significant effect on the 2MNQ yield and 2MN conversion as discussed in section 2.4.1.1. Based on the results from the one factor approach, 2MNQ yield increases when reaction conditions are increased. There reaction conditions are the reaction temperatures below 180°C, reaction time, hydrogen peroxide volume and catalyst amount. The 2MNQ yield decreased as the reaction time increased at reaction temperature, 180°C. For the effect of the substrate amount and solvent volume, highest yields and conversions were obtained at 1 g and 10 ml, respectively.

Table 5-5 illustrates the best results obtained from investigating the one factor approach for this system. Under optimal conditions obtained by Anunziata, *et al.*, (2004) for the hydroxylation of 2MN to 2MNQ over Ti-MCM-41 (Table 2-14) as indicated in section 2.4.1.1, the averages of the 2MN conversion and 2MNQ selectivity were 65% and 90%, respectively. This study obtains lower 2MNQ selectivity in comparison to Anunziata, *et al.*, (2004). An explanation for this could be that Anunziata, *et al.*, (2004) conducted experiments at higher reaction temperatures with low reaction times, more hydrogen peroxide volumes and catalyst amounts than this study. These reactions conditions have a pivotal impact on 2MNQ selectivity as shown in literature and this study. This study did however obtain higher 2MN conversions than Anunziata, *et al.*, (2004).

**Table 5-5 Best results from one factor approach for the hydroxylation of 2MN to 2MNQ over Highly ordered mesoporous material with 1 g 2MN and 10 ml MeCN**

Temperature [°C]	Amount of catalyst [mg]	H <sub>2</sub> O <sub>2</sub> [ml]	Time [hours]	Conversion 2MN [ mol%]	2MNQ selectivity %	2MNQ yield %
150	200	6	4	97	80	50
150	100	6	6	97	86	42
180	100	6	2	99	87	48

#### 5.2.4.2 Factorial Design

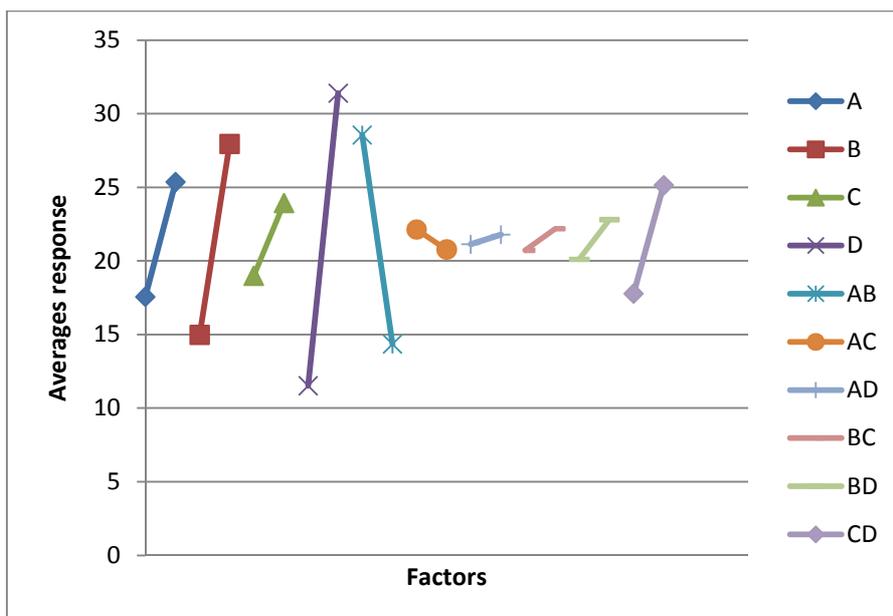
From the one factor approach, reaction conditions that increased when the 2MNQ yield increased were the reaction temperature, reaction time, catalyst amount and hydrogen peroxide volume. To get an understanding of the interaction between these reaction conditions, a preliminary two-level full factorial design is prepared with 2MNQ yield as the response factor. Therefore, a 2<sup>4</sup> experimental design is prepared, meaning 16 runs were conducted and no replicates were performed for this design. In a two-level factorial design, each factor only takes on two values, for example, high and low. For all experiments conducted in this design, 10 ml solvent and 1 g substrate were used based on the results from Figure 5-37 and Figure 5-39, respectively. Table 5-6 illustrates the 2<sup>4</sup> full factorial design with the high and low values and a letter representing each factor.

**Table 5-6 The 2<sup>4</sup> experimental design plan**

Letter	Factor	Low	High
A	Time (hours)	2	4
B	Temperature(°C)	150	180
C	Catalyst(mg)	50	100
D	Hydrogen Peroxide(ml)	3	6

The high and low values from Table 5-6 were chosen based on conclusions drawn from section 5.2.4.1. The low and high values for the reaction temperature and reaction time are 150°C and 180°C and 2 hours and 4 hours, respectively. The high and low values for hydrogen peroxide volume are 6 ml and 3 ml, respectively. The low and high values for catalyst amount are 50 mg and 100 mg, respectively.

To get an understanding of which factors and interactions are significant to the 2MNQ yield, the average response per factor level is determined. The average response per factor level is the average response of the high level of a factor to the low level average response of the same factor. Figure 5-40, illustrates the average response per factor level for this design.

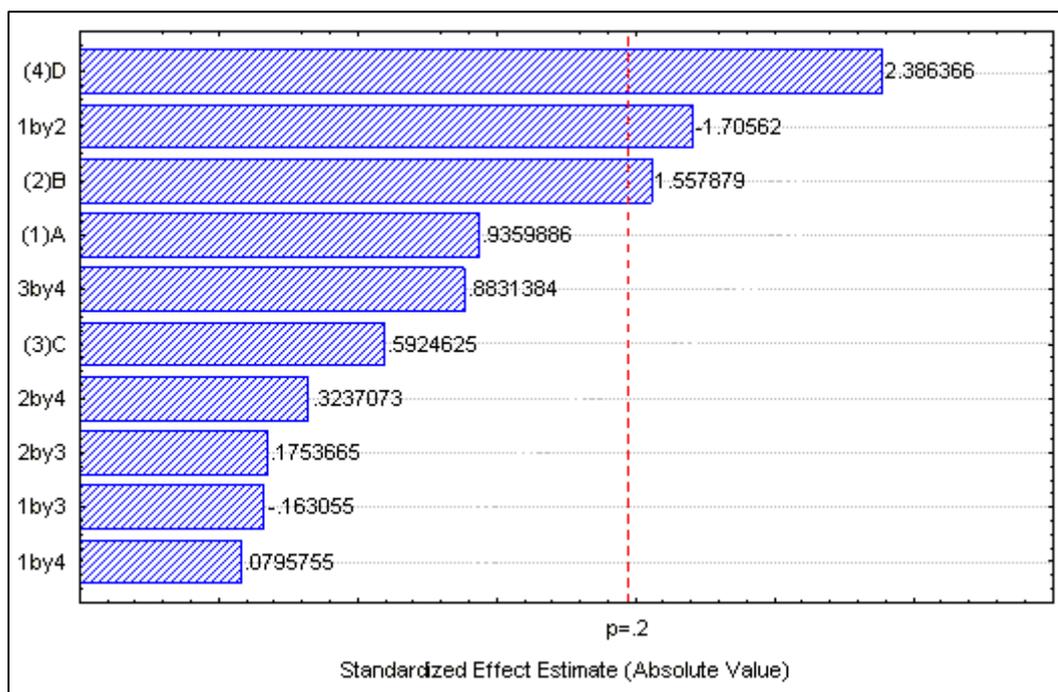


**Figure 5-40 Plot of the average response per factor level**

Figure 5-40 shows main factors A, B and D and interactions AB and CD are important to the 2MNQ yield. The main factor having the most influence on the yield is the hydrogen peroxide volume (D) followed by the reaction temperature (B) and reaction time (A). Between the important interactions, reaction temperature-reaction time (AB) is more significant toward the yield than the catalyst amount-hydrogen peroxide volume (CD). From Figure 5-40, the main factor C and interactions AC, AD, BC and BD do not have a major effect on the yield.

The gradients for the main factors and interaction CD are positive, this means increasing from the low level to the high level will result in a yield increase. The interaction AB is negative, therefore, increasing the interaction will result in a yield decrease. Hence, main factors A, B, D and interaction CD must be increased, whereas decreasing interaction AB will increase the 2MNQ yield. A possible explanation for a negative gradient for interaction AB is because at the high level temperature (180°C), highest 2MNQ yields will be achieved at the low level time (2 hours) because longer reaction times at this reaction temperature will favour over-oxidation products.

Thus far, factors and interactions that are significant to the yield are based on non-statistical techniques. It is important to verify these results with statistical techniques, a pareto chart( $\alpha=0.2$ ) generated from Statistika™ is illustrated in Figure 5-41. In this study, factors affecting the 2MNQ yield with a certainty of 80% are identified. It is always best to have a confidence level of 95% or higher but results in the 80% to 90% range should not be ignored. These results may indicate trends and provide clues about how to improve the process (<http://www.malwarwick.com/learning-resources/confidence-level-calculator.html>,2010)



**Figure 5-41 Pareto chart of standardized effects**

The factors identified with 80% confidence level for this design are the hydrogen peroxide volume, reaction temperature and the reaction time-reaction temperature interaction. The hydrogen peroxide volume has the most influence on the yield followed by the reaction temperature-reaction time interaction and reaction temperature. Based on Figure 5-41, the reaction time and catalyst amount-hydrogen peroxide volume interaction are not significant to the yield.

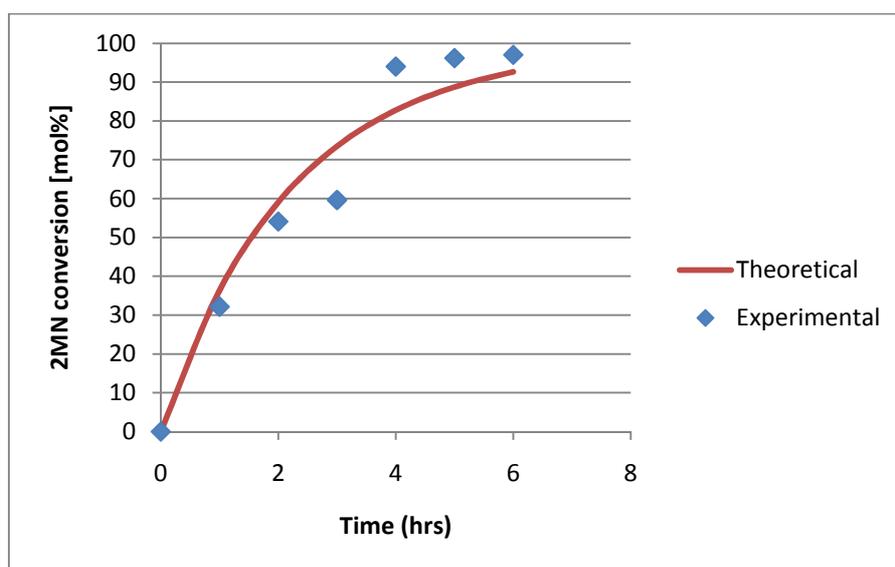
These results do not correspond to the Box-Behnken design conducted by Anunziata, *et al.*, (2004) because the Box-Behnken design identified all main factors and interactions between reaction temperature-reaction time, hydrogen peroxide volume-reaction time and catalyst amount-reaction time as important to the 2MNQ yield (mentioned in section 2.4.1.1). From Figure 2-11, the Box-Behnken identified the reaction time having the most influence on the yield, whereas hydrogen peroxide volume has the most influence in this study.

From this study, it appears that the only interaction that has a significant effect on the 2MNQ yield is the reaction time-reaction temperature interaction. It can be observed from the optimum reaction conditions obtained from Anunziata, *et al.*, (2004) in Table 2-14, the reaction temperatures are high with low reaction times. This is in agreement with the observation obtained in this study about the reaction time-temperature interaction. The increased 2MNQ yield in the Anunziata, *et al.* (2004) study can also be attributed to the fourfold higher volume of hydrogen peroxide that was used

### 5.2.5 Kinetic Modelling

The experimental data obtained during the hydroxylation of 2MN is kinetically expressed as a kinetic order expression as illustrated in Equation 4-9. Anunziata, *et al.*, (1999) suggested an overall first-

order rate equation for the hydroxylation of 2MN to 2MNQ over zeolites as discussed in section 2.4.1.1. An overall first-order model only takes one reagent in consideration but for the hydroxylation of 2MN to 2MNQ two reagents are present. From studies conducted in literature for similar processes it was proposed that the oxidant and substrate assume first order dependence (Burton, 2006). This resulted in an overall second-order rate reaction. Therefore, the process experiments for this study are fitted to a theoretical overall second-order kinetic model. Figure 5-42 shows a comparison between the experimental and theoretical second-order model for the hydroxylation of 2MN to 2MNQ with highly ordered mesoporous material as catalyst.



**Figure 5-42 Comparison between the theoretical and experimental 2MN conversion with the following reaction conditions: 150°C; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%); 10 ml MeCN; 1 g 2MN; 100 mg Highly ordered mesoporous material**

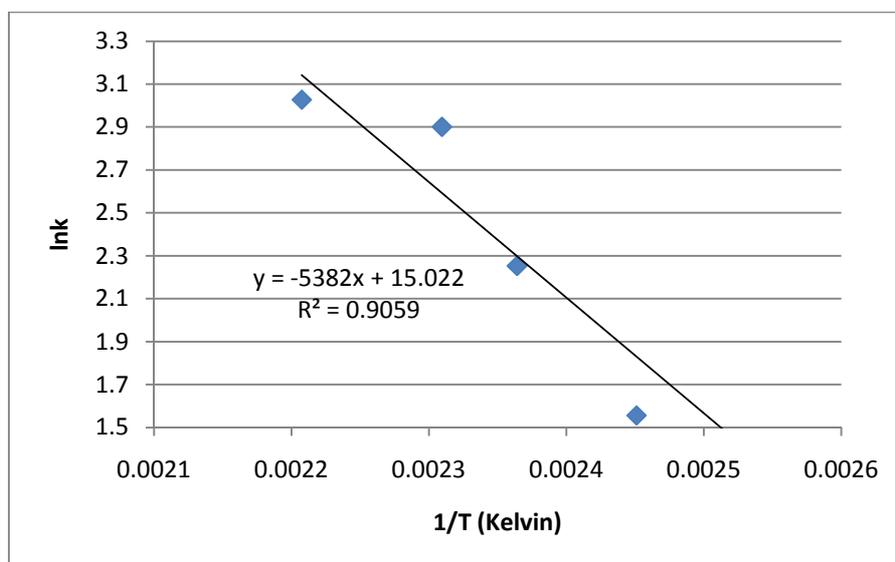
The fit of the theoretical model to the experimental data is important because one wants an accurate rate constant that fits well with the experimental data. From Figure 5-42 it appears the experimental data does not fit perfectly on the theoretical model. A possible explanation is that only one data point can be obtained from an experimental run because experiments are conducted in a pressurised autoclave. It is suggested that by modelling a process in such a manner, it affects the kinetic modelling accuracy of the system.

All 2MN rate constants are calculated by solving the differential equation obtained after fitting the concentration-time data to an overall second-order rate equation. Rate constants are strongly dependent on temperature as stated from literature (Fogler, 1999). The relationship between the reaction temperature and rate constant for this study is shown in Table 5-7. The rate constant increases as the reaction temperature increases for this study.

**Table 5-7 Influence of reaction temperature on the rate constants based on an overall second-order model for 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone over highly ordered mesoporous material**

$k_{2MN}$ [ml/gmol.hr]	Temperature [°C]
4	120
5	135
10	150
18	160
21	180

The Arrhenius plot can determine the activation energy of a reaction and is generated by calculating the rate constant for different reaction temperature intervals. It is based on Equation 4-19 and the Arrhenius plot for this study is illustrated Figure 5-43.



**Figure 5-43 Arrhenius plot of the second-order rate constant for the oxidation of 2-methylnaphthalene over the Highly ordered mesoporous material**

The Arrhenius equation is important because it gives the temperature behaviour of reaction rate constants within experimental accuracy over various temperature ranges (Fogler, 1999). From Equation 4-19, a plot of  $\ln k$  versus  $1/T$  should be a straight line with a slope proportional to the activation energy. It is suggested that the results obtained from Figure 5-43 presents a straight line. Even though experimental runs at temperature 135°C and 160°C were only conducted at one time intervals, whereas experimental runs were conducted at various time intervals for the other temperature intervals. By conducting an experimental run at only one time interval, it limits the accuracy for determining the rate constant with nonlinear least square regression analysis. The

slope of the curve in Figure 5.43 presents  $(-E/R)$ , this means the activation energy for this reaction is 45 kJ/mol. The activation energy is the minimum energy that must be possessed by the reacting molecules before the reaction will occur (Fogler, 1999). Anunziata, *et al.*, (1999) obtained an activation energy of 31 kJ/mol for the hydroxylation of 2MN to 2MNQ over zeolites. It is suggested that this implies that the rate of reaction for this study is more temperature sensitive than the process conducted by Anunziata, *et al.*, (1999) because the activation energy is larger.

## 5.2.6 Reusability of catalyst

The important question that should be addressed while investigating a liquid phase oxidation process over a solid catalyst, involves catalyst stability towards leaching and whether the catalyst truly acts heterogeneous (Maksimchuk, *et al.*, 2005). Thermogravimetric analysis and recycling of catalyst are conducted to test whether the catalyst truly acts as a heterogeneous catalyst and if leaching does occur in the process.

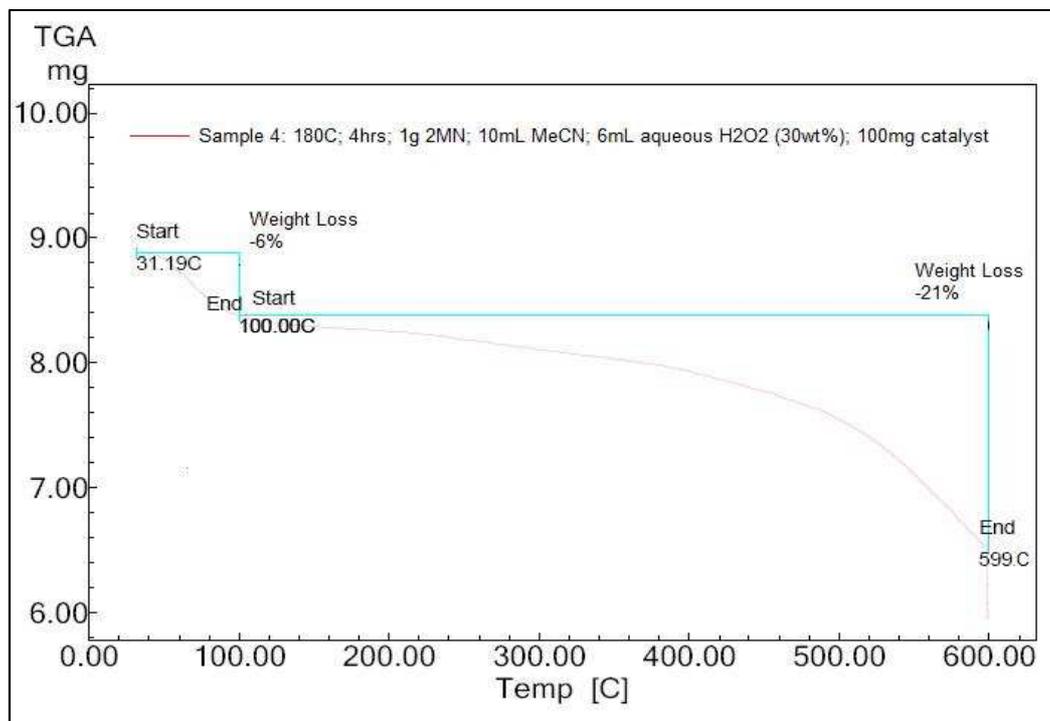
### 5.2.6.1 Thermogravimetric Analysis

Table 5-8 illustrates the thermogravimetric analysis of four different samples. Samples 1 and 2 are catalysts that were conducted at 150°C under different reaction conditions, whereas samples 3 and 4 are catalysts performed at 180°C under different reaction conditions. The total weight losses are 14%, 12%, 21% and 27% for samples 1, 2, 3 and 4, respectively. It appears that samples 1 and 2's weight loss is similar and the same occurred for sample 3 and 4. It is therefore suggested that samples with the same reaction temperature but under different reaction conditions produce weight loss in the same range.

**Table 5-8 Thermogravimetric analyses of various reaction conditions systems with Highly ordered mesoporous material as catalyst**

Sample	Reaction Conditions	Temperature [°C]	Weight loss%	Total weight loss%
1	150°C;1 hour, 1 g 2MN 10 ml MeCN; 6 ml H <sub>2</sub> O <sub>2</sub> ;100 mg	30-100	8	14
		100-600	6	
2	150°C;4 hours, 1 g 2MN 10 ml MeCN; 3 ml H <sub>2</sub> O <sub>2</sub> ;100 mg	27-100	8	12
		100-600	5	
3	180°C;2 hours, 1 g 2MN 10 ml MeCN; 3 ml H <sub>2</sub> O <sub>2</sub> ;100 mg	33-100	9	21
		100-600	12	
4	180°C;4 hours, 1 g 2MN 10 ml MeCN; 6 ml H <sub>2</sub> O <sub>2</sub> ;100 mg	31-100	6	27
		100-600	21	

The thermal patterns for the four samples are distinguished between two steps. The two step pattern for sample 4 is illustrated in Figure 5-44.



**Figure 5-44 TGA graph for sample 4: 180°C; 4 hours; 1 g 2MN; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30wt%); 100 mg Highly ordered mesoporous material**

The first weight loss step occurs between 27-100°C while the second step between 100-600°C for the various samples. It is suggested that the solvent and substrate can be responsible for the two step weight loss based on the conclusions drawn from Table 2-6. In this case, the first step is due to the solvent MeCN and the substrate 2MN is responsible for the second step. The thermogravimetric analysis therefore, indicates that there are no contents left on a catalyst after an experiment that will alter the catalytic activity and selectivity.

### 5.2.6.2 Recycling of catalyst

To test if the highly ordered mesoporous material act as a truly heterogeneous catalyst for this process, a comparison between experiments with the original (fresh) catalyst and recycled catalyst under the same reaction conditions. Figure 5-45 and Figure 5-46 illustrate the comparison of the original with the recycled catalyst under the same reaction conditions.

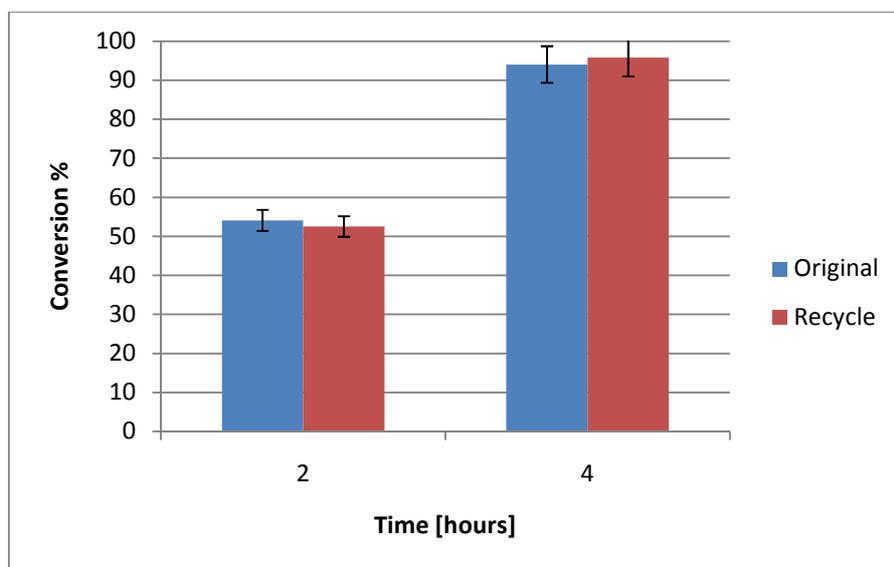


Figure 5-45 Recycling of Highly ordered mesoporous material catalyst at 150°C;1 g 2MN;100 mg catalyst; 10 ml MeCN;6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

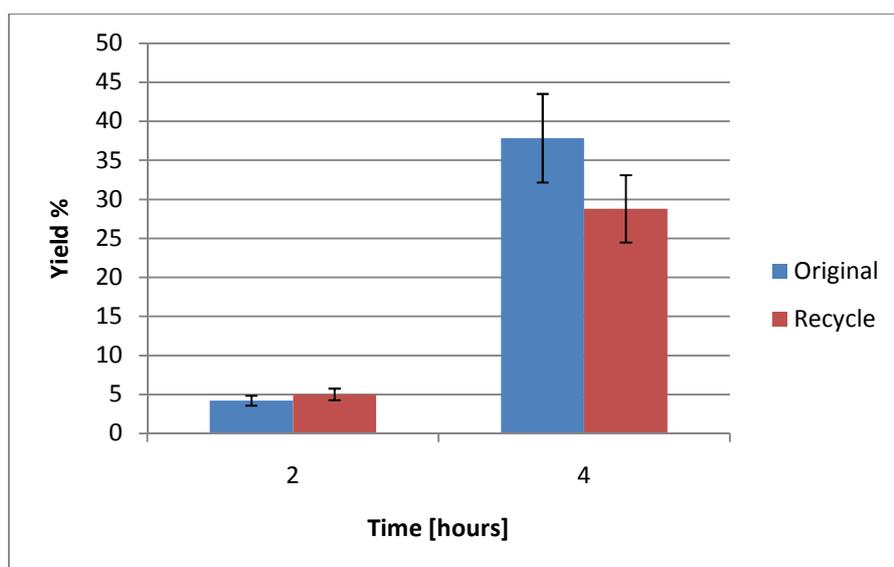


Figure 5-46 Recycling of Highly ordered mesoporous material catalyst at 150°C;1 g 2MN;100 mg catalyst; 10 ml MeCN;6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

Figure 5-45 indicates 2MN conversion for the original catalyst and recycled catalyst at 2 and 4 hours, whereas Figure 5-46 presents the 2MNQ yield. From Figure 5-45 and Figure 5-46, it appears that there is a difference between the substrate conversion and 2MNQ yield obtained from the original and recycled catalyst but it is within 7% error margin. For catalysts that did not act in a truly heterogeneous manner, the conversion decreased 2-3 times when the catalyst was reused compared to the fresh catalyst (as mentioned in section 2.2.4.). Therefore, it is suggested that the highly ordered mesoporous material behaves as a true heterogeneous catalyst for this process because the catalyst can be recycled without losing its catalytic activity and selectivity for at least two catalytic cycles. It is suggested that these results strongly support the absence of catalytic deactivation. This implies that the catalyst do not suffer from titanium leaching. Therefore, this process follows scenario 1 (the metal does not leach into the solution and the highly ordered mesoporous material is truly heterogeneous in this study) with regards to the different scenarios for heterogeneous catalyst in the liquid phase (as discussed in section 2.2b).

## 6 CONCLUSIONS & RECOMMENDATIONS

The results and discussions led to the following conclusions and recommendations regarding this research:

The characteristics and morphology of Ti-MCM-41 and the highly ordered mesoporous material for this study are consistent with literature findings but not catalysts Ti-MMM-2 and Ti-MMM-2(P123). It was suggested that the reason for this was because a different silicate source was used in this study than in literature. This confirms the importance of following the exact procedure for synthesising a catalyst. From literature, both the highly ordered mesoporous material and Ti-MMM-2(P123) possessed micropores and mesopores but in this study, the highly ordered mesoporous material was the only redox molecular sieve possessing both micropores and mesopores. It is therefore, recommended to synthesise Ti-MMM-2 and Ti-MMM-2(P123) with the same silicate source as literature and observe the effect it has on the hydroxylation of 2MN to 2MNQ.

All catalysts synthesised for this study successfully oxidized 2MN to 2MNQ and the by-products are either not harmful to the environment or have potential uses in alternative applications. Therefore, the processes in this study are environmentally friendly because low E-factors are produced. The products formed from this study are 2MNQ, 2-naphthaldehyde, 2MNL, menadione epoxide and 3-ethoxy-4-methoxyaldehyde. These findings correspond to results found in literature.

This study confirms that the process system, reaction conditions and catalyst type have a major impact on the products formed, 2MN conversion, 2MNQ selectivity and 2MNQ yield. The process system was improved by immersing the autoclave in a deep bath containing silicon oil. The process system can be improved further by using oil with a higher heat capacity than silicon that is able to withstand the high reaction temperatures. The effect reaction conditions have on the hydroxylation of 2MN to 2MNQ with the various catalysts synthesised were investigated to determine which catalyst obtained the highest 2MN conversion and favoured the formation of 2MNQ. The catalyst achieving the highest 2MN conversion and favouring 2MNQ formation in most cases was the highly ordered mesoporous material.

The hydroxylation of 2MN to 2MNQ over the highly ordered mesoporous material with H<sub>2</sub>O<sub>2</sub> as oxidant and MeCN as solvent was investigated in more detail to observe the effect reaction conditions have on the 2MNQ yield. This was done by a one factor approach and a factorial design. The results from the one factor approach clearly indicated that as the hydrogen peroxide volume increased from 1 ml to 6 ml, the 2MN conversion and 2MNQ yield also increased. The conversion increased with increasing the reaction temperature and reaction time. The 2MNQ yield increased with increasing reaction time at reaction temperature 120°C and 150°C but decreased with increasing the reaction time at 180°C. It was suggested that the reaction favours over-oxidation as the reaction time increases at 180°C. Therefore, reactions conducted at 180°C should be conducted

at reaction times lower than 4 hours. It was found that the conversion was almost constant with a change in catalyst amount, while the yield increased with increasing the catalyst amount. The yield reached a maximum point with a change in solvent volume and substrate amount. From the one factor approach it was found that 2MNQ yield increased when reaction conditions were increased. The reaction conditions were reaction time, catalyst amount, hydrogen peroxide volume and reaction temperatures, 120°C and 150°C. These observations are consistent with previous findings in literature and these reaction conditions acted as the factors for the preliminary factorial design.

Based on the factorial design, high 2MNQ yields can be achieved by increasing the reaction temperature and hydrogen peroxide volume while decreasing the reaction temperature-reaction time interaction. This was based on an 80% confidence level and further investigations should be conducted to improve the confidence level and generate a prediction equation. A more detailed factorial design should be conducted with more replicates or a three level with replicates. Based on the non-statistical and statistical techniques, the hydrogen peroxide volume had the most influence on the 2MNQ yield followed by the reaction time-reaction temperature interaction and reaction temperature. For this study, the hydrogen peroxide volume could not be increased to a higher peroxide volume than 9 ml because the autoclave could not withstand the pressure, causing the reactor to explode. Therefore further studies should be conducted with a bigger reactor in order to use higher hydrogen peroxide volumes than in this study.

The highest 2MNQ yields and 2MN conversions obtained for the hydroxylation of 2MN to 2MNQ over the highly ordered mesoporous material in this study were in the ranges 48-50% and 97-99%, respectively. This occurred at reaction temperatures 150°C and 180°C with 6 ml hydrogen peroxide volume, 10 ml MeCN, 1 g 2MN, 100 mg and 200mg catalyst and reaction times of 2 hours, 4 hours and 6 hours.

It was suggested that the kinetic modelling of the reaction data with an overall second-order kinetic model gave a good fit even though only one data point could be obtained from an experimental run because experiments were conducted in a pressurised autoclave. This study clearly showed the relationship between rate constants and the reaction temperature. To determine more accurate rate constants more experimental runs should be conducted at various reaction times for reaction temperature 135°C and 160°C.

Thermogravimetric analysis indicated that there are no contents left on the highly ordered mesoporous material after an experiment that would alter the catalyst activity and selectivity. The only contents found on the catalyst were the substrate and solvent. This process is therefore, efficient because the highly ordered mesoporous material performs in a truly heterogeneous manner, not losing any catalytic activity and selectivity after two catalytic cycles. The catalyst should be recycled for more cycles to see whether the catalyst will deteriorate over extended reaction times.

The highly ordered mesoporous material is therefore, an ideal catalyst to improve the process for the hydroxylation of 2MN to 2MNQ with H<sub>2</sub>O<sub>2</sub> as oxidant and MeCN as solvent because it obtained the highest conversions and yields of the desired product. This study proves that microporous/mesoporous catalysts are more favourable than catalysts only possessing mesopores for oxidizing bulky substrates. As a result, this study opens the door for improving the hydroxylation of bulky substrates because it provides an environmentally friendly process resulting in high conversions and desired product yields. Therefore, further studies should be conducted for other bulky substrates with the highly ordered mesoporous material as catalyst.

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## 8 APPENDIX A

### 8.1 Adsorption isotherms

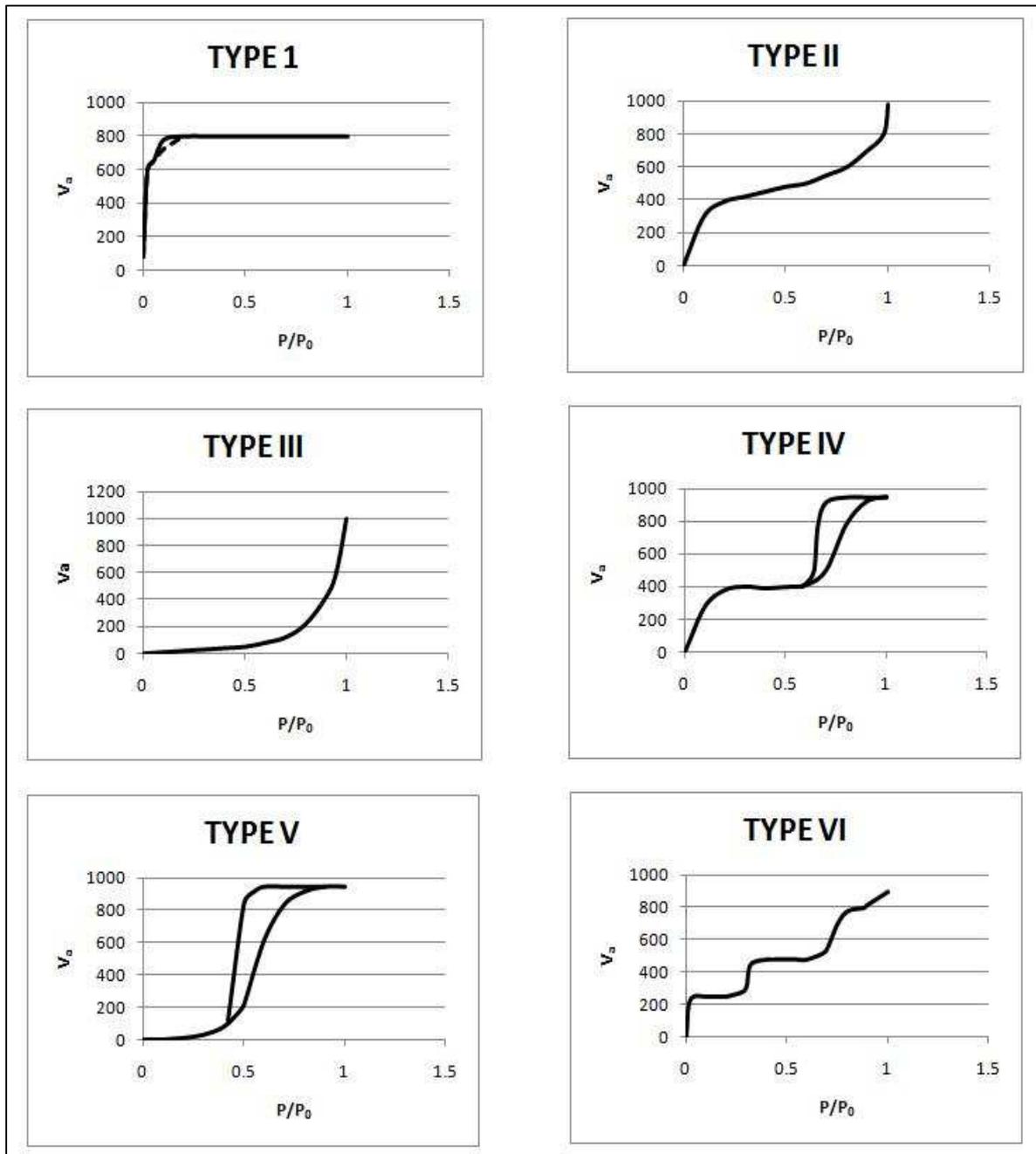


Figure 8-1 The six basic adsorption isotherm types (Lowell, *et al.*, 1984)

## 9 APPENDIX B

### 9.1 Gas Chromatography

Table 9-1 Gas Chromatography method designed for this process

Initial column temperature	80°C
Initial column hold time	5min
Final column temperature	250°C
Column rate in °C/min	2
Column hold time	0min
Injector temperature	280°C
Detector temperature	300°C
Program time	90min

Table 9-2 Response Factor for the various components

Component	Response Factor
Biphenyl	1
2-Methylnaphthalene	0.82
2-Methyl-1,4-naphthoquinone	0.85
2-Methyl-1-naphthol	0.47
2-Naphthaldehyde	0.83
3-Ethoxy-4-methoxyaldehyde	0.57
Menadione epoxide	0.70

## 10 APPENDIX C

### 10.1 List of Chemicals

Table 10-1 List of Chemicals

Chemical	Purity	Supplier
Hexadecyltrimethylammonium bromide	Min. Assay $\geq 97\%$	Merck
Tetramethylammonium hydroxide	25% wt-% aqueous solution, p.a	Aesar
Titanium isopropoxide	95%	Alfa Aesar
Pluronic (P123)	-	BASF
TiOSO <sub>4</sub> (Titanium oxysulfate-sulfuric acid complex hydrate)	-	Sigma-Aldrich
Sodium Trisilicate	Na <sub>2</sub> O: 18-20% ; SiO <sub>2</sub> : 62-65%	Fluka
Hydrochloric acid	30-34% aqueous solution	Merk
Sodium Silicate	Na <sub>2</sub> O: 10.6% ; SiO <sub>2</sub> : 25.6%	Sigma-Aldrich
Tetraethoxide titanium	Purum p.a. $\geq 97\%$	Sigma-Aldrich
Sulphuric acid	98%	Kimix
2-Methylnaphthalene	97%	Sigma-Aldrich
2-Methyl-1,4-naphthoquinone	98%	Sigma-Aldrich
Hydrogen peroxide	30 wt% aqueous solution, p.a.	Sigma-Aldrich
2-Methylnaphthaldehyde	98%	Sigma-Aldrich
2-Methyl-1-naphthol	98%	Sigma-Aldrich
3-Ethoxy-4-methoxybenzaldehyde	99%	Sigma-Aldrich
Biphenyl	Purum p.a. $\geq 98\%$ (HPLC)	Fluka
Acetonitrile	$\geq 99.9\%$	Sigma-Aldrich
Acetone	Min 98%	Merk

## 11 APPENDIX D

### 11.1 Adsorption isotherms for synthesised catalysts

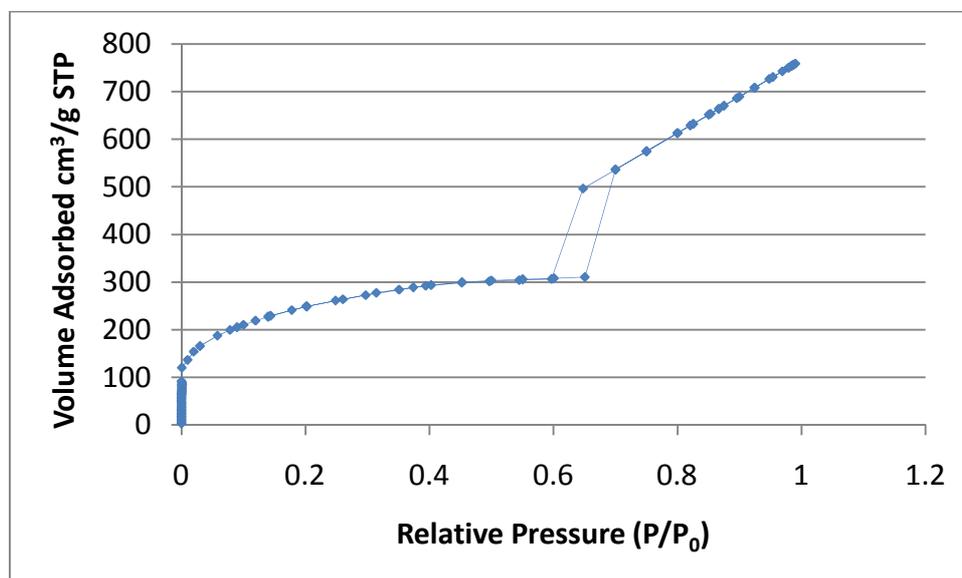


Figure 11-1 Nitrogen adsorption-desorption isotherms for hydrothermally synthesised calcined Ti-MMM-2 at 408K after 14hours

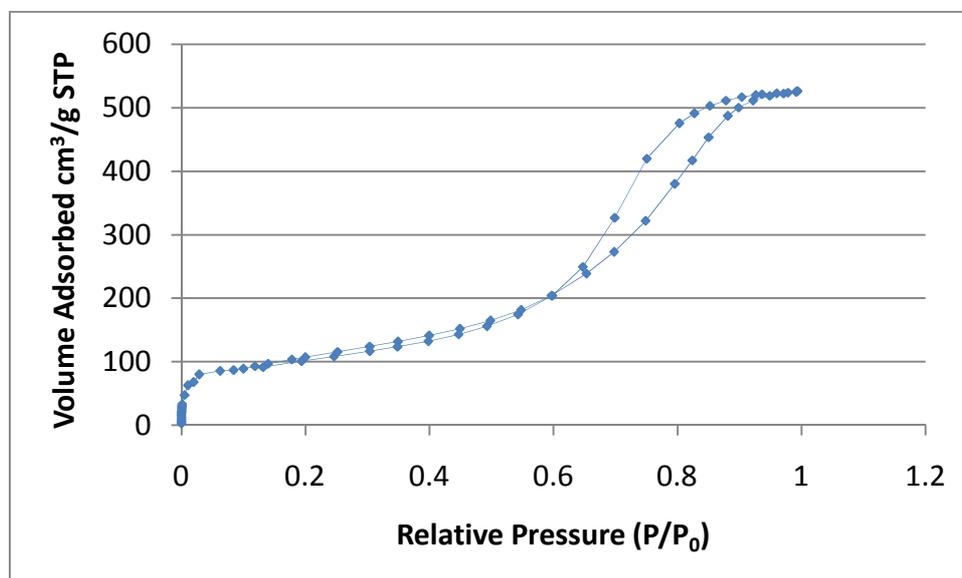


Figure 11-2 Nitrogen adsorption-desorption isotherms for hydrothermally synthesised calcined Ti-MMM-2 (P123) at 408K after 14hours

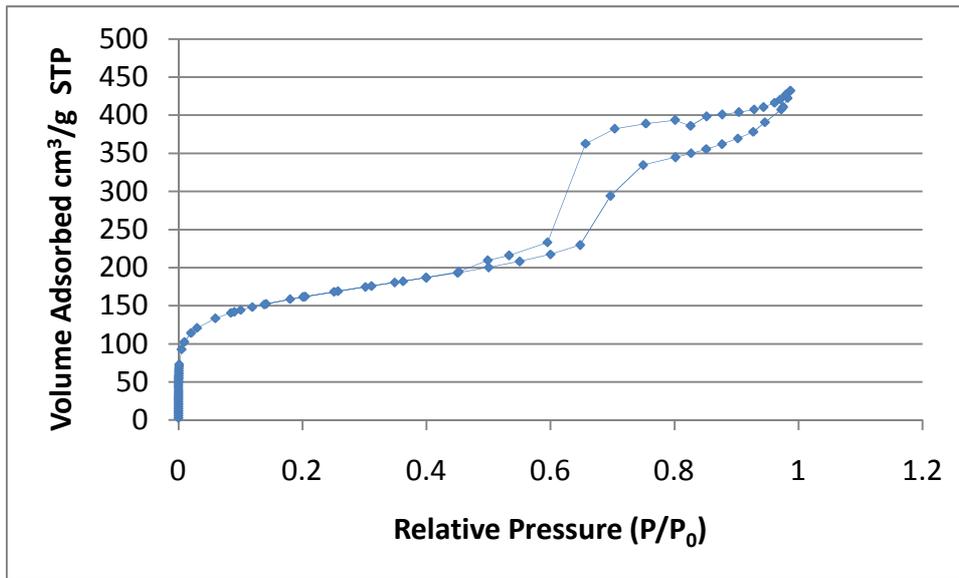


Figure 11-3 Nitrogen adsorption-desorption isotherms for hydrothermally synthesised calcined Highly ordered mesoporous material at 408K after 14hours

## 12 APPENDIX E

### 12.1 Pore size distributions for synthesised catalysts

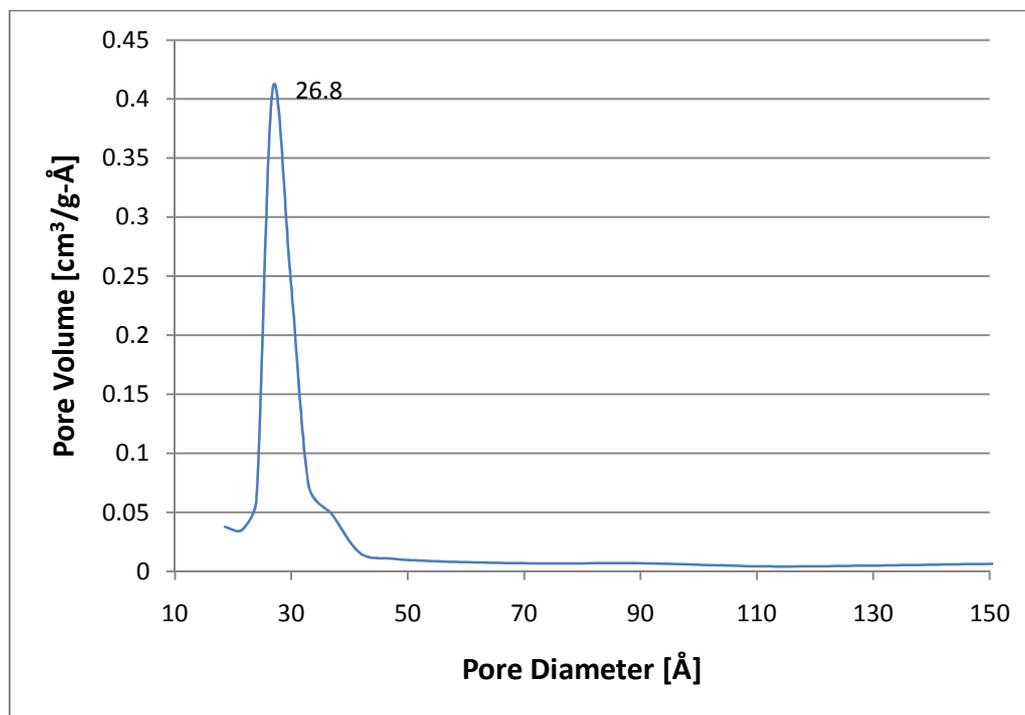


Figure 12-1 Pore size distribution (BJH method) for Ti-MCM-41

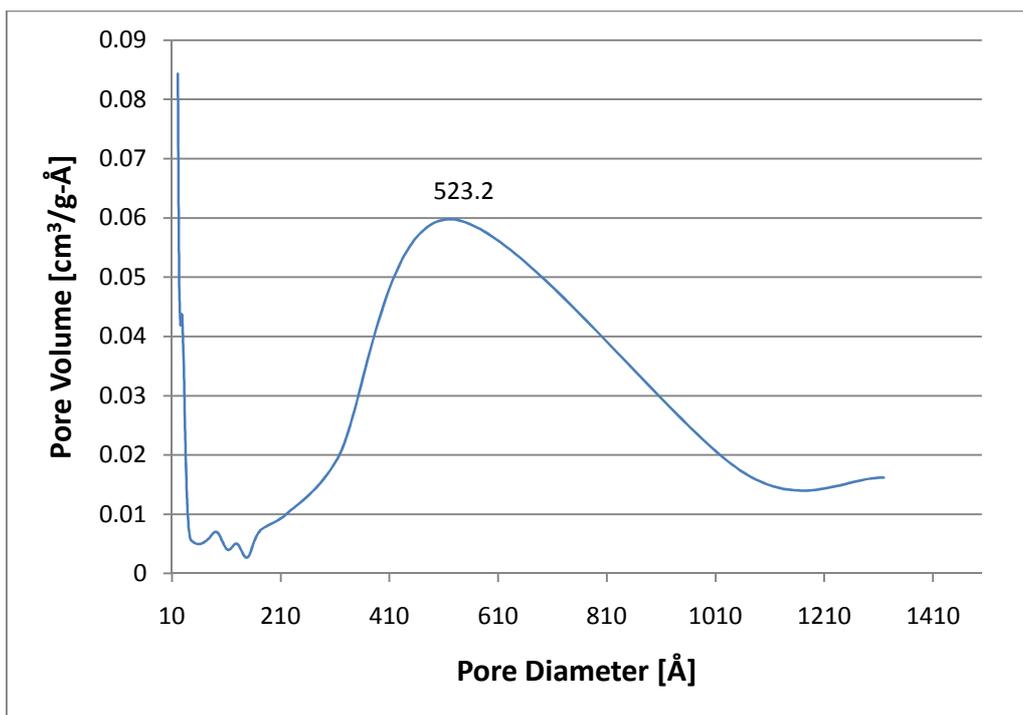


Figure 12-2 Pore size distribution (BJH method) for Ti-MMM-2

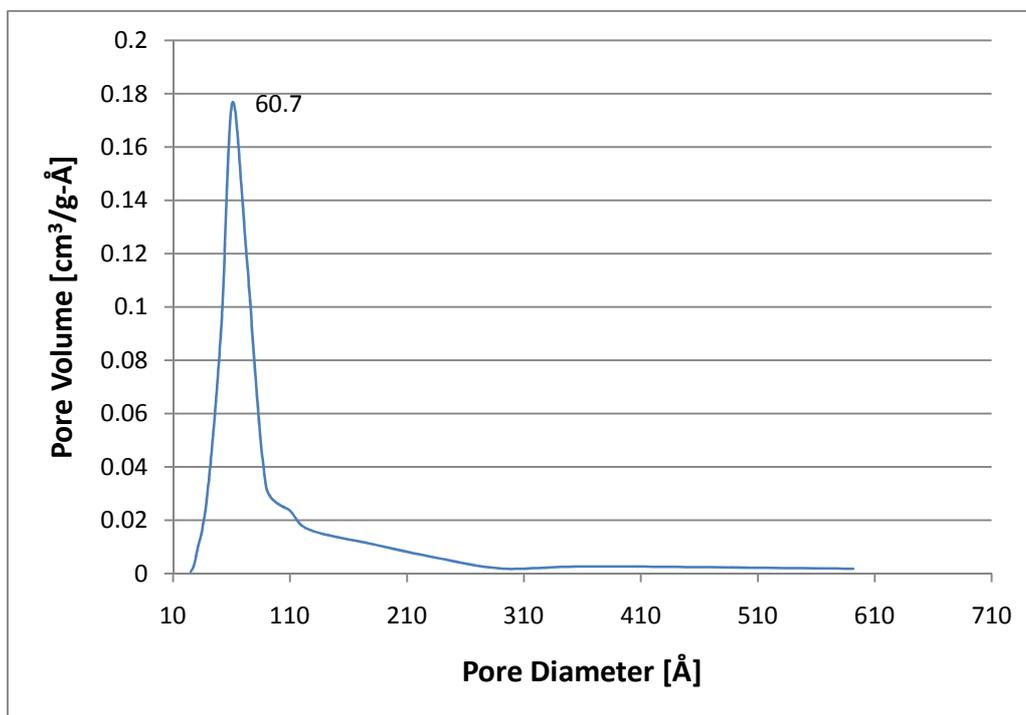


Figure 12-3 Pore size distribution (BJH method) for Ti-MMM-2 (P123)

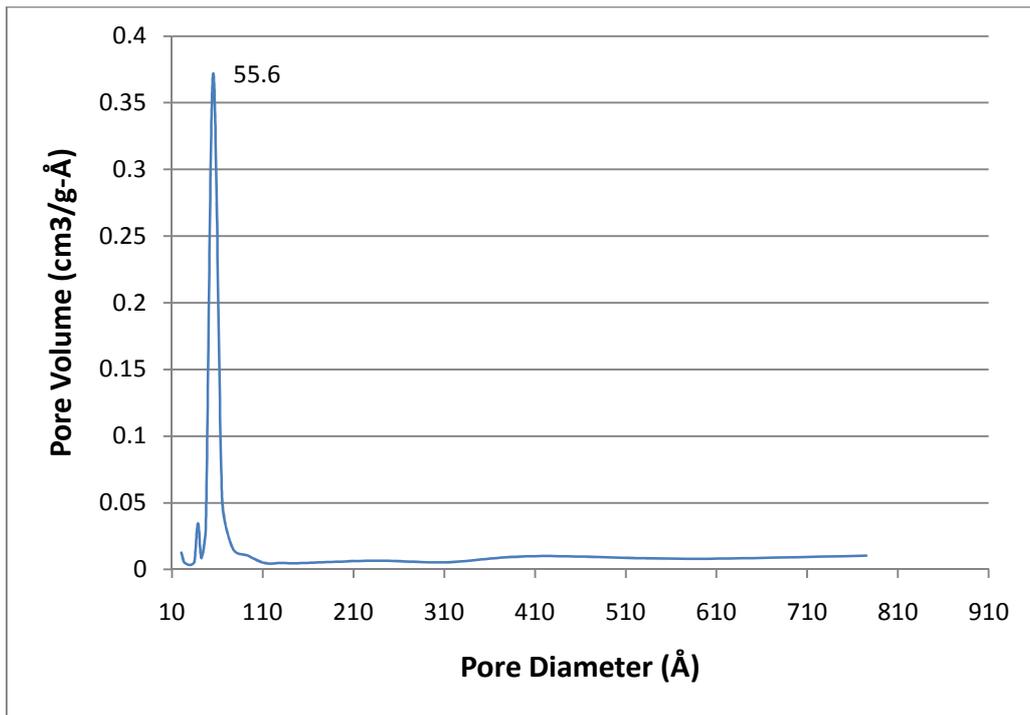


Figure 12-4 Pore size distribution (BJH method) for Highly ordered mesoporous material

## 13 APPENDIX F

### 13.1 t-Plots for synthesised catalysts

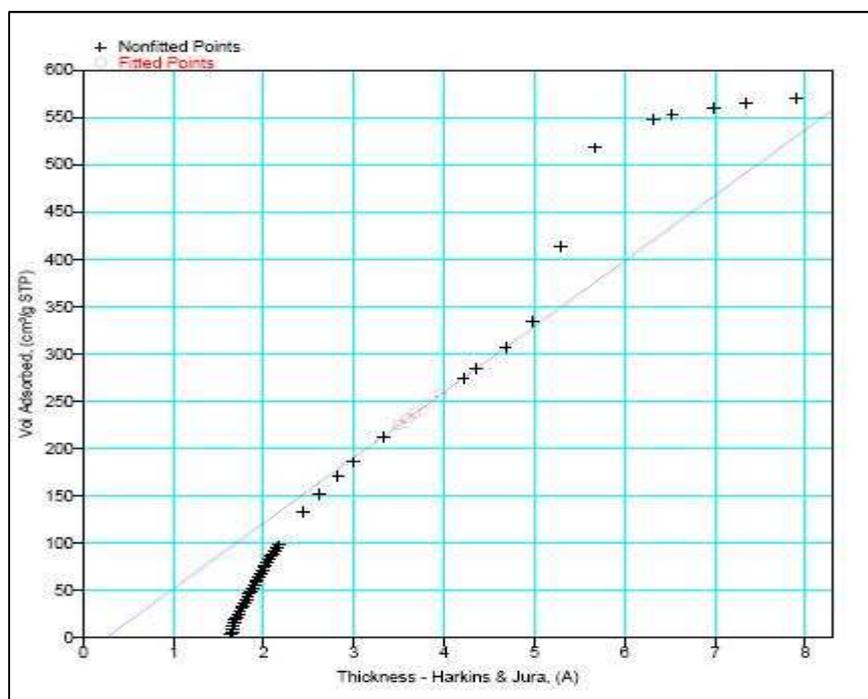


Figure 13-1 t-plot for Ti-MCM-41

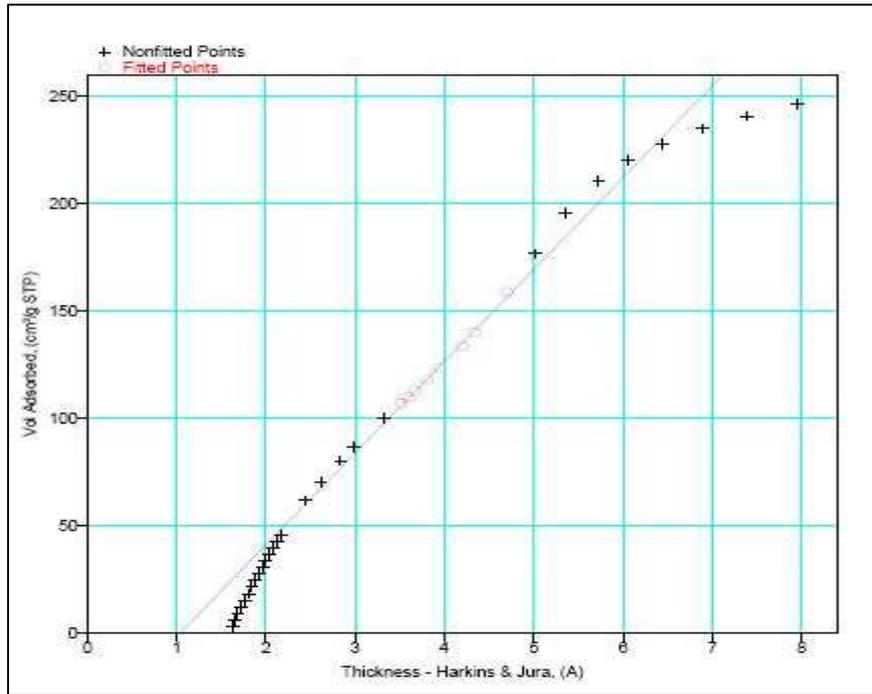


Figure 13-2 t-plot for Ti-MMM-2

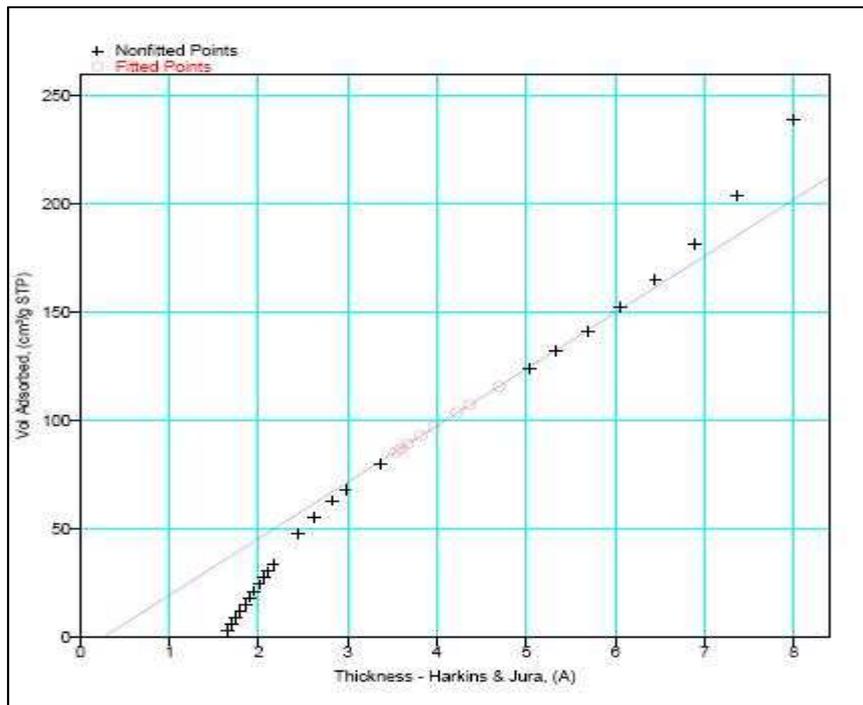


Figure 13-3 t-plot for Ti-MMM-2(P123)

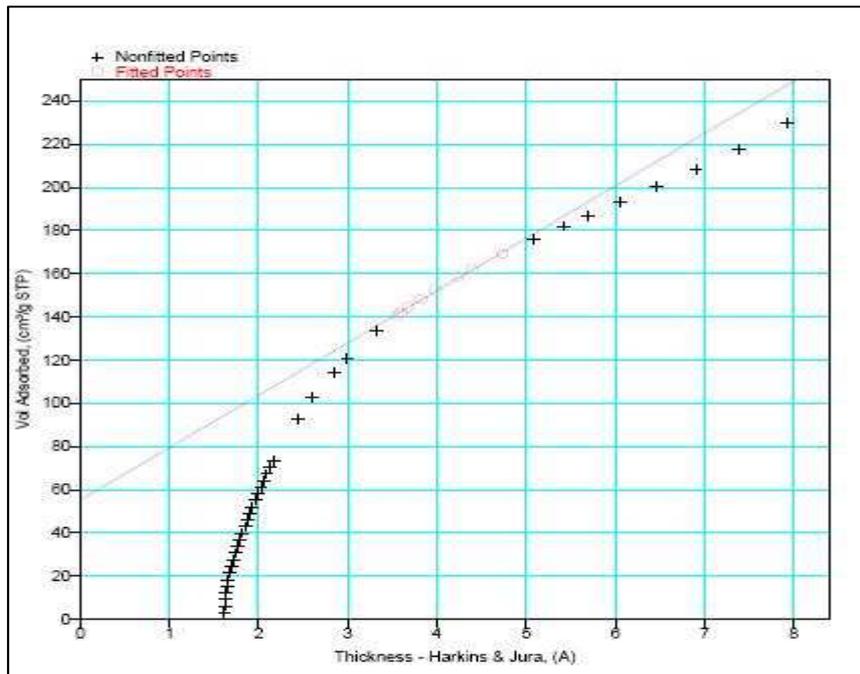


Figure 13-4 t-plot for Highly ordered mesoporous material

## 14 APPENDIX G

### 14.1 Selectivity for various catalysts from effect of process system

Table 14-1 Product selectivity of various process system at 100 mg Ti-MCM-41; 150°C; 1 g 2MN; 10 ml MeCN; 6 ml H<sub>2</sub>O<sub>2</sub> (30 wt%)

Time	2 Hours		4 Hours		6 Hours	
	Glycol	Silicon	Glycol	Silicon	Glycol	Silicon
Selectivity of 2MNQ %	27	38	47	44	58	68
Selectivity of 2-naphaldehyde %	73	29	53	31	42	22
Selectivity of 3-ethoxy-4-methoxy %	-	33	-	25	-	10

Table 14-2 Product selectivity of various process system at 100 mg Ti-MMM-2; 150°C; 1 g 2MN; 10 ml MeCN; 6 ml H<sub>2</sub>O<sub>2</sub> (30 wt%)

Time	2 Hours		4 Hours		6 Hours	
	Glycol	Silicon	Glycol	Silicon	Glycol	Silicon
Selectivity of 2MNQ %	25	33	77	71	90	79
Selectivity of 2-naphaldehyde %	75	33	23	9	10	15
Selectivity of 3-ethoxy-4-methoxy %	-	34	-	20	-	7

## 15 APPENDIX H

### 15.1 Selectivity for various catalysts from the effect of reaction conditions

120°C

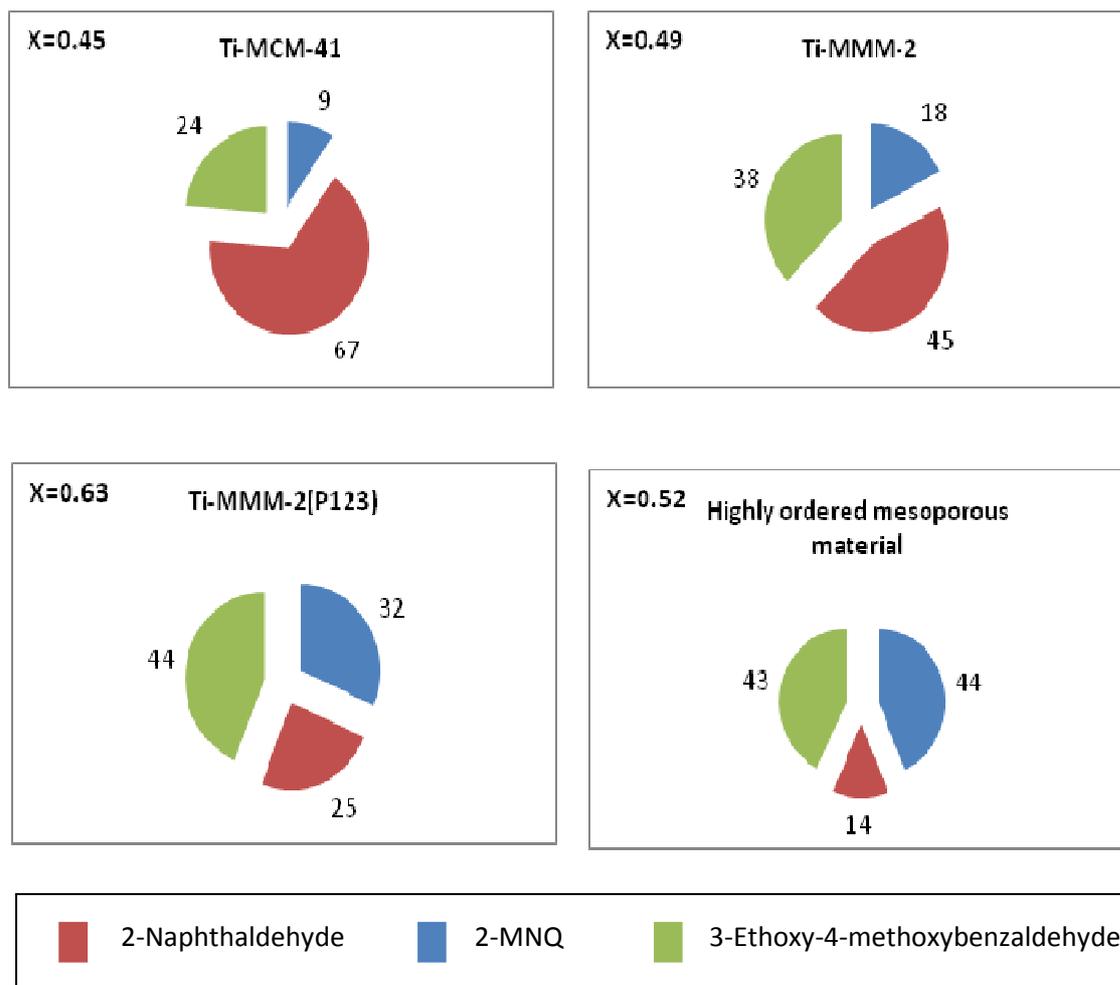


Figure 15-1 Selectivity for various catalysts at 120°C; 2 hours; 1 g 2MN; 100 mg catalyst, 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30wt%)

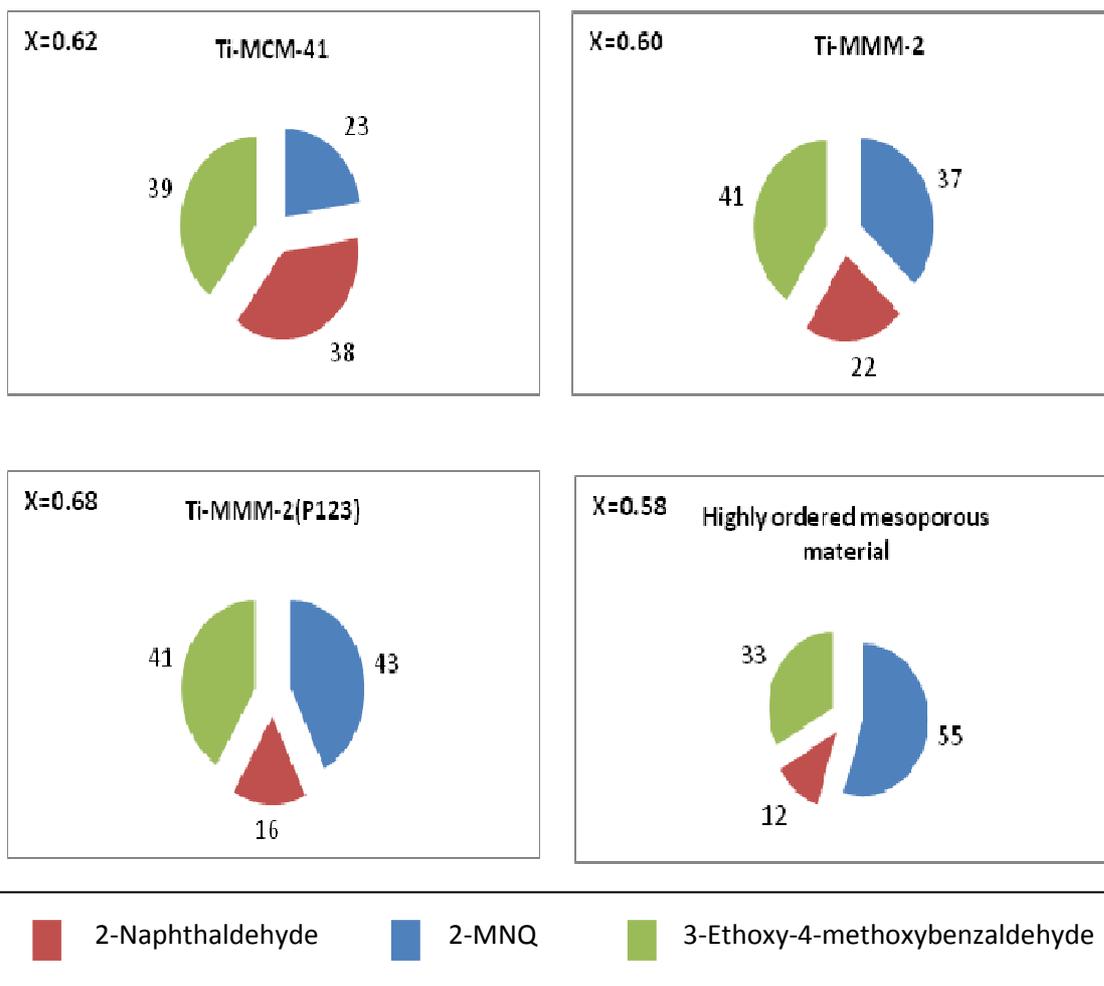


Figure 15-2 Selectivity for various catalysts at 120°C ; 6 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**150°C**

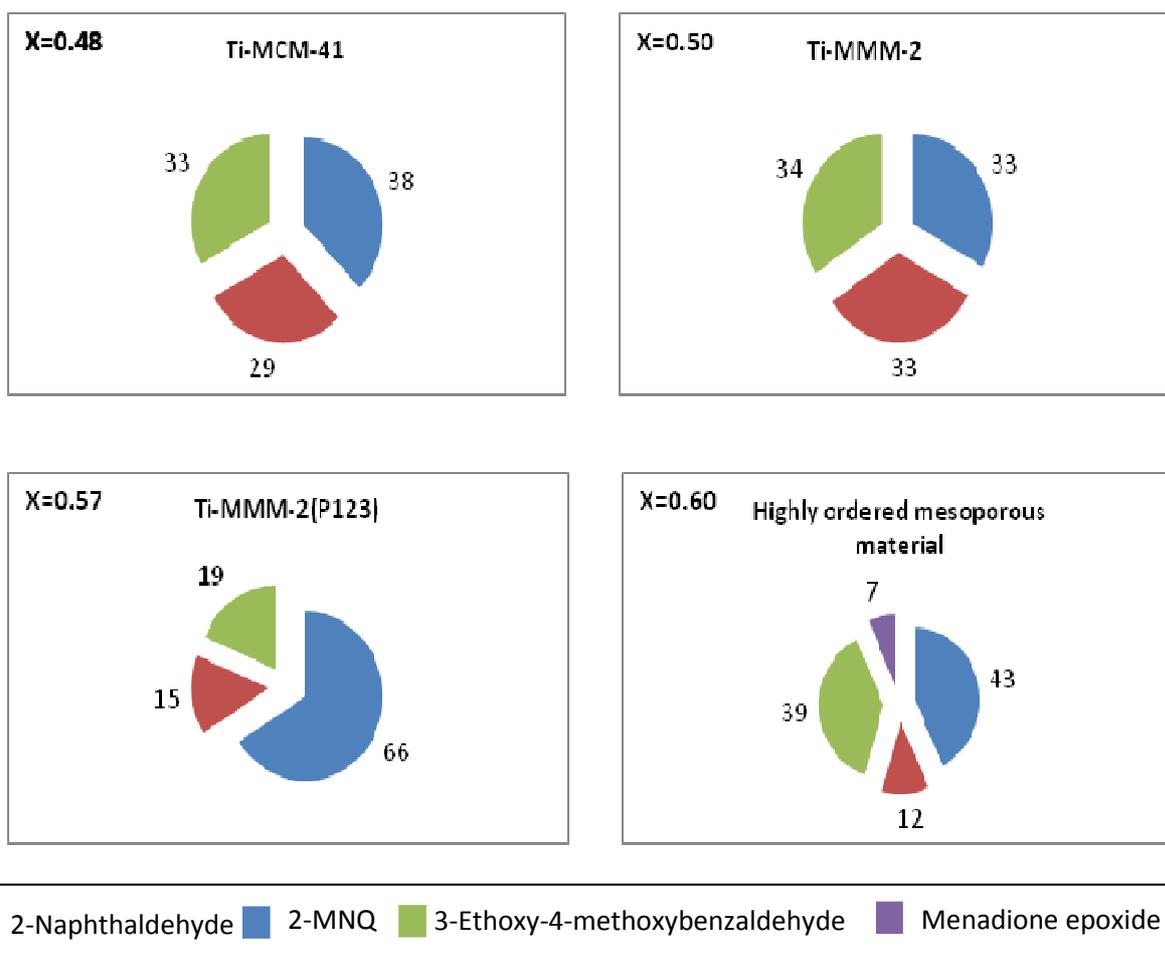


Figure 15-3 Selectivity for various catalysts at 150°C; 2 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

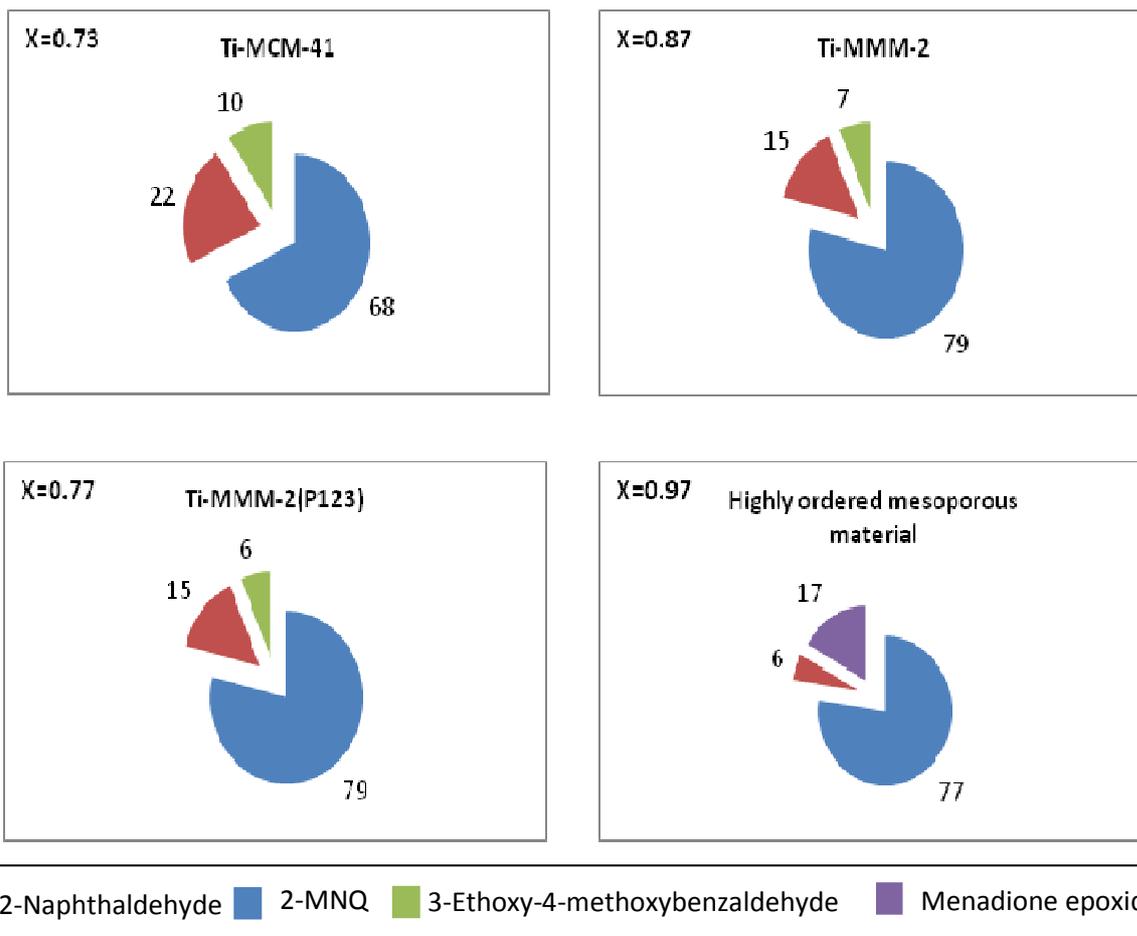
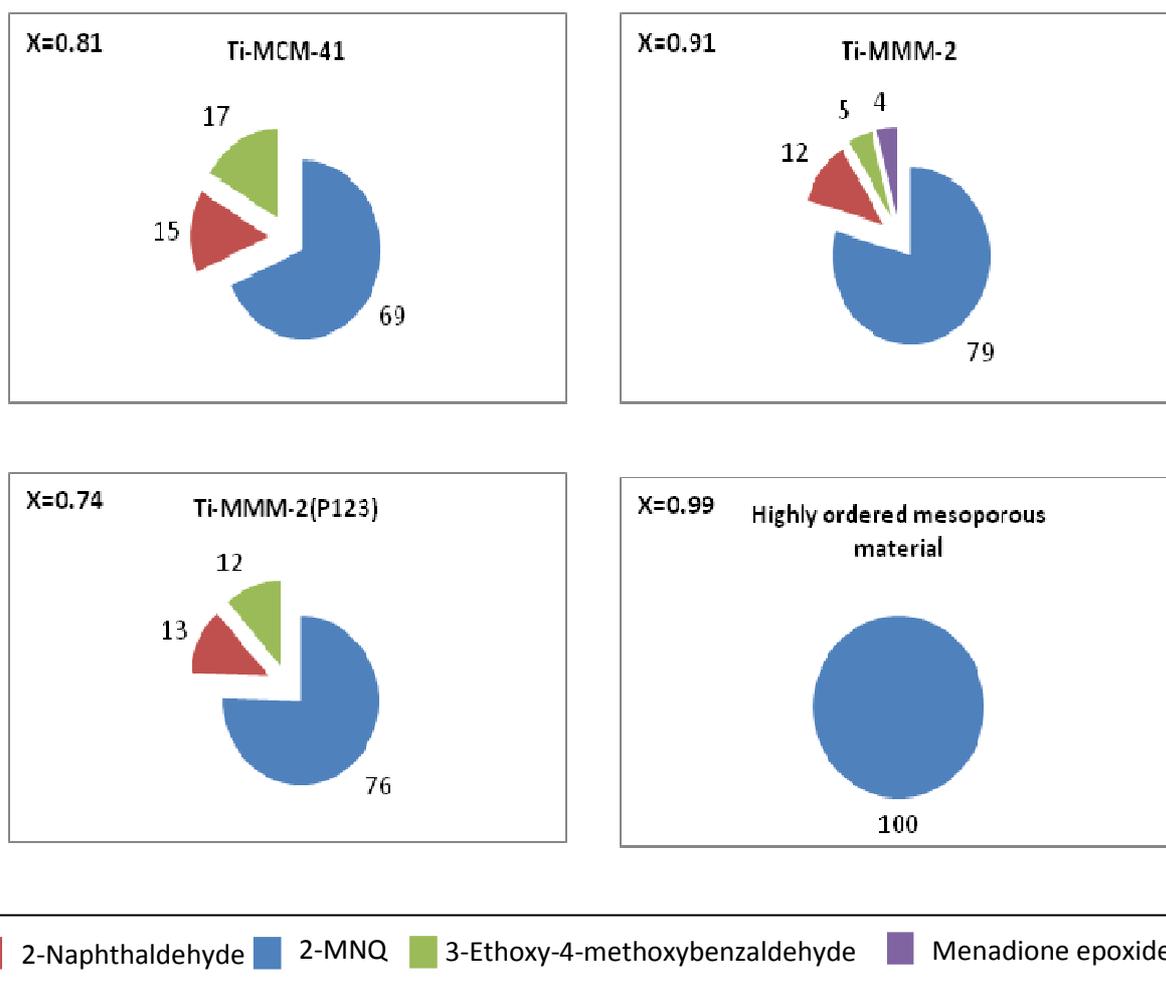


Figure 15-4 Selectivity for various catalysts at 150°C ; 6 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**180°C**



**Figure 15-5 Selectivity for various catalysts at 180°C; 2 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)**

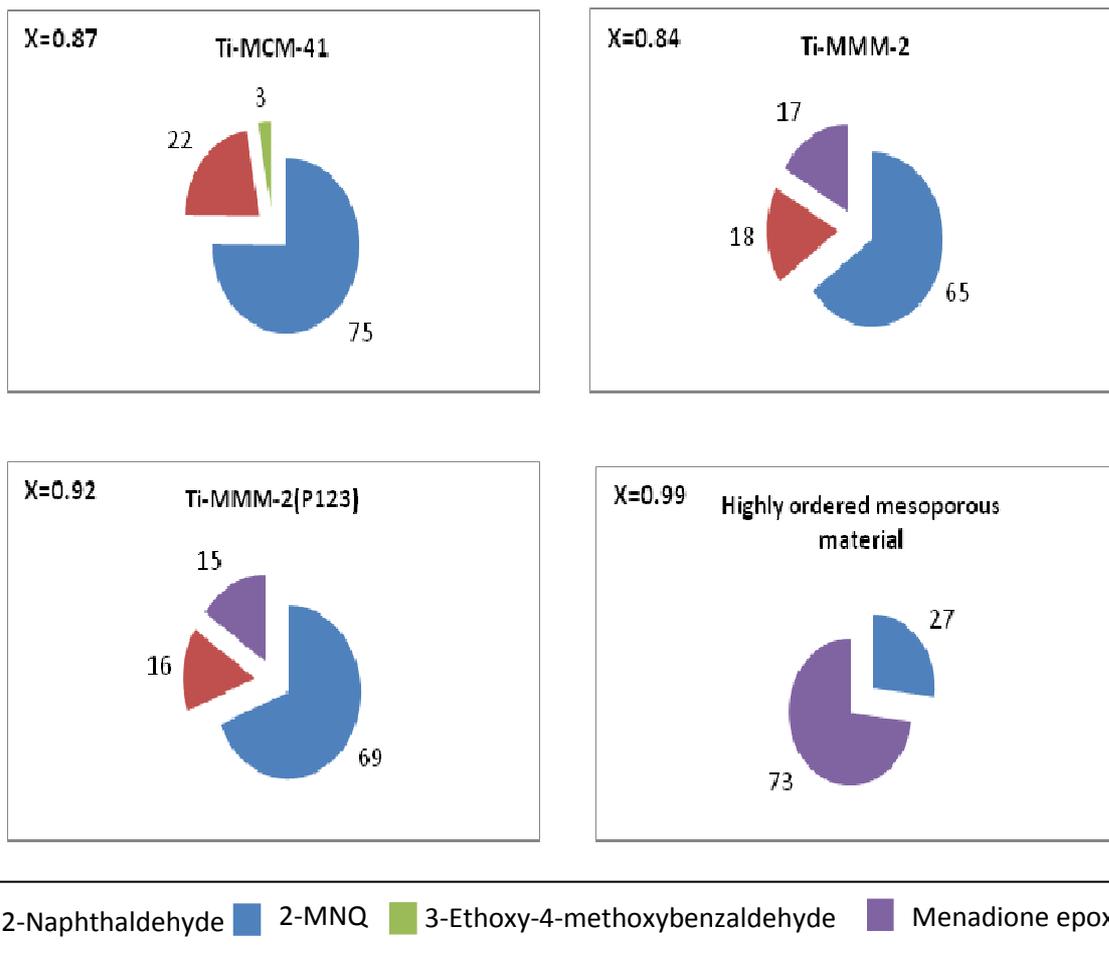


Figure 15-6 Selectivity for various catalysts at 180°C; 6 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**Hydrogen peroxide 9 ml**

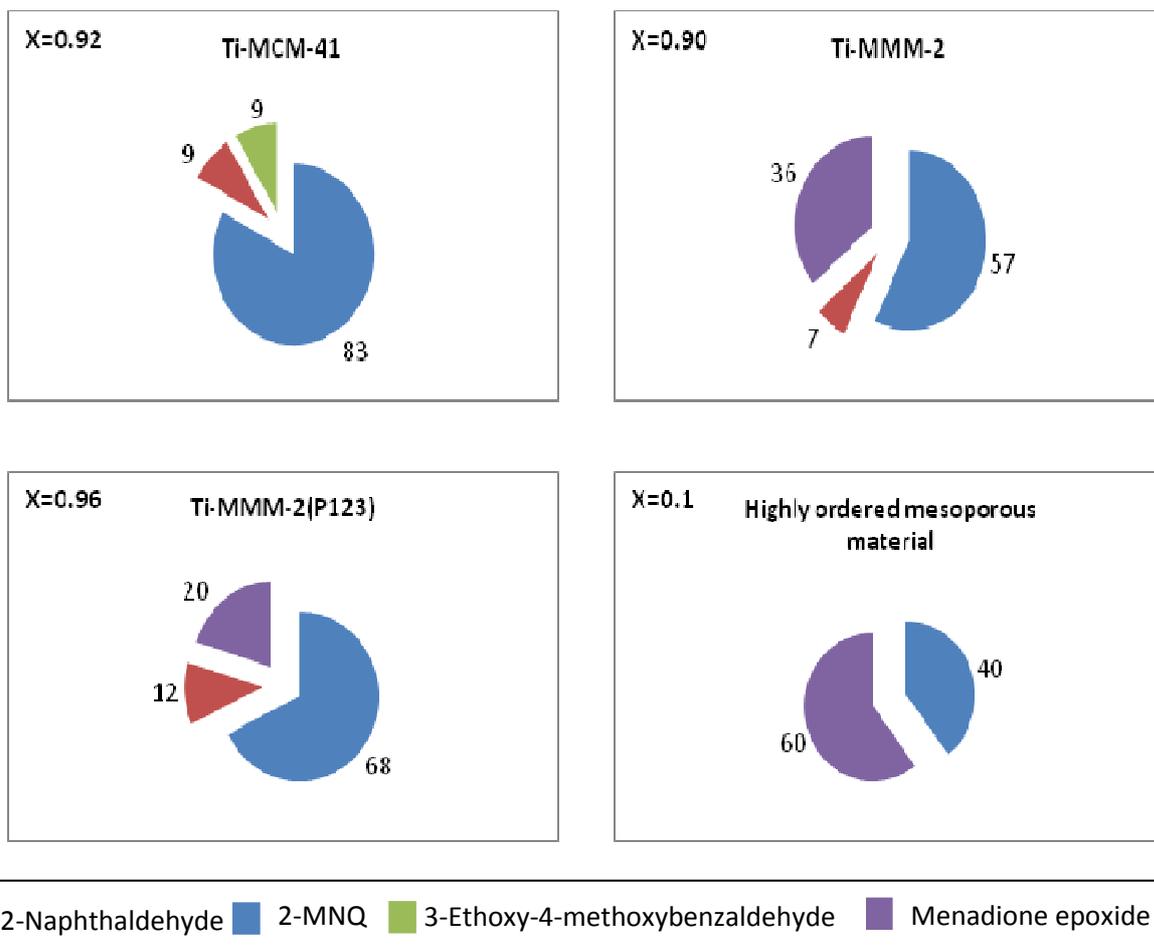


Figure 15-7 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 100 mg catalyst; 10 ml MeCN; 9 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**Substrate 0.5 g**

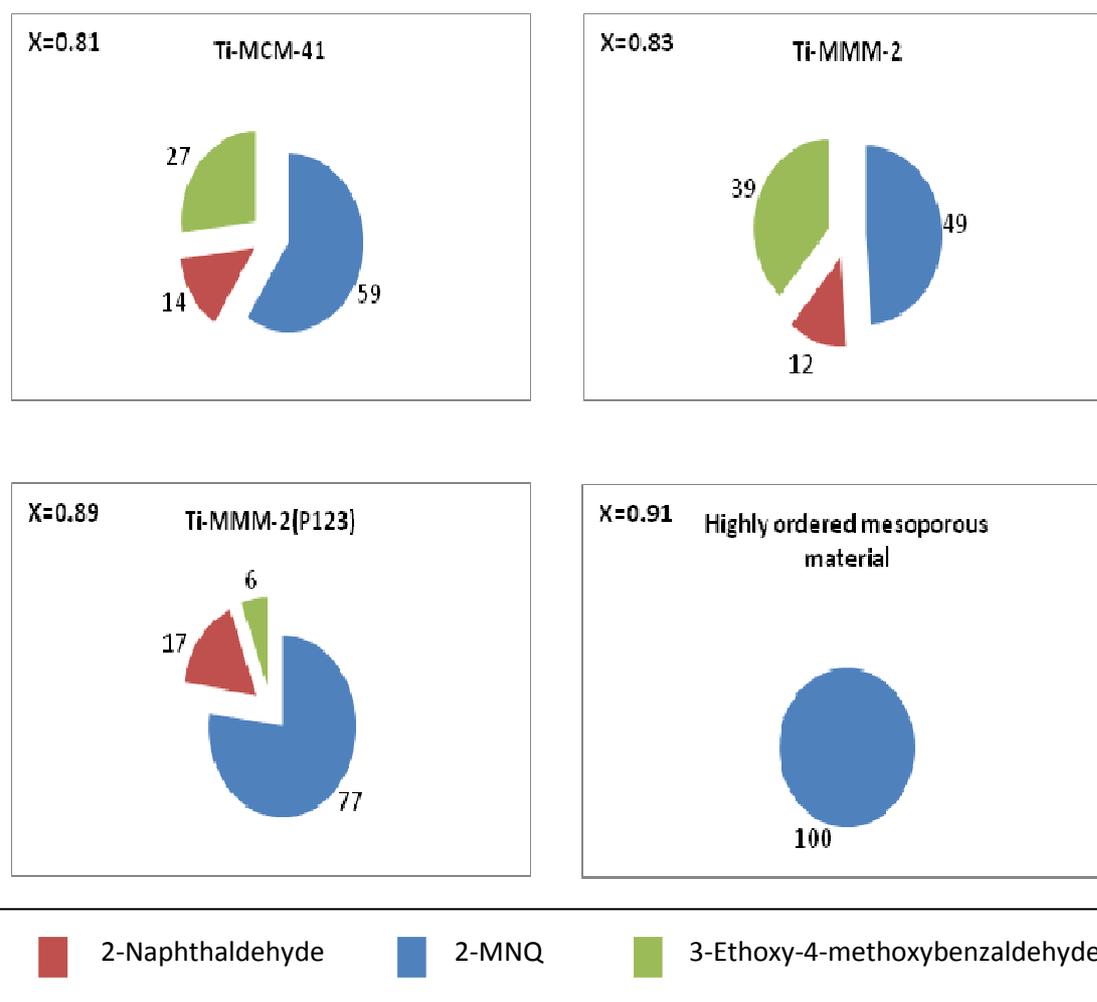


Figure 15-8 Selectivity for various catalysts at 150°C; 4 hours; 0.5 g 2MN; 100 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**Catalyst 50 mg**

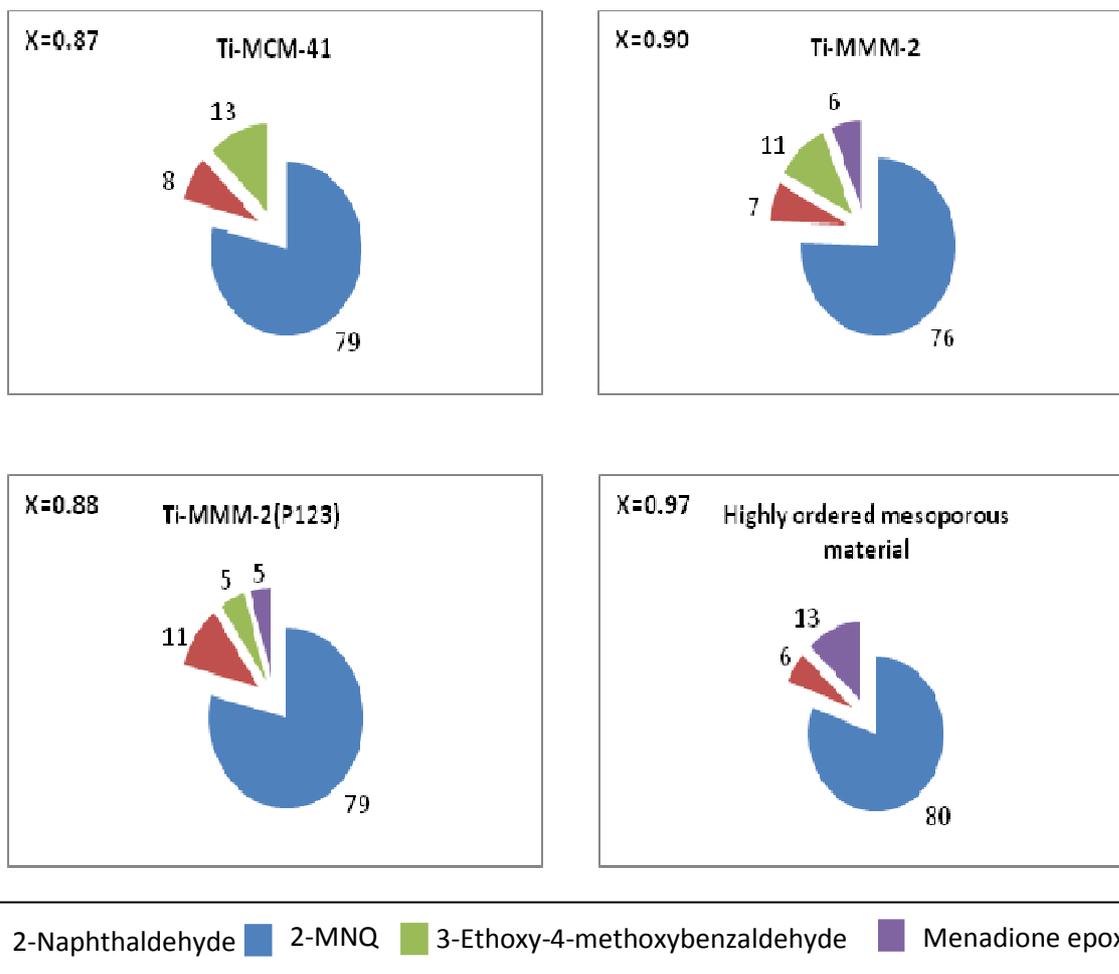


Figure 15-9 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 50 mg catalyst; 10 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

**Solvent 5 ml**

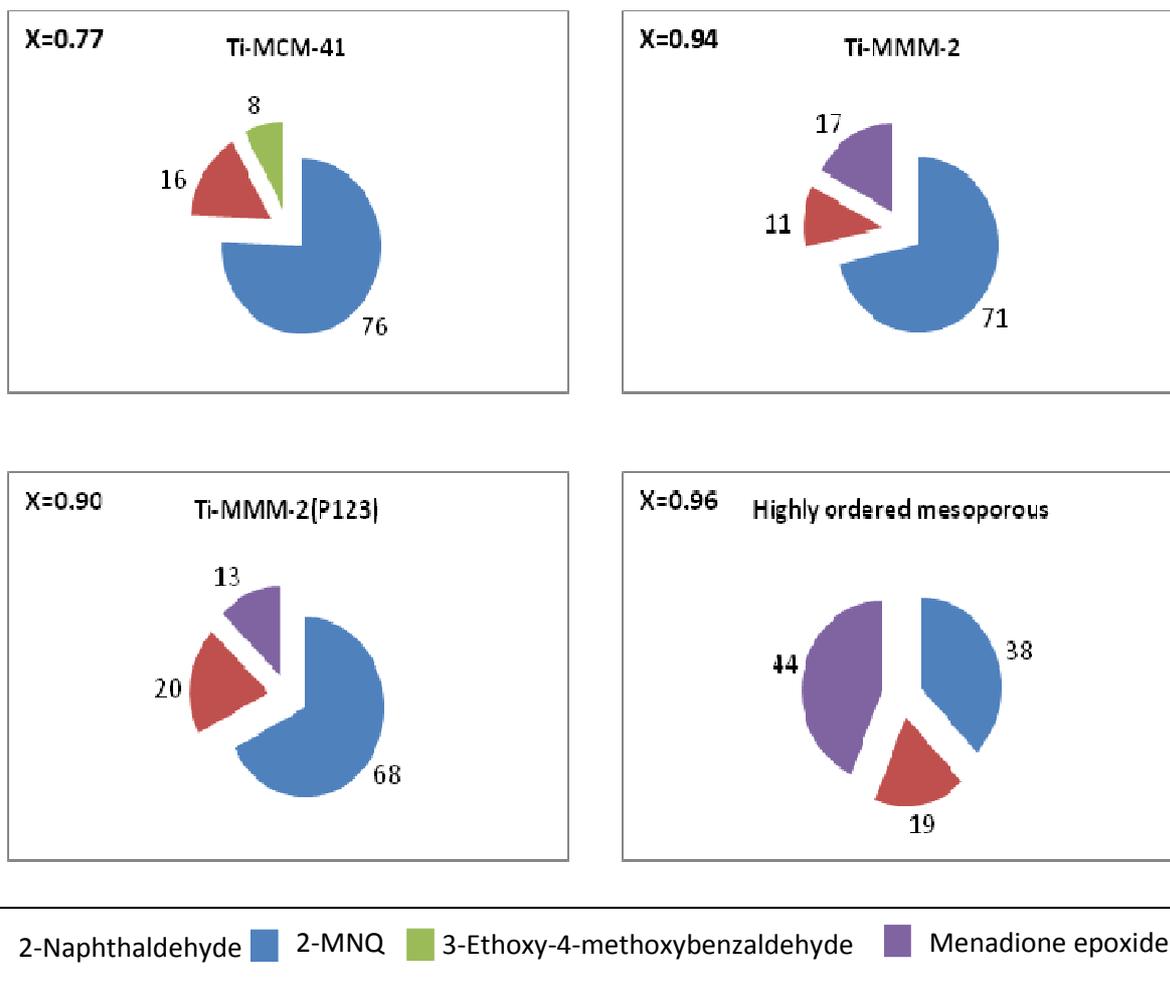


Figure 15-10 Selectivity for various catalysts at 150°C; 4 hours; 1 g 2MN; 100 mg catalyst; 5 ml MeCN; 6 ml aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%)

