"SULFUR, NITROGEN REMOVAL FROM MODEL FUEL BY USING OXIDATIVE METHOD"

by

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May, 2015

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Major Project

Submitted in partial fulfilment of requirements
for the degree of

Maters of Technology

In

Chemical Engineering
(Environment Process Design)

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May, 2015

Dedicated

To My Late Grandmother Vandana Gopalkrishna Shah
And
My Family

Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Nirma University and has not been submitted elsewhere for a degree.
2. Due acknowledgement has been made in the text to all other material used.

Disha Yogeshkumar Shah

Undertaking for the Originality of the Work

Shah Disha (13mche11) gives the undertaking that the major project entitled "Sulfur, Nitrogen removal from model compounds by using oxidative Methods" submitted by me, towards partial fulfilment of the requirements for the degree of Masters in Technology in Chemical Engineering (Environment Process Design), Institute of Technology, Nirma University, Ahmedabad is the original work carried out by me and I give the assurance that no attempts of plagiarism has been made. I understand that in the event of my similarity found subsequently with any published work or any dissertation work elsewhere it will result in severe disciplinary action.

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This is to certify that the Major Project entitled " SULFUR, NITROGEN REMOVAL FROM MODEL FUEL BY USING OXIDATIVE METHODS " submitted by Miss DISHA SHAH (13MCHE11), towards the partial fulfilment of the requirements for the degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Institute of Technology, Nirma University, Ahmedabad is the record of work carried out by her under our supervision and guidance. The results embodied in this major project are based on literature and research in RIL R&D.This data is based on proprietary catalyst of RIL and hence only RIL reserves the rights to patent,publish and present the data.

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Disha Yogeshkumar Shah

Abstract

Thiophene and its aromatic derivatives are the major sulphur compounds usually present in petroleum fractions as a pollutant. Oxidative desulfurization using Titanium Silicate (TS-1) as catalyst provides a promising deep desulfurization process which is an alternative to traditional HDS. The oxidative desulfurization of thiophene in a synthetic mixture of thiophene and octane was investigated with the commercial catalyst (TS-1) loaded with different metals like iron, molybdenum, cerium by incipient wetness impregnation method. The oxidizing agent used for the reaction was 30 wt% hydrogen peroxide. Catalyst were characterized by X-ray Diffraction, SEM/EDS, BET surface Area, TPD. Among all the catalysts examined the iron loaded on TS-1 catalyst showed the highest conversion .The different parameters that affect ODS reaction like speed of agitation, catalyst particle size, thiophene to hydrogen peroxide ratio, catalyst quantity and reaction temperature were studied. All the process parameters were optimized.

The study of nitrogen compounds was carried out at different temperature and also the effect on sulfur (Thiophene) conversion in presence of nitrogen compound (Quinoline) was studied. On the basis of this the kinetics of the reaction was carried out and activation energies were calculated.

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Chapter 1

Introduction

1.1 Introduction to Refinery

The crude oil is refined to produce various products like gasoline, diesel, naptha, coke, kerosene, etc. through various refining processes namely distillation, hydrotreating, catalytic reforming, fluid catalytic cracking, coker, steam reforming, hydrocracking, alkylation, etc. Crude consists of various components like organic, inorganic, gases materials. Crude oil is obtained from wells mainly from deep sea drilling and ground wells. Crude oil is pale yellow to dark green in color with low viscosity. This color is due to various factors like impurities present in the form of organic compounds, metals, etc. Once the crude is drilled out from wells it is transferred through pipe lines (provided proper safety and heating) for further upgradation. The various products fuels, lubricating oils, waxes, asphalt, petrochemicals are obtained after refining processes. Gasoline, diesel, lubricating oil, bitumen, etc are products which are used on daily basis for transportation, road building, etc. which can only be obtained through series of processes in refinery. Crude consists of oxygenated, sulfur, nitrogen containing compounds which act as impurities and create problem for environment by generating SO_x, NO_x, carbonaceous materials [1].

The crude oil in the form of petrol, diesel, gasoline and jet fuel are used in vehicles. In this crude oil, the sulfur is present in various forms like organic compounds, inorganic compounds, hydrogen sulfide and elemental sulfur. The major portion of sulfur compounds are in the form of organic sulfur with over 200 sulfur containing organic compounds Classification of organic compounds can be done as : (I) aliphatic and aromatic thiols, and its oxidation products (bisulfides); (II) aliphatic and aromatic thioethers; (III) heterocycles based in thiophenic ring: thiophene, benzothiophene (BT), and dibenzothiophene (DBT) and its alkyl derivatives In general the crude oils with higher density contains high percent of sulfur. This variation in sulfur content from less than 0.1% to greater than 5% depends on the crude type and its source. The main sulfur compounds found in gasoline are thiophenic and non-thiophenic compounds, and in diesel oil benzothiophene and dibenzothiophene are the main source of sulfur [2].

The main objective of hydrotreating is to remove is to remove sulfur as well as other compounds which are undesirable and detrimental to the stability and meeting specifications of the product with respect to its performance and environment. Such compounds for example are - unsaturated hydrocarbons, nitrogen from refinery process streams. More stringent specifications, particularly those related to environment impact, has resulted in extensive application of hydrotreating processes as shown in Fig.1.1.

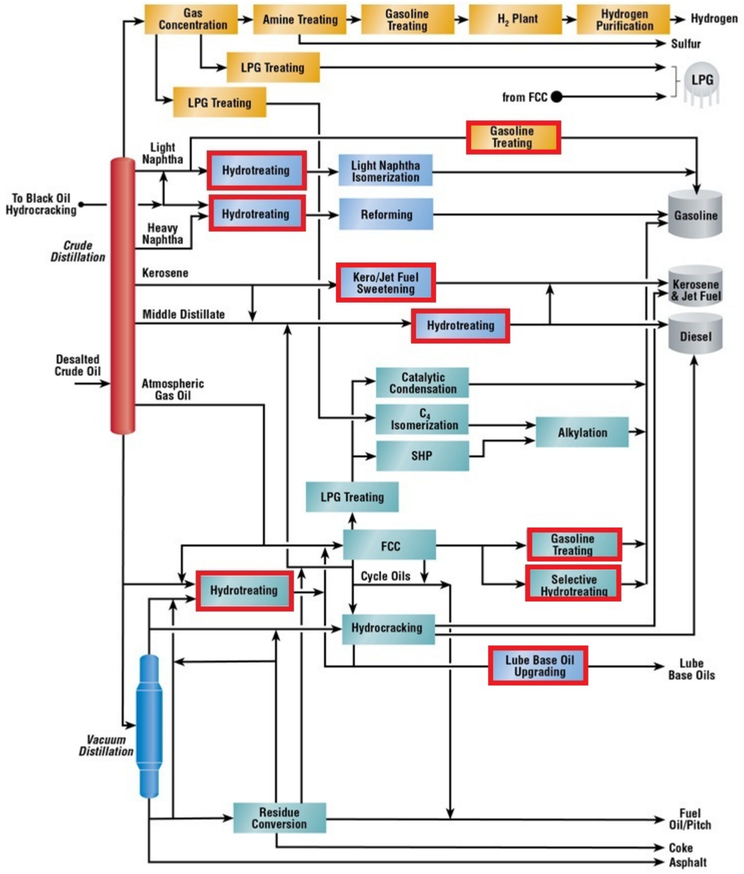
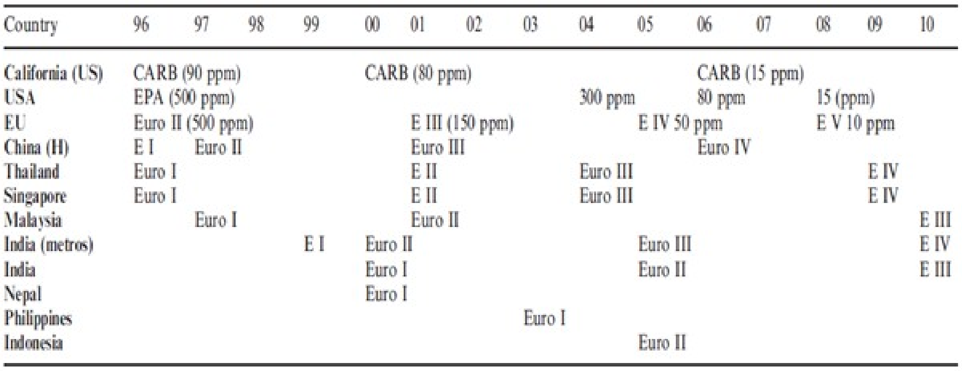


Figure 1.1: Refinery flow sheet

1.2 Sulfur Regulation

The quality of crude is deteriorating day by day and the sulfur reduction has become so important. In most of the western countries since past two decades the government has imposed strict legislative regulation for decreasing the sulfur content in transportation fuel. The sulfur content of diesel fuels had been limited to 15 ppm from a level of 500 ppm in 2006 by the U.S. Environmental Protection Agency [3]. In Europe the environmental regulations for on-road diesel fuels called for sulfur content reductions from the level of 350 to 50 ppm by 2005 and to 10 ppm by 2009 [4]. In India EURO IV standard has regulated the maximum sulfur content in gasoline and diesel at to 50 ppm since April 1, 2010 [5] Bharat Stage V standard specifies a maximum of 10 parts per million (ppm) of sulfur in fuel as against 50 ppm in Bharat Stage IV and Bharat Stage III 150 ppm [6] . Table 1.1 shows the roadmap of emission standard worldwide[7].

Table 1.1: Roadmap of emission standards worldwide



Country	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
California (US)	CARB (90 ppm)				CARB (80 ppm)						CARB (15 ppm)				
USA	EPA (500 ppm)								300 ppm		80 ppm		15 (ppm)		
EU	Euro II (500 ppm)					E III (150 ppm)				E IV 50 ppm			E V 10 ppm		
China (H)	E I	Euro II				Euro III					Euro IV				
Thailand	Euro I					E II			Euro III					E IV	
Singapore	Euro I					E II			Euro III					E IV	
Malaysia		Euro I				Euro II									E III
India (metros)				E I	Euro II					Euro III					E IV
India					Euro I					Euro II					E III
Nepal					Euro I										
Philippines								Euro I							
Indonesia										Euro II					

Crude consists of oxygenated, sulfur, nitrogen containing compounds which act as impurities and create problem for environment. The combustion of this sulfur contaminated fuel produces vast amount sulfur oxide into the atmosphere. These sulfur oxides are in the form of sulfur dioxide and sulfur trioxide which along nitrogen oxides with (NO_x) leads to poor air quality, acid rain and depletion of ozone layer. The presence of sulfur compounds in petroleum products leads to premature breakdown of combustion engine and also the corrosion in refinery equipment. Also sulfur poisons many catalysts that are used in the refining or catalytic conversion of gaseous effluents. Except these, sulfur compounds cause gum formation in gasoline fraction. Emission of SO_2 and sulfate particulate matter endangers public health and welfare [2].

1.3 Desulfurization

Desulfurization is defined as the removal of sulfur and sulfur containing compounds from hydrocarbons or hydrocarbon mixtures derived from petroleum or natural gas.

1.3.1 Hydro desulfurization (HDS)

Hydrodesulphurization is a conventional refinery process which involves catalytic treatment with hydrogen to convert the various sulfur compounds (e.g., mercaptans, disulfides, thiophenes, benzothiophenes and dibenzothiophenes), to H_2S and sulfur- free organic compounds at high temperature and high pressure of hydrogen typically in the range of 290^oC to 455^oC and 70 to 80 bar respectively. The alkyl-substituted derivatives are considered to be the most refractory sulfur compounds in the fuels due to the steric hindrance of the alkyl groups in HDS. Certain factors that limit the process are as follows

- With the HDS process it is difficult to remove last traces of sulfur without affecting the octane number.
- The necessity of pretreating the catalyst with a sulfur-containing stream prior to use in order to form the required metal sulfide phases.
- The catalyst cannot be regenerated The alkylated dibenzothiophenes are difficult to remove by this process, particularly in terms of requiring conditions that are much more severe and that substantially raise the fuel cost and reduce fuel production rates [7].

1.3.2 Biodesulfurization

Biodesulfurization is an enzymatic process to remove the organic sulfur compounds from the petroleum feed stock. This desulfurization process uses bacteria as catalyst or can be termed as biocatalyst for the removal of sulfur compounds. This process can take place under two conditions aerobic and anaerobic conditions. The research work done till date have reported following reduction for sulfur. The sulfur-specific desulfurization microbes can achieve 57% reduction in BT content 90% reduction in DBT content , 50% reduction in some of the alkyl derivatives of DBTs , higher than 80% desulfurization in HDS treated diesel and higher than 45% desulfurization in heavy oil. The certain disadvantages of the process are

1. Environmental conditions such as operating temperature, solvent used, toxin and nutrient availability to which the biological and enzymatic reactions are highly sensitive.
2. Besides, a pre- HDS treatment is usually required to provide a relatively low sulfur fuel.
3. Till date the biodesulfurization has been tested on bench scale. Pilot-plant tests are still under development with cost estimation and more detailed designs [7].

1.3.3 Adsorptive Desulfurization

An adsorptive desulfurisation process is developed to remove sulfur from various petroleum fractions including FCC gasoline. In the process solid sorbent is used and the process is based on moving bed technology .In the entire process the sorbent is counter currently brought in contact with the sulfur rich hydrocarbon stream. From the top of the adsorber the desulfurized hydrocarbon stream is obtained and spent adsorbent at the bottom. The spent sorbent is circulated into the reactivation reactor where organosulfur compounds and some adsorbed hydrocarbons are desorbed from the sorbent surface. The regenerated sorbent is recirculated back to the adsorber as shown in Figure 1.2 [7]. The research study related to this states that alumina is used as the sorbent and operates up to $240^{o}C$ at low pressure with a hydrocarbon/sorbent weight ratio of around 1.4. The same experimental condition in pilot plant experiments for FCC feedstock (1276 ppm S) and coker naphtha (2935 ppm) led to 90% reduction in sulfur.

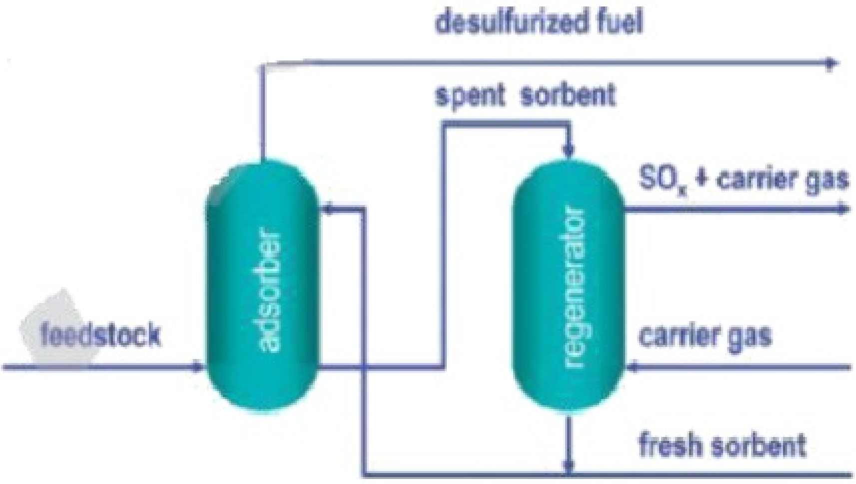


Figure 1.2: Adsorptive desulfurization

Reactive Adsorption

In reactive adsorption the sulfur rich stream comes in contact with solid sorbent in presence of hydrogen. Transition metals supported on base oxides are widely used in this process e.g. Cu/ZnO, Ni/Al_2O_3, Ni/ZnO, etc. Taking Ni/ZnO in consideration Nickel will react with the S-containing molecules under hydrogen to form NiS and then these sulfide ions are transferred to ZnO to form ZnS. In the course of the adsorption, the S-atom is removed from the molecule and retained by the sorbent on which it forms a sulfide phase, whereas the hydrocarbon is returned to the final product without any structural changes. The spent sorbent is continuously withdrawn from the reactor and transferred to the regenerator section. In a separate regeneration vessel, the sulfur is burned off the sorbent and SO_2 is sent to the sulfur plant. There are certain challenges for the process like developing an adsorbent with high adsorption capacity selectively for adsorption of aromatic sulfur compounds that are not removed by HDS. The regeneration of adsorbent is also difficult and requires frequent solvent washing and calcination. Moreover in order to minimize the number of turnovers large adsorbent beds are required. Repeated calcinations can also lead to a loss of surface area due to sintering; reducing the amount of sulfur a bed can remove [7].

1.3.4 Oxidative Desulfurization

Oxidative desulfurization is considered to be an alternative desulfurization processes to remove the aromatic sulfur compounds from the petroleum fractions which cannot be removed by hydrodesulfurization and meet the environmental norms. In ODS heavy sulfides are oxidized to sulfones in presence of oxidizing agent without breaking any carbon–sulfur bonds. The sulfoxides and sulfones produced after ODS have increased relative polarity, and are preferentially extracted using a non-miscible solvent .Oxidative desulfurization consists of two steps oxidation followed by extraction. The different types of oxidants used for ODS are: Air, oxygen, Hydrogen peroxide, Organic peracids, TBHP (tert-butyl hydroperoxide), Nitric acid, nitrogen oxides, ozone and combinations of any of the above. The different types of catalysts includes metals like titanium, vanadium, Cobalt, Iron, Chromium, Molybdenum or combination supported on alumina, silica-alumina, silica, natural and synthetic zeolite , MCM-41, SBA-15, TS-1, Ti-Beta, Ti-HMS, Ti-MWW, Siral-1. The catalysts used for the oxidative desulfurization of thiophene and its derivatives are TS-1, Ti-beta.Ti-HMS, alumina based catalysts.

1.3.5 General background of Catalysis

The Greek meaning of Catalysis is to “break down”. A catalyst facilitates a chemical reaction by lowering the activation energy of the reaction pathway. Catalyst increases the reaction rate and therefore the efficiency of the overall chemical process by lowering the activation energy as shown in Fig. 1.3[8]. In other words catalyst can be defined as “a substance, which increases the rate at which a chemical reaction approaches towards equilibrium, without itself becoming permanently involved in the reaction.” A catalyst can therefore only accelerate the rate of reaction, which is already thermodynamically feasible. Besides being responsible for a higher activity, catalyst also directs a reaction that influences the selectivity of a chemical process. In this respect, it is no wonder that more than 85 % of all bulk and fine chemicals are produced with the aid of catalysts.

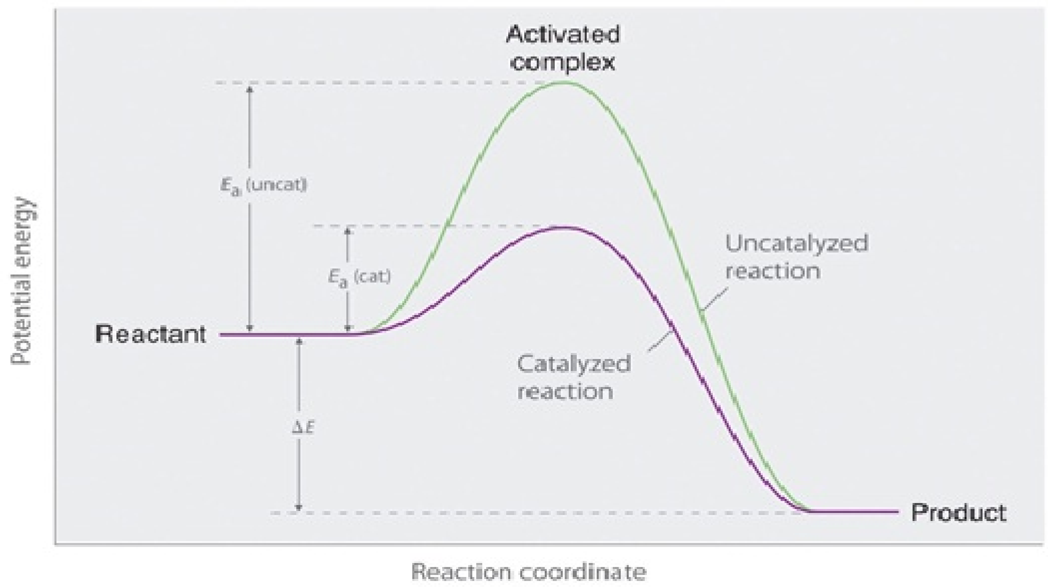


Figure 1.3: Catalysis and activation energy

Catalysis is divided in three types depending on the catalyst materials i) Bio-catalysis ii) Homogeneous catalysis and iii) Heterogeneous catalysis. In this section, only homogeneous and heterogeneous catalysis are considered. Bio-catalysis includes catalyst in the form of enzyme, cell etc. These are considered as ideal catalyst, as they can be operated in aqueous medium at room temperature and atmospheric pressure and with nearly 100 % selectivity. These catalysts were used for various reactions such as oxidation, reduction, etc. Homogeneous catalysis have reactants and products are in one phase. The homogeneous catalysts are more reactive and selective. When reaction system is differentiated with two or more phase then it is called as Heterogeneous Catalysis. In this type mainly the catalyst is in solid phase and products and / or reactants are generally in different phase. This area has been mostly exploited by researcher from last few decades, due to the high selectivity, easy separation and reusability of catalyst by simple procedure. On the basis of these advantages heterogeneous catalysis has become the basis of industrial and environmental chemistry during the last century[8].

1.4 Objective and Significance of the work

Significance of the work:

Lot of research and work has been carried out to obtain Ultra Low Sulfur (ULS) fuel. Because of the strict legislation by government to reduce the sulfur below 10 ppm it is necessary to find an efficient way to produce it.Many catalysts and oxidants have been reported as discussed in the literature Survey. Till date no work has been carried out on Fe/TS-1, Mo/TS-1 and Ce/TS-1 for desulfurization of petroleum fuel. So this work focuses on the synthesis, characterization of Fe/TS- 1, Mo/TS-1 and Ce/TS-1 as a catalyst and to optimize the process conditions and calculate the kinetics of reaction.

Objectives of work

1. To develop an alternative method for removal of sulfur which is more suitable for oxidation of thiophene in the gasoline range.
2. To modify the catalyst property to achieve higher conversion for Thiophene.
3. Preparation, Characterization and evaluation of the catalyst
4. Study the effect of nitrogen present along with the sulfur during oxidative desulfurization.
5. Kinetics of the reaction

1.5 Outline of thesis

The thesis will be presented in the following chapters:

- Chapter 2 presents literature review of oxidative desulfurization, followed by its detailed mechanism, along with the catalyst and the oxidizing agent used. The review describes the work done on till date on Oxidative Desulfurization.
- Chapter 3 gives a detail on materials and instruments used for catalyst preparation and explains the experimental work carried out. The chapter includes the techniques and procedures for catalyst preparation, characterization and evaluation using two dimensional gas chromatography.
- Chapter 4 gives results and discussion of experimental work done and kinetic analysis.
- Chapter 5 gives conclusion followed by bibliography.

Chapter 2

Literature Survey

2.1 Introduction

Oxidative desulfurization is the process of oxidation of divalent sulfur by oxygen to form hexavalent sulfur and sulfone under mild operating conditions. The reaction of oxidative desulfurization takes place under mild conditions.

The advantages of this process are

- Eliminates the use of expensive hydrogen in the process in comparison to HDS process.
- The refractory sulfur compounds that cannot be removed by HDS process can be easily converted by ODS process by oxidation of sulfur compounds followed by extraction.
- ODS avoids the aromatic and olefin saturation, and thus low octane number.
- ODS can lower the sulfur amount in petroleum fraction without negative impact on capital investment. Therefore, ODS has great potential to be complementary process to traditional HDS for achieving deep desulfurization [7], [9].

2.2 Mechanism of ODS

To understand the ODS mechanism thiophene is taken as a model compound. The reaction is a series reaction where thiophene is first oxidized to thiophene sulfoxide and water which is subsequently oxidized by another H_2O_2 molecule to form thiophene sulfone and water as a by product

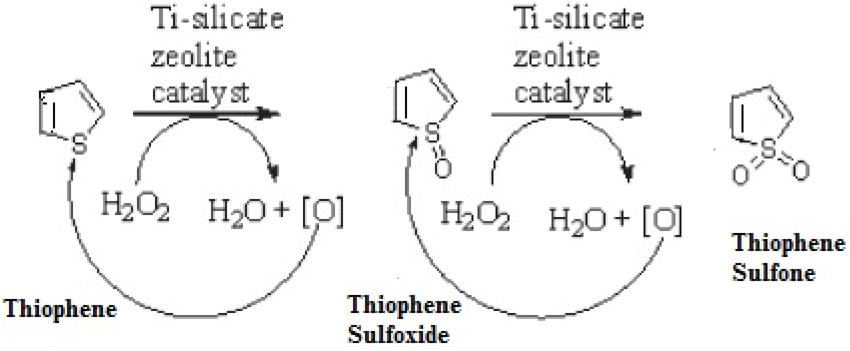


Figure 2.1: Reaction mechanism of ODS of thiophene

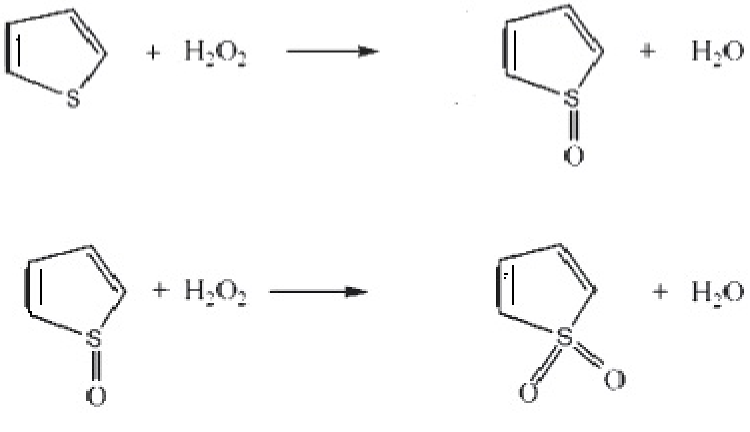


Figure 2.2: Reaction Scheme of ODS of thiophene

2.3 Catalysts

For oxidative desulfurization of thiophene and its derivatives in presence of oxidizing agents like hydrogen peroxide many catalysts has been reported like Titanium silicate ($TS-1$) [10], Ti-beta[10, 11], $Ti-HMS$[11]. Moreover $Ti/MCM-41$ has also been reported to be effective for thiophene conversion in presence of $H_2O_2.HCOOH$ [12]. Transition metal like Fe supported on MCM-41 has been reported to be effective for removal of DBT [13]. Also vanadium based catalysts supported on MCM-41 and Al_2O_3 has been reported to be effective for benzothiophenic compound. $Zr-ZSM-5$ supported on $SBA-15$ mReactive Adsorption olecular sieves and $Ti/SBA-15$ has been reported effective for ODS of light cycle oil [14], [15].

2.4 Oxidizing Agents

Potential catalytic oxidative routes have reported to produce low sulfur fuels which include various types of oxidants like Nitrous oxide and air [16], ozone [17], molecular oxygen with Pt/CeO_2, $CuO/ZnO/Al_2O_3$, Cu/CeO_2 as catalyst, Oxygen with iron for thiophenic compound [18]. Hydrogen peroxide with phosphotungstic acid supported on ceria for DBT removal has also been reported. Heterogeneous titanium (IV) catalyst and organohydroperoxide oxidant, such as tert-butyl hydro peroxide (TBHP), cumyl hydroperoxide (CHP) and/or ethylbenZene hydroperoxide (EBHP), has been reported to be effective for the selective oxidation and removal of refractory sulfur compounds from diesel fuel [19]. Hydrogen peroxide has been reported to show good oxidative desulfurization with titanium substituted molecular sieves like $TS-1, Ti-Beta$ [11] In oxidative desulfurization processes most widely used oxidizing agent is hydrogen peroxide (H_2O_2) and it is considered as "green" reagent. When the ODS reaction takes place in presence of hydrogen peroxide, water and oxygen are the only by products. These by products have no adverse effect on the environment. The degradation of hydrogen peroxide can be illustrated in the following chemical equation 2.1 :

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{2.1}$$

Table 2.1: Oxygen-donor Oxidants

Sr.No	Oxidant	Active Oxygen (% wt.)	By-Product
1	Hydrogen Peroxide (pure)	47.1	H_2O
2	O_3	33.3	O_2
3	HNO_3	25.4	NO_x
4	$t - BuOOH$	17.8	$t - BuOH$
5	$H_2O_2(30\% wt.)$	14.1	H_2O

For safety purpose, aqueous solution of 30% wt. of hydrogen peroxide is more commonly used. Although pure hydrogen peroxide has a high active oxygen ratio, dilution effect should be considered as it would significantly reduce the active oxygen ratio [20]. Active oxygen ratios of some common oxidizing agents are listed in Table 2.1.

Chica et al [21] performed the oxidative desulfurization on model sulfur compounds (thiophene, 2-methylthiophene, benzothiophene, 2-methylbezothiophene, dibenzothiophene, 4- methyldibenzothiophene, and 4, 6-dimethyldibenzothiophene) and partially hydrotreated industrial diesel fuel using TBHP as an oxidizing agent. The catalysts used were $Ti - MCM - 41$ calcined, Ti-MCM-41 silylated, MoO_x/Al_2O_3. Catalyst Deactivation was reported due to adsorption of the high polar sulfones on the surface of Ti-MCM-41C and MoO_x/Al_2O_3. However, silylating Ti-MCM-41 being a more hydrophobic catalyst the amount of adsorbed sulfones decreased significantly increasing catalyst life.

Baoshan Li et al [13] performed the ODS on DBT as a model compound using hydrogen peroxide as an oxidizing agent and $Fe - MCM - 41$ as a catalyst. The mesoporous structure of MCM-41 did not collapse until the Fe content reached up to 13.21 wt. %. The catalyst activity started to decrease due accumulation of Fe_2O_3 and it was detected with iron content higher than 11.75%. The ODS of DBT in presence of hydrogen peroxide at 50^oC exhibited high conversion for DBT removal. Even after being recycle for four times the sulfur removal did not decline.

Abdalla et al [22]synthesized $(Bu_4N)_4H_3(PW_{11}O_{39})/MCM-41$ a catalyst which is mesoporous in nature and performed ODS of FCC (fluidized catalytic cracking) cycle oil, DBT and thiophene under mild reaction conditions. Even after dispersion of tetrabutylammonium encapsulated lacunary Keggin units TBA–POM on MCM-41 surface the structure did not collapse and this was confirmed with characterization results. For DBT the sulfur content was reduced from 500ppm to 1ppm and for thiophene it reduced from 320ppm to 2 ppm of sulfur. Also ODS of real FCC cycle oil with 974 ppm S reduced the sulfur contents to a level of 27.3 ppm.

Sengupta et al [10] carried out the oxidative desulfurization of benzothiophene with three different catalysts TS-1(commercial microporous), TS-1 (mesoporous), Ti-beta (mesoporous) in presence of 30% aqueous hydrogen peroxide. Among all three different Titanum silicate catalysts, TS-1 gave the highest conversion after three hours of reaction at 60^oC. Mesoporous TS-1 is found to give a conversion of 85.6%, while Ti-beta and commercial microporous TS-1 give conversions of 45.74 and 25.31%, respectively, under the same experimental conditions.

Jose et al [23] carried out the oxidative desulfurization of thiophene in a synthetic mixture of thiophene in iso-octane.The catalyst used was copper loaded on titanium silicate-1 (TS-1) in presence of 30 wt% hydrogen peroxide as oxidizing agent. The conversion obtained was around 93% and also the kinetics of reaction were carried out which gave the activation energy of 38.46 kJmole-1.

Kye-Sung Cho et al [15]studied the effects of nitrogen compounds(indole, quinoline, carbazole),aromatics, and aprotic solvents on the oxidative desulfurization (ODS)of refractory sulfur compounds in presence of Ti-SBA-15 as catalyst and TBHP as oxidizing agent.. These results suggested that the oxidized sulfur and nitrogen compouns were highly souble in aromatic and aprotic solvent., minimizing the deposit of oxidized product on the surface of catalyst.

Lina Yang et al.[24] performed the ODS of DBT in isooctane using HPWA-SBA-15 as a catalyst and TBHP as an oxidant. $HPWA-SBA-15$ has the typical structure of mesoporous molecular sieve SBA-15 and Keggin structure of $H_3PW_{12}O_{40}$ (HPWA). Desulfurization capacity of HPWA-SBA-15 was compared with that of other catalysts including SBA-15 modified with phosphorous acid or boric acid and microporous materials involving USY, $H\beta\, and\, ZSM-5$ molecule sieves modified with HPWA.The experiment results indicate that HPWA-SBA-15 has the highest desulfurization rate among so many catalysts involved in this paper at low temperature and atmospheric pressure. Not strong chemical action exists between sulfone and HPWA through hydrogen bond, and this chemical action is broken at 513 K, at this temperature HPWA and the molecular sieve are both stable, therefore the HPWA-SBA-15 may easily restore the catalytic activity.

Jeong et al. [25] performed the ODS of 4, 6 dimethyldibenzothiophene using TBHP as a oxidant in presence of he reported that for ODS reactions 15 wt.% molybdenum oxide loaded on Siral 1 is highly active. For model compounds and for LCO containing 8000 ppm sulfur Mo/Siral 1 with 3wt% of bismuth oxide gives better catalytic performance and stability of the catalyst is for 300 hours. The oxidation activity of catalyst decreases as the basicity of support increases was indicated from the results. Catalytic performance during ODS correlates well with the molybdenum oxide dispersion and acidic properties of the support.

Akbari et al[26] synthesized $MoO_3/\gamma - Al_2O_3$ catalyst by incipient wetness impregnation (IWI) method and performed the ODS on (BT), dibenzothiophene (DBT) and 4, 6-dimethyl dibenzothiophene in presence of hydrogen peroxide. After 1 hour reaction, 97.0%, 95.0% and 55.0% conversion is reached for DBT, 4, 6-DMDBT and BT with 10wt. % Mo.

Wang et al [27] synthesized pure mesoporous silica MCM-41, SBA-15, MCM-48 and carried out ODS on DBT, 4,6DMDBT using TBHP as an oxidant. 4, 6-DMDBT can be more easily oxidized than DBT using TBHP as oxidant on SiM41C catalyst.

Caero et al [28] carried out ODS of benzothiophenic compounds prevailing in diesel using hydrogen peroxide as an oxidizing agent. The oxidation activity of DBTs in presence of nitrogen compound (indole) for V catalyst supported on niobia or alumina gave higher catalytic activity than all the other catalysts (niobia > alumina > SBA-15 > titania > ceria > Al– Ti mixed oxide), supported on titania.

Otsuki et al [29] carried out the ODS of model sulfur compounds, real feeds, i.e., SR-LGO and VGO in presence of hydrogen peroxide and formic acid and tried to investigate the relationship between the electron densities of sulfur atoms and reactivities. The sulfur compounds with low electron density like thiophene (5.696), 2-methyl thiophene (5.706) did not oxidize. But compounds with high electron density like benzothiophene, DBT, etc. oxidized to sulphones.

Ishihara et al [30] performed the oxidation of LGO which contained 39 ppm of sulfur in presence of 16 wt% Mo/Al_2O_3 as a catalyst and hydrogen peroxide as an oxidizing agent. The oxidizing agent to sulfur ratio was kept 15:1.After the oxidation and adsorption on silica gel the sulfur reduced to 5ppm which was remarkable. With the same process conditions nitrogen containing model compounds were treated and the denitrogenation performance decreased in the order indole > quinoline > acridine > carbazole. In LGO the N content decreased from an initial value of 13.5 ppm to a value of 0.8 ppm. Kinetics indicated that the reaction is pseudo first order reaction.

Jia et al [31] studied the effect of removal of sulfur from model fuel (Thiophene in octane) in presence of Ti-containing catalyst and hydrogen peroxide as a oxidizing agent in the presence of N-containing compounds. From different nitrogen compounds pyrrole and pyridine had adverse effect on removal rate of sulfur whereas Quinoline and indole did not influence the oxidation of thiophene. The adsorption of pyridine and quinoline on catalyst is stronger than that of sulfides because of basic nature of nitrides.

Selvavathi et al [32] reported the study oxidation of refractory sulfur compounds in presence of Ni-Mo catalyst (catalyst used for HDS) and TBHP as an oxidizing agent. The temperature of the reaction was in the range of 80 to 120^oC.The bulkier compounds got oxidized at higher temperature of 120.When the kinetics was carried out for the reaction the rate constant values were higher in comparison to HDS for bulkier compounds. The apparent activation energies obtained were in the range of 27–30 KJ/mol for C_2DBTs and 32–34 KJ/mol for C_3 and C_3^+DBTs.

From the literature survey it can be concluded that oxidation of thioethers into sulfoxides and sulfones in presence of hydrogen peroxide and redox solid catalyst such as Ti-containing zeolites It was expected that these catalysts could also be active in the sulfoxidation of aromatic sulfur compounds, such as thiophene, benzothiophenes, and dibenzothiophenes, all well known as refractory compounds in the HDS process. The use of Ti-containing molecular sieves as catalysts in oxidative desulfurization reaction has been already reported. The transition metals like Fe, Mo, V, Cu etc has been reported to show good oxidative desulfurization with different supports like MCM-41,Al_2O_3, TS-1 etc. To our knowledge not much literature concerning Fe, Mo, Ce substituted on Titanium silicate has been published till now. From this it was concluded that till date no work is carried out on transition metals which shows good redox properties supported on TS-1.So three different metals were chosen like molybdenum, iron and cerium and that were impregnated on titanium silicate (TS-1).

Chapter 3

Materials and Methods

This chapter presents a detailed description on the chemicals used during catalyst preparation and experiments in the present study. The experimental set-up, catalyst characterization techniques, and analysis of reaction mixture are also described in this chapter.

3.1 Materials

3.1.1 Chemical used in catalyst preparation

Ferric Nitrate was procured from Fischer Scientific and cerium nitrate hexahydrate and Ammonium heptamolybdate were supplied by S D Fine Chem Ltd. Titanium Silicate was procured from Clean Science. Hydrogen peroxide (30%, v/v) was supplied by Fischer Scientific.

3.1.2 Model sulfur compounds

In the present research work, thiophene is used as model sulfur compounds present in fuel oil. The physical properties and purity of this chemical according to the respective company specification are listed in Table3.1

Table 3.1: Details of the model sulfur and the nitrogen compounds

Compound	Properties	Sources
Thiophene	Molecular weight = 84.14 g/mol, Density= 1.061 g/cm^3, Purity= 99 %	Sigma Aldrich, India
Quinoline	Molecular weight = 129.16 g/mol, Density= 1.03 g/cm^3, Purity= 99 %	Sigma Aldrich, India

3.1.3 Oxidizing agent and solvent

Hydrogen peroxide (30% w/w aqueous solution) was used as oxidizing agent in this study. The H_2O_2 used has been procured from Fischer Scientific, India and has a density of $1.11g/cm^3$.The solvent used was octane for the preparation of model fuel.

Table 3.2: Details of the solvent

Solvent	Parameters	Value	Sources
Octane	Boiling point Molecular Weight Appearance Density	125^oC 114.23 g/mol Colourless liquid $703kg/m^3$	Sigma Aldrich, India

3.2 Characterization Techniques

The characterization of the catalyst is an important aspect in order to obtain information about molecular nature and structure of the active component to prepare the catalyst and also helps in optimizing industrial catalytic processes. No single technique is available to get the complete information about the surface structure of the active component and it is an impossible task to a single discipline of the subject to get comprehensive overview of the molecularities of the surface. Characterization of heterogeneous catalyst refers to the measurement of its characteristics which are those physical and chemical properties of the catalyst assumed to be responsible for its performance in a given reaction. More specifically, the characteristics of a catalyst include:

- The nature of its basic building blocks, i.e. chemical composition of the bulk and surface of the solid;
- The arrangement of these basic building blocks or architecture e.g. bulk and solid structure of the solid; size and size distribution, crystallite morphology, porosity, and surface area;

- Surface chemical properties such as valence state, acidity, reactivity with different molecules, surface energy and surface electronic state;
- The aggregate properties such as aggregate or particle size, magnetic properties, density, mechanical strength and attrition resistance;
- Catalytic properties i.e. activity, selectivity and activity stability

Objectives of characterization include a) understanding relationships among physical, chemical and catalytic properties i.e. relating catalytic structure and function. B) elucidating causes of deactivation, designing procedures for regeneration and choosing catalyst properties to minimize such deactivation. C) determining physical and chemical properties for purposes of catalyst marketing, reactor design, modelling and process optimization. D) ensuring quality control in catalyst manufacturing. There are three basic principles of characterization which can usefully guide the efforts of an investigator i.e. a) not all tools are equal. Each has its basic advantages and limitations. B) the wisdom of using more than one tool to provide complementary data on catalysts properties has been well demonstrated. C) for the industrial setting, the most productive techniques historically are those applied to the working surface of the catalyst. The commercial catalyst TS-1 and the synthesized catalyst Fe/TS-1, Ce/TS-1 and Mo/TS-1 were characterized by different characterization Techniques like X-ray diffraction, BET surface area analysis, Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS).

3.2.1 BET surface area and pore size distribution

BET surface area analysis is a technique used to determine the specific surface area of powders, solids and granules, the values are expressed in meter square per gram. Clean solid surfaces adsorb surrounding gas molecules and Brunauer, Emmett and Teller theory (BET) provides a mathematical model for the process of gas sorption. This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption and is used to measure total surface area and pore size analysis of nanopores, micropores and mesopores. The BET surface area measurement is crucial in understanding the aluminos of a material, as material reacts with its surroundings via its surface, a higher surface area material is more likely to react faster, dissolve faster and adsorb more gas than a similar material with a lower surface area. Typical analysis would include:

- Specific surface area BET surface area analysis using Nitrogen, or Krypton for low surface area materials.

Pore size analysis:

- Mesopore analysis using traditional Kelvin equation models such as BJH, or advanced DFT based models.
- Micropore analysis. Accurate measurement of micropores requires high vacuum, accurate low pressure transducers and advanced pore modelling calculations such as Quanta-chrome's range of DFT micropore models.
- Pore size distributidioxide and sulfur trioxide which along nitrogen oxides with (NO_x) on by: pore diameter, pore volume and pore surface area.
- Percentage of porosity

Surface area determination is an important factor in determining the catalyst performance, a method of assessing the efficiency of catalyst supports and promoters. The surface area measurements can be used to predict catalyst poisoning and provide reasons for the deactivation of the catalyst either due to poisoning or due to sintering. The BET (Brunner, Emmett and Teller) equation is based on the extension of Langmuir theory to multilayer adsorption. The basic equation to find the surface area is as follows 3.1:

$$\frac{P}{V_{adsorbed}(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \tag{3.1}$$

Where P= equilibrium adsorption pressure, P_0= saturated vapour pressure of the adsorbent, V_{ads}= volume (in ml) adsorbed at STP at pressure P, V_m = volume of adsorbate required to form a monolayer coverage, C=constant related to heat of adsorption. According to the BET method a plot of $P/(V_{ads}(P_0 - P))$ Vs $P/P_0$is a straight line (in the range of P/P_0: 0.05 -0.3) with slope $(C-1)/V_m C$and intercept $1/V_m C$. By knowing these intercept and slope values V_m can be calculated and further specific surface area can be calculated as follows Specific surface area (m^2/g) = $[(V_m x N_A)/$ (22414 x $W_t)]$ x A_m, where V_m= monolayer volume in ml at STP, N_A= Avogadro number, A_m= mean cross sectional area of adsorbate molecule (0.162 nm^2 for N_2), Wt= weight of the catalyst in grams.

Surface area and pore volume of the support and calcined catalysts were measured on a Micrometrics Autochem 2020 instrument. The sample (0.25 g) was evacuated at $300^o C$ for 4 hours prior to measurement. In the next step, nitrogen adsorption and desorption isotherms were measured at liquid nitrogen temperature. The Brunauer-Emmett-Teller (BET) area was estimated by N_2 adsorption at relative pressures (P/P_0) between 0.02 and 0.12, where P and P_0 are the measured and equilibrium pressures, respectively. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure close to 0.995. The nitrogen desorption branch was chosen for the pore size analysis. The pore size distribution was established by applying the Horvath-Kawazoe and Barrett-Joyner-Halenda (BJH) method.

3.2.2 X-ray Diffraction

X-ray diffraction (XRD) was used to obtain the crystallographic structure and chemical composition of solids. The XRD patterns of the support and the prepared catalysts were obtained using a Rigaku bench top XRD (miniflex 600) with Cu ($K\alpha$) radiation (1.5418 Å) operated at 40 kV and 15 mA. The catalysts were crushed to fine powders prior to measurement. The observed peaks were assigned by referring to the International Centre for Diffraction Data (ICDD) database. X-ray diffraction is a technique to identify the crystallinity of catalysts. This technique is based on the knowledge that each compound in catalyst has a different diffraction pattern. The crystallinity can be determined by comparing the intensity of a number of particular peaks to the intensity of the same peaks obtained by standard samples. The diffraction pattern is plotted based on the intensity of the diffracted beams. These beams represent a map of reciprocal lattice parameter, known as Miller index (hkl) as a function of 2θ, which satisfies Bragg equation: $n\lambda = 2dsin\theta$ where n is an integer number, l is the wavelength of the beam d is interplanar spacing and θ is a diffraction angle. Equation $n\lambda = 2dsin\theta$ is obtained from Bragg diffraction as shown in Figure 3.1. Powder XRD pattern were recorded for all the samples in order to verify the formation and structure of various microporous materials. The diffraction patters were recorded in the 2θ range of 5-80^o using a Rigaku miniflex 600 X-ray diffractometer. The scan speed and step size were 2.5^omin^{-1} and 0.02^o, respectively.

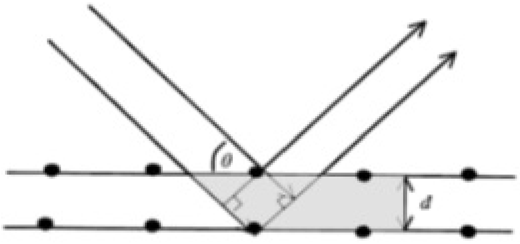


Figure 3.1: Braggs diffraction

3.2.3 Morphological Analysis: Scanning Electron Microscope

Scanning electron microscopy is an extremely powerful technique for obtaining information on the morphology and structural characteristics of catalysts. There are some advantages in this technique, which are great depth of focus, the possibility of direct observation of external form of real objects, and the ability to switch over a wide range of magnification, so as to zoom down to fine detail on some part identified in position on the whole object. The scanning electron microscope achieves its resolution by scanning a finely focused beam of very short-wavelength electrons, about $10 - 100\AA$in diameter, across a surface and by detection of either the backscattered or secondary electrons in a raster pattern in order to build up an image on a television monitor. Because of its very low numerical aperture, the SEM has an extreme depth of field so that thick objects can be visualized in focus from top to bottom. The SEM, unlike light microscopes, is limited to a surface view only. Nothing is learned visually about the interior of the specimen. It does, however, permit the production of dramatic black-and-white images. Scanning electron microscopy (SEM) is used to view the surface morphology. In addition, energy dispersive spectroscopy (EDS) yields qualitative information on elemental composition. The SEM and EDS characterization of the catalyst particles was performed using a HR-FEM scanning electron microscope with an EDAX energy dispersive spectrometer.

3.3 Catalyst preparation

3.3.1 Catalyst Synthesis

Titanium silicate is a novel catalyst which is able to catalyze a series of selective oxidations. Transition metal-substituted TS-1 molecular sieve have been found to be active, stable and selective solid catalysts for catalytic oxidation of a variety of organic substrates using O_2, hydrogen peroxide etc. Three different catalyst viz. Fe/TS-1, Ce/TS-1 & Mo/TS-1 were prepared with commercial Titanium Silicate as a support. $5Wt\%$ of iron,cerium and molybdenum were loaded on TS-1.

3.3.2 Synthesis of Fe/TS-1

The catalyst was synthesized using incipient wet impregnation method. Ferric nitrate was the metal salt used for impregnating iron on Titanium silicate (TS-1). 7.38 g of Ferric Nitrate was dissolved by dropwise addition of water (6.6

ml) and was put for stirring at 400-600 rpm at room temperature in a small beaker. The solution was stirred till the solution became homogeneous. TS-1 which was already weighed (19 gram) in a separate beaker was impregnated with this metal solution. Then the catalyst was allowed to dry for 24 hours at 110^oC and then it was calcined for 7 hours at 550^oC.

3.3.3 Synthesis of Ce/TS-1

The catalyst was synthesized using incipient wet impregnation method. Cerium nitrate hexahydrate was the metal salt used for impregnating cerium on Titanium silicate (TS-1). 3.099 g of Cerium Nitrate hexahydrate was dissolved by dropwise addition of water (6.6 ml) and was put for stirring at 400-600 rpm at room temperature in a small beaker. The solution was stirred till the solution became homogeneous. TS-1 which was already weighed (19 gram) in a separate beaker was impregnated with this metal solution. Then the catalyst was allowed to dry for 24 hours at 110^oC and then it was calcined for 7 hours at 550^oC.

3.3.4 Synthesis of Mo/TS-1

The catalyst was synthesized using incipient wet impregnation method. Ammonium heptamolybdate was the metal salt used for impregnating cerium on Titanium silicate (TS-1). 1.8610 g of Ammonium heptamolybdate was dissolved by dropwise addition of water (6.6 ml) and was put for stirring at 400-600 rpm at room temperature in a small beaker. The solution was stirred till the solution became homogeneous. TS-1 which was already weighed (19 gram) in a separate beaker was impregnated with this metal solution. Then the catalyst was allowed to dry for 24 hours at 110^oC and then it was calcined for 7 hours at 550^oC.

3.4 Experimental Procedure

3.4.1 Oxidative desulfurization procedure

The oxidation reactions were carried out in a three- necked glass reactor having capacity of 250 mL. The reactor was fitted with a glass reflux condenser, thermometer and 4 bladed-glass stirrer with the provision of speed regulation. The temperature of the reactor was maintained with a thermostatically controlled water bath with $\pm\ 1^oC$ temperature variation. The schematic diagram of the reactor set-up is presented in Figure 3.2.

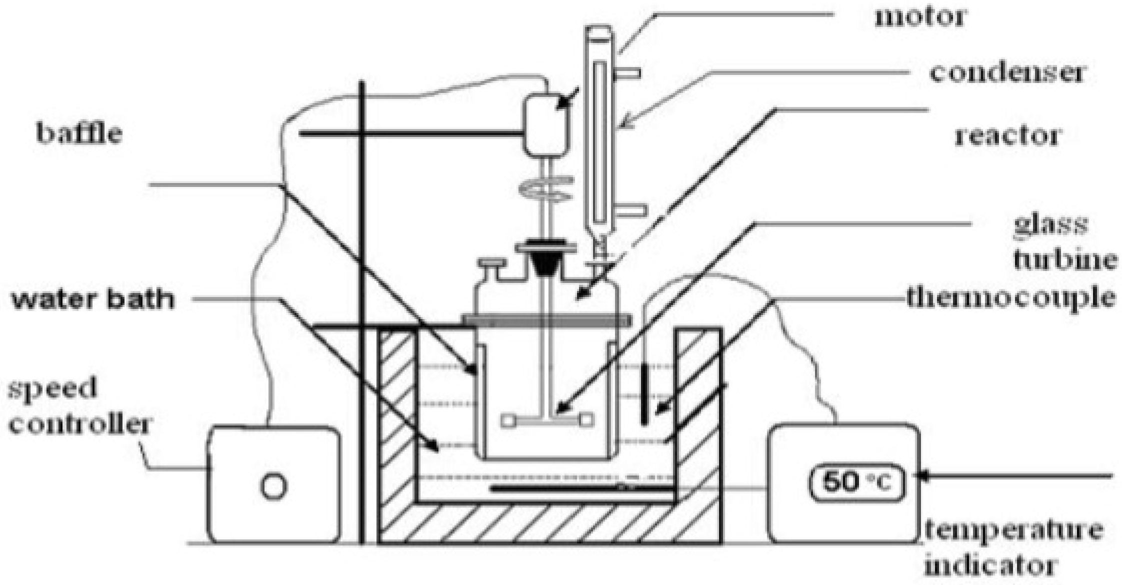


Figure 3.2: Schematic diagram of experimental set-up

3.4.2 Preparation of model fuel sample

The sulfurated model solution used in each experiment was prepared by adding a weighed amount of the selected sulfur compound (thiophene) in 50 mL octane (99.5%, Sigma Aldrich, India), to give an elemental sulfur concentration at desire level (2000 ppm of S), that is indicative of a real sample. The solution was then utilized to the heterogeneous catalytic oxidative desulfurization process, as described below. In a typical experiment the water bath was set a desired temperature and then the model fuel of 2000ppm was added into the three necked flat bottom flask. Once the temperature was achieved 1 gram of the catalyst was added into the solution. Then hydrogen peroxide (oxidizing agent) was added and was stirred at the speed of 400 rpm and the reaction was continued for 3 hours. The ratio of hydrogen peroxide to sulfur was kept 10:1.The ratio of catalyst to solvent was 0.02:1.The products were withdrawn periodically at different time interval of 15mins, 30mins, 60 mins, 120 mins &180 mins. The products were analyzed in 2 dimensional gas chromatography.

3.5 Two Dimensional Gas Chromatograph

2-D GC consists of 2 column in particular non-polar followed by polar column in series. The separation of molecules takes placed based on boiling point in first column (15 m length) and based on polarity in the second column. The columns are placed in two ovens namely first column is placed in main oven and second column is in auxiliary oven installed in main oven. Second column is normally of 5 m length out of which one meter will be used for creating loop and remaining will be placed in secondary oven. Cold and hot jet modular is installed in such a way it will be freezing the flow of column using nitrogen at -90 ^oC and heating using hot nitrogen at 280 to 300 ^oC at the junction of second column loop. The modulation of cold and hot jet is set in such a way that ice formation should be observed on the outer wall of column for few seconds (preferably 3 – 5 seconds) who will be easily removed using hot jet flow in milli-seconds.

SCD: SCD is used for the quantitative determination of various sulfur organic species like hydrogen sulfide, mercaptans, thiophenes, benzothiophenes & sulfides in hydrocarbon samples. It is a very sensitive and useful technique to characterize crude oils of different origin. Sulfur speciation is essential during oil catalytic processing in the refineries. Basically, the SCD signal derives from the formation of SO_2. Which generates light when falling back into the neutral state

NCD: It detects organic nitrogen compounds, the NCD responds to ammonia, hydrazine, hydrogen cyanide and NO_X. . The hydrogen and oxygen plasma in the combustion tubes converts all nitrogen compounds to nitric oxide at temperatures greater than 180^oC.

$$R - N + H_2 + O_2 \rightarrow NO + CO_2 + H_2O$$

$$NO + O_3 \rightarrow NO_2{*} \rightarrow NO_2 + hv$$

Nitric oxide reacts with ozone to form electronically excited nitrogen dioxide. The excited nitrogen dioxide emits light in the red and infrared region of the spectrum (600-3200 nm) when it relaxes to its ground state. The light emitted is directly proportional to the amount of nitrogen in the sample. Before the analysis of the sample the two dimensional gas chromatography was calibrated with different ppm of sulfur and nitrogen. Figure 3.3 and 3.4 represents the calibration of gas chromatography for thiophene and quinoline.

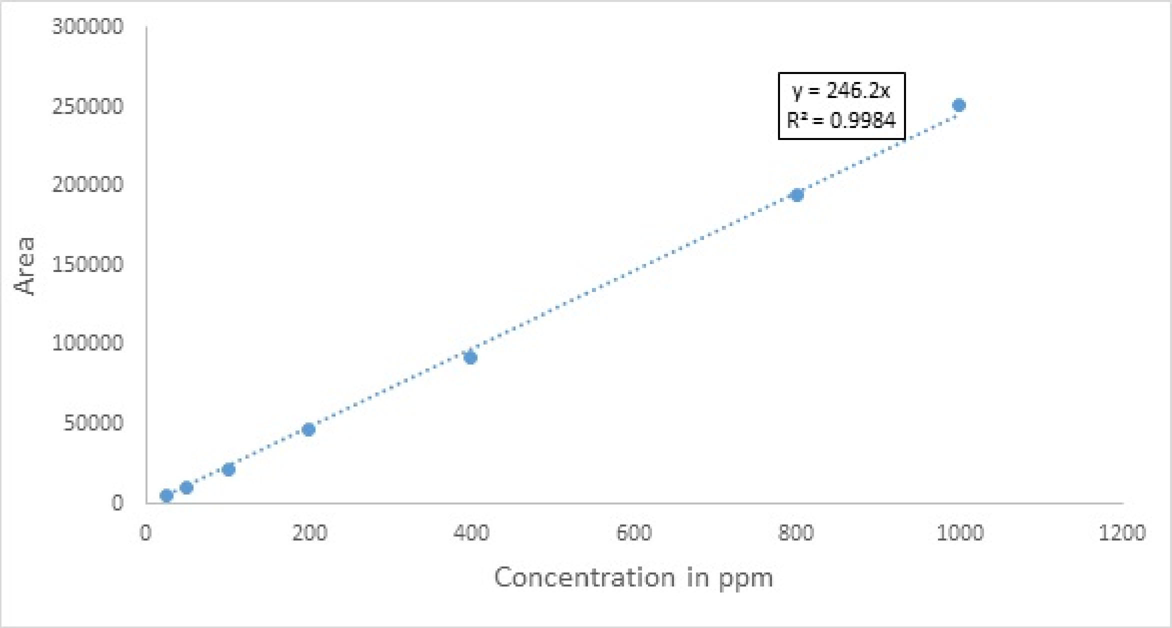


Figure 3.3: Calibration curve of GC for thiophene

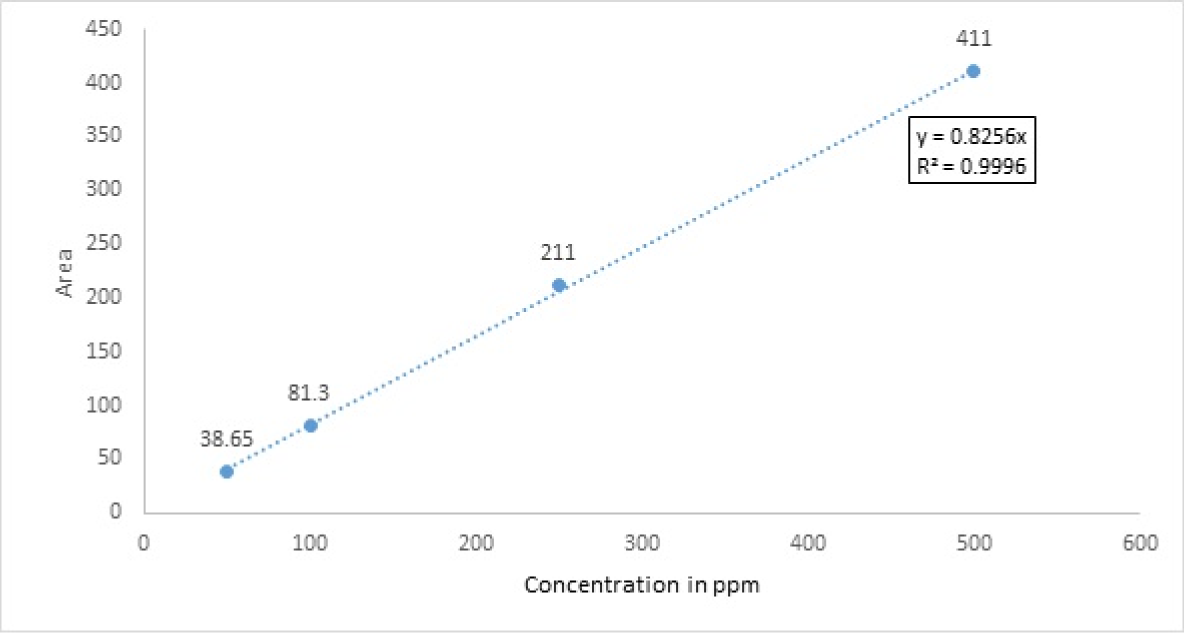


Figure 3.4: Calibration curve of GC for Quinoline

The Oxidation of thiophene and quinoline is clear from the Fig.3.5 and 3.6

3.5.1 Conversion or removal of sulfur compounds from model fuel

The removal or conversion of a given sulfur compound was calculated using its initial concentration at 0 min (C_0) and concentration after t minutes of reaction (C_t). The percentage conversion$X_A$is expressed as 3.2,

$$X_A = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \tag{3.2}$$

assuming that the total volume and mass of the reaction mixture were constant.

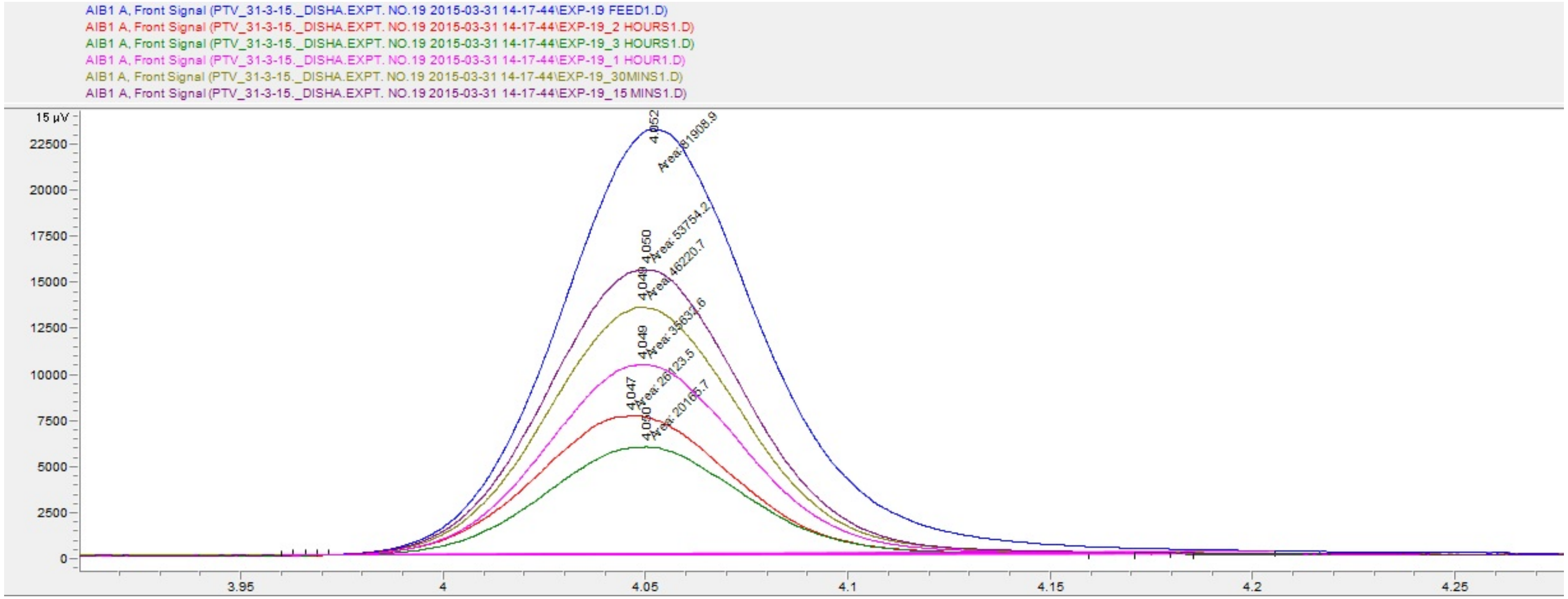


Figure 3.5: Chromatogram of feed and product (Thiophene)

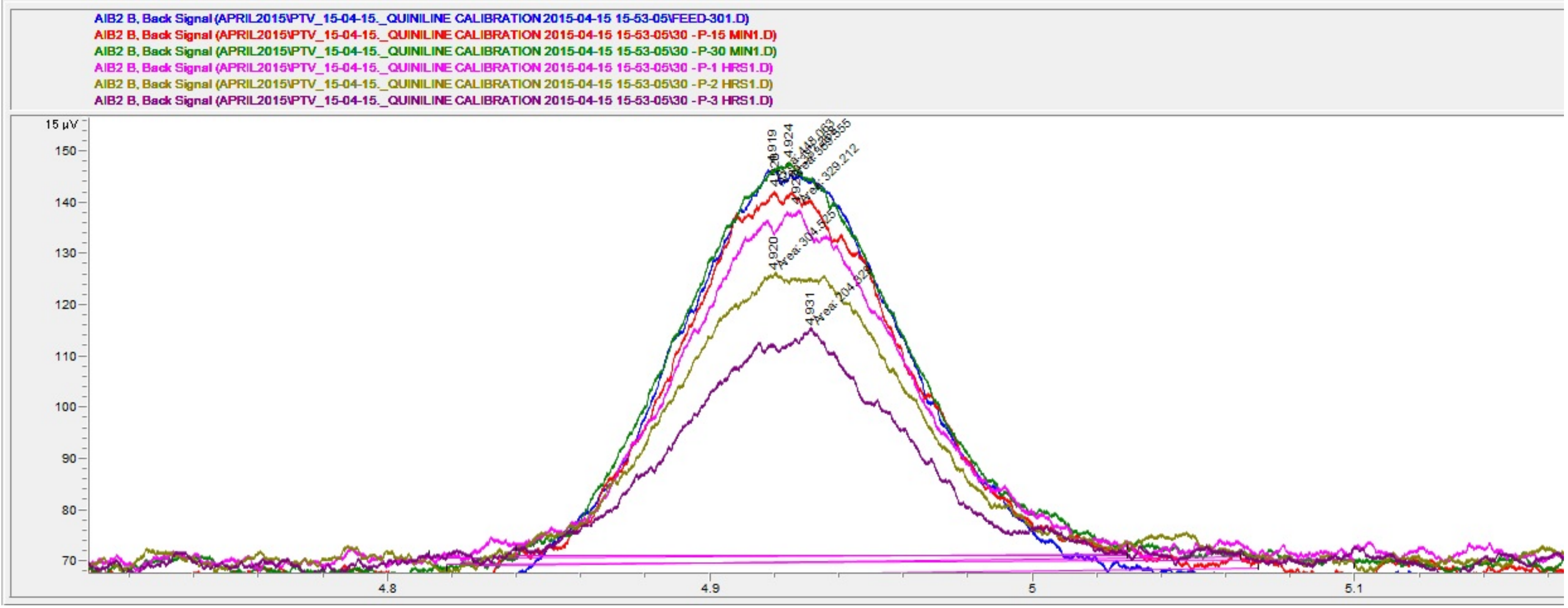


Figure 3.6: Chromatogram of feed and product (Quinoline)

Chapter 4

Results and Discussions

The characterization of catalysts were done by using X-ray diffraction for crystal structure and phase identification, BET surface area for measurement for the structural properties of catalyst,SEM/EDS study for the metal dispersion on catalyst. The experimental results of oxidation of sulfur using the synthesized catalysts are discussed in this chapter. The reduction in sulfur was analyzed using two dimensional gas chromatography.

4.1 XRD pattern of TS-1, Fe/TS-1, Ce/TS-1 and Mo/TS-1

Figure 4.1, 4.2, 4.3 shows the XRD patterns of $Fe/TS-1, Ce/TS-1$and $Mo/TS-1$ calcined at 550^oC.XRD analysis of TS-1 used before and after metal loading reveals that even after metal loading the characteristic peaks of TS-1 are intact. The analysis also depicts presence of high crystallinity before and after metal loading. The characteristic peaks of TS-1 at 2θ are observed at 24.4^o and 29.3^o. This also indicates that the metals are evenly distributed on TS-1.

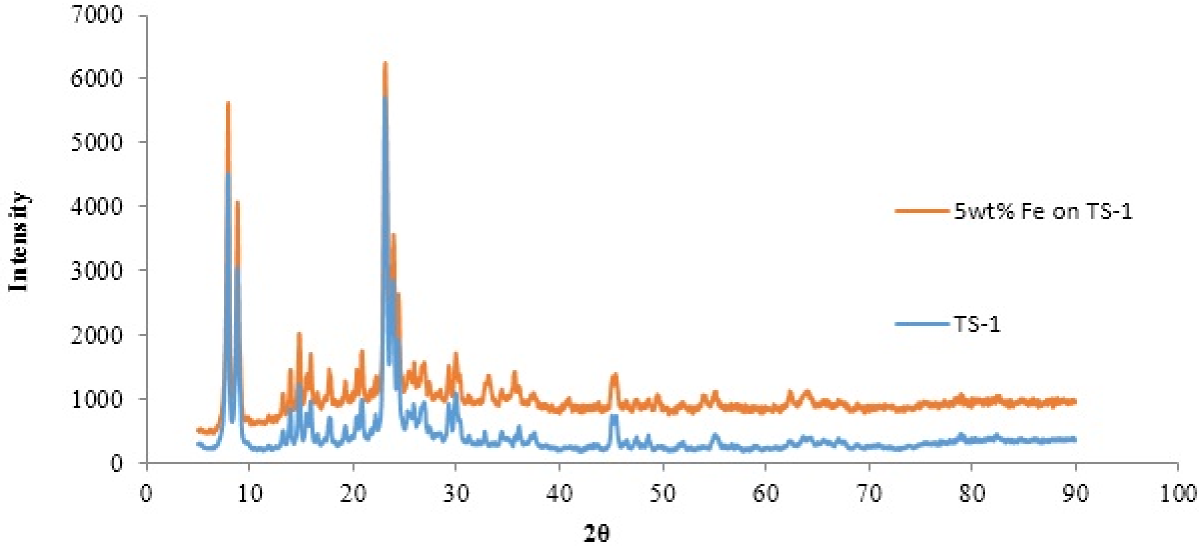


Figure 4.1: XRD pattern of Fe/TS-1

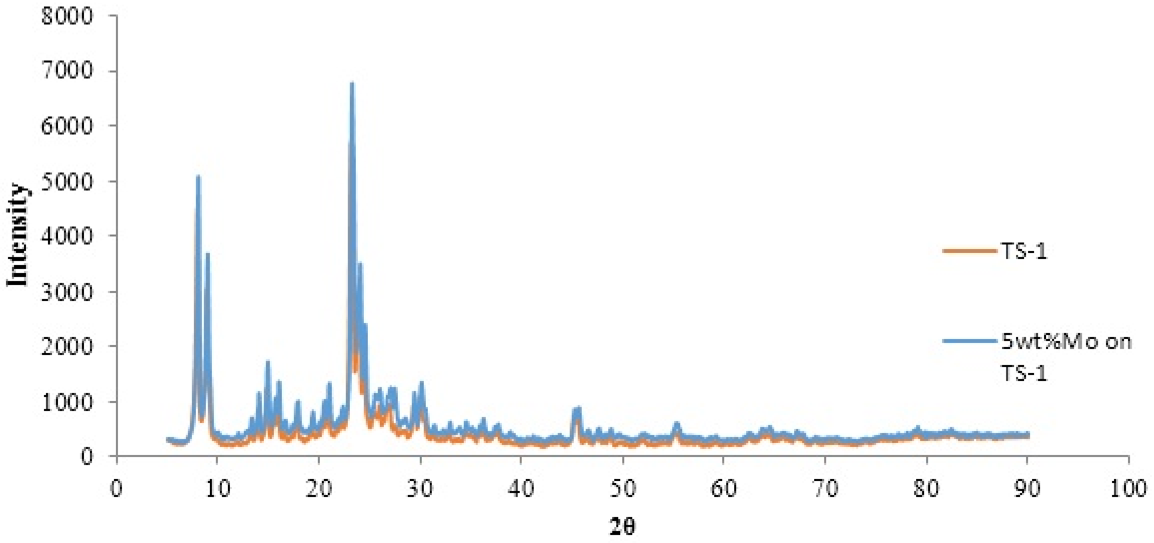


Figure 4.2: XRD pattern of Mo/TS-1

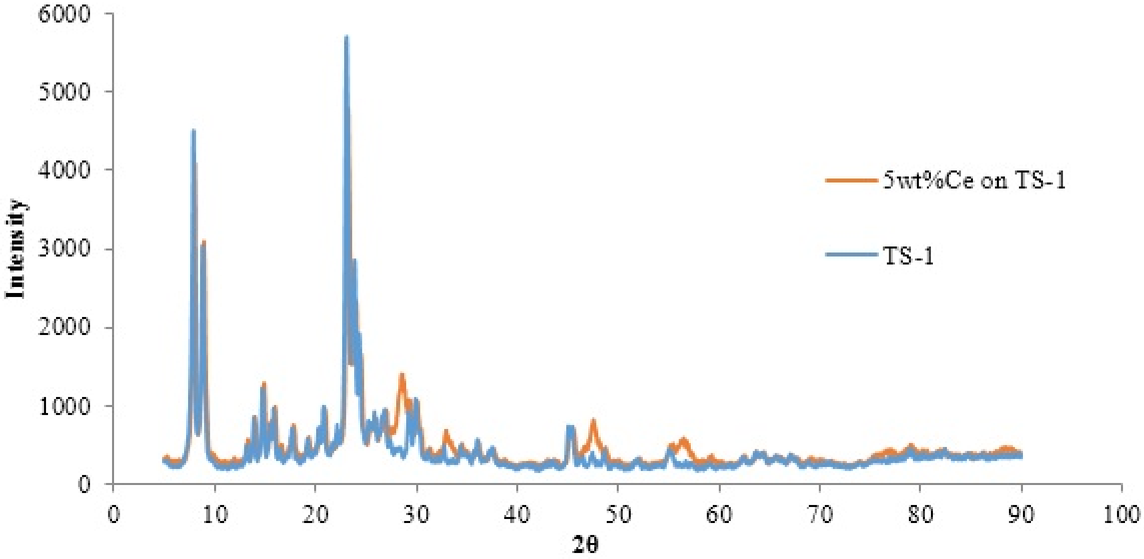


Figure 4.3: XRD pattern of Ce/TS-1

4.2 Bet Surface Area

The surface area and pore volume of all samples prepared, were measured using a static volumetric system. The surface area was calculated using multi point Brunauer-Emmett and Teller surface area method and the total pore volume was calculated from amount of nitrogen adsorbed at relative pressure P/P0 of 0.97. Figure4.4 shows the nitrogen adsorption-desorption isotherms measured on three catalysts. It can be seen that all samples shows type III adsorption isotherms based on IUPAC's classification and show no rapid initial uptake of gas and occur when the forces of adsorption in the first monolayer are relatively small. It can be seen that all three catalysts are microporous with average diameter [33].

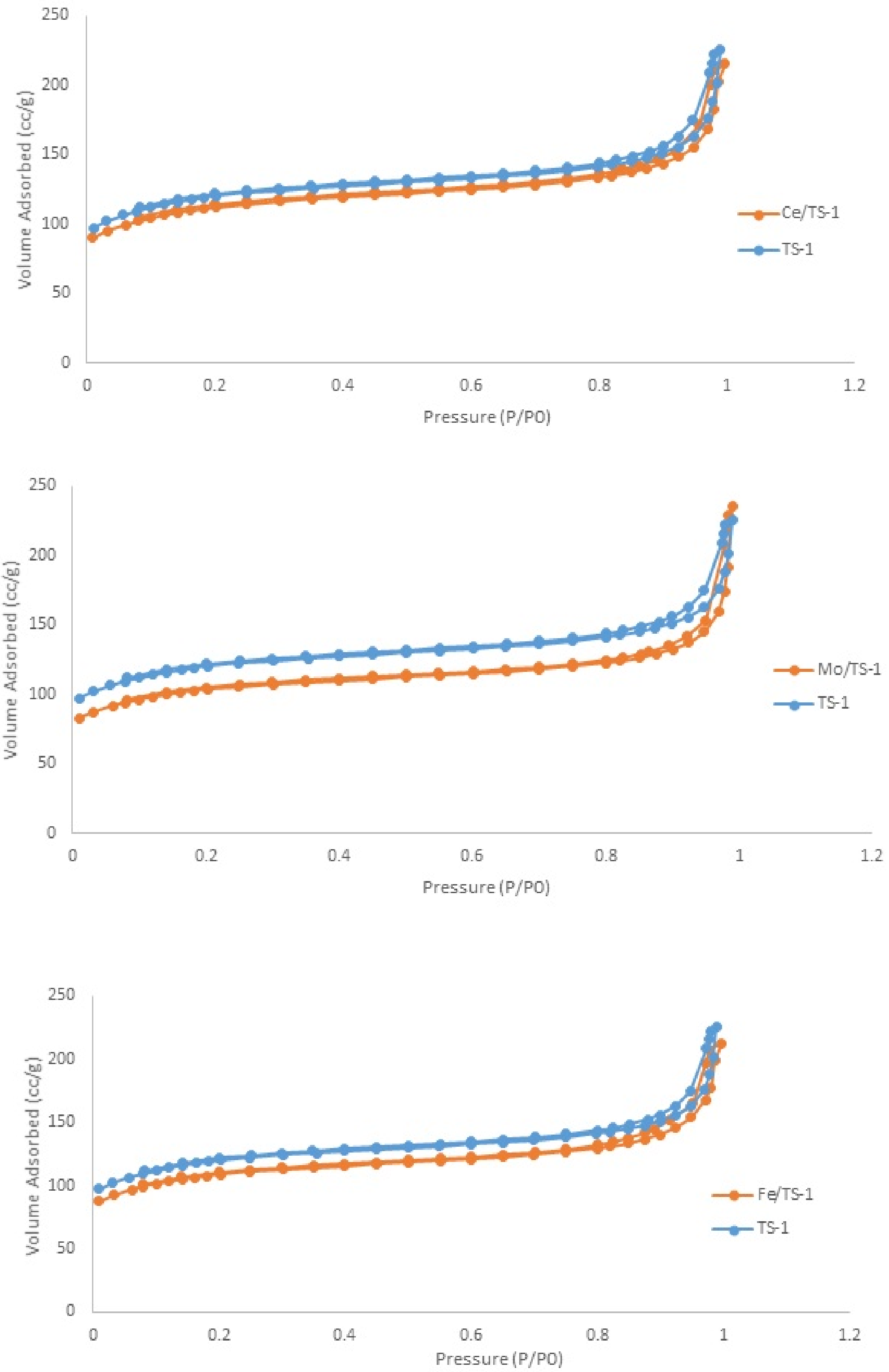


Figure 4.4: N2 adsorption-desorption isotherm of TS-1,$Ce/TS-1$, $Mo/TS-1$, $Fe/TS-1$

From Table4.1 it is clear that there is reduction in pore volume and it is because of mouth pore plugging due to the metals located on the surface.

The change in physical properties after metal loading may be because of the increase in atomic radii of metals. Reduction in surface area of Fe, Ce and molybdenum can be attributed to the dispersion of metals on the TS-1. This assumption is supported by SEM-EDS analysis.

Table 4.1: Structural properties of catalyst

Sr.No	Catalyst	Surface Area (m^2/g)	Pore Volume (ml/g)	Pore Diameter (Å)
1	$TS-1$	438	0.35	32
2	$Fe/TS-1$	402	0.26	28
3	$Ce/TS-1$	396	0.31	31
4	$Mo/TS-1$	378	0.27	27

4.3 SEM/EDS Results

The SEM/EDS images of $Mo/TS-1, Fe/TS-1 and Ce/TS-1$ were taken on cross sectional area of each catalyst. This study was done under high vacuum mode.Fig 4.5, 4.6, 4.7 shows the SEM and SEM/EDS images of synthesized catalysts.

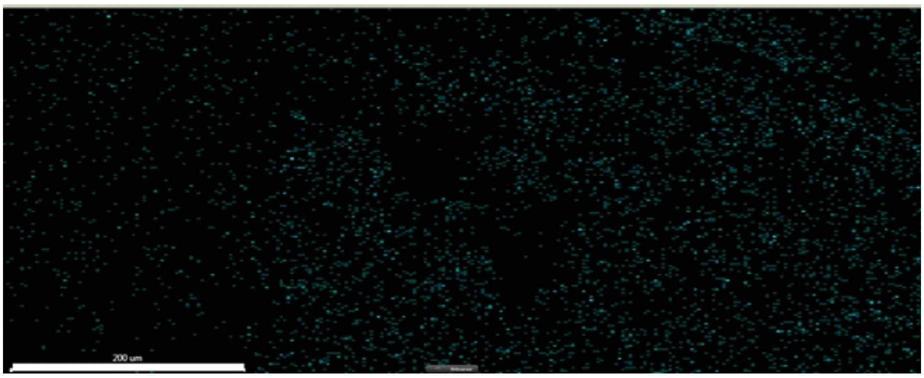


Figure 4.5: SEM/EDS of $Fe/TS-1$

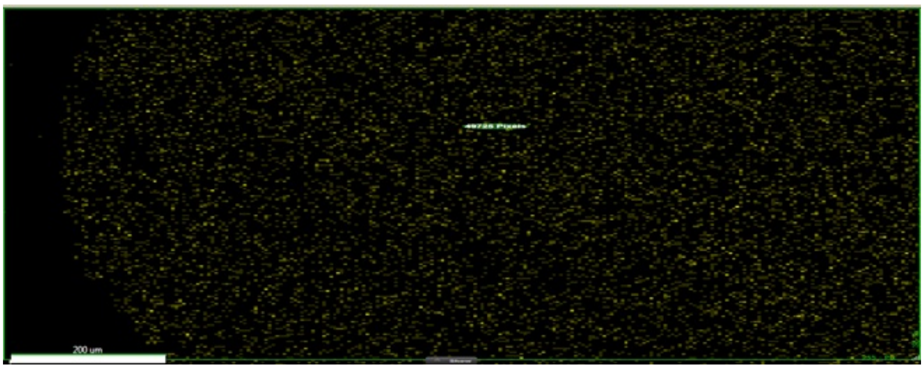


Figure 4.6: SEM/EDS of $Ce/TS-1$

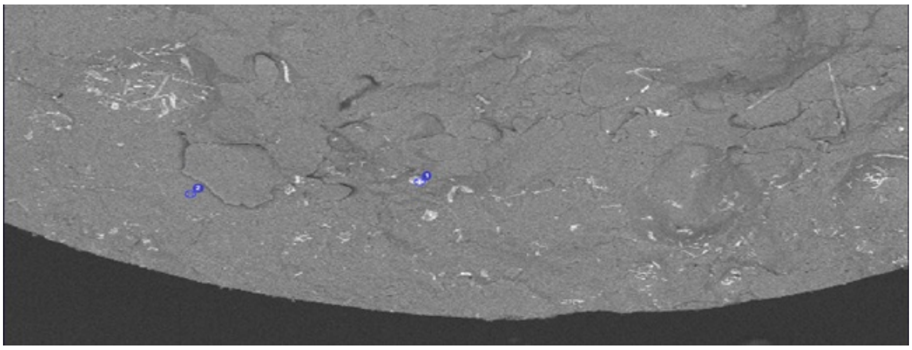


Figure 4.7: SEM of $Mo/TS-1$

In case of iron and cerium the metals are observed to be uniformly dispersed on catalyst surface as compared to molybdenum. The bright spots in case of molybdenum is may be because of charging of sample under SEM-EDS experimental conditions and agglomeration of molybdenum. The dispersion of metal is directly linked to the activity of catalyst (catalyst activity evaluation shows lowest activity for molybdenum based catalyst).

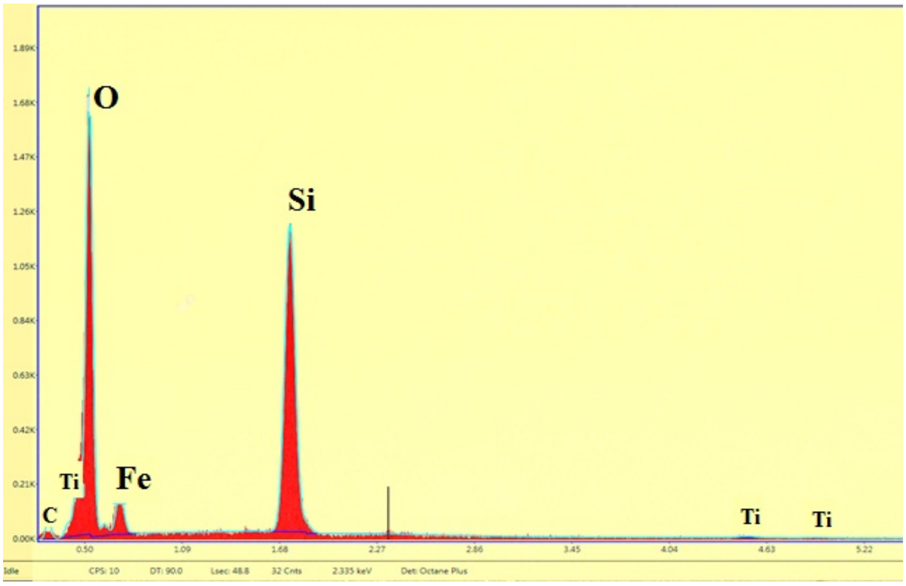


Figure 4.8: Surface Spectrum of $Fe/TS-1$

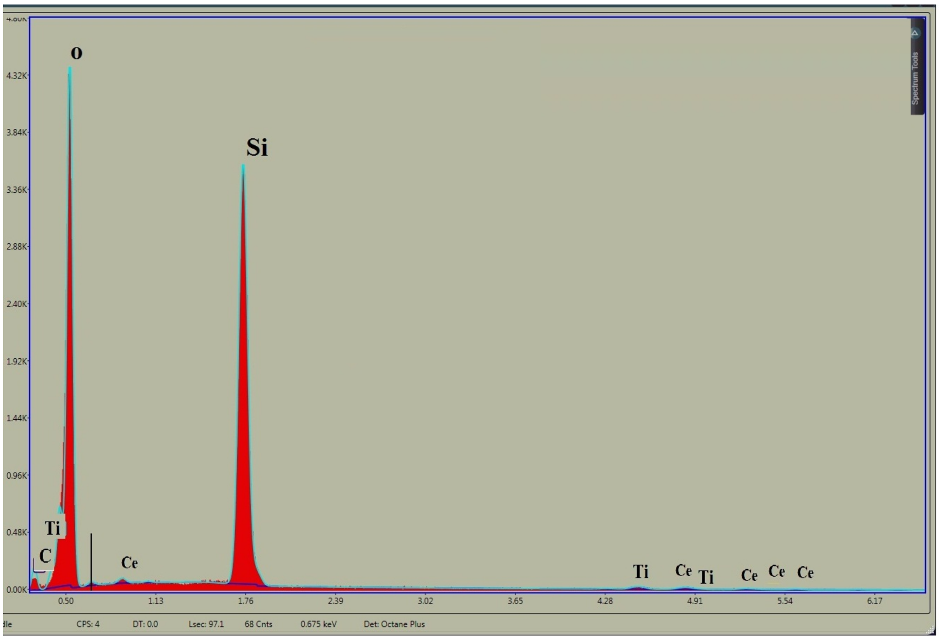


Figure 4.9: Surface spectrum of $Ce/TS-1$

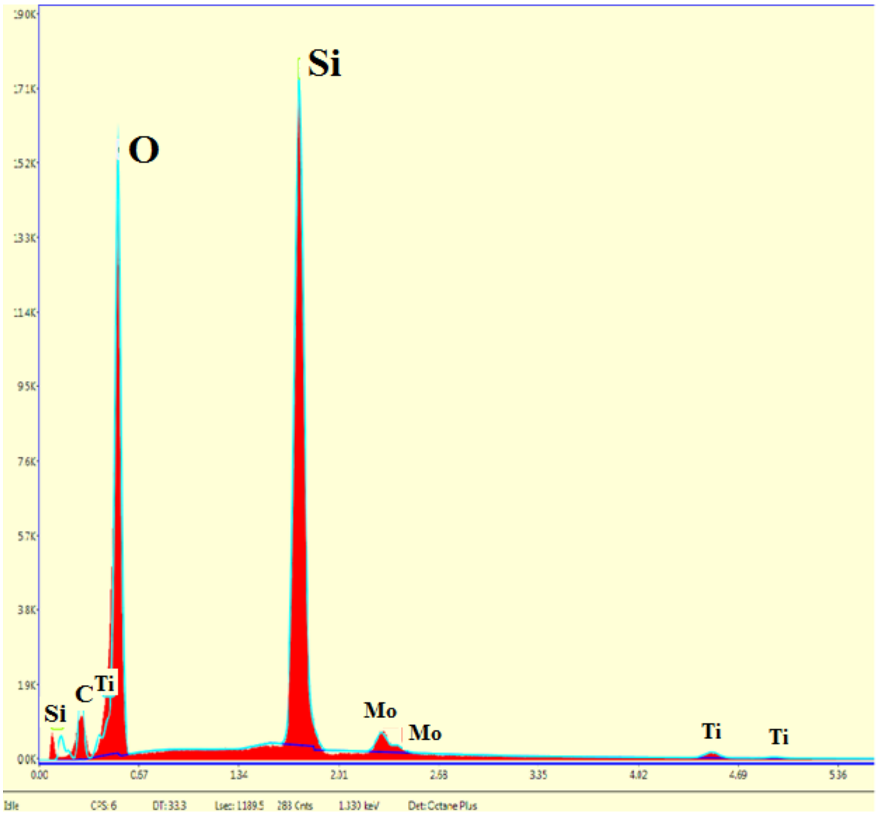


Figure 4.10: Surface spectrum of $Mo/TS-1$

The spectrum analysis of prepared catalysts supports the presence of titanium, silica, molybdenum, cerium and iron in the synthesized catalysts.

4.4 Oxidation of Thiophene

Over synthesized catalysts the oxidation reaction of sulfur compounds by hydrogen peroxide led to corresponding sulfoxides (1-oxides) and sulfones (1, 1-dioxide) as major products. The oxidation of Thiophene was carried out using three different catalyst Fe/TS-1, Ce/TS-1 and Mo/TS-1 as a catalyst with hydrogen peroxide as oxidizing agent under identical conditions. From these three catalysts Fe/TS-1 gave the highest conversion. In ODS reaction speed of agitation, particle size of catalyst, oxidant to substrate ratio, catalyst quantity and reaction temperature were the significant parameters and the effects of these parameters were studied on the oxidation of thiophene.

4.4.1 Effect of metals

The oxidation of thiophene was first evaluated for three different catalysts $Fe/TS-1, Ce/TS-1$ and $Mo/TS-1$ under identical conditions like stirrer speed of 400 rpm, temperature was 40^0C, catalyst size was 200-300µm, catalyst quantity was 1 gram and $H_2O_2 : S$was 10:1 Fig.4.11 clearly shows that Fe/TS-1 gives the highest conversion of 70%.Hence for the further studies Fe/TS-1 was selected.

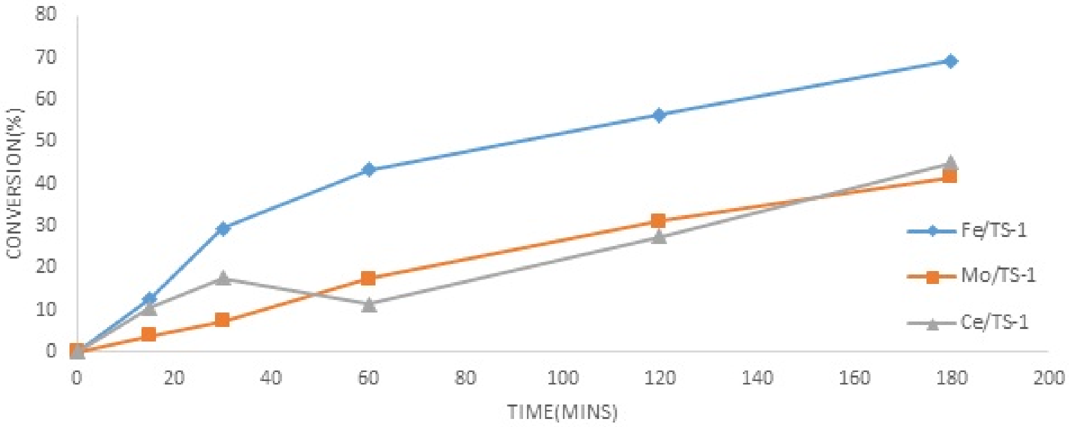


Figure 4.11: Effect of metals
Stirrer speed=400 rpm, temperature: 40^oC, catalyst size: 200-300µm, catalyst quantity=1 gram, $H_2O_2 : S$=10:1

4.4.2 Effect of speed of agitation

In order to eliminate the effect of external mass transfer resistance for heterogeneous reaction containing a solid catalyst the reaction was carried out at different stirring speed i.e. 400 rpm, 800 rpm, 1000 rpm and 1200 rpm. The results were as shown in figure 4.12. Conversion increased with stirring speed up to 800rpm after that increase in stirring speed did not affect thiophene conversion. Thus it was assumed that the reaction was free from mass transfer resistance at 800 rpm. Hence all the subsequent reactions were carried out at 800 rpm to obtain a proper kinetic data whereas when Copper was impregnated on TS-1(Cu/TS-1) it was free of external mass transfer resistance at 1000 rpm and catalyst quantity used was 0.4 gram, copper loading was 1.05wt% and solvent was i-octane as reported in literature[23].

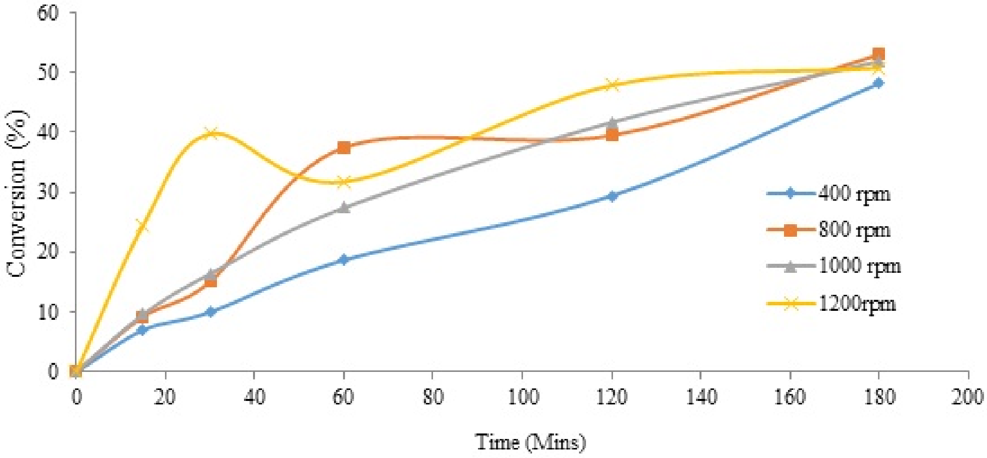


Figure 4.12: Effect of speed of agitation
Temperature: 40^oC, catalyst size: 400-500µm, catalyst quantity= 1 gram, $H_2O_2 : S$=10:1

4.4.3 Effect of catalyst particle Size

Reaction was carried out at different particle sizes to eliminate the effect of interparticle mass transfer resistance. Reaction was carried out using different particle sizes i.e. 100-181 µm, 181-250 µm, 400-500 µm and 710-850 µm. The result of conversion as a function of time is presented in the Figure 4.13.The results obtained when compared with Cu/TS-1 reaction was free of interparticle mass transfer resistance at 460 micron particle size as reported in literature with conversion around 20% in 60 mins as per literature [23].

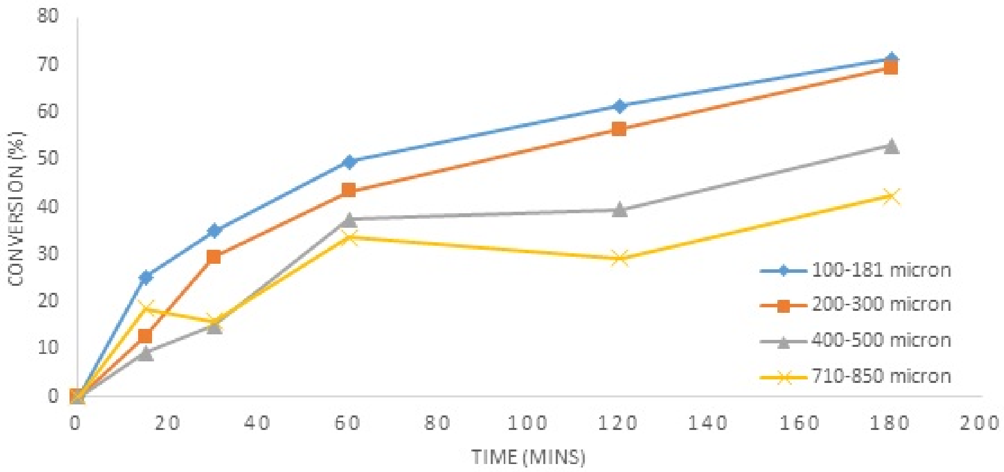


Figure 4.13: Effect of catalyst particle Size
Temperature: 40^oC, Stirrer speed: 800 rpm, catalyst quantity: 1 gram,
$H_2O_2 : S$=10:1

4.4.4 Effect of Oxidant to substrate ratio

The above experiments were carried out with an excess of hydrogen peroxide (10:1). According to the stoichiometry of the reactions only 2 moles of H_2O_2 are consumed per mole of sulfone produced. In order to determine influence of the hydrogen peroxide concentration on thiophene four ratios were taken 20:1,10:1,4:1,2.5:1.The lowest stoichiometric ratio (2.5:1) was set slightly above the actual stoichiometric ratio (2:1) in order limitations of the oxidant reagent and to achieve complete conversion of thiophene. From the trend observed in Fig.4.14 it was concluded that conversion increased with increase in oxidizing to substrate ratio. The Conversion obtained from 20:1 and 15:1 was almost same. So for further experiments the hydrogen peroxide: Substrate ratio was 15:1. These results when compared with the literature it was observed that the at 250 mins 85% conversion was obtained with 1:15 and in the present case 100% conversion in 180 mins [23].

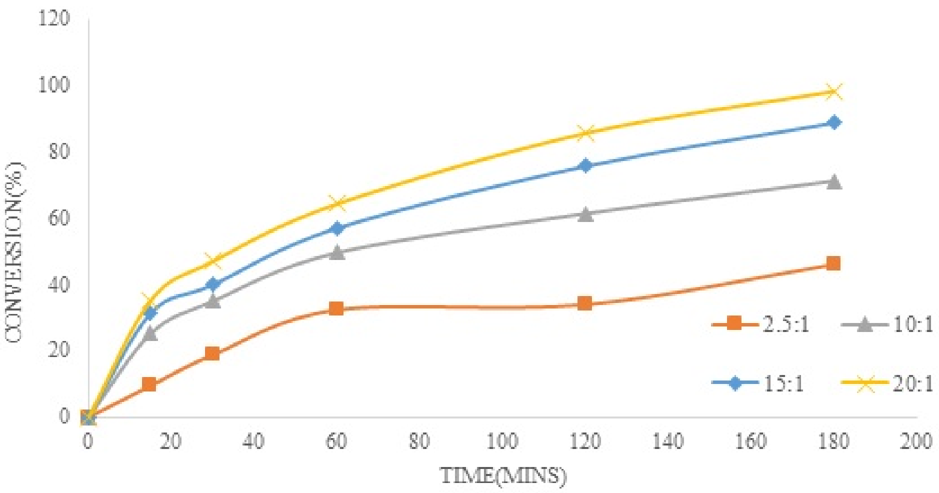


Figure 4.14: Effect of oxidant: substrate ratio
Temperature: 40^oC, Stirrer speed: 800 rpm, catalyst quantity: 1 gram, ,
catalyst size: 100-181µm

4.4.5 Effect of catalyst quantity

In order to determine the effect of catalyst quantity on thiophene the reaction was carried out using 0.5g, 0.75g, 1g and 1.5g of catalyst in a constant volume mixture. Thiophene conversion was increased with increasing catalyst quantity as shown in Fig.4.15.

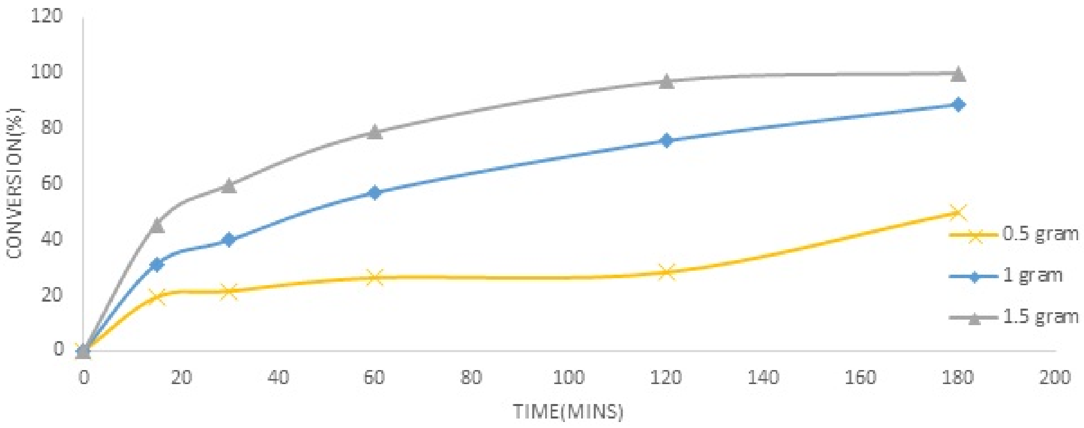


Figure 4.15: Effect of catalyst quantity
Temperature: 40^oC, Stirrer speed: 800 rpm, $H_2O_2 : S$=15:1, catalyst size:
100-181µm

4.4.6 Effect of temperature

Reactions were done at 40, 50 and 60^oC to study the effect of temperature on thiophene conversion. The results stated that the conversion increases with increase in temperature as shown in Fig.4.16. The rise in temperature has led to a remarkable increase in conversion. This is because the rate constant k increases with increase in temperature as given by Arrhenius law.From the literature it was reported that 93% conversion was obtaind at optimized conditions at 60^0C [23].

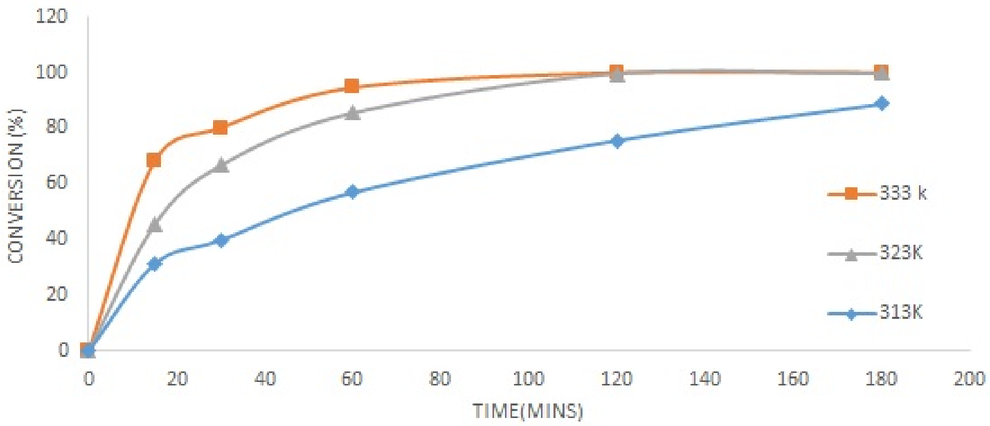


Figure 4.16: Effect of temperature (Sulfur)
Stirrer speed: 800 rpm, $H_2O_2 : S$=15:1, catalyst size: 100-181µm, catalyst quantity=1 gram.

4.5 Oxidation of quinoline over synthesized catalyst

The effect of Nitrogen compounds on oxidative desulfurization was also studied with the optimized process conditions, as nitrogen compounds inhibit the ODS reactions. Quinoline was taken as a nitrogen model compound to study effect of nitrogen on desulfurization rate oi thiophene.The catalyst remained the same i.e./TS-1 for these studies also. The experiments were carried out at different temperature and rest of the parameters that is rpm, oxidizing agent to sulfur ratio and catalyst to sulfur ratio remained the same.

4.5.1 Effect of temperature on Nitrogen Compounds

Reactions were done at 40, 50 and 60^oC to study the effect of temperature on quinoline conversion. The results stated that the conversion increases with increase in temperature as shown in Fig 4.17.

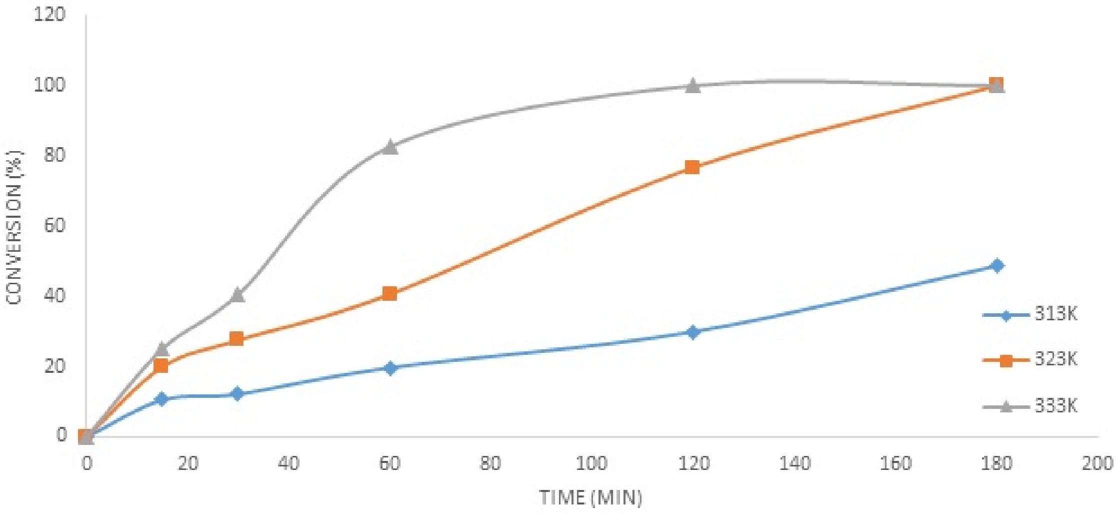


Figure 4.17: Effect of temperature (Nitrogen)
Stirrer speed: 800 rpm, $H_2O_2 : S$=15:1, catalyst size: 100-181µm, catalyst quantity=1 gram.

4.6 Effect of temperature on mixture (Sulfur and Nitrogen)

The graph in Fig.4.18 shows that with increase in time nitrogen and sulfur both are converted. When the oxidation of only quinoline was carried out at same process conditions the quinoline conversion was 48.68% in 180 minutes whereas in combination with sulfur the nitrogen is consumed within 120 minutes.. According to the literature nitrogen oxidation will continue with sulfur conversion. For these still more study with different tempertaure has to be carried out.

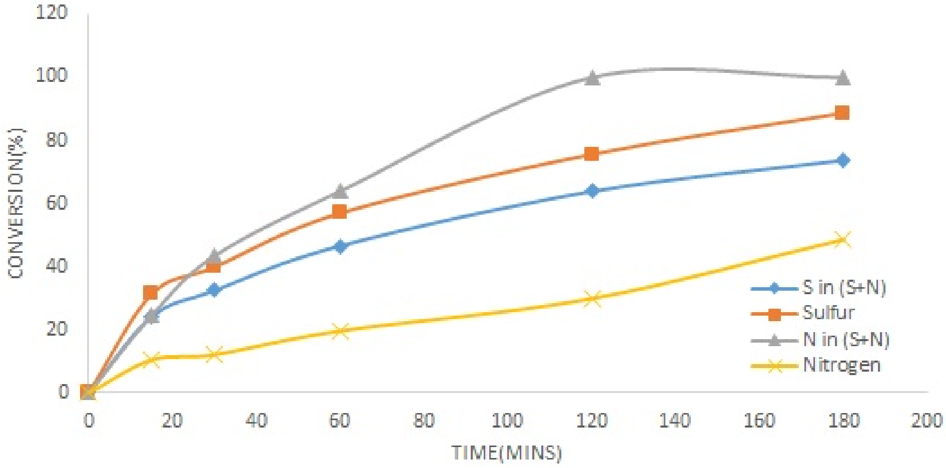


Figure 4.18: Effect of temperature (S &N mixture)
Stirrer speed: 800 rpm, $H_2O_2 : S$=15:1, catalyst size: 100-181µm, catalyst quantity=1 gram.

4.7 Kinetics of thiophene oxidation

The kinetics of oxidation was studied under the condition of different temperature ranging 40 , 50 and 60^oC.The kinetics of the reaction is of great importance and it is found by assuming pseudo first order reaction. The general equation for writing the rate of equation is,

$$A + B(excess) \rightarrow C + D$$

$$Thiophene + H_2O_2 \rightarrow ThiopheneSulfone + Water$$

The rate law can be written as,

$$\frac{d[C_{thio}]}{dt} = -k[C_{H_2O_2}][C_{thio}]$$

$$\frac{d[C_{thio}]}{dt} = -k'[C_{thio}]$$

$$k' = k[C_{H_2O_2}]$$

The plot of ln (C_0/C_t) Vs time gives a linear plot as shown in Fig. 4.19. This straight line was observed to pass through origin and this confirms the kinetics of pseudo first order reaction. The slope of the straight line was calculated to find the rate constant. The apparent rate constant k' is calculated. From that the rate constant is calculated.

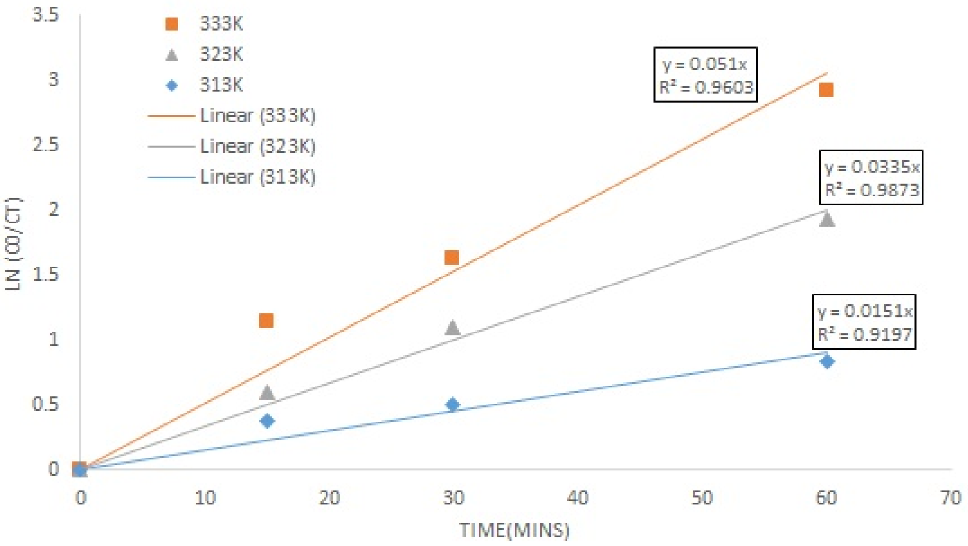


Figure 4.19: Pseudo-first order rate constant for different temperatures (sulfur)

Table 4.2: Rate constant for $Fe/TS-1$ for Thiophene

Temp	$T^{-1}(K^{-1})$	k'(apparant)	$kmin^{-1}$	R^2
40	0.0032	0.0151	0.0086	0.9197
50	0.0031	0.0335	0.0190	0.9873
60	0.0030	0.0510	0.0289	0.9603

The plot lnk Vs T^{-1} gives the value activation energy based on Arrhenius equation which is shown in Fig.4.20.

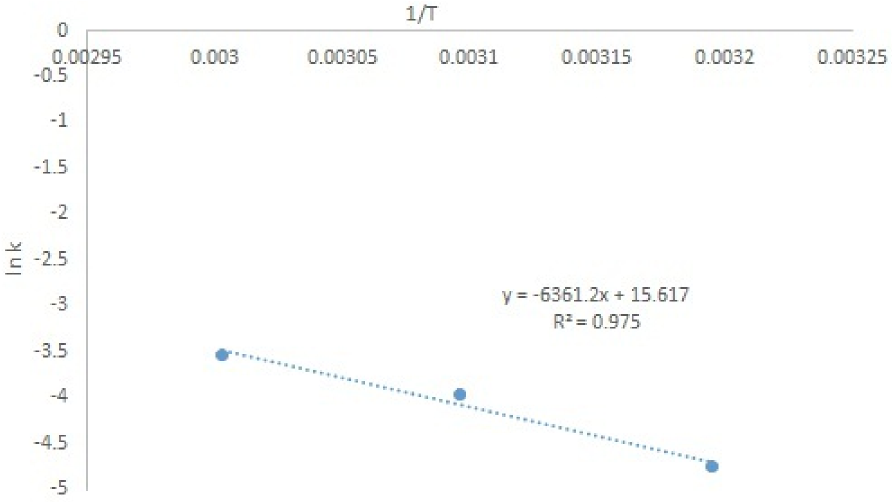


Figure 4.20: Arrhenius activation energies for thiophene oxidation

$$lnk = \frac{-E_a}{RT} + lnk_0$$

$$Slope = -E_a/R = -6361.2$$

$$E_a = 52.887 kJmol^{-1}$$

A plot was obtained and by analyzing the graph the activation energy Ea was calculated as 52.887 $kJmol^{-1}$.The activation energy value confirms that the reaction is kinetically controlled with negligible mass transfer resistance.

4.8 Kinetics of Quinoline oxidation

The kinetics of oxidation was studied under the condition of different temperature ranging 40 , 50 and 60^oC.The kinetics of the reaction is of great importance and it is found by assuming pseudo first order reaction. The general equation for writing the rate of equation is,

$$A + B(excess) \rightarrow C + D$$

$$Quinoline + H2O2 \rightarrow Polymeric\,compounds\,containing\,N\,and\,O.$$

The rate law can be written as,

$$\frac{d[C_{quinoline}]}{dt} = -k[C_{H_2O_2}][C_{quinoline}]$$

$$\frac{d[C_{quinoline}]}{dt} = -k'[C_{quinoline}]$$

$$k' = k[C_{H_2O_2}]$$

The plot of ln (C_0/C_t) Vs time gives a linear plot as shown in Fig.4.21. This straight line was observed to pass through origin and this confirms the kinetics of pseudo first order reaction. The slope of the straight line was calculated to find the rate constant. The apparent rate constant k' is calculated. From that the rate constant is calculated.

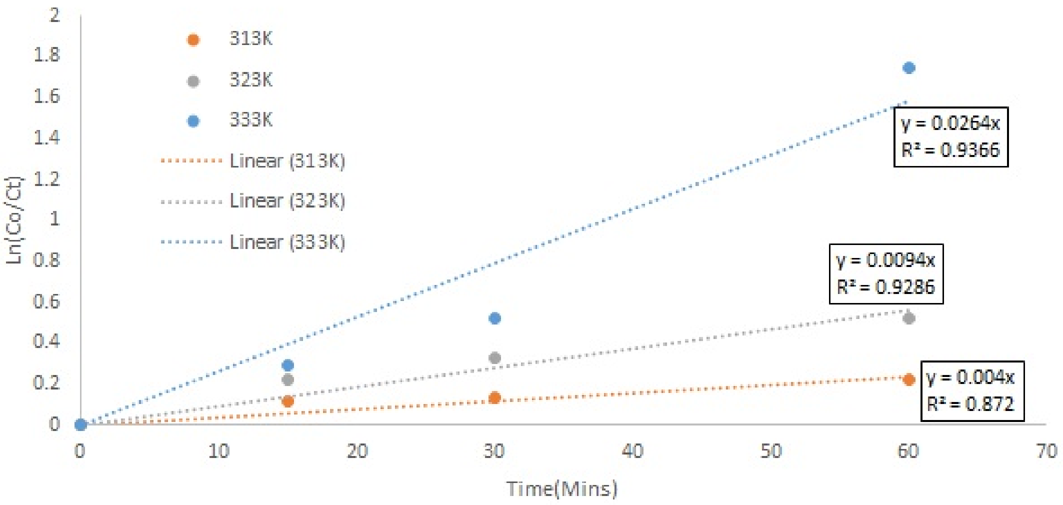


Figure 4.21: Pseudo-first order rate constant for different temperatures (Nitrogen)

Table 4.3: Rate constant for $Fe/TS-1$ for Quinoline

Temp	$T^{-1}(K^{-1})$	k'(apparant)	$kmin^{-1}$	R^2
40	0.0032	0.0040	0.0023	0.8720
50	0.0031	0.0094	0.0053	0.9286
60	0.0030	0.0264	0.0150	0.9366

The plot lnk Vs T^{-1} gives the value activation energy based on Arrhenius equation which is shown in Fig.4.22.

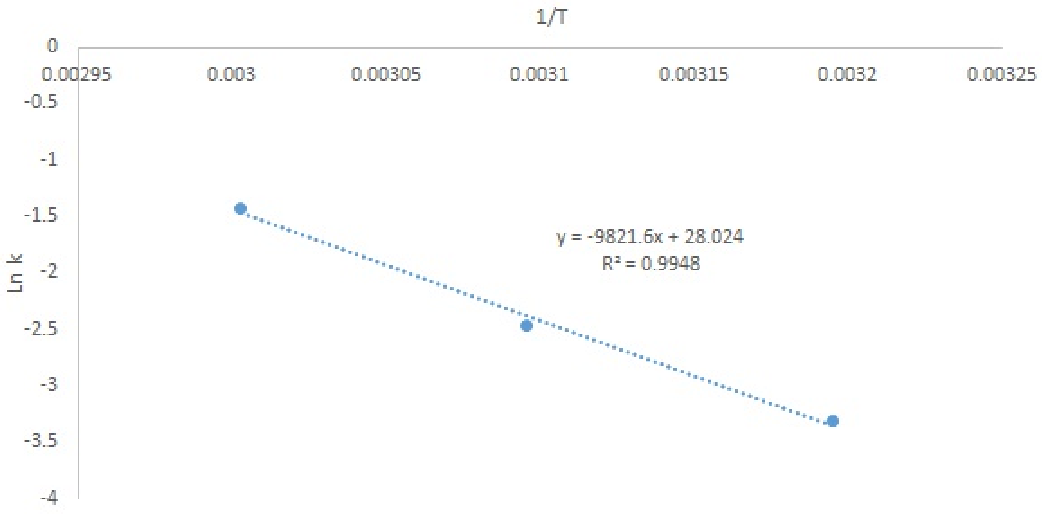


Figure 4.22: Arrhenius activation energies for Quinoline oxidation

$$lnk = \frac{-E_a}{RT} + lnk_0$$

$$Slope = -E_a/R = -9821.6$$

$$E_a = 81.65\, kJmol^{-1}$$

A plot was obtained and by analyzing the graph the activation energy Ea was calculated as 81.65 $kJmol^{-1}$.

It is concluded from above results that with the help of catalyst Fe/TS-1 and in presence of 30 wt % hydrogen peroxide thiophene and quinoline got oxidized to 100% and the process conditions like speed of agitation =800 rpm,temperature = 333 K,$H_2O_2 : S$ratio=15:1,catalyst quantity= 1 gram were optimized. On the basis of this optimized conditions kinetics of both the compounds were calculated and resultant activation energies for thiophene and quinoline were 52.887 $kJmol^{-1}$ and 81.65 $kJmol^{-1}$ respectively.

Chapter 5

Conclusions

Three different catalysts Fe/TS-1, Mo/TS-1, and Ce/Ts-1 were prepared using incipient wetness impregnation method. The characterization of the catalyst were done using BET surface area, X-ray diffraction and SEM/EDS. With the help of these three synthesized catalysts and in presence of 30 wt % of hydrogen peroxide the oxidation of thiophene as a sulfur model compound in octane was carried out. The evaluation of the reactions were done using two dimensional gas chromatography. The results have shown a high conversion of 70% increase in conversion with Fe/TS-1. For the further reactions Fe/TS-1 was used. Also the parameters including speed of agitation, catalysts particle size, oxidant to sulfur ratio, catalyst quantity and temperature were tested. The conversion obtained with Fe/TS-1 was 100% with following conditions, stirrer speed=800rpm, temperature=60^oC, $Thiophene : H_2O_2$ratio = 1:15, amount of catalyst =1.0 gram and catalyst size = 100-180 µm. Also the oxidation of quinolone as nitrogen model compound was carried out on Fe/TS-1 as a catalyst and hydrogen peroxide as an oxidizing agent. 100% conversion was obtained with following conditions, stirrer speed=800rpm, temperature=60^oC, $Thiophene : H_2O_2$ratio = 1:15, amount of catalyst =1.0 gram and catalyst size = 100-180 µm.The kinetics of the reaction was studied and found that it obeys pseudo first order reaction. The activation energy Ea of the Fe/TS-1 with thiophene was 52.887 $kJmol^{-1}$ and with quinoline was 81.65 $kJmol^{-1}$.

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