NANOCLUSTER METAL OXIDE CATALYST FOR LIGNIN OXIDATION TO PLATFORM CHEMICALS

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ABSTRACT

This study involves the valorization of model compound of lignin, a naturally abundant bio-polymer, to harness benefit in terms of chemicals and energy source for human utilization. Mixed metal cobalt titanium oxides $CoTiO_3$ and composite with titania $CoTiO_3/TiO_2$ were prepared by solution phase method and applied for the liquid phase catalytic oxidation of a lignin model compound, vanillyl alcohol to vanillin. The morphology, phase composition and crystal structure of the freshly prepared and reused $CoTiO_3$ and $CoTiO_3/TiO_2$ catalyst were studied by using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Raman spectroscopy. The analysis supported properties of optimal heterogeneous catalyst in lieu of their phase composition, generation of highly dispersed metallic cobalt and high surface. The oxidation process of vanillyl alcohol used H_2O_2 as an oxygen source. The vanillyl alcohol conversion was influenced by various experimental conditions such as reaction time, temperature, molar ratio of reactants, catalyst loading, nature of solvent and reaction medium. The bimetallic oxide catalysts were synthesized efficiently to perform the high conversion and selective oxidation of vanillyl alcohol into fine chemicals, such as vanillin and vanillic acid. In the presence of NaOH in acetic acid and isopropanol solvents, the $CoTiO_3$ catalyst exhibits remarkable conversion of 99% and excellent selectivity of 99.8% to vanillin, respectively. On the other hand, in the case of $CoTiO_3/TiO_2$ catalyst, the highest conversion (99%) was registered in the acetic acid as a solvent with presence of NaOH while without catalyst the recorded conversion was 80%. These could be attributed to the formation of peracetic acid. The oxidation reaction mechanism over the catalyst was postulated based on the analysis of products using high performance liquid chromatography (HPLC) analysis. It has been discovered that $CoTiO_3$ and $CoTiO_3/TiO_2$ catalyst can retain its performance without significant change in the catalytic activity after four consecutive cycles.

ABSTRAK

Logam campuran kobalt titanium oksida $CoTiO_3$ dan gabungan dengan titania CoTiO3/TiO2 yang disediakan dengan kaedah fasa penyelesaian telah dinilai bagi fasa pengoksidaan pemangkin cecair vanillyl alkohol untuk vanillin menggunakan H_2O_2 sebagai sumber oksigen. Morfologi, komposisi fasa dan struktur kristal CoTiO3 pemangkin baru disediakan dan digunakan semula telah dikaji dengan SEM, EDX, XRD, XPS dan spektroskopi Raman. Penukaran Vanillyl alkohol dipengaruhi oleh pelbagai keadaan eksperimen seperti masa reaksi, suhu, nisbah tindak balas molar bahan, pemangkin pemuat, sifat pelarut dan tindak balas medium. Dengan kehadiran pemangkin CoTiO3, aktiviti yang lebih tinggi iaitu 91% mencatatkan lebih pemangkin dengan media berasid selepas 5 jam masa tindak balas. Sementara pemilihan yang cemerlang vanillin 99% telah dicapai dalam media asas. Pemangkin CoTiO3/TiO2, penukaran tertinggi (99%) telah ditemukan dalam asid asetik sebagai pelarut dengan kehadiran NaOH tanpa penukaran rekod adalah 80%. Ini boleh menjadi sifat kepada pembentukan asid paracetic. Mekanisme tindak balas pengoksidaan lebih pemangkin diandaikan berdasarkan produk pemerhatian daripada analisis HPLC itu. Ia telah mendapati bahawa CoTiO3 dan CoTiO3/TiO2 pemangkin boleh mengekalkan prestasinya tanpa perubahan ketara dalam aktiviti pemangkin selepas empat kitaran berturut-turut.

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CH_3COOH	Acetic acid
[Amim]Cl	1-allyl-3-methylimidazolium chloride
($[C_4mim]PF_6$)	1-butyl-3-methylimidazolium hexafluorophosphaste
($[C_4mpyr]PF_6$)	1-butyl-1-methylpyrrolidiniumhexafluorophosphaste
($[C_4mim]PF_6$)	1-butyl-3-methylimidazolium
($[C_6mim]CF_3SO_3$)	1-hexyl-3-methylimidazolium trifluoromethanesulfonate
$Fe(Cl_8TTPPS_4)$	5,10,15,20-tetrakis (2′, 6′-dichloro-3′- sulfonatophenyl) porphyrin
Fe-($TPPS_4$)	5,10,15,20-tetrakis (4′ -sulfonatophenyl) porphyrin,
Br	Bromine
C	Carbon
$CoCl_2$	Cobalt chloride
$CoTiO_3$	Cobalt titinate
FESEM	Field-Emission Scanning Electron Microscope
Au	Gold
HBr	Hydrogen bromide
H_2O_2	Hydrogen peroxide
MgO	Magnesium oxide
Ni	Nickel
Pt	Platinum
POM	Poly oxo metalates
Ru	Ruthenium
SBA-15	Santa Barbara amorphous
NaOH	Sodium hydroxide
Na_2O_2	Sodium peroxide

TiO2 : Titanium dioxide

H_2O : Water

XPS : X-ray Photoelectron Spectroscopy

XRD : X-ray Powder Diffraction

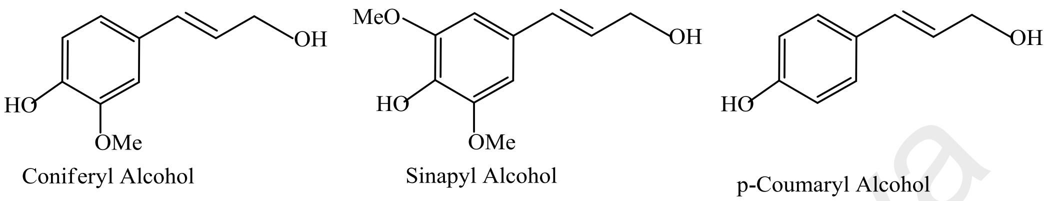
Zr : Zirconium

CHAPTER 1: INTRODUCTION

1.1 Background

Lignin is the second most abundant naturally occurring compound after cellulose, which is frequently found as an integral part in the plants. This lignin contributes 30% of weight and 40% of energy content of the lignocellulosic biomass (Sakakibara, 1980; G. Wang & Chen, 2016). Thus, lignocellulosic bio-refinery obtains a huge amount of lignin, which aims the valorisation of lignin as energy and resource of initial materials for the chemical industries with the development of accurately sustainable and efficient bio-refinery processes (Albini & Protti, 2016; Glasser & Sarkanen, 1989; Wooley et al., 1999). More significantly, lignin has been denoted as the only renewable source of aromatic fine chemicals and has become an interesting future opportunity for the conversion of lignin to discrete molecules or classes of lower molecular weight aromatic, monomeric building blocks for organic synthesis and polymer productions (Bozell et al., 1995; Bozell et al., 2000; Dimmel et al., 2002). It is a natural polymer of three phenyl-propanoid polyphenols mainly linked with the arylglycerol ether bonds between coniferyl alcohol (G-type), phenolic para-coumaryl alcohol (H-type), and sinapyl alcohol (S-type) units (Adler, 1957; Lebo et al., 2001) which is presented in Figure 1. 1. Gymnosperms lignin consists of mostly G-type lignins. Moreover, a mixture of G-and S-type lignin is also produced from the dicotyledonous angiosperms (Varman & Saka, 2015). All these three types of lignin can be found in quantities in monocotyledonous lignin (GSH-lignin) (Lange et al., 2013; Vanholme et al., 2010). These polyphenolic composite material have been used to bind the celluloses closely to each other and protect the wall of the cell from pathogenic attack (Adler, 1977; Onal & Karaduman, 2016).

Lignin degradation is generally identified as delignification, which plays a vital role in paper production (Stevens & Verhé, 2004) and the synthesis of many commodity chemicals such as drugs, pharmaceuticals and perfumes (Fan et al., 2009). This delignification has been done by catalytic oxidation which produces functionalized, monomeric or oligomeric products that can serve as starting materials for other valorization processes in the pharmaceutical and chemicals industries.



Coniferyl Alcohol Sinapyl Alcohol p-Coumaryl Alcohol

Figure 1. 1: Natural monomer of coniferyl alcohol (G-type), sinapyl alcohol (S-type) and phenolic para-coumaryl alcohol (H-type) units

Because of the complexity of lignin, most of the lignin oxidation studies were performed from lignin model compounds and are very well documented in literature (Badamali et al., 2013; Hwang et al., 2008; Kapich et al., 2010; Rochefort et al., 2002). Several novel strategies for oxidation of lignin and lignin model compounds have been studied, such as electrochemistry (Pan et al., 2012; Richardson et al., 2012), use of mesoporous materials (Badamali et al., 2013) and photocatalysis (Tonucci et al., 2012).

These studies reveal that some issues need to be resolved, such as the lack of selectivity, catalyst decomposition, low amounts of lignin required and difficult separation of products after the reactions are completed. These limitations can be overcome by utilizing an appropriate heterogeneous catalysts they offer several benefits over their homogenous counterparts such as the separation, reusability and easy handling. Different types of noble metal-based heterogeneous catalysts such as Au/CeO_2, Pt/C, Ru/TiO_2 etc. have been proposed for this purpose and such reactions are mediated by the use of alkali (Shen et al., 2010; Y. Zhang et al., 2011).Although noble metal catalysts exhibit high activity for oxidation reactions, they can be expensive, minimizing their potential for commercial applications (Guo & Wang, 2011). Oxides of other transition metals, such as titanium, chromium, manganese, cobalt and copper are also recognized to be effective catalysts for the oxidation reactions. Among these metals, titanium and cobalt are the most attractive because of their strong capability for dioxygen activation (through metal–O_2 adduct formation) and because these are more cost efficient compared to noble metals. Recently, a mixed metal-based catalyst of cobalt and manganese oxide ($CoMn_2O_4$) was found to be an active species for oxidation reactions and catalyzed oxidation of vanillyl alcohol to vanillin (Jha et al., 2014).

In light of this study, we were attracted and motivated towards the mixed-metal cobalt titanium oxide system. The preparation, characterization and detailed catalytic performance of $CoTiO_3$ and $CoTiO_3/TiO_2$ mixed metal oxide catalyst for liquid phase oxidation of vanillyl alcohol mediated with H_2O_2 have been reported in this dissertation. The catalytic reaction parameters such as reaction time, mass loading of catalyst, influence of temperature, molar ratio, and reusability of the $CoTiO_3$ and $CoTiO_3/TiO_2$ catalyst have also been systematically carried out during current study.

1.2 Problem statement

The upgrading for higher value of lignin into production of chemical feed stocks represents a real challenge in terms of sustainability and environmentally protection. In the context of sustainable development and green chemistry, lignin value-add program represent an important opportunity to reduce dependency of fossils-based material for chemicals. Despite the good results obtained from lignin or lignin model compound oxidation, some systems suffer from different limitation including catalyst decomposition, lack of selectivity for lignin and low amounts of lignin required e.g., in electrochemical studies, and difficulties in separation of products after completion of the reactions. In some events, it needs high temperature for oxidation reaction and it is economically infeasible. Thus a few methods are not suited for higher production of platform chemicals. The shift from homogeneous to heterogeneous reduces discharge of chemicals into water affluents system besides its advantage in separation process between catalyst and products/remaining feed. Current heterogeneous reported still suffer from low activity and poor selectivity, when using metals-supported based catalysts. To our best knowledge, for the first time, we will develop and optimize in this study mixed metal oxide nano catalyst for lignin model compound oxidation to platform chemicals.

1.3 Research objectives

Since Nano composite materials possess unique and beneficial properties, they can be used for a wide variety of applications. Here we focused our studies on,

1. To synthesis new multifunctional supported $CoTiO_3$ and $CoTiO_3/TiO_2$ catalysts via solution phase method.
2. To demonstrate the above catalysts for oxidation of single aromatic model compound, vanillyl alcohol at different parameters temperature, molar ratio, catalyst loading, solvent and reaction time.
3. To demonstrate the reusability of the above catalysts for oxidation of vanillyl alcohol.

1.4 Outline of the dissertation

This dissertation comprises of five chapters. The contents of the individual chapters are outlined as follows:

Chapter 1: This chapter has briefly described the background information regarding the potential reasons for lignin model compound oxidation with catalyst and negative impact of some catalysts, currently available techniques for lignin model compound oxidation, significance of using metal oxide nano catalyst, research gap and study objectives. It highlights problem statement, and thus rationalizes the objective and scope of research designed.

Chapter 2: A review of literatures on existing methods to oxidation reaction with various types of catalyst for lignin model compound to platform chemicals, oxidation reaction with homogeneous and heterogeneous catalyst system, lignin model compound oxidation with ionic liquids and electro catalysis are included.

Chapter 3: In this chapter, the materials, procedures, equipment, instruments, synthesis of catalyst, characterization of catalyst, typical method for the oxidation of vanillyl alcohol and the proposed reaction mechanism are presented and described.

Chapter 4: This chapter presented two catalyst systems prepared, i.e. $CoTiO_3$ and CoTiO3/TiO_2 followed by their characterization data and analysis, as well as their catalytic performance. It is divided into two main Sub-sections, Section 4.1 $CoTiO_3$ catalyst system, and Section 4.2 $CoTiO_3/TiO_2$ catalyst system. Each section discussed about the composition, structural and morphological properties of the $CoTiO_3$ and $CoTiO_3/TiO_2$ catalysts. Further, the liquid phase oxidation of vanillyl alcohol by $CoTiO_3$ and $CoTiO_3/TiO_2$ catalysts with different parameters such as reaction time and temperature, mole ratio and reusability of catalysts are discussed. Additionally, influence of basic medium and solvent are illustrated here.

Chapter 5: This is the last chapter, which summarizes the dissertation with some concluding remarks and recommendations for future works.

CHAPTER 2: LITERATURE REVIEW

2.1 Lignin

Lignin is a high molecular weight polymer composed of alkylphenol units (Park et al., 2016). It is the largest renewable source of aromatic polymer in nature, but is chemically recalcitrant to breakdown because of its complicated heterogeneous structure (Collinson & Thielemans, 2010). As a complex aromatic macromolecule, it provides strength and rigidity to cell walls and tissues of all vascular plants by acting as glue between the polysaccharide filaments and fibres (Kuswytasari et al., 2015). In addition, lignin is involved in water transport in plants and forms a barrier against microbial destruction by protecting the readily assailable polysaccharides (Hofrichter, 2002). From the chemical point of view, lignin is a heterogeneous, optically inactive polymer consisting of phenylpropanoid inter units, which are linked by several covalent bonds (e.g. aryl-ether, aryl-aryl, carbon-carbon bonds) (Sidhu, 2012). For the cleavage of these type of covalent bonds, a number of methods are used for the production of lignin model compound from lignocellulose, especially lignin, such as solvolysis including hydrolysis, hydrocracking (hydrogenolysis), pyrolysis, and alkaline oxidation (Pandey & Kim, 2011; Zakzeski et al., 2010). Extensive removal of the functional groups present on the lignin model compound by oxidation to yield platform chemicals such as aldehyde, phenol, benzene, toluene, and xylene like aromatic compounds (Zakzeski, et al., 2010). These compounds are then reacted using existing catalytic technology developed for petroleum refineries to produce bulk and fine chemicals.

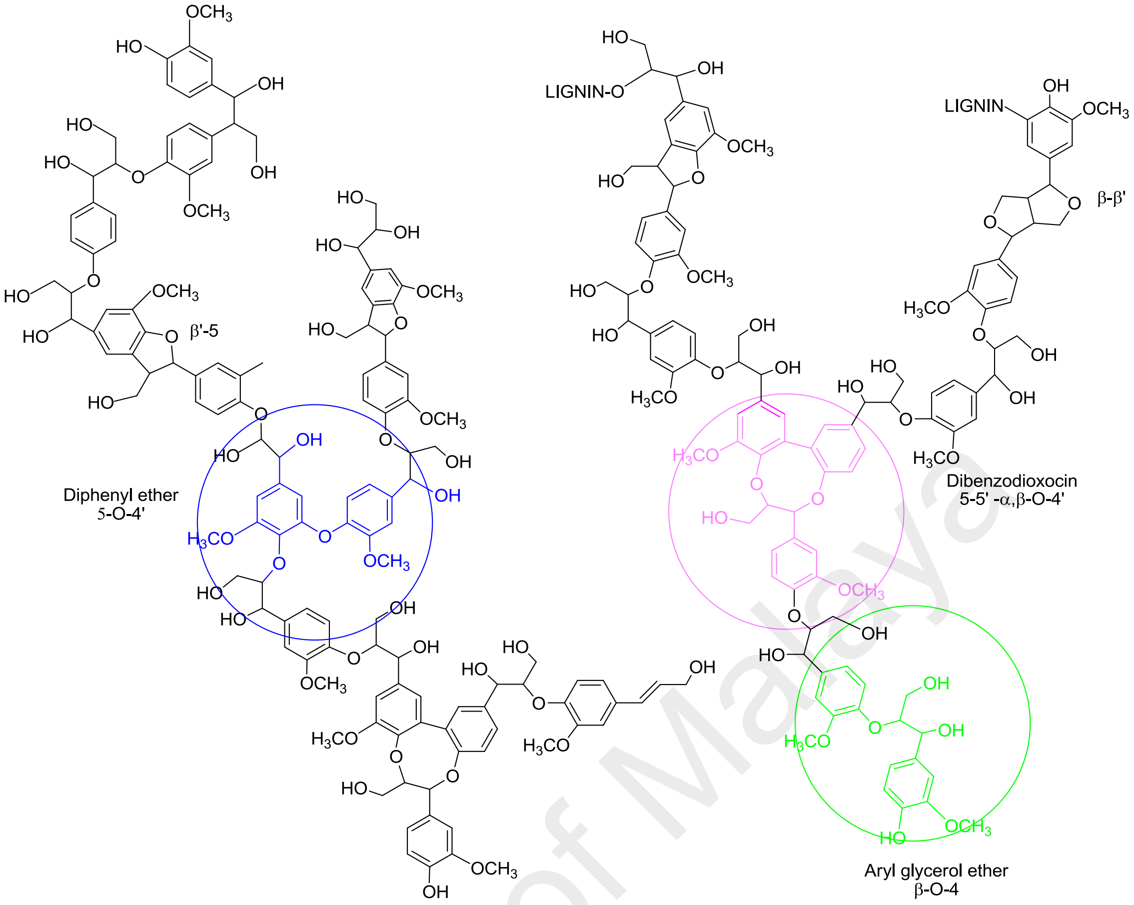


Figure 2. 1: Common chemical structural linkage in lignin (H. Wang et al., 2013)

2.2 Different type of linkages in lignin model compounds

Most research in homogeneous and heterogeneous catalysis are focused on using model compounds that mirror the representative linkages in lignin (Joffres et al., 2013). The most important linkages of lignin are β-O-4, 5-5, *β*-5, α-O-4 and 5-O-4' which are presented in Figure 2. 1. The most significant reactions of model compounds having a β-O-4 linkage involve disintegration of that linkage to produce the coniferyl, p-coumaryl, and sinapyl alcohol building block type’s simpler model compounds. Figure 2. 2 shows the structure of the model compounds having the β-O-4 linkages. On the other hand, several types of secondary products have been produced throughout the disintegration of 3-hydroxypropaldehyde and arenes containing various aldehyde or alkane side chains. These secondary products are further transformed into specific lignin model compounds such as coniferyl, p-coumaryl, and sinapyl alcohol. Oxidation of coniferyl alcohol to form vanillin or oxidation of the aromatic ring to form quinone is very common side reaction.

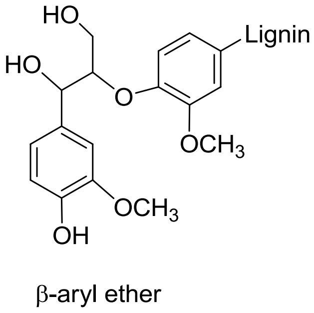


Figure 2. 2: Lignin model compound mimicking the β-O-4 linkage (Chakar & Ragauskas, 2004).

Figure 2. 3 shows the carbon-carbon (5-5) bonds in lignin. These bonds are difficult to break due to its chemical stability. Even many of these linkages tend to retain during the pulping process (Chakar & Ragauskas, 2004). Model compounds including these linkages normally have dimeric arenes containing variable number of methoxy and hydroxyl groups attached with the arenes, similar to dimers of coniferyl or *p*-coumaryl alcohols. Oxidation of model compounds containing a 5-5 bond also can provide the products containing additional ether linkages in addition to the 5-5 bond. The oxidative cleavage of the arene ring can yield the polycarboxylic acids.

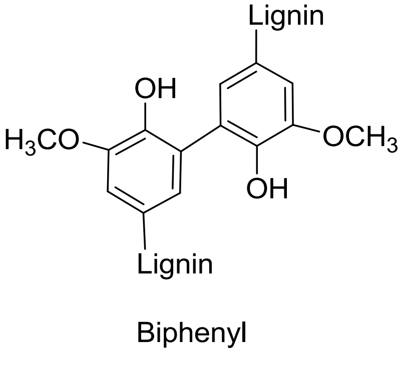


Figure 2. 3: Lignin model compounds mimicking the 5-5’ linkage (Zakzeski et al., 2010).

The lignin model compounds mimicking β-5 linkage are presented in Figure 2. 4. Usually in that case, a five-membered ring connects two aromatic structures via both carbon-carbon and carbon-oxygen bond. In order to obtain vanillin or vanilic acid from lignin model compounds, both of these bonds are further required to undergo cleavage. The disruption of only one bond (i.e., the α-O-4 ether linkage) forms β-1 linkage compounds with other products containing the β-5 linkage.

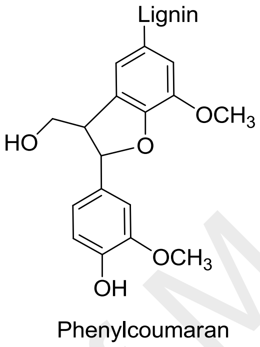


Figure 2. 4: Lignin model compounds mimicking β-5 linkage (Zakzeski et al., 2010).

Figure 2. 5 shows the 5-O-4' linkage model compound (Zakzeski et al., 2010). However, modern nuclear magnetic resonance (NMR) spectroscopy analysis does not endorse the presence of noncyclic α-O-4 moietes. It was proposed earlier that these α-O-4 linkages exist only as fragment of the dibenzodioxocin or phenyl coumaran structural units. The 4-O-5 aryl-aryl ether linkage in lignin mainly results from oligomer-oligomer couplings which further leads to the branching of the polymereric structure.

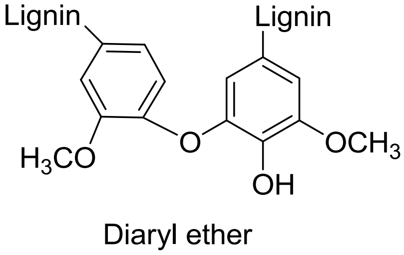


Figure 2. 5: Lignin model compounds mimicking the 5-O-4 linkage (Zakzeski et al., 2010).

2.3 Oxidative routes for platform chemicals

De-polymerization of primary linkages inside lignin macromolecules produces monomers of different aromatic compounds. These aromatic compounds are often extremely functionalized with aldehyde, ether, alcohol or acidic groups. These monomeric compounds after reduction can yield simple hydrocarbons, or after oxidation can make aromatics with enlarged structure having targeted functional groups. The oxidation process requires the application of catalysts which can selectively disrupt the linkages in lignin to produce precise aromatic alcohols, acids, aldehydes, and other specifically functionalized aromatics that are challenging to yield. Although these aromatic compounds are highly functionalized; yet they are deficient of some synthetic steps from petroleum feed stocks, or require expensive platform molecules. An example of high-value product is vanillin ("3-methoxy-4-hydroxybenzaldehyde") which is prepared from vanillyl alcohol, lignin model compound (Figure 2. 6). The scheme has been already used to produce vanillin from softwood lignin (Adler, 1957). Vanillin is used extensively in foods and perfumes because of its flavor. It is also used as an essential chemical for pharmaceuticals production (Zakzeski et al., 2010). The coniferyl alcohol derivatives are 3,4-dimethoxy fragment, which can be converted from veratryl alcohol to veratryl aldehyde. Veratryl alcohol itself is an important target compound for biomass valorization. Other products include acids, quinones and aliphatic carboxylic acids mainly produced from oxidative cleavage of benzene ring. The monolignols p-coumaryl alcohol is the least functionalized monomer unit of lignin macromolecule. Oxidation of *p*-coumaryl alcohol also produces aldehyde, acid, quinone and other products.

Among the oxidation reactions, oxidation of R group often an alkyl group into 4-hydroxybenzaldehyde is more prominent (Korstanje et al., 2010). Furthermore, oxidation of this compounds can also yield acid, aldehyde and quinone which was demonstrated by previous researchers (Partenheimer, 2009). Several metalloporphyrin catalysts efficiently can oxidize the hydroxyl functional groups on the aromatic ring to form quinones or, in some instances; oxidative cleavage of the benzene ring itself can form noncyclic carboxylic acids. Thus several efforts have been made for the conversion of lignin to lignin model compounds to obtain different types of alcohols to other desirable molecules. Figure 2. 7, Figure 2. 8, and Figure 2. 9 depict the oxidation reactions of *p*- coumaryl, coniferyl and sinapyl type lignin model compounds to platform chemicals.

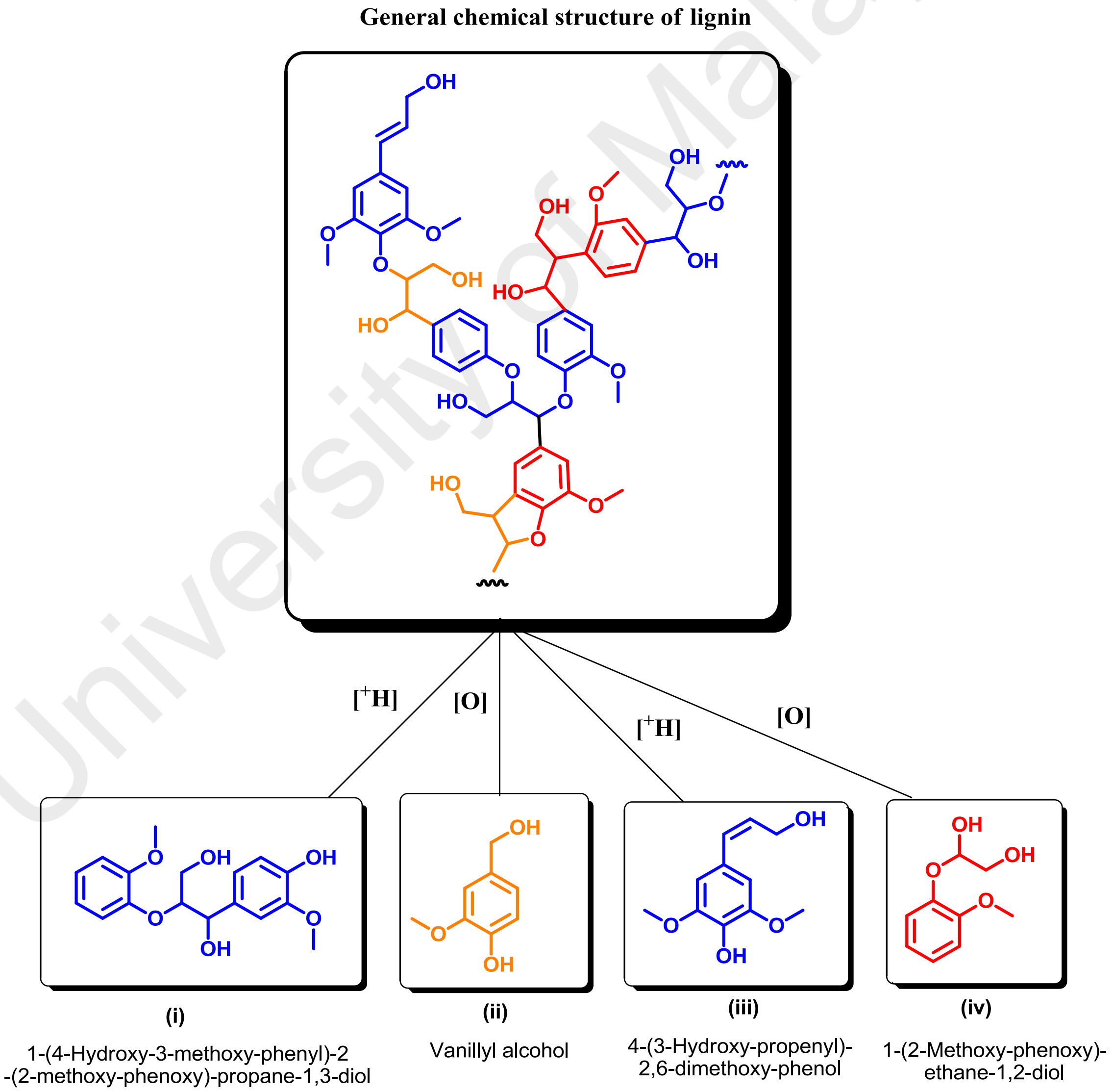


Figure 2. 6: Lignin to several types of lignin model compounds (R Bourbonnais et al., 1997).

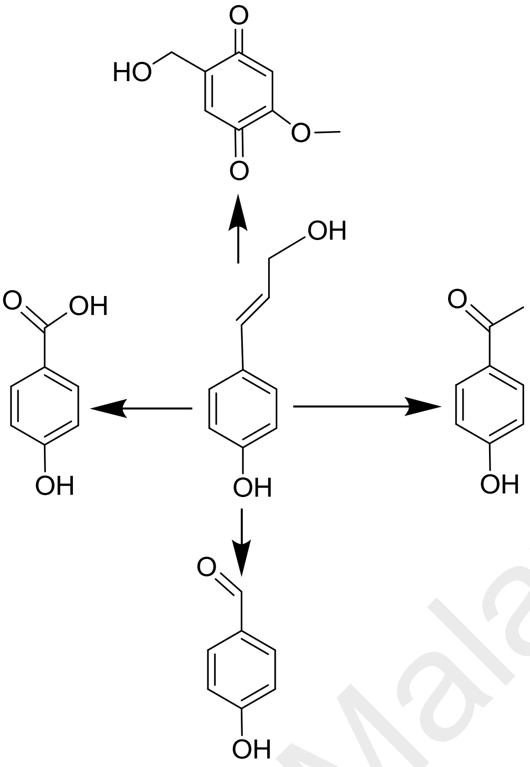


Figure 2. 7: Oxidation reaction of *p*-coumaryl alcohol resembling lignin model compounds to various products (Zakzeski et al., 2010).

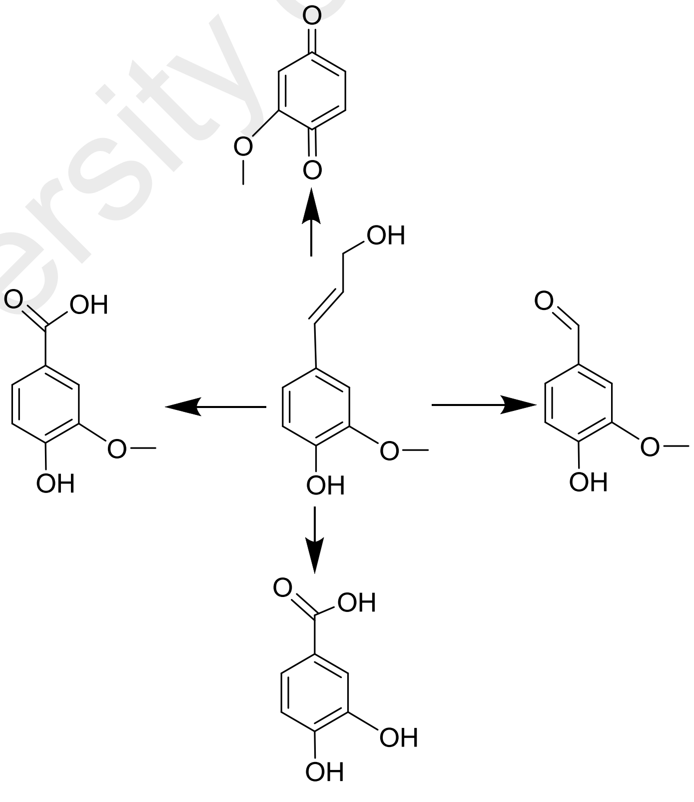


Figure 2. 8: Oxidation reaction of Coniferyl alcohol resembling lignin model compounds to various products (Zakzeski et al., 2010).

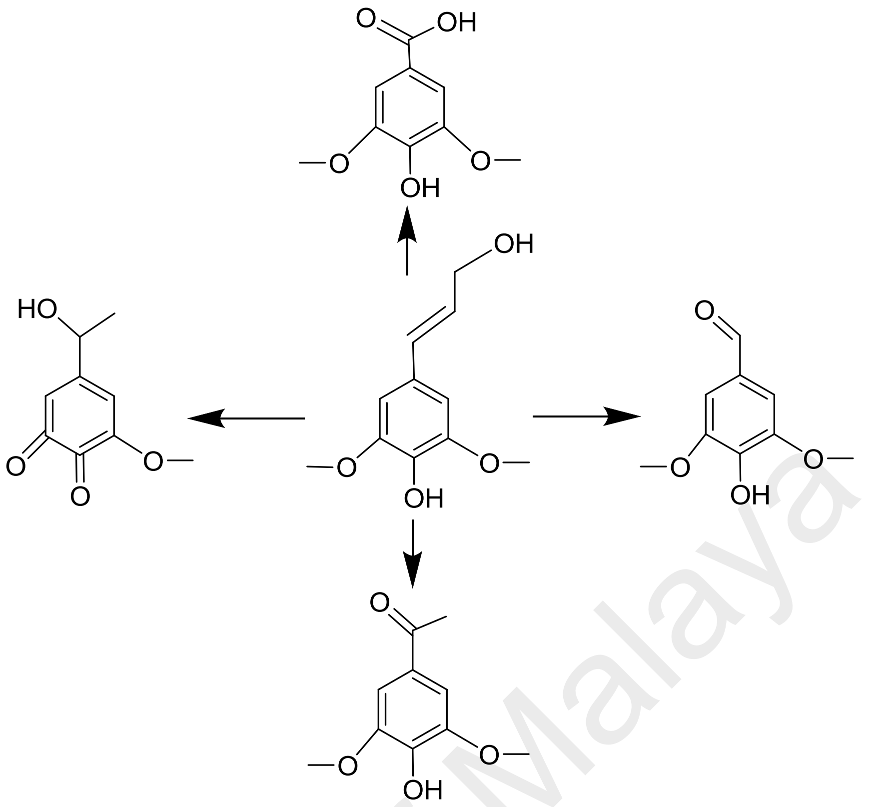
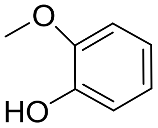
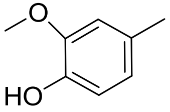
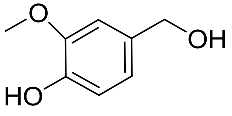
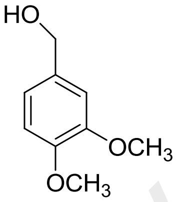
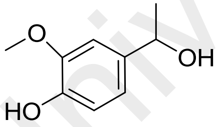
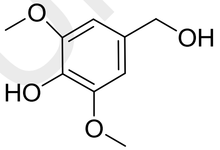


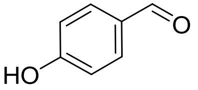
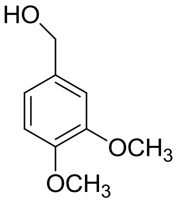
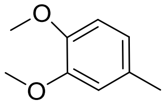
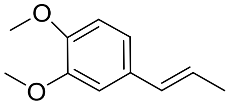
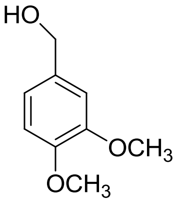
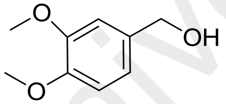
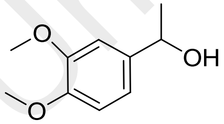
Figure 2. 9: Oxidation reaction of Sinapyl alcohol resembling lignin model compounds to various products (Zakzeski et al., 2010).

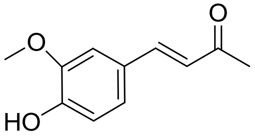
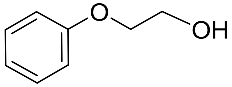
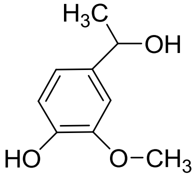
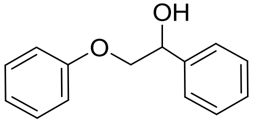
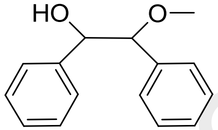
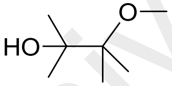
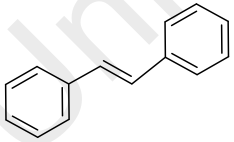
2.4 Lignin model compounds

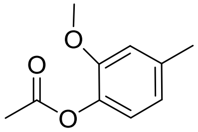
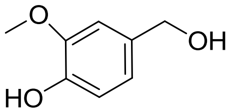
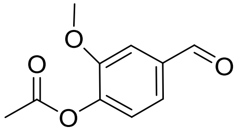
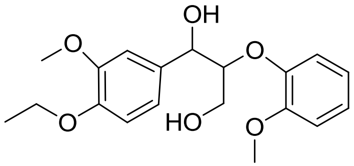
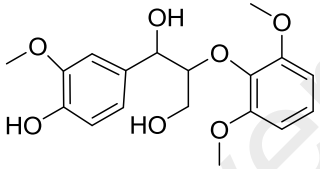
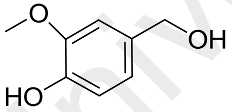
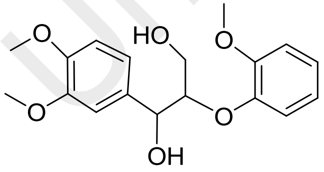
Lignin oxidation is essential to produce more complex aromatic compounds in order to achieve some additional functionality. The majority proportion of lignin oxidation studies were accomplished using model compounds for the complexity of lignin. These lignin model compounds provide several platform chemicals which have been used for organic chemical synthesis and it itself can provide targeted fine chemicals. The complexity and variability of lignin has impelled the usage of numerous simpler, low molecular weight lignin model compounds. The model compounds of lignin have been used for many primary purposes. Firstly, to have linkages that are similar to those found in the lignin polymer and thus their reactivity can give understanding about the oxidation reaction of the polymer structure as a whole. Secondly, the development of methods for extracting value added chemicals. Finally, the model compounds present fewer analytical challenges relative to the complicated lignin polymer. Usually, they often contain only one type of linkage in the model compound making analysis of the reaction paths and catalytic performance correspondingly simplified (Zakzeski et al., 2010).

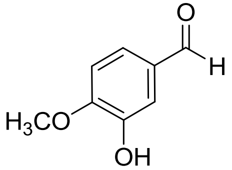
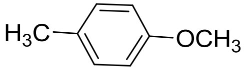
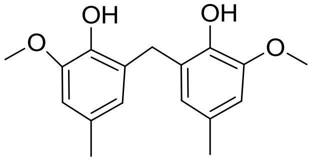
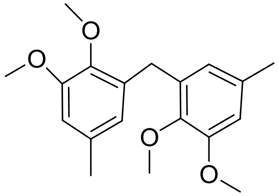
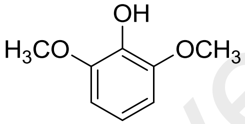
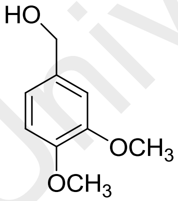
Table 2. 1: The list of major lignin model compounds, catalysts, and products of the oxidation reaction reported in literature (Chatel & Rogers, 2013; Zakzeski et al., 2010)

Model Compounds	**Structure**	**Catalyst/ Oxidant/ Solvent**	**Major Products**	**Ref.**
Guaiacol (2-methoxiphenol)		Manganese acetate/ air/ water acetonitrile mixture	Polyguaiacols	(Hwang et al., 2008)
3-methoxy-4-hydroxytoluene		Manganese acetate/ fungal manganese peroxidases/ water	Aldehydes, carboxylic acids	(Kapich et al., 2010)
Vanillyl alcohol (4-(hydroxylmethyl)-2-methoxyphenol)		Methyltrioxiorhenium/ H_2O_2/ acetic acid	4-hydroxy-3-methoxybenaldehyde, 4-hydroxy-3-methoxybenzoic acid	(Crestini et al., 2006)
Veratryl alcohol(3,4-Dimethoxybenzylalcohol)		Methyltrioxiorhenium/ H_2O_2/ acetic acid	3,4dimethoxybenaldehyde 3,4dimethoxybenzoic acid	(Crestini et al., 2005)
Apocynol (1,2-(4-hydroxy-3-methoxyphenoxy) ethanol)		Mesoporous silica materials/ H_2O_2/CH_3CN (microwave)	Acetovanillone, vanillin, 2-methoxybenzoquinone	(Badamali et al., 2013)
Syringyl alcohol (4-(hydroxymethyl)-2, 6-dimethoxyphenol)		Manganese acetate/ O_2/ acidic water	methanol	(Sugimoto et al., 2000)

4-hydroxybenzaldehyde		Co/ Mn/ Zr/ Br catalyst/ O2/ Acetic acid	4-hydroxybenzoic acid	(Partenheimer, 2009)
Veratryl alcohol (3,4 Dimethoxyalcohol)		Mn(TSPc)Cl, 4-Methoxyacetophenone, H_2O_2Fe(TSPc),$KHSO_5$,	Veratryl aldehyde (3,4 Dimethoxyaldehyde)	(Sorokin et al., 1997)
3,4-dimethoxytoluene		Co/ Mn/ Br catalyst/ O2/ Acetic acid	Corresponding Carboxylic acid, methy-3,4-dimethoxybezoate	(Partenheimer, 2004)
1-(3,4-dimethoxyphenyl)-1-propane		Binucleus manganese complexes/ H_2O_2/ water	Corresponding ketones, epoxides and aldehyde	(Alves et al., 2003)
Veratryl alcohol 4-hydroxy-3-methoxytoluene		CoTSPc,O_2,H_2O	Veratraldehyde 2,2'-dihydroxy-3,3'dimethoxy 5,5' –di dimethylbiphenyl	(Watanabe & Archer, 1994)
Veratryl alcohol ((3,4-dimethoxyphenyl) methanol)		Laccase/ water and electrolysis/ water	Ketone, veratraldehyde	(Rochefort et al., 2002)
1-(3,4-dimethoxyphenyl) ethanol		Binucleus manganese complexes/ H_2O_2/ water	Ketone, veratraldehyde	(Alves et al., 2003)

Vanllideneacetone ((E)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one		Copper hydroxide/ O_2/ water	Vanillin	(Tarabanko et al., 2004)
2-phenoxyethanol		Dipicolinate vanadium complexes/ air/ DMSO	Phenol/ formic acid	(Hanson et al., 2010)
2-hydroxyethyl apocynol		Fe(TF5PP)Cl, H2O2, Fe(TF_5PS_4)Cl, magnesium monoperoxyphthalate	Acetovanillin 2-methoxy phenol	(Chatel & Rogers, 2013)
1-phenyl-2-phenoxyethanol		Dipicolinate vanadium complexes/ air/ DMSO	Phenol/ benzoic acid/ formic acid	(Hanson et al., 2010)
1,2-diphenyl-2-methoxyethanol		Dipicolinate vanadium complexes/ air/ DMSO	Benzaldehyde, methanol, 2-methoxy-1,2-diphenylethan-1-one	(Hanson et al., 2010)
Pinacol monomethyl ether		Dipicolinate vanadium complexes/ air/ DMSO	Formic acid	(Hanson et al., 2010)
(E)-1,2-diphenylethen		Binucleus manganese complexes/ H_2O_2/ water	Corresponding epoxides	(Alves et al., 2003)

3-methoxy-4-acetoxytoluene		Manganese acetate/ fungal manganese peroxidases/ water	Aldehydes, carboxylic acids	(Kapich et al., 2010)
Veratryl alcohol		Co(salen)/SBA-15,O_2,Co(salen),NaOH/H_2OCHCl$_3$	Veratraldehyde,alkaline,3,4 dimethoxy benzaldehyde,quinone	(Jayaseeli et al., 2015)
3-methoxy-4-acetoxybenzaldehyde		Manganese acetate/ fungal manganese peroxidases/ water	Aldehydes, carboxylic acids	(Kapich et al., 2010)
1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol		Methyltrioxorhenium/ H_2O_2/ acetic acid	4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one, 2,6-dimethoxyphenol	(Crestini et al., 2006)
1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol		Methyltrioxorhenium/ H_2O_2/ acetic acid	4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one, 2,6-dimethoxyphenol	(Crestini et al., 2006)
Vanillyl alcohol		[Co(N-Me salpr)],Co-sulphosalen/H_2O_2	Veratraldehyde,3,4 dimethoxybenzaldehyde,	(Räisänen et al., 2013)
1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol		Cobalt acetate or manganese acetate/ O_2/ acetic acid	4-methoxybenzaldehyde and derivatives	(Dicosimo & Szabo, 1988)

3-methoxy-4-acetoxybenzaldehyde		$Co(OAc)_2$ /$Mn(OAc)_2$ /HBr	3-methoxy-4-acetoxybenzaldehyde	(Partenheimer, 2009)
4-methoxytoluene		O_2/CH3COOH	4-methoxytoluene	(Partenheimer, 2009)
2,20- dihydroxy-3,30-dimethoxy-5,50-dimethyl-diphenyl methane		Methyltrioxorhenium/ H_2O_2/ acetic acid	2-hydroxy-5(hydroxymethyl)-3-methoxybenzoic acid, 2-(2-hydroxy-5-hydroxymethyl)-3-methoxyphenyl)acetic acid	(Crestini et al., 2006)
2,20,3,30-tetramethoxy-5,50-dimethyl-diphenyl methane		Methyltrioxorhenium/ H_2O_2/ acetic acid	2-(2,3-dimethoxy-5-methylphenyl)acetic acid	(Crestini et al., 2006)
2,6-dimethoxyphenol, Coniferyl alcohol		M. albomyceslaccase 1-allyl-3-methylimidazolium	2,6-dimethoxyphenol, Coniferyl alcohol	(Lahtinen et al., 2013)
Veratryl alcohol		Task specific ionic liquid-salen-Co-hexaflurophosphate	Veratryl aldehyde	(Sonar et al., 2011)

2.4.1 Lignin model compounds oxidation by heterogeneous catalysts

Heterogeneous oxidative catalysts have played a vital role in pulp and paper industries to eliminate lignin and other compounds from wood pulps for increasing the final paper product quality. Several types of lignin heterogeneous oxidation catalysts and their results are summarized in Table 2. 1. Generally, most of the catalysts involved titanium dioxide (Portjanskaja et al., 2009) or supported valuable metals (Pt/TiO_2) (Ma et al., 2008), are able to effectively degrade the lignin by using ultraviolet light. This TiO_2 catalyst increased the photooxidation efficiency of lignin with the addition of small quantities of Fe^{2+} (Portjanskaja & Preis, 2007). The ultraviolet light was required to displace the valence-band electrons in the titanium dioxide catalyst, as it initiates the oxidation reactions (Portjanskaja et al., 2009). There were some other catalysts such as Ni/MgO used in gasification of lignin to produce hydrogen, methane and carbon-dioxide (Furusawa et al., 2007), or CH_3ReO_3 used to immobilize on polystyrene or poly(4-vinyl pyridine) (Crestini et al., 2006). The methylrhenium trioxide catalyst was used for the oxidation of monomeric, dimeric, phenolic, and nonphenolic lignin model compounds in addition to sugar cane lignin and red spruce kraft lignin for treatment of kraft pulp. Veratryl and vanillyl alcohol were oxidized to the acids, aldehydes, and quinones in up to 49% yield with the balance forming polymeric products (Crestini et al., 2006). The oxidation of isoeugenol and *trans*-ferulic acid to produce vanillin from CH_3ReO_3 catalyst in the presence of hydrogen peroxide was reported by Herrmann and co-workers (2001) (Herrmann et al., 2001). By considering the reaction conditions, this catalyst was able to breakdown the carbon-carbon double bond in order to produce either aldehyde or acid. This catalyst was found to neutralize through the formation of a perrhenate species after 1000 to 2000 cycles, but a one-pot method to reactivate the catalyst was described (Herrmann et al., 2000). The applicability of Pd/Al_2O_3 catalysts for the alkaline lignin oxidation from sugar cane bagasse in both batch slurry and constant fluidized-bed reactors was recently reported by Sales and co-workers (2007) (Sales et al., 2007). About 0.50 g of syringaldehyde and 0.56 g of vanillin were attained from 30 g of lignin at 393 K after 2 h (Widegren & Finke, 2003).

Bhargava and co-workers (2007) studied the catalytic wet oxidation of ferulic acid using single-metal (copper), bi-metal (copper-nickel, copper-cobalt, and copper-manganese), and multi-metal (copper-nickel-cerium) alumina-supported catalysts, copper and copper-manganese kaolin-supported catalysts, and multi-metal oxide (copper-cobalt-manganese and copper-iron-manganese) catalysts (Bhargava et al., 2007). Cu-Ni-Ce/Al_2O_3 catalysts were the most dynamic, but were susceptible to catalyst leaching (Bhargava et al., 2007). Cu-Mn/Al_2O_3 was the most stable and was second to Cu-Ni-Ce/Al_2O_3 in terms of movement of the nine catalysts studied (Bhargava et al., 2007). Zhang and co-workers (2007) justified the use of perovskite-type oxide $LaFe_{1-x}Cu_xO_3$ (x = 0, 0.1, 0.2) for the wet aerobic oxidation of lignin by citing the aspiration to replace “toxic” metal ions (*i.e.*, Sr, Ce, Co, and Mn) in pervoskite-type oxides with “nontoxic” iron to avoid the environmental pollution (J. Zhang et al., 2009).

2.4.2 Lignin model compounds oxidation with electro catalysts

Various electrochemical researches were carried out depending on the lignin degradation on several electrodes. The anodic oxidation of lignin model compounds in methanol and the breakage of the C_α-C_β bond through the formation of radical cations were elaborately analyzed by the Pardini and co-workers (Andersen & Wayner, 1999; Robert Bourbonnais et al., 1998). It was observed that oxidation peak potentials as elucidated from cyclic voltametry are prejudiced by substrate structure but not solution pH (Hu et al., 1997). Parpot and coworkers (2009) studied the electrochemical degradation of kraft lignin in batch and flow cells on platinum, gold, nickel, copper, DSA-dioxide, and led-dioxide anodes (Parpot et al., 2009). Lignin was transformed into vanillin, but required nonstop extraction in order to avoid its additional oxidation reaction (Parpot et al., 2009). Previous researchers had successfully completed the electrochemical decolorization of wastewater effluent stream where a lead sheet was used as anode (Zaied & Bellakhal, 2009). One of the major limitation of this electrochemical procedures is the requirement of lower concentration of lignin and thus, the conduct of big amounts of lignin which is essential for any efficient commercial process has not yet been possible (Shankar et al., 2009; Shiraishi et al., 2012).

2.4.3 Lignin model compounds oxidation by homogeneous catalysts

The lignin model compound oxidation process with homogeneous catalysts is one of the most attractive approaches for the fabrication of fine chemicals from lignin. The selective oxidation is also possible with these homogeneous catalysts which were previously stated in the literatures (Zakzeski et al., 2010). Moreover, these catalysts show various beneficial properties such as wide range usability of ligands, high influence on activity due its steric and electronic characteristics, solubility, and stability, which make them appropriate for the oxidation of lignin (Happ et al., 2010; Lange et al., 2013; Vidal-Ferran et al., 1998). There are six types of homogeneous catalysts based on the set of ligand were used for the oxidation of lignin, which are elaborately described in the following section.

2.4.4 Lignin model compounds oxidation by Metalloporphyrin catalysts

Metalloporphyrin complexes have been widely applied for the selective oxidation of lignin model compound to produce valuable fine chemicals (Gonçalves & Benar, 2001; Parton et al., 1994). An elaborate review on lignin and lignin model compounds oxidation with these metalloporphyrin complexes was studied by Crestini and Tagliatesta and presented in (Simoes et al., 2009). The lists of all types of metalloporphyrin catalyzed reactions are presented in Table 2. 1. Figure 2. 10 presents the structure of various porphyrin and phthalocyanine based catalysts and the oxidation pathways for veratryl alcohol to veratryl aldehyde using metal porphyrin complexes as a catalyst are depicted in Figure 2. 11.

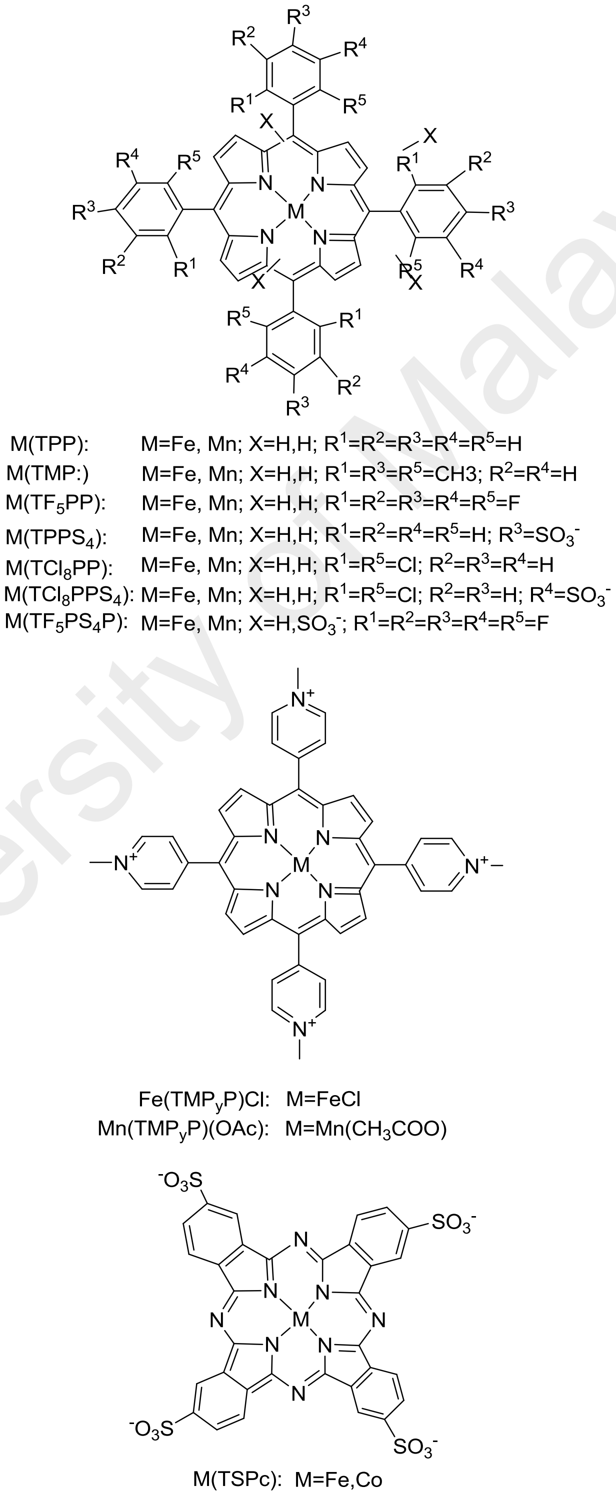


Figure 2. 10: Structures and designations of reported porphyrin and phthalocyanine catalysts used for lignin oxidation (Zakzeski et al., 2010).

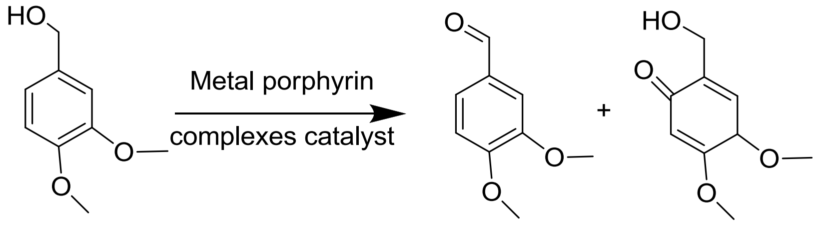


Figure 2. 11: Oxidation of veratryl alcohol.

A tetraphenylporphyrinato iron (III) chloride complex with the *tert*butylhydroperoxide was used by Shimada and co-workers (1984) in order to breakdown the carbon-carbon bond of the model compound 1,2-diarylpropene-1,3-diol at the temperature of 293 K(Shimada et al., 1984).The main products of the oxidation involved 3-methoxy-4-ethoxybenzaldehyde (54% yield on the oxidant), and formaldehyde (Shimada et al., 1984). The oxidation of lignin model compounds was analyzed by Zhu and Ford (1994) utilizing iron (III) and manganese (III) meso-tetraphenylporphyrin and phthalocyanine complexes (Watanabe & Archer, 1994). Moreover, an iron porphyrin catalyst was used by Artaud and co-workers (1993) for oxidation of α,β-diarylpropane lignin dimer model compounds (Artaud et al., 1993). The metal porphyrin was observed to oxidize the α,β,-diarylpropane through four primary reactions includingC_α-$C_\beta$propyl side chain cleavage, phenyl-C_α bond cleavage, oxidation of the dimethoxyaryl nucleus to form quinone,and opening of the dimethoxyaryl ring to form a muconicacid dimethyl ester (Policar et al., 1996). A major drawback of porphyrin complexes is the susceptibility to degradation with excess oxidant, particularly H_2O_2, or through the formation of catalytically inactive μ-oxo species (Korstanje et al., 2010).

2.4.5 Lignin model compounds oxidation by Metallosalen catalysts

Cobalt (salen=[*N*,*N′*-bis(salicylidene)ethane-1,2-diaminato]) complexes are one of the most promising catalysts for lignin oxidation. The usage of the polymer supported Schiff base complexes, including Co(salen), for the oxidation of lignin model compound was studied by Gupta and co-workers (2009) (Gupta et al., 2009). Figure 2. 12 shows the Co(salen) structures and its related complexes. The summary of these catalyzed reactions is presented in Table 2. 1.

Bozell and co-workers (2001) confirmed that the Co(salen) was able to oxidize the aromatic compound phenolic groups to produce benzoquinones in up to 90% yield in 18 h (Bozell et al., 2001). Moreover, Drago and coworkers (1986) also showed that the Co(salen) complexes with molecular oxygen, rapidly oxidizedlignin and lignin model compound, isoeugenol, to vanillin (Drago et al., 1986). These Co(salen) complexes are more suitable compared with the above mentioned metalloporphyrin complexes as they have various advantages such as easier to synthesize, relatively stable, and cheaper (Sippola et al., 2004). Badamali and coworkers (2009) immobilized the Co(salen) on SBA-15 and showed its effective lignin model compound (apocynol) oxidation reaction using microwave heating (Badamali et al., 2009). An another lignin model compound (veratryl alcohol) oxidation catalyzed by Co(salen) was also investigated by Kervinen and co-workers (2003) (Kervinen et al., 2003).The typical turnover frequencies are ranged between 2.8×10^{-3} and 4.1×10^{-3} s^{-1} for these types of complexes with total turnover numbers around 300. Moreover, Canevali and co-workers (2002) reported the oxidative degradation of various types of lignin model compounds using Co(salen) catalysts (Canevali et al., 2002). Research with the electron paramagneticresonance spectroscopy stated that two phenoxy cobaltradicals are involved for the phenolic compounds oxidation mechanism. Limited research on these Co(salen) complexes for the oxidation of lignin have been performed, and according to Badamali and co-workers (2009), the complexes need to be investigated in greater detail (Badamali et al., 2009).

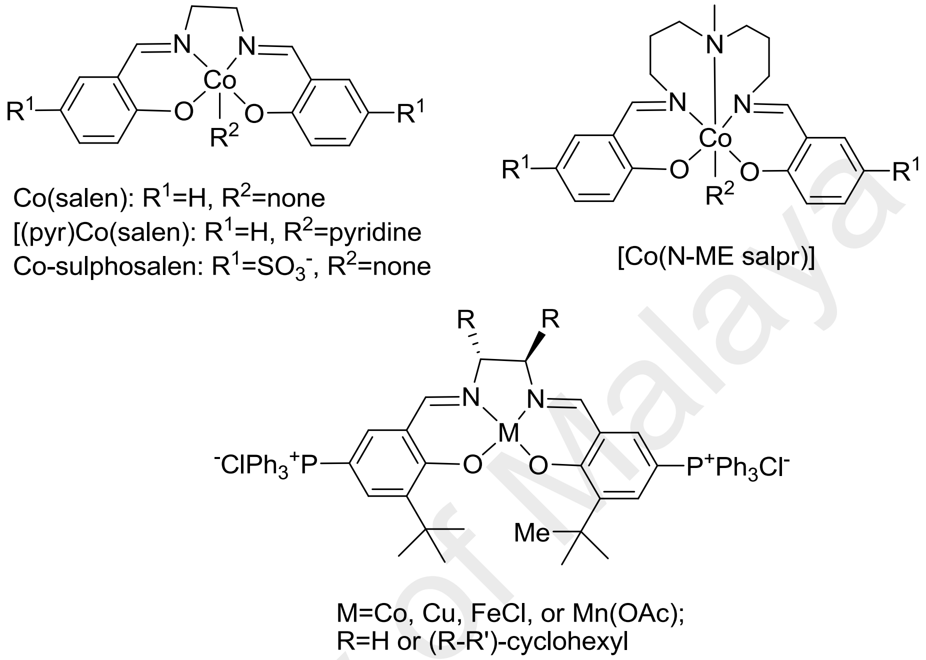


Figure 2. 12: Structure of Co(salen) and related complexes(Badamali et al., 2009).

2.4.6 Lignin model compounds oxidation by Nonporphyrinic catalysts

Collins and co-workers used a series of iron-TAML (tetraamido macrocyclic ligand) complexes (Collins, 2002). These catalysts were active, selective, and extremely effective as oxidation catalysts (Collins, 2002; Popescu et al., 2008). A μ-oxo-bridged diiron(IV)-TAML complex was reported for the selective oxidation of aromatic alcohols ("benzyl, 4-chlorobenzyl, 4-nitrobenzyl, 4-methoxybenzyl, and cinnamyl alcohols") to the corresponding aldehydes but it was not specifically used yet in lignin and lignin model compounds valorization (Chanda et al., 2006). Chen and co-workers (2003) revealed the use of $[(Me_4DTNE)Mn(IV)_2(\mu\text{-}O)_3](ClO_4)_2$, where DTNE is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane, or $[(Me_3TACN)Mn(IV)_2(\mu\text{-}O)_3](PF_6)_2$, where TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane, and H_2O_2 to bleach pine kraft-AQ pulp. It was reported that this catalyst was more effective for delignification of softwood pulps over hardwood pulps (C.-L. Chen et al., 2003a, 2003b). The structures of these complexes are presented in Figure 2. 13. Table 2. 1 summarizes the use of Mn-DTNE and Mn-TACN catalysts for pulp delignification. Cui and co-workers (1999) stated that $[(Me_4DTNE)Mn(IV)(\mu\text{-}O)_3Mn(IV)](ClO_4)_2$ readily oxidized various lignin model compounds with H_2O_2 to aldehydes and alcohols (Cui et al., 1999).This catalyst preferentially epoxidated C-Cdouble bonds conjugated with aromatic moieties.

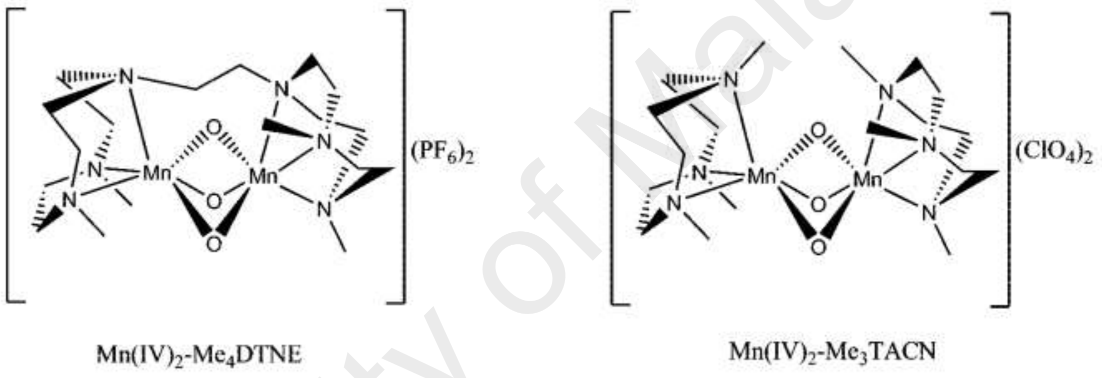


Figure 2. 13: Structures of $[(Me_4DTNE)Mn(IV)_2(\mu\text{-}O)_3](PF_6)_2$ and $[(Me_3TACN)Mn(IV)_2(\mu\text{-}O)_3](ClO_4)_2$ (Cui et al., 1999).

2.4.7 Lignin model compounds oxidation by Polyoxometalates (POMs) based catalysts

The POMs were developed as delignification catalysts in order to replace the chlorine-based pulp bleaching techniques, which increased the amount of chlorine in local environment, with environmentally benign oxidation processes (Evtuguin et al., 1998). This POMs catalysts were able to degrade the *β*-O-4 linkages in lignin, which was demonstrated by Kim and co-workers (2007) (Sik Kim et al., 2007). A list of lignin oxidation reactions with POM based catalysts is summarized in Table 2. 1.The oxidation of various lignin model compounds was performed by considering the structural properties of the lignin model compounds on the kinetics (Sik Kim et al., 2008). The kinetic experiments with POMs catalysts of composition $Na_{5(+1.9)}[SiV_{1(-0.1)}MoW_{10(+0.1)}]$ for the degradation of 1-(3,4,5-trimethoxyphenyl)ethanol to the corresponding aldehydes was carried out by Yokoyama and coworkers (2004) (Yokoyama et al., 2004).They observed a rate constant of16.80 s^{-1} at453 K, an activation energy of 68.4 kJ mol^{-1}, and frequency factor of 1.28×106 s^{-1} for the reaction of 1-(3,4,5-trimethoxyphenyl)ethanol to 1-(3,4,5-trimethoxyphenyl)ethanol (Yokoyama et al., 2004).

On the other hand, the $H_3PMo_{12}O_{40}$ catalysts was used for the selective oxidation of kraft pulps to platform chemicals ("vanillin, methyl vanillate, ethyl vanillate, and other monomeric products") in the presence of oxygen and either methanol or ethanol (Voitl & Rohr, 2009). Gaspar and coworkers (2007) carried out the oxidative delignification of homoveratryl and homovanillyl alcoholwith Mn(II)-substituted heptamolybdo-pentavanadophosphate polyanions, which produce various simpler substituted aromatic compounds (Gaspar et al., 2007).

2.4.8 Lignin model compounds oxidation by Metal salt based catalysts

The oxidation reaction of lignin and its model compounds with the help of metal salt-based catalysts in presence of O_2 were elaborately analyzed and reported in literature (Pandey & Kim, 2011). These metal salt-based catalysts were developed in order to perform the selective oxidation of aromatic hydrocarbons such as to produce terephthalic acid from *p*-xylene. for the production ethylene terephthalate (Partenheimer, 1995). The single-electron oxidation of lignin model compound "1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol using Co(II) acetate and Mn(II) acetate" through cleavage of the C_{α}-C_{β}bond, which was reported by Dicosimo and Szabo in (Dicosimo & Szabo, 1988). Partenheimer (2009) also reported that the lignin oxidation by utilizing Mn(II)acetate/Zr(IV)acetate/ Co(II)acetate/ HBr catalyst solution to produce several aromatic products (vanillic acid, vanillin, syringic acid, and syringaldehyde) (Partenheimer, 2009). Hwang and co-workers (2008) were used Mn(III) acetate as a polymerization catalyst of guaiacol to polyguaiacol (Hwang et al., 2008), and performed a mechanistic study using $CuSO_4$ catalyst in order to oxidize the lignin model compound to yield vanillin (Tarabanko et al., 1995). The primary identifiable products included of the aromatic aldehydes, acids and ketones, with the production of syringaldehyde and vanillin were around 15% (Xiang & Lee, 2001). Moreover, the oxidation of syringyl alcohol by using Mn(III) acetate and molecular oxygen was also studied by Sugimoto and coworkers (2000) (Sugimoto et al., 2000). Furthermore, the mechanistic research was executed by Tarabanko and co-workers (2004) with the help of copper oxide as a catalyst (Tarabanko et al., 2004). Groups of ferulic acid found in the renewable resource are transformed with hydrogen peroxide by using manganese sulfate hydrate with a Ni, Co, or Cu co-catalyst (Gasser et al., 2012). Finally, Villar and co-workers (1997) utilized Co(II) and Cu(II) salts to oxidize hardwood kraft lignin in alkaline medium to yield syringaldehyde, vanillin, and other acids in the presence of molecular oxygen (Villar et al.,1997).

2.4.9 Lignin model compounds oxidation by Miscellaneous catalyst systems

A comparative study between the enzymatic such as laccase, lignin peroxidase and nonenzymatic such as lead tetraacetate, Fenton’s reagent, catalysts was carried out by Bohlin and coworkers (2007), which showed the differences in selectivity of the oxidation of lignin model compound in β-O-4 linkage (Bohlin et al., 2007). Again, Rochefort and co-workers (2002) studied a reaction process in which hexacyanoruthenate (II) or tris-(4,4′-dimethyl-2,2′-bipyridine) iron (II) was used in the presence of an electron transport mediator (1-hydroxybenzotriazole) for the oxidation of veratryl alcohol to yield veratryl aldehyde (Rochefort et al., 2002). This electron transport mediator assisted the lignin model compound oxidation reaction and the system activity was compared with the enzymatic oxidation and the electrochemical oxidation (Rochefort et al., 2002). Moreover, the oxidation of veratryl alcohol using Cu(II) sulfate and 1,10-phenanthroline (phen) in alkaline, aqueous solutions to produce veratryl Aldehyde was performed by Korpi and co-workers (2007) (Korpi et al., 2007).

2.4.10 Lignin model compounds oxidation by ionic liquids

A list of several ionic liquids, catalysts and oxidant is presented in Table 2. 1. The performance of a laccase enzyme to catalyze the coniferyl alcohols oxidation process with allyl-3-methylimidazolium chloride ([Amim]Cl) in an aqueous medium was analyzed by Lahtinen et al. (2013) (Lahtinen et al., 2013). In this oxidation process, the ionic liquid increased the substrate and products solubility, which further formed the β-O-4, β−β, β-5, and α-C=O/β-O-4 dimers, α-O-4/β-O-4 trimers, and a coniferyl alcohol dehydropolymer.

Kumar et al. (2007) analyzed the veratryl alcohol oxidation process with two water-soluble iron(III) porphyrins as catalysts [iron(III) 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrin, (Fe(Cl$_8$TTPPS$_4$)) and iron(III) 5,10,15,20-tetrakis (4′-sulfonatophenyl)porphyrin, (Fe-(TPPS$_4$))]; hydrogen peroxide as oxidant; and 1-butyl-3-methylimidazoliumhexafluorophosphaste ([C$_4$mim][PF$_6$]) as solvent (Kumar et al., 2007). Veratraldehyde was produced as a major product for both catalysts with 69% and 83% yields in the presence of Fe(TPPS$_4$) and Fe(Cl$_8$TTPPS$_4$), respectively.

On the other hand, several primary alcohols were selectively oxidized into their corresponding acids or aldehydes with very high efficiency by using various ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphaste ([C$_4$mim][PF$_6$]), 1-butyl-1-methylpyrrolidinium hexafluorophosphaste ([C$_4$mpyr]-[PF$_6$]), or 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([C$_6$mim][CF$_3$SO$_3$]). The oxidation of lignin model compounds (veratryl alcohol and vanillyl alcohol) using [C$_4$mim][PF$_6$] as solvent with the conversion (yield) of 96% (94%) and 94% (82%), respectively, to the corresponding aldehydes, which was reported by Jiang and Ragauskas (2007) (Jiang & Ragauskas, 2007). Zakzeski et al. (2010) studied the oxidation of lignin model compounds (5,5 ′ model compounds and β-O-4 model compounds) in the presence of O_2 as oxidant and 1-ethyl-3-methylimidazolium diethyl phosphate ($[C_2mim]-[Et_2PO_4]$) as solvent (Zakzeski et al., 2010). The benzyl functionality in veratryl alcohol was also selectively oxidized to form veratraldehyde, presenting excellent turnover frequency (1440 and 1300 h^{-1} using $CoCl_2·6H_2O$ and Co(salen), respectively), 1300 h^{-1} using $CoCl_2·6H_2O$ and Co(salen), respectively) (Zakzeski et al., 2010). However, phenolic functional groups contained in guaiacol, syringol, and vanillyl alcohol remained intact, although the benzyl alcohol group in the latter was oxidized to form vanillin.

In the last few years, some innovative approaches for oxidation of lignin and lignin compounds have been investigated, such as electrochemistry (Pan et al., 2012; Richardson et al., 2012), use of mesoporous materials (Badamali et al., 2013), photocatalysis (Tonucci et al., 2012) and use of vanadium-based catalysis (Hanson et al., 2012).

These studies reveal that some issues need to be addressed properly, such as the lack of selectivity, decomposition of the catalyst, low amounts of lignin required and difficult separation of products after the reactions are completed. These problems can be overcome by designing a suitable heterogeneous catalyst. These types of catalyst may offer many advantages such as easy handling, separation and reusability. Although noble metal catalysts exhibit high activity for oxidation reactions, they can be expensive, minimizing their potential for commercial applications (Guo & Wang, 2011). Oxides of other transition metals, such as titanium, chromium, manganese, cobalt and copper are also known to be effective catalysts for oxidation reactions. Among these metals, titanium and cobalt are the most attractive because of their strong capability for dioxygen activation (through metal–O2 adduct formation) and because these are more cost effective compared to noble metals. $CoTiO_3$ and $CoTiO_3/TiO_2$ mixed metal oxide catalyst for liquid phase oxidation of vanillyl alcohol mediated with H_2O_2 carried out this current study for maximum conversion and selectivity.

CHAPTER 3: EXPERIMENTAL DETAILS

3.1 Materials and chemicals

Table 3. 1 shows the list of chemicals used for the preparation of catalysts and their subsequent reactions. All the reagents used were of analytical grade and without further purification.

Table 3. 1: Chemicals used for the catalyst preparation and catalytic reaction.

No.	Chemicals	Company	Purity (%)
1.	Cobalt (II) acetate tetra hydrate	Merck	99
2.	Titanium (IV) iso-propoxide	Sigma-Aldrich	98
3.	Vanilly alcohol	Sigma-Aldrich	98
4.	Hydrogen peroxide	Sigma-Aldrich	30
5.	Acetic acid	Merck	96

3.2 Synthesis of $CoTiO_3$ and $CoTiO_3/TiO_2$catalysts

In a typical synthesis, 1.0 g (4.0 mmol) cobalt (II) acetate tetrahydrate was dissolved in 25 mL methanol in a 100 mL Schlenk tube fitted with an inert gas/vacuum line adapter and magnetic stirrer. Titanium (IV) iso-propoxide (1.2 mL) (4.0 mmol) was added drop by drop with a syringe to the solution. The contents were stirred for 4 h to obtain a clear purple solution. The reaction mixture was evaporated to dryness under vacuum to produce a deep purple solid. The as synthesized solid was grounded to fine powder and calcined in air at a rate of 2 ˚C/min until 500 ˚C, and was kept at this temperature for 6 h in order to obtain the $CoTiO_3$ and $CoTiO_3/TiO_2$ catalysts. The flowchart of the catalyst production process is presented in Figure 3. 1.

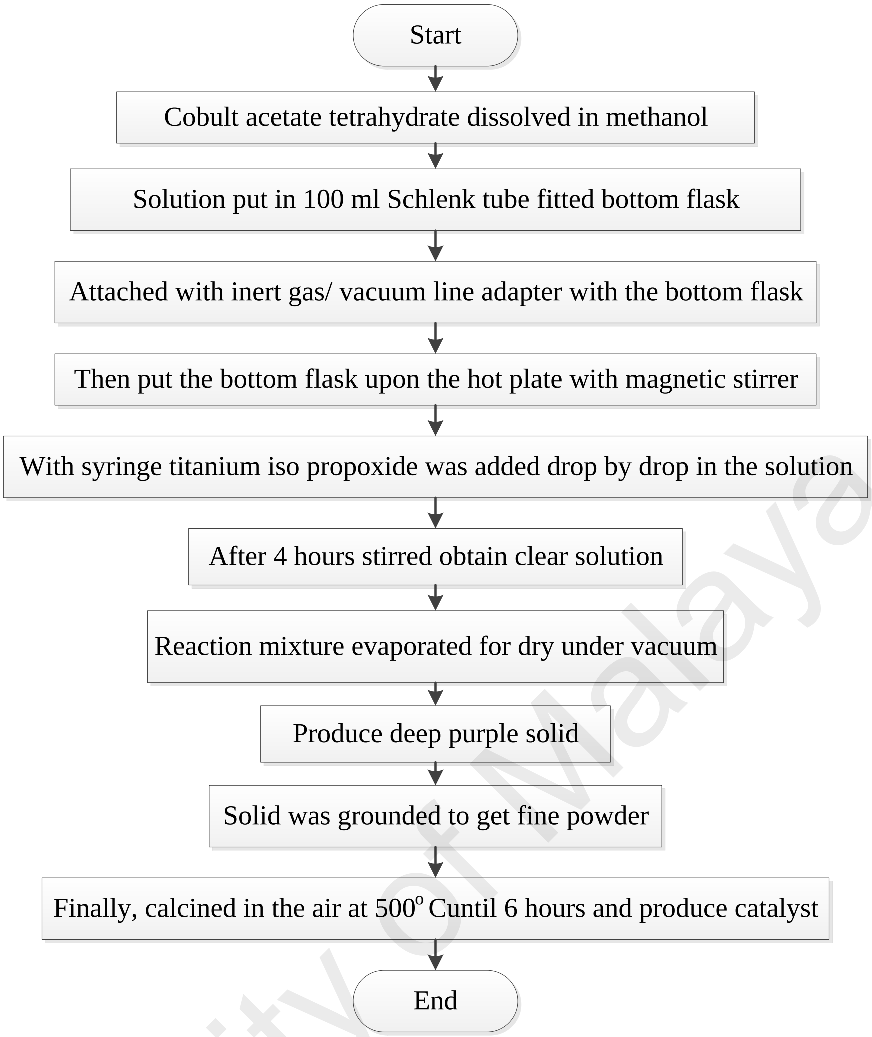


Figure 3. 1: Flow chart of the catalyst production.

3.3 Catalyst characterization

3.3.1 Fourier transform Raman (FT-Raman) analysis

Infrared (IR) spectroscopy techniques are extensively used for chemical analysis. However, it provides only the partial information on the vibrational structure of most polyatomic species. In fact, selection rules apply to IR light absorption phenomena, so that only vibrational modes that are associated with changes of the molecular dipolar moment can be directly excited. The application of IR spectroscopy to catalysis and surface chemistry was first stated in 1937 by Buswell and coworkers (Rao & Ravishankar, 2000). Most metal oxides only absorb radiation in the low-energy IR region (below 1000 cm^{-1}) while most gaseous or volatile molecules absorb strongly in the higher energy IR region (4000–1000 cm^{-1}). In this study, the formation of metal oxide was monitored using FTIR spectroscopy. The spectra were recorded on a Shimadzu FTIR- 8201 PC spectrophotometer in the wave number range of 400 – 4000 cm^{-1}. The samples were made into KBr pellets (1 wt. %) or as such in DRIFT mode. In general, neat KBr was used as a reference material.

3.3.2 X-Ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive method for the quantitative and qualitative analysis of crystalline materials in powder or solid form. It helps in determining the crystallinity, phase purity, crystal structure and crystallite size of catalyst materials (Menon, Galvita, & Marin, 2011).The XRD method involves interaction between the incident monochromatized X-rays (like Cu Kα or Mo Kα) with the atoms of a periodic lattice (Figure 3. 2). X-rays scattered by the atoms in an ordered lattice interfere constructively as described by Bragg's law: $n\lambda = 2d \sin\theta$, where, λ is the wavelength of the X-rays, *d* is the distance between two lattice planes, θ is the angle between the incoming X-rays and the normal to the reflecting lattice plane and n is an integer known as the order of reflection (McFarland & Metiu, 2013; Menon et al., 2011).

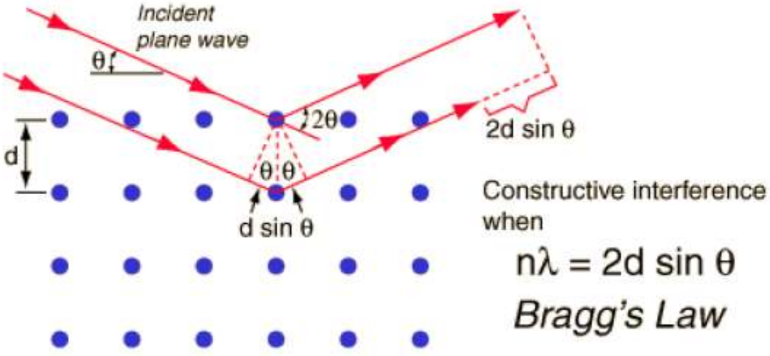


Figure 3. 2: X-ray diffraction from crystal planes (Jha, 2013).

The mesoporous materials were characterized using an X’Pert Pro (Philips) diffractometer with Cu-Kα radiation (λ = 0.15406 nm) and a proportional counter as a detector. A divergent slit of 1/32◦ on the primary optics and an anti-scatter slit of 1/16◦ on the secondary optics were used to measure the data in the low-angle region. The rest of the catalysts were analyzed using a Rigaku Geigerflex X-ray diffractometer with Ni filtered Cu-Kα radiation (40 kV, 30 mA). The XRD patterns were measured in the 2θ range of 0.5–10º in the case of mesoporous (PTA/MCM 41 and SO_3H-Fe_3O_4@MCM-41) materials and 5 – 80° in the case of metal cation-exchanged montmorillonite clay catalyst at a scan rate of 5.3º min^{-1}, respectively. Crystallite size of the materials was determined using the Scherrer equation: $L = K\lambda/\beta\cos\theta$, where θ and λ are the Bragg’s angle and wavelength of incident X-ray radiation, respectively. K is a constant approximately taken as 0.9; β is the line width on the 2θ scale in radians. Qualitative phase analysis of the catalysts was done based on the comparison of the line positions and intensity distributions of a set of reflections of the catalyst sample with a data base (JCPDS). In case of mixed oxides, XRD is the best technique to study the effect of dopant on the host oxide. It can measure the newly form crystalline phase due to the dopant present in the mixed oxide. Peak widths are fitted to the Debye−Scherrer equation to determine crystallite size. Shifts due to the substitution doping are often interpreted using Vegard’s rule, which states that there is a linear relationship between the concentration of a substitution dopant and the change in the lattice parameter. As an added complication, the lattice parameters of small nanocrystals depend on crystallite size, and it is not sure whether the observed lattice parameters shift is due to doping or to the small size of the crystallites.

3.3.3 Field emission scanning electron microscopy (FESEM) / energy dispersive X-ray spectroscopy (EDX)

SEM images and EDX elemental analyses were analyzed by Hitachi FESEM SU furnished with Oxford INCA 200 Energy Dispersive X–ray microanalysis System "Carl–Ziess SMT, Oberkochen, Germany; Oxford Instruments Analytical, Bucks. U.K.". The thin powdered sample was first mounted on to a SEM specimen stub with double–sided sticky tape before being scanned with the electronic microscope.

The specimen was coated with gold and left to dry for about 10–20 min prior to analysis. The analysis was operated at an accelerating voltage of 20 kV and a working distance of 9.2 mm.

3.3.4 Temperature programmed reduction (TPR) and oxidation (TPO)

The technique temperature programmed oxidation and reduction typically involves monitoring surface (or bulk) processes between the solid catalysts and its gaseous environment via continuous analysis of the gas phase composition as the temperature is raised. TPR is a widely used tool for the characterization of metal oxides, mixed metal oxides, and metal oxides dispersed on a support. A thermal conductivity detector (TCD) is used to measure changes in the thermal conductivity of the gas stream. TPR is a method in which a reducing gas mixture (5% H_2 in argon) flows over the sample while the temperature is increased linearly. The experiment permits the determination of the total amount of hydrogen consumed, from which the degree of reduction and, thus the average oxidation state of the solid material after reduction can be calculated. However, reduction of metal oxide is strongly dependent on the morphology and particle size (Chang, Zhang, Xia, Zhang, & Xing, 2012). Similarly, in TPO experiment, pre-reduced sample was subjected to oxygen flow (10% O_2 in He, 25 ml/min.) with linear heating. The amount of oxygen consumption gives the reduced species in a catalyst material. In the present work, both the TPR/TPO experiment was carried on Micromeritics 2720 chemisorb instrument (Figure 3. 3).

Figure 3. 3: Micromeritics 2720, instrument.

3.3.5 X-Ray photoelectron spectroscopy (XPS) analysis

XPS is based on the observation of the photoelectric effect and also known as electron spectroscopy for chemical analysis (ESCA), in which a photon reaching a sample can liberate an electron, which subsequently escapes into the vacuum (Figure 3. 4). XPS detects only those electrons that have actually escaped into the vacuum of the instrument. This technique biased towards the top few atomic layers ($\sim 1-10$ nm) of the solid (Bulam, Nekrasov, Passet, & Foshkin, 1988). In brief, XPS is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that present at the surface in concentration greater than approximately 1 atomic percent.

Furthermore, XPS is able to give the information of the elemental stoichiometry of the near-surface region, which is frequently different from the bulk composition. The catalytic function is mainly dependent on surface composition and electronic properties, which makes XPS a popular surface analytical tool. The amount of the XPS peak (I_A) is strongly dependent on (i) the incoming photon flux, (ii) the concentration of the given element, (iii) its photoionization cross-section (which is excitation-energy dependent), (iv) the mean free path of the emitted photoelectron, and (v) further instrumental parameters (such as photoelectron collection and detection efficiency). The atom fraction of any element in a sample can be calculated by defining atomic sensitivity factors (S, as an overall factor summing up the effects of iii–v) as:

$$X_A = (I_A / S_A) / \sum (I_i / S_i) \tag{3.1}$$

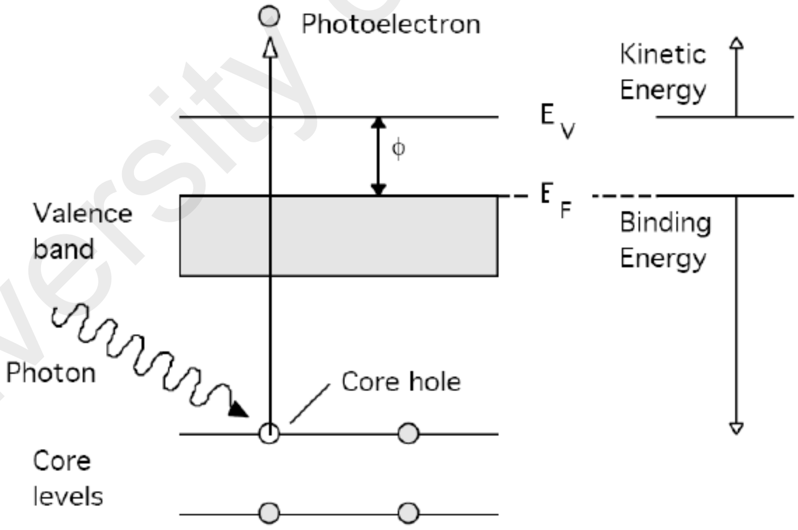


Figure 3. 4: Schematic presentation of the operation principle of XPS (Jha, 2013).

XPS data of different catalysts were collected on a VG Scientific ESCA-3000 spectrometer using a non-monochromatised Mg Kα radiation (1253.6 eV) at a pressure of about 1×10^{-9}Torr (pass energy of 50 eV, electron take off angle 55) and overall resolution 0.7 eV determined from the full width at half maximum of the $4f_{7/2}$ core level of the gold surface. The error in the binding energy values were within 0.1 eV. The binding energy values were charge-corrected to the C1s signal (284.6 eV).

3.4 Typical method for the oxidation of vanillyl alcohol

The overall procedure of this research is graphically presented in Figure 3. 5. The oxidation reaction was carried out in a 50 ml two-necked round bottom flask fitted with a water-cooled reflux condenser. In a typical oxidation reaction, the calculated quantities of vanillyl alcohol (0.15 g, 1.0 mmol) and acetonitrile (25 mL) were added to round bottom flask and kept on magnetic stirrer with oil bath at 358 K. After the desired temperature was attained, specific amount of catalyst was added while stirring (850 rpm) followed by H_2O_2 (0.2 ml, 2.0 mmol). About 0.5 ml of reaction mixtures was withdrawn periodically by means of a syringe and filtered for analysis by HPLC.

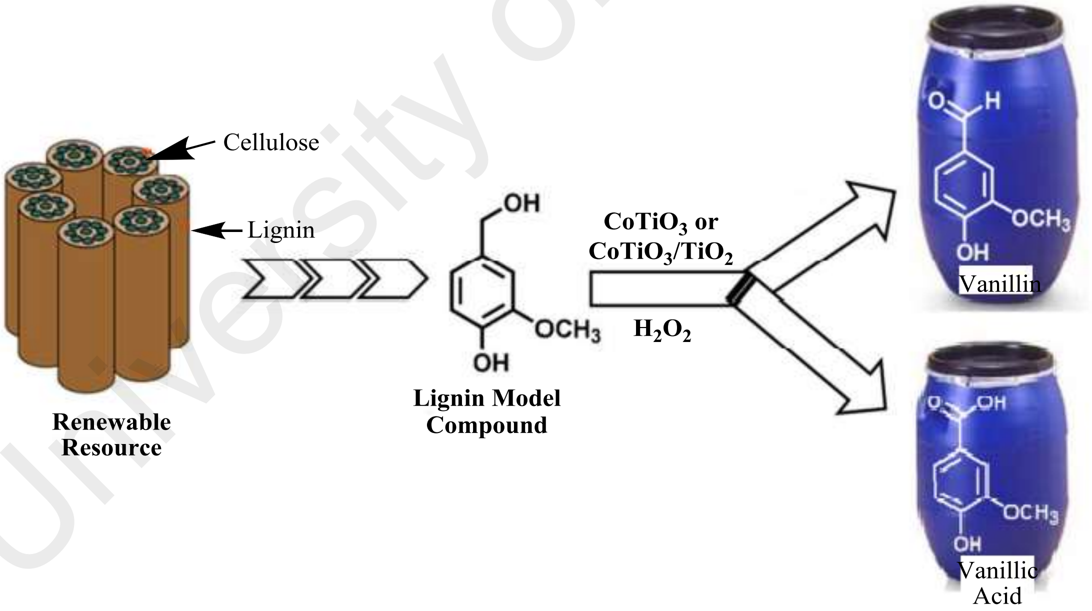


Figure 3. 5: Graphical representations of the research.

3.4.1 Product analysis and identification

The progress of the reaction was observed by analyzing the filtrate into Agilent High-performance liquid chromatography (HPLC) equipped with an ultraviolet detector. The HPLC analysis was carried out on a 25 cm RP-18 column. The products and reactant were identified by using a UV detector at λ_{max} = 270 nm. Aqueous acetonitrile (15%) with (1%) acetic acid was used as a mobile phase at a column temperature of 28 °C and a flow rate of 1.0 ml min^{-1}.

The HPLC is a method in analytical chemistry, which is used to identify, separate, and quantify each of the components in a mixture. It depends on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out the column.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 $CoTiO_3$ catalyst

4.1.1 Structural characterization

The phase composition and chemical formula of the as-synthesized Co-Ti oxide catalyst were determined from XRD and the resultant X-ray pattern is presented in Figure 4. 1 (blue line). A careful matching of the fresh Co-Ti oxide XRD pattern with the standard inorganic crystal structure database available in PANalytical X'Pert HighScore Plus" software identifies the formation of $CoTiO_3$ as a catalyst product. The cobalt titanium oxide ($CoTiO_3$) (ICSD = 00-001-1040) crystallizes in the rhombohedral crystal system with cell parameters a = b = 5.0440, c = 13.9610 A˚; $\alpha = \beta = 90^o \gamma = 120^\circ$and is identified by its peaks at 2θ = 24.0, 32.9, 35.4, 40.6, 49.2, 53.5, 60.3, 63.7, 71.4, 75.3, 84.1 and87.9 produced by their Miller indices (012), (104), (110), (113), (024), (116), (214), (300), (119), (220), (134) and (226) correspondingly. All peaks in XRD pattern showed excellent matching with standard pattern (ICSD library card (00-001-1040) in terms of their peak position, 2θ value and d-spacing (Figure 4. 2). No possible crystalline impurities such as Co_2O_3, Co_3O_4 and TiO_2 were detected from XRD pattern. This clearly indicates the formation of pure crystalline $CoTiO_3$ at 500 ˚C.

After performing the catalytic oxidation reaction, the reused catalyst was again characterized by XRD (Figure 4. 1, green line) in order to observe any change in its phase composition and chemical identity. It was worth to notice that no significant change in the composition and phase was detected and finger prints of reused catalyst were similar to the fresh $CoTiO_3$in terms of its peak position and 2θ values.

Both the XRD patterns were dominated by the peak at $2\theta = 32.9^\circ$ also revealed that $CoTiO_3$ product was well crystallized. However the crystallinity of the reused catalyst was reduced as compared to the freshly prepared $CoTiO_3$.

Recent literature implies that attempts to synthesize pure $CoTiO_3$ generally require higher temperatures exceeding 600 °C and often produce TiO_2 and Co_2TiO_4 as impurity phases (Anjana & Sebastian, 2006; Kapoor, Uma, Rodriguez, & Klabunde, 2005; Zhou, Lee, Kim, Kim, & Kang, 2006). Furthermore, it needs prolonged annealing at higher temperature of 700 °C to enhance the crystallinity of the material. On the other hand, in the present case, solution method was used at a relatively low temperature of 500 °C to furnish a high crystalline $CoTiO_3$ product free from all other titania and cobalt oxide phases.

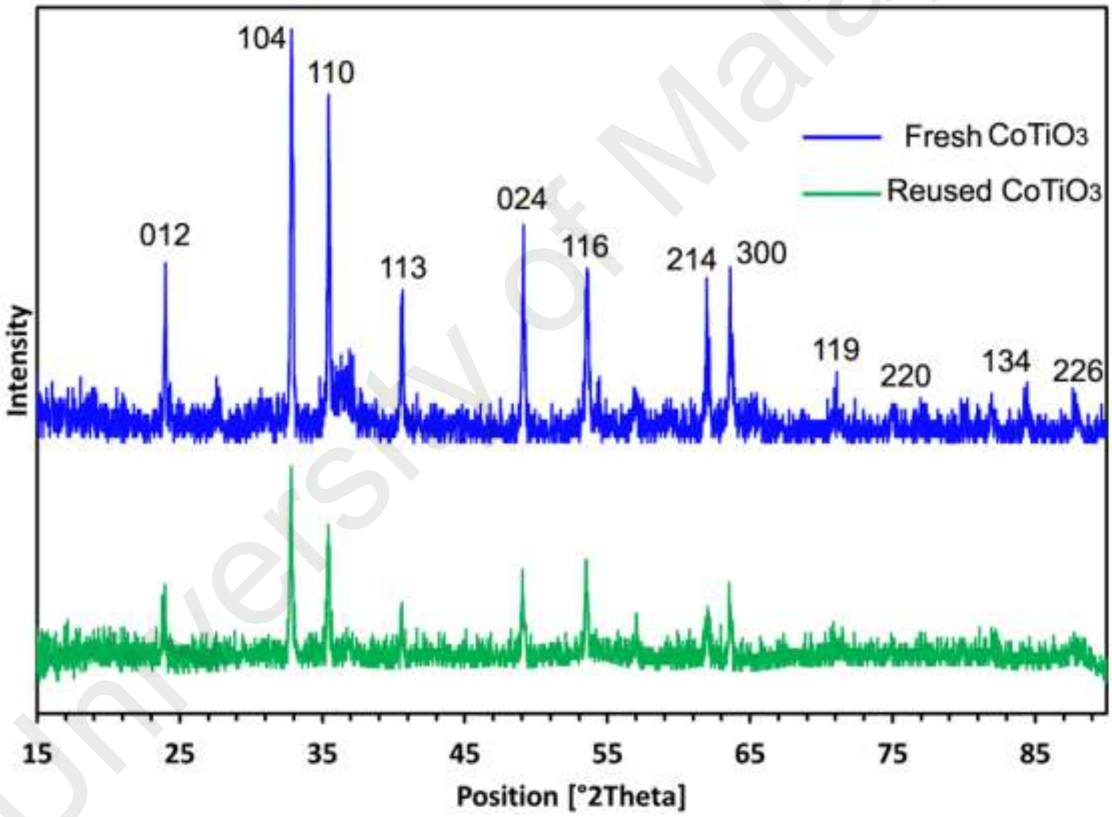


Figure 4. 1: X-ray diffractogram of freshly prepared $CoTiO_3$ (blue line) catalyst prepared at 500 °C. Green line represents the X-ray diffractogram of reused catalyst after performing the oxidation reaction.

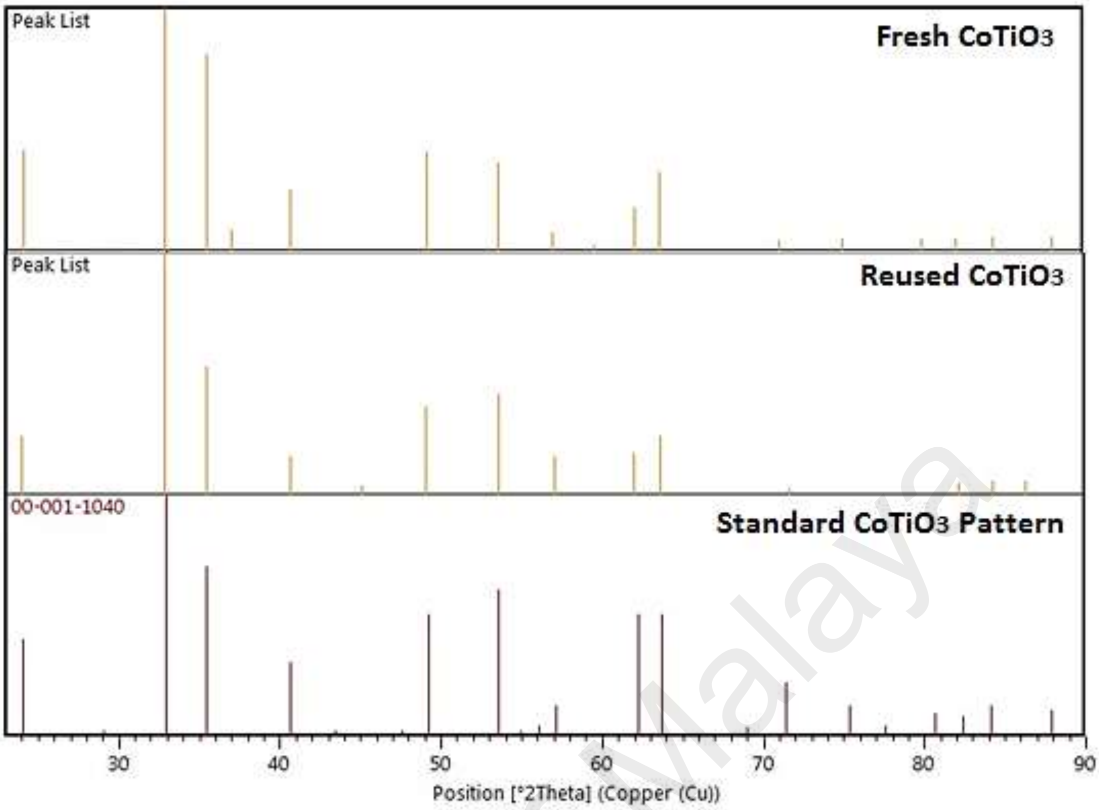


Figure 4. 2: Comparison of XRD pattern of freshly prepared $CoTiO_3$; reused $CoTiO_3$with standard ICSD library card (00-001-1040).

The cobalt titanate phase that was identified from the XRD pattern was further confirmed by Raman spectroscopy as shown in Figure 4. 3. The Raman scattering vibration modes detected at 193, 208, 237, 267, 335, 383, 480, 521 and 689 cm^{-1} are characteristic of ilmenite $CoTiO_3$. The Raman spectroscopy results are in good agreement with our XRD pattern and also matched well with the previously reported Raman data for the $CoTiO_3$materials (Zhou et al., 2006).

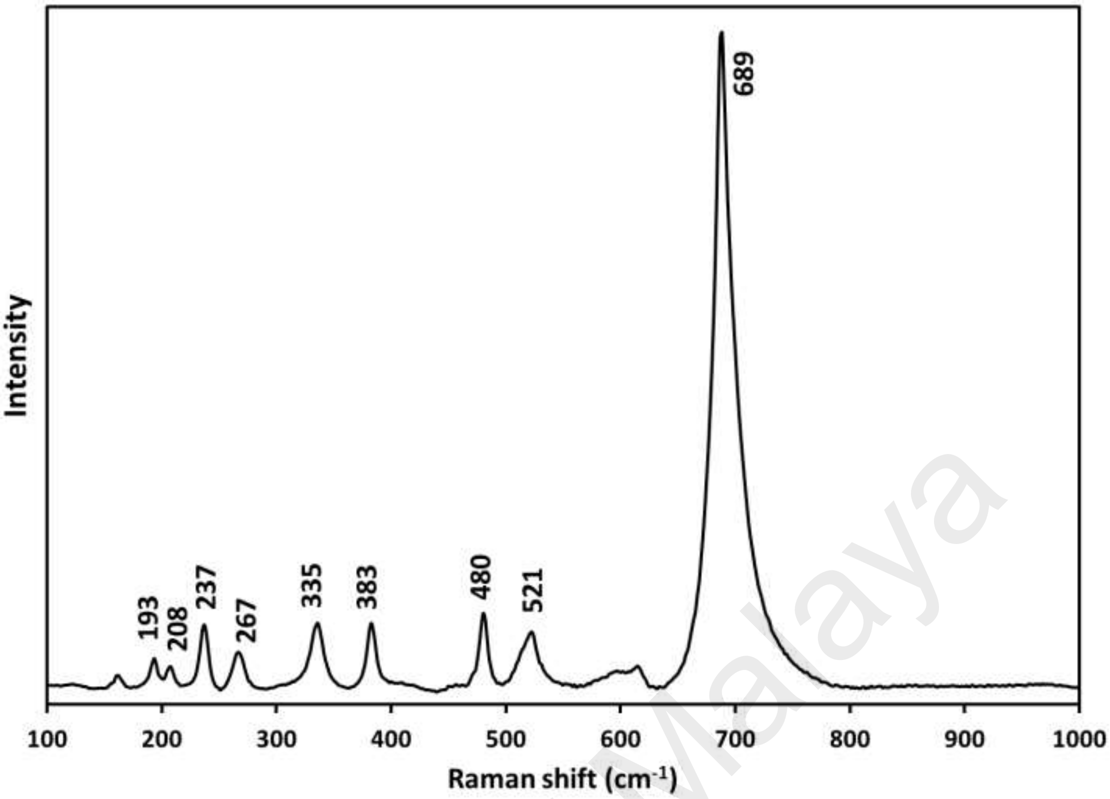


Figure 4. 3: Raman spectrum of $CoTiO_3$ catalyst.

4.1.2 Morphological studies

The change in surface morphology of the as-synthesized $CoTiO_3$ catalyst before and after vanillyl alcohol oxidation reaction was studied by scanning electron microscopy and images as shown in Figure 4. 4. Before carrying out the catalytic reaction, $CoTiO_3$ catalyst was comprised of large size crystallites (Figure 4. 4a) and high resolution image revealed the rough and stony surface of the catalyst (Figure 4. 4 b). It is generally believed that the rough surface of the catalyst because of its high surface area can better perform the catalytic action as compared to smooth and plane surface which has less surface area. After execution of the oxidation reaction the morphology of $CoTiO_3$ changes to oval shaped crystallites which exhibited smooth and plane surface (Figure 4. 4 c and d).

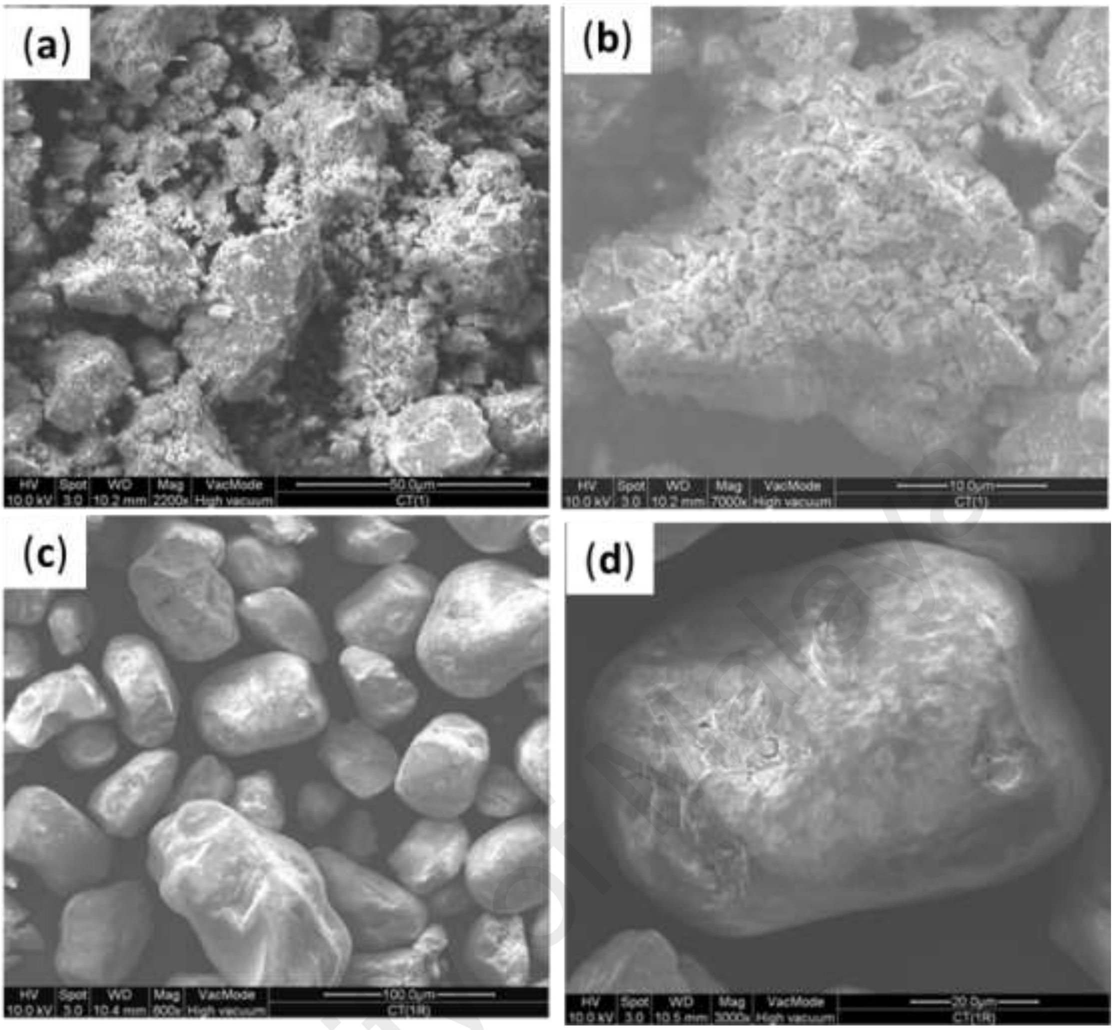


Figure 4. 4: SEM images of $CoTiO_3$ catalyst (a and b) before vanillin oxidation reaction; (c and d) after vanillin oxidation reaction.

4.1.3 Compositional studies

The stoichiometric composition of the catalyst before and after the catalytic oxidation reaction was established from energy dispersive X-ray analysis and EDX spectra shown in Figure 4. 5. It was found that the elemental composition of the catalyst before and after catalytic oxidation reaction remains unchanged and EDX spectra showed the expected stoichiometric ratio indicating that the composition of the catalyst before and after oxidation reaction was $CoTiO_3$. The molar ratio of Co/Ti obtained from different peak areas of the EDX spectra was thus close to the expected 1:1 ratio of $CoTiO_3$.

Figure 4. 6 indicates the EDX mapping of $CoTiO_3$ catalyst before and after the catalytic oxidation reaction and reveals that Co, Ti and O atoms are homogeneously distributed throughout the catalyst's surface.

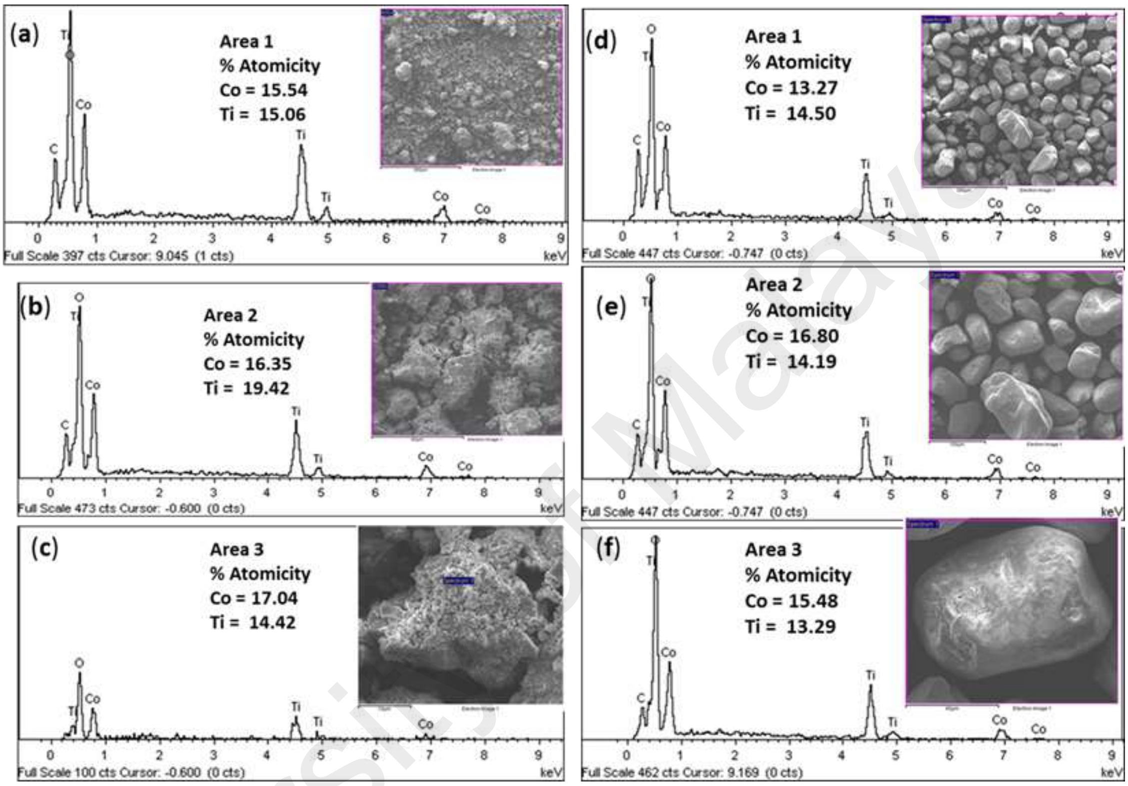


Figure 4. 5: EDX spectra revealing the stoichiometric composition of $CoTiO_3$ catalyst (a-c) before and (d-f) after oxidation reactions.

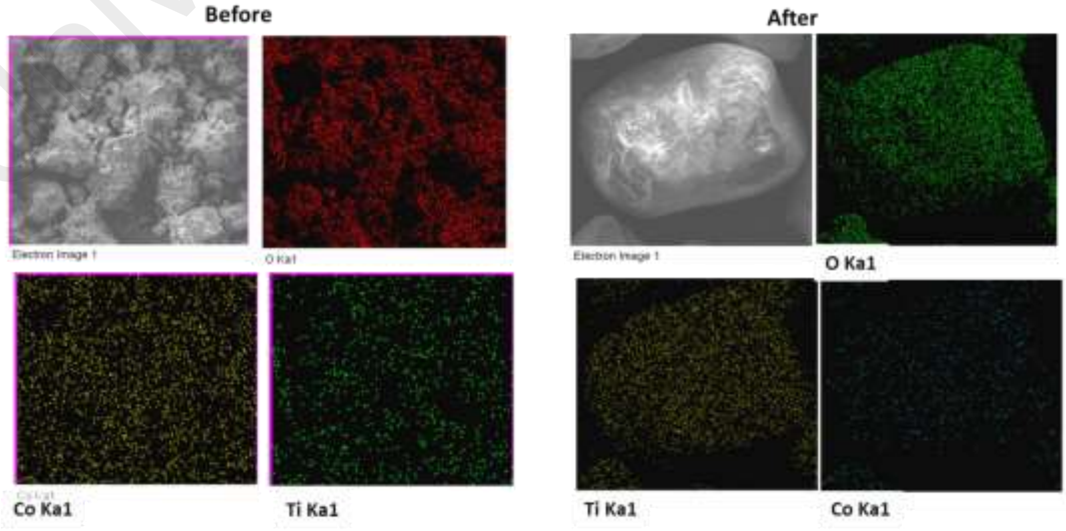


Figure 4. 6: EDX mapping revealing the distribution of Co, Ti and O atoms on the surface of catalyst before and after oxidation reactions.

4.1.4 The proposed reaction mechanism

Detection of oxidation products from the HPLC analysis suggests a free radical mechanism may be operating for vanillyl alcohol oxidation under the studied reaction condition. Figure 4. 7 illustrates the suggested mechanism for oxidation of vanillyl alcohol in present of H_2O_2. Initially the catalyst reacts with H_2O_2 to form the hydroperoxyl radial which is acting as a source of highly reactive oxidant, this in turn attack the catalyst forming an intermediate. The hydroperoxyl radical is a conjugate acid of superoxide anion ($O_{2.}^{-}$) which is a very important intermediate in combustion chemistry and known to play major roles in the oxidation reaction (Neumann & Levin-Elad, 1995; Singh & Selvam, 1996). Moreover, this chemical is more stable in atmosphere than superoxide. On the other hand, it is well known that the formation of hydroperoxyl radical can be through direct photolysis of H_2O_2 as well as through the Fentons reaction (Tumula et al., 2012). However, the vanillyl alcohol is activated on the catalyst surface. Then the electron rich hydroperoxyl attack the partially positive carbon and the hydrogen of the hydroxyl group abstraction by the oxygen molecular to produce activated oxygen species, which help to remove the hydroxyl from the hydroperoxyl to produce water as a by-product. Meanwhile, the vanilloxy cation releases a proton which is attacked by electron rich oxygen of the hydroperoxyl group and forming the final acid product. Another possibility is that the electron rich oxygen of the hydroperoxyl group attacks the proton on activated oxygen species (on catalyst) and forms the final vanillin product. It has found that when the reaction medium was more basic, the formation of aldehyde product increased. This could be due to the formation of superoxide rather that hydroperoxyl radical which preferentially attack the hydrogen on activated oxygen species (on catalyst) than the proton of vanilloxy carbon.

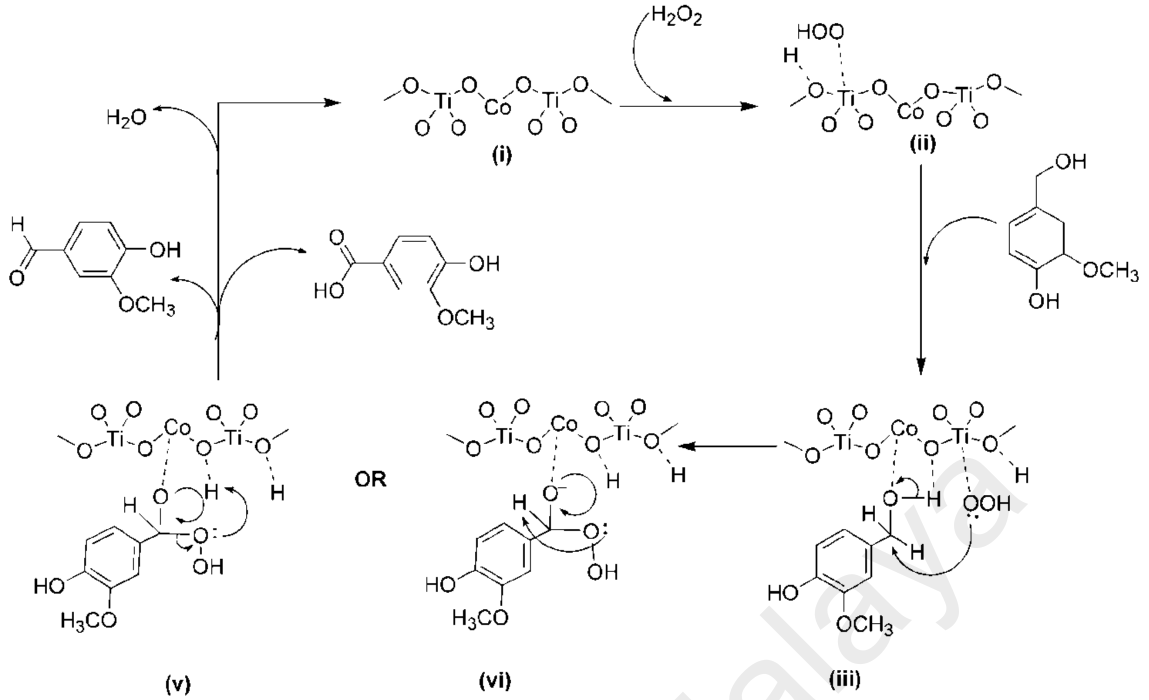


Figure 4. 7: The suggested mechanism for the formation of main oxidation product (vanillin and vanillic acid) from vanillyl alcohol in presence of CoTiO3.

4.1.5 Liquid phase oxidation of vanillyl alcohol over CoTiO$_3$ catalyst

To determine the optimum reaction condition of vanillyl alcohol oxidation various reaction parameters were studied such as effect of time, catalyst amount, and molar ratio of vanillyl alcohol:H$_2$O$_2$, reaction temperature, solvent type and the effect of alkaline medium on the reaction. Under the optimum reaction condition, the oxidation of vanillyl alcohol without catalyst did not show any activity and the reusability analyses were also investigated. Moreover, the reactions were performed under optimum reaction conditions in alkaline medium. The idea behind using base is probably to deprotonate the phenolic-OH to form the phenoxy anion, which is more reactive and easier to perform, favours coordinate to CoTiO$_3$ and resulting more selectivity to vanillin and increasing the activity (Burriel et al., 2005). The reaction scheme for the oxidation of vanillyl alcohol is shown in

Figure 4. 8.

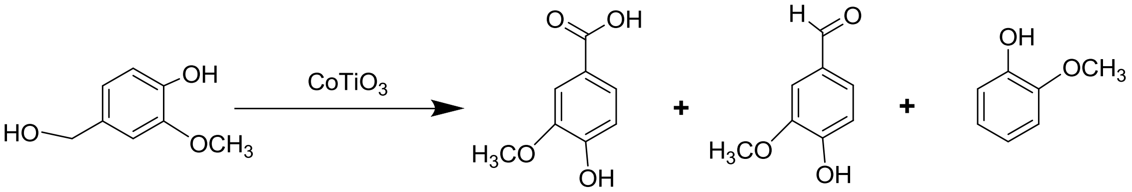


Figure 4. 8: Liquid phase oxidation of vanillyl alcohol products in $CoTiO_3$ catalyst.

4.1.5.1 Influence of reaction time

The effect of reaction time on vanillyl alcohol conversion and selectivity to vanillic acid and vanillin were studied for $CoTiO_3$ and the results are shown inFigure 4. 9. The conversion increased slowly from 28% to 67% when the time increased from 30 min. to 5 h. However, further extending the reaction time to 6 h did not improve the oxidation. Based on the highest conversion, the 5 h reaction time was selected as an optimum time for this catalytic system. However, the selectivity of vanilic acid was found to decrease from 87% to 77% with increase in time. This decrease was consistent with the increased selectivity of vanillin from 10% to 19% in reaction time 30 min. to 5 h.

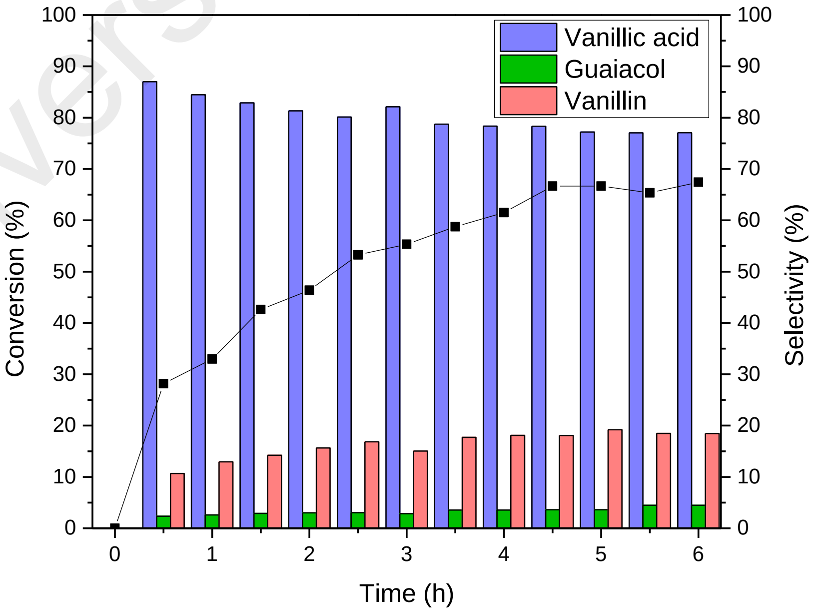


Figure 4. 9: Effect of time on conversion and selectivity. Reaction condition: amount of $CoTiO_3$ (100 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.1.5.2 Catalytic activity with different mass of catalyst

The prepared catalyst was tested in liquid phased oxidation of vanillyl alcohol. As illustrated in Figure 4. 10, as the mass of the catalyst increased the conversion of vanillyl alcohol to corresponding product was found to increase sharply from 24%, to 67% when the catalyst mass used was increased from 25 to 100 mg. The selectivity of acid formatting was found to slightly decrease as the catalyst mass was increased. However, further increase in the catalyst mass to 125 mg resulted in a decrease in vanillyl alcohol conversion to 59%. The reason behind that could be due to the rapid decomposition of H_2O_2 over the large surface area available with a higher mass catalyst (Chuang et al., 2010). As a result, the selectivity of vanillin was observed to slightly increase with the decreased in the formation of vanillic acid. On the other hand, the absence of the catalyst leads to maximum value of 3% vanillyl alcohol conversion to vanillic acid.

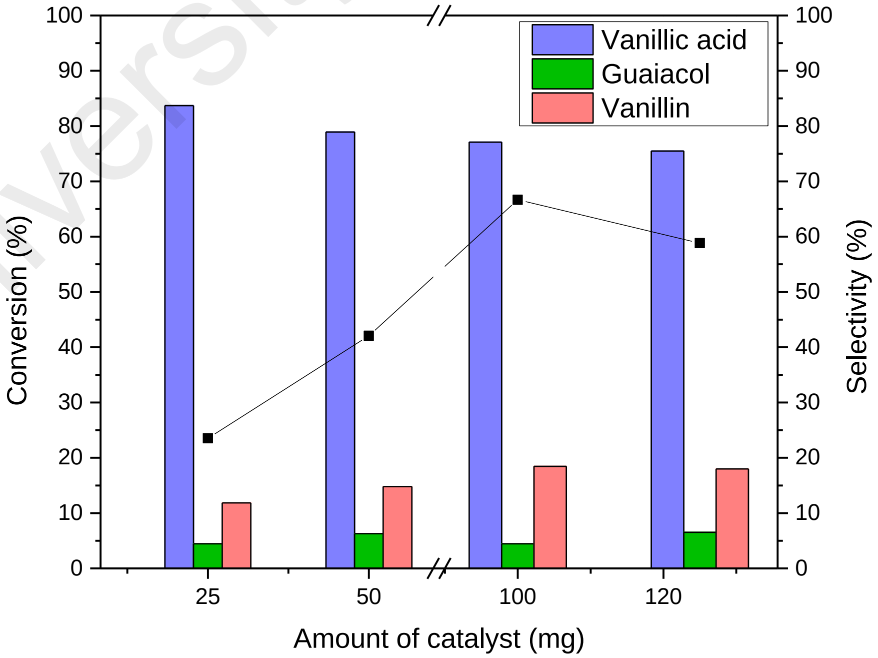


Figure 4. 10: Effect of catalyst loading on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.1.5.3 Influence of temperature

The reaction temperature was found to have a great influence on the conversion of the reaction. Thus, in the oxidation of vanillyl alcohol, the effect of temperature on the reaction was studied in the range of 338-363 K (Figure 4. 11). The reaction was conducted at a fixed parameter (vanillyl alcohol: H_2O_2 molar ration 1:2 and a catalyst amount of 100 mg in 25 ml acetonitrile). The conversion was found to increase from 51% at 338 K to 72% at 363 K. The plausible explanation for this observation could be due to the enhanced decomposition of H_2O_2 at high temperature (Chuang et al., 2010). However, there is no significant change in the selectivity of vanillic acid and vanillin at different temperature. Therefore, 358 K was preferred as suitable reaction temperature for the subsequent optimization studies, since there are moderate conversion and rapid decomposition of H_2O_2.

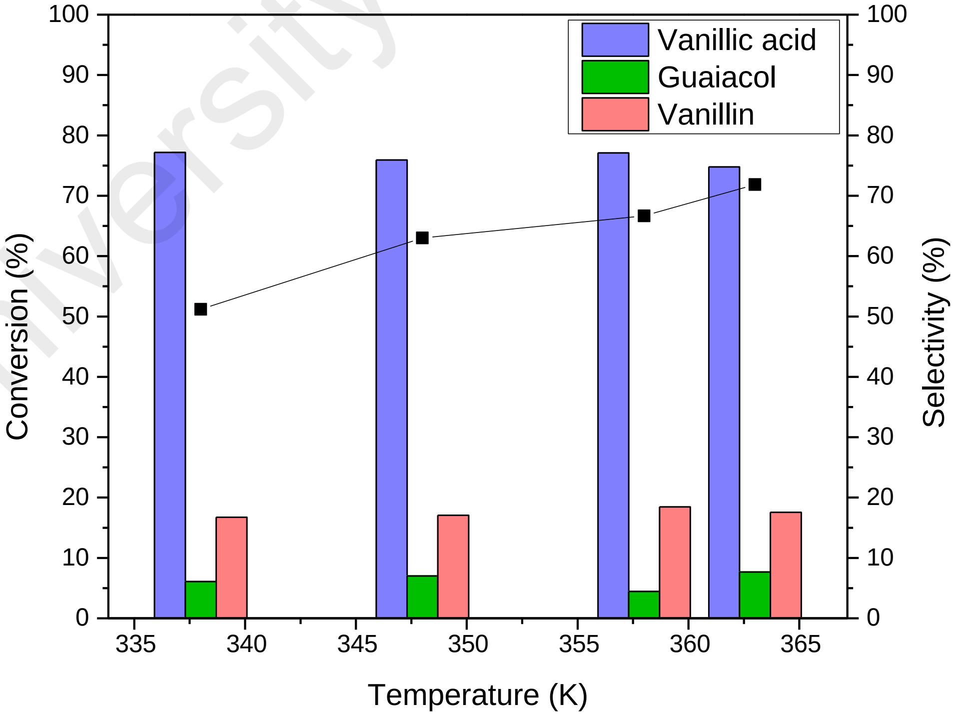


Figure 4. 11: Effect of reaction temperature on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillyl alcohol: H_2O_2 (1:2); amount of $CoTiO_3$ (100 mg); acetonitrile as solvent (25 ml).

4.1.5.4 Influence of H_2O_2 mole ratio

To determine the optimum ration of H_2O_2 needed for this oxidation of vanillyl alcohol reactions, 4 different ratios were studied. The results obtained from the reactions are shown graphically in Figure 4. 12. The conversion ranges from 51-67% for 1 to 4 H_2O_2 molar ratios. However, the results clearly showed that when H_2O_2 is used in more than equimolar ratio (vanillyl alcohol:H_2O_2, 1:2, 1:3), the conversion significantly increased (67%). Generally, the decomposition of H_2O_2 produced water as a byproduct (Jha & Rode, 2013), and that might poison the catalyst by adsorbing strongly to the catalyst $CoTiO_3$ surface, blocking the active sites and thus inhibiting the conversion of vanillyl alcohol to further products. Furthermore, decomposition of H_2O_2 increased the formation of vanillic acid, decreased the formation of guaiacol. In contrast, vanillin formation did not significantly change. It can be seen from Figure 4. 12, that an increase in H_2O_2 more than 2 equimolar ratio, does not significantly change the performance of the catalyst.

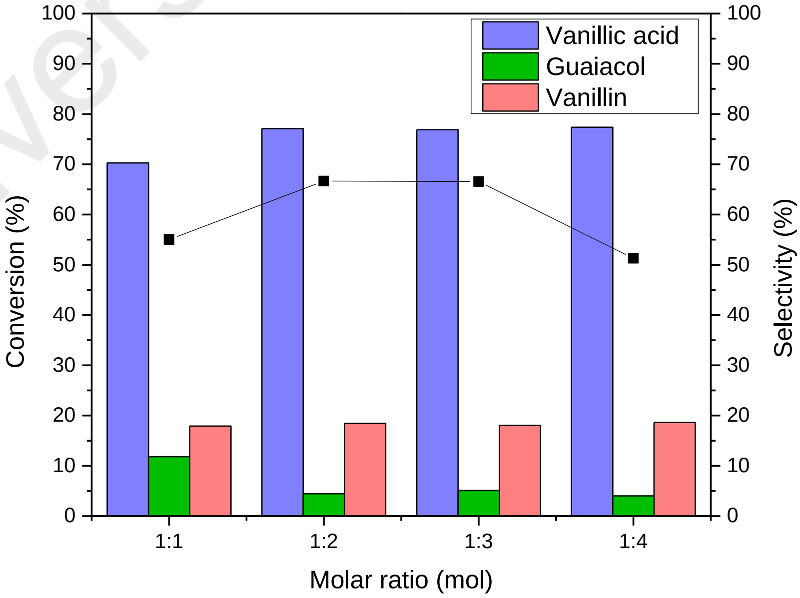


Figure 4. 12: Effect of molar ratio on conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3$ (100 mg); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.1.5.5 Reusability of the catalyst

In order to study the stability of $CoTiO_3$ heterogeneous catalyst, the reusability test was carried out. After observing the completion of the reaction with a fresh catalyst which was carried out as mention in typical method for the oxidation of vanillyl alcohol, the liquid contents were removed from the flask and $CoTiO_3$ catalyst was washed several times with acetone. Then, it was dried under vacuum at 100 °C for 2 h. This dried catalyst was reused in a second cycle for the oxidation of vanillyl alcohol and a similar procedure was followed for four subsequent oxidation cycles. The results are depicted inFigure 4. 13. It can be observed that the vanillyl alcohol conversion decreased *ca*. 15 % and 20 % after the third and fourth cycle of reuse, respectively. However, the selectivity of the vanillic acid and vanillin was slightly changed after the third recycle. To further confirm the catalytic nature of $CoTiO_3$ after the fifth reuse, the reused catalyst was investigated by XRD, SEM and Raman spectroscopies.

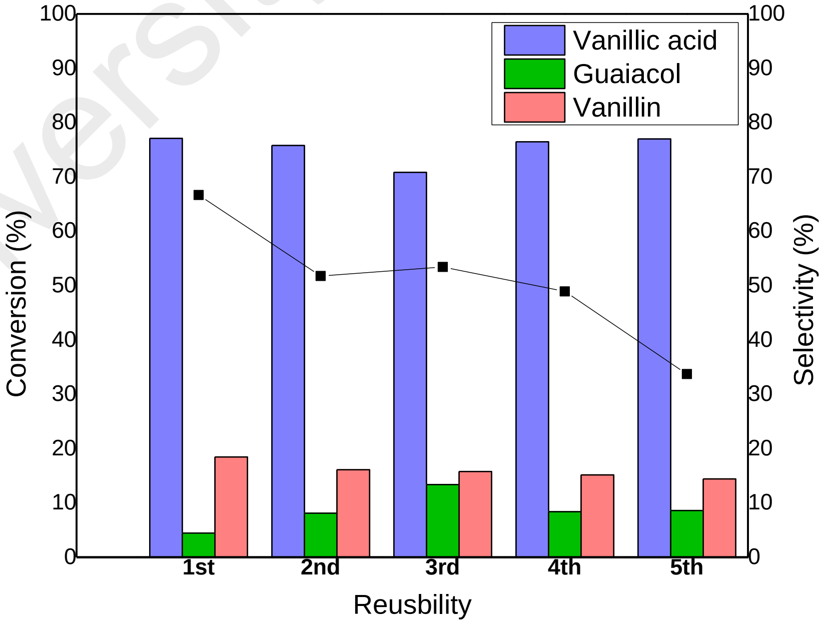


Figure 4. 13: Effect of re-used catalyst (reusability) on conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3$ (100 mg);

molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.1.5.6 Influence of solvent

The influence of natural solvents on the oxidation of vanillyl alcohol and vanillin was investigated using sixth different solvent systems with 100 mg catalyst mass and 1:2 vanillyl alcohol:H_2O_2 molar ratio. The results are shown in Figure 4. 14. Based on the experiment, highest conversion was achieved in acetic acid (91%) followed by ethyl alcohol (70%), acetonitrile (67%), *N*,*N*-dimethyl formaldehyde (35%), tetrahydrofuran (20%) and acetone (1%). Keeping the above fact in view, it is understood that the increasing conversion by using acetic acid as a solvent was directly proportional to the formation of peracetic acid, which was *in-situ* generated by reaction between acetic acid and H_2O_2 in the presence of an acid catalyst (Farook, Thiam-Seng, & Andas, 2012). This in turn accelerated the reaction and acted as an oxidant source for the oxidation reaction, as shown in Figure 4. 15. Additionally, the selectivity of vanillin was significantly increased when acetic acid was used as a solvent compared to other solvents. This could be due to the possibility of the formation of higher O_2 than the hydroxyl radical. Nonetheless, acetic acid was chosen as the optimal solvent media due to the formation of peracetic acid, and this led to higher conversion and increased the selectivity to vanillin. So, under these reaction conditions, peracetic acid plays a major role in the oxidation of vanillyl alcohol to vanillin, and conversely, in the oxidation of vanillyl alcohol to vanillic acid a major role is played by H_2O_2.

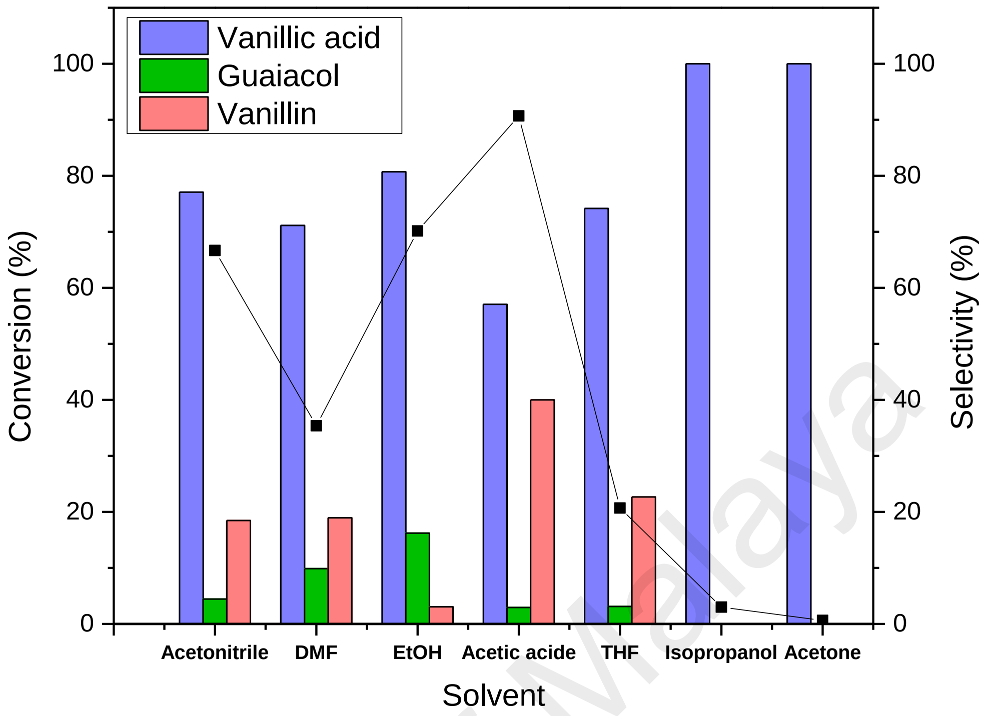


Figure 4. 14: Effect of solvent on vanillyl alcohol conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3$ (100 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K).

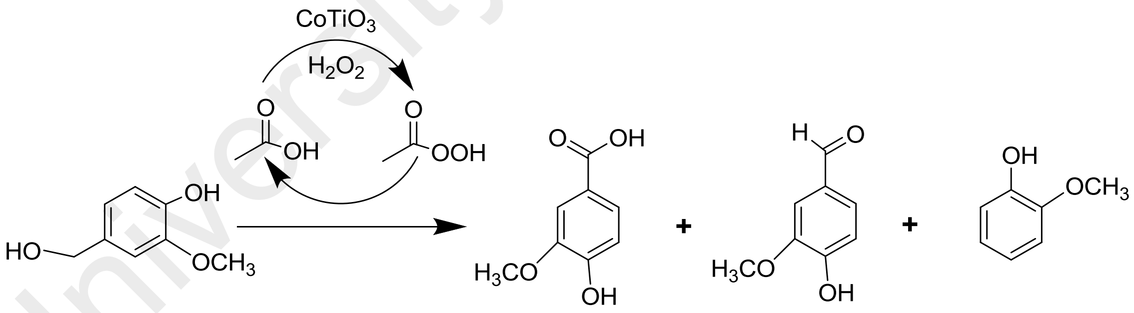


Figure 4. 15: Role of formation peracetic acid in oxidation of vanillyl alcohol by $CoTiO_3$ Catalyst.

4.1.5.7 Influence of basic medium

The effect of NaOH on the conversion and selectivity of aldehyde product (vanillin) in the oxidation of vanillyl alcohol is displayed in Figure 4. 16 A. The added amount of the base (NaOH) used was equivalent to H_2O_2 (2.0 mmol). The role of using alkaline condition was probably to deprotonate the phenolic to form the phenoxy anion. In addition, it seems that the generation of sodium peroxide occurs immediately after adding H_2O_2 to alkaline oxidation reaction mixture (Eq. 4.1 and 4.2). The latter, can be used as an oxidizing agent as well as oxygen source that enhances and accelerates the reaction activity and the selectivity towards aldehyde. However, due to poor solubility of NaOH in acetonitrile, the acetic acid and isopropanol were chosen to examine the effect of alkaline on the oxidation of the vanillyl alcohol reaction. Referring to Figure 4. 165 B, it is obvious that the highest conversion was achieved with acetic acid (99 %) followed by isopropanol (91%). On the other hand, the selectivity of vanillin was found to be higher in isopropanol (100%) than acetic acid (68%). A comparable oxidation reaction in presence of isopropanol as solvent and without a base led to much lower conversion (3%) of vanillyl alcohol. As a result, this hypothesis indicates that the alkaline medium plays an important part in the selective oxidation of the vanillyl alcohol process.

$$\mathrm{H_2O_{2\,(aq)} + 2NaOH_{(s)} \rightarrow Na_2 + 2H_2O} \qquad 4.1$$

$$\mathrm{Na_2O_2 + 2H_2O \rightarrow O_2 + 4NaOH} \qquad 4.2$$

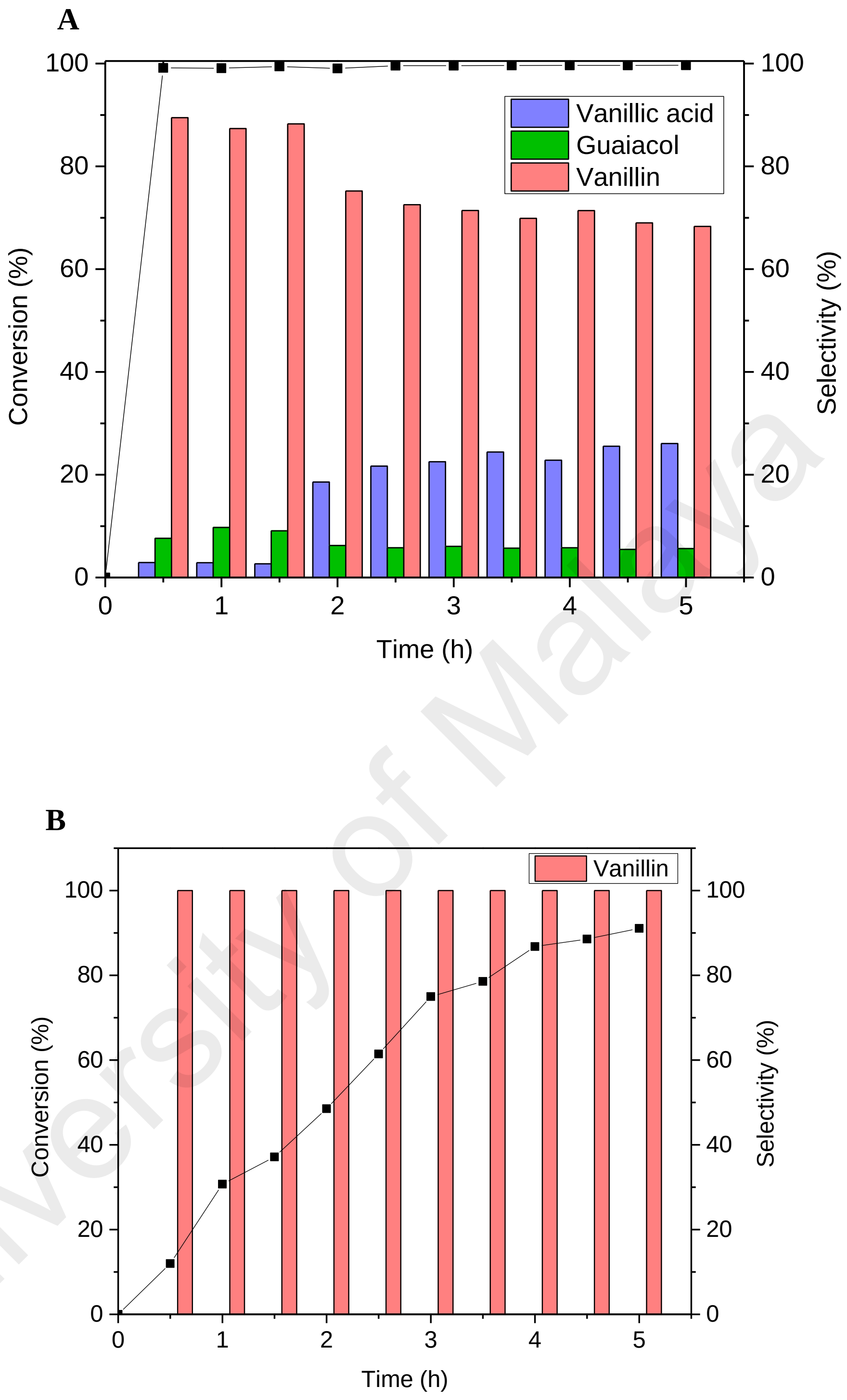


Figure 4. 16: Effect of basic media on conversion and selectivity. Reaction condition: amount of $CoTiO_3$ (100 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); A): acetic acid (25 ml), B): isopropanol (25 ml).

4.2 $CoTiO_3/TiO_2$ composite catalyst

4.2.1 Structural characterization

Cobalt (II) acetate tetrahydrate and titanium (IV) iso propoxide in 1:2 ratios were dissolved in methanol and solution was stirred for 4h. All volatiles were evaporated under reduced pressure and the pink colour solid was obtained. This solid was calcined at 500˚Cfor 6 h to yield a dark green color powder. In order to determine the phase composition and chemical formula, the green powder was subjected to powder XRD analysis and the resultant X ray diffractogram is presented in Figure 4. 17 (green line). A careful matching of the XRD pattern with the inorganic crystal structure database available in PANanalytical X' pert HighScore Plus" software identifies the growth of $CoTiO_3$ (ICOD=00-001-1040) and TiO_2 (00-002-0494) phases in the resultant product. The as–synthesized cobalt titanium oxide($CoTiO_3$) crystalizes in the orthorhombic crystal system with cell a=b=5.0440, c=13.9610A˚; α=β=90˚ and γ=120˚ and is identified by its peaks at 2θ =24.0, 32.9, 35.4, 40.6, 49.2, 53.5, 60.3, 63.7, 71.4, 75.3, 84.1 and 87.9^o produced by the Miller indices (012), (104), (110), (113), (024), (116), (214), (300), (119), (220), (134) and (226), respectively. In X-ray diffractogram reflections related to $CoTiO_3$ are labelled as "X" and the peaks indicated by "Y" at 2θ=27.4 (110), 36.1 (101), 54.40 (211), 68.9 (301), and 84.2(400) are attributed to TiO_2 which exists in the form of tetragonal rutile crystal system of space group P42/mnm and cell parameters of a=b=4.5800, c=2.9500A˚ and α=β=γ=99.48˚. All peaks in XRD pattern show excellent matching with standard pattern $CoTiO_3$ and rutile TiO_2 in terms of their peak position, 2θ value and d- spacing. No possible crystalline impurities of Co_2TiO_4 and other phases of TiO_2 were identifies form XRD pattern. This clearly indicates the formation of crystalline composite of $CoTiO_3$/ TiO_2 at 500˚C.

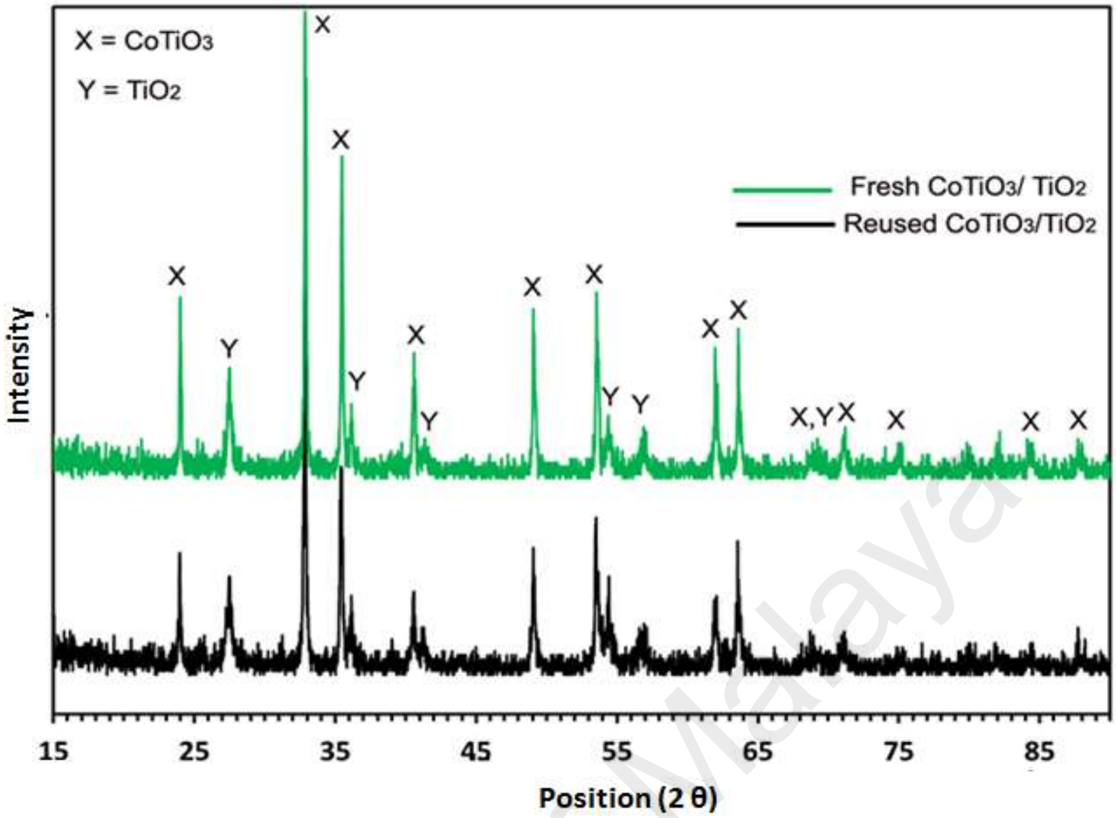


Figure 4. 17: X-ray diffractogram of freshly prepared $CoTiO_3$/ TiO_2 (green line) catalyst prepared at 500 ˚C. Black line represents the X-ray diffractogram of reused catalyst after performing the oxidation reaction.

The as-synthesized $CoTiO_3/TiO_2$ composite oxides were tested for the catalytic oxidation of vanillyl alcohol and after performing the catalytic reactions in order to monitor the change in morphology and composition. The powder catalyst was again investigated by XRD analysis and X-ray diffractogram is presented in Figure 4. 17 (black line).

It is worth to notice that no significant change in the phase composition was detected, and the finger prints of the reused catalyst were similar to the fresh $CoTiO_3/TiO_2$ in term of its peak position and 2θ values. Both XRD patterns are dominated by peak at 2θ=32.85˚, however, the intensities of crystalline peaks of the reused catalyst was reduced as compared to the freshly prepared $CoTiO_3$.

The cobalt titanate and titania phases that were identified from XRD pattern of the composite oxide catalyst were further confirmed by Raman spectroscopy as is shown in Figure 4. 18. The absorption modes detected at 207, 237, 266, 335, 382, 451, and 695 cm^{-1} are characteristic of ilmenite $CoTiO_3$. While the peaks at 161and 603 cm^{-1} reveal the presence of rutile phase. These results agree well with our XRD pattern and were also in agreement with the reported Raman data for $CoTiO_3$ and TiO_2phases.

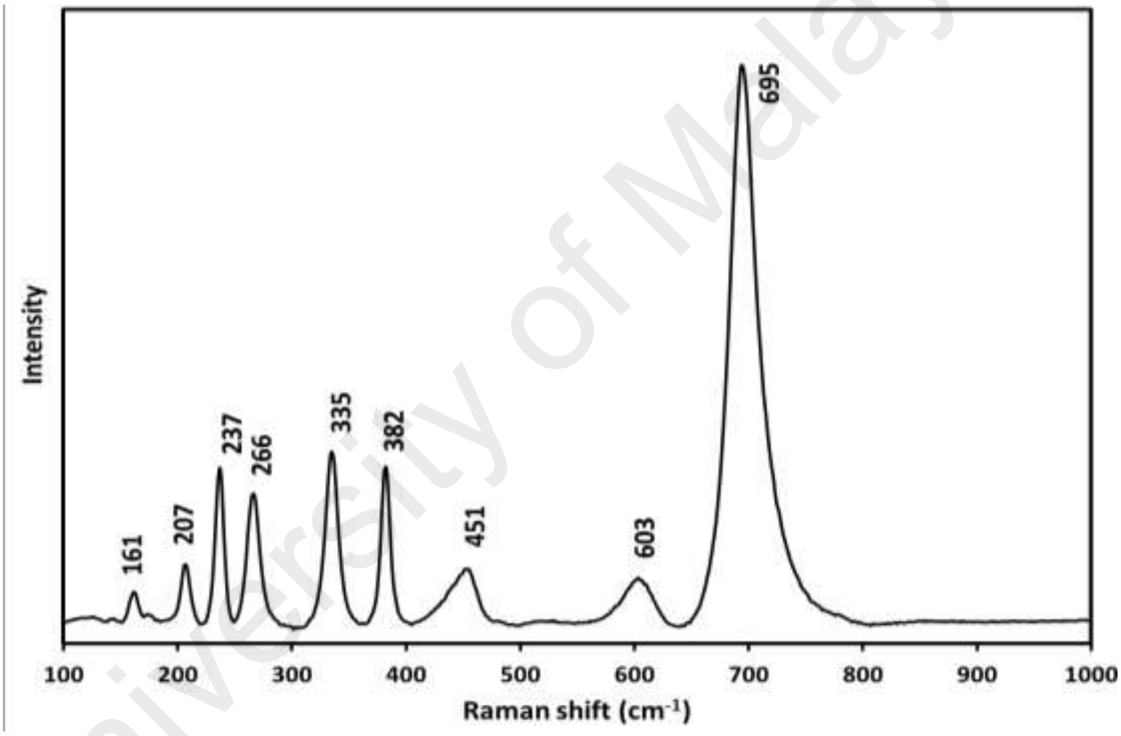


Figure 4. 18: Raman spectrum of $CoTiO_3/TiO_2$ catalyst.

4.2.2 Morphological studies

The change in surface morphology of the as-synthesized $CoTiO_3/TiO_2$ catalyst before and after vanillyl alcohol oxidation reaction was studied by scanning electron microscopy and images are shown in Figure 4. 19. Before carrying out the catalytic reaction, $CoTiO_3/TiO_2$ catalyst was comprised of large size crystallites (Figure 4. 19a), and high resolution image reveals the rough and stony surface of the catalyst (Figure 4.

19b). It was generally believed that the rough surface of the catalyst was because of its high surface areas which can better perform the catalytic action as compared to smooth and plane surface which has less surface area. After carrying out oxidation reaction, the morphology of $CoTiO_3/TiO_2$ changes to oval shaped crystallites which exhibit smooth and plane surface (Figure 4. 19 c and d).

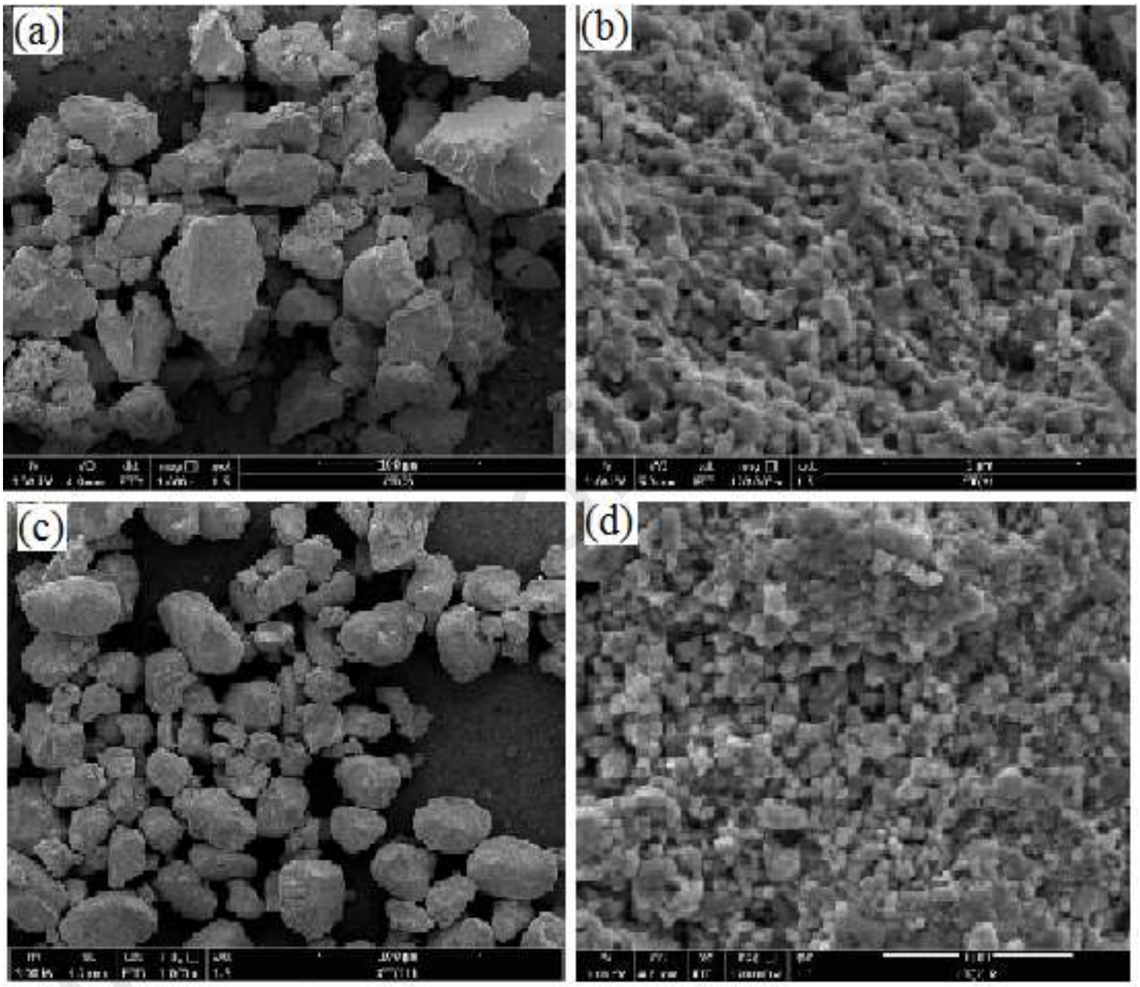


Figure 4. 19: Surface topographic images of $CoTiO_3/TiO_2$ composite catalyst (a and b) before vanillin oxidation reaction; (c and d) after vanillin oxidation reaction.

4.2.3 Compositional studies

The stoichiometric composition of the catalyst before and after the catalytic oxidation reaction was established by energy dispersive X-ray analysis and EDX spectra as shown in Figure 4. 20. It was observed that the elemental composition of the catalyst before and after catalytic oxidation reaction remained unchanged and EDX spectra showed the expected stoichiometric ratio indicating that the composition of the catalyst before and after oxidation reaction was $CoTiO_3/TiO_2$. The molar ratio of Co/Ti obtained from different peak areas of the EDX spectra was close to the expected 1:1 ratio of $CoTiO_3$/ TiO_2. Figure 4. 21 indicates the EDX mapping of $CoTiO_3/TiO_2$ catalyst before and after the catalytic oxidation reaction and reveals that Co, Ti and O atoms are homogeneously distributed throughout the catalyst’s surface.

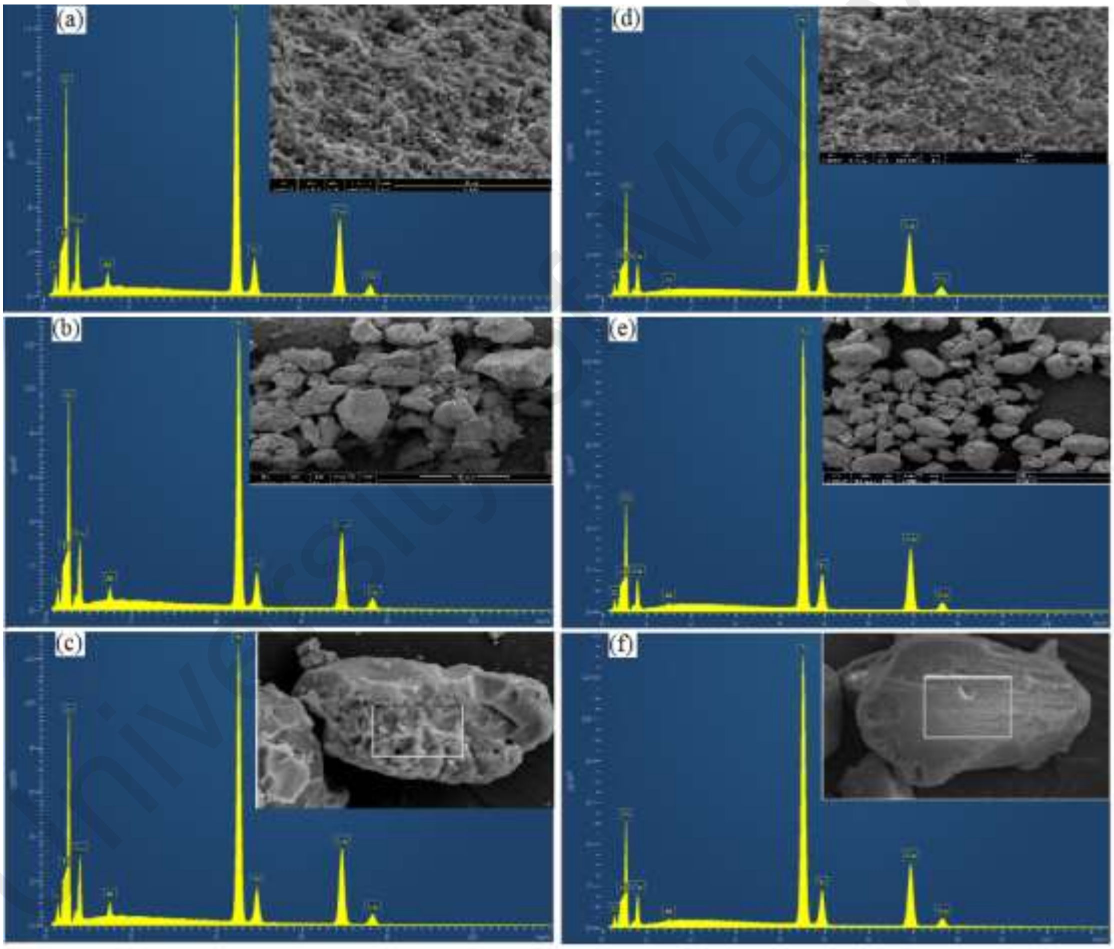


Figure 4. 20: EDX spectra revealing the stoichiometric composition of $CoTiO_3/TiO_2$catalyst (a-c) before and (d-f) after oxidation reactions.

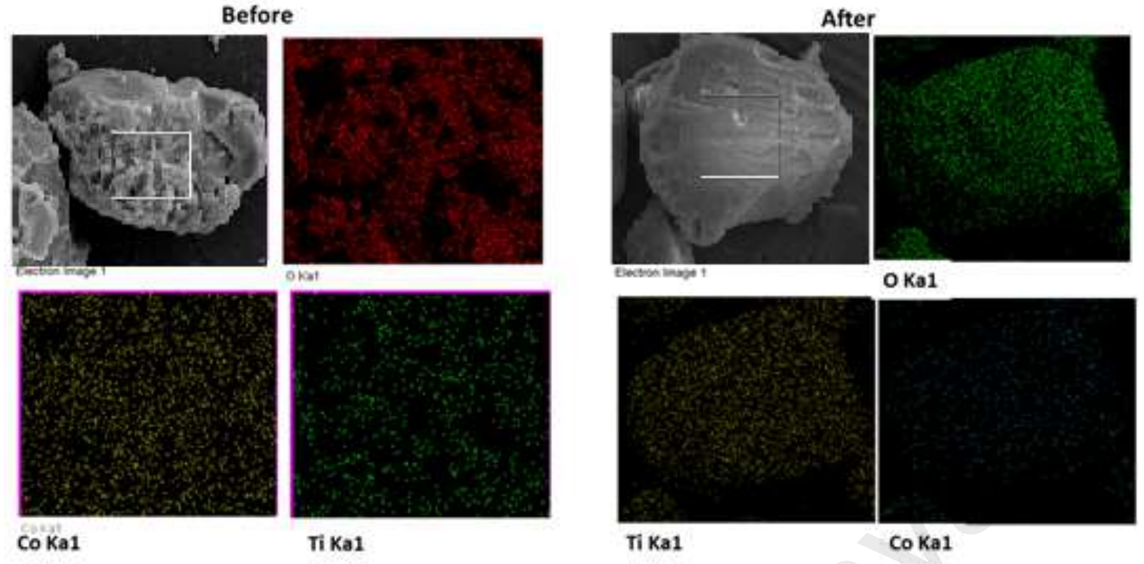


Figure 4. 21: EDX mapping revealing the distribution of Co, Ti and O atoms on the surface of catalyst before and after oxidation reactions.

4.2.4 Liquid phase oxidation of vanillyl alcohol over $CoTiO_3/TiO_2$ composite catalyst

To determine the optimum reaction condition of vanillyl alcohol oxidation, various reaction parameters were studied such as effect of time, catalyst amount, and molar ratio of vanillyl alcohol: H_2O_2, reaction temperature, solvent type and the effect of alkaline medium on the reaction. Under the optimum reaction condition, the oxidation of vanillyl alcohol without catalyst did not show any activity. The reusability analyses were also performed, but no activity was recorded. Moreover, the reactions were also performed under optimum reaction conditions in alkaline medium. The idea behind using base is probably to deprotonate the phenolic-OH to form the phenoxy anion, which is more reactive and easier, favours coordination to $CoTiO_3$ and resulting higher selectivity to vanillin and increasing the activity (Burriel et al., 2005). The reaction scheme for the oxidation of vanillyl alcohol is shown in Figure 4. 22.

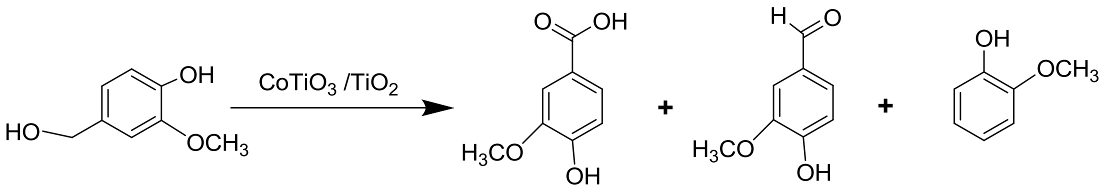


Figure 4. 22: Liquid phase oxidation of vanillyl alcohol products in $CoTiO_3/TiO_2$ catalyst.

4.2.4.1 Influence of reaction time

The effect of reaction time on vanillyl alcohol conversion and selectivity to vanillic acid and vanillin were studied for $CoTiO_3/TiO_2$ and the results are shown in Figure 4. 23. The conversion increased slowly from 16% to 52% when the time was increased from 30 min to 4h. However, further extending the reaction time to 6h did not improve the oxidation. Based on the highest conversion, the 4h reaction time was selected as an optimum time for this catalytic system. However, the selectivity of vanilic acid was found to decrease from 82% to 75% within time increase, this decrease was consistent with the increased selectivity of vanillin from 15% to 21% in reaction time 30 min to 4h.

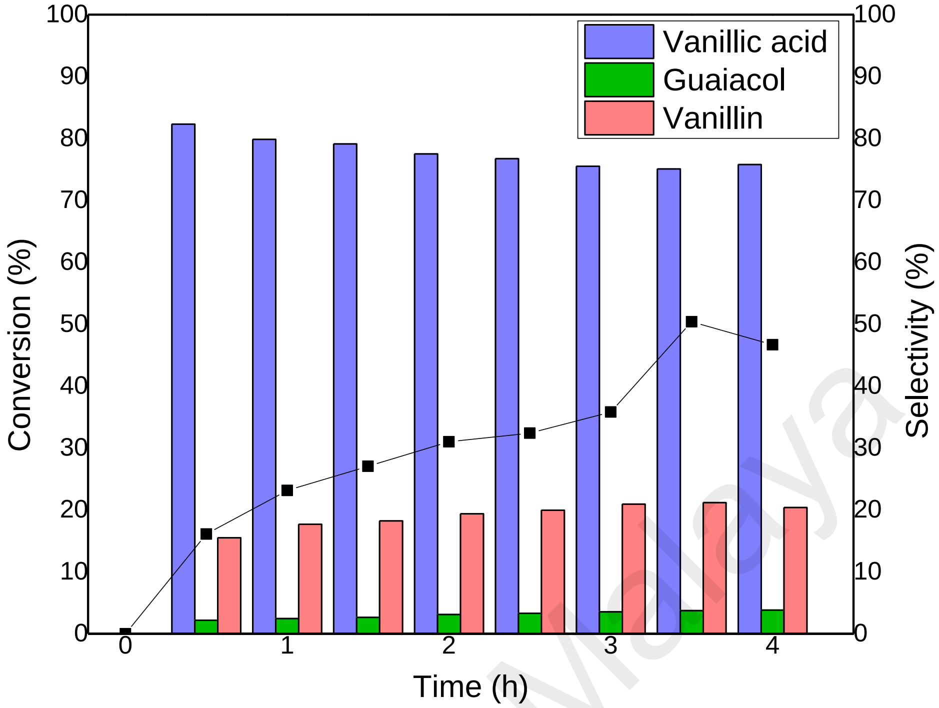


Figure 4. 23: Effect of time on conversion and selectivity. Reaction condition: amount of $CoTiO_3/TiO_2$ (50 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.2.4.2 Catalytic activity with different mass of catalyst

The prepared catalyst was tested in liquid phased oxidation of vanillyl alcohol. As illustrated in Figure 4. 24, as the mass of the catalyst increased, the conversion of vanillyl alcohol to corresponding product was found to increase sharply from 24% to 47% when the catalyst mass used was increased from 25 to 50 mg. The selectivity of acid formation was found to slightly decrease as the catalyst mass was increased. However, further increase in the catalyst mass to 125 mg resulted in a decrease in a vanillyl alcohol conversion to 40%. The reason behind that could be due to the rapid decomposition of H_2O_2 over the large surface area available with a higher mass catalyst (Chuang et al., 2010). As a result, the selectivity of vanillin was observed to slightly increased with the decreased in the formation of vanillic acid. On the other hand, the absence of the catalyst leads to maximum value of 3% vanillyl alcohol conversion to vanilic acid.

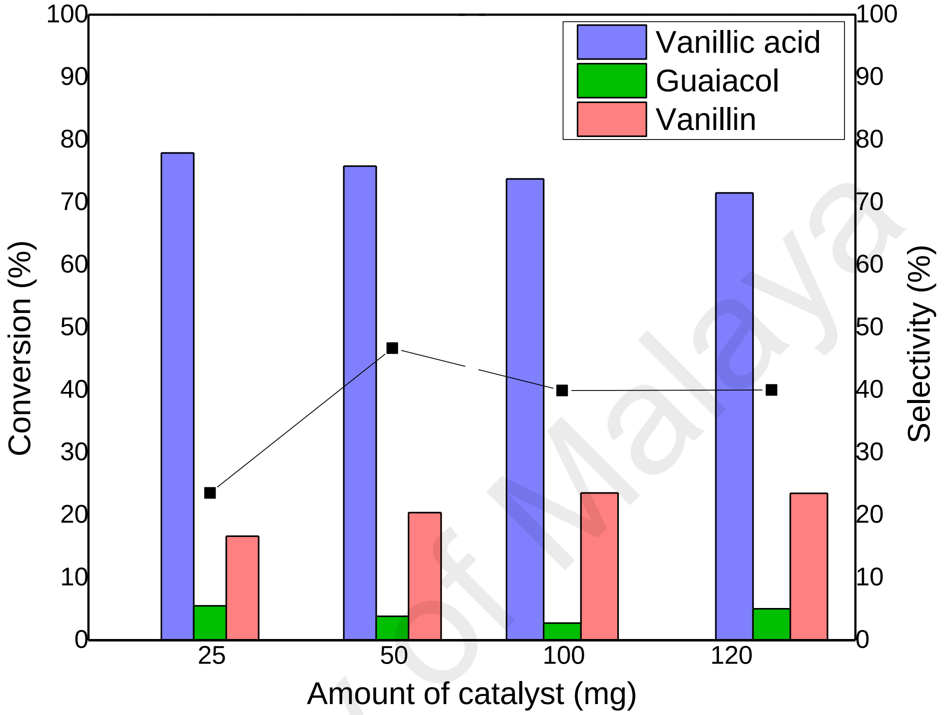


Figure 4. 24: Effect of catalyst loading on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.2.4.3 Influence of temperature

The reaction temperature was found to have a great influence on the conversion of the reaction. Thus, in the oxidation of vanillyl alcohol the effect of temperature on the reaction was studied in the range of 338-363 K (Figure 4. 25). The reaction was conducted at a fixed parameter (vanillyl alcohol: H_2O_2 molar ratio 1:2 and a catalyst amount of 50 mg in 25 ml acetonitrile). The conversion was found to increase from 16 % at 338 K to 47 % at 363 K. The plausible explanation for this observation could be due to the enhanced decomposition of H_2O_2 at high temperature (Chuang et al., 2010). However, there was no significant change in the selectivity of vanillic acid and vanillin at different temperature. Therefore, 358 K was preferred as suitable reaction temperature for the subsequent optimization studies, since there are moderate conversion and rapid decomposition of H_2O_2.

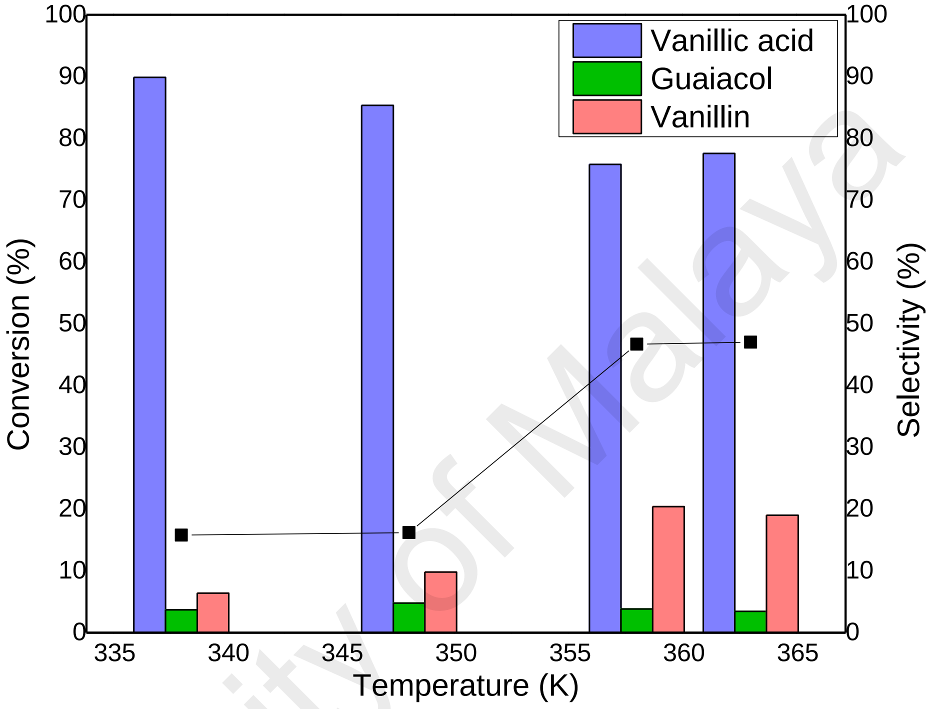


Figure 4. 25: Effect of reaction temperature on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillyl alcohol: H_2O_2 (1:2); amount of $CoTiO_3/TiO_2$ (50 mg); acetonitrile as solvent (25 ml).

4.2.4.4 Influence of H_2O_2 mole ratio

To determine the optimum ratio of H_2O_2 needed for this oxidation of vanillyl alcohol reactions, 4 different ratios were studied. The results obtained from the reactions are shown graphically in Figure 4. 26. The conversion ranged from 22-46% for 1 to 4 H_2O_2 molar ratios. However, the results clearly showed that when H_2O_2 was taken in more than equimolar ratio (vanillyl alcohol: H_2O_2:1:2, 1:3), the conversion significant increased (~46%). Generally, the decomposed of H_2O_2 produced water as by-product (Jha & Rode, 2013), and that might poison the catalyst by adsorbing strongly to the catalyst $CoTiO_3/TiO_2$ surface and blocked the active site, thus inhibiting conversion of vanillyl alcohol to other products. Furthermore, decomposition of H_2O_2 increased the formation of vanillic acid, while the formation of vanillin did not significantly change. Unlike, it can be seen from Figure 4. 26, which indicates that an increase in H_2O_2 in more than 2 equimolar ratios did not significant change in the performance of the catalyst.

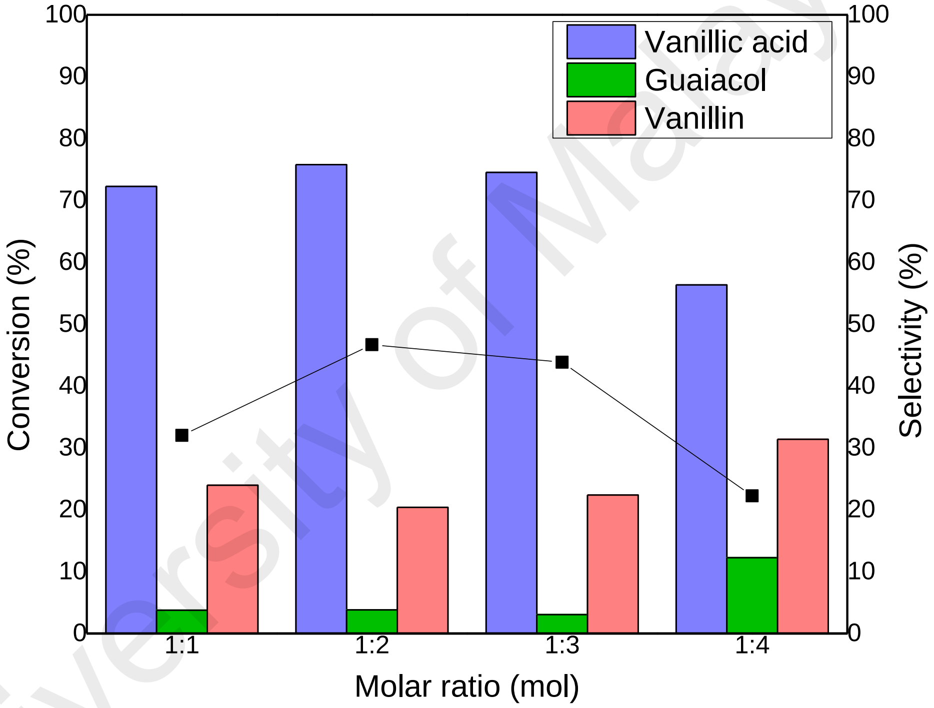


Figure 4. 26: Effect of molar ratio on conversion and selectivity. Reaction condition: reaction time (5 h); amount of$CoTiO_3/TiO_2$ (50 mg); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.2.4.5 Reusability of the catalyst

In order to study the stability of $CoTiO_3/TiO_2$ heterogeneous catalyst, the regeneration test carried out. After observing the completion of the reaction over a fresh catalyst which was carried out as mention in typical method for the oxidation of vanillyl alcohol, the liquid contents were removed from the flask and $CoTiO_3/TiO_2$ catalyst washed several times with acetone. Then dried under vacuum at 100 °C for 2 h. This dried catalyst was reused in a second cycle for the oxidation of vanillyl alcohol and a similar procedure was followed for four subsequent oxidation cycles, the result is depicted in Figure 4. 27. It can be observed that the vanillyl alcohol conversion decreased very slowly after the third and fourth reuse. However, the selectivity of the vanillic acid and vanillin was found with slight changes after third recycle. To further confirm the catalytic nature of $CoTiO_3/TiO_2$ after the fifth cycle, the reused catalyst was subjected to XRD, SEM and Raman analysis.

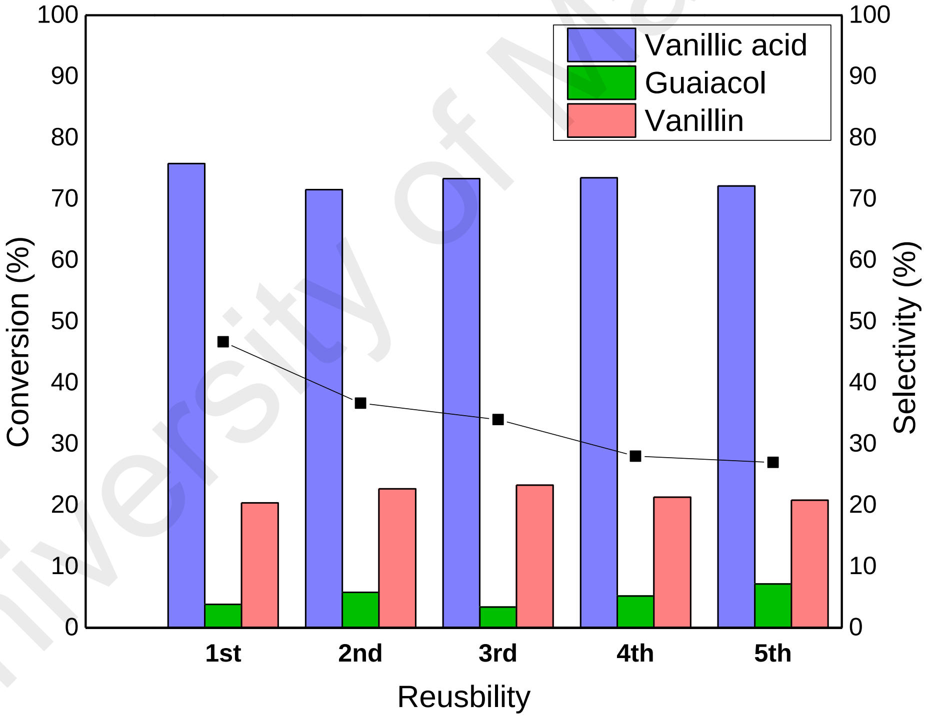


Figure 4. 27: Effect of re-used catalyst (reusability) on conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3/TiO_2$ (50 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

4.2.4.6 Influence of solvent

The influence of solvents on the oxidation of vanillyl alcohol and vanillin selectivity were investigated over sixth different solvent system with 50 mg catalyst mass and 1:2 vanillyl alcohol: H_2O_2 molar ratio, the result is represented in Figure 4. 28. Based on the experiment, highest conversion was achieved in acetic acid (80%) followed by ethyl alcohol (70%), acetonitrile (46%), *N*,*N*-dimethyl formaldehyde (35 %), tetrahydrofuran (20 %) and acetone (1%). Keeping the above fact in view, it is understood that the increasing conversion by using acetic acid as a solvent was directly proportional to the formation of peracetic acid which was *in-situ* generated by reaction with acetic acid and H_2O_2 in the presence of an acid catalyst. And this in turn accelerated and acted as an oxidant source for the oxidation reaction, as shown in Figure 4. 29. However, the selectivity of vanillin was significant increased when acetic acid used as a solvent compared to other solvents, this could be due to the possibility of formation O_2 higher than radical hydroxide. Nonetheless, acetic acid was chosen as the optimal solvent media due to formation of peracetic acid and this led to higher conversion and increases the selectivity to vanillin. So under these reaction conditions, in the oxidation of vanillyl alcohol to vanillin, a major role is played by peracetic acid conversely to oxidation of vanillyl alcohol to vanillic acid.

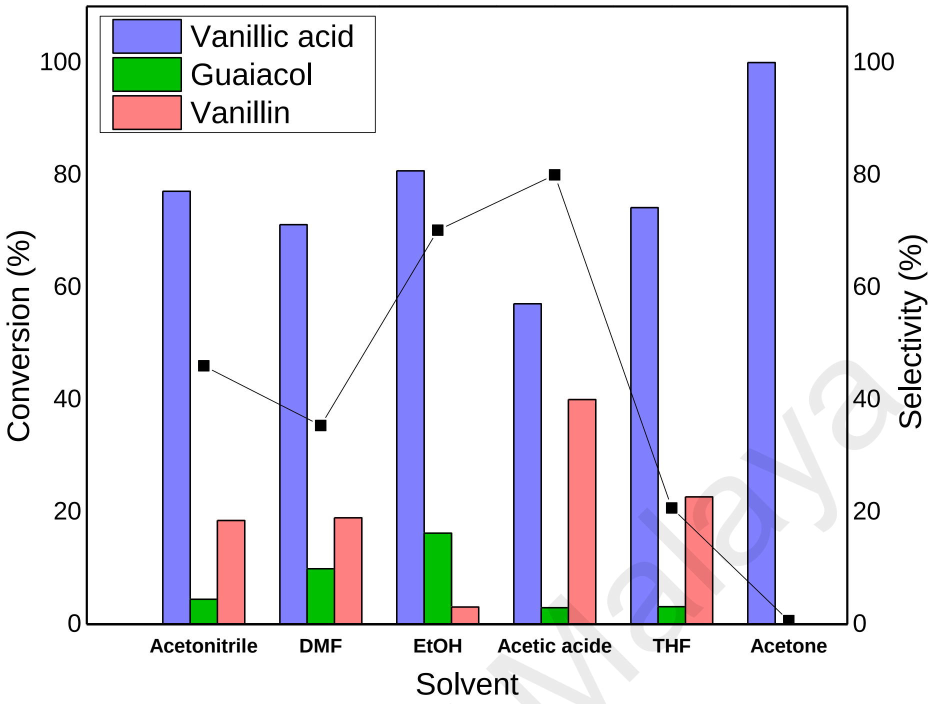


Figure 4. 28: Effect of solvent on vanillyl alcohol conversion and selectivity. Reaction condition: reaction time (4 h); amount of $CoTiO_3/TiO_2$ (50 mg); molar ratio of vanillyl alcohol: H_2O_2 (1:2); reaction temperature (358 K).

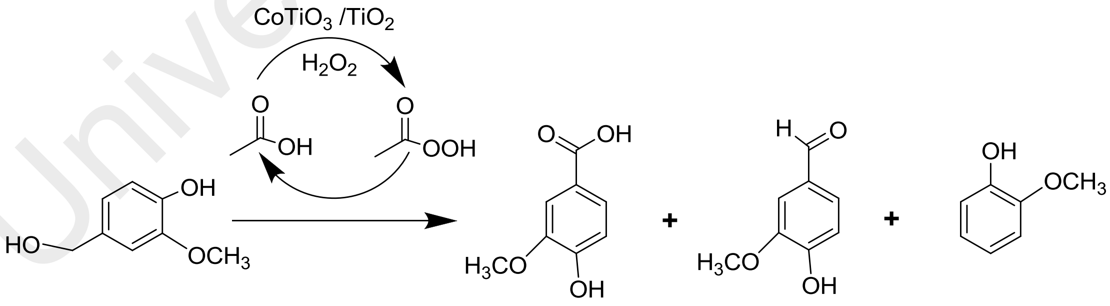


Figure 4. 29: Role of formation peracetic acid in oxidation of vanillyl alcohol by $CoTiO_3/TiO_2$ Catalyst.

4.2.4.7 Influence of basic medium

The effect of NaOH on the conversion and selectivity of aldehyde product (vanillin) in the oxidation of vanillyl alcohol is displayed in Figure 4. 30. The adding amount of the base (NaOH) has been used equivalent to H_2O_2 (2.0 mmol).The role of using alkaline is probable to deprotonate the phenolic to form the phenoxy anion, In addition, it seems that the generation of sodium peroxide occurs immediately after adding H_2O_2 to alkaline oxidation reaction mixture. The latter, can be used as an oxidizing agent as well as oxygen source and that enhance and accelerate the reaction activity and the selectivity of aldehyde. However, due to poor solubility of NaOH in acetonitrile, acetic acid was choosen to examine the effect of alkaline on the oxidation of the vanillyl alcohol reaction. It is observed that the highest conversion achieved with acetic acid (99%).

$$H_2O_{2\,(aq)} + 2NaOH_{(s)} \rightarrow Na_2O_2 + 2H_2O \qquad 4.3$$

$$Na_2O_2 + 2H_2O \rightarrow O_2 + 4NaOH \qquad 4.4$$

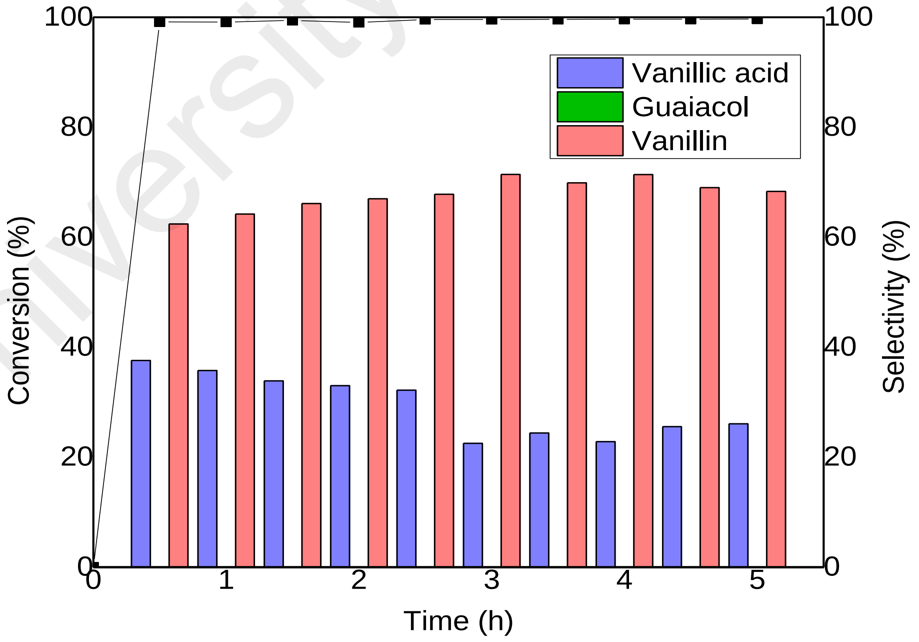


Figure 4. 30: Effect of basic media on conversion and selectivity. Reaction condition: amount ofCoTiO$_3$/TiO$_2$ (50 mg); molar ratio of vanillyl alcohol: H$_2$O$_2$ (1:2); reaction temperature (358 K); acetic acid (25 ml) NaOH (0.15 gm).

CHAPTER 5: CONCLUSION AND FUTURE WORKS

5.1 Conclusion

The $CoTiO_3$ and $CoTiO_3/TiO_2$ catalyst were prepared by mixing equimolar $Co(OAc)_2$ and Ti(i $Pro)_4$ in methanol followed by calcination at 500 °C. The as synthesized $CoTiO_3$ and $CoTiO_3/TiO_2$ materials were characterized by XRD, SEM, EDX and Raman and subsequently employed for the catalytic oxidation of vanillyl model compound with the co-promoter of H_2O_2 in acid and base medium. Presences of titanium species were responsible for their enhanced catalytic activity.

In the presence of $CoTiO_3$ catalyst, oxidation of vanillyl alcohol produced vanillin product as the major component in basic condition (99.8%) while the highest conversion was obtained in the acid medium (99%). On the other hand, in case of $CoTiO_3/TiO_2$ catalyst, the highest conversion (99%) was registered in the acetic acid as a solvent in presence of NaOH while in the absence of NaOH, the vanillin conversion was 80%. These could be attributed to the formation of peracetic acid. However, no products were obtained without the presence of the catalyst. In the present study, we identified that $CoTiO_3$ possesses excellent catalytic properties which could be used for practical applications. Through a simple regeneration technique, the prepared catalyst was found to be stable and could be reused several times with just a minor loss in activity observed initially.

5.2 Future works

In future, the multifunctional cobalt titanate over Titania-dioxide nano catalysts will be developed to oxidize the lignin model compound (veratryl alcohol) to platform chemicals. Moreover, SBA-15 supported gold catalyst will also be developed for the oxidation of vanillyl and veratryl alcohol and further characterized with SEM, EDX, XRD, RAMAN, TPO, and XPS.

LIST OF PUBLICATIONS AND PAPERS PRESENTED

Academic journals:

1. Sharifah Bee Abd Hamid, **Mariom Zamila Shilpy**, and Md.Eaqub Ali. "Green Catalytic Approach for the Synthesis of Platform Chemicals from Palm Tree Lignin."*Advanced Materials Research* 925 (2014): 62-66
2. **Mariom Zamila Shilpy**, Tammar Hussein Ali, Muhammad Ali Ehsan, Sharifah Bee Abd Hamid and Md Eaqub Ali. "Performance of cobalt titanate towards H_2O_2 based catalytic oxidation of lignin model compound", *RSC Advances 5.97 (2015): 79644-79653.*
3. **Mariom Zamila Shilpy**, Tammar Hussein Ali, Muhammad Ali Ehsan, Sharifah Bee Abd Hamid and Md Eaqub Ali. "Nanocomposite of $CoTiO_3/TiO_2$ oxides for liquid phase catalytic oxidation of Vanillyl alcohol", *RSC Advances* – **under preparation**.

International conferences:

1. Sharifah Bee Abd Hamid, **Mariom Zamila Shilpy**, and Md. Eaqub Ali. "Green Catalytic Approach for the Synthesis of Platform Chemicals from Palm Tree Lignin." *Advanced Materials Research* 925 (2014): 62-66.

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