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Hydroxylation of Aromatic Compounds over Zeolites

by

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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and to my knowledge has not been previously submitted at any university for a degree.

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Date ...25 February 2009....

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SYNOPSIS

Aromatic precursor compounds are derivatives that play an important role in biosystems and are useful in the production of fine chemicals. This work focuses on the catalytic synthesis of 2-methyl-1, 4-naphthoquinone and cresols (para- and ortho) using aqueous hydrogen peroxide as an oxidant in liquid-phase oxidation of 2-methylnaphthalene and toluene over titanium-substituted zeolite TS-1 or Ti-MCM-41.

Catalysts synthesised in this work were calcined at 550°C, extensively characterised using techniques such as X-ray Fluorescence for determining the catalyst chemical composition; BET for surface area, pore size and micropore volume; Powder X-ray diffraction for determining their crystallinity and phase purity and SEM was used to investigate the catalyst morphologies. The BET surface areas for Ti-MCM-41 showed a surface area of 1025 m²/g, and a 0.575 cm³/g micropore volume. However, zeolite TS-1 showed a BET surface area of 439 m²/g and a 0.174 cm³/g micropore volume.

The initial experiments on 2-methylnaphthalene hydroxylation were performed using the normal batch method. After a series of batch runs, without any success as no products were generated as confirmed by GC, a second experimental tool was proposed. This technique made use of the reflux system at reaction conditions similar to that of the batch system. After performing several experimental runs and optimising the system to various reactor operating conditions and without any products formed, the thought of continuing using the reflux was put on hold. Due to this, a third procedure was brought into

perspective. This process made use of PTFE lined Parr autoclave. The reactor operating conditions were changed in order to suit the specifications and requirements of the autoclave. This process yielded promising results and the formation of 2-MNQ was realised. There was a drawback when using an autoclave as only one data point was obtained, at the end of each run. Therefore, it was not possible to investigate reaction kinetics in terms of time.

Addition of aqueous hydrogen peroxide (30 wt-%) solution in the feed was done in one lot at the beginning of each reaction in all oxidation reactions, to a reactor containing 2-methylnaphthalene and the catalyst in an appropriate solvent of choice (methanol, acetonitrile, 2-propanol, 1-propanol, 1-pentanol, and butanol), with sample withdrawal done over a period of 6 hours (excluding catalytic experiments done with a Parr autoclave as sampling was impossible).

As expected, 2-methylnaphthalene oxidation reactions with medium pore zeolite TS-1 yielded no formation of 2-methyl-1, 4-naphthoquinone using various types of solvents, with a batch reactor, reflux system, or a Parr PTFE autoclave. This was attributed to the fact that 2-methylnaphthalene is a large compound and hinders diffusion into zeolite channels.

With the use of an autoclave, Ti-MCM-41 catalysed reactions showed that the choice of a solvent and reaction temperature strongly affect 2-methylnaphthalene conversion and product selectivity. This was proven after comparing a series of different solvents (such as methanol, isopropanol, *n*-propanol, isobutanol, *n*-pentanol and acetonitrile) at different temperatures. Only reactions using acetonitrile as a solvent showed 2-MNQ. Formation of 2-MNQ, indicating that acetonitrile is an appropriate choice of solvent for this

system. The highest 2-methylnaphthalene conversion (92%) was achieved at 120 °C, with a relative product selectivity of 51.4 %. Temperature showed a major effect on 2-MN conversion as at lower reaction temperature 100°C, the relative product selectivity (72%) seems to enhance; however, the drawback is the fact that lower 2-methylnaphthalene conversions (18%) are attained. Another important point to note is the fact that using an autoclave (with acetonitrile as a solvent), 2-methyl-1-naphthol was generated as a co-product.

Toluene hydroxylation reactions were only performed using the original batch method as this process seemed to work well and generating satisfactory results. It was therefore, not a necessity to continue with the use of the reflux or PTFE Parr autoclave. Aqueous hydrogen peroxide (30 wt-%) solution was added to a reactor containing water, or excess toluene, or acetonitrile solutions and passed over a zeolite TS-1 as catalyst with sample withdrawal done at 40, 60, 120, 180, 240, 300, and 360 min.

With water or acetonitrile as a solvent, calculated cumulative toluene consumption was observed to increase, with higher formation of either para- or ortho- cresol. In the triphase system at 80 °C, with water as a solvent, the desired para- cresol (0.009 mol/dm³) was the only observed product. For lower reaction temperature (60 °C), ortho-cresol was obtained at a concentration of 0.004062 mol/dm³ after 2 hours.

In reactions with using acetonitrile as a solvent, ortho-cresol (0.065 mol/dm³) was the favoured product; para- cresol (0.02 mol/dm³) was obtained at lower concentrations. When using acetonitrile as a solvent, cumulative toluene consumption (4.23 %) increased rapidly with time over a period of 6 hours and

the selectivity to ortho- cresol formation was highly favourable (5.72 mmol/mmol), especially at lower reaction time of 4 hours. Comparing both solvents, cumulative toluene consumption was strongly affected by choice of a solvent used in each reaction, and higher cumulative toluene consumption was obtained in acetonitrile (4.24%) than in water (0.46%) at reaction temperature 80°C.

In reactions with excess toluene, para-cresol was the favoured product. Cumulative toluene consumption was observed to increase slightly with reaction time (0.024 mol/dm³ after 4 hours).

Kinetic modelling of the reaction data obtained in toluene oxidation reactions was done with assumptions based on the first order model in both toluene and hydrogen peroxide. For the model, however, unselective decomposition of aqueous hydrogen peroxide was ignored. With all the data sets obtained in water as a solvent or excess toluene, the proposed model generated a good fit, with a reasonable fit obtained with acetonitrile as a solvent.

Toluene rate constants are strongly affected by solvent effects. This was seen when water was used as a solvent, at a reaction temperature of 80 °C giving a toluene rate constant of $1.87 \times 10^{-5} \text{ dm}^{-3}/\text{mol.m}^2.\text{min}$; using acetonitrile, the toluene rate constant was $1.34 \times 10^{-4} \text{ dm}^{-3}/\text{mol.m}^2.\text{min}$. In absence of a solvent (excess toluene), toluene rate constant was observed to decrease up to approximately $6.85 \times 10^{-6} \text{ dm}^{-3}/\text{mol.m}^2.\text{min}$. Solvent effects in toluene oxidation enhanced product formation, with para-cresol favoured when using water as a solvent, or ortho- cresol using acetonitrile as a solvent, while in absence of a

solvent (excess toluene), this reaction was slightly hindered although para-cresol was the favoured product.

In conclusion, it has been shown that the hydroxylation of different aromatic compounds over zeolites conducted in this study generated interesting findings. In 2-MN hydroxylation over Ti-MCM-41 as a catalyst, only acetonitrile is an appropriate choice of solvent using an autoclave. In addition, zeolite TS-1 is not a suitable catalyst for 2-MN hydroxylation reactions. It is ideal to optimise an autoclave in order to investigate reaction kinetics and optimum selectivity. Toluene hydroxylation reactions yielded para and ortho-cresol as expected with either water or acetonitrile as a solvent. No meta-cresol was formed. The kinetic model fitted generated a good fit with water as a solvent or excess toluene, with acetonitrile as a solvent generating a reasonable fit.

OPSOMMING

Aromatiese voorloper verbindings is afgeleides wat 'n belangrike rol speel in biosisteme en is bruikbaar vir die vervaardiging van fyn chemikalieë. Hierdie werk fokus op die katalitiese sintese van 2-metiel-1, 4-naftokwinoon en kresols (para- en orto-) deur gebruik te maak van waterige waterstofperoksied as 'n oksidant in die vloeistoffase-oksidasie van 2-metielnaftaleen en toluen oor titaniumvervangde zeoliet TS-1 of Ti-MCM-41.

Die katalis was verkalk by 550°C en ekstensief gekarakteriseer deur van tegnieke soos X-straal-fluoresensie gebruik te maak om die chemiese komposisie van die katalis vas te stel; BET is gebruik vir oppervlakarea, poriegrootte en mikroporievolume; Poeier-X-straal-difraksie is gebruik om die kristaliniteit en fase suiwerheid vas te stel en SEM om die morfologie van die katalis te ondersoek. Die BET-oppervlakarea vir Ti-MCM-41 het 'n area van 1025 m²/g opgelewer en 'n 0.575 cm³/g mikroporie volume. Zeoliet TS-1 het 'n BET-oppervlakarea van 439 m²/g en 'n 0.174 cm³/g mikroporievolume getoon.

Die aanvanklike eksperimente op 2-metielnaftaleen hidroksilasie was uitgevoer op die gewone enkelladingmetode. Na 'n reeks van enkelladinglopië sonder die suksesvolle vorming van enige produkte, soos bevestig deur gaskromatografie (GK), word 'n tweede eksperimentele opstelling voorgestel. Hierdie tegniek maak gebruik van die terugvloeiende sisteem by reaksietoestande soortgelyk aan dié van die enkelladingsisteem. Na die uitvoering van 'n aantal eksperimentele lopië en die optimering van die sisteem na verskeie reaktorbedryfstoeestande het steeds geen produkte gevorm nie en die gebruik van die terugvloeiende sisteem is gestaak. 'n Derde prosedure is dus ontwikkel wat gebruik maak van 'n PTFE-gelynde Parr-outoklaaf.

Die reaktorbedryfstoestand is aangepas om by die spesifikasies en vereistes van die outoklaaf te pas. Belowende resultate is verkry met die vorming van 2-MNQ. Ongelukkig is dit met die outoklaaf slegs moontlik om een lesing te kry aan die einde van elke lopie, daarom was dit nie moontlik om die reaksiekinetika as 'n funksie van tyd te bepaal nie.

Die reaktor bevat 2-metielnaftaleen en die katalis in 'n gepaste oplosmiddel (metanol, asetonitriël, 2-propanol, 1-propanol, 1-pentanol en butanol). Waterige waterstofperoksied (30 m-%) oplossing was op een slag aan die begin van elke reaksie hierby bygevoeg. Monsters is geneem oor 'n tydperk van 6 uur (uitgesluit die katalitiese eksperimente gedoen met die Parr outoklaaf omdat die neem van monsters onmoontlik was).

Soos verwag het geen reaksie plaasgevind met die gebruik van medium poriegrootte zeoliet TS-1 nie. Dit word toegekryf aan die hoë komposisie van 2-metielnaftaleen wat diffusie in die zeolietkanale verhinder.

Met die gebruik van 'n outoklaaf het Ti-MCM-41 gekataliseerde reaksies getoon dat die keuse van oplosmiddel en reaksietemperature 'n groot invloed het op 2-metielnaftaleen se omsetting en produkselektiwiteit. Dit was bewys deur 'n reeks oplosmiddels te vergelyk by verskeie temperature. Slegs reaksies wat van asetonitriël as oplosmiddel gebruik maak het 2-MNQ gevorm wat aandui dat dit 'n gepaste keuse is vir die sisteem. Die hoogste omsetting was 92 % by 120°C met 'n relatiewe produkselektiwiteit van 51.4 %. Die temperatuur toon 'n beduidende effek op 2-MN omsetting bv. by 'n laer temperatuur van 100°C is die relatiewe produkselektiwiteit hoër (72 %), maar ten koste van 'n laer omsetting (18 %). Nog 'n belangrike punt om te noem is die vorming van 2-

metiel-1-naftol as byproduk met die gebruik van die outoklaaf met asetonitriël as oplosmiddel.

Tolueen hidrosilasie reaksies is slegs uitgevoer volgens die oorspronklike enkelladingmetode aangesien dit bevredigende resultate gee. Die Parr-outoklaaf is dus nie verder gebruik nie. Waterige waterstofperoksied (30 m-%) oplossing was bygevoeg by 'n reaktor wat óf water- óf oormaat tolueen- óf asetonitriël- oplossings bevat en is toegelaat om te vloei oor 'n zeoliet TS-1 katalis. Monsters was geneem by 40, 60, 120, 180, 240, 300 en 360 minute.

Met water of asetonitriël as oplosmiddel word waargeneem dat die berekende kumulatiewe tolueengebruik toeneem by 'n optimum reaksietemperatuur van 80°C met 'n hoë produksie van para- of orto-kresol. In die drie-fase sisteem by 80°C met water as oplosmiddel was die verlangde para-kresol (0.009 mol/dm³) die enigste waarneembare produk. Vir laer reaksietemperatuur (60°C) is 0.004062 mol/dm³ orto-kresol verkry na 2 ure.

Reaksies wat van asetonitriël as oplosmiddel gebruik maak begunstig die vorming van orto-kresol (0.065 mol/dm³); para-kresol (0.02 mol/dm³) was teenwoordig in laer konsentrasies. Verder het die kumulatiewe tolueenverbruik (4.23 %) drasties toegeneem met tyd oor 'n tydperk van 6 uur en die selektiwiteit vir orto-kresol vorming was baie gunstig (5.72 mmol/mmol), veral by 'n laer reaksietyd van 4 ure. Deur albei oplosmiddels te vergelyk kan waargeneem word dat 'n hoër kumulatiewe tolueenverbruik verkry is met asetonitriël (4.24 %) as met water (0.46 %) by 80°C.

In reaksies met oormaat toluen is para-kresol die begunstige produk. Die kumulatiewe toluenverbruik het effens toegeneem met 'n toename in reaksietyd (0.024 mol/dm³ na 4 ure).

Die kinetiese modelering van die reaksiedata verkry in toluenoksidasiereaksies was uitgevoer met die aanname gebaseer op die eerste-orde-model in beide toluen en waterstofperoksied. Die onselektiewe dekomposisie van waterige waterstofperoksied nie in ag geneem nie. Vir al die datastelle met water of oormaat toluen as oplosmiddel het die voorgestelde model goed gepas. Die gebruik van asetonitriël as oplosmiddel het die model redelik gepas.

Toluën reaksiesnelheidkonstantes is baie beïnvloed deur die oplosmiddeleffekte. Dit was waargeneem dat wanneer water as oplosmiddel gebruik is by 'n reaksietemperatuur van 80°C die reaksiesnelheidkonstante $1.87 \times 10^{-5} \text{ dm}^{-3}/\text{mol} \cdot \text{m}^2 \cdot \text{min}$ is. Asetonitriël as oplosmiddel lewer $1.34 \times 10^{-4} \text{ dm}^{-3}/\text{mol} \cdot \text{m}^2 \cdot \text{min}$. In die afwesigheid van 'n oplosmiddel (oormaat toluen), neem die reaksiesnelheidkonstante toe tot ongeveer $6.85 \times 10^{-6} \text{ dm}^{-3}/\text{mol} \cdot \text{m}^2 \cdot \text{min}$. Oplosmiddeleffekte in toluenoksidasie het produkvorming verhoog met para-kresol begunstig as water die oplosmiddel is en orto-kresol in die geval van asetonitriël as oplosmiddel, terwyl in die afwesigheid van 'n oplosmiddel (oormaat toluen) die reaksie effens verhinder was alhoewel para-kresol steeds die begunstige produk was.

In gevolgtrekking, dit is bewys dat die hidroksilasie van verskillende aromatiese verbindings oor zeoliet uitgevoer in die studie die volgende interessante bevindinge opgelewer het. In 2-MN hidroksilasie oor Ti-MCM-41 as katalis is slegs asetonitriël 'n gepaste keuse vir oplosmiddel met die gebruik van 'n

outoklaaf. Zeoliet TS-1 is nie 'n gepaste katalis vir 2-MN hidroksilasie reaksies nie. Dit is gewens om 'n outoklaaf te optimeer om sodoende die reaksiekinetika en optimum selektiwiteit te ondersoek. Tolueenhidroksilasie reaksies lewer para- en orto-kresol soos verwag met óf water óf asetonitriël as oplosmiddel. Geen meta-kresol het gevorm nie. Die kinetiese model lewer 'n goeie passing met water en met oormaat tolueen as oplosmiddel en 'n redelike passing vir die gebruik van asetonitriël as oplosmiddel.

DEDICATION

I want to dedicate this piece of work to my late mother Nowinile Priscilla Gqogqa. These past two years have not been the best years after her tragedy in January 2006 when I started with my masters, I feel at least this work will make her proud and her soul rest in peace.

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Nomenclature

Abbreviations

AAS	Atomic Absorption Spectroscopy
BET	Brunauer-Emmett Teller Isotherm
GC	Gas Chromatography
GC-MS	Gas Chromatography- Mass Spectra
HPLC	High Performance Liquid Chromatography
IR	Infra-Red
SEM	Scanning Electron Microscopy
UV-VIS	Ultraviolet- Visible
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
EDX	Energy Dispersive X-ray
1-OH—2MN	1-hydroxy-2-methylnaphthalene
DOH-2MN	Dihydroxy-2-methylnaphthalene
2-M-1,4-DOHN	2-methyl-1,4-dihydroxy-naphthoquinone
2-M-1-OHN	2-methyl-1-hydroxy-naphthalene
Fe	Iron
Ti	Titanium
MNL	2-methyl-1-naphthol

Indices

0	Initial
MN	Methylnaphthalene

MNQ	2-Methy-1, 4- naphthoquinone
Ox	Oxidant (hydrogen peroxide)
Tol	Toluene
O	Ortho cresol
P	para cresol

Symbols

A_i	Absolute area of species i	[a/u]
C_i	Concentration of species i	[mmol/dm ³]
k_i	Formation or consumption rate constant of compound i	[dm ³ /mmol.m ² .s]
M_r	Molar mass	[g/mol]
m	Mass	[g]
n_i	Moles of species i	[mol]
r_i	Rate of formation/ consumption of compound i	[mmol.s.m ²]
RF_i	Response factor of species i	
S_i	Molar selectivity of species i	[%]
T	Reaction time	[hr, min]
V_i	Volume of compound i	[ml or dm ³]
X_i	Conversion of species i	[mol-%]
x_i	Mass fraction of species i	
y_i	Molar fraction of species i	

1. Introduction

It is of high importance in organic synthesis to develop and implement chemical processes that reduce or avoid the generation of waste and hazardous substances that are detrimental and harmful to the environment and therefore, cause pollution. In general, catalytic oxidation is a useful protocol that is used industrially for hydrocarbon feedstock conversion leading to the production of industrial chemicals on a large scale (Sheldon, R.A., 1993). Selective oxidation of aromatic compounds offers an efficient access to substituted 1, 4-quinones that exhibit biological activity and are used importantly in the synthesis of medicines and production of fine chemicals (Khavasi, H.R., et al., 2002; Zalomaeva, O.V., et al., 2006; Pérollier, C., et al., 2005; Kholdeeva, O.A., et al., 2005; Minisci, F., et al., 1992).

An aromatic compound is an organic compound that contains a benzene ring and characterised by the presence of alternating double bonds within the ring. Aromatic compounds tend to undergo ionic substitution, with the replacement of hydrogen, bonded to the ring with some other group. Processes that are currently adopted generate a lot of interest focusing on developing oxidation reactions that make use of cleaner waste-avoiding oxidants that are safer and more environmentally friendly, to substitute stoichiometric processes that generate large toxic waste.

An aromatic compound such as toluene has been neglected in the last decade in favour of phenol and this aromatic compound has attracted a lot of attention and focus in the field of catalysis. There is little information known in the literature regarding reactions involving oxidation of toluene, reaction kinetics

and mechanisms. Selective oxidation of toluene produces cresols (para, ortho, and meta cresol), used industrially as chemical intermediates.

1.1. Selective Oxidation of 2-methylnaphthalene

The major focus on heterogeneous catalysts instead of reactions involving homogeneous catalysts has been assigned mainly to environmental concerns, the elimination of waste production and avoiding the use of toxic or hazardous materials (Zalomaeva, O.V., et. al., 2006; Sheldon, R.A., 2000). The fine chemical industry abounds with processes involving classical “stoichiometric” technologies such as sulfonation, nitration, chlorination, bromination, diazotization, and Friedel-Crafts alkylations. These stoichiometric processes produce large quantities containing aqueous effluents of inorganic salts (Sheldon, R.A., 1993). Therefore, there is a growing need for high atom utilisation low-salt processes, like catalytic oxidations, hydrogenations and carbonylations (Sheldon, R.A., et al., 1994). By definition, atom utilisation is a process generated by dividing molecular weight of a desired product by the sum of molecular weights of all products formed in a process.

The major drawback in the production of fine chemicals and specialities is the use of stoichiometric rather than catalytic technologies and also the use of stoichiometric reagents such as potassium dichromate and potassium permanganate (which results in deposition and formation of toxic waste) other than using heterogeneous catalysts (Sheldon, R.A., 1993; Sheldon, R.A., et al., 1994; Sheldon, R.A., 2000). The nature of waste is an important factor and a more sophisticated approach to develop cleaner processes and is expressed in terms of environmental quotient (EQ), described as the E- factor. By definition, the E- factor is the mass ratio of waste to the desired product (Sheldon, R.A., et

al., 1994). The high importance of knowing the actual impact of toxic waste deposited in the environment resulted in the introduction of the “environmental quotient (EQ)”, defined as:

$$EQ = E \text{ (kg waste/ kg product)} \times Q \text{ (unfriendliness quotient)}$$

The environmental acceptability E-factors for aromatic oxidation are shown in Table 1.

Table 1: Environmental acceptability E- factors for aromatic oxidations (Sheldon, R.A., 1993)

Industry Segment	Product Tonnage	E-factor (Kg By-Products/ Kg Products)
Oil Refining	10 ⁶ - 10 ⁸	Ca. 0.1
Bulk Chemicals	10 ⁴ - 10 ⁶	< 1 – 5
Fine Chemicals	10 ² – 10 ⁴	5 -50
Pharmaceuticals	10 – 10 ³	25 -> 100

As mentioned above, stoichiometric oxidation of aromatic compounds results in large amounts of toxic heavy metal waste (Zalomaeva, et. al., 2006; Shi, F., et al., 2007). A typical problem, as illustrated in Figure 1, is the production of synthetic vitamin K₃ (2-methyl-1, 4-naphthoquinone, menadione, 2-MNQ) via the stoichiometric oxidation of 2-methylnaphthalene (2-MN) with chromic acid (CrO₃) in sulphuric acid.

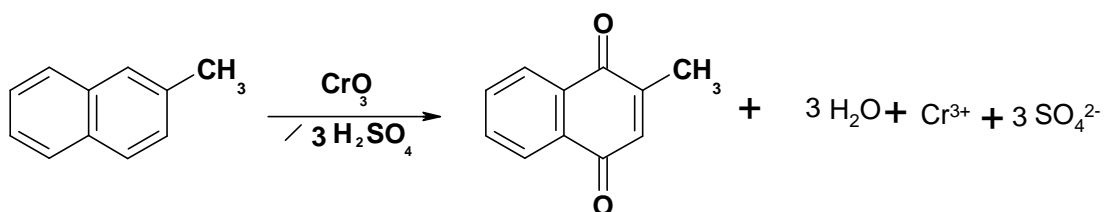


Figure 1: Stoichiometric oxidation of 2-methylnaphthalene with chromium in sulphuric acid. Redrawn from (Kholdeeva, O.A., et al., 2005).

Although, this stoichiometric reaction generates quinones with reasonable yields, the very low active oxygen content in the used oxidants leads to a significant amount of waste, causing a lot of serious ecological hazards when disposed, producing about 18 kg of inorganic waste per 1 kg of target product (Sheldon, R.A., 1996; Zalomaeva, O.V., et al., 2006; Kholdeeva, O.A., et al., 2005; Narayanan, S., et al., 2002; Herrmann, W.A., et al., 1999; Shi, F., et al., 2007).

Recent investigations in literature illustrate the best method for selective oxidation of 2-methylnaphthalene is achieved with glacial acetic acid and sulphuric acid as catalyst, generating high yields (approximately 80 %). It is noteworthy, a major drawback of all the existing stoichiometric oxidation procedures is the use of acidic solvents like acetic acid, or the necessity to add inorganic acid catalysts, resulting in environmental pollution and more serious corrosion problems on a large scale (Shi, F., et al., 2007). The establishment of cleaner catalytic, environmentally friendly methods using catalytic quantities of metal complexes immobilised on solid support such as zeolites has been proposed because zeolites provide selective aromatic oxidation and allow their easy separation from the reaction mixture (Shi, F., et al., 2007; Zalomaeva, O.A., Sorokin, A.B., 2006). Therefore, in heterogeneous processes, instead of the traditional oxidants, for example, potassium dichromate, oxidants like oxygen, hydrogen peroxide or percarboxylic acid are applied.

Production of 2-methyl-1, 4-naphthoquinone in catalytic oxidation reactions in liquid phase is of major interest as this product is environmentally friendly and avoids product contamination by traces of transition metals (Kholdeeva, O.A., et al., 2005; Shi, F., et al., 2007). In this research work, the main focus is on

studying the feasibility of producing 2-methyl-1,4-naphthoquinone via the hydroxylation of 2-methylnaphthalene with hydrogen peroxide which is a potentially “green” process with minimal toxic side products.

Another interesting part in the synthesis of 2-methyl-1, 4-naphthoquinone is the focus on economics. Vitamins are classified as typical fine chemicals, with prices above US \$10 per kg and production volumes of about 1000–10,000t per annum. However, few known vitamins are classified in the class of bulk chemicals. The application of 2-methyl-1, 4-naphthoquinone has been intense in the animal feed industry, due to high costs of phylloquinone (vitamin K₁). The synthesis of phylloquinone is important for use in infant formula, medical foods, and pharmaceuticals. However, the addition of 2-methyl-1, 4-naphthoquinone to animal feed is important specifically to poultry rations since chemotherapeutic agents against coccidiosis and parasitic diseases inhibit intestinal synthesis and increase the dietary requirements of the chicken (Reto, M., et al., 2007).

In addition, there is a high demand for production of 2-methyl-1, 4-naphthoquinone and its derivatives as 2-methyl-1, 4-naphthoquinone possesses more antibleeding activity than phylloquinone and menaquinone (vitamin K₂). The major drawback for using 2-methyl-1, 4-naphthoquinone is its toxicity. This problem is solved by using water soluble analogs of 2-methyl-1, 4-naphthoquinone instead, namely, menadione sodium bisulphate (MSB), menadione sodium bisulphite complex (MSBC), and menadione dimethyl-pyrimidinol bisulphite (MPB), which are less toxic, adsorb more efficiently and are more adequate for Human consumption (Wagner A.F. and Folkers K, 1964).

1.2. Selective Oxidation of Toluene

The hydroxylation of toluene has some similarities to the hydroxylation of 2-methylnaphthalene. However, this is a simpler system with less potential intermediate and side-products. Although progress has been reported in using hydrogen peroxide and titanium zeolites in the oxidation of benzene, toluene, xylene and anisole, reaction kinetics for the formation of cresols are still unknown.

In general, toluene is a low cost, readily available chemical that has been neglected in favour of phenol. The market price reports for meta-cresol worth \$6.60/Kg, with ortho-cresol market price of \$4.70 /Kg and para-cresol worth \$2.80/Kg respectively (<http://www.infobanc.com>). Hydroxylation of toluene as illustrated in Figure 2 produces cresols, which are used industrially, medicinally and as chemical intermediates.

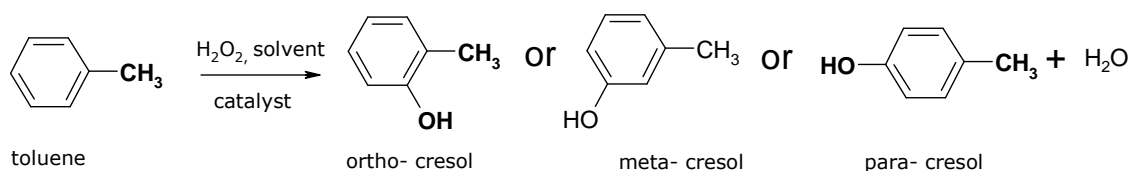


Figure 2: Different types of cresols produced from the selective hydroxylation of toluene.

The formation of functional organic compounds like cresols using zeolites, leads to a well-known paradox of heterogeneous catalysis, known to be caused by high polarity of cresol compared with the relatively unpolar reactant toluene. A product inhibition and a subsequent deactivation of the zeolite are assumed to play a major role, with previous studies focused mainly on the effect of different catalysts and system phases (Kumar, R., et al., 1998).

However, the purpose of this project is to investigate the possibility of enhancing the selectivity and yield of para- cresol through a variation of system parameters, such as temperature and assessing solvent effects in the production of these cresols. It has been reported that most industries providing cresols produce equivalent amounts of the three cresols, with by- products, e.g., aldehydes and dihydroxy compounds as expected products. Laboratory synthesised cresol mixtures are known to consist of only the para- and ortho- products (Marchal, C., et al., 1993; Kumar, R., et al., 1999; Kumar, R., et al., 1998).

Initial work at the University of Stellenbosch investigating toluene hydroxylation reactions with hydrogen peroxide using an in-house synthesised zeolite TS-1 catalyst, observed the production of para-cresol to enhance with increasing reaction temperature, with very low ortho- cresol formation. In water as a solvent, a product yield of 4.6% at 80 °C compared to 0.18% at 60 °C was obtained. With methanol as a solvent, no product formation was attained. It was suggested that tar formation is rapid in this case and hinders catalytic activity. In conclusion, the improved product selectivities and yields are obtained at elevated reaction temperatures, thus water as a solvent favours formation of para-cresol, and no meta-cresol was found with HPLC with all reactions (Engelbrecht, J.M.M., 2006).

2. Research Objectives

This chapter provides a brief description of the research objectives. This work focuses on the hydroxylation of two aromatic compounds, namely, 2-methylnaphthalene and toluene.

2.1 2 - Methylnaphthalene Hydroxylation

Over the past decades, a lot of research has been done in the synthesis of phenolic derivatives with aqueous hydrogen peroxide as an oxidant and titanium-substituted molecular sieves. Industrially, however, the stoichiometric processes employed in the oxidation of 2-methylnaphthalene, as described in section 1.1, produced large amounts of toxic waste. Therefore, there is a growing need for cleaner processes (Kholdeeva, O.A., et. al., 2005; Sheldon, R.A., 1993; Zalomaeva, O.V., et. al., 2006).

This study aims to investigate the selective oxidation of 2-methylnaphthalene with aqueous hydrogen peroxide as an oxidant over titanium- substituted zeolites and mesoporous materials as catalysts. Factors that affect 2-MN conversions and generation of 2-MNQ are carefully investigated. These factors include: (i) solvent effects, (ii) reaction temperature, (iii) catalyst type, and (iv) the best catalytic procedure that generates 2-MN conversions and better 2-MNQ yields.

The effect of using different types of solvents in 2-methylnaphthalene oxidation is monitored by employing a wide range of primary alcohols to long chains alcohols, and nonprotic solvents. The type of solvents that were investigated

include: methanol, n-butanol, n-propanol, iso-propanol, n-pentanol and acetonitrile.

In this work, synthesised catalysts (TS-1 or Ti-MCM-41) are extensively characterised, hence, diffusion constraints and the suitable catalyst choice that generates higher 2-MN conversions and higher 2-methyl-1, 4-naphthoquinone (2-MNQ) yield is assessed by performing catalytic reactions over zeolite TS-1 or Ti-MCM-41 as catalysts.

The effect of different procedures was investigated by employing the normal batch method, or the reflux technique or the Parr PTFE autoclave. This study is a feasibility study, investigating factors that might enhance reproducibility of 2-methyl-1, 4-naphthoquinone yields and generate higher selectivities, therefore, providing higher 2-methylnaphthalene conversions. According to our knowledge, there has been challenges in catalytic oxidations of 2-methylnaphthalene with only Anunziata (1999)'s work reporting a comparative study concerning the use of Ti-containing zeolites (TS-1) and titanium mesoporous materials (Ti-MCM-41), with little information regarding the reaction mechanisms and other products that might be generated other than 2-MNQ. Therefore, this research work has a tremendous interest and is a challenging reaction in catalysis with very little work done in the past decade.

2.2. Toluene Hydroxylation

In literature, studies on toluene hydroxylation have been neglected while much work has focused on phenol, with phenol reactions leading to the formation of hydroquinone and catechol.

Production of cresols from toluene oxidation is a major goal, industrially and chemically. The study aims to investigate the selective hydroxylation of toluene using aqueous hydrogen peroxide as an oxidant over zeolite TS-1 as a catalyst.

This work focuses primarily on determining system conditions that enhance product selectivity and generates good yields of expected cresols (that is, para and ortho). This is achieved by investigating the effects that changes in the system parameters have on the yield and selectivity of cresols. The factors that were investigated include: (i) the choice of a solvent used (ii) reaction temperature. Solvent effects were investigated by employing water or acetonitrile as solvents or by performing the reactions with toluene in excess.

2.3. Hypotheses

2.3.1 2 - Methyl naphthalene Hydroxylation

The following hypothesis was proposed based on the findings in literature:

2-MN conversion and 2-MNQ yield can be enhanced by choosing a suitable solvent, reaction temperature and a catalyst type that allows diffusion of 2-MN reactant.

2.3.2. Toluene Hydroxylation

The proposed hypothesis for this part of work was:

A set of reaction parameters that generate the yield and selectivity of para or ortho-cresol may be achieved when one or a combination of system conditions, such as reaction temperature and choice of a solvent are varied.

3. Literature Review

3.1. Hydroxylation of Aromatic Compounds

3.1.1. 2- Methyl-naphthalene hydroxylation

The need to create materials with high selectivities and yields using titanium-substituted zeolites and mesoporous materials has triggered a lot of interest in the synthesis of 2-methyl-1,4-naphthoquinone (2-MNQ).

The catalysed hydroxylation of 2-methylnaphthalene with aqueous hydrogen peroxide as an oxidant, leading to 2-methyl-1,4-naphthoquinone has been a challenging goal in catalysis research as first published by Anunziata et al. (1999). The production of 2-methyl-1,4-naphthoquinone has mainly pharmaceutical applications due to its function as a blood coagulant, attributed to being essential for the functioning of several proteins involved in blood clotting. Two commonly known natural occurring forms are phylloquinone, synthesised by plants, and a range of vitamins synthesised by bacteria, using repeating 5-carbon units in the side chain of the molecule designated as menaquinone-n (MK-n). 2-methyl-1,4-naphthoquinone is the synthesised form of vitamin K (<http://lpi.oregonstate.edu/>).

In addition, the most commonly known biological role of vitamin K is that of the required coenzyme for a vitamin K-dependent carboxylase that catalyses the carboxylation of the amino acid, glutamic acid, resulting in its conversion to gamma-carboxyglutamic acid (Gla). Although, vitamin K-dependent gamma-carboxylation occurs only on specific glutamic acid residues in a small number

of proteins, it is critical to the calcium-binding function of those proteins (<http://lpi.oregonstate.edu/>).

The ability to bind calcium ions (Ca^{2+}) is required for the activation of the 7 vitamin K-dependent clotting factors (normally found in the liver) in the coagulation cascade (referring to a series of events dependent on each other to stop bleeding through clot formation), with the core of this coagulation cascade made up by factors II (prothrombin), VII, IX, and X. Risks in clot formation block the flow of blood in arteries of the heart, brain, or lungs, resulting in massive heart attacks, stroke, or pulmonary embolism, respectively (Wagner, A.F., and Folkers, K., 1964; (<http://lpi.oregonstate.edu/>; Reto, M., et al., 2007).

McDowell (1989) found vitamin K (substituted 1, 4-naphthoquinones) to be required in infants mostly due to poor placental transfer and absence of bacterial synthesis in the newborn's gut. Adults also develop a deficiency under conditions where fat absorption is impaired or suffering from liver disease, resulting in lower blood levels of vitamin K-dependent clotting factors and increased risk of uncontrolled bleeding (haemorrhage, produces bleeding in the skin, subcutaneous tissue, GI tract, umbilical cord, and intracranium). However, haemorrhage develops due to inadequate supplies of the bile which results to hypotherbinemia (Wagner A.F. and Folkers K, 1964).

Approximately, 40 - 50 % of the average person's daily requirement is derived from plant sources (phylloquinone, vitamin K_1) and the remainder from microbial synthesis (menaquinone, vitamin K_2), with the range of 2-200 μg vitamins K per kilogram body weight. Deficiency can be prevented by phylloquinone injection at birth (Eitenmiller, R.R. and Landen, W.O. Jnr., 1999).

An estimated recommended daily dose of 1-2 mg vitamin K for newborn infants or 2-5 mg daily to the parturient mother is administered (McDowell, L.R., 1989). The preferred daily requirement of adults is estimated to be about 1mg (Marks, 1975; RDA, 1980), with minimal daily requirement as low as 0.03 µg/kg body weight (Frick, P.G., et. al., 1967). The routine administration of phylloquinone, either maternally or neonatally, for the prevention of haemorrhage in the infant, has been questioned. It has been suggested that synthetic water- soluble analogs of menadione be administered in doses of 2-5 mg for the mother or 1- mg for the infant only in situations such as premature delivery, anoxia, or erythroblastosis which are normally conducive to neonatal haemorrhage. (Wagner A.F. and Folkers K, 1964).

The synthesised 2-methyl-1, 4-naphthoquinone cannot be used for human consumption due to its toxicity, however its water soluble analogs, namely, sodium bisulphate (MSB), menadione sodium bisulphite complex (MSBC), and menadione dimethyl-pyrimidinol bisulphite (MPB), can be administered in the absence of bile more than phylloquinone, which is poorly absorbed (Wagner A.F. and Folkers K, 1964).

3.1.1.1. Relationship between Structure and Activity

The effect of antihemorrhagic activity in vitamin K compounds is found only in 1, 4- naphthoquinone series. Highest activities are achieved when a synthesised compound consist a 2-methyl substituent. In addition, an increase in the number of carbon atoms in the 2- methyl substituent lowers activity significantly. The double bond at 2'-position of the 3- substituent is the only centre of unsaturation which increases activity (Wagner A.F. and Folkers K, 1964).

The presence of a hydroxyl on either the 1, 4- naphthoquinone nucleus or in the side chain resulted in the loss of activity. The structure - activity requirements for the effective reversal of vitamin K antagonists are different from those required to prevent the characteristic hemorrhagic syndrome in the dietary-induced deficiency. Only the derivatives with a comparative large substituent at the 3- positions are effective in reversing the antagonism of dicumerol in the rat and dog. Derivatives with less than eight carbon atoms in the side chain are essentially inactive. Methyl branching or unsaturation in the side chain are not essential for activity, but such functional groups enhance activity (Wagner A.F. and Folkers K, 1964).

3.1.1.2. Antagonists

Deficiency of vitamin K is brought about by ingestion of dicumerol (which are produced by molds), an antagonist of vitamin K, or introduced by feeding of sulfonamides (in monogastric species) at levels sufficient to inhibit intestinal synthesis of vitamin K. Mycotoxins, toxic substances produced by molds, are also antagonists causing vitamin K deficiency. Hemorrhagic disease of cattle described in the 1920s was traced to consumption of moldy sweet clover hay. The destructive agent is found to be dicumarol, a substance produced from natural coumarins. When toxic hay or silage is consumed by animals, hypoprotheminemia results, presumably because dicumarol combines with the proenzyme to prevent the formation of the active enzyme, for the synthesis of prothrombin (Wagner A.F. and Folkers K, 1964). Dicumarol also serves as an anticoagulant in medicine to slow blood coagulation in people afflicted with cardiovascular disease to avoid intravascular blood clots, just as vitamin K under other conditions increases the coagulation time. Thus, vitamin K will

overcome this action by dicumarol. Goplen and Bell (1967) have showed in cattle that phyloquinone is much more potent as an antidote to dicumarol than is 2-methyl-1, 4-naphthoquinone. The most successful dicumarol for the long term lowering of vitamin K- dependent clotting factors is warfin which is widely used as a rodenticide.

3.1.1.3. Types of Vitamin K

Mechanical, chemical and physical properties of different types of vitamin K are listed in Table 2.

Table 2: Different types of Vitamin K (Eitenmiller, R. R., and Landen, W.O. Jnr.; 1999; Frick, P.G., et al., 1967; McDowell .R., 1989)

Vitamin Type	K	Chemical Nature	Chemical Formula	Properties	Crystal Form	Sources
Phylloquinone (Vitamin K ₁)		3-methyl-3-phytyl-1,4-naphthoquinone	C ₃₁ H ₄₆ O ₂	Only one double bond as a 20 side chain derived from 4 isoprenoid units. Exist naturally on its trans- form.	No crystals; yellow oil	Synthesised by plants such as green leafy vegetables
Menaquinone-6 (Vitamin K ₂)		2-methyl-3-(prenyl) _n - 1, 4 - naphthoquinone	C ₄₁ H ₅₆ O ₂	Consists up to 13 prenyl groups in the unsaturated 35 C side chain of 7 isoprenoid units	Yellow crystals	Bacterial synthesis in stomach by microorganisms such as <i>Microflora</i>
Menadione Vtamin K ₃		2-methyl- 1, 4- naphthoquinone	C ₁₁ H ₈ O ₂	No side chain at position 3. A derivative of all vitamin K compounds	Bright yellow crystals	Synthesised form

3.1.2. Toluene Hydroxylation

The demand of toluene has started to increase more importantly, due to a critical feedstock for a few important chemicals. Toluene has a wide range of uses in the chemical industry. Some of these uses are, depending on location, the production of benzene by dealkylation, the application as an aromatic solvent, the production of toluene sulfonic acids or cymenes that lead to the formation of cresols, production of toluene diisocyanate through nitrotoluene intermediates and the manufacture of the oxidation products benzaldehyde, benzoic acid to phenol, and benzyl alcohol (Mukhopadhyay, A.K., 2005; Franck, H.-G. and Stadelhofer, J.W., 1988).

In liquid phase catalytic oxidation of toluene, hydrogen peroxide donates the hydroxyl group to the aromatic ring. This hydroxyl substitution depends on the mechanism of the reaction which is determined by reaction parameters, for example solvent effects and temperature variation. The substitution of a hydroxyl group leads to the formation of three cresol isomers as shown in Figure 3. In oxidation of toluene using aqueous hydrogen peroxide as an oxidant, water is a by-product. Side reactions such as formation of aldehydes and methylbenzene diols may result due to further oxidation and prolonged reaction time.

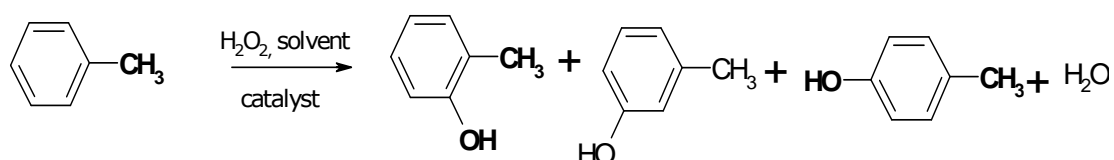
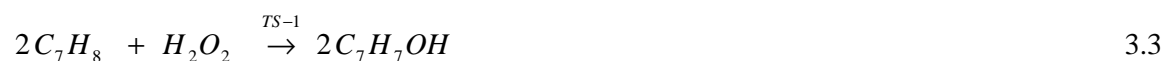
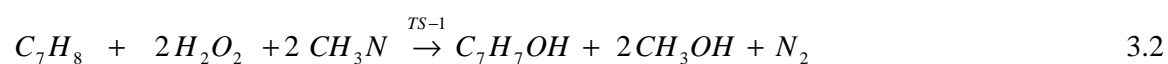
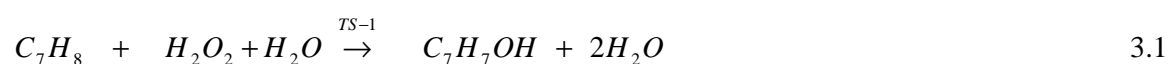


Figure 3: Formation of cresols from toluene hydroxylation reaction.

In literature, the only by product that is mentioned to be generated in toluene reactions catalysed by TS-1 is water. However, in this work the by products that may form in hydroxylation of toluene using hydrogen peroxide as oxidant in water or acetonitrile as solvents over TS-1 catalyst are presented by the balanced chemical reactions derived as follows:



By definition, cresols are the mono-methyl derivatives of phenol that were discovered in coal tar in 1854 by a scientist Alexander Wilhelm Williamson. For a very long period, coal tar was the most important source of cresols in the industry until the mid- 1960's as the natural source of cresols became inadequate (Franck, H.G., and Stadelhofer, J.W., 1988). The production of synthetic cresols from toluene opened up new developments for these products. However, the isolation of pure p-cresol from an isomeric mixture of m-, p-, o-cresols was a serious problem in organic synthesis (Mukhopadhyay, A.K., 2005).

3.1.2.1. Relationship between Structure and Activity

The effect of how the hydroxylation occurs to the methyl group is of high importance. The result of toluene hydroxylation generating either ortho-, para- and meta- carbocation products is determined by nucleophilic attack at the methyl group. It is known that all cresol intermediates are resonance stabilised,

but the ortho and para are reported to be more stabilised than the meta-cresol. Therefore, for both the para and ortho intermediates, a resonance form places the positive charge directly on the methyl-substituted carbon, where it is in a tertiary position and can best be stabilised by the electron-donating inductive effect of the methyl group. However, the para and ortho intermediates are lower in energy than the meta intermediate and, as a result, these intermediates form faster (McMurry, J., 2000).

3.1.2.2. Different Types of Cresols

The physical and chemical properties of cresols are illustrated in Table 3.

Table 3: Different types of cresols (Mukhopadhyay, A.K., 2005)

Cresol Type	Chemical Formula	Properties	OH- Position
Ortho-cresol	C ₇ H ₈ O	Melting point: 31 °C Boiling point: 191 °C	Ortho position (Most stable)
Meta- cresol	C ₇ H ₈ O	Melting point: 12 °C Boiling point: 202 °C	Meta position
Para- cresol	C ₇ H ₈ O	Melting point: 34 °C Boiling point: 201 °C	Para position (Most stable)

3.2. Heterogeneous Catalysts

In oxidation reactions, the major disadvantage of using homogeneous catalysts is associated with problems concerning catalyst separation that may result in contamination of the target product with hazardous transition metal compounds

(Kholdeeva, O.A., et al., 2002). Due to increasing environmental concerns, the quest for cleaner catalytic methods such as using heterogeneous catalysts instead of homogeneous catalysts, in the production of fine chemicals and specialities is of great demand (P  rollier, C., et al., 2005). The obvious advantage of heterogeneous catalysts in liquid phase oxidations is the ease of recovery, recycling and suitability for continuous fixed-bed operation (Sheldon, R.A., and Dakka, J., 1994).

A typical example of a heterogeneous catalyst is observed employing a Ti^{IV}/SiO_2 catalyst with aluminium replacing titanium in the Si-O-Al cluster instead of the normal Si-O-Ti cluster as illustrated in Figure 4.

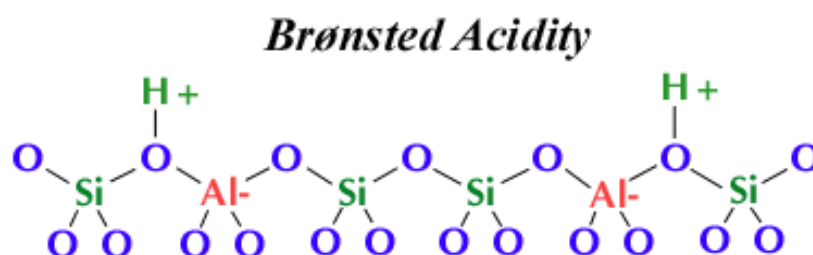


Figure 4: Acid-based zeolite catalysts with Br  nsted acid sites, containing H^+ ion localised near a bridging Si-O-Al cluster (<http://atom.ecn.purdue.edu/~thomsonk/projects.html>).

In liquid phase oxidation, heterogeneous catalysts can be divided into 3 categories, namely: (i) supported metals (e.g. Pt/ C), (ii) supported metal ions and complexes (metal ions on ion exchange resins, metal- ion exchange zeolites and metal encapsulated in zeolites), (iii) supported oxo-metal (oxidic) catalysts (Ti^{IV}/SiO_2 and redox molecular sieves) (Sheldon, R.A., and Dakka, J., 1994).

By definition, heterogeneous catalysts are zeolites which are microporous crystalline solids with cages of molecular dimension that accept or reject in a selective way certain reactants or products, on the basis of their shape. There are four desirable attributes of a heterogeneous catalyst that include activity, selectivity, stability and accessibility. Activity, selectivity, and stability are attributes that also apply in homogeneous catalysis, but accessibility is an attribute specific to catalysis by solids. Another drawback that led to limited use of homogeneous catalysts is generally attributed to the concern that the homogeneous oxidations are unselective, as a result of unhindered accessibility, yielding a complex mixture of potentially valuable products which requires an elaborate refinery for separation (Hucknall, D.J., 1974).

In oxidation reactions a major key in obtaining cleaner processes is selectivity. There are various commonly used types of selectivity that include: chemoselectivity (competing reactions at different functional groups), regioselectivity (ortho versus para substitution in aromatics), and stereoselectivity (enantio- or diastereoselectivity) (Sheldon, R.A., and Dakka, J., 1994). The incorporation of redox sites in the zeolite network creates selective oxidation catalysts with optimal activities and selectivities. In addition, zeolites with titanium (Ti) or vanadium (V) catalyse the selective oxidation of alkanes, aromatics and epoxidation of olefins (Anunziata, O.A., et al., 2004).

Behind the chemical functioning of heterogeneous catalysts, diffusion of heat and mass into and out of their surface is always an important principle irrespective of whether the catalysts are porous or not. However, the lacking gradients of concentration and temperature hinders the process of transporting reactants, products and generation of heat.

Despite all the advantages mentioned above, the use of heterogeneous catalysts in liquid phase reactions does have some serious problems, especially when using aqueous hydrogen peroxide as an oxidant. This is of concern due to the possibilities of leaching of the metal ion into the solution when aqueous hydrogen peroxide is used. But this problem may be overcome by reducing the water concentration in the reaction mixture or alternatively making the catalyst surface hydrophobic, to minimise the problem of catalyst stability (Kholdeeva, O.A., et al., 2002). The use of nanostructured catalysts is sometimes recommended to enhance the catalytic activity, resulting in increased surface area (Kesavan, V., et al., 2002).

3.2.1. Zeolite Catalysts

The concept of zeolite applications as acid catalysts in the field of catalysis began in 1756 with the classification of zeolites based on their molecular size. The reason why the use of zeolites is preferred in heterogeneous catalysis is attributed to their unique porous properties. Current methods use zeolites in a variety of applications with an estimate of the growing market of several million tons per annum, e.g., the petrochemical industry, selective synthesis of chemical intermediates, and other industrial processes such as methanol to gasoline processes (MTG) (Kreisberg, J., 1996; Corma, A., et al., 1996).

Zeolites and related molecular sieves are largely being used for various catalytic applications because of their unique structural and textual properties. The major advantage of zeolites and related molecular sieves as heterogeneous catalysts over the homogeneous catalysts is that they avoid contamination of the effluents, which are becoming increasingly difficult to

dispose of (Carvalho, A., et al., 1997). Their properties, such as pore dimension, hydrophobicity, acidity or basicity, can be tailored over a broad range allowing the preparation of highly selective catalysts. Pore size limitations of the microporous zeolites limit the use of bigger molecules for catalytic conversions inside the zeolitic channels (Laha, S.C., et al., 2002).

When defining zeolites, they are usually described as crystalline microporous inorganic solids containing large voids and channels, giving the material an internal pore system as well as interstitial spaces between the crystallites. These molecular sieves encompass materials comprising silicates, aluminosilicates, aluminophosphates, metalloaluminates, and germinates (IZA, 2005). Two main characteristics of the zeolites that need to be considered are: acidity and pore diameter. Zeolites encompass hundreds of Brønsted or Lewis acid centers that can catalyse some of the same reactions as in homogeneous, solution phase, catalysis (Kreisberg, J., 1996). One reason for their success is the possibility of modifying the Brønsted acid strength which can then be adapted to the acidity needed for a particular reaction as shown in Figure 5. Zeolites are thermally stable, have high adsorption capacities, and are able to preactivate reactant molecules due to the presence of strong electric fields and electronic confinement (Corma, A., et al., 1997).

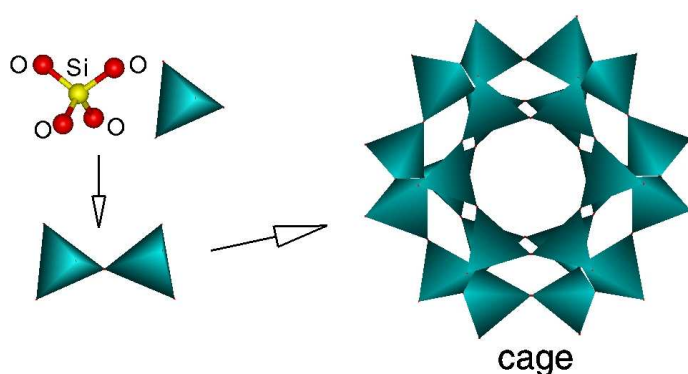


Figure 5: Schematic diagram of the framework structure of zeolites, <http://www.bza.org/zeolites.html>.

It is known that the active sites responsible for the catalytic performance are located inside the zeolite pores, and accessibility of the active sites to reactant molecules for catalyst activity and selectivity, depends solely on the diameter of zeolite channels (Blasco, T., et al., 1993). These acid sites can be adjusted by exchange with other ions and this has been reported to be quite important since most reactions catalysed by zeolites involve proton transfer or at least activation by a Brønsted or Lewis acid (Kreisberg, J., 1996). A defining feature of zeolites is that their frameworks are made up of 4-connected networks of atoms. These materials exhibit a tetrahedral structure, with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedra can then link together by their corners to form a rich variety of structures as shown in Figure 5. The framework structure of zeolites contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter, meaning, the limiting pore sizes are roughly between 3 and 10 Å in diameter (IZA, 2005; <http://www.bza.org/zeolites.html>).

Since the mid-1960's, the shape selectivity of zeolites has found many applications. The term shape selectivity is based on the concept of pores of

certain zeolites where chemical reactions that are catalysed, are of the same order of size as the molecular dimensions of the reacting molecules. The application of shape selectivity is classified according to the size and shape of reacting molecules, as certain molecules may or may not diffuse through the zeolite channels. Some potential reaction products can, for steric reasons, not form in the zeolite pores. Another shape-selective property of zeolites is their use in molecular adsorption. This can be shown by preferential ability to adsorb certain molecules, while excluding others with a wide range of applications of molecular sieving based on these properties. In other cases, different types of molecules enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite as shown in Figure 6.

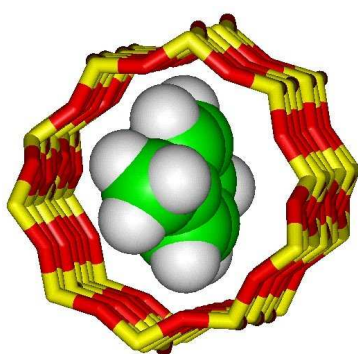


Figure 6: Schematic diagram showing the diffusion of para-Xylene adsorption in the channels of silicalite, <http://www.bza.org/zeolites.html>

Zeolites containing cations in their frameworks are extensively used as desiccants due to their high affinity for water. These zeolites have application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. (<http://www.bza.org/zeolites>).

In a number of fine chemicals syntheses, crystalline aluminophosphates that exhibit shape selectivity similar to that of zeolites, but with lower acidity, are also used. One of the most important recent developments in the chemistry of zeolites and related molecular sieves has been the incorporation of transition metal cations, such as Ti^{4+} , into zeolite framework of mesoporous structures, increasing the possibility of solid-catalysed oxidation reactions in liquid phase with alkylperoxides (Gontier, S., and Tuel, A., 1995). For processes used mostly in selective oxidations involving zeolite catalysts, the catalyst use and synthesis procedure are of utmost importance as aromatic oxidation is strongly dependent on the quality of the catalyst. It is worth mentioning that different synthesis parameters affect activity and selectivity of the catalyst to such a greater extent (Sheldon, R.A., and Dakka, J., 1994).

A problem encountered in selective oxidation catalysis using soluble oxometal species is associated with: (i) Propensity of certain oxometal species (titanyl, $Ti^{IV} = O$) towards oligomerisation to inactive μ -oxo complexes, (ii) oxidative destruction of organic ligands (Sheldon, R.A., and Dakka, J., 1994).

There are several advantages of redox molecular sieves as compared to the more conventional heterogeneous oxidative catalysts, namely:

- The possession of regular microenvironment. Unlike amorphous materials, such as silica and alumina, zeolites and related molecular sieves have highly homogeneous internal structures with uniform, well defined cavities and channels.
- Site- isolation of redox metal centres prevents deactivation via di-/ oligomerisation of active $M=O$ species.

- Enhanced stability towards leaching of the metal.
- Possibility for shape selective catalysis.
- More pronounced solvent effects- the molecular sieve can be considered as a second solvent that extracts the substrate out of the bulk solvent
- Possibility of 'fine tuning' the size and the hydrophobic/ hydrophilic character of the redox cavity to give 'tailor made' oxidation catalysts (Sheldon, R.A., and Dakka, J., 1994)

Molecular sieves containing small amounts of catalytically active transition metals show remarkable activity in selective oxidation in liquid phase with aqueous hydrogen peroxide under mild conditions. Pârvulescu et al. (2004), reported these properties to result from high dispersion of metal ions as isolated species on the support with an ordered structure and pore-dimensions. This metal is introduced on the molecular sieves in two different ways, namely ion exchange or direct synthesis. The incorporation of two different metals might create materials with different or new redox and acid properties; this can combine the high activity of some metal ions and the high selectivity of others in aromatic oxidation. Although zeolites have been long exploited in chemical industry as solid catalysts, there is a widespread demand for novel large-pore materials for use as: (i) ion-transport membranes in fuel cell technology, (ii) molecular sieves in separation technology, and (iii) novel materials for nanostructured electronic devices.

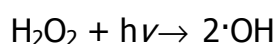
<http://atom.ecn.purdue.edu/~thomsonk/projects.html>.

3.2.1.1. Titanium Silicate-1 (TS-1)

In oxidation reactions, the use of titanium silicate-1 (TS-1) has found wide range of applications from photography to polymer industries and pharmaceuticals (Klaewkla, R., et al., 2006). The major use of this zeolite is for production of hydroquinone and catechol from phenol hydroxylation using aqueous hydrogen peroxide as an oxidant. The zeolite TS-1 was firstly developed and synthesised by Enichem. Ever since its discovery, this zeolite has been proven to be a highly efficient heterogeneous catalyst of liquid- phase oxygenation reactions of various organic compounds using aqueous hydrogen peroxide as oxidant. Examples of such oxidation reactions includes, alcohol oxidation, olefin oxidation, phenol and aromatic hydroxylation, and ammoxidation of cyclohexanone to cyclohexanone oxime (Trukhan, N.N., and Kholdeeva, O.A, 1993).

In the synthesis of hydroquinone and catechol, zeolite TS-1 generates higher phenolic conversion and para-hydroxylation activity, interpreted as shape selectivity effect. Higher photocatalytic activity is, however, achieved with TS-1 than TiO₂ for CO₂ reduction, with the reason mainly due to the efficient formation of the hydroxyl radical ($\cdot\text{OH}$) from hydrogen peroxide and the close proximity of $\cdot\text{OH}$ radicals to the reactant molecules (Klaewkla, R., et al., 2006).

When light intensity generated is high, hydrogen peroxide is reported to react with light, leading to the formation of $\cdot\text{OH}$ radicals, regardless the presence of the catalyst (Klaewkla, R., et al., 2006).



3.4

This ·OH radical produced can rapidly react with most organic compounds. The formation of the ·OH radicals is more easily on the titanium-hydroperoxo species, with unstable hydroperoxidic species formed by interaction of framework titanium in TS-1 with hydrogen peroxide, than from H₂O₂. When water is added, one of the Ti -O-Si bond is hydrolysed, hence the tetra-coordination is kept intact. Addition of another water molecule generates a pentacoordinated titanium species. An approach to isolate redox metal in stable inorganic matrices, thereby creating oxidation catalysts with interesting activities and selectivities, is to incorporate them in a zeolite framework (Sheldon, R.A., 1993; Sheldon, R.A., 1996; Corma, A., et al., 1996; Sheldon, R.A., and Dakka, J., 1994; Liu, H., et al., 2005).

Zeolite TS- 1 exhibits quite remarkable activities and selectivities, such as epoxidation of ethylene at ambient temperature in aqueous tert-butanol with 30 wt-% aqueous hydrogen peroxide, affording ethylene oxide in 96% selectivity at 97% conversion (Sheldon, R.A., 1993). Reactions catalysed by TS-1 are limited to molecules that can easily fit into micropores (5.1 x 5.5 Å) of this catalyst. Due to this limitation, application of zeolites is still limited to the transformations of molecules small enough to enter their pores, therefore, restricting oxidation of larger molecules (Carvalho, W.A., et al., 1997; Sheldon R.A., 1996; Trukhan, N.N., and Kholdeeva, O.A, 1993).

Unlike the Group IV–VI metal oxide based catalysts, titanium-silicalites are active in the presence of diluted aqueous solutions of hydrogen peroxide, whereas anhydrous organic hydroperoxides, such as tert- butylhydroperoxide (TBHP), are the oxidants of choice for the former catalysts. These differences can be partially ascribed to the hydrophobic character of TS-1, which favours

the adsorption of the organic substrates over the more polar water molecules present in the aqueous peroxide solution, thus maintaining the Ti sites inside the zeolite pores in an organic-rich environment (Corma, A., et al., 1996).

The IZA (2006) database describes the framework of TS-1 as a three-dimensional pore structure with interconnecting 10-membered ring channels. The sinusoidal channels are parallel to the [100] direction, with pore opening dimensions, which are interconnected with straight, two-dimensional pore channels (parallel to the [010] direction) with free pore dimensions of 5.3 x 5.6 Å. After several reports and considerations, TS-1 has been proven to be a remarkable redox catalyst in numerous friendly environmental applications but not efficient in the oxidation of more space demanding substrates having diameter larger than ~5.5 Å (Ungureanu et al., 2003). However, to overcome this limitation and to improve the performance of Ti-zeolites, novel large pore structures are synthesised (Sheldon, R.A., and Dakka, J., 1994).

3.2.1.2. Titanium- Beta (Ti- β)

As mentioned in section 3.2.1.1., TS-1 was found to be an active and selective catalyst in selective oxidation reactions with small diameter molecules. This limitation led to the incorporation of titanium (IV) into medium pore, high-silica zeolite ZSM-48 characterised by three-dimensional channel system, with several advantages such as resistance to blockage by extraneous materials. However, this zeolite is found to be catalytically inactive, probably due to the existence of extraframework Ti species as changes in unit cell diameter and Infrared data are consistent with titanium being incorporated into framework positions (Corma et al., 1996; Keiko et al., 1996; Sheldon, R.A., and Dakka, J.,

1994). After this investigation, the synthesis of a 12-membered ring zeolite Ti-Beta (Ti- β) was proposed (Blasco, T., et al., 1993)

The incorporation of titanium into larger pore molecular sieves, for example zeolite Ti- β (7.6x 6.4 Å), allows the catalysis of bulkier molecules such as alkanes and alkenes by using hydrogen peroxide as an oxidant (Sheldon, R.A., 1996; Corma, A. et. al., 1994). Due to this advantage, Ti-beta is more active than TS-1 for the oxidation of bulkier substrates (Corma, A., et al., 1996). Zeolite Titanium- β has a large pore size zeolite consisting of a three-dimensional framework, characterised by two interconnecting main channel systems of 12-ring atoms, which make up the rings controlling diffusion through the channels (IZA, 2006). The two-dimensional straight pore channels are parallel to all crystallographically equivalent axes (i.e. along x, y, and z) of the cubic structure (the <100> direction), with pore opening dimensions of 6.6 x 5.6 Å, parallel to the [001] direction (IZA, 2005).

Early research conducted by Blasco, et al. (1995), investigated the possibility of Ti zeolites as oxidation catalysts and found that the introduction of Ti- β has been one step forward in the preparation of zeolite oxidation catalysts, although the application of this zeolite is still limited to molecules smaller than 7Å. This has been found to be the limitation for the use of Ti zeolites as selective oxidation catalysts in the field of fine chemicals. Therefore, there was a need for production of molecular sieve oxidation catalysts with pore diameter larger than 7Å. The difference in structures of TS-1 (MFI) and Ti-Beta is shown in Figure 7.

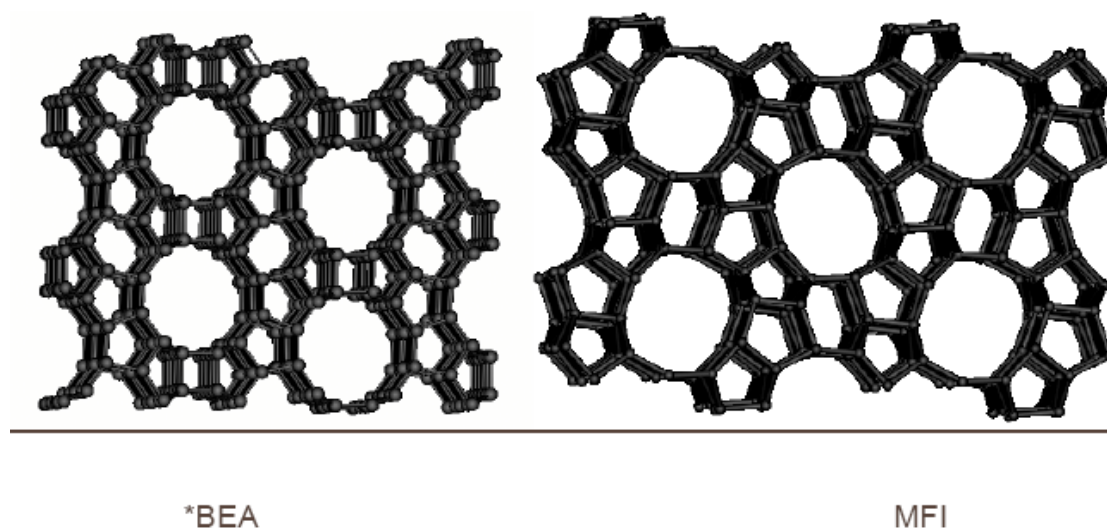


Figure 7: Two zeolite structures (Zeolite Beta and MFI) (Genov, MSc. K.A., 2004)

3.2.2. Mesoporous Silicate Materials

Significant advances in heterogeneous catalysis for liquid phase oxidation reactions have been made since the discovery of mesoporous molecular sieves (M41S; a collective name for a family of crystalline mesoporous molecular sieves with a regular and well-defined mesoporous system) and their extension to new mesostructured silica containing Ti in tetrahedral coordination environment (Ungureanu, A., et al., 2003; Beck, J.S., et al., 1992). The novel family of M41S was discovered by Mobil Research and Development Corporation in 1992, and attracted numerous researches into its catalytic application in bulky molecule reactions (Yuan, Q., et al., 2006; Keiko, A.K., and Tatsumi, T., 1996; Beck, J.S., et al., 1992). These mesoporous (alumina) silicate materials, with well-defined pore sizes of 15 – 100 Å, break past the pore-size constraint (<15 Å) of microporous zeolites (Ying, J.Y., et al., 1999). The extremely high surface areas (> 1000 m²g⁻¹) and precise turning of pore sizes are among the many desirable properties that have made mesoporous materials the focus of great attention.

By definition, mesoporous materials are typically amorphous or paracrystalline solids such as silicas, transitional aluminas, or modified materials such as pillared clays or silicates (Beck, J.S., et al., 1992). According to the IUPAC definition, all inorganic solids containing pores with diameters in the range of 20 – 500 Å are considered mesoporous materials, which include: M41S, aerogels, and pillar layered structures (Ying, J. Y., et al., 1999).

Various types of mesoporous materials with new structures and well-ordered pore arrays have been synthesised, which offer large surface areas, uniform pore size distributions, and tunable pore diameters. Amongst them, MCM-41 is the most promising support for the immobilisation of homogeneous catalysts and heterogeneous catalysts (Ying, J.Y., et al., 1999). These models are predicated upon the presence of surfactants in a solution to guide the formation of the inorganic mesostructured from the solubilised inorganic precursors such as in Figure 8.

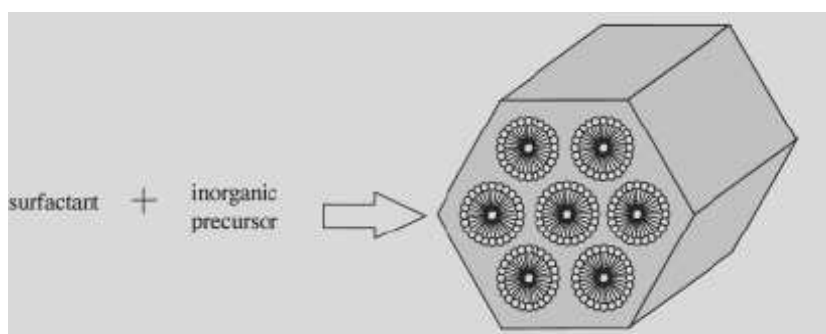


Figure 8: Schematic presentation of general formation of MCM-41 from inorganic precursors and organic surfactants (Ying, J.Y., et al., 1999).

When compared to TS-1 zeolites, Ti-containing mesoporous molecular sieves suffer from the two drawbacks: (i) hydrophilic surface due to the large population of defect silanol groups, (ii) the amorphous nature of their pore walls. These disadvantages are reported to limit their applications, especially in the oxidation reactions involving aqueous hydrogen peroxide since surface silanols strongly attract water molecules thereby limiting the access of the organic substrates to the active sites. Notably, surface silanol groups can be suppressed by two strategies: (i) post-synthesis Ti species grafting, (ii) silinasation (Ungureanu, A., et al., 2003).

Other reactions in literature, for example, production of 2, 3, 5-trimethyl-*p*-benzoquinone through the oxidation of 2, 3, 6-trimethylphenol has been achieved by the use of Ti, Si-catalyst-based process. This process however has the following important advantages [Kholdeeva, O.A., et al., 2002]:

- High activity combined with high selectivity.
- True heterogeneity of the catalyst, which can be separated by simple filtration.
- No Cl- containing reactants and solvents (lack of transitional metal impurities and Cl- containing by-products).
- No corrosion problems.

3.2.2.1. Mesoporous Ti-MCM-41

Owing to pore size limitations of zeolites, a new family of mesoporous molecular sieves, designated as MCM-41, was discovered in the laboratories of the Mobil Oil Company and opened new possible applications of these materials, especially when synthesised in the presence of cations other than Si.

These materials have found a wide application for the verification and improvement of applicability of classical methods for pore size analysis (Choma, J., and Jaroniec, M., 2007).

As mentioned above, MCM-41 and its analogues received great interest because of their very high surface areas (typically 800- 1000 m² g⁻¹) and peculiar porosity. This mesoporous material has been shown to be an excellent support for preparing bifunctional catalysts, presenting a superior activity and selectivity than conventional supports, such as alumina, silica- alumina, and even zeolites (Blasco, T. et al., 1998).

A defining feature of MCM-41 is their narrow and tunable nanopore size distribution in the range of 20-100 Å, which is suitable for the synthesis of fine chemicals and pharmaceuticals. Under typical conditions, as developed by Laha, S.C., et al. (2002), MCM-41 exhibits a hexagonal array of one-dimensional mesopores, with a narrow pore size distribution. This is achieved through a proper choice of surfactant as the template, auxiliary chemicals, and reaction conditions.

Anunziata et al. (2004) stated that Ti-MCM-41 contain isolated titanium atoms which are responsible for its catalytic activity in the selective oxidation of organic substrates with aqueous hydrogen peroxide. This oxidation occurs via formation of titanium peroxo-species facilitating the direct insertion of oxygen into the aromatic ring.

3.3. Catalyst Synthesis and Characterisation

The evaluation of methods of synthesis in the preparation of nanostructured materials, their instrumental characterisation, and determination of catalytic behaviours used to investigate the relation between catalytic structure - activity is of vital importance (Anunziata, O.A., et al., 2004).

3.3.1. Synthesis Medium

A catalyst is a chemical product characterised by its composition and its method of preparation, from the nature of its precursor salts of the active agents, through the conditions of the unit operations used for constructing the catalyst. A solid catalyst is known to be evaluated with reference to its activity and selectivity. The activity of a catalyst determines the rate of conversion whereas the selectivity of the catalyst determines the quality of the product. Therefore, it is essential that the development and preparation method of the catalyst be conducted with expertise and proper training to ensure the synthesised catalyst carries physicochemical and crystallographic characteristics within the framework of its function (Ertl, E., et al., 1999).

When synthesising a zeolite catalyst, the incorporation of transition metal cations into the framework of pure silica polymorphs of zeolites is not easy and usually limited to less than 3 wt%. The reason for this is due to cations having radius larger than that of Si^{4+} , therefore, incorporation of these metals into zeolite framework distorts the catalyst (Gontier, S., and Tuel, A., 1995).

The synthesis method of zeolite TS-1 has received a lot of attention and has a very broad scope as this zeolite has been of interest in the field of catalysis ever since its discovery. Zeolite TS-1 discovery has been a milestone in zeolite and heterogeneous catalysis due to the fact that this catalyst is an active, highly selective, and environmentally friendly catalyst for a number of industrially important organic oxidation reactions in the presence of aqueous hydrogen peroxide solution. However, there is a growing need of synthesising a zeolite of high quality with the MFI structure.

The synthesis of TS-1 is usually carried out using the hydrothermal procedure. According to Fan et al. (2008), using different synthesis methods in the synthesis of zeolite TS-1, affects the coordination states of Ti species in the sample. Another important discovery is that monitoring the pH of the synthesis gel is also of high importance as differences in sample purity and the degree of crystallinity may be encountered. The pH should can be kept around 12.0 (which is more appropriate for the depolymerisation of the silica and construction of the zeolite framework) by employing the use of tetrapropyl ammonium hydroxide (TPAOH) as a template instead of tetrapropyl ammonium bromide (TPABr), which provides pH values between 4.0-9.0, hence leading to formation of impure TS-1 that are contaminated with cristobalite, quartz and rutile (Borin, M.F., et al., 2006).

On the other hand, in the synthesis of Ti-MCM-41, there are two synthesis approaches that have been used in the past decade, namely the hydrothermal or the sol-gel technique. However, recent methods in the literature show hydrothermal procedure to be the preferred technique. Investigations conducted by Anunziata et al. (2004) showed that the synthesis of mesoporous

Ti-MCM-41 catalyst using the hydrothermal procedure produces titanium species that are tetrahedrally coordinated. The linear increase in this coordination is observed to be 5 fold when the sample is hydrated, which contrasted with the sol-gel procedure, where titanium-sites have higher coordination, which is independent of the degree of hydration. This condition is attributed to the fact that sol-gel technique is less active, hence, the selectivity is very poor as been observed using X-ray Fluorescence Spectroscopy (XAFS). In catalytic oxidations, leaching of Ti^{4+} cations out of the zeolites or amorphous silica depends strongly on the pH. Ti leaching is observed to be less serious when less polar solvents like dichloromethane or aprotic solvent such as acetonitrile are used with hydrogen peroxide as an oxidant with titanium substituted mesoporous materials (Anunziata, O. A., et al. 2004).

During the synthesis, the exclusion of alkali ions (K^+ and Na^+) from the synthesis gels of titanosilicates is very crucial as even trace amounts of these ions in the template solution result in catalyst samples with very poor catalytic properties and poor crystallinity, even though spectroscopic characterisation can indicate a high purity material (Blasco, T., et al., 1995). A major disadvantage of using alkali salts is that, after pH adjustments or addition of alkali solutions, the alkali salts formed have a strong electrolytic effect. Such salts may cause solidate to crystallise instead of a zeolite type material. When required, it is advantageous to introduce, particularly for reaction mixtures of low SiO_2/Al_2O_3 ratios, aluminium in the anionic form, that is sodium aluminate (Robson, H. and Lillerud, K.P.; 2001).

Addition of alkali cations raises another concern as these cations are known to poison the titanium sites. Therefore, it is recommended that prior to use,

commercially supplied template solutions must be tested using Atomic Absorption Spectroscopy (AAS) to confirm their alkali content; with concentrations less than 50 ppm ideal (Tamarasso, M., et al., 1983; Notari, B., 1988). Under the above mentioned conditions, an optimum OH/SiO₂ ratio of 0.26 can be obtained. Another investigation conducted by Blasco et al. (1995) reported higher ratios of alkali cations to result in less crystalline materials with ill-defined X-ray Diffraction.

Prior to characterisation, calcination of synthesised zeolites is of high importance. Calcination is a process for the removal of template and water from the zeolite pores using higher temperatures and calcination conditions must be carefully monitored. Studies by Blasco et al. (1995), revealed that upon calcination, a cell contraction of 2-4 Å is observed in Ti-MCM-41; with the cell parameter values (a_0) of a good crystalline Ti-MCM-41 (2-4 Å) higher than the pure siliceous material. This is an indication of titanium incorporation into the tetrahedral network.

It is noteworthy that, the synthesis of ordered silica (Si-MCM-41) is faster in the presence of oxyanions than in its absence. However, at the same promoter concentration, the synthesis time required for obtaining a well-ordered MCM-41 material decreased with increasing charge/ radius ratio of the central cation of the corresponding promoter oxyanions as it has been already observed previously in the case of zeolites (Kumar, R., et al., 1998). The catalytic activity of Ti-MCM-41 is also studied with the effect of different promoters as illustrated in Figure 9.

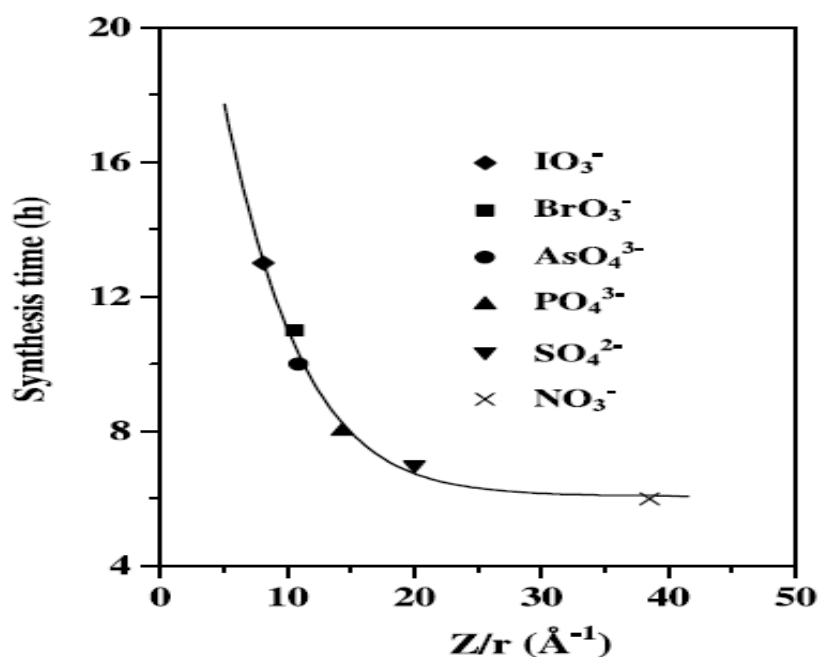


Figure 9: Correlation between the synthesis time and the charge/ radius (Z/r , \AA^{-1}) ratio of the central cation of the promoter in the synthesis of Si-MCM-41) (Laha, S.C, and Kumar, R., 2002)

As in Figure 9, addition of small amount of promoter oxyanions such as phosphate, arsenate, sulfate, chlorate, bromate, and iodate to the synthesis precursor mixture of zeolites and silica- based microporous materials, reduces the crystallisation time considerably. These observations led Laha and Kumar (2002) to further investigate the effect of different oxyanions on MCM-41. Thus, at the same promoter concentration, the effect of different promoters in the synthesis of MCM-41 materials depended on the polarising ability of the promoter oxyanion. The higher the polarising ability of the promoter central cation, the lower the synthesis time.

The use surfactants such as cetyltrimethylammonium halide (or hydroxide) or tetramethylammonium hydroxide as a mineraliser under autogeneous pressure is of high importance. Laha and Kumar (2002) reported the use of a refluxing

gel mixture at atmospheric pressure under stirring for the synthesis of MCM-41 type mesoporous materials. Mobil researchers proposed a “Liquid Crystal Templating” mechanism based on similarity between liquid surfactant assemblies (lyotropic phases) and M41S. The common constraints being mesostructure dependence on the hydrocarbon chain length of the surfactant tail group. With MCM-41 (having hexagonal packed cylindrical pores) as M41S representative, two mechanistic pathways were postulated as in Figure 10.

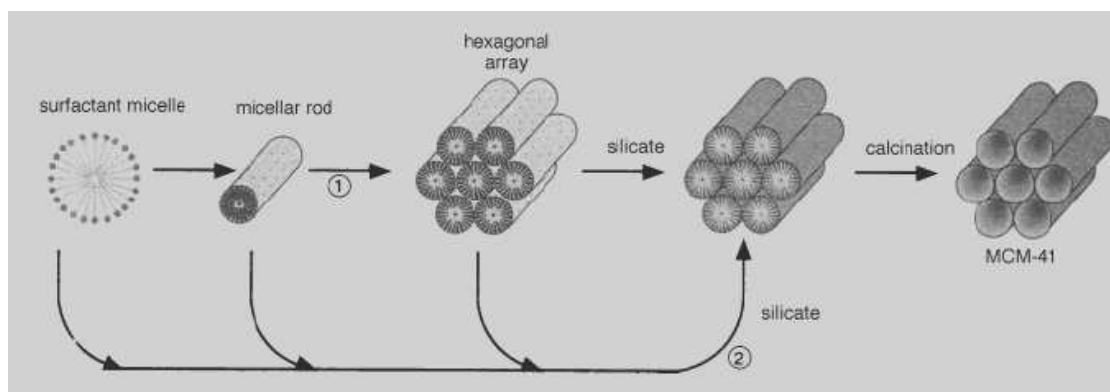


Figure 10: Two possible pathways of LC mechanism. Redrawn from (Ying, J. Y., et al., 1999).

In Figure 10, the aluminosilicate precursor species are occupying the space between the pre-existing hexagonal lyotropic liquid crystal (LC) phases and deposited on the micellar rods of LC phase. The organics mediated, in some manner, the ordering of the surfactants into the hexagonal arrangement (Ying, J.Y., et al., 1999).

The method of synthesis as described above can be crucial when developing a catalyst. This is proven by an observation that was made when methods of synthesising Ti-MCM-41 gave contrasting results. This phenomenon was

observed when Si-MCM-41 was crystallised as “short winding worms” with diameters between $1.5 \times 10^4 \text{ \AA}$ and $2.5 \times 10^4 \text{ \AA}$ and lengths between $1.0 \times 10^4 \text{ nm}$ and $2. \times 10^4 \text{ nm}$ as investigated by Carvalho et al. (1997). These findings contrasted with the hexagonal crystals obtained by Kresge et al. (1992), with the size of ca. $2.0 \times 10^4 \text{ \AA}$. The differences in diameter were mostly based on the stirred synthesis used by Carvalho et al. (1997) irrespective to static autoclaves used by Kresge et al (1992).

3.3.2. Catalyst Characterisation

Characterisation methods such as X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Atomic Absorption Spectroscopy (AAS), Nitrogen adsorption-desorption isotherm, UV-Vis, Infrared (IR), and Scanning Electron Microscopy (SEM), are used to investigate either vibrations, absorption, framework, crystallinity and chemical composition of zeolites and mesoporous materials, and the incorporation of Ti^{4+} into the zeolite framework. The use of these techniques give an insight into the coordination state of Ti in mesoporous Ti-MCM-41 samples that is crucial for proper understanding of their structure and catalytic behaviour.

In work done by Srinivas et al. (2003), the local structure of Ti is different in different titanosilicates obtaining two types of framework: (i) tetrapodal $(\text{SiO})_4 \text{Ti}$ structures in activated TS-1 catalysts, and (ii) Ti atom in Ti-MCM-41 (prepared by grafting method) to possess a tripodal $(\text{SiO})_3 \text{Ti} (\text{OH})$ structure. Titanium sites in these different structural environments generate reactive oxygen species having different structures and reactivities.

According to Blasco et al. (1995), when synthesising Ti-MCM-41, wall thickness between the pores is eventually an important parameter in determining the catalytic behaviour of this material and this wall is constructed by no fewer than three tetrahedral TO_4 , belonging to edge sharing 3-, 4-, or 5-membered rings of the tetrahedra. A typical characteristic of mesoporous type material, is an inflection ($P/P_0 = 0.2-0.3$) given by nitrogen adsorption – desorption isotherms. The inflection depends on the mesopore diameter with sharpness indicating the uniformity of the narrow pore size distribution. Porosity for catalytic oxidations is examined with the use of X-ray Diffraction (XRD), with the presence of four Bragg angles indicating metallosilicates with highly ordered pore system and high porosity. Observations with XRD also show most intense peaks of the crystalline materials are indexed in a hexagonal unit cell. Comparatively, differences between Ar pore diameters and a a_0 value, wall thickness has been estimated approximately $\sim 7-9 \text{ \AA}$ (Carvalho, W.A., et al., 1997).

With the use of Infrared spectroscopy, titanium- containing MCM-41 shows a band at 960 cm^{-1} , which indicates incorporation of this metal into the framework. In pure silicate or aluminosilicate materials, this band has been assigned to the Si-O stretching vibrations of Si – O $^-$ R $^+$ groups, as R $^+$ = H $^+$ in the calcined state. When aluminium is incorporated into the tetrahedral network, a_0 values of aluminium- containing MCM-41 are higher than the pure siliceous counterparts (Blasco, T., et al., 1995).

Another method of characterisation employs the DR-UV visible spectroscopy which is a very sensitive probe for examining the presence of extra framework titanium in zeolite. An intense band centered at ca. $215 \pm 5 \text{ nm}$ can be observed on the spectra, with a shoulder a wavelength approximately $\sim 270 \text{ nm}$

corresponding to partially polymerised coordinated Ti species. Lack of this band at ~330 nm indicates the absence of titanium anatase in the crystals (Blasco, T., et al., 1995).

However, in general, oxidation reactions evoke three types of oxo-titanium species namely: (i) hydroperoxo-, (ii) peroxo-, and (iii) superoxo - titanium.

In the case of zeolite TS-1, when contacting this zeolite with aqueous hydrogen peroxide, oxo-titanium species are generated by showing a characteristic absorption band in DRUV-visible spectrum in the region of 300-500 nm with this band attributed to a ligand- to- metal charge transfer transition, of a peroxo moiety interacting with a framework Ti center (Srinivas, A., et al., 2003).

3.4. Reaction Mechanism

A reaction mechanism describes the transition state at which the bonds are broken or the order at which bonds are formed and also generates information on relative rates. In addition, a reaction mechanism must also account for the order at which molecules react and how the overall reaction proceeds. In this work, the mechanism that shows the possible sequence of steps in the hydroxylation of 2-MN or toluene with aqueous hydrogen peroxide using titanium- substituted zeolites or mesoporous materials as catalysts is described in the subsections below.

3.4.1. Formation of 2-methyl-1, 4-naphthoquinone

The hydroxylation of 2-methylnaphthalene is shown in Figure 11. The desired product formed during this reaction is 2-methyl-1, 4-naphthoquinone (MNQ).

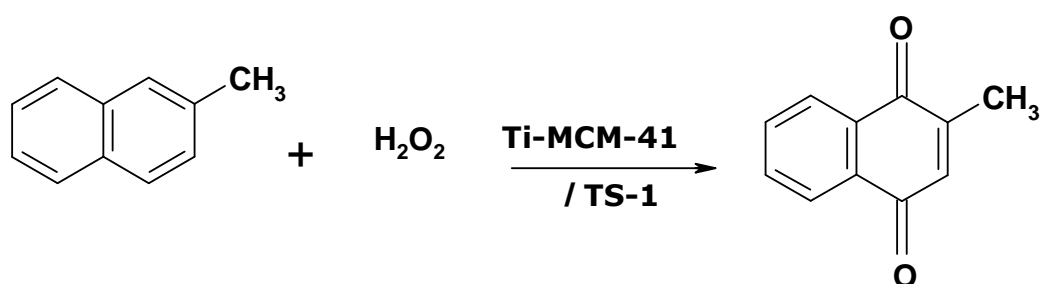
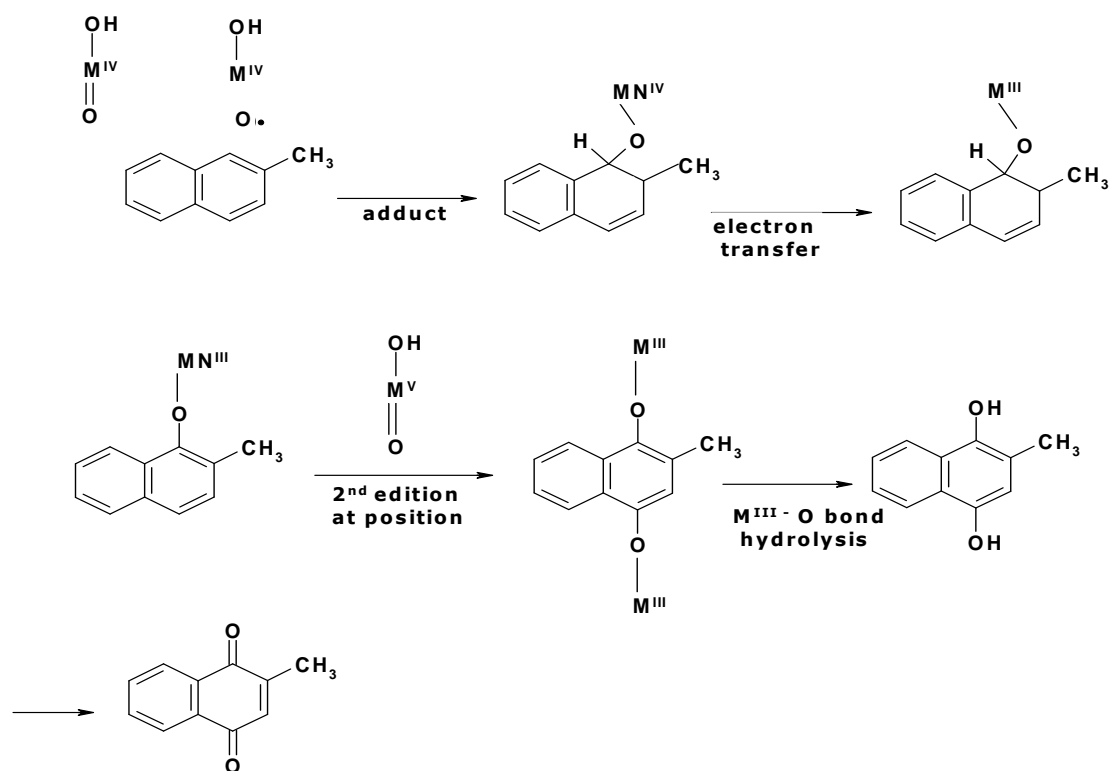
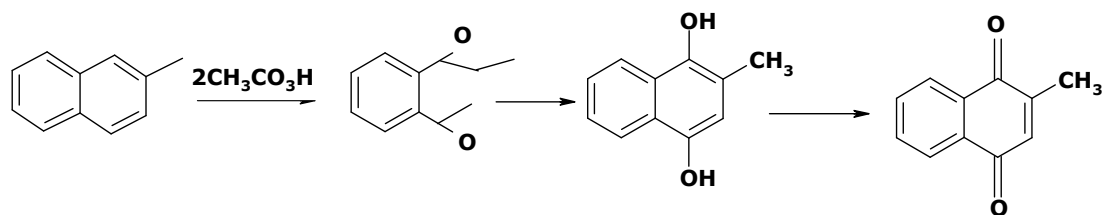


Figure 11: Hydroxylation of 2-methylnaphthalene with aqueous peroxide to 2-methyl-1, 4-naphthoquinone

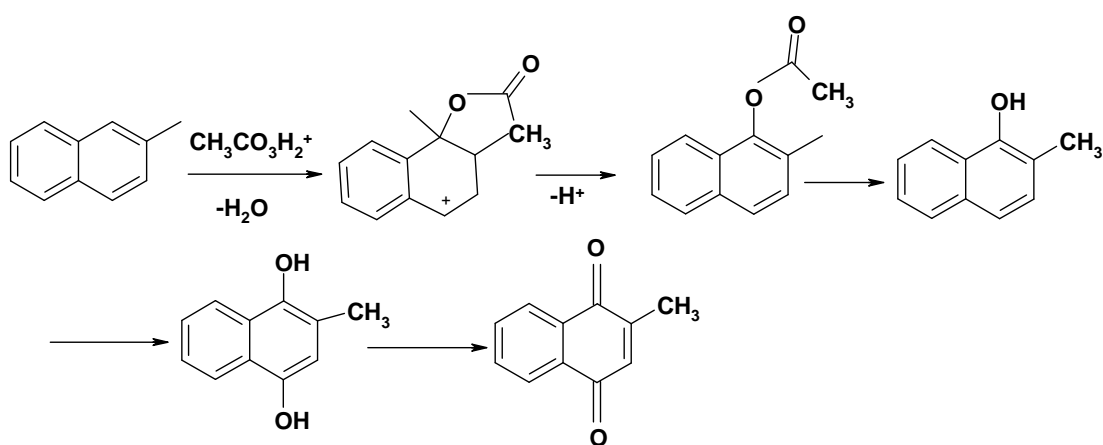
It is of high interest to show reaction mechanisms generating 2-MNQ than employing the use of zeolites. Other reactions show that other methods in literature generated 2-MNQ through the oxidation of 2-MN with the use of Iron metalloporphyrins catalysts. These reaction schemes are helpful in providing possible ideas on other compounds that are likely to form as described by detailed mechanisms in Scheme 1, Scheme 2 and Scheme 3.



Scheme 1: Mechanism of KHSO_5 oxidation of 2-methylnaphthalene catalysed by metalloporphyrins in aqueous solution. Redrawn from Song, R., et al., 1997.



Scheme 2: Epoxidation pathway. Modified and redrawn from Bohle, A., et al., 2006.

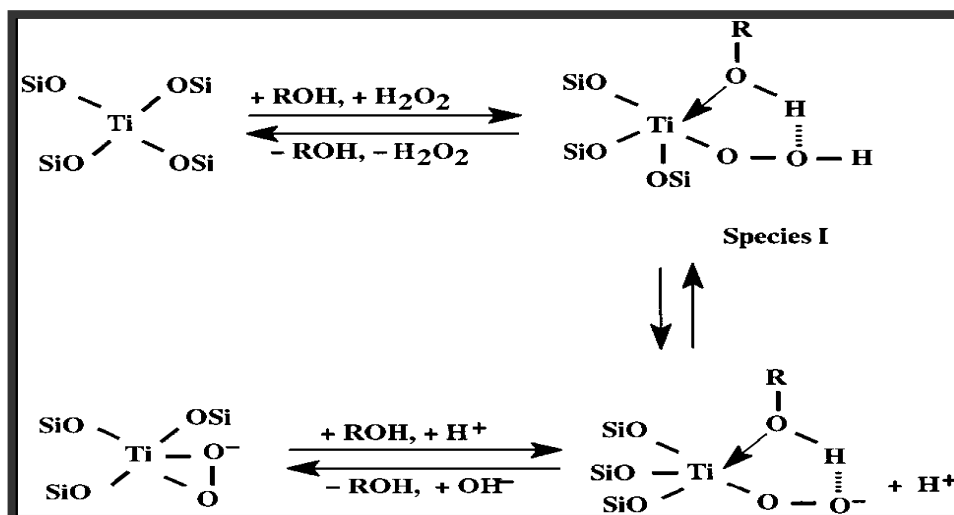


Scheme 3: Aromatic substitution pathway. Redrawn from Bohle, A., et al., 2006.

It is clearly seen from the reaction scheme 1 that an electron transfer followed by hydrolysis generate the formation of 2-methyl-1,4- dihydroxy- naphthalene thus leading to the formation of 2-MNQ. In addition, when using acetic acid in the oxidation of 2MN as in Scheme 2, a ring opening occurs followed by hydrolysis, generating 2-MNQ. In addition, the disadvantage of scheme 2 and 3 make use of homogeneous systems in acetic acid solution.

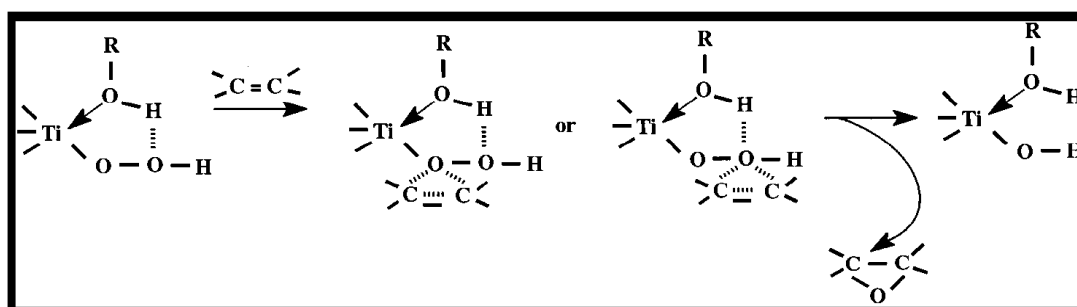
Another important aspect to take into consideration is the role played by solvents in a reaction mechanism. Using TS-1 as catalyst, the role played by protic solvents on the oxidation activity of TS-1 is explained assuming the formation of a stable five-membered structure as shown in species I in Scheme

4, where the protic molecule, ROH, coordinates the Ti centers and stabilises the Ti- peroxy complex through hydrogen bonding. Acids and bases modify species I according to the following equilibria:



Scheme 4: Showing the relevant role played by protic solvents on the oxidation activity of TS-1 (Corma, A., et al., 1999).

Effect of protic solvents in reactions with TS-1 is explained by the mechanism in Scheme 5.



Scheme 5: Proposed mechanism illustrating the effect of protic solvents (Corma, A., et al., 1999).

For both protic and aprotic solvent reactions, activity increases with solvent polarity. However, the increase is much more pronounced with the aprotic solvents. The use of protic solvents enhances the activity of TS-1 for the epoxidation of olefins. This positive effect of protic solvents is explained assuming the formation of a cyclic species I (Scheme 4) prior to the approximation of the olefin to the Ti-peroxo complex.

In the case of nonprotic solvents, which would not form the cyclic species I, the order of reactivity observed i.e., acetonitrile>acetone>methanol, which may be explained by the increase of substrate concentration in the hydrophilic pores of Ti-beta as the polarity of the solvent increases. Indeed, the higher the solvent polarity, the higher the concentration (Corma, A., et al., 1999).

The formation of the cyclic adducts (species I in Scheme 4) to account for the selectivity and kinetic features of TS-1 has been proposed. However, since the alcohol oxidation may involve the activation of a C-H bond, the competition between the alcohol substrate and protic solvents for adsorption on the Ti sites is established. This competition must be extended to the water molecules in the case of the hydrophilic Ti-beta catalyst. Competition between the alcohol substrate with protic solvents and water molecules is determined to decrease the reactivity of the catalyst. In the case of aprotic solvents this competition between substrate and solvent for adsorption on the Ti sites does not occur (Corma, A., et al., 1999).

3.4.2. Formation of Cresols

Toluene is an aromatic substituted benzene, with a methyl group, which has an electron- donating inductive effect that behaves as an ortho or para director. Selective hydroxylation of toluene in liquid phase might occur either para, ortho, or meta to the methyl group, giving three carbocation intermediates. Ortho, para and meta intermediates are resonance stabilised. However, during ortho and para attack, a resonance form places the positive charge directly on methyl- substituted carbon, where it is in a tertiary position and can be stabilised by the electron- donating inductive effect of the methyl group. Ortho and para intermediates form faster than meta because of these intermediates are lower in energy.

Toluene hydroxylation reaction leading to the formation of para- and ortho- and meta- cresol is shown in Figure 12.

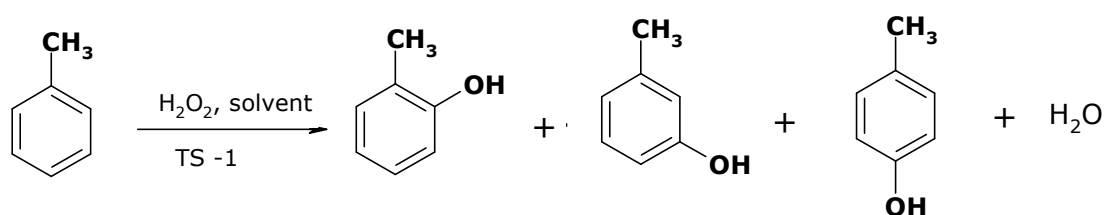


Figure 12: Toluene hydroxylation with aqueous hydrogen peroxide over TS-1 to para-, ortho-, and meta- cresol.

A more detailed reaction mechanism including the intermediate carbocations and the extent at which an electron- donating effect occurs is shown in Figure 13. Note that the ortho and para carbocations are more stable than the meta-

carbocation, which means that the ortho and para cresols will form more readily.

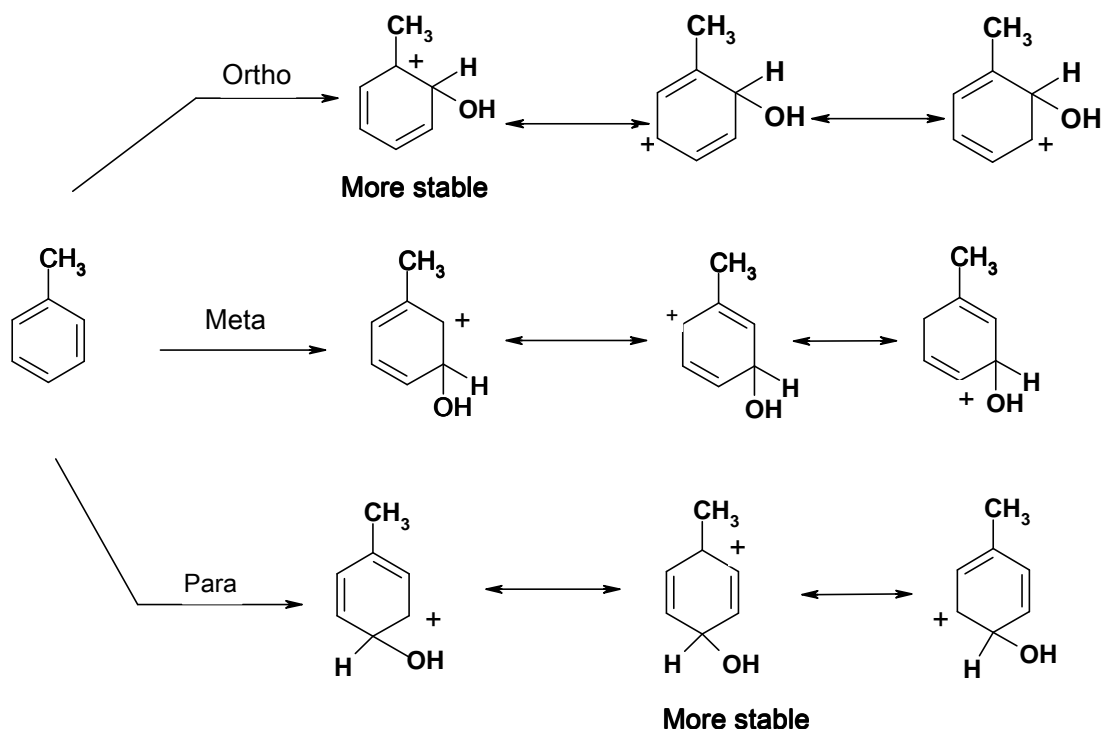


Figure 13: Carbocation intermediates in the hydroxylation of toluene. *Ortho* and *para* intermediates are more stable than the *meta*-intermediate because the positive charge is on a tertiary carbon rather than a secondary carbon. (McMurry, J., 2000).

Solvent effects on toluene hydroxylation have been observed to have great influence on the reaction mechanisms. When water is used as a solvent, ring opening by nucleophilic attack is expected. When TS-1 is suspended in water – H₂O₂ mixtures, the Ti⁴⁺ species become six coordinate, retaining three Ti –O– Si bonds, which are considered to anchor Ti within the microporous framework.

In TS-1 catalysed reaction triol by- product formation can be commonly observed. The interaction of these triols with the active sites of TS-1 can be observed as in Figure 14.

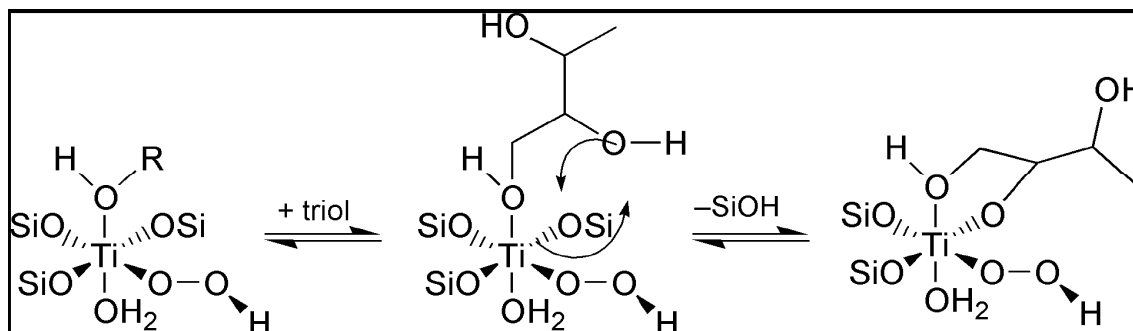


Figure 14: Mechanism for interaction of triols with the active site of TS-1. (Davies, L., et al., 2000)

3.4.3. Geometric Effect

3.4.3.1. TS-1

The use of TS-1 in selective oxidation reactions is restricted to reactions of relatively small molecules, due to diffusion limitations which result from active sites that are situated in a channel system of about 5.5 Å average diameters (Anunziata, O. A., et al. 2004). In general, zeolite pore size controls the product formation. For larger pores intracrystalline diffusion is expected to be faster. Investigations by Kulkarni et al. (1998), where 1-naphthol oxidation to 2-methyl-1-naphthol was studied; yields obtained (58.4 and 13.4) decreased with increase in the Weight Hourly Space Velocity (WHSV) (for example, 0.50 h⁻¹ and 1.0 h⁻¹ respectively). This proved the reaction to be diffusion controlled.

Control of surface activity is more important especially for zeolites, because of the possibility of controlling product selectivity by an adequate dimensionalisation of their pores and cavities (Corma, A., et al., 1997).

Using zeolite TS-1 in selective oxidation reactions has been advantageous as TS-1 possess two unique features. The incorporation of Ti into the microporous silicate framework increases the hydrophobicity and enables use of hydrogen peroxide as an oxidant. Another feature is the stability of TS-1 under reaction conditions avoiding leaching of Ti metal into solutions during reactions.

3.4.3.2. Ti-MCM-41

In 2-methylnaphthalene oxidation, activity and selectivity are the most crucial parameters towards product recovery. However, a lot of work still needs to be done in determining the reaction path and the effect of the pore size of the catalyst used in this work. Comparison of product selectivities obtained with the medium pore titanium silicate TS-1 and Ti-MCM-41 can indicate whether shape selectivity effects and the role of pore geometry are influential in the hydroxylation reaction i.e. 2-MN would be able to enter the TS-1 pores.

Investigations from previous research demonstrated the amount of catalyst used in a catalytic reaction, is amongst the crucial factors affecting the product yield of the desired product. A study performed by Anunziata et al. (2004), illustrated oxidation of 2- methyl-naphthalene carried out varying the amount of the catalyst from 20 to 200 mg in each reaction, with results obtained showing selectivity of 2-methyl-1, 4-naphthoquinone (vitamin K₃) increasing with conversion of 2-methylnaphthalene, that is, conversion increase with the yield of 2-methyl-1, 4-naphthoquinone; suggesting a first- order dependence. The value of first –order rate constant k is used to characterise the catalyst activity (Anunziata, O.A., et al., 1999). Catalyst ration, augmentation of the amount of catalyst up to the optimal value of 5 mol% (mol Ti/mol MNL = 0.05) led to

growing selectivity of MNQ at 100% MNL conversion. Without any catalyst, 51% conversion of MNL can be attained, with no MNQ production (Kholdeeva, .O.A., et al, 2005).

3.5. Process Operation

In the past decade, initial research done on oxidation of 2-methylnaphthalene was achieved by using sulphuric acid solutions of chromic acid (Fischer, L.F., 1940; Sheldon, R.A., 1993) and problems with disposal of large volumes of toxic waste were experienced as mentioned in chapter 1. Further studies, as patented by Sankarasubbier et al. (US 6579994B2, 2003), claimed that oxidation of 2-methylnaphthalene using hydrogen peroxide in the presence of acid catalysts (homogeneous systems) generates higher 2-MN conversions and higher selectivities. However, there were major drawbacks such as reuse of the catalyst as disposal of acid is not environmentally safe. Thus far, there is still a growing need for the oxidation of 2-methylnaphthalene as a lot of information and processes regarding this molecule are still limited.

3.5.1. Literature Methods for Selective Oxidation of 2-Methylnaphthalene

Oxidation of aromatics generally lacks selectivity due to coupling of reactions caused by phenoxy radicals; hence a novel practical method of oxidation of aromatics is very interesting (Khavasi, H.R., et al., 2002). It is of interest to include other reactions of 2-methylnaphthalene catalysed by different catalysts such as ruthenium (II) complexes. In a recent publication, the synthesis of ruthenium (II) complexes with tridentate nitrogen ligands and their applications in oxidation catalysis, arose interest in demonstrating the utility of such

complexes in arene oxidation. The difference in ruthenium complexes can be illustrated in

Table 4 (Shi, F., et al., 2007).

Table 4: Selective oxidation of 2-methylnaphthalene using different ruthenium (Ru) catalysts. Redrawn from (Shi, F., et al., 2007), catalyst used 4: Ru (II) (terpyridine) (2, 6-pyridinedicarboxylate), t = 1h, 1mmol starting material, 0.5 ml H₂O, ratio 2:3 = ratio between desired product: regioisomeric product.

Run	Catalyst (mol %)	T (°C)	1/H ₂ O ₂	Conversion (%)	Yield (%)	Selectivity (%)	Ratio of 2:3
1	4 (0.2)	40	1:7	67	51	77	2.8:1
2	5 (0.2)	40	1:7	65	32	50	2.7:1
3	6 (0.2)	40	1:7	91	26	29	2.9:1
4	7 (0.2)	40	1:7	88	53	61	2.5:1
5	4 (0.2)	40	1:3:6	58	50	86	2.9:1
6	4 (0.2)	40	1:3:6	70	54	77	3.2:1
7	4 (0.2)	40	1:7	67	51	77	3.1:1
8	4 (0.2)	40	1:7	88	64	73	3.0:1
9	4 (0.2)	40	1:10	65	49	75	2.9:1
10	4 (0.2)	40	1:10	97	52	54	3.0:1
11	4 (0.5)	40	1:7	73	56	77	2.9:1
12	4 (0.1)	40	1:10	58	41	71	2.9:1
13	4 (0.2)	40	1:3:6	99	56	56	2.8:1

According to exploratory experiments conducted by Shi et al. (2007), selective oxidation of 2-methylnaphthalene with approximately 2.3 equivalents hydrogen peroxide using Ruthenium (Ru) catalysts yields the corresponding 1,4 - naphthoquinones in 56% isolated yield with catalyst turnover frequency (TOF) of 840h⁻¹ (desired product 2-methyl-1, 4-naphoquinone and regioisomeric product 6-methyl-1, 4-naphthoquinone respectively). However, further investigation proved no significant influence of catalyst on the ratio of quinones obtained, which is observed to be between 2.5:1 and 2.9:1.

In a study of catalysts with Ti incorporated into the framework, Anunziata et al. (2004), obtained 2-methylnaphthalene conversions and product selectivities as illustrated in Table 5.

Table 5: Conversion and product selectivity over different catalysts in standard conditions: 100mg, T= 100°C, H₂O₂ = 6ml, 2MN= 1g, t = 4 hours (Anunziata et al., 2004)

Catalyst	Ti, Fe (mol %)	2MN conversion	H ₂ O ₂ X/ selectivity	Product selectivity (mol %)		
				1OH-2MN	DOH-2MN	2MNQ
TS-1	1.81	10	15/58	34	11	55
Ti-Beta	1.80	11	16/60	34	3	63
Ti-MCM-41	1.82	28	38/64	55	10	35

X = conversion

3.5.1.1. Effect of the amount of the catalyst

Product selectivity is a function of amount of catalyst and the resulting variation of 2-MN conversion. 2-methyl-1, 4- naphthoquinone selectivity and yield increase with the increase in 2MN conversion, with the formation of quinone occurring through consecutive (but very fast) steps. This linearity is shown as in Figure 15: Product selectivity as a function of 2-MN conversion, catalyst amount: 20, 5, 75, 100, 150, 200 mg, T = 393K, H₂O₂ = 6ml, 2MN = 1g, solvent = 10ml, t = 10h (Anunziata et al., 2004). Initially the reaction rate increases almost linearly with the increase in catalyst amount, suggesting first-order dependence (Anunziata, O.A, et .al., 2004; Anunziata, O.A, et .al., 1999).

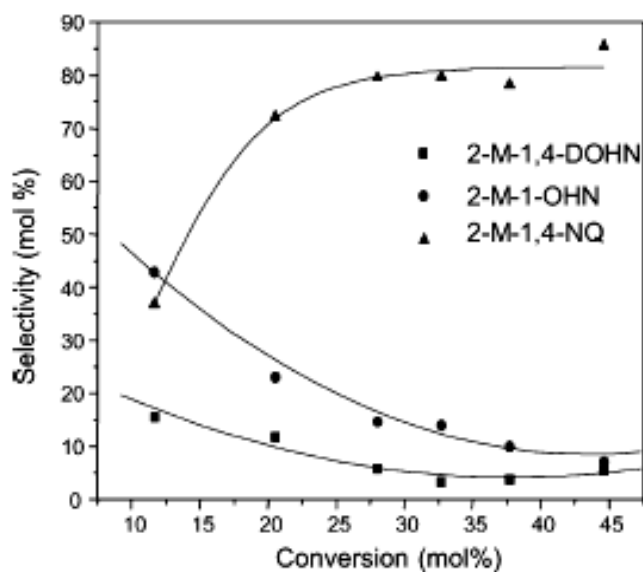


Figure 15: Product selectivity as a function of 2-MN conversion, catalyst amount: 20, 5, 75, 100, 150, 200 mg, T = 393K, H₂O₂ = 6ml, 2MN = 1g, solvent = 10ml, t = 10h (Anunziata et al., 2004).

3.5.1.2. Effect of oxidant type and concentration

The major task of fine organic synthesis is the selective oxidation of organic compounds by environmentally friendly and cheap oxidants, such as molecular oxygen and hydrogen peroxide (Trukhan, N.N., and Kholdeeva, O.A., 2003). In production of fine chemicals, a broader choice of oxidant such as hydrogen peroxide rather than oxygen or air is preferred. Even though hydrogen peroxide is more expensive per kilogram than molecular oxygen, it is often a choice for fine chemicals because of the simplicity of operation (lower fixed costs) and cheaper technological equipment. Other than price and simplicity of handling, the two important factors influencing hydrogen peroxide are namely: (i) the nature of the co-product which is important in an environmental context and (ii)

the percentage available oxygen which directly influences the productivity (kg product per unit reactor volume per unit time) (Sheldon, R.A., 1993).

Different potential oxidants that are used in catalytic oxidation reactions are listed in **Table 6**.

Table 6: Potential Oxygen donating species used for selective hydrocarbon oxidation reaction (Sheldon, R.A., 1993)

Potential Donor	Active Oxygen [weight %]	By-product of Oxidation
Hydrogen Peroxide, H ₂ O ₂	47.0	H ₂ O
Ozone, O ₃	33.3	O ₂
Tert-butylhydroperoxide, TBHP	17.8	t-BuOH
Sodium Chlorate, NaClO	21.6	NaCl
Sodium Bromate, NaBrO	13.4	NaBr
Nitric acid, HNO ₃	25.4	NO _x

In hydrocarbon oxidation reactions, hydrogen peroxide is the most suitable oxidant when compared to other oxidants as shown in

Table 6. Hydrogen peroxide reagents are also potentially ideal oxygen transfers. This is attributed to its non-toxic by-product, water; and this oxidant has been known as clean and having a high oxidation potential (Lukasiewicz, M., et al., 2006; Sheldon, R.A., 1993). In addition, the use of hydrogen peroxide in oxidation reactions is attributed to several advantages such as (Fraile, J.M., et al., 2003):

- ❖ Ease of handling
- ❖ High active oxygen content
- ❖ Absence of by-products.

In contrast with reactions involving hydrogen peroxide, organic oxidants such as tert-butylhydroperoxide can be readily recycled, with the overall process requiring extra step to afford water as a by-product. Linear increase in peroxide concentration is proportional to increase in its active oxygen content (Sheldon, R.A., 1993).

The oxidation reaction of many organic compounds using hydrogen peroxide requires a metal catalyst (Lukasiewicz, M., et al., 2006). According to Sheldon's (1993) investigations, the different metal-catalysed oxidation reactions using hydrogen peroxide as an oxidant, are divided into two categories depending on the type of catalyst used: (i) one involving a peroxometal active catalyst-oxygen species (ii) oxometal pathways. Metals that are strong oxidising agents in high oxygen states such as Ru^{VI} , Cr^{VI} , V^{V} , Ce^{IV} , react via oxometal pathways whilst weakly oxidising metal ions such as Mo^{VI} , W^{VI} , Zr^{IV} , Ti^{IV} , involve peroxometal species in the selective oxidative dehydrogenation step.

It is noteworthy that when hydrogen peroxide is added in only one lot at the beginning of the reaction, in oxidation reactions involving triphase systems, the formation of secondary products is likely to occur at increased rate at the beginning of the reaction and decreases with time (Bhaumik, A., et al., 1998). This is attributed to the fact that hydrogen peroxide decomposes as the reaction progresses. In addition, 2-MN conversion increases almost proportionally with the hydrogen peroxide concentration, i.e., first order dependence of the peroxide concentration is observed (Anunziata, O.A., et al., 2004).

Increasing hydrogen peroxide concentration in catalytic hydroxylation of 2-methylnaphthalene has several effects as shown in Figure 16.

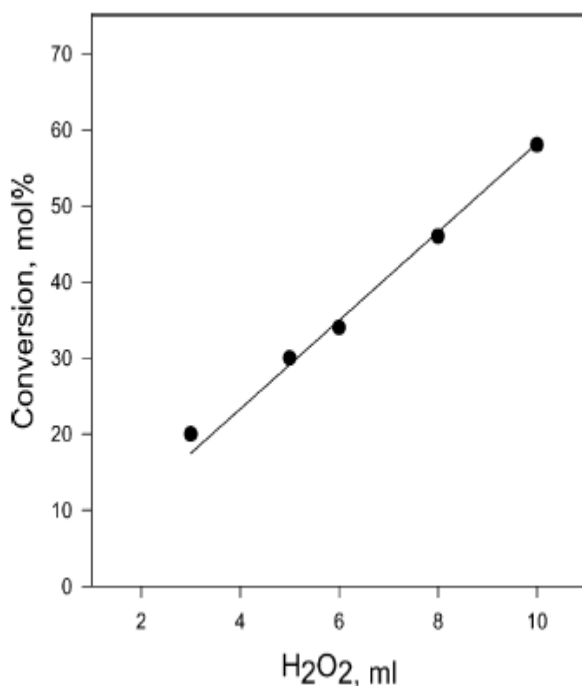


Figure 16: Conversion vs. hydrogen peroxide volume (30%wt, w/w) in the oxidation of 2-methylnaphthalene. Catalyst = 100mg, T- 393K, 2MN = 1g, solvent = 10ml, t= 10h (Anunziata, O.A., et.al, 2004).

2-MN conversion enhances linearly with increasing hydrogen peroxide concentration. Further research conducted in literature investigated the effect of an oxidant in 2-MN oxidation catalysed by iron (III) porphyrins catalysts using different oxidants, proved that considerable yields of 1,4- naphthoquinone are obtained with metachloroperbenzoic acid as oxidant; the use of tert-butylhydroperoxide and hydrogen peroxide, showing no catalytic effect (Khavasi, H.R., et al., 2002). The overall reaction rate for selective oxidation of 2-methylnaphthalene can be described as:

$$r = k [\text{cat}]^{-1} [\text{H}_2\text{O}_2]^1$$

3.5

$$\gamma = k' [\text{H}_2\text{O}_2]^1 \quad 3.6$$

$$\ln (1-X) = -k' t \quad 3.7$$

3.5.1.3. Reaction Temperature

Catalytic oxidation of aromatics requires elevated temperatures for the synthesis of hydrocarbons and quinones (Khavasi, H.R., et al., 2002).

In a study conducted by Anunziata et al. (2004), increasing temperature in the selective oxidation of 2-methylnaphthalene using aqueous hydrogen peroxide and titanium- containing zeolites generated enhanced 2-MN conversions. This was proven by 25 mol% 2-MN conversion obtained at 100 °C; with further temperature increase required to generate higher 2-MN conversions, although boiling points of the reactants must be taken into consideration ensuring that formation of side reactions is minimal. Product selectivities for 2-methyl-1, 4 - naphthoquinone increased to about 70 mol % at 100 °C. 2-methyl-1, 4 - naphthoquinone yield achieved 40.5 mol% at 150 °C (Anunziata, O.A., et al., 2004).

In a comparative study showing the variation of the relative spectral intensity per mole of Ti; the different titanosilicates are presented graphically as a function of temperature when interacted with aqueous hydrogen peroxide leading to the total signal intensity (200) at 200K. With decrease in temperature, this value was observed to increase steeply and below ~175K, the increase was less marked. The total spectral intensity of different titanosilicates (at 80K) decrease in the order: amorphous Ti- SiO₂ > Ti-MCM-41 > Ti-β > TS-1 (Srinivas, A., et al., 2003).

3.5.1.4. Solvent Effects

The vast majority of chemical reactions are performed in solutions. Therefore, the use of a solvent in oxidation reactions fulfils several functions during a chemical reaction as a solvent solvates the reactants and reagents so that they dissolve. Another important advantage of using a solvent in oxidation reactions is to provide a means of temperature control, either to increase the energy of the colliding particles so that they react quicker, or to absorb the heat that is generated during the exothermic reaction. Due to the reasons mentioned, it is highly desirable to develop eco- friendly methods for production of organic fine chemicals. One major problem encountered in various chemical processes is the use of large quantities of organic solvents that are detrimental to the environment and create problems with product separation and solvent recycle, that are energy intensive steps (Kumar, R., et al., 1999; Bhaumik, A., et al., 1998).

Corma et al. (1999), showed that the nature of the solvent has a major influence on reaction kinetics and product selectivity during oxidation reactions over zeolite TS-1. Thus, methanol and other protic solvents exhibit to enhance the catalytic activity of zeolite TS-1 for the epoxidation of propylene and other lower alkenes, provided that the size of the solvent is small enough to enter the pores of the medium pore TS-1. By definition, a protic solvent is a solvent that has a hydrogen atom bound to oxygen, for example, oxygen as in a hydroxyl group or nitrogen as in an amine group. It is known that the molecules of such solvent can donate an H⁺ (proton). Conversely, aprotic solvent cannot donate a proton. However, polar aprotic solvents are solvents that share ion dissolving

power with protic solvents but lack acidic hydrogen and these solvents generally have high dielectric constants and high polarity

(http://en.wikipedia.org/wiki/Protic_solvent).

Research done by Corma et al. (1999) on Ti-MCM-41 has distinguished two possible explanations for decrease in activity when using aprotic solvents such as:

- Additional adsorbed alcohol or water could become a barrier hindering diffusion of substrates and products while also decreasing the amount of adsorbed substrate thereby decreasing the intrinsic rate.
- The additional alcohol or water molecule is competing with hydrogen peroxide for the coordination at the titanium sites, thus reducing the amount of the catalytic active species.

When alcohols are employed as solvents, activity allows strong deactivation, which is caused by acid catalysed by-product formation. Several approaches to theories of solvent effects indicated that in order to explain the effect of protic solvents on the kinetics of oxidation of alcohols over TS-1, differences in the kinetic orders when using methanol, t-butanol, and water can be interpreted on the basis of differences in adsorption between the protic solvent and the alcohol substrate. However, when the reaction rates are much less affected by the type of solvent used, this can be explained assuming that the solvent does not take part in the slow step of the reaction mechanism (Corma, A., et al., 1999).

The nature of a solvent greatly affects selectivities in oxidation of 2-methylnaphthol using hydrogen peroxide as an oxidant over a titanium-substituted mesoporous catalyst. This was proven in a study when 2-methylnaphthol oxidation at reaction temperature 80 °C using acetonitrile as a

solvent generated high selectivities of 75%, 27% in acetone as a solvent, 17% in methanol as a solvent, and 38% in ethyl acetate (Kholdeeva, O.A., et al, 2005).

Another important aspect that is worthy to mention is adsorption. Adsorption inside the molecular sieves is remarkably different in TS-1, than in Ti-MCM-41 and Ti, Al- β . In general, Ti-MCM-41 has a lower affinity for the n-alkanes, as reflected in much lower k values. However, significant increase in k values is observed if an experiment is run in nonprotic solvent such as acetone or acetonitrile. The sorption of 2-alkanols on catalysts mentioned above seem to be governed by interaction of OH⁻ groups with the polar channel walls and only to a lesser extent by the hydrocarbon part of the molecule. Nonprotic solvents cannot compete with the alcohol group of the injected tracer compound, thus high K values result.

3.5.2. Selective Oxidation of Toluene

Generally, toluene has three classes of reactions, namely electrophilic substitution, side-chain reactions and cleavage of the methyl-phenyl bond. However, from an industrial point of view the most important electrophilic substitutions are nitration and chlorination with the cleavage of the bond between the methyl group and the aromatic ring of toluene occurring during dealkylation to produce benzene, with biphenyl as a reported by-product (Franck, H.-G. and Stadelhofer, J.W., 1988).

When reviewing studies reported in the literature, there is little information with limited research that has been done in terms of process operation and operating reactor conditions and mechanisms in oxidation of toluene in liquid

phase compared to information on 2-MN oxidation and more research still need to be conducted.

It is shown in

Table 7 that there is a high production of para- cresol in tri-phase system with water as a solvent with titanium zeolites used as catalysts.

Table 7: Toluene hydroxylation reactions: Catalyst = either TS-1 or MMATS, reaction time =6, 12 hrs (Kumar, R., et al., 1998).

Substrate	Solvent	H ₂ O ₂ Efficiency (%)	X (mol%)	mmol Toluene/ gram cat.	p : o	Products (mol%)	
						p-cresol	o-cresol
Toluene	Tri- water (TS-1)	15.2	14.8	50	1.35	55.9	41.4
	Bi-/acetone (TS-1)	5.6	5.5	50	0.41	28.4	69.7
	Bi-/ acetonitrile (MMATS)	39	26.6	108.5	1.18	16.5	14.0

In triphase system, the reaction is mainly taking place inside the zeolite channels of TS-1, whereas under bi-phase TS-1/H₂O₂ system, the active sites responsible for the reaction are generated on the external surface of zeolite catalyst (Kumar, R., et al., 1999). Observations by Keshavaraja, et al. (1995), stated that MMATS catalyst favours the oxidation of the methyl group side chain which is more predominant (approximately ± 69% product selectivity) than the hydroxylation of an aromatic ring, thereby enhancing the formation of cresols, with this process assumed to involve free radical routines in the reaction mechanism.

3.5.3. Conclusions Drawn from Studies Conducted in Literature and Relevance to this Study

Oxidation is one of the major and industrially important processes and is widely used in the synthesis of low and high volume chemicals and in the pharmaceutical industry. Furthermore, the stoichiometric technologies that scientists have used in recent times, using homogeneous catalysts suffer from several disadvantages such as production of large amounts of toxic wastes that are detrimental and hazardous to human health and causes a lot of environmental pollution.

However, previous work reported in the literature regarding the oxidation of aromatic compounds has been useful and of importance to this study. Many attempts were patented where 2-methylnaphthalene was oxidised in vapour phase, with oxygen using a vanadium-based catalyst. The drawback of this process is the fact that in order to attain high selectivity with the use of a vanadium-based catalyst, the 2-MN conversion was suppressed to a very low level (Matsumoto, Y., et al., U.S. 5,637,741,1997). In addition, low yields of 28-40% obtained by this process were attributed to the fact that excessive heat was generated during the reaction since the oxidation of the methyl group of 2-MN to carbon dioxide and water, and the conversion of naphthalene nucleus were both exothermic. Therefore, the use of vanadium- based catalysts is still a reluctant choice. Other processes in the oxidation of 2-methylnaphthalene employed the use of cerium compounds as catalysts (Kreh, R.P., U.S. Pat. No. 4,701,245, 1987). The drawback of this process is the fact that ceric ion has a potential of representing an excellent one electron oxidant. In addition, cerium

has not been used on an industrial scale because of its association with poor reactivity and selectivity.

As explained in chapter one, homogeneous systems in the oxidation of 2-MN generated a lot of toxic waste about ± 18 kg (Sheldon, R.A., 1996; Zalomaeva, O.V., et al., 2006; Kholdeeva, O.A., et al., 2005; Narayanan, S., et al., 2002; Herrmann, W.A., et al., 1999; Shi, F., et al., 2007). It is noteworthy that there is still a growing need to investigate and conduct more research on the subject as there is still a lot of information unknown regarding reaction mechanism and the reaction kinetics.

Oxidation of toluene has been neglected in the past decade in favour of phenol and its derivatives. As a result, a limited number of publications are reported in the literature and do not provide much information on the reaction kinetics and investigation of rate constants. In addition, more research and studies that focus on the use of toluene as a reactant in oxidation reactions involving heterogeneous systems is still required. The advantages of toluene oxidation processes are less formation of by-products, low costs, minimum waste production and the fact that these processes work well with environmental standards.

However, the work that is reported in the literature is a guideline to processes that were conducted and provided more insight into developing a protocol of manipulating reaction parameters in such a way that will generate high product yields and better conversions. Therefore, more work still needs to be conducted.

4. Research Design and Experimental Methodology

This chapter provides a description of the experimental setup and apparatus, procedure and experimental conditions, and the techniques employed for data analysis.

4.1. Catalyst Synthesis and Preparation treatment

The method of catalyst preparation has effects on the activity of the catalysts. It is of high importance to use reagents of high purity and accuracy when one is synthesising the catalysts used in this work. In this research work, the first phase involved the syntheses of titanium silicate – 1 (TS-1) and mesoporous Titanium–MCM-41 (Ti–MCM-41), both synthesised using hydrothermal procedures. Well established synthesis procedures were employed and all catalyst samples obtained were extensively characterised. Catalyst synthesis was carried out in the absence of aluminium. Reagents used in this work were used directly as obtained from the suppliers without further purification. The use of propylene or Teflon flasks prevents contamination during crystallisation. Glass vessels were excluded as silica, aluminium and boron are known to be leached out of glass (Robson H., and Lillerud K.P., 2001).

4.1.1. Synthesis of mesoporous Ti-MCM-41

Large crystallites of mesoporous Ti-MCM-41 were prepared using a hydrothermal procedure in the absence of aluminium and other alkali cations. Mesoporous Ti-MCM-41 crystallites are obtained by crystallising a gel of the approximate molar ratio composition:

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1 SiO₂ : 0.40 CTABr: 0.26 TMA : 0.26 OH : 0.017 TiO₂ : 24 H₂O₂

The large crystallites of mesoporous Ti-MCM-41 were synthesised according to the procedure described by Blasco et al. (1996). In a typical synthesis, a solution of 9.7 g Cetylammmoniumbromide (CTABr, Merck; a 29 wt% solution, prepared by adding 24g of H₂O to 9.7 g CTABr) was used. To this solution, 25 wt% tetramethylammoniumhydroxide (TMAOH, Alfa; 25 wt% TMAOH prepared by dissolving 6.3g of TMAOH in 0.25 g H₂O) was slowly added. This mixture was stirred in a propylene container, using a laboratory electric stirrer, giving a milky solution, which indicated that a homogenised mixture was attained. To this mixture, 4g of silica (aerosol Degussa 200) was added followed by the addition of 0.34g titanium isopropoxide (Sigma) as titanium source.

Crystallisation was carried out in 125 ml Parr PTFE- lined stainless steel autoclaves. Prior to autoclaving, the gel was aged for 24 hours at room temperature in the 125 ml Parr PTFE- lined stainless steel autoclave. This gel was heated under static autogeneous pressure at 125 °C for 14 hours without any rotation or stirring. The system was under autogeneous pressure, whereby the pressure inside the reactor was self-generated and experienced no other external influence.

After the crystallisation, the Parr autoclave was cooled by immersion in water at room temperature. The zeolite obtained was washed three times with deionised water and filtered under vacuum. Finally, the solid was dried for 14 hours at 80 °C, yielding ± 9.6g cream-yellow solid.

4.1.2. TS-1 Synthesis

Small crystallites of TS-1 were synthesised according to the method described by Tamarasso et al (1983). This synthesis was performed in two batches under the same reaction conditions except one batch was dried at room temperature due to technical problems and the other run dried at 80 °C (according to synthesis procedure). TS-1 crystallites were prepared from a starting gel with the following chemical composition:

0.125 TiO₂ : 8.25 SiO₂ : 247.5 H₂O : 3.75 TPA- OH

In a typical synthesis 20.4g tetraethylorthosilicate (TEOS, Si (OC₂H₅)₄; Merck) was mixed with 0.32g tetraethylorthotitanate (Ti (OC₂H₅)₄; Merck) at 35°C. The resulting milky solution was stirred in a propylene container. Slow addition of 21.25g tetrapropylammoniumhydroxide (40% solution in water, Alfa) to the reaction mixture was performed in a water bath at 0°C to prevent hydrolysis. Ethanol originating from tetraorthosilicate and tetraethylorthotitanite reagents was evaporated from the gel for approximately an hour at 80°C. Addition of 19.6g deionised water was performed to restore the loss of water during evaporation and to return to the initial volume, with a final pH of 12.2.

This gel was then transferred to a 125 ml Parr PTFE-lined stainless steel autoclave and heated under autogeneous pressure and static conditions at 170°C for 48 hours, without agitation. After the crystallisation time, the Parr PTFE-lined stainless steel autoclave was immersed on ice for 2 hours for cooling.

Then, the crystalline product was washed with deionised water three times, filtered under vacuum and dried overnight at room temperature. A white powder was obtained ($\pm 5.5\text{g}$ and $\pm 5.0\text{g}$ respectively).

4.1.3. Calcination

Calcination was performed at high temperatures to remove the template from the synthesised catalysts. Calcination decreases the coordination number from five or six to four in titanium species (Adam, W., et al., 1997). For both TS-1 and mesoporous Ti-MCM-41, the calcination temperature was 550°C . The synthesised catalysts were put into the furnace 25°C at a heating rate of $0.1^{\circ}\text{C}/50\text{s}$ until 550°C was reached. At 550°C , the holding time was 6 hours. After this calcination time, the furnace was switched off and both synthesised catalysts were taken out and cooled to room temperature, then weighed.

4.2. Catalyst Characterisation

A number of different spectroscopic techniques have been used for physical and chemical characterisation of the synthesised calcined samples.

4.2.1. Catalyst Chemical Composition (XRF and SEM)

Elemental analysis for determining the presence of alkali cations (Na^+ , Al^{3+} , K^+) and other elements, as well as the titanium and silicon content in the samples, was determined using X-Ray Fluorescence on a Philips 1404 Wavelength Dispersive spectrometer, fitted with a Rh tube and six analysing crystals, while the detectors are a gas-flow proportional counter, scintillation detector or a

combination of the two. Samples were analysed on a powder briquette at 60 kV and 40 mA tube operating conditions. Pressure was kept low at 10 Pa under reflux. An EDX chemical analysis was also performed using Scanning Electron microscopy (SEM), explained in detail in section 4.2.2.

4.2.2. Scanning Electron Microscopy (SEM)

Crystal sizes, morphologies, and chemical composition (using EDX system) of both synthesised, calcined catalysts were investigated using a Leo 1430VP Scanning Electron Microscope fitted with Backscatter, Cathodoluminescence, variable pressure and energy dispersive detectors, as well as a Link EDX system.

Samples were mounted on carbon paper to avoid electron conductance and coated with a thin gold film prior to scanning the images, to prevent surface charging and protect from thermal damage from the electron beam with the flow of carbon dioxide, current of 15mA and system vacuum approximately 1.3×10^{-2} Pa. The instrument was operated at an accelerating voltage of 40 kV, a tilt angle of 0° and an aperture size of 30 μm , and a working distance of 7mm.

4.2.3. X-ray Powder Diffraction (XRD) Analysis

4.2.3.1. Ti-MCM-41

Examination of crystallinity and determination of phase purity of Ti-MCM-41 was performed using Powder X-ray diffraction patterns, collected in air at room temperature on a Bruker D8 Advanced Powder Diffractometer.

The instrument used Cu-K α radiation of wavelength ($\lambda = 0.1542$ nm) and was generated at 40KV and 25mA. For synthesised calcined Ti-MCM-41, scanning was done at the lower angle 2θ at the range of 1 to 10 at counting time of 30s for 15 min; with the step size of 0.05 2θ A. A slit divergence of 3 ° was used.

4.2.3.2. TS-1 (Small crystals)

Powder X-ray diffraction patterns for the analysis of crystallinity and determination of phase purity of zeolite TS-1 were collected in air at room temperature on a Bruker AXS D8 Advanced Powder Diffractometer.

The instrument used Cu-K α radiation of wavelength ($\lambda = 0.1232$ nm) and was generated at 40KV and 30mA. For synthesised calcined TS-1 sample, scanning was done at the range of 5 to 50° 2θ , with step size of 0.04 2θ and 10 second counting time. A slit divergence of 3 ° was used. For the TS-1, better XRD patterns were obtained over 90 minutes.

4.2.4. BET- Nitrogen Absorption Isotherm

Surface areas and micropore volumes of the samples were determined using a Micromeritics ASAP 2010 (Accelerated Surface Area and Porosimetry System).

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Prior to analyses, 0.6g of sample was first degassed under vacuum at 90°C for 1 hour. Then the temperature was increased to 300°C and degassed overnight.

The first step was to get rid of any moisture that might be trapped in the pores. This must be done gently at higher temperatures, otherwise the water will "escape" too quickly and might damage the pores. The BET analysis was performed at 77.35 K and the BJH method was applied to calculate the pore diameters. The BJH method is a procedure for calculating pore size distributions using the Kelvin equation that involves an imaginary emptying of condensed adsorptive in the pores in a stepwise manner as the relative pressure is likewise decreased. The Surface areas were determined by t-plot method.

4.3. Experimental Batch Hydroxylation Reactions

4.3.1. Apparatus

Several apparatus have been utilised in this work. The three experimental set-ups employed are as follows:

- I. The first set-up tested was the one previously employed for the studies of the hydroxylation of phenol (Burton, R., 2006). A 24 ml glass closed-batch reactor immersed in the water bath was used. The reaction was maintained at the correct temperature by placing a water bath on a magnetic stirrer/ heater unit. The reactor vessel was equipped with a Mininert® valve teflon sample port so that the reaction samples could be

withdrawn through the reaction at specified sampling intervals. The reaction set-up is shown in Figure 17.

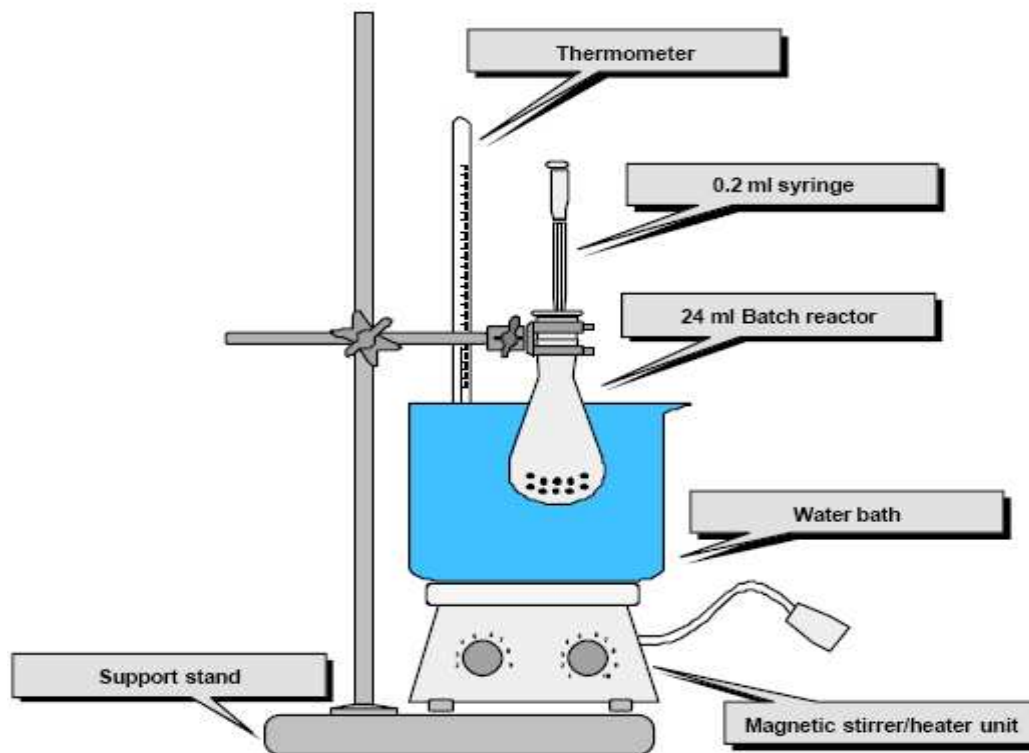


Figure 17: Experimental setup used in the 2-methylnaphthalene and toluene hydroxylation reactions (Burton, R., 2006).

Prior to conducting each run, the heater plate was calibrated so that the correct temperature could be maintained. The heater- water bath temperature was calibrated between 60 °C and 80 °C.

As the first method described above didn't yield good results, a second procedure was proposed.

- II. Figure 18. Illustrates the second set-up. The heating mantle was placed in a magnetic stirrer/ heater unit, to ensure that the reaction was performed under constant stirring and uniform temperature.

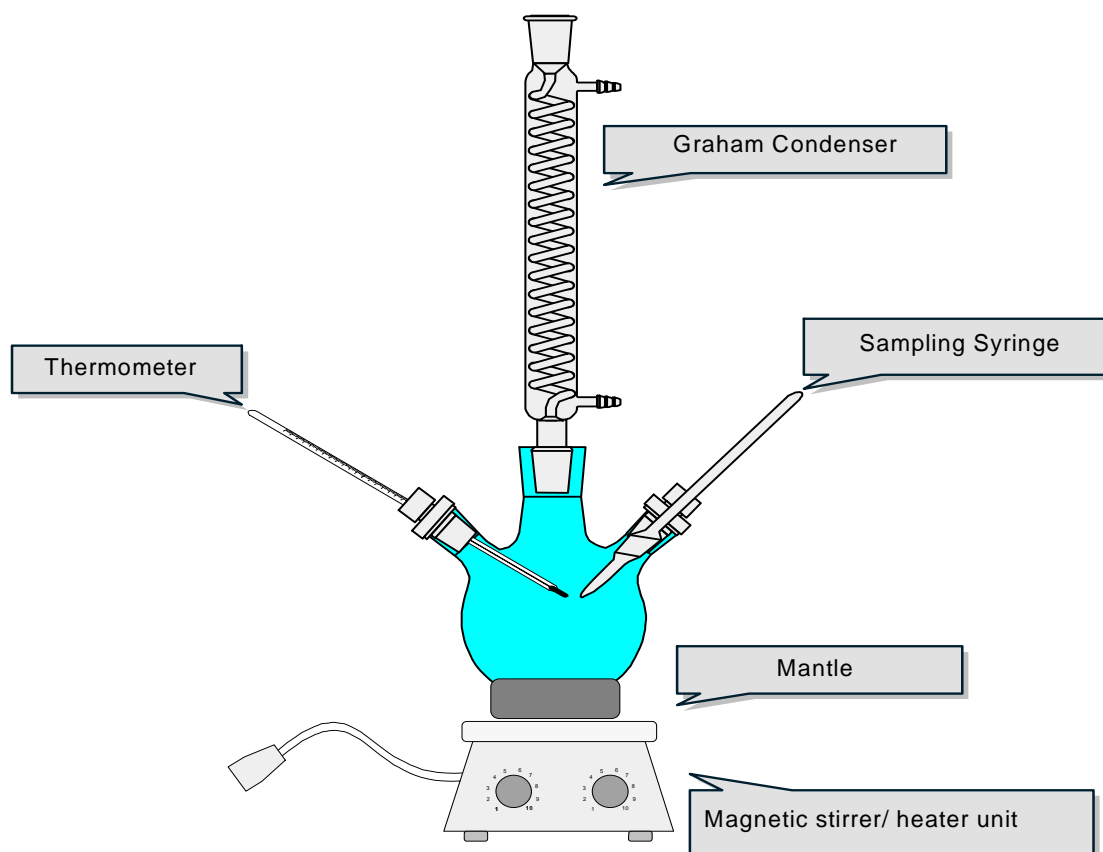


Figure 18: Experimental setup for a reflux apparatus in 2-MN hydroxylation.

The flask consists of three necks. A thermometer was immersed to ensure that the reaction mixture was maintained at a correct temperature, with the sampling syringe immersed for sample withdrawal at certain time intervals. The use of PTFE sample ports with screw-thread Quickfit adapters ensured that samples were only in contact with glass and PTFE, as well as to minimise any evaporation losses.

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The heater mantle was calibrated prior to conducting any experiment to minimise temperature variations.

- III. The third procedure was found to be the most suitable. This apparatus consisted of a Parr PTFE-lined stainless steel autoclave, immersed in a polyethylene glycol oil bath, ensuring that the reaction temperature was kept at correct temperature as shown in Figure 19.

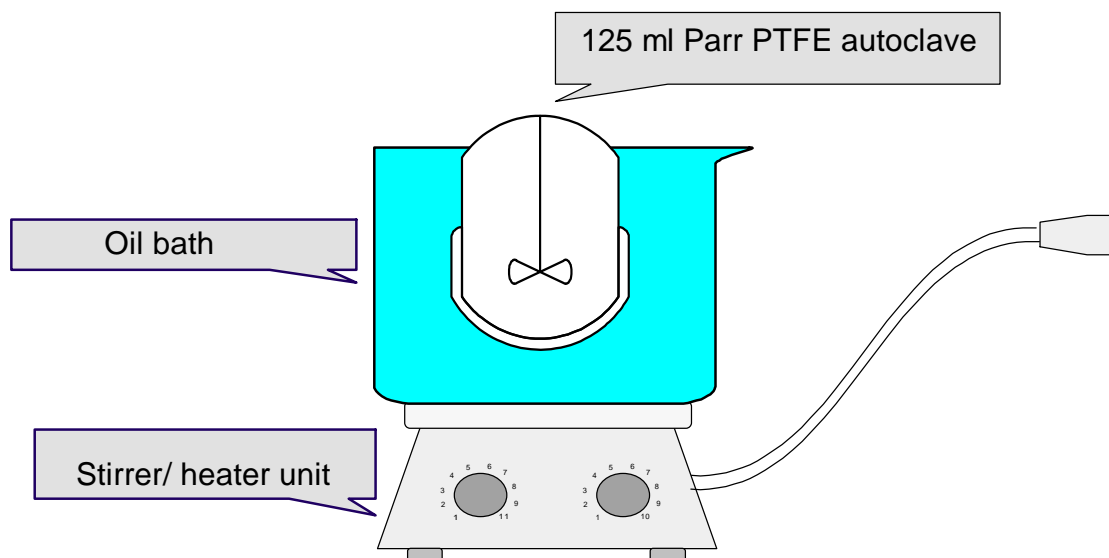


Figure 19: Experimental setup for a Parr PTFE autoclave apparatus in 2-MN hydroxylation.

The heater – oil bath temperature was calibrated and monitored between 80 °C and 120 °C. At constant time intervals, temperature checks were performed using a thermostat to ensure that constant temperature was maintained throughout the reaction.

4.3.2. Experimental Conditions and Procedures

4.3.2.1. 2-methylnaphthalene Hydroxylation

2-methylnaphthalene oxidation was performed using 30 wt-% hydrogen peroxide as an oxidant over TS-1 or Ti-MCM-41 as catalysts. The stoichiometric amount of hydrogen peroxide was in the range of 1.0 – 6ml. Due to the fact that this was primarily a feasibility study, various experimental set-ups were tested to determine which option was the best for determining the reaction activity and selectivity.

- i. Reactions in the original set-up (I) were carried out as follows:

Initially, 0.5 – 1.0 g 2-methylnaphthalene was dissolved in 3 - 10 ml of an appropriate solvent (either methanol, n – butanol, n – propanol, isopropanol, n – pentanol, or acetonitrile) and dissolved under constant stirring until a homogenised mixture was obtained. 0.1 -0.5 g of synthesised calcined catalyst (either Ti-MCM-41 or TS-1) was then added (2-methylnaphthalene: catalyst mass ratio was ca. 2.5) and adsorption equilibrium was attained at a reaction temperature (60- 80°C) by allowing the suspension to stir for approximately 12 hours before starting the reaction to reach adsorption equilibrium.

After adsorption equilibrium had been attained, the catalytic reaction was started by addition of between 1.0 ml – 6ml 30 wt% hydrogen peroxide (Sigma-Aldrich, AR, 30 wt% stabilised solution) at time zero to the catalyst and 2-methylnaphthalene- solvent solution. In all reaction runs, hydrogen peroxide was added as a single portion.

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Aliquots of reaction samples (0.2 ml) were withdrawn at specified time intervals through a septum with a microlitre syringe (without removing reactor cap) for analysis. This sample was directly transferred into a 4ml sample vial (fitted with Teflon-lined septa), then diluted with 3 ml of the same solvent used in the reactor (either methanol, *n* – butanol, *n* – propanol, isopropanol, *n* – pentanol, or acetonitrile), and then prior to filtration, 1ml of the diluted sample was withdrawn, and reserved for Iodometric titration. The remaining sample was filtered over a sterile 0.22 μm Millipore filter (Millex – GV). The samples were labelled and cooled at 0°C to prevent further reaction and hydrogen peroxide decay prior to analysis.

Samples were taken at 15, 30, 60, 120, 180, 240, 300, 360, and 420 minutes (the total reaction time was 7 hours).

(ii). Catalytic experiments using reflux technique (set-up II) were performed according to the same procedure as detailed and outlined in (i) above, except at slightly higher reaction temperatures (80- 120°C).

(iii). Using a Parr Teflon – lined autoclave (set-up III), the above mentioned procedure could not be used as sampling was only done after 6 hours due to the fact that the autoclave was completely sealed. Therefore increasing reactant concentrations was proposed in order to meet the reactor conditions and to have a sample recovered after each reaction. It was assumed that changing operating conditions would alter conversion and product yield. For all reactions, 1g 2- methylnaphthalene was placed in the PTFE liner, 0.1g of either zeolite TS-1 or mesoporous Ti-MCM-41 was used comparably for each run, 10 ml solvent of interest (methanol, *n*-propanol, isopropanol, acetonitrile),

temperature (70 - 120°C) under constant stirring, using a heating unit for 6 hours. Adsorption was attained over night at room temperature (± 12 hours). To start the reaction, 6 ml H_2O_2 was added.

After the total reaction time had been reached, the autoclave was placed in cold water for an hour for cooling. 0.5ml was then withdrawn and placed in a 4ml vial and diluted with 3ml of the solvent being used, then filtered using a sterile 0.22 μm Millipore filter (Millex – GV) to remove the catalyst. 1ml sample was withdrawn for iodometric titration, and the remaining sample kept at 0°C for analysis.

Catalyst recovery or recycling was performed on the remaining sample on the reactor port for each experimental run by filtration, extensive washing with the solvent used in the reactor, and drying at room temperature; half of the original mass was obtained (for example, 0.063g at 110°C in acetonitrile solvent).

Sample analysis was performed using Gas Chromatography and GC-MS Spectroscopy as detailed in section 4.4.

4.3.2.2. Toluene hydroxylation reactions

Further catalytic batch hydroxylation experiments were performed using a normal batch reactor as in apparatus I. Because toluene is not a larger aromatic substrate, as compared to 2-methylnaphthalene, and was more reactive, the initial batch system (set-up I) was adequate for these experiments.

Reaction conditions consisted of either 1.2g Toluene, 0.12g catalyst (TS-1), and 5ml of solvent (either water or acetonitrile), or for the experiments in excess

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toluene (0.657g toluene) and 0.12g catalyst. The reaction temperature was controlled between 60 – 80 °C, depending on boiling points of the solvent used. The reactants were allowed to adsorb on the catalyst at room temperature for ±12 hours prior to reaction. The reactor was suspended into an oil bath at the desired temperature, under constant stirring for one hour to reach thermal stability. To start the reaction, 0.5ml of the 30 wt-% hydrogen peroxide solution was added. Sampling was done by withdrawal of 0.2 ml sample from the reactor at every 40, 60, 120, 180, 240, 300, and 360min.

0.2ml sample was placed in a 4ml vial, diluted by 3ml solvent used in the reaction, filtered using a sterile 0.22 µm Millipore filter (Millex – GV), labelled and stored for analysis at 0°C to prevent further oxidation and hydrogen peroxide decomposition. Prior to storage, 1ml of the diluted sample was withdrawn for determination of hydrogen peroxide concentration by iodometric titration.

4.4. Product and Sample Analysis

Several analytical techniques such as: standard iodometric titration (for the determination of H₂O₂ concentration in samples), Gas Chromatography, and Gas Chromatography with Mass Spectrometry (GC – MS), were used.

4.4.1. Standard Iodometric Titration

Iodometric titration is a redox reaction using sodium thiosulphate as a reducing agent specifically to titrate iodine. This method is used for the determination of concentration of the oxidising agent solution, with liberation of iodine. In iodometric titration, starch can be used as an indicator as it adsorbs iodine that

has been released. This absorption will change the solution to turn dark blue colour, which disappears when titrated with sodium thiosulphate, thus end point has been achieved.

4.4.2.1. Titration Procedure

To limit the influence of iodine's volatility, the titrations were performed in cold solutions in conical flasks with constant stirring, preventing local excesses of thiosulphate. The preparation of chemical reagents used in the titration are as detailed in **APPENDIX A**. The use of acid solutions as reported by Christian (1994) is due to reactions between many oxidising agents and iodide being promoted by high acidity.

The method of titration used in this work has been adopted and modified from Pan, Y. et al., 2003. In a typical titration, 50 ml of dilute sulphuric acid (0.1 M) was placed in a 250 Erlenmeyer flask, with nitrogen gas bubbled through the flask at a higher rate of 250 ml (NTP)/ min in the acid solution for 2 minutes to purge any oxygen and carbon dioxide present in the flask prior to injecting the dilute organic reaction sample.

Approximately, 1 ml of the diluted reaction sample was added all at once to the flask, with the nitrogen gas flow slowed to approximately 120 (NTP)/ min. 5 ml 1 wt% potassium iodide solution was added slowly to the flask, with agitation using a magnetic stirrer to ensure complete and homogenised mixing. One drop of 2 wt% ammonium molybdate solution was added to accelerate the reaction and decomposition of hydrogen peroxide with the liberation of iodine.

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The reaction was allowed to stand for 1 minute to reach equilibrium and the solution turned a goldish – brown colour.

This mixture was slowly titrated with sodium sulphate solution (*ca.* 0.04019 N) until the solution turned pale – yellow. The titration was performed rapidly to minimise air oxidation of iodide, with sufficient stirring to prevent local excess of thiosulphate, as thiosulphate is decomposed in acid solution. 1 ml of starch indicator solution is not added at the beginning of the reaction where iodine concentration is high, instead was added slowly under agitation when the iodine colour turns pale yellow, yielding a deep violet/ blue solution. Two reasons for this phenomenon are attributed to (i) iodine – starch complex slow dissociation, with a diffuse endpoint resulting when large amount of iodine were adsorbed on starch. (ii) Most iodometric titration reactions being performed in strongly acidic medium and starch investigated to have tendency to hydrolyse in acid solution. The titration mixture was further titrated with thiosulphate solution until the solution turned colourless, indicating the endpoint had been reached. Then, the total volume of sodium thiosulphate used to reach the endpoint was recorded, and hydrogen peroxide concentration present in the organic samples was calculated.

4.4.2. Gas Chromatography

Gas chromatography (GC) is the widely used technique for qualitative and quantitative analysis, whereby components of a vaporised sample are separated as a consequence of being partitioned between a mobile gaseous phase and a liquid or solid stationary phase held in a column. Elution in a GC is brought about by the flow of an inert, gaseous, mobile phase. In contrast to other separation techniques, the mobile phase does not interact with the

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molecules of the analyte; its function is mainly to transport the analyte through the column. Thus, this mobile phase must be chemically inert, with helium the most common mobile-phase gas used, although argon, nitrogen and hydrogen can also be used (Skoog, D.A., et al., 2004).

Currently, gas chromatography is one of the most important and the most economic of all separation methods. Its applicability ranges from the analysis of permanent gases and natural gas to heavy petroleum products, oligosaccharides, lipids and also aromatic compounds (Günzler, H., and Williams, A., 2001).

Chromatography is extensively used for the ultimate identification and determination of the vitamins, with GC specifically, the most convenient method of separation of vitamin K compounds. Prior to this, biological methods were distinguished to be the best for identification and determination of vitamin K groups, although due to several disadvantages such as (i) inaccuracy, (ii) expense, and (iii) slowness a demand for the development of physicochemical methods has been high (Heftmann, E., 1966). Due to the disadvantages mentioned, the development of chromatographic techniques replaced the biological methods.

The low volatility of vitamin K compounds requires high column temperatures. Chromatograms obtained by liquid chromatography (LC) and UV detection are often complex with poor resolution of vitamin K compounds from chromatographic interferences.

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Other separation methods such as High Performance Liquid Chromatography (HPLC) for vitamin K analysis were also developed for certain vitamin K compounds. This method was also found to be an analytical tool to investigate the vitamin as well as the interconversion of vitamin K to its 2, 3- epoxide. High Performance Liquid Chromatography can be suitable due to its high sensitivity, specificity, and accuracy (McDowell, L.R., 1989).

For either methylnaphthalene or toluene hydroxylation reactions, the analysis system used in this study was a GC-Varian 3400 connected to a FID detector, equipped with a 50m x 0.25mm bounded phase SGE capillary column made of fused silica. For quantitative identification of 2-methyl-1, 4-naphthoquinone, biphenyl was used as an internal standard for methylnaphthalene hydroxylation.

In a previous study conducted at the Department of Process Engineering, Stellenbosch University, (Engelbrecht, 2006) when analysing cresols using HPLC (High Performance Liquid Chromatography), a problem with separation of para and ortho cresol peaks was experienced as the peaks overlapped. The meta-cresol peak however, formed a separate peak. According to the investigations using HPLC, meta- cresol was not produced during the reactions with toluene as a feed reactant. Therefore, although the meta and para peaks could not be separated effectively on the GC, this method was preferred for analysis of the reaction samples. Kumar and Bhaumik (1998), when performing GC analysis reported formation of para and meta cresol to be inseparable as one peak was obtained, and this has been problematic in terms of separating the meta- from para-cresol. The ortho cresol forms a separate peak. Due to our reaction mechanisms and solvent effects, however, the

formation of meta-cresol in this work is not expected; therefore, this is not a problem and meta-cresol formation is totally omitted.

Using the GC, for identification of cresols from toluene hydroxylation, with water as a solvent, phenol was used as an internal standard. However, the use of phenol as internal standard is a reluctant choice as phenol is expected to react in the GC with hydrogen peroxide present in the sample, leading to the formation of benzoquinone. The extent of benzoquinone formation during sample analysis was determined by allocating a benzoquinone peak. However, solubility of toluene in water is very low as toluene is mostly immiscible with water and forms an organic layer. Samples with either acetonitrile as solvent or excess toluene were analysed using ethylbenzene as an internal standard.

4.4.3. Gas Chromatography – Mass Spectroscopy (GC - MS)

GC-MS use came into consideration with 2-MN oxidation data obtained at reaction temperature 110 and 120 °C using Ti-MCM-41 as catalyst with acetonitrile as a solvent. The reason why only 2-MN samples were taken for further analysis with GC-MS was the generation of products that were unidentified by the GC. Toluene oxidation reactions when using water or acetonitrile as a solvent, no side products were detected. Therefore, due to this it was not necessary to perform GC-MS analysis for toluene samples.

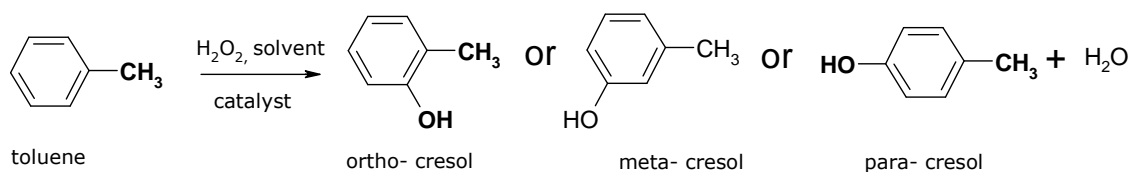
In general, GC-MS is a very powerful technique combining gas chromatography with mass spectroscopy is known as Gas Chromatography – Mass Spectroscopy. Mass spectroscopy is a sophisticated technique producing, separating, and detecting ions in the gas phase (Christian, G.D., 1994). This

technique has found various applications due to the following uses (i) identification and quantitation of volatile and semivolatile organic compounds in complex mixtures, (ii) Determination of molecular weights and elemental compositions of unknown organic compounds in complex mixtures, (iii) Structural determination of unknown organic compounds in complex mixtures both by matching their spectra with reference spectra and by a prior spectral interpretation (Hites, R.A, handbook, year not given).

For this work, catalytic oxidation reaction samples of 2-methylnaphthalene analysed by GC (reaction temperatures of 110 and 120°C), were further analysed using agilent MSD 5975 GC-MS, consisting a HP-5MS 5% phenyl methyl siloxane 30m x 0.25mm x 0.25µm column. Biphenyl was used as an internal standard.

4.5. Kinetic Modelling

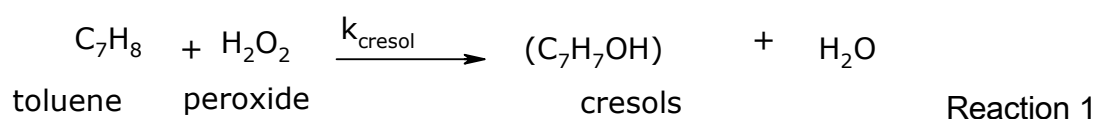
The rate of disappearance of toluene due to hydroxylation depends on temperature, solvent effects and reactant mixture composition. For this research work, rate constants were determined using initial reaction rates. Kinetic reactions were obtained by fitting the concentration-time profile data obtained in catalytic oxidation of toluene. Liquid – phase hydroxylation of toluene with aqueous hydrogen peroxide gives:



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In the above reaction, toluene is assumed to react with hydrogen peroxide, with introduction of one OH⁻ group leading to formation of cresols, with side reactions expected to result to the formation of aldehydes and dihydroxy compounds (methylbenzenediols).

Toluene hydroxylation is expressed by the following independent reaction:



In the presence of light, hydrogen peroxide is degraded and undergoes decomposition according to the following reaction:



For data modelling purposes, in synthesis of cresols, assumptions made are based on hydrogen peroxide reacting only with toluene forming ortho-, meta-, and para- cresols.

The data obtained from toluene hydroxylation experiments can be fitted in concentration time profiles with the following second order kinetic expressions, first order in both toluene and hydrogen peroxide as clearly explained in Burton (2005)'s work, with kinetic reaction rate expressions for reactants and products explained as follows:

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$$-r''_{\text{tol}} = \frac{1}{S_T} \cdot \frac{dC_{\text{tol}}}{dt} = k_{\text{tol}} \cdot C_{\text{tol}} \cdot C_{\text{ox}} \quad [4.1]$$

$$r''_{\text{par-}} = \frac{1}{S_T} \cdot \frac{dC_p}{dt} = -k_p \cdot C_{\text{tol}} \cdot C_{\text{ox}} \quad [4.2]$$

$$r''_o = \frac{1}{S_T} \cdot \frac{dC_o}{dt} = -k_o \cdot C_{\text{tol}} \cdot C_{\text{ox}} \quad [4.3]$$

Whereby:

r''	=	Rate of consumption/ generation per unit external surface area of catalyst [$\text{mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
k_i	=	Reaction rate constant [$\text{dm}^6 \cdot \text{mmol}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
S_T	=	Total external surface area of catalyst [m^2/dm^3]
C_i	=	Concentration of species i [mol/dm^3]
t	=	time [min]

In order to simplify the equations, the following abbreviations were used identifying the reacts and product used in catalytic experiments:

Tol	=	Toluene
Ox	=	Oxidant (H_2O_2)
p	=	p-cresol
o	=	o-cresol

The design equation for a batch reactor, written in terms of conversion of toluene is illustrated by:

$$\frac{dX_{\text{tol}}}{dt} = \frac{-r_{\text{tol}} \cdot V}{N_{\text{tol},0}} \quad [4.4]$$

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It has been shown that in liquid-phase reaction, where the total reactor volume remains constant, the design equation can be expressed in terms of concentration as follows:

For the irreversible liquid-phase reaction, the rate law is expressed by:

$$-r_{\text{tol}} = k_{\text{tol}} \cdot C_{\text{tol},t} \cdot C_{\text{ox},t} \quad [4.5]$$

The toluene and hydrogen peroxide concentrations at time t can be expressed in terms of the toluene conversion, and initial toluene concentration (C_{tol}) and molar ratio of hydrogen peroxide to toluene (Θ_{ox}) at the start of the reaction:

$$C_{\text{tol},t} = C_{\text{tol},0} \cdot (1 - X_{\text{tol}}) \quad [4.6]$$

$$C_{\text{ox},t} = C_{\text{tol},0} \cdot (\Theta_{\text{ox}} - X_{\text{tol}}) \quad [4.7]$$

The rate law of toluene consumption can be expressed by substituting equations [4.6] and [4.7]:

$$-r_{\text{tol}} = k_{\text{tol}} \cdot C_{\text{tol},0}^2 \cdot (1 - X_{\text{tol}}) \cdot (\Theta_{\text{ox}} - X_{\text{tol}}) \quad [4.8]$$

The design reaction for a batch reactor, can be generated by substituting equation [4.8] into equation [4.4]

$$\frac{dX_{\text{tol}}}{dt} = k_{\text{tol}} \cdot C_{\text{tol},0}^2 \cdot (1 - X_{\text{tol}}) \cdot (\Theta_{\text{ox}} - X_{\text{tol}}) \quad [4.9]$$

By solving equation [4.9], the following expression is obtained:

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$$\frac{dX_{tol}}{(1 - X_{tol}) \cdot (\Theta_{ox} - X_{tol})} = k_{tol} \cdot C_{tol,0} \cdot dt \quad [4.10]$$

Integrating, between t_1 and t_2 generates the following equation:

$$\frac{1}{(\Theta_{ox} - 1)} \cdot \ln \frac{\Theta_{ox} - X_{tol}}{\Theta_{ox} \cdot (1 - X_{tol})} \Big|_{X_{t1}}^{X_{t2}} = k_{tol} \cdot C_{tol,0} \cdot (t_2 - t_1) \quad [4.11]$$

Raising the exponent:

$$\frac{\Theta_{ox} - X_{tol}}{\Theta_{ox} \cdot (1 - X_{tol})} = \exp[k_{tol} \cdot C_{tol,0} \cdot t (\Theta_{ox} - 1)] \quad [4.12]$$

The calculated toluene conversion can be obtained by rearranging and solving equation [4.12] as follows:

$$X_{tol} = \frac{\Theta_{ox} \cdot (1 - \exp[k_{tol} \cdot C_{tol,0} \cdot t (\Theta_{ox} - 1)])}{(1 - \Theta_{ox}) \cdot \exp[k_{tol} \cdot C_{tol,0} \cdot t (\Theta_{ox} - 1)]} \quad [4.13]$$

The rate constant for toluene consumption was obtained by solving to minimise the error between the theoretical and calculated conversion by changing the value of the rate constant. Determination of toluene consumption rate constant was achieved by Least squares Regression. Microsoft excel solver was used, with error of sum of squares of the differences between the theoretical toluene conversions and calculated toluene conversions to the minimum.

5. Results and Discussion

5.1. Catalyst Physical and Chemical Characterisation

5.1.1. Titanium- MCM-41

The synthesised Ti-MCM-41 used in this work was easily isolated from the hydrothermal process after 14 hours by washing the recovered solid catalyst with distilled water, filtering and drying at crystallisation temperature (408K), with $\pm 6.22\text{g}$ of total solid catalyst recovered after drying at 353K for 13 hours. After calcination, this solid catalyst was characterised using different techniques and procedures.

Firstly both X-ray Fluorescence Spectroscopy (XRF) and Scanning Electron microscopy (SEM) were used to investigate the chemical and elemental composition (XRF and SEM) and morphology (using only SEM) as detailed in

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Table 8. The use of XRF for chemical analysis was attributed to problems experienced with AAS.

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Table 8: Elemental analysis performed using either XRF or SEM spectroscopes on calcined Ti-MCM-41 catalyst.

Element/ Compound	X-ray Fluorescence (compound %)	SEM-EDX (wt %)	Si/Ti Ratio
AlO ₃	0.01	-	43.1 (EDX) 35.77 (XRF)
SiO ₂	84.98	39.7	
TiO ₂	1.86	1.11	
CaO	0.03	-	
K ₂ O	0.04	-	
Fe ₂ O ₃	0.05	-	
MgO	0.04	-	
MnO	0.01	-	
P ₂ O ₅	0.01	-	
Si		30.9	
Ti		0.72	
O	-	57.7	
Cu	-	0.26	
C	-	10.4	

As

indicated

in

Table 8, chemical analysis using X-ray Fluorescence (XRF) shows lower Si/Ti ratios of 35.77 compared with 43.1 obtained using Scanning Electron Microscopy (SEM). Notably, chemical analysis done by XRF technique is ideal and reliable as this technique is designed for rapid and accurate whole sample analysis, as compared with SEM which focuses on quantitative chemical analysis on a fixed spot, with expected errors ranging from 0.5 to 0.2 wt% for the analysis of major elements. In addition, the SEM focuses on the surface rather than the bulk of the material. Although no aluminium was incorporated during catalyst synthesis, traces of 0.01 wt% aluminium were reported with XRF. The Ti/Al ratio of ca. 186 or alternatively Si/Al = 8498 was assumed to be negligible with no effect on catalyst structure and composition.

Comparing the Si/Ti ratios obtained from this work with the values obtained by Blasco et al. (1995), the values are within the accepted range. Blasco et al. (1995) synthesised Ti-MCM-41 obtaining Si/Ti ratios of *ca.* 58.8, as measured using Atomic Absorption Spectroscopy (AAS). Bhaumik and Tatsumi (2000) stated pure Ti-MCM-41 synthesised with a Si/Ti molar ratio of 60, is of high purity. The limit of incorporation is restricted up to Si/Ti =30 for Ti-MCM-41 in the presence of organic modification, with Si/Ti =60 for pure Ti-MCM-41 in the synthesis gel. In this study, the Si/Ti molar ratio was 59 in the synthesis gel under static conditions. The difference in results here may be due to the choice of measured technique.

Scanning electron microscopy was also used for the determination of Ti-MCM-41 morphology, synthesised by hydrothermal procedure at 10 μ m magnification as shown in Figure 20 and 30 μ m magnification as indicated in **APPENDIX D**.

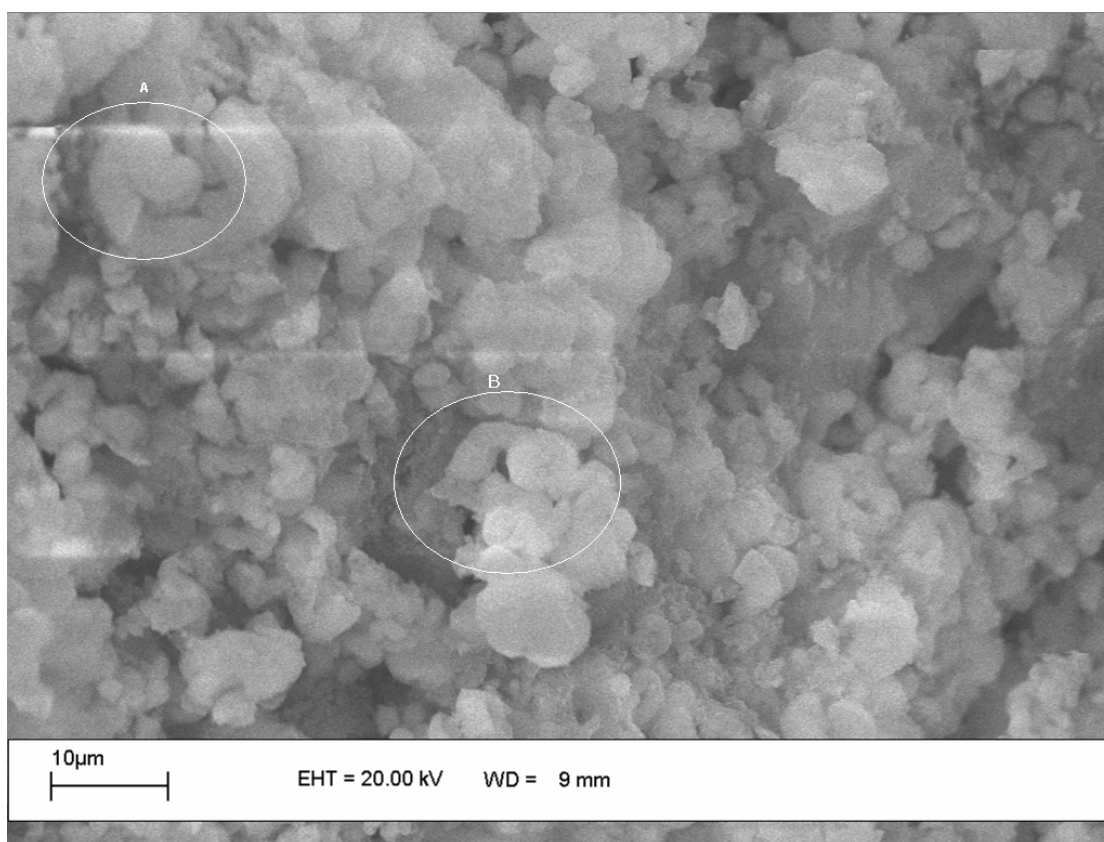


Figure 20: SEM micrograph of titanium- MCM-41, with Si/Ti of 45.7, on a 30 μm scale obtained at 408K after 14 hours.

Ti-MCM-41 catalyst synthesised in this work exhibits two different types of particle morphology as indicated by round rings in Figure 20. A hexagonal shaped structure (A) and worm-like structures (B) were obtained. The hexagonal shaped structures and winding worm structures observed with Ti-MCM-41, clearly emphasised that the catalyst synthesised definitely belongs to the M41S family and is of high purity. It is noteworthy that the hexagonal structure is the major feature of the Ti-MCM-41. However, the particle size of Ti-MCM-41 was too complex to define or estimate as this mesoporous material has a tendency to form agglomerates, thus the homogeneity of Ti-MCM-41 was

assumed to indicate that there are no physical isolated crystals of the microporous or mesoporous in Ti-MCM-41.

In describing the crystallinity and phase purity of calcined Ti-MCM-41 catalyst, X-ray Powder Diffraction (XRD) was used. To achieve this analysis, powder diffraction diagrams were obtained by measuring intensity, shape and width of diffraction lines at a lower diffraction angle 2θ (maximum diffraction angle = 10). A detailed XRD chromatogram is clearly illustrated in Figure 21.

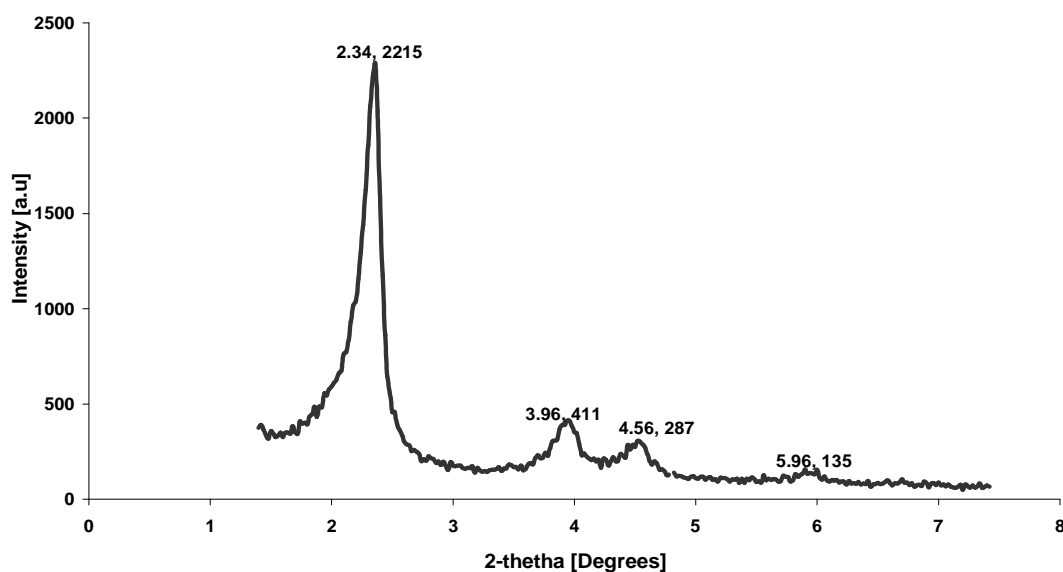


Figure 21: XRD patterns for hydrothermally synthesised calcined Ti-MCM-41 at 408K after 14 hours.

The well-defined XRD patterns were found to be indexed on the basis of four Bragg peaks, with the most intense peak of crystalline mesoporous material indexed at $2\theta \sim 2.34^\circ = 2215$, $2\theta \sim 3.96^\circ = 411$, $2\theta \sim 4.56^\circ = 287$, with the smallest peak indexed at $5.96^\circ = 135$.

The presence of four peaks as in Figure 21, indicate a typical low diffraction peak, which is the major characteristic of Ti-MCM-41 structure at the lower angle 2θ . In agreement with work done by Berenguer-Murcia et al. (2003), the presence of smaller peaks confirmed presence of the long- range order in Ti-MCM-41. It also emphasises that the synthesised sample is Ti-MCM-41 without any lamella phase impurities.

Further characterisation on Ti-MCM-41 catalyst adopted the use of nitrogen-adsorption isotherm, a standard procedure and technique preferred for surface area determination, porosity, and micropore volume. The surface area of Ti-MCM-41 has been evaluated from physisorption isotherm data using a widely used method invented by Brunauer – Emmett – Teller (BET). After analysis, a nitrogen adsorption – desorption isotherm was generated as indicated in Figure 22.

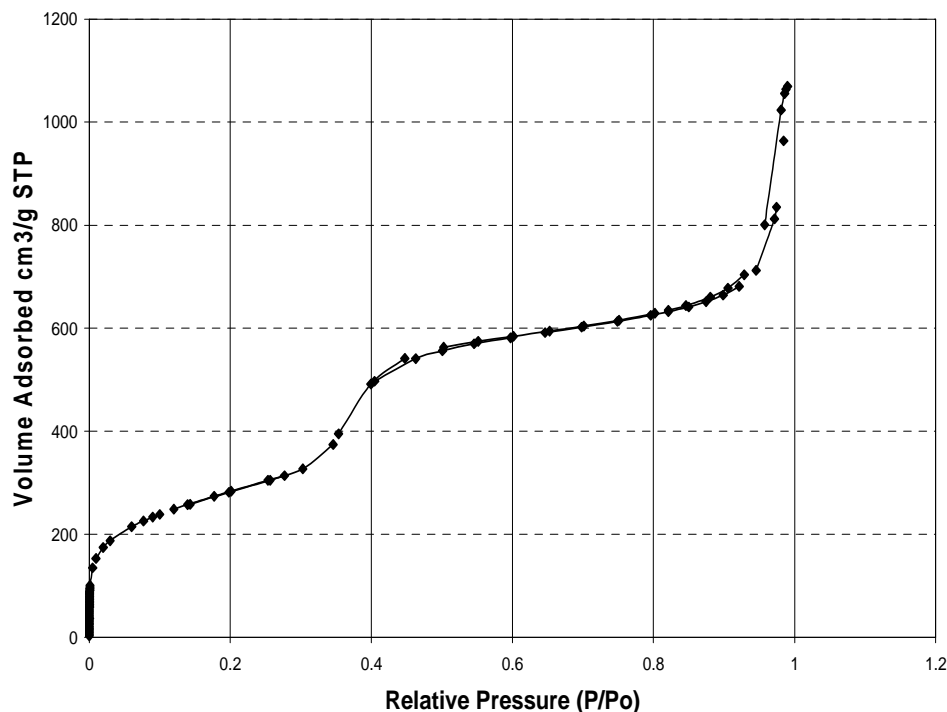


Figure 22: Nitrogen adsorption - desorption isotherms for hydrothermally synthesised calcined Ti-MCM-41 at 408K after 14 hours.

The first step feature of the isotherm is represented by the microporous phase (P/P_0 0 – 0.4) with a knee-shaped curve between 0 and 0.2 indicating the beginning of the middle section providing a measure monolayer capacity within the micropores (that is, the amount of adsorbate required to cover the surface with a complete monomolecular layer). A second step feature of the isotherm is the formation of the mesopore phase (P/P_0 0.4 – 0.8). This phase illustrates that the synthesised catalyst in this work possesses the characteristics of the MCM41s family (mesoporous materials, for example Ti-MCM-41 family). The last step feature of the isotherm is the double step features of the isotherm generating a hysteresis loop and the plateau at high P/P_0 . These features

clearly indicate that the isotherm obtained is from a material with multiple pore sizes.

Using the BET method, a large total surface area of 1025 m²/g was obtained which included an external surface area of 436.6 m²/g, and a micropore area of 588.8 m²/g. A BJH adsorption pore distribution reported an accumulative pore volume of 1.47 cm³/g at a cumulative pore surface area of 1110.4 m²/g, whereas for desorption BJH method gave a cumulative pore volume of 1.72 cm³/g at a cumulative pore surface area of 1346.9 m²/g. The values for surface area evaluation are in agreement with values obtained by Beck et al. (1992), as well as Blasco et al. (1995). Noteworthy, the pores are filled with liquid adsorptive, especially in the case of mesopores filling. Due to this assumption, the micropore volume was determined using a t-plot method; generating a value of 0.575 cm³/g.

The BJH method for calculating pore size distributions using Kelvin equation generated an adsorption pore diameter of 53.1 Å, with BJH desorption average pore diameter of 51.0 Å. These values are within the acceptable range as compared with the average pore diameter of 50.4 Å obtained using the BET method. However, the BET method is used most importantly to investigate surface areas. Compared to literature study conducted by Blasco et al (1995), an estimate pore diameter in the range of 20-100 Å. The catalyst synthesised in this study complies and falls within the diameter range expected for mesoporous materials.

In conclusion, from the physico-chemical data analysed; it is evident that the synthesised Ti-MCM-41 belongs to the mesoporous class and the adsorption of each layer takes place within an expected range of P/P_0 and also with features of mesoporous materials.

From different characterisation procedures used, it is observed that the synthesised material belongs to the M41S family as it resembles characteristics of the Ti-MCM-41 class as clearly shown by the XRD pattern in Figure 21. With chemical analysis, the X-ray fluorescence technique is more important for assessment and interpretation of quantitative chemical analysis of both trace and major elements or compounds present in zeolite Ti-MCM-41, thus, providing reliable results compared to scanning electron microscopy which only focuses analysis on a fixed catalyst surface, with chemical composition of elements identified only in that specific spot.

5.1.2. Titanium Silicate- 1

Zeolite TS-1 was synthesised in two batches under the same synthesis conditions for 48 hours at the crystallisation temperature (443K). The second synthesis was performed due to technical problems with the first batch and concerns with contamination; for example, after synthesis the first batch was dried at room temperature and the second batch was dried at ideal temperature 80°C. The second batch was used for performing catalytic experiments. No difference was detected of any form between the two catalysts as confirmed by characterisation methods that were used. Moderate yields of approximately ± 5.4 g were obtained. Upon calcination at high temperatures (550°C), a dramatic

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decrease of catalyst mass (approximately 3.1g and 2.7g) was observed. This decrease in mass can be attributed to the removal of water and template from the zeolite channels. After calcination, the zeolite was characterised using different techniques and procedures.

Firstly X-ray Fluorescence spectroscopy (XRF) and scanning electron microscopy (SEM) were used to determine the elemental composition and determination of catalyst morphology (SEM only). A detailed elemental composition analysis is shown in Table 9.

Table 9: Elemental analysis performed using either XRF or SEM spectroscopes on calcined TS-1 catalyst.

Element/ Compound	X-ray Fluorescence (compound %)	SEM-EDX Microscopy (compound %)		Si/Ti ratio
AlO ₃	0.00	Analysis 1	Analysis 2	45.51 (EDX 1) 35.37 (EDX 2) 23.4 (XRF)
SiO ₂	86.78	97.85	96.92	
TiO ₂	3.71	2.15	2.74	
CaO	0.02	-		
K ₂ O	0.27	-		
Fe ₂ O ₃	0.04	-		
MgO	0.02	-		
MnO	0.01	-		
P ₂ O ₅	0.01	-		

As observed in Table 9, there is a large difference in Si/Ti ratios as obtained with the SEM and XRF techniques. These results are still under investigation

as the TS-1 synthesised in this work appeared to form large crystals; however, small crystallites were expected. A second EDX analysis was performed generating Si/Ti values of 35.37. These values were higher than XRF analysis. The SEM and EDX analysis for this zeolite showed problems with assigning morphology and ratio of Si:Ti. In general, the Si/Ti ratios reported by SEM are not reliable as they reveal information on a fixed surface of the catalyst sample compared to XRF analysis as it detects and investigates all the elements present in the analysed sample. The morphology of the synthesised zeolite TS-1 as determined using SEM is shown in Figure 23.

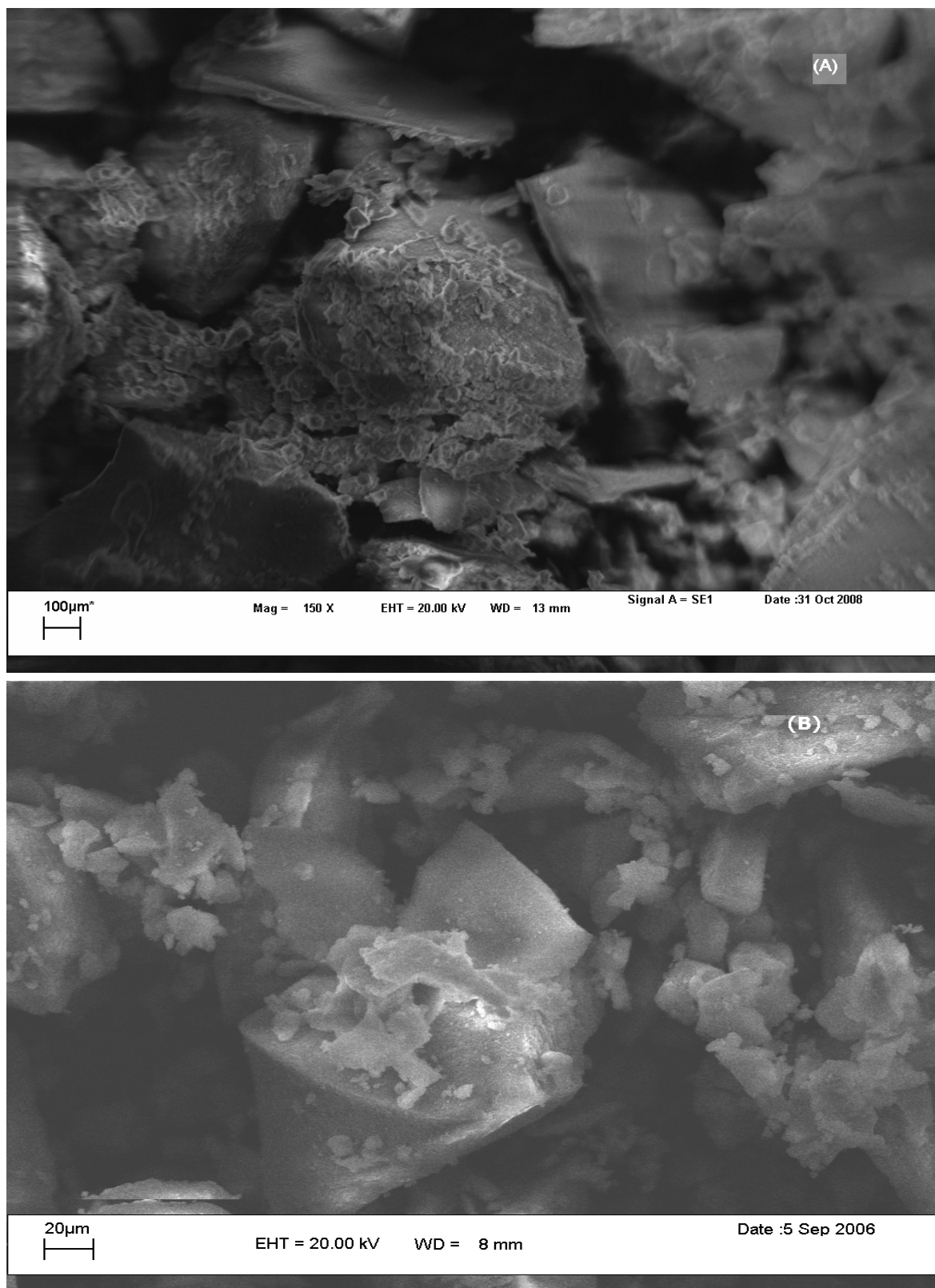


Figure 23: SEM micrograph of calcined TS-1, with Si/Ti of 32.7, on a 30 µm (A) and 20 (B) µm scale obtained at 443K after 48 hours respectively.

Structural morphology of zeolite TS-1 synthesised in this work was not clearly distinguished by SEM as shown in Figure 23. It is seen that the crystals are large and as a result it is not possible to state conclusively whether the synthesis yielded a hexagonal or cubic structure as expected. Even at higher magnification, morphologies were unclear. Zeolite TS-1 chromatograph showed white spots of the scattered solid sample during analysis. It is worth mentioning that the synthesised zeolite TS-1 in this work is suspected to form large crystals instead of smaller crystals synthesised. In addition, the particle size was difficult to attain as the crystallites formed agglomerates.

Wilkenhöner et al (2001), in the synthesis of TS-1, obtained large crystallites of this zeolite which were coffin shaped with dimensions of $45 \times 10 \times 3 \mu\text{m}$, with the straight channels of zeolite structure being in the direction of the small axis ([010] direction). However, results obtained by Wilkenhöner et al. (2001) adopted a different synthesis procedure from the procedure used in this work that was adopted by Tamarasso et al. (1983); therefore, the difference in crystallites shapes and size is not known whether it is attributed to difference in synthesis procedures. It is worth mentioning that the synthesis method used by Tamarasso et al. (1983) was taken from IZA official synthesis book and this makes his method more valuable and recommended for use in zeolite synthesis.

X-ray Powder Diffraction (XRD) is a technique used for analysing crystallinity and phase purity of zeolite TS-1. Powder diffraction peaks were analysed by measuring the angles at which the X-ray beam of wavelength is diffracted by the sample. Therefore, the information on the analysed sample was given in

terms of position, shape, intensity and width of the diffraction lines. Diffraction diagrams for zeolite TS-1 are shown in Figure 24.

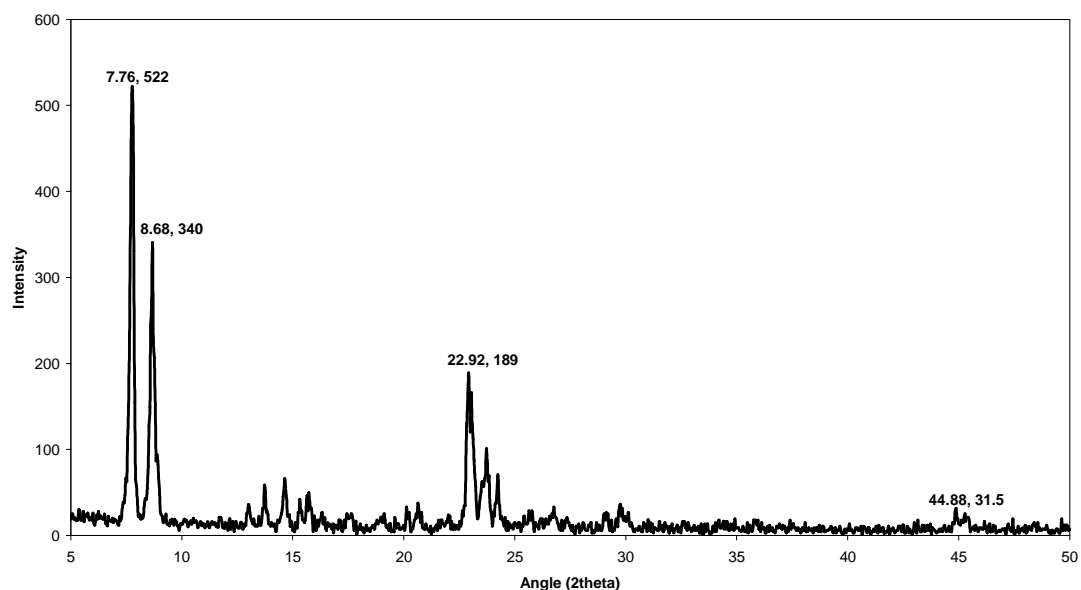


Figure 24: XRD patterns for synthesised calcined TS-1 at 443K after 48 hours.

The diffraction spectra in Figure 24, was measured at a higher level 2θ , with the angle increased up to 50° . Narrow diffraction lines with higher intensities were observed at $7.56 - 7.80$ and $22.84 - 23.04$ angles 2θ , assumed to indicate the homogeneity in the alloy composition. Zeolite TS-1 synthesised in this work is of high purity and possesses good crystalline structure. This diffraction pattern also illustrates Ti incorporation in the zeolite framework.

In conclusion, diffraction patterns as presented by the Powder X-ray diffraction technique proves that zeolite TS-1 synthesised in this work has framework structural features of the MFI type zeolite. However, this is in contradiction with

results obtained using EDX-SEM as these results raise concern as higher values were generated compared to results obtained by the XRF.

Quantitative analysis using Nitrogen adsorption - desorption isotherms for zeolite TS-1 is used for investigating the surface areas, micropore volumes, and the pore diameters. Physisorption isotherms given by BET method are illustrated as in Figure 25.

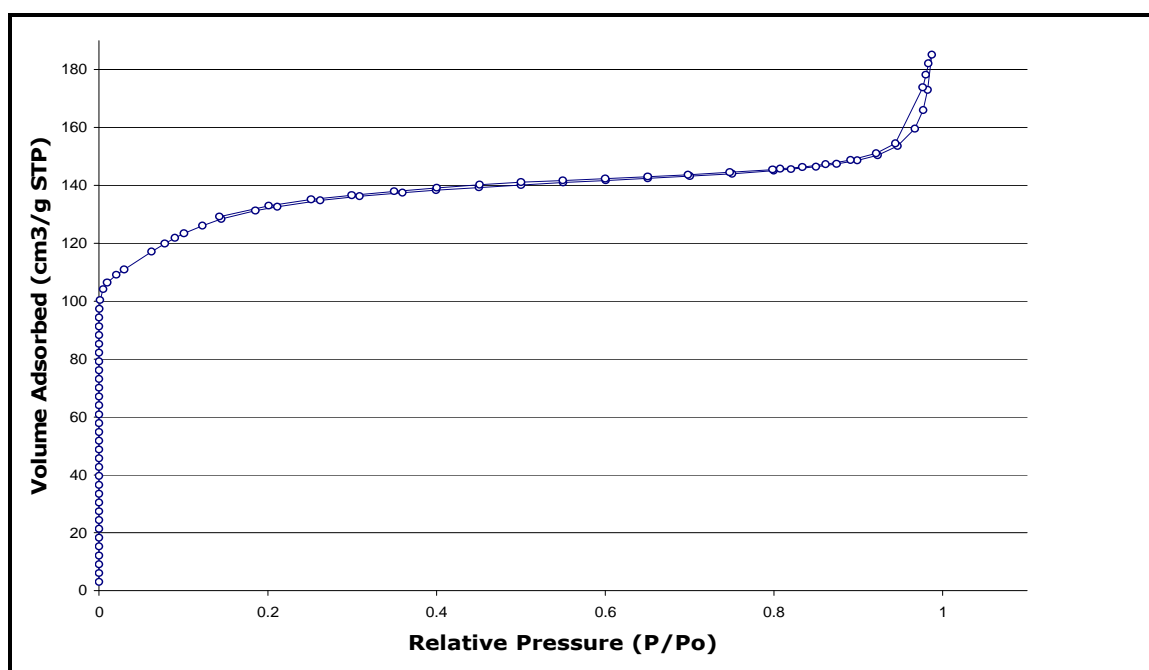


Figure 25: Nitrogen adsorption - desorption isotherms for hydrothermally synthesised calcined TS-1 at 443 K after 48 hours.

Physisorption isotherm shown in Figure 25, exhibit hysteresis of flattened shape compared to isotherm of Ti-MCM-41, with adsorption and desorption curve following different paths. This type of isotherm is straightforward, thus reversible and concave to the relative pressure, hence results from adsorption taking place from narrow pores of zeolite TS-1 (by the process of micropore filling).

Using the BET approach, a total surface area of 457.1 m²/g was obtained. This value includes both the external surface area (196.9 m²/g) and the micropore area (260.8 m²/g). However, a BJH adsorption cumulative surface area of pores (40.7 m²/g) was obtained as well as a BJH desorption cumulative surface area of pores (84.7 m²/g). A t-plot method was used in evaluation of total micropore volume generating a 0.118 cm³/g. A BJH adsorption pore distribution reported accumulative pore volume of 0.091 cm³/g and a desorption BJH method generated a cumulative pore volume of 0.115 cm³/g.

With all the information regarding the physical and chemical characterisation of this zeolite, short conclusions are made based on the observations and the data obtained. The TS-1 synthesised in this work belongs to the MFI family and the BET results obtained are acceptable and within the normal range and this is also proven by the XRD pattern as the structural crystallinity and phase purity lies in the range of MFI class. However, results obtained using SEM are not as expected, as several analysis at different magnifications were made but the morphology of the zeolite was still unknown and unclear. The use of Ti-Beta was not considered due to the difficulties in synthesis procedure of this zeolite.

5.2. Catalytic Experiments

5.2.1. Selective Oxidation of 2-methylnaphthalene

The proposed focus of this study was to perform the oxidation of 2-methylnaphthol as a precursor substrate in liquid phase using heterogeneous

processes employing use of zeolites and mesoporous materials with aqueous hydrogen peroxide as an oxidant. However, limitations with high costs of 2-methylnaphthol, approximately ±R1200.00 per 1g (Sigma- Aldrich, 2006), hindered any possibilities of using this reagent in our reactions as a feed substrate. Therefore selective oxidation of 2-methylnaphthalene, which is a known precursor to 2-methylnaphthol, in liquid phase was proposed. The advantage of this choice is the fact that it was expected that 1, 4-naphthoquinone derivatives, for example, 2-MNQ will also be formed from the oxidation of 2-methylnaphthalene.

Selective oxidation of 2-methylnaphthalene using aqueous hydrogen peroxide as oxidant was investigated on both Ti-MCM-41 and TS-1 as catalysts as detailed in subsections below.

5.2.1.1. Ti- MCM-41

Ti-MCM-41 is a mesoporous material with larger pore diameter. Therefore, in the oxidation of 2-methylnaphthalene, Ti-MCM-41 was expected to allow diffusion of this bulkier molecule into the catalyst's active sites and enhancing conversion and production of 2-methyl-1, 4-naphthoquinone.

Initial experiments in the oxidation of 2-methylnaphthalene were performed using a batch system (c.f. apparatus I in section 4.3.1.), and second experiments were done using the reflux system (c.f. apparatus II in section 4.3.1.). Reaction conditions involved employing use of different solvents (methanol, isopropanol, *n*- propanol, *n*-butanol, *n*- pentanol, and acetonitrile).

Chapter 5: Results and Discussion

The temperature was varied between 60 and 120 °C, with sample withdrawal done every 15, 30, 60, 180, 240, 300, 360 and 420 min.

A complete list of the conditions investigated is summarised below in Table 10.

Table 10: List of conditions investigated

Reactor	Solvent choice	Reactor Temperature (°C)
Batch system Reflux system Parr PTFE autoclave	Methanol	60 – 80 °C (batch) 80 – 120 °C (reflux) 80 – 120 °C (autoclave)
	n-propanol	
	Iso-propanol	
	n-butanol	
	n-pentanol	
	Acetonitrile	
	Iso-propanol	
	Acetonitrile	

With experiments conducted using batch and reflux methods showed no 2-MN conversion as reported by the GC. This was due to the fact that the original batch method is an ideal process in similar oxidation reactions with smaller aromatic compounds and this technique is suitable for reactants that are not heavier and bulkier. However, it was clear that neither the original batch nor the reflux system was effective for the hydroxylation of 2-MN. This was attributed to the fact that a sufficiently high temperature could not be achieved with the batch method.

In all catalytic successful experiments performed, production of 2-methyl-1, 4-naphthoquinone was achieved by using a PTFE Parr autoclave (c.f. apparatus III). However, using set-up III there are some limitations and drawbacks such as inability to perform sampling during the reaction. This led to problems in modeling the reaction data in terms of concentration- time profiles as only one data point was obtained at the end of each run. Another observation was the fact that even using set-up III, only acetonitrile as a solvent generated 2-methyl-1,4-naphthoquinone as a product as compared with other solvents such as n-butanol, iso-propanol, n-propanol, methanol, and n-pentanol that were used without generation of 2-MNQ.

The use of water as a solvent was completely avoided in reaction systems involving Ti-MCM-41 catalyst due to the hydrophilic character of this material, with assumptions based on the fact that the internal surface consists of mainly Si-O groups, leading to water competing with hydrogen peroxide for coordination with the active sites. Catalytic performance would therefore be hindered if water was used in Ti-MCM-41 catalysed reactions.

The effect of temperature on 2-MN conversion using Ti-MCM-41 is shown in Figure 26.

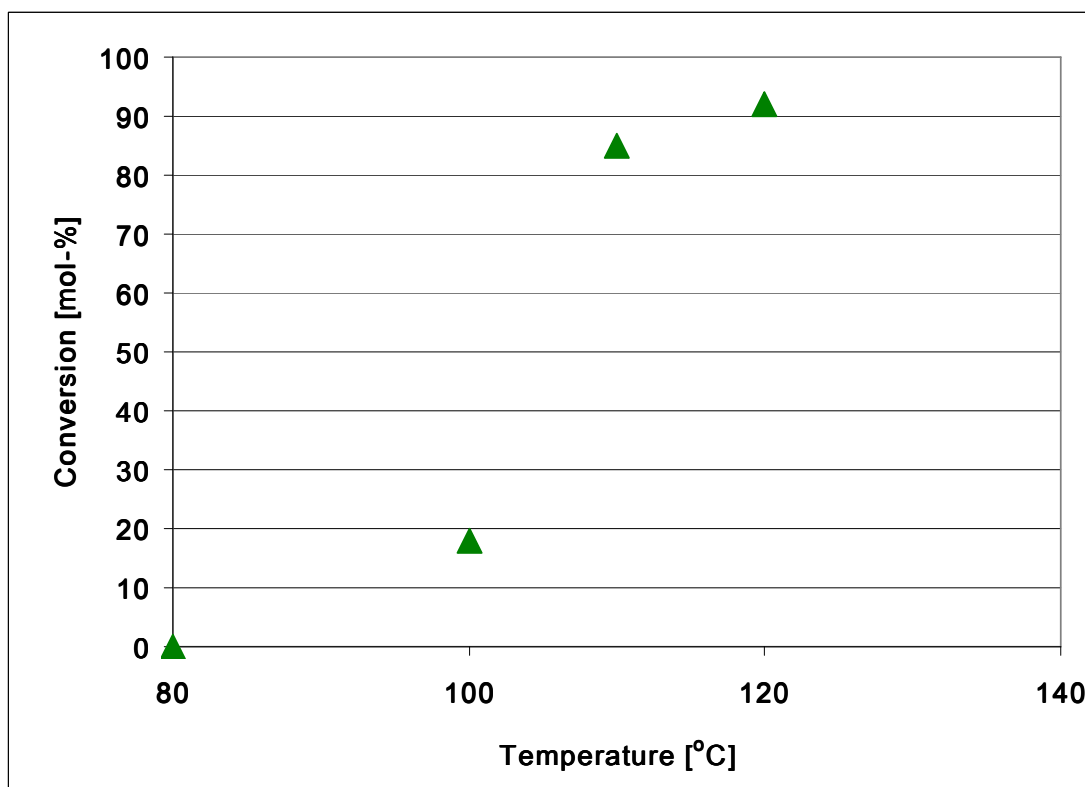


Figure 26: Breakthrough curve for 2-MN conversion as a function of temperature. Catalyst (Ti-MCM-41 = 0.1g, 2-MN = 1g, hydrogen peroxide = 6ml, acetonitrile = 10ml).

It was observed that no reaction occurred at 80 °C. Increasing reaction temperature to 100°C, an 18 mol-% 2-MN conversion was observed. 2-methylnaphthalene conversions generating 2-MNQ enhanced with temperature increase as illustrated by higher conversions of 85 mol-% at 110°C and 92 mol-% at 120°C respectively as summarised in Table 15 (APPENDIX C). At higher reaction temperature (120°C), higher 2-MN conversions are obtained, however, the rate of side products formation increases.

The peaks were identified using GC and the formation of products other than 2-methyl-1,4-naphthoquinone was observed as shown by a GC chromatogram in APPENDIX B (Figure 52). The main side product observed in 2-MN reactions was 2-MNL.

The effect of reaction temperature on relative product selectivity was investigated as shown in Figure 27.

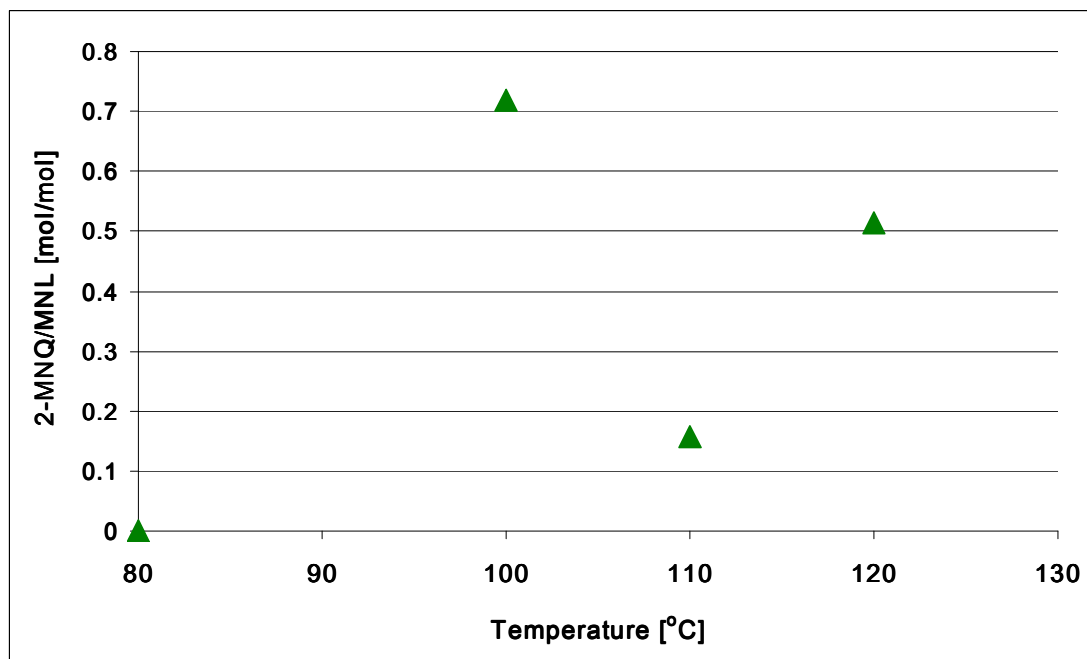


Figure 27: Relative 2-MNQ selectivity as a function of temperature (Ti-MCM-41 = 0.1g, 2-MN = 1g, hydrogen peroxide = 6ml, acetonitrile = 10ml, temperature 80 – 120 °C)

As observed in Figure 27, the oxidation of 2-methylnaphthalene using aqueous hydrogen peroxide also showed the formation of significant amounts of 2-methylnaphthol as a product. The extent at which this product was formed was obtained by calculating relative product selectivities (2-MNQ/ MNL), that is, the formation of 2-methyl-1, 4- naphthoquinone relative to that of 2-methylnaphthol in the reactor as a function of temperature. It is important to note that 2MNL is an expected intermediate in the formation of 2-MNQ so the production of 2MNL during hydroxylation of 2-MN is neither unexpected nor desired.

Another important finding was that performing the reactions at temperatures above the boiling point of solvents led to the formation of additional undesired products. It was thought that this was due to over oxidation of the products and/or oxidation of an undesired position of the 2-MN.

The results obtained while using Ti-MCM-41 catalysed reactions showed that 2-MN conversions obtained in this study are higher than those reported in literature by Anunziata, et al. (1999) where a highest conversion of 28 mol-% was reported. Yet, Anunziata, et al. (1999) achieved 28% conversion using 1g of 2-MN which is similar to the quantity used in this study. Figure 27 also shows that the relative selectivities at different reaction temperatures using Ti-MCM-41 are inconsistent. This decrease in selectivity at 110 °C (0.157mol/mol) can be attributed to the formation of the unidentified products that were obtained other than the expected 2-methyl-1,4- naphthoquinone. The change at reaction temperature 120 °C (0.514 mol/mol) shows that as the temperature increases, selectivity to product formation is enhanced. The extent at which this occurs was evaluated by plotting absolute amounts of 2MNQ and 2MNL relative to temperature as shown in Figure 28.

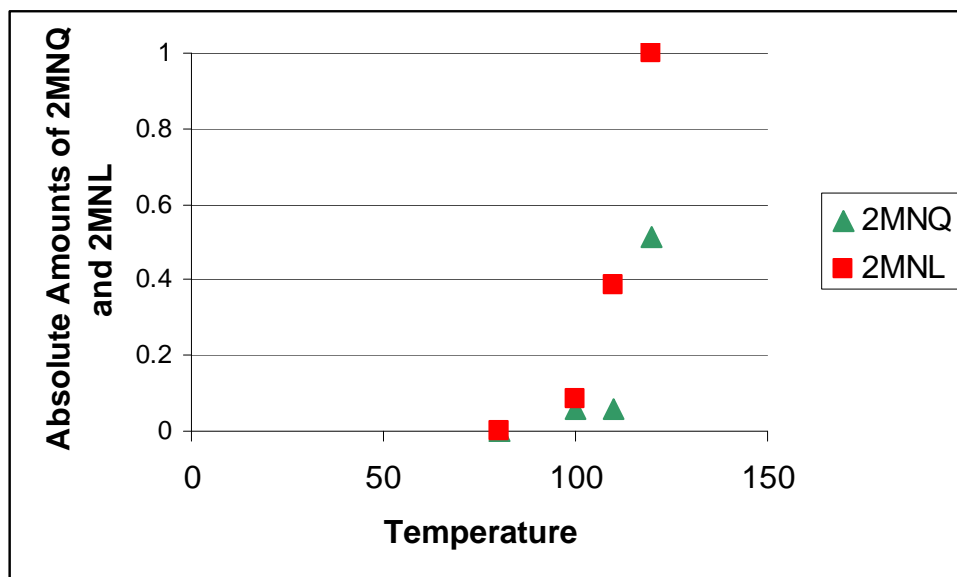


Figure 28: Absolute amounts of 2MNQ and 2MNL vs. temperature (Ti-MCM-41 = 0.1g, 2-MN = 1g, hydrogen peroxide = 6ml, acetonitrile = 10ml, temperature 80 – 120 °C)

It is observed in Figure 28 that as the reaction progresses, with temperature increase, the formation of secondary products is enhanced. This is seen with the amount of 2MNL enhanced, with a decrease in 2MNQ.

The generation of unidentified products observed from using the GC led to further analysis of the products using GC-MS as shown in

Figure 29.

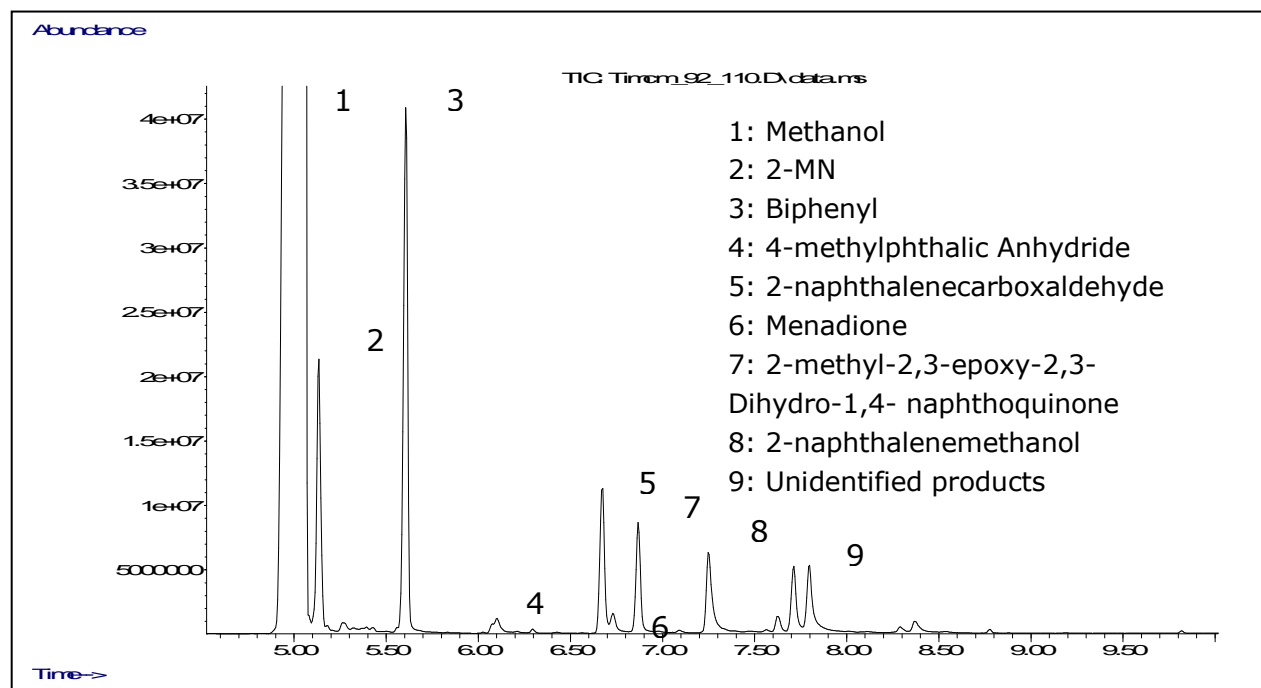


Figure 29: Components identified by GC-MS. Catalyst (Ti-MCM-41 = 0.1g, 2-MN = 1g, hydrogen peroxide = 6ml, acetonitrile = 10ml, Temperature = 110 °C).

The quantitative analysis using GC-MS as shown in

Figure 29 provided information on compounds that were unidentified as compared with data generated using GC as illustrated in **APPENDIX B (Figure 52)**. Several compounds that the GC-MS identified included 4-methylnaphthalic anhydride; benzofuran that is produced in very small amounts (peak too small to be seen on the GC-MS spectra); 2-naphthalenecarboxaldehyde; 2-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone and 2-naphthalenemethanol identified instead of 2-MNL that was identified by the GC. 2-naphthalenemethanol and 2-MNL have the same chemical composition and structural features, therefore, this is not problematic.

Possible mechanisms for the formation of observed products:

In Ti-MCM-41 catalysed reactions with acetonitrile solvent, with the data obtained using GC-MS spectroscopy, the methyl substituent is present on position 4 on the carbon position of the benzene ring, thus leading to the formation of 4-methylphthalic anhydride. Phthalic anhydrides are useful as intermediates in the chemical synthesis of herbicides and particularly in the synthesis of certain herbicides used to protect cereal crops. In addition, phthalic anhydrides are generally prepared by the processes of Diels- Alder reaction, where a carbon- carbon bond is formed. The mechanism is shown as in Figure 30.

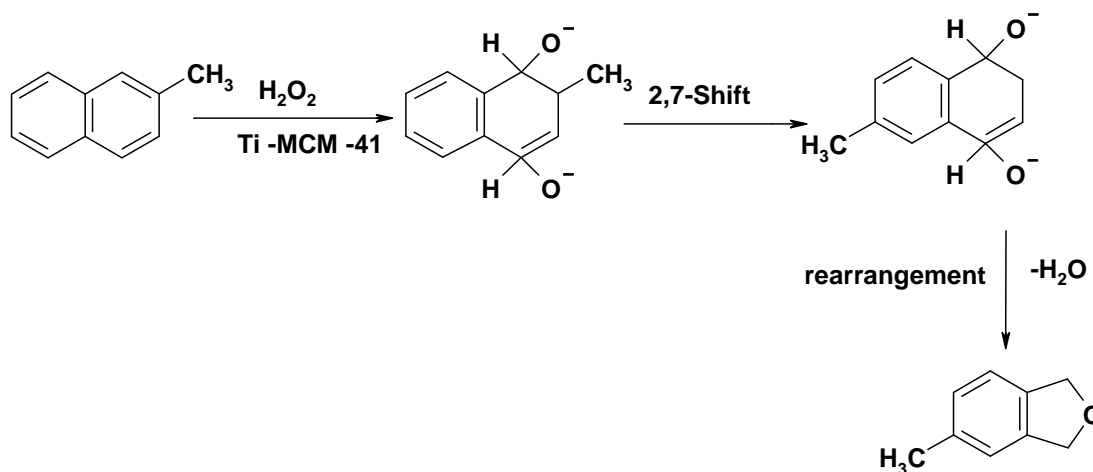


Figure 30: Mechanism of 4-methylphthalic anhydride formation from 2-MN oxidation using Ti-MCM-41, aqueous hydrogen peroxide and acetonitrile solvent. Catalyst =0.1g, 2-MN=1g, solvent=10ml, H_2O_2 = 6ml

In Figure 30, oxidation of 2-MN generated electrophiles, followed by a 2,7 CH₃ shift. This reaction further was seen to undergo the Claisen-cope rearrangement, which was a [3,3]-sigmatropic reaction of a 1,5-diene to give another 1,5-diene, followed by dehydrogenation. The oxygen atom in the carbon chain became the carbonyl group in the product, thus the C=O bond was significantly more stable than a C=C bond.

However, the same rearrangement was observed in 2-MN hydroxylation reaction leading to the formation of benzofuran and methanol. Benzofuran is a heterocyclic compound consisting of fused benzene and furan rings. In this work, benzofuran was formed from selective oxidation of 2-methylnaphthalene by o-alkylation, with dehydrogenation. This reaction occurred on the aromatic ring of 2-methylnaphthalene whereby oxidation occurs, with the methyl group, in this case a leaving group at the alpha position, followed by dehydrogenation into a benzofuran. This mechanism is illustrated as in Figure 31.

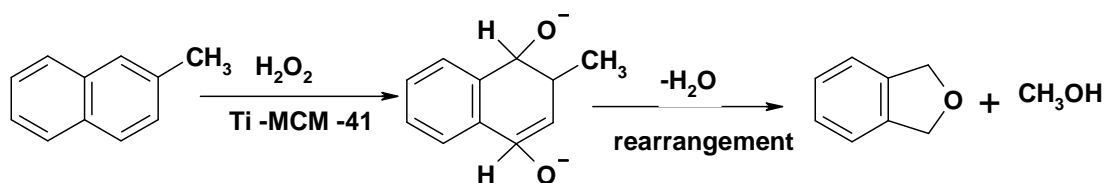


Figure 31: Mechanism of benzofuran formation from 2-MN oxidation using Ti-MCM-41, aqueous hydrogen peroxide and acetonitrile solvent. Catalyst =0.1g, 2-MN=1g, solvent=10ml, H₂O₂= 6ml

Formation of 2-naphthalene carboxyaldehyde clearly indicated that the reaction occurred on the methyl group of 2-methylnaphthalene. With aqueous hydrogen

peroxide as an oxidant, oxidation of a methyl group generating an aldehyde is clearly shown in Figure 32.

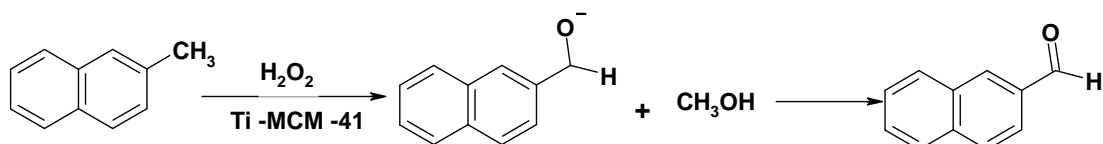


Figure 32: Mechanism of 2-naphthalene carboxyaldehyde formation from 2-MN oxidation using Ti-MCM-41, aqueous hydrogen peroxide and acetonitrile solvent. Catalyst =0.1g, 2-MN=1g, solvent=10ml, H₂O₂= 6ml

Production of 2-naphthalene-1- methanol from 2-methylnaphthalene oxidation in Ti-MCM-41 catalysed reaction was of great achievement. 2-methyl-1-naphthol (2-naphthalenemethanol) was an initiation and proposed substrate for this study, however, due to its high costs, use of this aromatic substrate in hydroxylation reactions was impossible. Side chain or methyl group oxidation of 2-methylnaphthalene led to the formation of this compound. The reaction showing how this reaction takes place is illustrated in Figure 33.

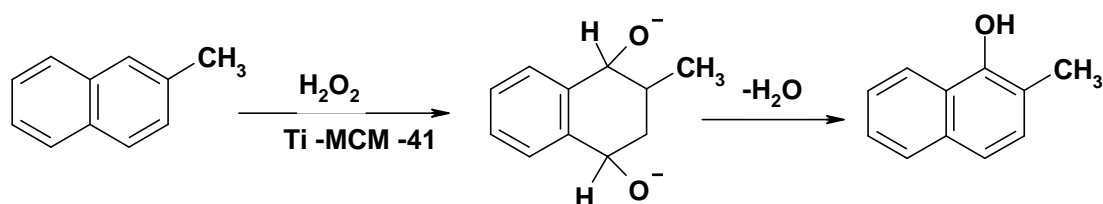


Figure 33: Mechanism of 2-naphthalenemethanol formation from 2-MN oxidation using Ti-MCM-41, aqueous hydrogen peroxide and acetonitrile solvent. Catalyst =0.1g, 2-MN=1g, solvent=10ml, H₂O₂= 6ml

It is observed that oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone is further oxidised, with the reaction directly occurring on the

aromatic ring. This is a Diels- Alder reaction mechanism whereby the naphthoquinone ring undergoes hydrolysis leading to the formation of 2-methyl-2,3-epoxy-(2,3-dihydro)-1,4-naphthoquinone. The mechanism by which this occurs is shown in Figure 34.

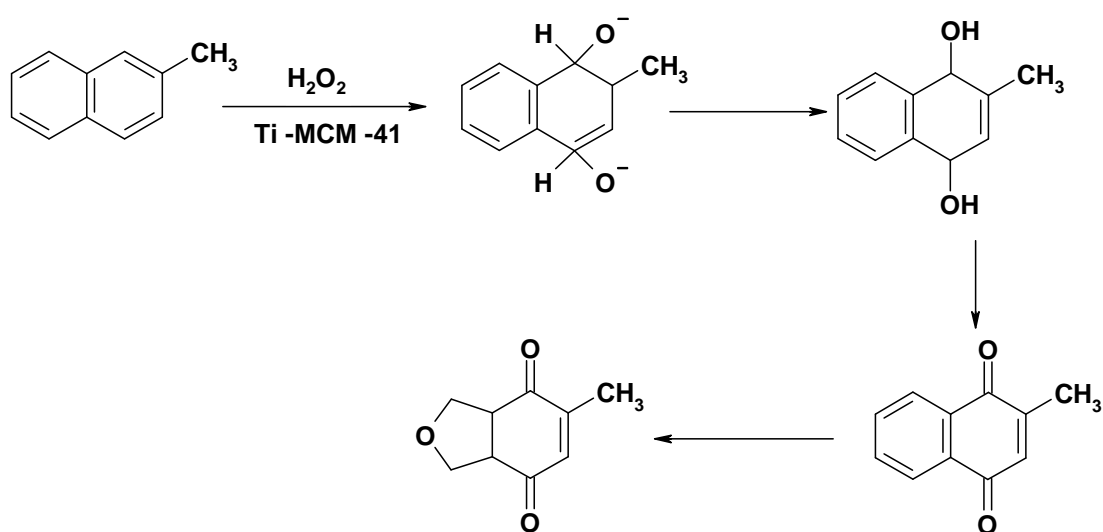


Figure 34: Mechanism of 2-epoxy-1,4-naphthoquinone formation from 2-MN oxidation using Ti-MCM-41, aqueous hydrogen peroxide and acetonitrile solvent. Catalyst =0.1g, 2-MN=1g, solvent=10ml, H₂O₂= 6ml.

The results presented in literature for 2-MN oxidation over Ti-MCM-41 and acetonitrile as a solvent presented no information on other compounds that are likely to form other than 2-MNQ, 2-methyl-1-hydroxy-methylnaphthalene, 2-methyl-dihydroxy-methylnaphthalene, and 2-methyl-1,4-OH- naphthoquinone.

However, Genov (2004) obtained 2-naphthalenemethanol and 2-naphthaldehyde when using Ti-Beta in 2-MN oxidation. Some of the compounds generated in this work as presented by the GC-MS (

Figure 29) are not reported in literature in 2-MN oxidation; therefore, it is of high interest to conduct further investigation on the products that are formed to minimise the rate of formation of unwanted products as the selectivity to 2-MNQ is influenced (for example, 0.157 mol/mol relative selectivity obtained at 110°C). Even though the selectivity was not optimised, it was still better than the homogeneous case with an E-factor of 18 (Sheldon, R.A., 1996).

After performing reactor experiments, catalyst recovery was performed by washing the recovered solid with acetonitrile solvent three times (± 15 ml), followed by drying the zeolite at room temperature for ± 8 hours. After drying, half the original catalyst was recovered (± 0.063 g at 110°C and ± 0.052 g at 120°C). Loss in catalyst quantity is attributed to sample withdrawal performed at the end of each reaction for quantitative analysis (GC or GC-MS). For the determination of whether titanium leaching into solutions occurred during the reactions, repeat runs were performed using the used catalysts. Under the

same reaction conditions and at reaction temperatures 110 °C and 120 °C, no 2-MN conversion and no product formation was observed.

The conclusions that were drawn showed concern that the process used might not allow the used solid to be re-used in reactions and maybe the active sites of zeolite Ti-MCM-41 were blocked leading to the formation of unwanted products and hindering adsorption and diffusion of 2-methylnaphthalene. However, this assumption and the extent of how this happens has not been proven and a close investigation on this subject needs to be conducted for future research. Therefore, this led to impossibilities of distinguishing whether titanium metal leaches out of Ti-MCM-41 framework during reactions at reaction temperatures of 110 °C and 120 °C.

In conclusion, it was found that, despite testing a large range of conditions and reactor set-ups, only a limited set of experiments were successful. The work has, however, confirmed that it is possible to synthesise 2-MNQ from 2-MN using hydrogen peroxide as the oxidant but only when using acetonitrile as a solvent. In addition, this work has shown that high conversions of 2-MN are possible. It is recommended that further work be carried out in order to fully investigate the effect of hydrogen peroxide concentration and to optimise the reaction selectivity. It is worth mentioning that the catalysts used in this work were stored in tightly sealed containers at room temperature with no moisture absorbed.

After each reaction, the catalyst was filtered and removed to ensure that no reaction continued at 0 °C. The cooling process of the autoclave after each

reaction for an hour might have possible influence of further reaction, and the extent to which this occurs was not investigated.

5.2.1.2. TS-1

TS-1 catalysed reactions were performed using the normal batch method, reflux technique and the Parr PTFE autoclave. Reactions were carried out with acetonitrile, methanol, isopropanol, n-butanol, and n-pentanol as solvents. The initial standard conditions used for 2-MN oxidation employed the catalyst, substrate, oxidant, appropriate solvent, in the molar ratio of 1:5:2.5:20. Thus, temperature variations were to an optimum of (60 °C - 120 °C), small samples of reaction mixture (*ca.* 0.2ml) were taken for every 15, 30, 60, 120min, 180, 240, 300, 360, and 420min.

With 2-methylnaphthalene as a feed substrate, no reaction was obtained at reaction temperature (60 - 120 °C) using any of the reaction set-ups. The absence of reaction was attributed to diffusion limitations, as 2-MN is a large diameter molecule, whereas, TS-1 is a medium pore zeolite. In addition, there may be rapid deactivation of the external surface due to undesired formation of heavy aromatic (tar) compounds.

Anunziata et al. (2004), reported using zeolite TS-1 in selective oxidation of 2-MN with aqueous hydrogen peroxide, obtaining conversions of 10% and 55% selectivity to 2-methyl-1,4-naphthoquinone. Although the method used by Anunziata (2004) has not been clearly stated, the difference with the results in this work needs to be discussed. It is assumed from the paper (Anunziata,

2004) that the catalyst used had a very small particle size and, hence, a large external surface area. As the catalyst particle sizes in the work performed here were large, with a relatively smaller external surface area, it is assumed that Anunziata (2004) was seeing reaction only on the external surface, whereas that was not possible in this work. Anunziata's work has been used as a reference in this dissertation as the work he conducted is of vital importance to the study.

Another study conducted by Genov (2004) using a reflux technique in 2-MN hydroxylation over zeolite TS-1 and zeolite Ti-Beta with hydrogen peroxide as oxidant was reported. In Genov's work, 2-methylnaphthalene was oxidised at the aromatic ring over Ti-Beta as a catalyst to either 1- or 3- methylnaphthalene or in the side chain to 2-naphthalenemethanol and further oxidation to 2-naphthaldehyde. Hence, no 2-methyl-1, 4-naphthoquinone formation was reported. Very low conversions of 2-MN (0.6%) and 66.5% selectivity on the side chain and 33.5% selectivity in the ring oxidation were obtained. Therefore, in our work, it is possible that the GC was unable to detect such low conversions.

In conclusion, after performing several catalytic experiments using various solvents of different polarities and different methods, this sample of zeolite TS-1 proved unsuitable for reactions involving bulkier substrate, such as 2-methylnaphthalene and the use of this zeolite in such reactions must be avoided.

5.2.2. Toluene hydroxylation

Selective oxidation of toluene in the liquid phase, generating cresols using aqueous hydrogen peroxide as the oxidant and zeolites as catalysts is a complex and difficult process. Due to time constraints such as the effect of varying the reactant and oxidant concentration was not investigated although it is assumed that they will have an effect on the reaction rate and selectivity.

In a recent study conducted by Engelbrecht (2006), investigating toluene hydroxylation, the HPLC technique was used to prove that there was no meta-cresol formed during the reactions. In toluene hydroxylation, the use of HPLC is not advantageous as the overlapping of ortho- and para-cresol peak is observed, with only the meta-cresol having a completely separate peak. However, HPLC is of advantage when investigating the formation of meta-cresol during the reactions. The use of GC was therefore proposed as this technique generates an ortho- cresol peak separately, even though meta and para-cresol peaks overlapped. This decision was made after several experiments done by Engelbrecht (2006) proved that meta-cresol is not formed in these reactions. This also proven by papers that are reported in literature (Kumar, R., et al., 1989; Kumar, R., et al., 1999; Marchal, C., et al., 1993), stating that laboratory synthesised mixtures are known to consist of only para and ortho-cresol. In addition, meta-cresol is only generated industrially not on a laboratory bench.

For all experimental runs, the standard conditions used for toluene hydroxylation reactions over TS-1/ H₂O₂ system employed the catalyst (TS-1,

0.1g): aromatic substrate (2-MN, 1g): oxidant (H_2O_2 , 6ml) at ratios of 1:12:5 respectively. Zeolite TS-1 catalysed reactions were performed under either triphase conditions with water as the dispersion medium; or under biphasic system with acetonitrile as a co-solvent; or performed in excess toluene.

It is worth mentioning that in some reactions there are stages whereby cumulative toluene consumption may seem to slightly decrease with time as the reaction progresses. This can be attributed to the calculation of 2-MN conversion that was obtained from the products formed in the reaction and the possibility that other products that are formed may lead to a decrease in conversion. In this case, tar formation might hinder the formation of products and lead to decrease in 2-MN conversion.

Initial data obtained from the toluene hydroxylation reaction at various temperatures over zeolite TS-1 in a triphase system, using water as a solvent is shown in Figure 35. During experiments, care was taken with sampling and sample analysis, especially with batch catalytic reactions using water as a solvent (as two liquid phases are normally formed, i.e. an organic and an aqueous phase).

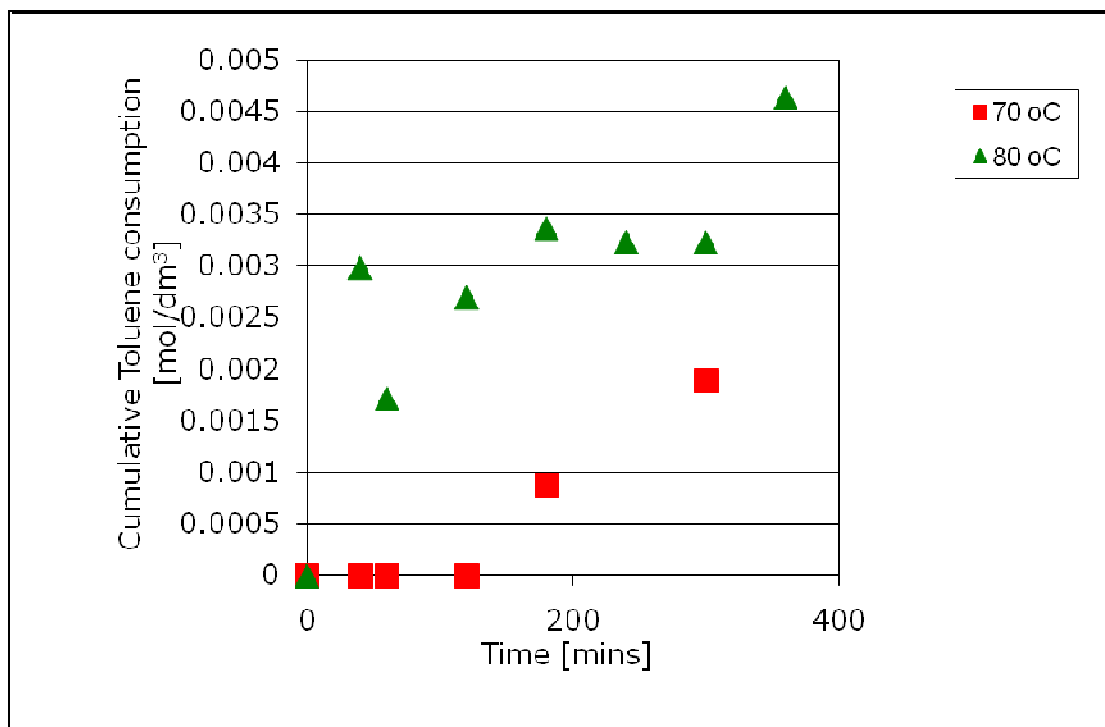


Figure 35: Cumulative toluene consumption versus time at 70 and 80 °C with water as a solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, water = 5ml.

The reaction was also conducted at 60 °C but the results were inconsistent and it was concluded that this temperature was too low. It can be seen that the reaction rate increased with temperature.

With water as a solvent, toluene is consumed during the reaction at very low concentrations (max. 0.0045 mol/ dm³). This effect is attributed to the immiscibility of water with toluene, thus leading to the formation of a separate toluene organic phase. Effectively, toluene is excluded to a large degree from the catalyst surface. When using water as a solvent, the rate of ortho or para cresol production is shown in Figure 36 and Figure 37 respectively.

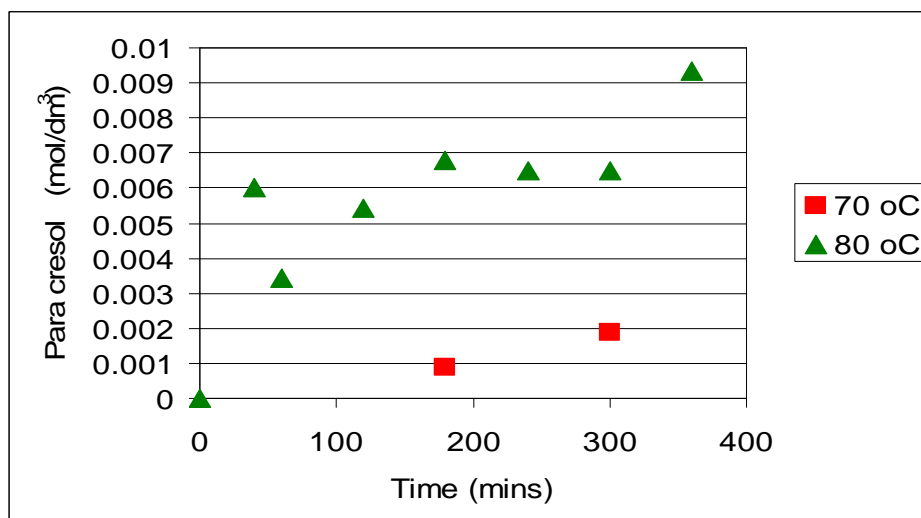


Figure 36: Para cresol concentration versus time at 70 and 80 °C with water as a solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, water = 5ml.

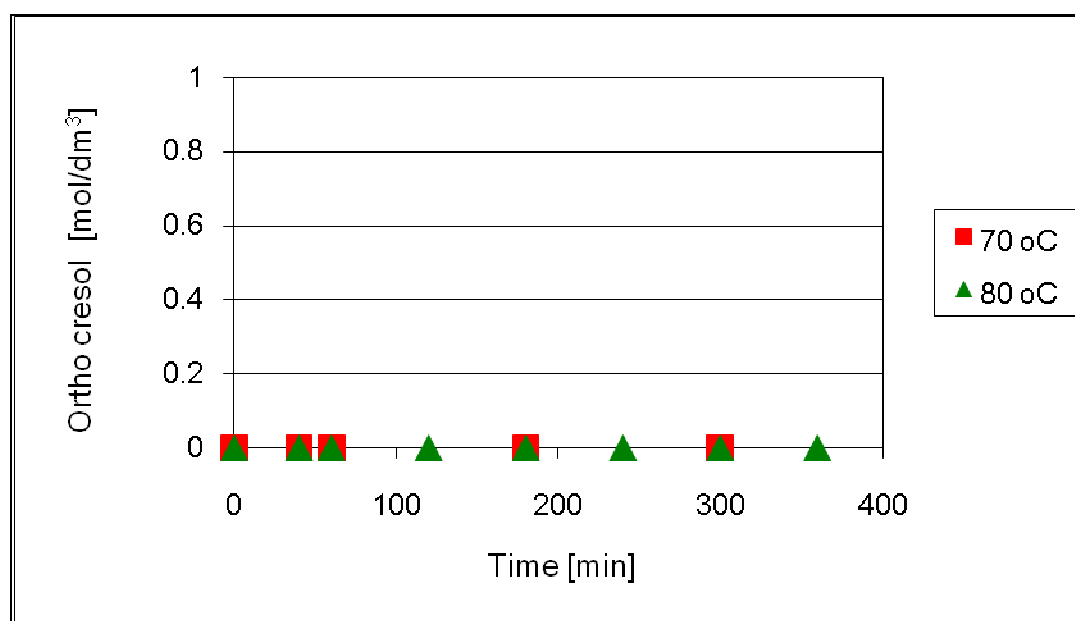


Figure 37: Ortho cresol concentration versus time at 70 and 80 °C with water as a solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, water = 5ml.

By comparing Figure 36 and Figure 37, it can be seen that formation of para - cresol is highly favoured. The formation of para- cresol is enhanced with reaction time and increases more rapidly at the beginning of the reaction. As the reaction progresses, the conversion slows. This is attributed to the fact that

as the reaction progresses, hydrogen peroxide decomposes unselectively; therefore this a drawback with using hydrogen peroxide in catalytic experiments. In addition, some high molecular weight compounds (tars) are formed, effectively slowing the reaction.

The data obtained in this work correlates well with results reported by Kumar et al. (1999), showing that when using water as a dispersion medium in TS-1/H₂O₂ system, the major product observed is the para-isomer. This is proven by the para-cresol generated at 80°C, with no ortho-cresol observed as in Figure 36 and 37. An advantage of using TS-1 is the hydrophobicity of this zeolite, and the restricted 10 –ring pore openings. When using water as a solvent, toluene is expected to compete more favourably with water for diffusion and adsorption once inside the zeolite channels. It is unfortunate that the triphase nature of this system hinders the toluene from accessing the catalyst particles in the first place and thus slows the overall reaction rate.

Only one sample in the run performed at 70 °C showed any ortho-cresol formation, with no ortho-cresol seen at 80 °C. On the Ti- zeolites, it is well known that water may complex with the active site (Wilkenhöner, 2001; Callanan, 2004) and thus increases the space constraints in the zeolite, effectively allowing only sufficient space for the para-isomer to form.

In conclusion, with water as a solvent the reaction is assumed to be occurring inside the pores of the zeolite. Noteworthy, this reaction is taking place without other factors hindering the catalytic effect (that is, lack of organic solvent hindering conversion of the aromatic substrate).

Toluene consumption in the presence of acetonitrile as a solvent is shown in Figure 38.

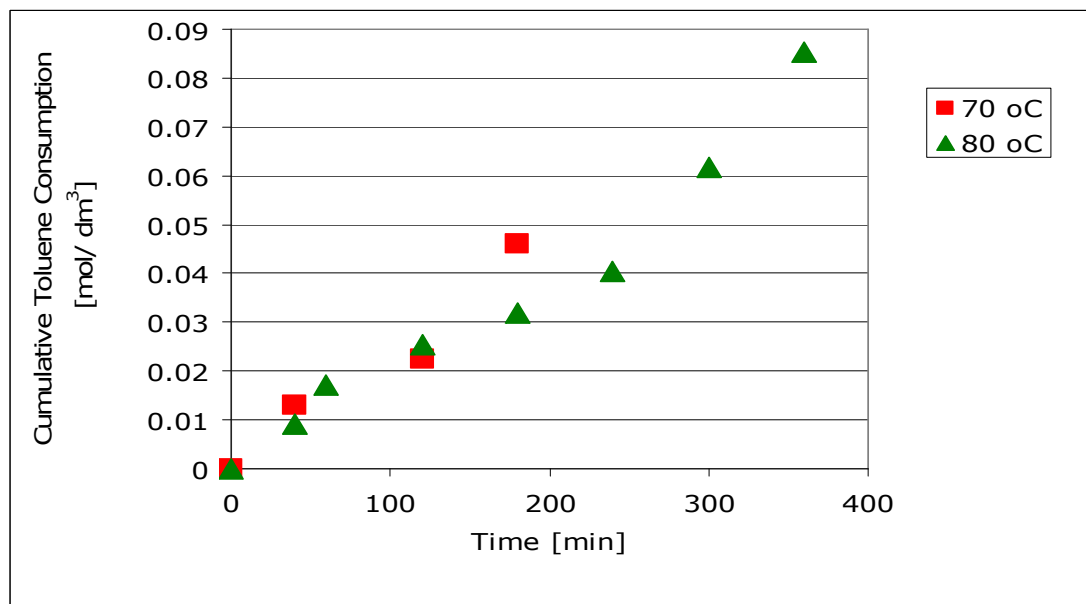


Figure 38: Cumulative toluene consumption versus time at 70 and 80 °C with acetonitrile as solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, acetonitrile = 5ml.

It can be seen from Figure 38 that the conversion of toluene increases steadily with reaction time, at both 70 and 80 °C when acetonitrile is used as a solvent. It is important to note that, unlike the previous experiment with water as a solvent, no deactivation of the catalyst is observed over the time period examined. In addition, the maximum toluene consumption is 9 times higher with acetonitrile as a solvent than with water as a solvent. The formation of ortho and para cresol as a function of time using acetonitrile as a solvent is shown in Figure 39 and Figure 40 respectively.

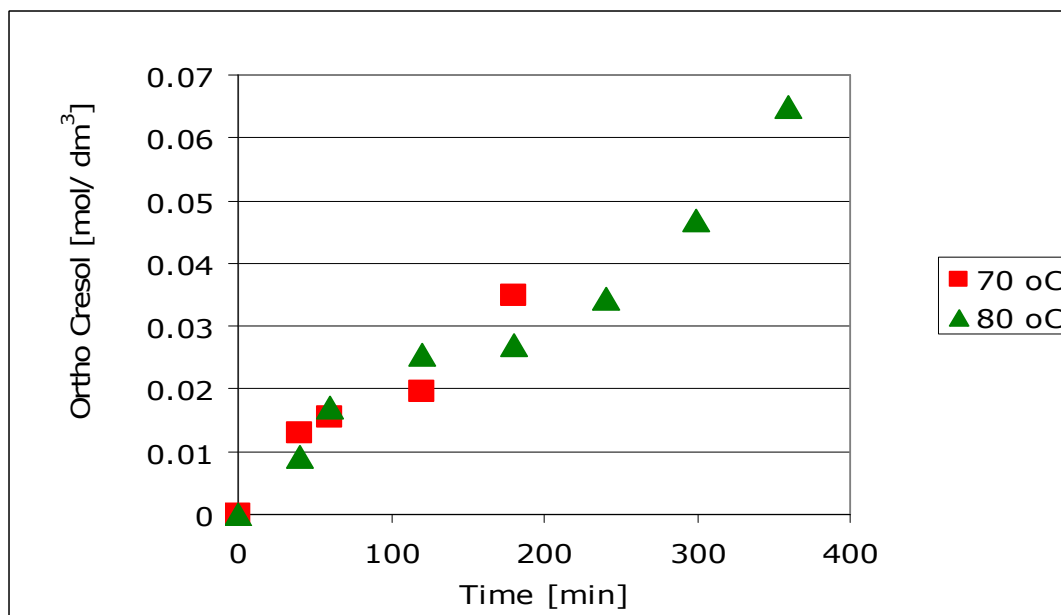


Figure 39: ortho-cresol concentrations versus time at 70 and 80 °C with acetonitrile as a solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, acetonitrile = 5ml.

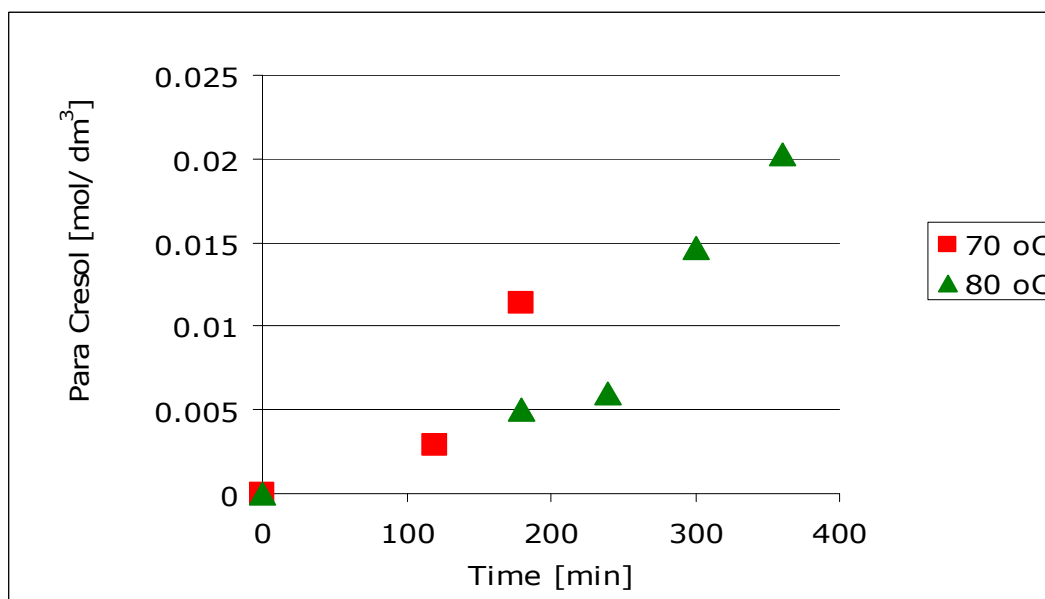


Figure 40: para-cresol concentrations versus time at 70 and 80 °C with acetonitrile as a solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, acetonitrile = 5ml.

Unlike the reactions performed with water as the solvent, in reactions using acetonitrile as a solvent, the formation of ortho cresol is more favoured than the formation of para cresol. This can be attributed to the fact that acetonitrile is non-polar and will therefore, not complex with the active sites, and not impose additional space constraints.

The effect of conversion on relative product selectivities is the ratio of ortho to para-cresol formed, shown here as a function of toluene conversion. Relative product selectivities are shown in Figure 41.

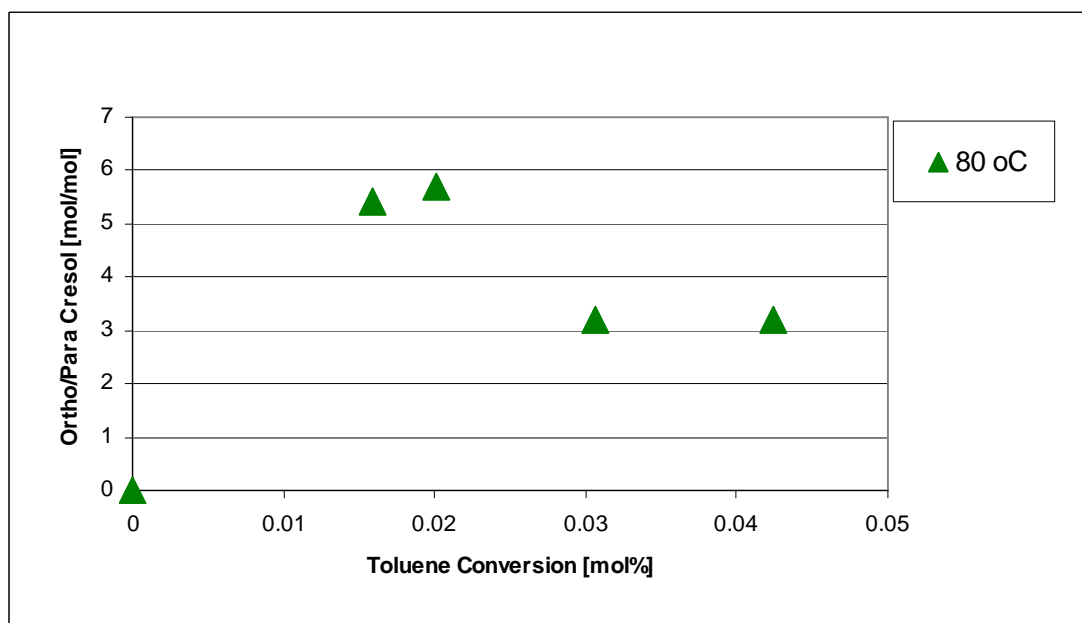


Figure 41: Product selectivities versus toluene conversion at 70 and 80 °C with acetonitrile solvent using zeolite TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, H₂O₂ = 0.5ml, acetonitrile = 5ml.

It may be seen that the ortho-cresol formation is favoured at low conversions, but decreases rapidly with increasing conversion. This may be attributed to over oxidation and decomposition of hydrogen peroxide with time.

This work also focused on performing catalytic experiments in the absence of any solvent. This was done by using excess of toluene in the feed (ca. 10.5 mol/dm³). The rate at which toluene is consumed during the catalytic reactions at 80 °C is shown in Figure 42. Due to the excess of toluene in the system, it was difficult to measure toluene consumption directly. The toluene consumption in this case is, therefore, calculated from the total product formation.

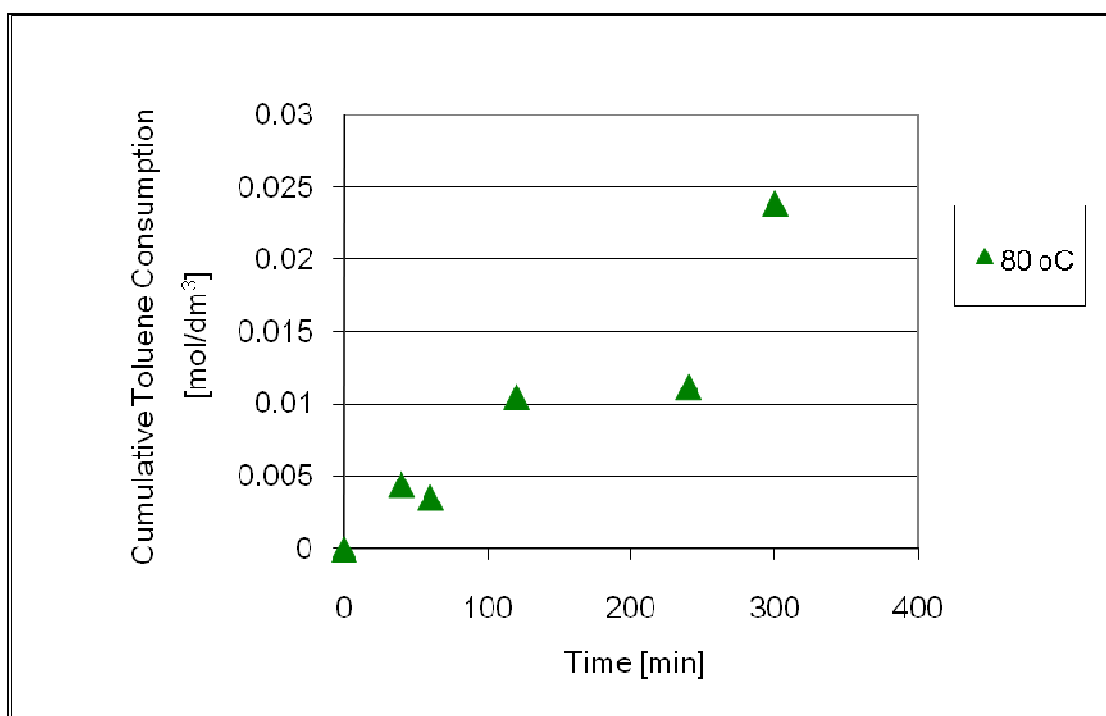


Figure 42: Cumulative toluene consumption versus time at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g, H₂O₂ = 0.5ml.

Lower reaction temperature 60 and 70 °C were not included with the results as the data sets were inconsistent, although toluene consumption was observed to slightly increase at the beginning of the reaction and gradually decreases as the

reaction progresses (after 120 min). Therefore, only data sets at 80°C showed that toluene consumption is enhanced with reaction time.

When toluene is in excess, the reaction favours the generation of para- cresol. This was proven with catalytic experiments conducted between reaction temperature 60 and 80°C (only 80°C reported). The effect of reaction temperature on para-cresol formation is shown in Figure 43.

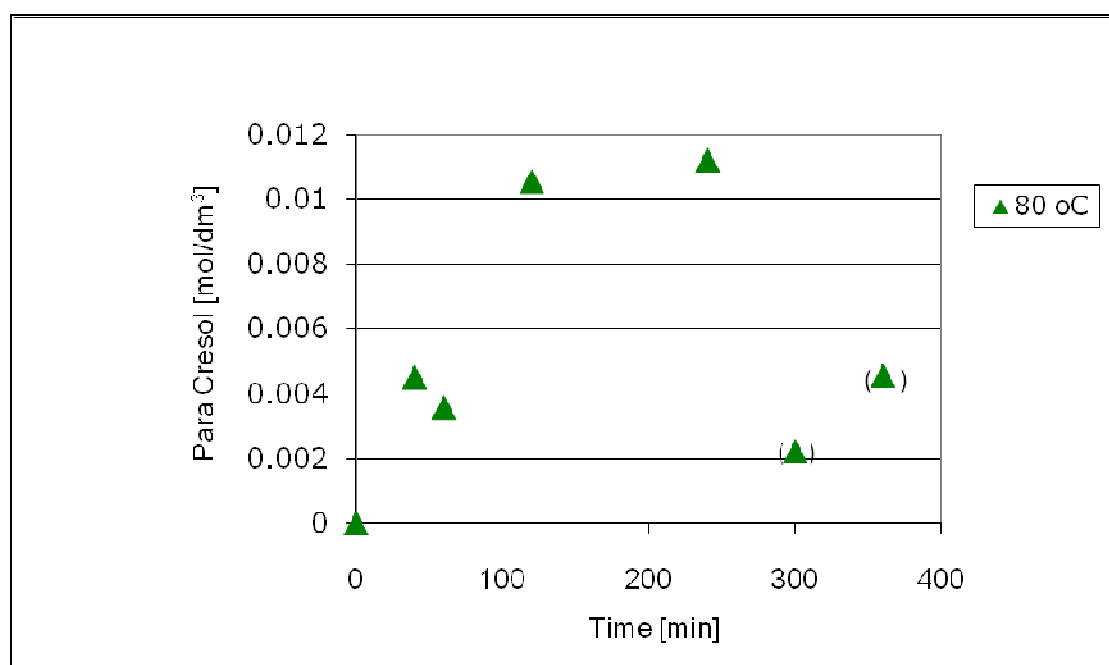


Figure 43: Para- cresol concentration versus time at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g, H₂O₂ = 0.5ml.

The data on Figure 43 indicates that para- cresol formation is highly favoured and the reaction progresses yielding higher para-cresol concentrations at the initial stages of the reaction. Reaction time of 2 hours is observed to be an optimum time for para-cresol formation as thereafter, the product concentration decreases as shown by data points in brackets. An assumption is made that

after a period of 2 hours, over oxidation may lead to decrease in para-cresol formation, enhancing the formation of tars. Ignoring the data sets produced after 2 hours, this might generate good data for modeling and investigating the rate at which para cresol is formed.

Formation of ortho- cresol during reactions with excess toluene is shown in Figure 44.

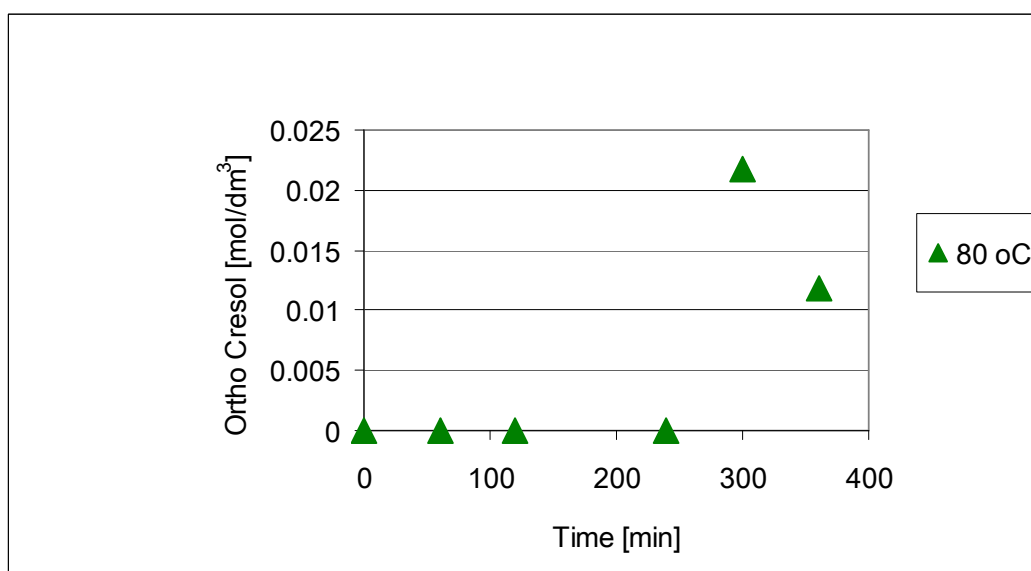


Figure 44: Ortho- cresol concentration versus time at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g, H₂O₂ = 0.5ml.

In excess toluene, ortho- cresol formation is not favoured. Ortho- cresol concentrations that were generated at reaction temperatures of 60 and 70°C were very low (ca. 4.18×10^{-6} and ca. 4.55×10^{-5} respectively). However, at reaction temperature 80°C, ortho- cresol concentration (ca. 0.0217) is generated with prolonged reaction time (over-oxidation).

Product selectivities were measured by monitoring the rate at which para-cresol is formed compared to ortho cresol production. The extent to which this ratio increases is observed as shown in Figure 45.

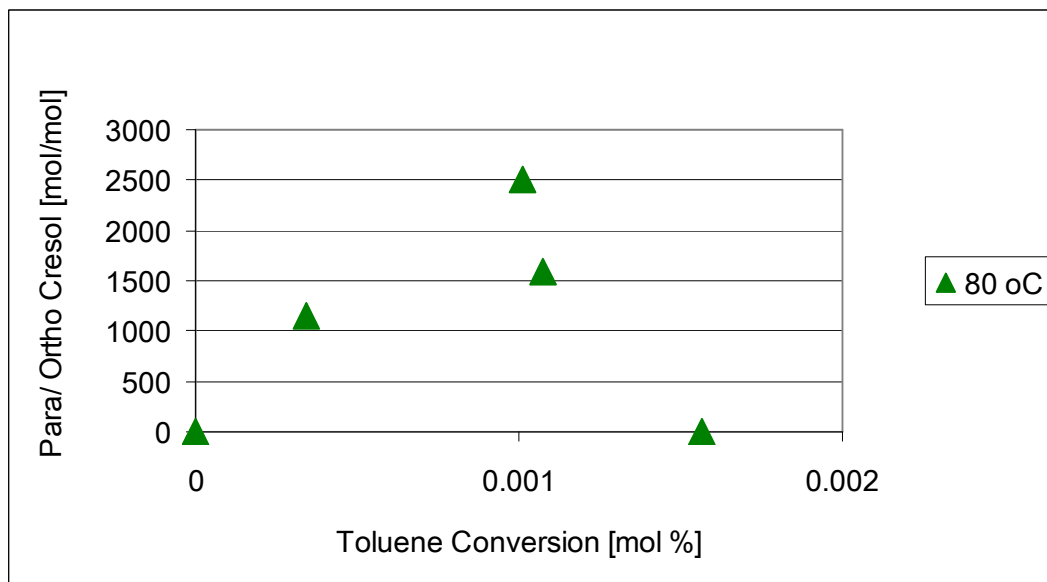


Figure 45: Product selectivities versus measured toluene conversion at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g, H₂O₂ = 0.5ml.

It is observed that the relative para/ortho selectivities increase with toluene conversion. Reaction temperature has a major effect on para-ortho cresol selectivities as illustrated in Figure 45. For reaction temperature 80°C, product selectivities enhance with increase in toluene conversion; with prolonged time the selectivities decrease. This decrease can be attributed to overoxidation.

Overall conclusion, concentrations of toluene in the feed with water or acetonitrile as a solvent consisted of *ca.* 2.01 mol/dm³ and *ca.* 10.46 mol/dm³ with excess toluene. At reaction temperature 80 °C, solvent effects show a major influence on toluene conversions and product formation; that is, higher conversions (approximately 3.23%) were obtained with acetonitrile as a solvent

and 0.464% with water as a solvent. Thus using acetonitrile as a solvent highly favours the formation of ortho-cresol, with para-cresol produced in relatively small amounts (ca. 0.0649 and ca. 0.0203 respectively), in the ratio of 3.20 o/p-cresol. This phenomenon is reversed with water as a solvent where the para-cresol is highly favoured with ca. 0.0093; not even trace amounts of ortho cresol detected at 80°C.

However, under solvent free conditions, with toluene in excess, para-cresol is highly favoured with ortho-cresol in small amounts (ca. 0.0217 and 0.0112 respectively). Product formation of p/o-cresol ratio is 1.94.

Previous studies conducted at the University of Stellenbosch by Engelbrecht (2006) on toluene hydroxylation using the same reaction conditions adopted in this work with methanol as a solvent observed that the use of methanol as a solvent in these reactions is not favourable. This was proven after performance of a series of experiments using methanol with no formation of cresols observed. Using both the batch and semi batch process generated no cresol formation after 6 hours at reaction temperature 60 °C.

From these observations, it may be concluded that acetonitrile is a suitable solvent of choice for toluene hydroxylation reactions catalysed by zeolite TS-1 for the production of ortho-cresol. If, however para-cresol is desired, then excess toluene should be used.

5.3. Rate Fitting and Kinetic Modelling

The experimental data generated from 2-methylnaphthalene reactions catalysed by Ti-MCM-41 as catalyst using set-up III generated only one data point at the end of each experimental run. This meant that kinetic modeling could only be performed on the toluene hydroxylation experiments where concentration versus time data was available.

Experimental data obtained during toluene hydroxylation reactions was kinetically expressed using a second order kinetic expression assuming first order in both toluene and hydrogen peroxide. As the analysis of hydrogen peroxide proved inconsistent, an estimate of hydrogen peroxide concentration during the reaction was calculated using the initial measured concentration and assuming no selective decomposition of H_2O_2 . The concentration of H_2O_2 could then be related to the toluene conversion [see equation 4.21], where θ_{peroxide} is the feed ratio of aqueous hydrogen peroxide to toluene. Details of the kinetic model used can be found in section 4.5.

Measured Toluene conversions were obtained by the summation of all products (ortho and para-cresol) divided by initial starting concentration of toluene in the feed. The calculated value of toluene conversion was obtained by using equation 4.27. A regression model was used to solve for the value of k . In this model the sum of errors between the measured and calculated values of toluene conversion was minimized by varying the value of the rate constant, k

(least squares regression). A comparison of the measured and calculated conversion versus time profiles for toluene hydroxylation with water as a solvent is shown in Figure 46.

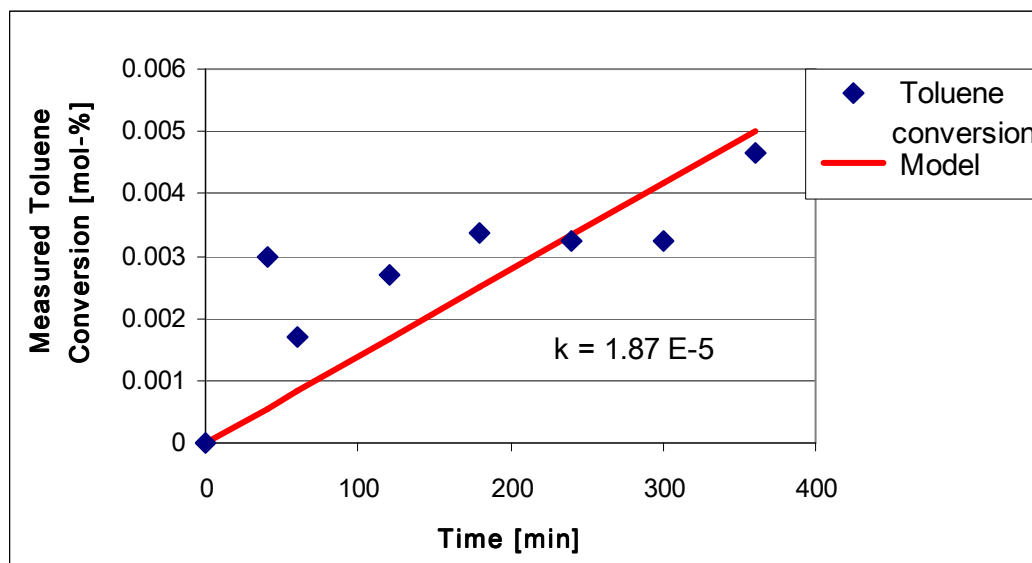


Figure 46: Kinetic modeling for all data points (measured toluene conversion) at 80°C with water as a solvent using TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, water = 5ml.

It can be seen that the model does not correspond well with the experimental data. This was attributed to the fact that hydrogen peroxide decomposes unselectively and that the concentration of hydrogen peroxide was therefore lower than predicted at longer reaction times. To obtain a better estimate of the rate constant, the data was refitted using only data up to 180 minutes reaction time. This is illustrated in Figure 47. Note that all measured data is shown even though only the data up to 180 minutes was used for modeling.

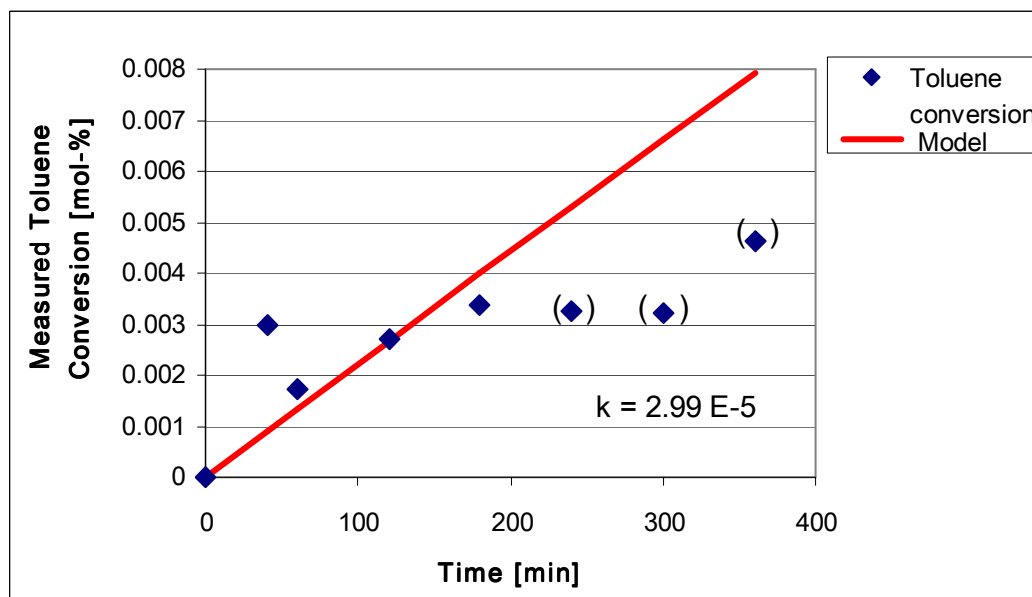


Figure 47: Kinetic modeling for data sets obtained up to 180 min (measured toluene conversion) at 80°C with water as a solvent using TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g, water = 5ml. Data points in brackets not used for model fitting.

It can be seen that the rate constant for the toluene hydroxylation in water increased from 4.16×10^{-6} at 70 °C to 1.87×10^{-5} at 80 °C when using only the initial data. When toluene is in excess, the model generated a better fit when all data was used to fit the model as illustrated in Figure 48.

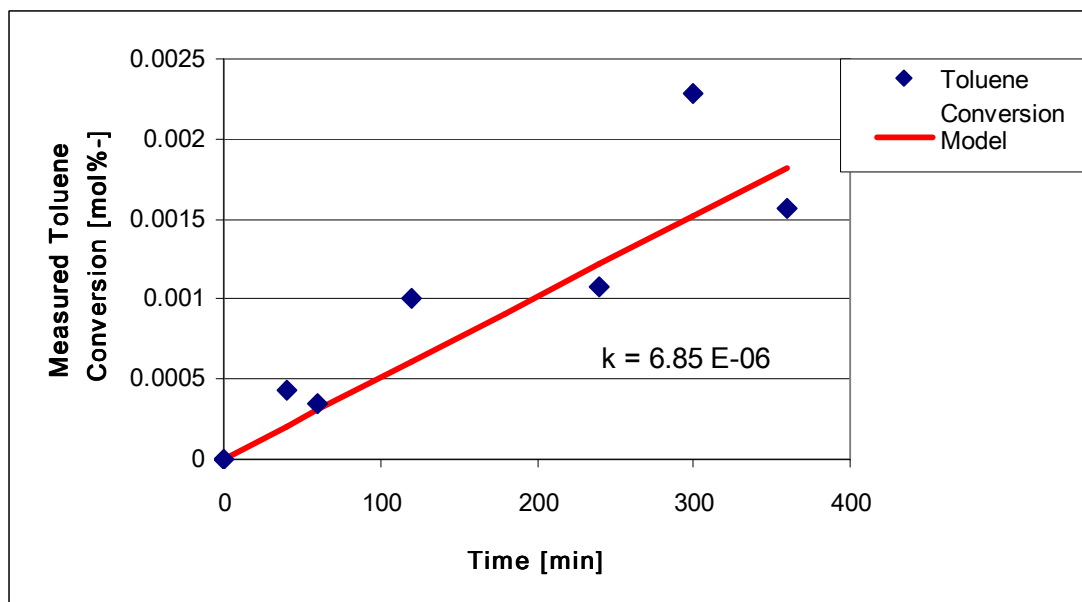


Figure 48: Kinetic modeling for all data points (measured toluene conversion) at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g.

However, using only the initial data still gave an increase in the modeled rate constant from 4.14×10^{-6} at 70 °C to 7.62×10^{-6} at 80 °C as illustrated in Figure 49.

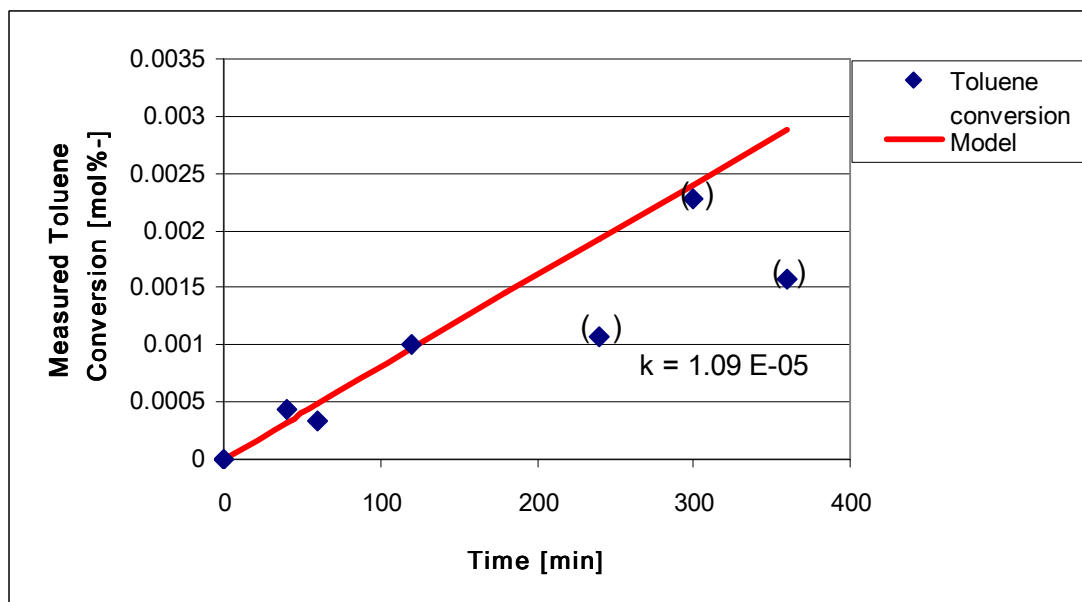


Figure 49: Kinetic modeling for data sets obtained up to 120 min (measured toluene conversion) at 80°C with excess toluene using TS-1 catalyst. Toluene = 6.257g, catalyst = 0.120g. Data points in brackets not used for model fitting.

In this case, only data up to 120 min was used for the kinetic model as there was no data point obtained at 180 min. Comparing the fit obtained at 120 min with fitting the model of all the data points with excess toluene, it was observed that, as in the case with water as a solvent, the measured data deviated from the predicted values at longer reaction times.

When using acetonitrile as a solvent, fitting the model at 80 °C generated a very good fit when using all data points. This can be observed as shown in Figure 50.

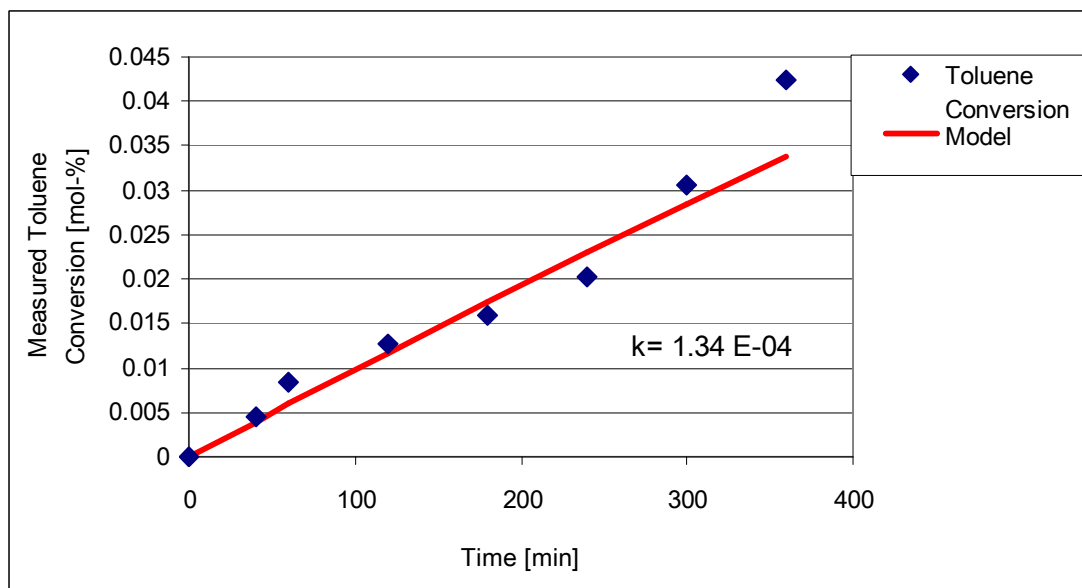


Figure 50: Kinetic modeling for all data points (measured toluene conversion) at 80°C with acetonitrile as a solvent using TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g.

In this case, only the initial data showed no major difference to the case where all data was used as illustrated in Figure 51.

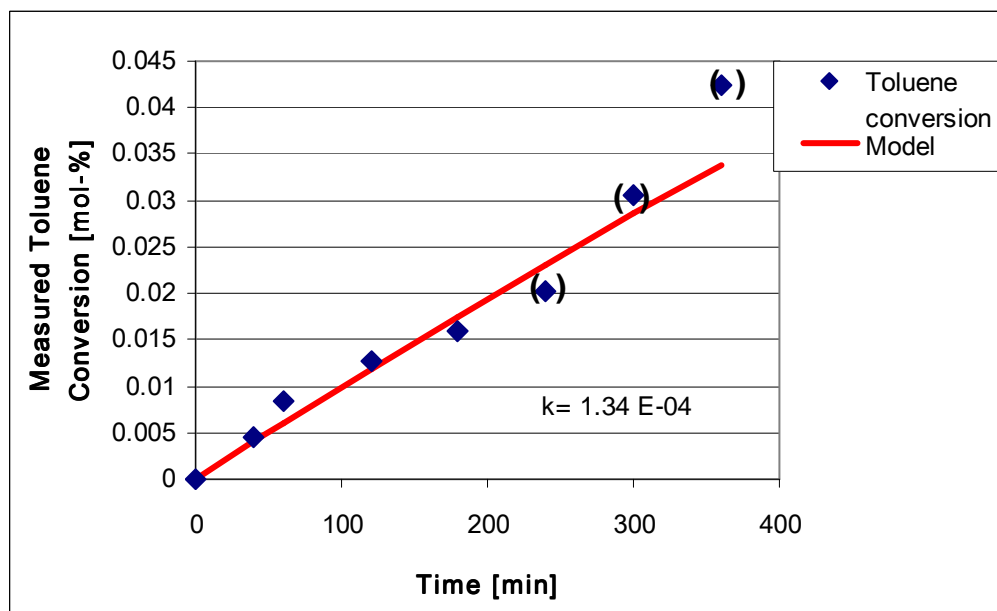


Figure 51: Kinetic modeling for data sets obtained up to 120 min (measured toluene conversion) at 80°C with acetonitrile as a solvent using TS-1 catalyst. Toluene = 1.202g, catalyst = 0.120g. Data points in brackets not used for model fitting.

It can be seen that solvent effects have a significant effect on the reaction rate and rate constants. The rate constants obtained for the experiments illustrated in Figure 46 to Figure 51, at 80 °C as well as the rate constants obtained at lower temperatures using all data fitted are summarised in Table 11. As expected, the temperature also has an effect on the observed rate constant. The only deviation from what is expected is that the effect of temperature when acetonitrile is used as a solvent is minimal.

Table 11: Reaction rate constant for toluene hydroxylation over TS-1. Catalyst = 0.120 g, toluene = 1.202g (water or acetonitrile as a solvent) or 6.257g (excess toluene), hydrogen peroxide = 0.5 ml.

Dispersion Medium	k_{toluene} ($\text{dm}^3/\text{mol}\cdot\text{m}^2\cdot\text{min}$)
Water (70°C)	2.62×10^{-6}
Water (80°C)	1.87×10^{-5}
Excess toluene (60°C)	1.97×10^{-6}
Excess toluene (70°C)	4.14×10^{-6}
Excess toluene (80°C)	6.85×10^{-6}
Acetonitrile (70°C)	1.30×10^{-4}
Acetonitrile (80°C)	1.34×10^{-4}

It was of high importance to obtain the initial reaction rates for toluene hydroxylation reactions. The initial reaction rates were obtained by calculating the rate of the reaction at time zero. This was achieved by taking into

Chapter 5: Results and Discussion

consideration the initial feed concentrations of toluene and hydrogen peroxide, and the rate constants obtained using the regression model. This information was fitted in the kinetic model as clearly stated in equation [4.19].

The initial rate of toluene consumption for different dispersion media, at different temperatures, are summarised in Table 12.

Table 12: Initial reaction rate in toluene hydroxylation reactions over TS-1. Catalyst = 0.120 g, toluene = 1.202g or 6.257g, hydrogen peroxide = 0.5 ml, solvent (water or acetonitrile = 5ml).

Dispersion Medium	Initial Reaction Rates (mol/L. min)
Water (70°C)	3.95×10^{-6}
Water (80°C)	2.81×10^{-5}
Excess toluene (60°C)	1.54×10^{-5}
Excess toluene (70°C)	3.23×10^{-5}
Excess toluene (80°C)	5.35×10^{-5}
Acetonitrile (70°C)	1.96×10^{-4}
Acetonitrile (80°C)	2.02×10^{-4}

In conclusion, the kinetic modeling has shown that toluene hydroxylation in acetonitrile generates the best fit with the proposed kinetic model. When performed in excess toluene, a reasonable fit was also obtained. In water, however, the unselective decomposition of hydrogen peroxide is severe, which means that this decomposition cannot be neglected when modeling the reaction. Extrapolation that was done proved that the model obtained with the 180 min data did not always fit the later data due catalyst decay.

6. Conclusions

The objective of this research was to investigate factors which affect the selective oxidation of 2-methylnaphthalene with aqueous hydrogen peroxide as an oxidant over TS-1 and mesoporous Ti-MCM-41 as catalysts. The factors considered were varying reaction temperature and the choice of solvent.

It was seen that TS-1 is an unsuitable catalyst for the hydroxylation of 2-MN at any conditions investigated. It may be concluded that TS-1, which is a medium pore zeolite cannot allow the larger substrate, 2-methylnaphthalene, to penetrate the active sites and for intra-particle diffusion to take place.

With data obtained with Ti-MCM-41, it was observed that better yields and conversions are generated using acetonitrile as a solvent. In addition, catalytic oxidation of 2-methylnaphthalene is strongly affected by reaction temperature. This was proven by higher 2-MN conversion (92%) attained at 120 °C when using acetonitrile as a solvent. The formation of 2-methyl-1, 4-naphthoquinone was also enhanced with increasing reaction temperature generating optimum relative selectivities of 51.4 % at 120 °C. It was found that in the oxidation of 2-MN it is possible to produce 2-methyl-1-naphthol (a proposed initial feed substrate for 2-methyl-1, 4-naphthoquinone production) as a co-product.

The use of the Parr autoclave made it difficult to obtain the reaction kinetics as only one data point was collected at the end of each reaction run.

Chapter 6: Conclusions

From toluene oxidation reactions, it is seen that the catalytic oxidation of toluene occurred predominantly on the aromatic ring leading to the formation of a para or ortho- cresol. In addition, with all the catalytic reactions performed, no meta-cresol was generated.

Using water as a solvent, para- cresol was the favoured product. This was attributed to the fact that the reactant (toluene) was faced with minimum or no competition from water for adsorption and diffusion in the channels of TS-1, thus leading to higher reaction rates. This led to para-cresol to be formed faster. Cumulative toluene consumption was observed to increase with reaction temperature, with a maximum obtained at 80 °C (approximately 0.464%).

When reactions were performed in excess toluene, para-cresol was the favoured product. However, with the increase feed concentration of toluene, formation of side products increased, with over-oxidation leading to poly aromatic compounds (tars) deposited onto the catalyst surface. This was assumed to block diffusion to and adsorption on the internal active sites, thereby allowing the reaction to take place only on the external surface. The reaction on the external surface of the catalyst is not selective to para-cresol.

Using acetonitrile as a solvent, cumulative toluene consumption increased with time and reaction temperature. Ortho-cresol was generated as the favourable product. An optimum reaction temperature of 80 °C was found to be adequate and desirable, generating high concentrations of ortho- cresol and higher cumulative toluene consumption.

Chapter 6: Conclusions

Kinetic modeling of reaction data was done using a second order kinetic modeling assuming overall first order dependence in both toluene and hydrogen peroxide. Using water as a solvent, fitting the data to a kinetic model generated a good fit, especially when the model was fitted at lower reaction time of 180 min. In excess toluene, a better kinetic model fit was attained when considering only the initial data (120 min).

It was seen that when using acetonitrile as a solvent, a good fit was generated. This was also proven when it made little difference whether only the initial data, or all the data were used. From these observations it can be concluded that acetonitrile is the suitable solvent for the generation of ortho-cresol in toluene hydroxylation reactions with hydrogen peroxide as the oxidant.

From the kinetic studies conducted, it was seen that the rate constant for toluene consumption was influenced by the type of solvent used in the reaction and the reaction temperature. This was proven in reactions with water as a solvent, whereby the rate constant was enhanced at 80 °C with a value of $1.87 \times 10^{-5} \text{ dm}^{-3}/\text{mol}\cdot\text{m}^2\cdot\text{min}$, and a value of $6.85 \times 10^{-6} \text{ dm}^{-3}/\text{mol}\cdot\text{m}^2\cdot\text{min}$ was attained with excess toluene. In addition, using acetonitrile as a solvent, the rate constant enhanced slightly with an increase in temperature ($1.30 \times 10^{-4} \text{ dm}^{-3}/\text{mol}\cdot\text{m}^2\cdot\text{min}$ at 70°C and $1.34 \times 10^{-4} \text{ dm}^{-3}/\text{mol}\cdot\text{m}^2\cdot\text{min}$ at 80°C). It was observed that for all reactions performed (acetonitrile, excess toluene, water), the initial reaction rates increased with reaction temperature. Therefore, it is conclusive that the results attained in toluene hydroxylation are accurately interpreted and analysed.

Chapter 6: Conclusions

An important point to note is the fact that the results that were generated in this study for toluene hydroxylation were obtained using larger particle size zeolite TS-1. This means that the catalyst used here had larger internal diffusion constraints, which explains the difference between the results obtained in literature and the results generated in this study.

7. Recommendations

For catalytic oxidation reactions involving 2-methylnaphthalene with mesoporous Ti-MCM-41, it is recommended that a Parr PTFE autoclave with a sampling port must be used to obtain better sampling and to improve experimental results in order to fit the reaction data to a suitable kinetic model in order to determine 2-methylnaphthalene consumed during reactions, the rate constants and the initial reaction rates. As this was a feasibility study, therefore, a lot of work on oxidation of 2-methylnaphthalene still need to be conducted to enhance conversions and product selectivities.

For future work, it can be highly recommended that other zeolite catalysts with higher surface areas and larger pore diameters other than mesoporous Ti-MCM-41 must be utilised as 2-methylnaphthalene is a larger compound and cannot diffuse and adsorb through medium pore zeolites such as TS-1 and Ti-Beta channels. This is recommended due to the fact that there was no conversion using set-up III attained with TS-1. First consideration should be given to other mesoporous catalysts, due to time constraints, other factors such as feed ratio of 2-MN: hydrogen peroxide, were not investigated and optimised when using set-up III, therefore, it is a need to further the research in this area. It is also recommended that the catalyst be tested for deactivation over a period of time and possibilities of catalyst poisoning.

For toluene hydroxylation reactions, this is a very complex and difficult reaction with little work done regarding toluene in the last decade, a lot of focus is still

Chapter 7: Recommendations

required that will enhance and generate better reaction rates and improving toluene conversions. It is also recommended to optimise the feed ratio of toluene : hydrogen peroxide, performing reactions in excess toluene starting at lower concentrations and improving para-cresol selectivity. This is proposed as water was observed not to be a proper solvent in toluene hydroxylation reactions as there were complications with sampling.

For future work, it will be ideal to use other zeolites other than TS-1 in toluene hydroxylation reactions as a comparison and to see whether compounds other than ortho and para-cresol might be obtained or generated at higher yields.

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9. APPENDIX A

9.1 Titration Reagent Preparation

Titration Chemical solutions used in this work were prepared as detailed below.

Sulphuric Acid

A dilute sulphuric acid solution was prepared by slowly adding 2.8 ml of sulphuric acid (98 mass %) to 500 ml flask of distilled water under constant stirring. This yielded an approximately 0.1 M solution.

Starch

For Iodometric titrations, an aqueous suspension of starch is used as indicator. However, β -amylose present in the indicator reacts with iodine to form an intensely violet-purplish coloured complex. A 1 wt-% per volume solution of starch indicator was prepared by dissolving 1.001 g of soluble starch (starch from potatoes, $(C_6H_{10}O_5)_n$, Fluka) in a little boiled distilled water to give a paste, which boiled distilled water was added to a 100 ml flask under constant stirring. The solution was kept in a stoppered flask and stored in a dark cupboard to prevent decomposition by direct sunlight.

Potassium Iodide

Iodide is completely oxidised by atmospheric oxygen. Therefore the solution must be kept in a glass-stopped flask and kept in a cool place preferably a dark cupboard where there is no direct sunlight.

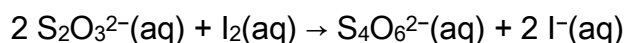
A 1 wt-% per volume solution was prepared by dissolving approximately 0.999 g potassium iodide crystals (KI, Merck) in a 100 ml flask of distilled water. Two important sources of errors involving titrations with iodine include: loss of iodine owing to its appreciable volatility and oxidation of acid solutions of iodide by oxygen from air. Atmospheric oxidation of iodide is negligible in neutral solutions, in the absence of the catalyst, but the rate of oxidation increases proportionally with the decrease in pH. Solutions containing excess of iodine and acid must not be allowed to stand longer before iodine titration, thus when prolonged time is necessary, the solution must be free from air prior to iodine addition.

Ammonium Molybdate Tetrahydrate

1.002 g ammonium molybdate tetrahydrate ($\text{H}_{24}\text{Mo}_7\text{N}_6 \cdot 4\text{H}_2\text{O}$, Fluka) was dissolved in 50 ml distilled water to give a 2 wt-% ammonium molybdate solution.

Sodium Thiosulphate

In Iodometric titrations, the thiosulphate anion reacts stoichiometrically with iodine reducing it to iodide as it is oxidised to tetrathionate:



Consequently boiled out water was used as sodium thiosulphate solutions prepared by ordinary distilled water are particularly unstable because distilled

water usually contains an excess of carbon dioxide, which may cause slow decomposition to take place resulting in the formation of sulphur.

This solution was prepared by dissolving 4.9880g sodium thiosulphate crystals ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in a boiled-out cool distilled water, making up to 500ml boiled distilled water in a stopped flask to produce an approximately 0.04019 mol per litre (0.04019- N) solution.

Three to four drops of chloroform were added to improve and stabilise the keeping qualities of the solution by inhibition of microbial decomposition. The flask was stored in the dark cupboard as exposure even to slight rays of light hastens decomposition.

10. APPENDIX B

10.1. Data Evaluation and Workup

10.1.1. Iodometric Titration

This method deals with the titration of iodine liberated in a chemical reaction. Strong reducing agents such as sodium thiosulphate react completely and rapidly with iodine even in acid solution. Upon titration with sodium thiosulphate solution, the iodine is removed and the reaction proceeds from right to the left.

For this work, a known concentration solution of sodium thiosulphate was used as a titrant, and the hydrogen peroxide concentration present in the samples determined quantitatively from the thiosulphate volume required for equivalence, and the known laws of stoichiometry.

The moles of thiosulphate required to reach the end-point were calculated as:

$$n_{\text{thiosulphate}} = C_{\text{thiosulphate}} \cdot V_{\text{equivalence}}$$

Moles of iodine formed through the oxidation of potassium iodide can be calculated using expression [4.7], whereby two moles of thiosulphate reduce one mole of iodine. However, the moles of hydrogen peroxide reduced can be calculated using equation [10.1]:

$$n \text{ H}_2\text{O}_2 = 0.5 \text{ C Na}_2\text{S}_2\text{O}_3 \cdot V_{\text{equivalence}} \quad [10.1]$$

This could help determine the hydrogen peroxide concentration in the reactor at specific reactor sampling intervals and whether the degree of dilution and aliquot volume can be obtained.

10.1.2. Aromatics Analysis

All 0.2 g samples withdrawn from the reaction mixture at specified time intervals were diluted with 3 ml solvent of choice, filtered on a 0.45 μm Millipore filter to remove the catalysts prior to GC-MS analysis. With 2-methylnaphthalene using Ti-MCM-41 samples, an estimate of ± 1.0 ml was further diluted with ethanol as acetonitrile is too volatile and would evaporate before it can be analysed/ detected by GC analysis.

Standards were prepared in a 5ml vial for every experimental run, dissolved in methanol as a solvent. The mass of the compounds used to prepare a standard for 2-MN oxidation experiments is shown in

Table 13.

Table 13: Mass of components used for preparation of standard for 2-MN oxidation reactions.

Component	Mass (g)
2-Methylnaphthalene (MN)	0.0234
Biphenyl	0.0216
2-Methyl-1,4-naphthoquinone (MNQ)	0.0175
Methyl-1-naphthol (MNL)	0.0102

A Hewlett Packard 5890 GC with FID detector was used to quantify and separate aromatic compounds present in each sample as shown in Figure 52. The GC was equipped with a 50 x 0.25 mm bounded phase SGE capillary column made of fumed silica operated at 250°C maximum, with injector 270°C and detector at 300°C. The operating flow rates were: air flow rate \approx 300 ml/min, hydrogen \approx 30 ml/min, mature gas \approx 30 ml/min. Helium gas was also used to separate aromatics from the reaction mixture. Dilution with ethanol was negligible as no effect on separation was obtained.

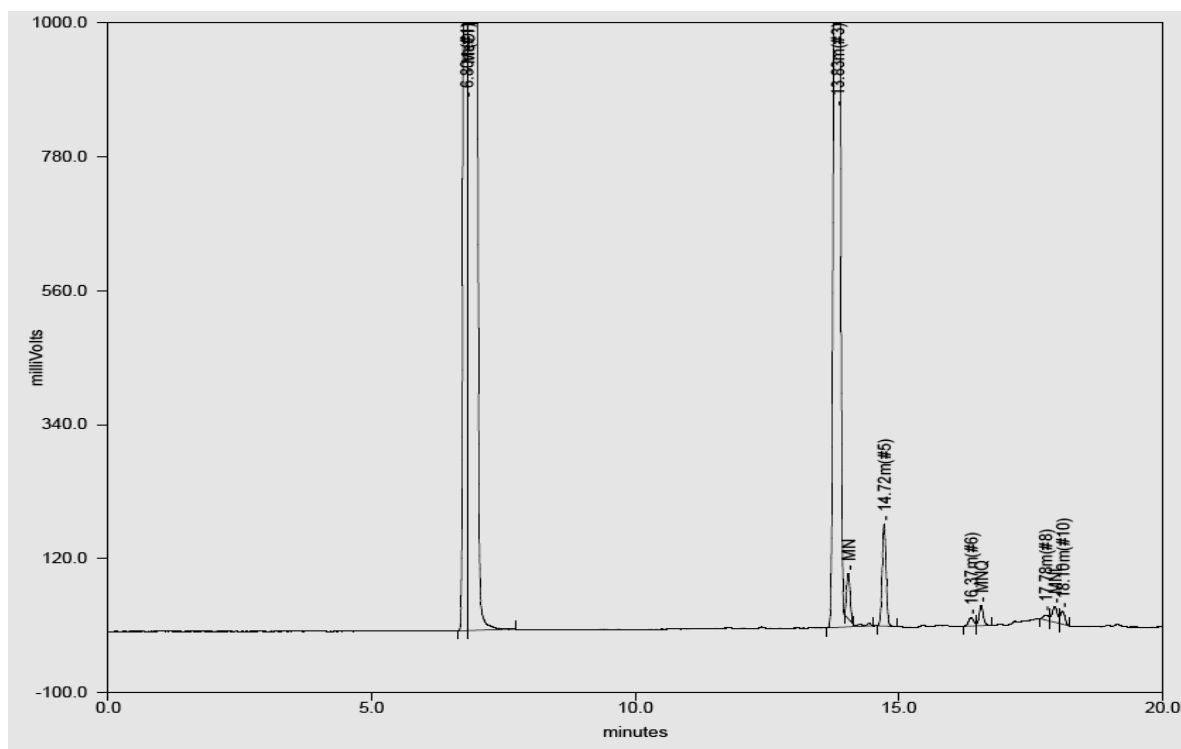


Figure 52: GC-FID trace showing identified peaks. Catalyst (Ti-MCM-41= 0.1g, 2-MN = 1g, H₂O₂ = 6ml, acetonitrile = 10, reaction temperature = 110 °C).

With preparations of dilute standard samples, biphenyl was used as an internal standard.

Species concentrations were determined relative to calibration standards of known concentration, and the aromatics were identified qualitatively by comparison of their retention times with those of 2-methylnaphalene, 2-methyl-1, 4-naphthoquinone, biphenyl, 2-methylnaphthol in the standards.

For GC-MS, the same mass fractions used in the preparation of standards for GC were used.

For toluene hydroxylation experiments, a Hewlett Packard 5890 GC with FID detector was used to quantify and separate aromatic compounds present in each sample. The GC was equipped with a 50 x 0.25 mm bounded phase SGE capillary column made of fumed silica operated at 200°C maximum, with injector 250°C and detector at 270°C. The operating flow rates were: air flow rate \approx 300 ml/min, hydrogen \approx 30 ml/min, mature gas \approx 30 ml/min. Helium gas was also used to separate aromatics from the reaction mixture. Dilution with ethanol was negligible as no effect on separation was obtained.

Two standards were prepared; for water and acetonitrile as a solvent, phenol as internal standard was used and ethylbenzene was used as internal standard for reactions performed in excess toluene. The standards were diluted up to 100ml using acetonitrile as solvent as toluene is immiscible with water and the summary of the components used is illustrated in

Table 14.

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Table 14: Mass of components used for preparation of standard for toluene oxidation reactions.

Phenol as internal standard		Ethylbenzene as internal standard	
Component	Mass (g)	Component	Mass (g)
Phenol	0.0476	Ethylbenzene	0.0469
Toluene	0.0466	Toluene	0.0460
p-cresol	0.0514	p-cresol	0.0510
o-cresol	0.0507	o-cresol	0.0507
m-cresol	0.0493	m-cresol	0.0491

Linear calibration curves for toluene, phenol, ortho-cresol, and para-cresol were expressed by plotting absolute area of each component as a function of concentration as shown in Figure 53.

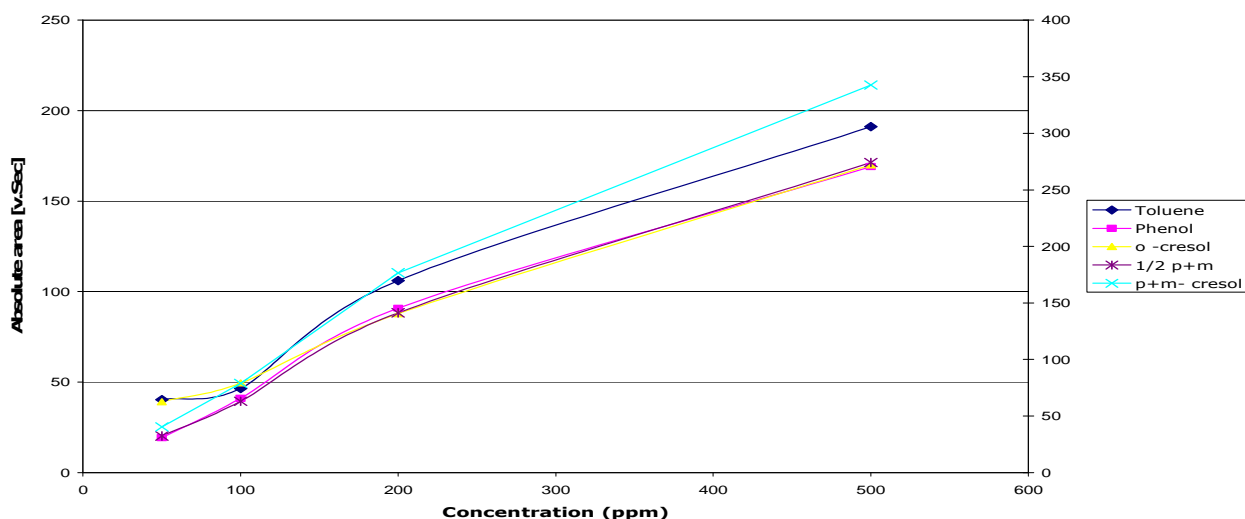


Figure 53: Linear calibration curve for toluene, phenol, ortho-cresol, and para-cresol.

The response factors of each compound can be calculated by using phenol (for water samples) and methylbenzene (for toluene in excess) as internal standard which is assigned a response factor of 1.

$$\frac{Area_i}{m_i} \times \frac{m_{phenol/EB}}{Area_{phenol/EB}} \quad [10.2]$$

The peaks in each catalytic sample analysed that are identified as toluene, ortho-cresol and para - cresol, based upon comparison of their retention times with those of the calibration solution species, are assigned these response factors. Unidentified compounds are assigned a response factor of 1.

Concentrations of each compound in the sample per 0.3 g/ml of total sample analysed were calculated using equation [10.3],

$$Area_i \times \frac{y}{Area_{phenol/EB}} \times \frac{1}{RF} \quad [10.3]$$

The concentration of compound *i* in the sample was generated from values obtained in equation [10.3], to a factor of a thousand divide by the 0.3. The concentration was expressed in g/ml. Therefore a molar mass of each compound was used to calculate concentration of each compound in a sample in mol/L.

In order to determine specific concentration of each compound in a mixture (mol/L), a factor of $\frac{3}{2}$ was taken into consideration.

Thus the final reactor concentration of each compound was attained with equation [10.4]

$$Conc_{mix} \times \frac{3.2}{0.2} \quad [10.4]$$

Molar fractions (y_i), calculated based on the molar masses of each species.

Toluene conversion was generated based on summation of product concentration as in equation [10.5].

$$X_{tol} = \frac{SUM [product\ concentration]}{C_{tol,0}} \times 100 \quad [mol-\%] \quad [10.5]$$

Therefore, when species concentrations are known, product yields, product p/o-ratio can be determined. Hydrogen peroxide efficiency cannot be clearly determined as the Iodometric titration gave suspicious concentrations and the results were not taken into account. Thus selectivities were not determined. The following equations were utilised for the determination product yields and product p/o- ratios.

$$P/o - ratio (t) = \frac{C_{para-cresol}}{C_{ortho-cresol}} \quad [mol/mol]$$

$$Y_i (t) = \frac{C_{tol,0} - C_{tol}(t)}{C_{i,0} - C_i(t)} \times 100 \quad [\%]$$

11. APPENDIX C

With 2-MN hydroxylation reactions, the data obtained is summarised in

Table 15.

Table 15: Conversions, relative selectivities of MNQ/MNL (mol/mol) as a function of choice of catalyst at reaction temperature (80 - 120°C). Catalyst= 0.1g, solvent (acetonitrile)= 10ml, H₂O₂ = 6ml.

Run	Catalyst	Temperature (°C)	2-MN Conversion [mol-%]	Relative selectivity [MNQ/MNL]
1	TS-1	(80-120)	0	0
2	Ti- MCM-41	80	0	0
3		100	18	0.720
4		110	85	0.157
5		120	92	0.514

12. APPENDIX D

12.1. Catalyst Characterisation

12.1.1. Scanning Electron Microscopy

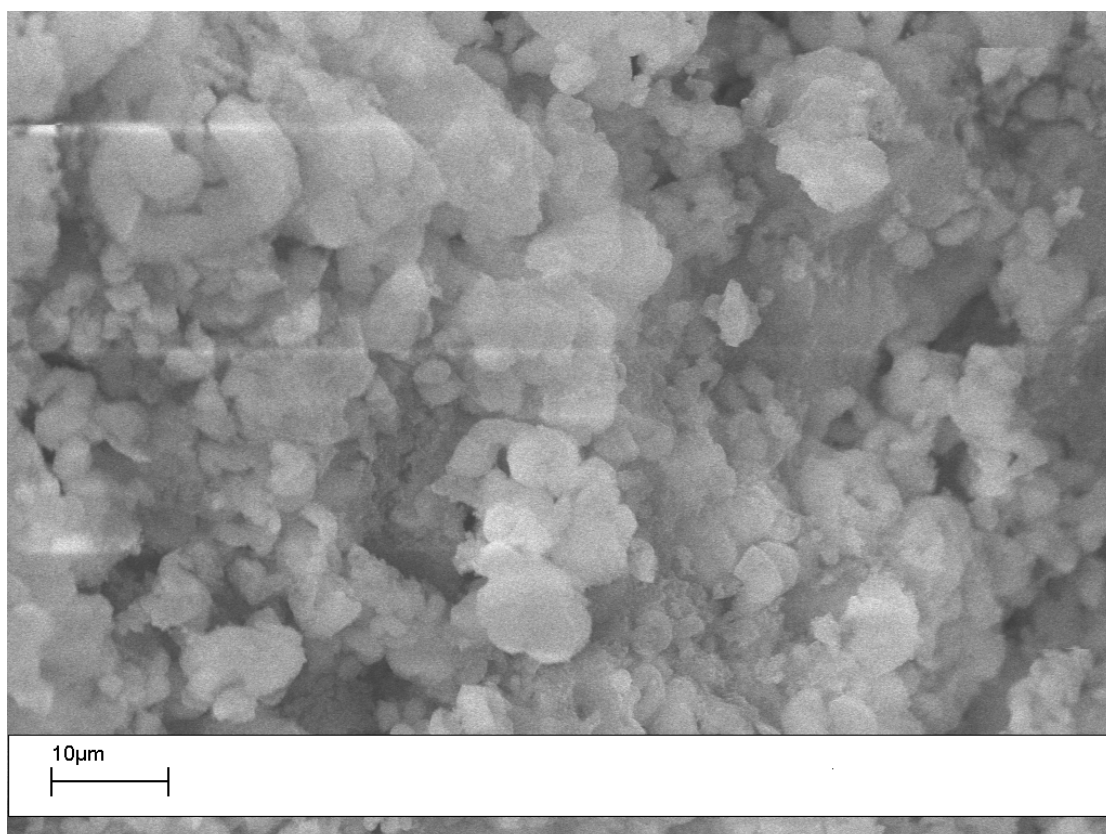


Figure 54: SEM micrograph of Ti-MCM-41. A hexagonal- shaped crystallite with surface area $1025 \text{ m}^2/\text{g}$

13. APPENDIX E

13.1. List of Chemicals Used

Table 16: List of Chemicals used in batch hydroxylation experiments

Reagent	Purity	Supplier
Acetonitrile	HyperSolv for HPLC	Sigma- Aldrich
Ethylbenzene	99%	Sigma- Aldrich
Hexadecyltrimethylammonium Bromide	97 % (for synthesis)	Merk
Hydrogen Peroxide	30 wt-% aqueous solution, p.a	Sigma- Aldrich
Meta-cresol	99% (GC)	Sigma- Aldrich
Methanol	99.9+ % HPL Grade	Sigma- Aldrich
Ortho-cresol	99+%	Sigma- Aldrich
Para-cresol	99 %	Sigma- Aldrich
Phenol	Min. assay 99%	Assoc. Chem. Enterprises
Tetrabutyl orthotitanate (Ti IV Oxide)	—	Aldrich
Tetraethyl orthosilicate	99.99 %	Fluka

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Tetramethylammonium hydroxide	25 % wt	(Alfa)
Reagent	Purity	Supplier
Tetrapropylammonium hydroxide	20% Sol. in H ₂ O (~1.0M)	Fluka
Titanium Isopropoxide	95 %	Alfa
Titanium Isopropoxide	Metals basis	(Alfa)
Toluene	99.5%	Sigma- Aldrich
1-Pentanol	99.0% (GC) p.a	Fluka
1- Propanol	CHROMASOLV® for HPLC	Sigma- Aldrich
2-Methylnaphthalene	97%	Sigma- Aldrich
2-methylnaphthol	98%	Sigma- Aldrich
2-methyl-1,4- naphthoquinone	98 %`	Sigma- Aldrich