EPOXIDATION OF SOYBEAN OIL OVER MESOPOROUS TITANIUM AND NIOBIUM INCORPORATED SBA-15 CATALYSTS

A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillments of the Requirements for the Degree of

MASTER OF SCIENCE

in Chemical Engineering

by
Mustafa KALKANDELEN

December 2019

İZMİR

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisor Prof. Dr. Selahattin YILMAZ for his guidance, contribution, advice and support during my studies. He was very kind, generous and patient to me all the time. Without him, I would have never been able to achieve what I have done in this study.

I am very thankful to my lab mate, research assistant Vahide Nuran MUTLU for her help and understandings during my studies.

I would like to thank research specialist Dr. Nesrin AHIPAŞAOĞLU and technical staff of chemical engineering department Ahmet KURUL and Nazil KARACA for their understandings, kindness and helps.

I would like to thank my parents Hasan and Güvercin KALKANDELEN and my siblings Pınar and Oktay KALKANDELEN for their material and moral support on me. They were always by my side and encouraged me to do my best. I'm very lucky to have such a great family.

ABSTRACT

EPOXIDATION OF SOYBEAN OIL OVER MESOPOROUS TITANIUM AND NIOBIUM INCORPORATED SBA-15 CATALYSTS

Soybean oil is an abundant, cheap and nontoxic biomass source and contains triglycerides with unsaturated fatty acids which can be easily modified by epoxidation. In this study, mesoporous Ti-SBA-15 with two different Si/Ti molar ratios, MoO_3/Ti-SBA-15 with two different MoO_3 mass ratios and Nb-SBA-15 with two different Si/Nb molar ratios were prepared as catalysts for soybean oil epoxidation reactions. Tertbutanol and ethyl acetate was used as solvent and H_2O_2 was utilized as oxidant. BET analysis indicated existence of high surface area of the catalysts which ranged between 650 and 950 m^2/g. XRD analysis indicated successful incorporation of Nb and Ti into SBA-15 structure. Epoxidation reactions were carried out successfully using Ti-SBA-15 and Nb-SBA-15 catalysts in tertbutanol at 75 ºC for 6 h. Utilizing ethyl acetate as solvent was caused undesired catalyst behaviour such as precipitation, gelation and aggradation. No further investigations were carried out with ethyl acetate. Epoxidation products were analysed with H-NMR, FTIR and analytic methods. Ti-SBA-15 catalysts provided only 10 % double bond conversion and 49 % epoxide selectivity. They were not very active. Nb-SBA-15 catalysts exhibited high acidity. They provided 28 % double bond conversion and 31 % epoxide selectivity. Best yield was obtained with Nb-SBA-15 (10) catalyst as 6.49 %. Stability tests of catalysts indicated that Nb and Ti did not leach whereas severe leaching was observed with Mo. Also, homogenous epoxidation reaction with H_2SO_4 was carried out for comparison with heterogenous catalysts. Results indicated that, heterogenous catalysts were not competitive with homogenous catalyst.

ÖZET

MEZOGÖZENEKLİ TİTANYUM VE NİYOBYUM KATKILANMIŞ SBA-15 KATALİZÖRLERİYLE SOYA YAĞI EPOKSİDASYONU

Soya yağı, ucuz, bol bulunan ve toksik olmayan bir biyokütle kaynağıdır ve doymamış yağ asitlerini ihtiva eden trigliseritleri içerir, bu doymamış yağlar epoksidasyonla kolayca modifiye edilebilirler. Bu çalışmada, farklı Si/Ti mol oranı olan iki Ti-SBA-15, farklı MoO_3 kütle oranı olan iki MoO_3/Ti-SBA-15 ve farklı Si/Nb mol oranı olan iki Nb-SBA-15 katalizörleri soya yağı epoksidasyonu için hazırlandı. H_2O_2 oksidant olarak ve tertbütanol ve etil asetat çözücü olarak kullanıldı. BET analiziyle katalizörlerin yüzey alanın yüksek olduğunu ve 650 ile 950 m^2/g arasında değiştiği belirlendi. Nb ve Ti'un SBA-15 yapısına başarılı bir şekilde yerleştirildiği XRD analiziyle belirlendi. Epoksidasyon reaksiyonları Ti-SBA-15 ve Nb-SBA-15 katalizörleri kullanılarak tertbütanol'de 75 ºC de 6 sa olarak başarılı şekilde gerçekleştirildi. Etil asetat'ın çözücü olarak kullanılması katalizörlerde pelteleşme, dibe çökme ve tabakalaşma gibi istenmeyen davranışlara sebep oldu. Bu yüzden etil asetat'ın çözücü olarak kullanımana devam edilmemiştir. Epoksidasyon ürünleri H-NMR, FTIR ve analitik metotlarla analiz edildi. Ti-SBA-15 katalizörleri sadece 10 % çift bağ dönüşümü ve 49 % epoksi seçiciliği sağladı. Katalizörlerin çok aktif olmadığı bulundu. Nb-SBA-15 katalizörlerinin daha yüksek asitliğe sahip olduğu bulunmuştur. Nb-SBA-15 katalizörleri 28 % çift bağ dönüşümü ve 31 % epoksi seçiciliği sağladı. En iyi epoksit verimi Nb-SBA-15 (10) katalizörüyle 6.49 % olarak elde edildi. Kararlılık testlerinden Mo'un yüksek miktarda sıvıya geçtiği bulunurken, Ti ve Nb'un kararlı olduğu bulunmuştur. Ayrıca, heterojen katalizörlerle karşılaştırmak için homojen epoksidasyon reaksiyonu H_2SO_4 ile gerçekleştirildi. Sonuçlardan, heterojen katalizörlerin homojen katalizörle rekabet edecek düzeyde olmadığı belirlendi.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

In the past few decades increasing concern about detrimental effects of petrochemicals and its derivatives on environment forced researchers to seek their replacements. Vegetable oils are a vast biomass resource that can be a good substitute for petrochemicals because they are cheap, easily available, biodegradable and non-toxic [1]. Soybean oil is one of the most produced vegetable oils and it contains triglycerides with mostly unsaturated double bonds which can be easily functionalized to produce value added chemicals by epoxidation. Epoxidized soybean oil uses as plasticizer and stabilizer in PVC resins and it's a starting materials for production of glycols, alkanolamines, polyols and polymers [2, 3].

Traditionally, epoxidation of vegetable oils carried out in the presence of a strong mineral acid, generally sulphuric acid, with in situ produced peracid which is also produced reaction between hydrogen peroxide and an acid. Until now, this is known the most catalytically active process for epoxidation. However, because of acid utilization, many drawbacks arises with this process such as equipment corrosion, product separation, side reactions and waste disposal [4]. Therefore, utilization of greener process is indispensable.

Recently, many afford were devoted to developing alternative processes instead of homogenous one. Heterogenous processes offers greener and sustainable reaction pathway, also they do not have aforementioned drawbacks, and thus many epoxidation reactions performed by employing heterogenous catalysts including acid resins, Ti-silicas, heteropoly acid and so on [4-8]. Throughout literature, there are many reports that indicate epoxidation properties of Nb and Ti when incorporated in a silica structure or used with a support [4, 9-11]. Both metals are not just active in epoxidation reactions but also have good stability against leaching [12, 13]. Also, as a transition metal, Mo demonstrated remarkably good catalytic activity in homogenous and heterogenous epoxidation reactions [14-16].

Moreover, when heterogenous systems considered, it's a three phasic system (oil, aqueous and solid) and because of that, utilization of a solvent is crucial which increases interaction between phases hence increases the yield. Many of solvents used in epoxidation reactions include, tertbutanol, toluene, ethyl acetate, hexane and so on [17-20]. Aside that, selection of a proper oxidant is important in both economic and environmental point of view. As an oxidant, molecular oxygen involves more active oxygen however it's not commonly used in liquid phase epoxidation reactions because of mass transfer limitation between phases causes lower yield [21]. On the other hand, hydrogen peroxide is a liquid substance, relatively cheap and gives only water as by product thus it is the most utilized oxidant in both homogenous and heterogenous processes [22].

In this study, Nb and Ti were incorporated to mesoporous SBA-15 structure with different Si/Nb and Si/Ti molar ratios by sol-gel method and MoO_3 was loaded on synthesised Ti-SBA-15 structure for two different amounts by incipient wetness impregnation. The catalysts were employed in soybean oil epoxidation reaction by utilizing tertbutanol and ethyl acetate as solvent and hydrogen peroxide as oxidant at 75 ºC for 6 h. Also, for comparison purposes, commercial homogenous epoxidation reaction was carried out.

CHAPTER 2

VEGETABLE OILS EPOXIDATION

2.1. Vegetable Oils

Vegetable oils are extracted from crops and they are abundant, cheap and non-toxic biomass sources. In 2017, 182.3 million ton vegetable oils produced annually and the most produced one is palm oil (33 %) although its cultivation occupies only 5.5 % of the total lands used for production of vegetable oils [23]. Vegetable oils are mainly used in food industry (80 %) and the rest is used for production of many chemicals like lubricants, soap and so on [24]. The main component of vegetable oils are triglycerides which are composed of three fatty acids bonded at a glycerol molecule as demonstrated in Figure 2.1 [25].

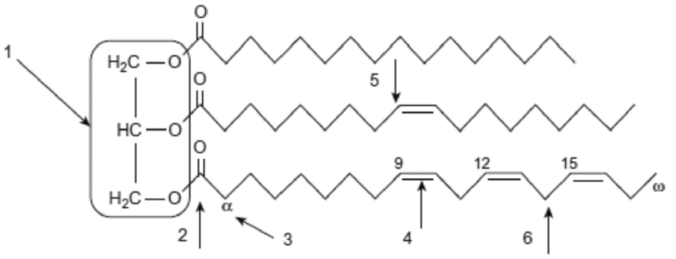


Figure 2.1. A typical triglyceride molecule: (1) glycerol linkage, (2) ester group, (3) α position of ester group (4) double bonds, (5) monoallylic position, and (6) bisallic position [25].

Carbon chain length of fatty acids inside vegetable oils ranges between 8-24 with between 0–7 carbon carbon double bonds. These contents can vary depending on growth condition, plant type and even seasons. Table 2.1 demonstrates main fatty acid composition and iodine values of different vegetable oils. Iodine values indicates double bond content of oil which measures by iodine absorbed by double bonds. Generally, iodine values expressed as milligram amount of iodine absorbed per 100 gram of oil [26].

Higher iodine values indicates higher double bond content and accordingly, from Table 2.1, linseed oil compromises the highest amount of double bonds (ranges between 168-204 mg I_2/100 g oil) due to its high linolenic acid content (56.6 wt %) which has

Table 2.1. Fatty acid composition of different vegetable oils [25].

	Fatty acid composition (*X*:*Y*, where *X* is the number of carbon atoms and *Y* is the number of double bonds), wt%					
Vegetable oil	**Palmitic (C16:0)**	**Stearic (C18:0)**	**Oleic (C18:1)**	**Linoleic (C18:2)**	**Linolenic (C18:3)**	**Iodine value (mg per 100 g)**
Soybean	11.0	4.0	23.4	53.3	7.8	117–143
Palm	42.8	4.2	40.5	10.1	—	44–58
Rapeseed/canola	4.1	1.8	60.9	21.0	8.8	110–126
Sunflower	5.2	2.7	37.2	53.8	1.0	110–143
Tallow	27.0	7.0	48.0	2.0	—	35–48
Lard	26.0	11.0	44.0	11.0	—	45–75
Butterfat	26.0	11.0	28.0	2.0	—	29–41
Groundnut	11.4	2.4	48.3	31.9	—	80–106
Cottonseed	21.6	2.6	18.6	54.4	0.7	90–119
Coconut	9.8	3.0	6.9	2.2	—	6–11
Palm kernel	8.8	2.4	13.6	1.1	—	14–24
Olive	13.7	2.5	71.1	10.0	0.6	75–94
Corn	10.9	2.0	25.4	59.6	1.2	102–130
Linseed	5.5	3.5	19.1	15.3	56.6	168–204
Sesame	9.0	6.0	41.0	43.0	1.0	103–116
Castor	1.5	0.5	5.0	4.0	0.5	82–88

three double bonds.

2.1.1. Soybean Oil

Soybean is the most cultivated oilseed crop and about 40.1 % lands (based on total lands employed by oilseed crops) occupied by soybean however, its oil content is relatively low (21 wt %) thus it is the second major vegetable oil production source after oil palm tree. In 2017, about 53.7 million ton of soybean oil produced in the world [27]. Table 2.2 demonstrates content of crude soybean oil. Triacylglycerols are the main components and rest is phospholipids, unsaponifiable matter, free fatty acids and traces of other. Some of these components effects oil quality negatively and quality of oil can be increased by refining namely a bland, stable and nutritious product can be obtained [28]. Primary fatty acid composition of soybean oil is demonstrated in Table 2.1. It contains about 85 wt % of unsaturated fatty acids, which are oleic acid (23.4 %), linoleic acid (53.3 %) and linolenic acid (7.8 %), and the rest is saturated fatty acids. Because of high unsaturation, its iodine value is high and ranges between 117-143 mg I_2/100 g oil.

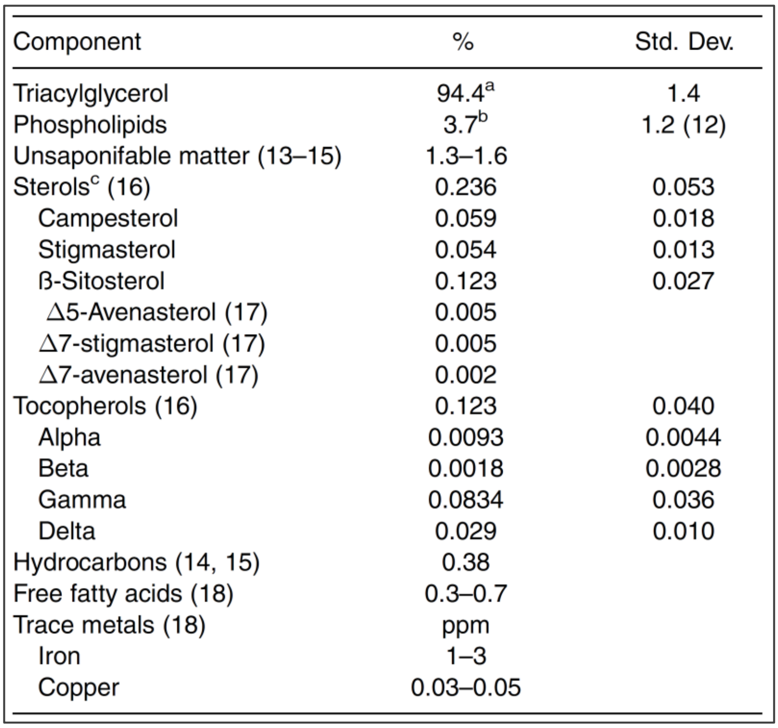
2.2. Epoxidation of Vegetable Oils

Vegetable oils epoxidation occurs at the fatty acid chain inside triglyceride molecule by addition of an oxygen atom to ethylenic unsaturation (double bonds) thus a cyclic ether form is obtained [29]. Figure 2.2 demonstrates comparison of epoxides structure with ether structure. The bond angle in ether structure is ideal, which is 109.5° and epoxides have a bond angle as 60° thus there is 49.5° angle strain on each corner of epoxides which makes them highly strained and highly reactive [30]. Epoxidized oils are biodegradable, non-toxic and natural hence they can be good substitutes for petroleum derived chemicals. Vegetable oil epoxide are used as stabilizers and plasticizers in PVC resins which improves resins flexibility, elasticity and stability. Moreover, they are used as raw material for production of various chemicals such as polymers, alcohols, glycols, alkanolamines, olefinic compounds and carbonyl compounds [29].

2.2.1. Epoxidation Methods

There are basically two important vegetable oil epoxidation methods:

Table 2.2. Typical composition of crude soybean oil [28].



Component	%	Std. Dev.
Triacylglycerol	94.4[a]	1.4
Phospholipids	3.7[b]	1.2 (12)
Unsaponifable matter (13–15)	1.3–1.6	
Sterols[c] (16)	0.236	0.053
Campesterol	0.059	0.018
Stigmasterol	0.054	0.013
ß-Sitosterol	0.123	0.027
Δ5-Avenasterol (17)	0.005	
Δ7-stigmasterol (17)	0.005	
Δ7-avenasterol (17)	0.002	
Tocopherols (16)	0.123	0.040
Alpha	0.0093	0.0044
Beta	0.0018	0.0028
Gamma	0.0834	0.036
Delta	0.029	0.010
Hydrocarbons (14, 15)	0.38	
Free fatty acids (18)	0.3–0.7	
Trace metals (18)	ppm	
Iron	1–3	
Copper	0.03–0.05	

[a] By difference.
[b] Based on 23 varieties chosen to represent a wide fatty acid composition.
[c] Based on 13 varieties chosen to represent a wide range of composition.

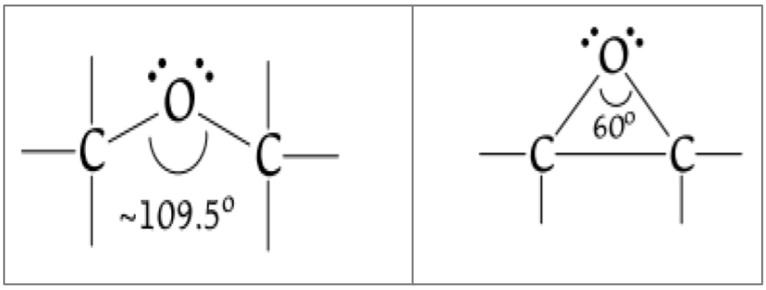


Figure 2.2. Structure of epoxides relative to ethers [30].

1) Homogenous catalytic epoxidation with carboxylic acids and hydrogen peroxide with or without liquid homogenous catalyst (enzymes or mineral acids). The system is biphasic which are organic and inorganic phases.

2) Heterogenous catalytic epoxidation with hydrogen peroxide or tertbutyl hydroperoxide. The system is triphasic which are organic, inorganic and solid phases.

2.2.1.1. Homogenous Epoxidation Method

Homogenous epoxidation is carried out in the presence of a mineral acid by in situ produced peracid. There are few mineral acids that used in epoxidation reactions which are H_2SO_4, HCI, HNO_3 and H_3PO_4. Among them, H_2SO_4 is the most used one because it provides better yield. Peracid is produced reaction between hydrogen peroxide and respective acid (e.g., formic acid, acetic acid). M-clorobenzoic, performic, perbenzoic and peracetic acid are some of the used peracids in the epoxidation reactions. Benzoic peracids offer higher activity however they are expensive and separation of them after reaction is more difficult thus performic and peracetic acids are the most used peracids [25]. In this system, there are two phases, one is organic phase and other one is inorganic phase. Inorganic phase includes aqueous hydrogen peroxide and respective reactant acid (formic or acetic acid) and by the reaction between them, peracid produces. Subsequently, produced peracid migrates into the organic phase, which is oil, and reacts therein to produce epoxidized oil in the presence of a mineral acid (e.g., H_2SO_4). After losing its oxygen, peracid (e.g., performic acid) becomes acid (formic acid) then migrates into inorganic phase again and follow the same cycle repeatedly. Figure 2.3 demonstrates taking place reactions during this cycle.

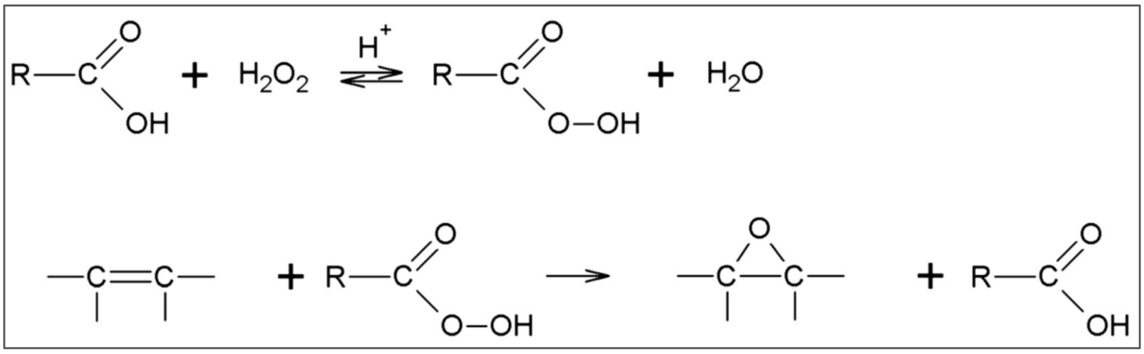


Figure 2.3. Reactions of conventional epoxidation process of soybean oil [25].

Conventionally epoxidation of vegetable oils is carried out with this method at temperatures between 65-70 ºC by using excess amount of hydrogen peroxide in the presence of H_2SO_4. The reaction is highly exothermic and because of that hydrogen peroxide and respective acid are added slowly in order to prevent overheating of reactor and ring opening reactions [29]. Possible ring opening products are given in Figure 2.4. The side reactions occur primarily because of the presence of acidic substances in the reaction medium. In the literature, some studies were performed to determine the heat of reaction for this system. The obtained results are demonstrated in Table 2.3. In any case, from Table 2.3, heat of reaction was found very high and the values ranges between 116-230 kj/mol. Although this method provides higher conversion and selectivity values, it has several drawbacks such as side reactions, strongly corrosive by products, non-recyclable wastes, and separation of catalyst [25].

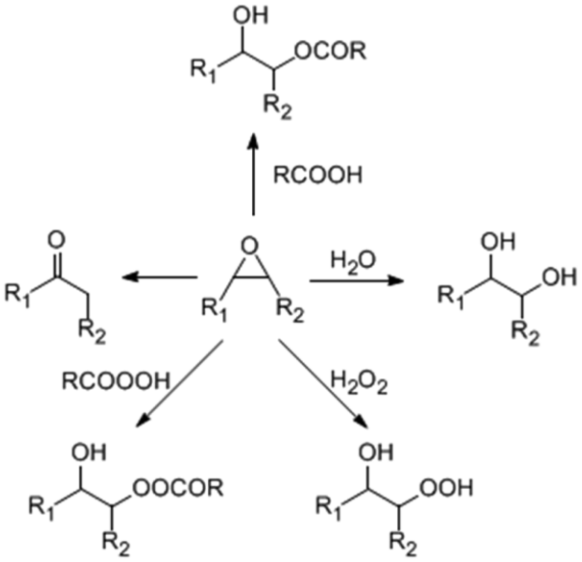


Figure 2.4. Possible oxirane ring opening reactions [31].

Table 2.3. Heat of reactions results determined in the literature studies [24].

	De Quadros et al.	Santacesaria et al.	Leveneur et al.	Vianello et al.
Heat of reaction (kj/mol)	-196	-230	-116	-193

2.2.1.2. Heterogenous Epoxidation Method

This method developed considerably recently due to increasing concerns about environment and depleting petroleum reservoirs. Epoxidation is carried out in the presence of a solid catalyst by using an oxidant and solvent. There are many types of oxidants but generally tert butyl hydroperoxide or hydrogen peroxide are used because they are relatively cheap and their by products are only alcohol and water, respectively. There are three phases in this system, which are catalyst (solid), oil (organic) and aqueous (inorganic) phases, hence, to assure more interaction between phases a solvent is used but its utilization is not imperative. In some cases, solvent can be used to prevent sudden increase of temperature by absorbing of heat. In this method, after completion of reaction catalyst can be easily separated from the reaction mixture and also none of the drawbacks, as in the homogenous one, are encountered. The acid utilization is minimal thus side reactions are diminished significantly. Throughout literature various types of heterogenous catalysts are employed including titanium, tungsten, molybdenum, niobium and alumina [29]. Microporous (Ti silicates) and mesoporous (SBA-15 and MCM-41) type materials are commonly used in epoxidation reactions. In both types, surface area, pore diameter and pore volumes are some of the important variables. Table 2.4 demonstrates some performed epoxidation studies in the literature within different catalytic systems.

Table 2.4. Different catalytic systems reported for the epoxidation of vegetable oils [25].

Substrate	Oxidant	Catalyst	Reaction conditions	Solvent	System efficiency (epoxy product yield) (%)	Ref. (year)
Homogeneous catalytic systems						
Rapeseed oil	$CH_3COOH + H_2O_2$	Sulphuric acid	65 °C, 6 h	—	66	24 (2010)
Grape seed oil	$CH_3COOH + H_2O_2$	Sulphuric acid	60 °C, 6 h	—	69	25 (2016)
Soybean oil	H_2O_2	CH_3ReO_3	30 °C, 2 h	Dichloromethane	95	26 (2002)
Soybean oil	TBHP	$[MoO_2(acac)_2]$	110 °C, 2 h	Toluene	54	27 (2010)
Lipases						
Soybean oil	H_2O_2	Novozym 435	50 °C, 4 h	Toluene	90	28 (2006)
Sapindus mukorossi seed oil	H_2O_2	Novozym 435	50 °C, 7 h	Toluene	90	29 (2011)
Karanja oil	H_2O_2	Novozym 435	40 °C, 10 h	Toluene	80	30 (2016)
Polyoxometalates						
Soybean oil	H_2O_2	A peroxopolyoxometalate $[PW_4O_{24}]^{3-}$ with dicationic long-chain alkyl imidazolium ionic liquids	80 °C, 2 h	—	80	31 (2014)
Soybean oil	H_2O_2	$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$	60 °C, 4 h	—	90	32 (2015)
Soybean oil	H_2O_2	$[MeN(n\text{-}C_8H_{17})_3]\{PO_4[WO(O_2)_2]_4\}$	40 °C, 3 h	—	99	33 (2012)
Soybean oil	H_2O_2	$[MeN(n\text{-}C_8H_{17})_3]\{PO_4[WO(O_2)_2]_4\}$ supported on modified halloysite nanotubes	40 °C, 3 h	—	12	33 (2012)
Soybean oil	H_2O_2	$[MeN(n\text{-}C_8H_{17})_3]\{PO_4[WO(O_2)_2]_4\}$ supported on palygorskite	50 °C, 2 h	—	79	34 (2014)
Heterogeneous catalytic systems						
Cottonseed oil	$CH_3C(O)OOH$	Amberlite IR-120	75 °C, 10 h	—	63	35 (2011)
Castor oil	$CH_3C(O)OOH$	Amberlite IR-120	50 °C, 10 h	Benzene	78	36 (2014)
Soybean oil	H_2O_2	$\gamma\text{-}Al_2O_3$	80 °C, 10 h	Ethyl acetate	48	37 (2016)
Soybean oil	H_2O_2	$Nb_2O_5\text{–}SiO_2$	80 °C, 5 h	Ethyl acetate	10	38 (2012)
Sunflower oil	TBHP	CoCuAl ternary layered double hydroxides	110 °C, 4 h	Toluene	69	39 (2015)
Soybean oil	TBHP	MoO_3/Al_2O_3	80 °C, 4 h	Toluene	16	40 (2014)
Soybean oil	H_2O_2	Amorphous Ti/SiO_2	90 °C, 54 h	*tert*-Butanol	87	41 (2004)
Soybean oil	TBHP	Meso-TS-1	80 °C, 4 h	Toluene	11	40 (2014)
Soybean oil	TBHP	Meso-Ti–MCM-41	60 °C, 24 h	Ethyl acetate	14	42 (2010)
Soybean oil	TBHP	Meso-Ti–HMS	60 °C, 24 h	Ethyl acetate	22	42 (2010)

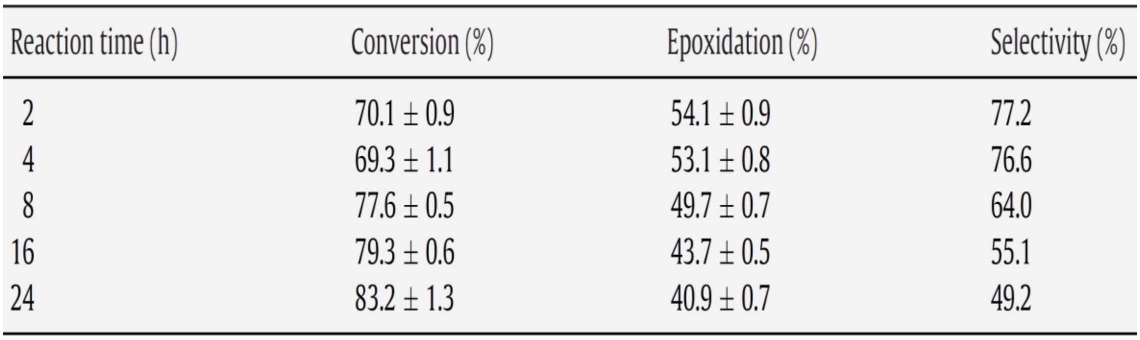
CHAPTER 3

LITERATURE SURVEY

3.1. Epoxidation by Homogenous Catalysts

In the study conducted by Farias et al. (2010), a molybdenum complex, which is $MoO_2(acac_2)$, was used as catalyst in epoxidation of soybean oil at 80 ºC and 110 ºC for 24 h. Toluene and anhydrous TBHP were used as solvent and oxidant, respectively. The catalyst was purchased and subjected to epoxidation reactions without any treatment. When soybean oil epoxidation reaction was performed at 80 ºC, conversion and epoxide selectivity were increased with time and reached 94.1 % for conversion and 41.9 % for epoxide selectivity at 16 h and remained constant after that time. In the case of epoxidation reactions at 110 ºC, soybean oil conversion and epoxide selectivity values are given in Table 3.1. Conversion increased from 70.1 % to 83.2 % with time however epoxide selectivity diminished (from 77.2 % to 49.2 %). They were ascribed that fact by formation of tertbutanol as by-product from TBHP which acted as an inhibitor. Under conditions tested, best results for soybean oil conversion (70.1 %) and epoxide selectivity (77.2 %) were obtained at 110 ºC for 2 h [16].

Table 3.1. Epoxidation of soybean oil at 110 ºC using the catalytic system $MoO_2(acac_2)$/TBHP[a], determined by H NMR spectroscopy [16].



Reaction time (h)	Conversion (%)	Epoxidation (%)	Selectivity (%)
2	70.1 ± 0.9	54.1 ± 0.9	77.2
4	69.3 ± 1.1	53.1 ± 0.8	76.6
8	77.6 ± 0.5	49.7 ± 0.7	64.0
16	79.3 ± 0.6	43.7 ± 0.5	55.1
24	83.2 ± 1.3	40.9 ± 0.7	49.2

[a] Reaction were carried out with toluene as solvent and molar ratios of anhydrous TBHP: number of double bonds in the oil: catalyst of 100:100:1. The results were calculated by H NMR, 5 % incertitude.

Wang et al. (2017) studied on soybean oil epoxidation with deep eutectic solvents (DESs) as catalyst by using commercial epoxidation reaction. DESs, which is choline chloride (ChCI), was purchased and modified by using three carboxylic acids (Oxalic acid, citric acid and malonic acid) as hydrogen bond donors. Modified DESs were denoted as ChCI-OA, ChCI-CA and ChCI-MA for oxalic acid, citric acid and malonic acid, respectively. Acidic strength of DESs in aqueous solution were investigated and it was found that acidic strenght of short chain carboxylic acids were higher than that of longer counterparts. Reaction products were analyzed with H-NMR and compared to common used titration method (HBr method). Results obtained from both analysis was similar which meant H-NMR is a strong method to analyse products.

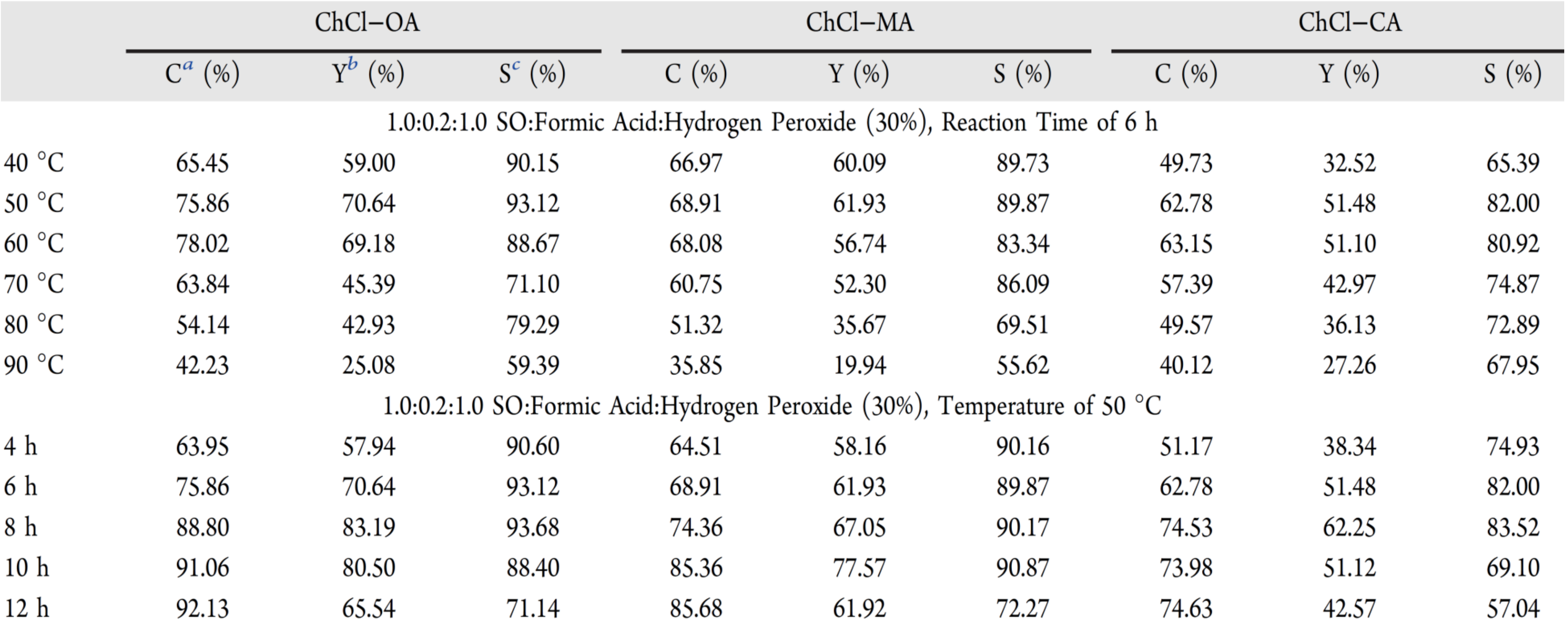
Firstly, epoxidation reactions were performed at different temperatures (40-90 ºC) for 6 h in order to investigate temperature effect on reaction. For ChCI-OA and ChCI-CA, the highest double bond conversion was obtained at 60 ºC but for ChCI-MA at 50 ºC. ChCI-OA and ChCI-MA gave higher epoxide selectivity than ChCI-CA. Overall, catalysts exhibited better catalytic activities at 50 ºC.

After selection of best temperature, they performed reactions further at various reaction times (4-12 h) in order to determine required time for best results of conversion and selectivity. Conversion of double bonds and epoxide selectivity increased, for all catalyst, with increasing time from 4 to 8 h and thereafter, conversion was increased still however, selectivity decreased after 8 h except for ChCI-MA (selectivity decreased after 10 h). When reactions were performed for 12 h, serious side reactions took place along with the main reaction thus 8 h was selected as optimal reaction time.

Under optimal test condition (8 h at 50 ºC), best results for double bond conversion (88.8 %) and epoxide selectivity (93.68 %) were obtained with ChCI-OA catalyst. Conversion, yield and selectivity results for all three catalysts are demonstrated in Table 3.2. Also, to investigate reusability of catalyst, ChCI-OA was used five consecutive runs. It was found that catalytic activity of catalyst almost remained same after five runs [32].

In the study performed by Vianello et al. (2018), effect of several process variables within commercial soybean oil epoxidation method were investigated. The variables investigated were presence and absence of sulphuric acid, effect of mixing program, amount of sulphuric acid and amount of acetic acid. In any case, hydrogen peroxide to double bond molar ratio was kept 1.5:1, reaction temperature was set to 60 ºC and reaction carried out for 4 h. Preliminary, epoxidation reaction was carried out in the absence of

Table 3.2. Epoxidation of soybean oil at different reaction temperatures and times in DESs [32].



	ChCl−OA			ChCl−MA			ChCl−CA		
	C[a] (%)	Y[b] (%)	S[c] (%)	C (%)	Y (%)	S (%)	C (%)	Y (%)	S (%)
1.0:0.2:1.0 SO:Formic Acid:Hydrogen Peroxide (30%), Reaction Time of 6 h									
40 °C	65.45	59.00	90.15	66.97	60.09	89.73	49.73	32.52	65.39
50 °C	75.86	70.64	93.12	68.91	61.93	89.87	62.78	51.48	82.00
60 °C	78.02	69.18	88.67	68.08	56.74	83.34	63.15	51.10	80.92
70 °C	63.84	45.39	71.10	60.75	52.30	86.09	57.39	42.97	74.87
80 °C	54.14	42.93	79.29	51.32	35.67	69.51	49.57	36.13	72.89
90 °C	42.23	25.08	59.39	35.85	19.94	55.62	40.12	27.26	67.95
1.0:0.2:1.0 SO:Formic Acid:Hydrogen Peroxide (30%), Temperature of 50 °C									
4 h	63.95	57.94	90.60	64.51	58.16	90.16	51.17	38.34	74.93
6 h	75.86	70.64	93.12	68.91	61.93	89.87	62.78	51.48	82.00
8 h	88.80	83.19	93.68	74.36	67.05	90.17	74.53	62.25	83.52
10 h	91.06	80.50	88.40	85.36	77.57	90.87	73.98	51.12	69.10
12 h	92.13	65.54	71.14	85.68	61.92	72.27	74.63	42.57	57.04

[a] Conversion of double bonds. [b] Epoxide yield. [c] selectivity.

sulphuric acid with acetic acid to double bond molar ratio 0.5:1. The result demonstrated that there was no conversion. After that, epoxidation reaction was carried out in the presence of 3 wt % (with respect to mass of oil) sulphuric acid by setting impeller speed to 500 rpm and increasing it to 1500 rpm for 30 s after 2 h. Under this condition, results were indicated complete conversion of double bonds and 77 % of epoxide selectivity hence the presence of sulphuric acid in the process was found crucial.

Thereafter, in order to investigate effect of mixing program, epoxidation reaction was carried out at same conditions as above in the presence of sulphuric acid but this time impeller speed was set to 500 rpm and it was increased to 1500 rpm for 30 s after every 20 min. The results demonstrated complete conversion of double bonds however epoxide selectivity was increased to 97 % and time for complete conversion of double bonds decreased by half an hour. They pointed out that, setting impeller speed to1500 rpm in the whole reaction time would be increase reaction kinetics and also selectivity however by researching through literature it was found that higher impeller speeds cause also degradation of soybean oil.

Moreover, effect of sulphuric acid amount was investigated by using 2 wt %, 3 wt % and 4 wt % sulphuric acid with respect to oil by keeping other variables constant. Time for complete conversion of double bonds were found as 4 h, 3.5 h and 3 h and epoxide selectivity as 97 %, 97 % and 94 % for 2 wt %, 3 wt % and 4 wt % sulphuric acid amounts, respectively. In order to investigate acetic acid amount, 0.5:1 and 1:1 acetic acid to double bonds molar ratios were studied. It was found that increasing acetic acid amount increased peroxyacetic acid formation and consequently faster reaction kinetics thus, time for complete conversion of double bonds were decreased by half an hour. However, epoxide selectivity was found as 97 % for 0.5:1 acetic acid to double bonds molar ratio whereas for 1:1 acetic acid to double bonds molar ratio as 89 %. From the results, best compromise was found for sulphuric acid as 3 wt % (with respect to oil) and acetic acid to double bonds molar ratio as 0.5:1 [24].

Recently, Piccolo et al. (2019), investigated effect of microwave heating on soybean oil epoxidation within traditionally used epoxidation method (H_2SO_4). Also, for comparison, epoxidation reaction was carried out with using conventional heating. Three temperatures (50, 60 and 70 ºC) and various stirring velocities were investigated. In order to investigate stirring velocities, temperature set to 60 ºC and time fixed at 3 h. In conventional heating it was found that low stirring velocities provided lower yields (10 %) and threshold stirring velocity was found between 250-300 rpm. Maximum yield (about 80 %) was obtained when stirring velocity was 450 rpm, higher velocities after this value were provided lower yields, because increasing stirring velocity further was caused more interaction between epoxide and acid therefore, accelerating side reactions.

For the case of microwave heating, investigated stirring velocities were between 45-145 rpm. Highest yield (90 %) was obtained at 45 rpm. Increasing stirring velocity to 145 rpm was decreased yield (82 %). After determination of ideal stirring velocities (45 rpm for microwave heating and 450 rpm for conventional heating), effect of temperature was investigated. Firstly, epoxidation reactions were carried out at 70 ºC. Maximum yield (about 90 %) was reached at 1.5 h for microwave heating and 3 h for conventional heating. When reactions were carried out at 60 ºC, maximum yield (about 90 %) was reached in 2 h for microwave heating and 4 h for conventional heating. At 50 ºC for 6 h, microwave heated reaction gave higher yield than conventional heated reaction (over 90 % for microwave heating and about 75 % for conventional heating). For microwave heated reaction, best compromise for yield (90 %) was obtained at 70 ºC for 1.5 h, however reaction must be shut down immediately after reaching maximum yield because microwave was speeded up side reactions also.

Moreover, microwave was ensured more uniform suspension even agitation was weak, and solution was preserved its stability longer duration after stopping process whereas after shutting down of process, fast phase separation was occurred in conventional heated reaction. As a conclusion, microwave heating require more equipment cost but it was decreased reaction time by half and was ensured high yield with lower stirring velocities [23].

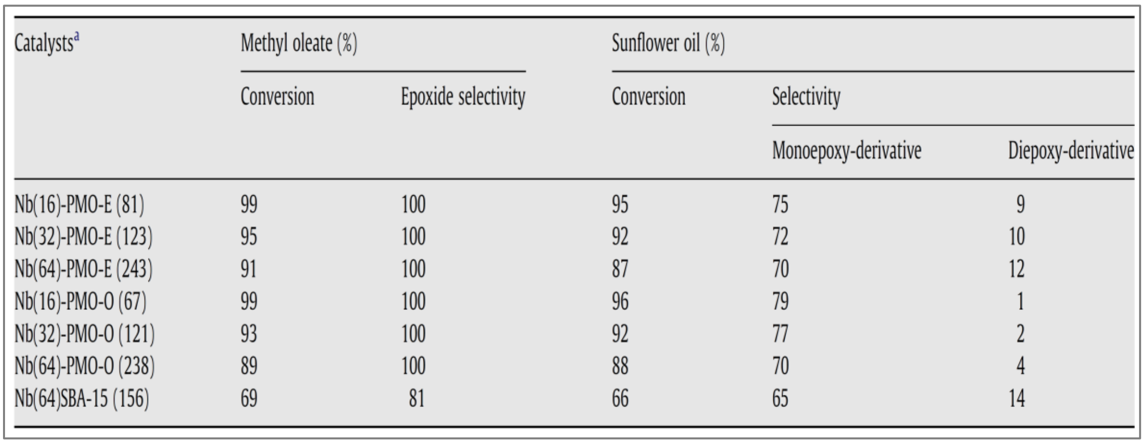
3.2. Epoxidation by Heterogenous Catalysts

In the study conducted by Feliczak et al. (2009), periodic ordered mesoporous organo-niobosilicas (Nb-PMOs) were synthesised in order to use in epoxidation of methyl oleate, fatty acid methyl ester (FAME) and oxidation of C18 fatty acid at 70 ºC for 24 h. Hexane and H_2O_2 was used as solvent and oxidant, respectively. The catalysts were bridged by two organic groups, which are ethane and octane, with three Si/Nb nominal molar ratios (16, 32 and 64) and they denoted them as Nb-PMO-E and Nb-PMO-O for ethane and octane bridged catalysts, respectively. Also, for comparison Nb-SBA-15 with Si/Nb molar ratio 64 was synthesised.

XRF results indicated that actual Si/Nb molar ratio of Nb-PMO-E and Nb-PMO-O catalysts were almost four times higher than nominal ratio. They explained that by competitiveness of bridged organic groups with niobium and acidity of synthesis medium whereas actual Si/Nb ratio for Nb-SBA-15 was found two times higher because of acidity of synthesis medium. From N_2 adsorption/desorption analysis surface area of Nb-PMO catalysts was found for Nb-PMO-E's between 720-950 m^2/g and for Nb-PMO-O's 320-400 m^2/g. Also, same analysis was indicated that pore size of Nb-PMO-E catalysts were higher than Nb-PMO-O catalysts. Results of performed methyl oleate and FAME mixture (obtained from sunflower oil) epoxidation reactions are given in Table 3.3.

Methyl oleate conversion was found very high (between 89-99 %) with organic bridged Nb-PMO-E and Nb-PMO-O catalysts and conversion increased with increasing niobium content for both catalysts. Also, 100 % epoxide selectivity obtained with these catalysts. Decrease of conversion (between 88-96 %) and epoxide selectivity (74-86 %) were found when FAME mixture was used as substrate in epoxidation reactions with organic bridged Nb-PMO catalysts. On the other hand, Nb-SBA-15 catalyst provided relatively lower conversion and selectivity values either using methyl oleate (69 % conversion and 81 % selectivity) or FAME mixture (66 % conversion and 79 % selectivity) as substrate. Moreover, they tested all catalyst four times in epoxidation reactions in order to investigate activity and reusability of catalysts. The results indicated that these catalysts preserve their activity and reusable at least four times [20].

Table 3.3. Epoxidation of methyl oleate and sunflower oil using different nioboorganosilicas and niobosilica [20].



Catalysts[a]	Methyl oleate (%)		Sunflower oil (%)		
	Conversion	Epoxide selectivity	Conversion	Selectivity	
				Monoepoxy-derivative	Diepoxy-derivative
Nb(16)-PMO-E (81)	99	100	95	75	9
Nb(32)-PMO-E (123)	95	100	92	72	10
Nb(64)-PMO-E (243)	91	100	87	70	12
Nb(16)-PMO-O (67)	99	100	96	79	1
Nb(32)-PMO-O (121)	93	100	92	77	2
Nb(64)-PMO-O (238)	89	100	88	70	4
Nb(64)SBA-15 (156)	69	81	66	65	14

Conditions: aqueous H_2O_2/substrate = (1 mmol/mmol); substrate/catalyst = 8 (v/v); 343 K, 24 h.
[a] The last two numbers in the brackets denotes real Si/Nb ratio.

In the study performed by Farias et al. (2011), a molybdenum complex, which was [$MoO_2(acac)_2$], immobilized on montmorillonite K10 clay in order to use in epoxidation of soybean oil and castor oil at 80 ºC. Toluene and anhydrous TBHP was used as solvent and oxidant, respectively. They examined different TBHP to double bond molar ratios ranging from 1 to 4. After immobilization of molybdenum complex, catalyst was denoted as K10-Mo. From N_2 adsorption/desorption and BET analysis, a slight increase of pore diameter and decrease of surface area and pore volume was observed. The catalyst exhibited type IV adsorption isotherms which indicated occurrence of mesoporous structure.

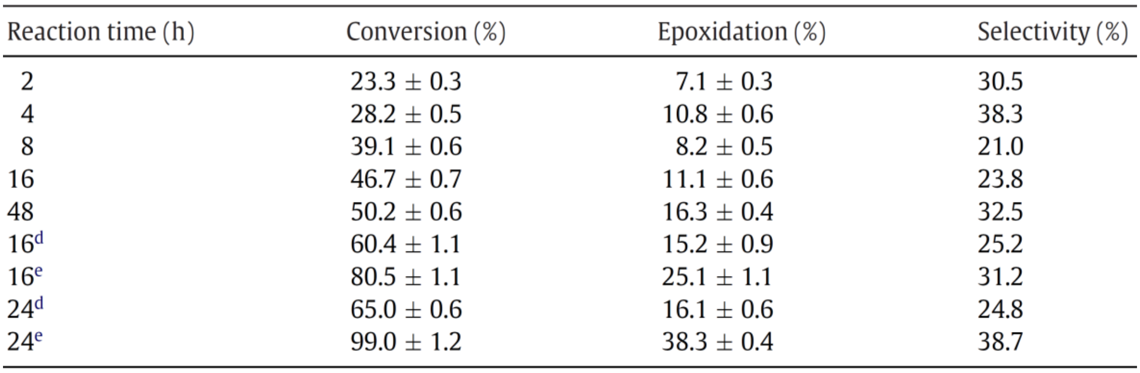
They carried out epoxidation reaction of castor oil for 24 h and of soybean oil for 48 h. Both substrates gave very high conversion (99 %) but castor oil provided better epoxide selectivity (58.5 %) with using excess amount of oxidant (TBHP/double bond molar ratio 4) for 24 h. Results obtained for soybean oil are given in Table 3.4. Conversion of soybean oil increased (from 23.3 % to 50.2 %) with time (from 2 h to 48 h) however selectivity decreased after 4 h (from 38.3 % to 32.5 %) when TBHP to double bond molar ratio was 1. Better soybean oil conversion (99 %) and epoxide selectivity (38.7 %) was found when TBHP to double bond molar ratio was 4 for 24 h of reaction time.

They also carried out catalyst reusability tests. After washing used catalyst, it was subjected to epoxidation reactions five times. It was found that conversion decreased (from 99 % to 85 %) after second use however epoxide selectivity (from 38.7 to 75 %) and catalyst activity increased after each use. This was attributed to loss of water in catalyst pores and non-leaching of molybdenum. Analysis of catalyst after first use was carried out. Results indicated that, surface area of catalyst was decreased significantly and catalyst exhibited type I adsorption isotherms but pore size increased and retained in mesoporous range [15].

Di Serio et al. (2012), studied soybean oil epoxidation with sol-gel prepared Nb_2O_5-SiO_2 catalysts, which had different molar Nb content, at 80 ºC for 300 min by using ethyl acetate and H_2O_2. Molar niobium content of synthesised catalysts were 0.025, 0.05 and 0.1 and they had denoted them as 2.5Nb, 5Nb and 10Nb, respectively. Performed epoxidation test results are given in Figure 3.1. It was found that increasing niobium content decreased double bond conversion (from 30 % to 18 %) but increased epoxide selectivity (from 8 % to 42 %). 2.5Nb was the most active catalyst however it gave the lowest epoxide selectivity (8 %).

Activity of 2.5Nb catalyst was attributed to existence of more moderate Lewis

Table 3.4. Catalytic activity of K10-Mo for the epoxidation reaction of soybean oil with TBHP[a] [15].



Reaction time (h)	Conversion (%)	Epoxidation (%)	Selectivity (%)
2	23.3 ± 0.3	7.1 ± 0.3	30.5
4	28.2 ± 0.5	10.8 ± 0.6	38.3
8	39.1 ± 0.6	8.2 ± 0.5	21.0
16	46.7 ± 0.7	11.1 ± 0.6	23.8
48	50.2 ± 0.6	16.3 ± 0.4	32.5
16[d]	60.4 ± 1.1	15.2 ± 0.9	25.2
16[e]	80.5 ± 1.1	25.1 ± 1.1	31.2
24[d]	65.0 ± 0.6	16.1 ± 0.6	24.8
24[e]	99.0 ± 1.2	38.3 ± 0.4	38.7

[a] Reaction conditions: molar ratio TBHP: oil double bonds: catalyst 100:100:1, reaction carried out at 80 ºC with toluene. The results are calculated by H NMR, 5 % of incertitude.
[epoxide]/[catalyst]*time (h^{-1}).
[d] molar ratio TBHP: oil double bonds 2:1.
[e] molar ratio TBHP: oil double bonds 4:1.

acid strength which were responsible for epoxidation reaction whereas strong Lewis acid sites causes H_2O_2 decomposition. Low selectivity was attributed to presence of more Bronsted acid sites in 2.5Nb, which were responsible for side reactions thus lowering epoxide selectivity. They determined existence of Bronsted and Lewis acid sites in catalysts by NH_3-TPD and basic probe (acetonitrile) adsorbed FTIR. Raman spectra and FTIR spectroscopy revealed that Nb were uniformly distributed in SiO_2 framework in 2.5Nb. It was also found that, NbO_4 and NbO_6 species were mostly formed in framework with the lower Nb content. However, at higher Nb content clustering of NbO_6 species were mostly prevailed.

Also, esterification (free fatty acid conversion) and transesterification (glyceride conversion) reactions were performed in order to further investigate acidic properties of catalysts. However these results were found to contradict the previous analysis results and this was explained by low sensitivity of test reactions [33].

In the study performed by Turco et al. (2016), γ-alumina was used as catalyst for the epoxidation of soybean oil and methyl oleate in ethyl acetate with H_2O_2 at 80 ºC. Here, for the relevance, results only associated with soybean oil was given. Catalyst was purchased and characterized by XRD, XRF and BET. From this characterization, existence of γ phase in alumina was confirmed. The catalyst was mostly consisted of alumina and was also included some other impurities. Surface area and mean pore diameter of catalyst was found 149 m^2 g^{-1} and 4.2 nm, respectively. It exhibited type IV adsorption isotherms which meant ink-bottle shape mesopores. Table 3.5 demonstrates

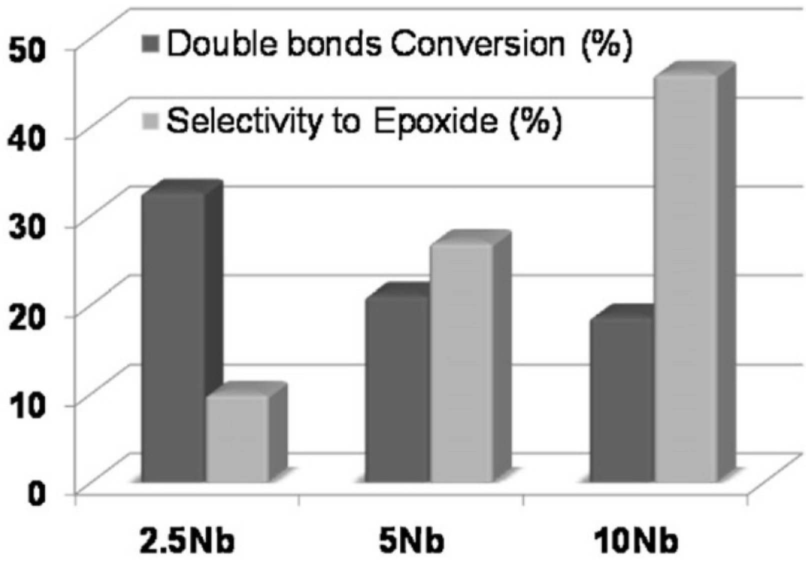
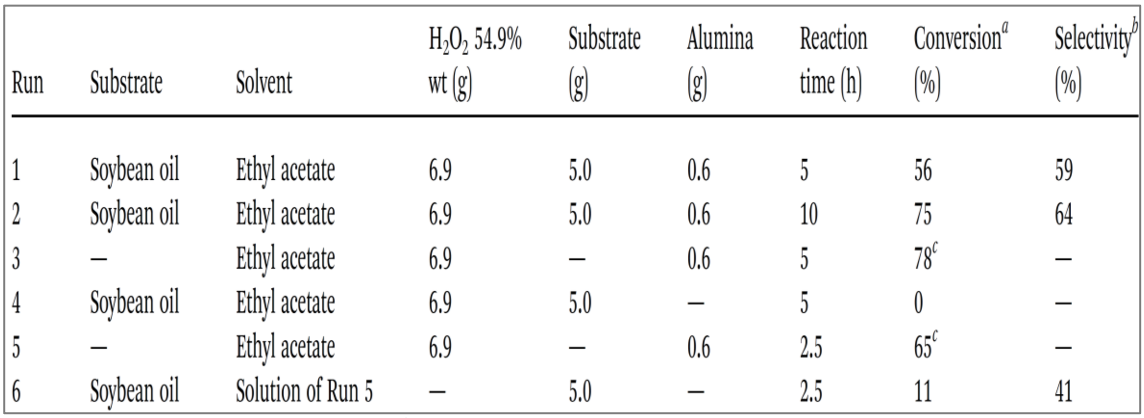


Figure 3.1. Epoxidation test results with Nb_2O_5-SiO_2 catalysts. [33].

Table 3.5. Effect of some parameters in soybean oil epoxidation system with conversion and selectivity values [34].



Run	Substrate	Solvent	H_2O_2 54.9% wt (g)	Substrate (g)	Alumina (g)	Reaction time (h)	Conversion[a] (%)	Selectivity[b] (%)
1	Soybean oil	Ethyl acetate	6.9	5.0	0.6	5	56	59
2	Soybean oil	Ethyl acetate	6.9	5.0	0.6	10	75	64
3	–	Ethyl acetate	6.9	–	0.6	5	78[c]	–
4	Soybean oil	Ethyl acetate	6.9	5.0	–	5	0	–
5	–	Ethyl acetate	6.9	–	0.6	2.5	65[c]	–
6	Soybean oil	Solution of Run 5	–	5.0	–	2.5	11	41

[a] Conversion of double bonds. [b] Selectivity to oxirane rings. [c] Conversion of H_2O_2. The standard deviations related to conversion and selectivity values are 2.8% and 1.8% respectively.

the different parameters and effect of change of these parameters in soybean oil epoxidation system [34].

They performed run 1 by using pre-determined operating conditions and double bond conversion and selectivity to oxirane were found as 56 % and 59 % respectively. In run 2, reaction time was doubled, and all other parameters kept same as in run 1. The catalyst was gave higher conversion (75 %) and selectivity (64 %) results. However, reaction stopped suddenly after 10 h. This incident is demonstrated in Figure 3.2. They suspected severe decomposition of H_2O_2, even though they used excess amount of H_2O_2 (H_2O_2 to double bond molar ratio was 4).

Thereafter, in order to investigate catalyst activity on H_2O_2 decomposition, run 3 was performed using previous conditions but without using soybean oil. After 5 h of reaction time, H_2O_2 decomposition was found as 78 %. Also, they performed run 4 to 6 in order to investigate catalyst interaction with solvent. Run 4 was performed without using catalyst, as a result no conversion was found. In run 5, they performed reaction for 2.5 h without using soybean oil. Subsequently, run 6 was performed without using H_2O_2 for 2.5 h by using mixture obtained in run 5. Even there was no oxidant added in run 6, considerable amount of soybean oil conversion (11 %) and selectivity to oxirane (41 %) was obtained. This was ascribed to decomposition of ethyl acetate to acetic acid in the presence of γ-alumina. Then, acetic acid was reacted with H_2O_2 to form peracetic acid. Hence, the reaction was carried out as like homogenous system. As conclusion, γ-alumina was found to be active in soybean oil epoxidation reaction. However it also promoted H_2O_2 and ethyl acetate decomposition thus caused ineffective utilization of both substances [34].

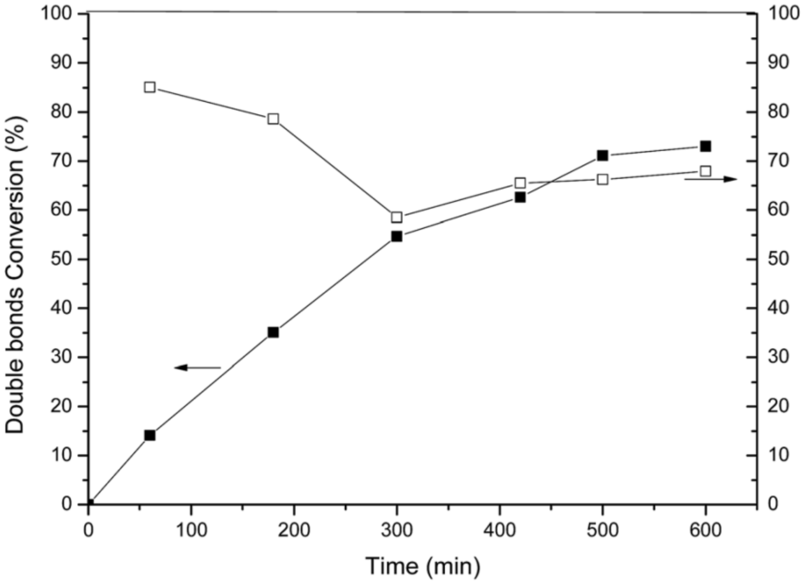


Figure 3.2. Performance (conversion and selectivity) of the γ-alumina catalyst as a function of reaction time in the epoxidation of soybean oil. [34].

In another study performed by Turco et al. (2017), H-Y zeolite was used as catalyst to investigate soybean oil epoxidation by in situ produced performic acid. They used soybean oil and formic acid as reactants and H_2O_2 as oxidant and epoxidation reactions was performed at 70 ºC. They purchased the catalyst and it contained 20 wt % alumina as binder. H-Y zeolite was chosen as catalyst because it promotes reaction between formic acid and H_2O_2 thus, decreasing induction time and also, its microporous structure prevents side reactions by hindering diffusion of bulky oil molecules inside.

When epoxidation reactions were performed, at first usage catalyst provide 58 % of double bond conversion at 3 h but after that time reaction stopped suddenly. They firstly explained this incident by pore blockage of catalyst with bulky soybean oil molecules. However, when they washed the catalyst and used it in the reaction again, it gave higher conversion than previous use. After fifth use, 89 % double bond conversion was achieved. Thereafter, they performed further tests to show that reaction stoppage was due to decomposition of performic acid and beside that, increase of conversion was because of chemically adsorbed soybean oil molecules on catalyst surface which poisoned active sites that was responsible of performic acid decomposition.

After these findings, they also performed reactions with pre-treated catalysts (pre-treated with epoxidized soybean oil (ESO) or soybean oil) to find best results for double bond conversion and oxirane selectivity. Results are given for pre-treated and not pre-treated catalysts in Figure 3.3. In Figure 3.3a it was demonstrated that double bond conversion with pre-treated catalysts (about 80 %) are higher than not pre-treated catalyst (about 60 %) and best conversion (83 %) was obtained with ESO pre-treated catalyst. Oxirane selectivities (for pre-treated catalysts and not pre-treated catalyst) are demonstrated in Figure 3.3b. Pre-treated catalysts gave similar oxirane selectivities (about 82 %) and not pre-treated catalyst gave higher oxirane selectivity (about 86 %) than pre-treated catalysts however overall yield (about 50 %) was found low with this catalyst. Consequently, better yield (% 79) was obtained when ESO pre-treated catalyst was used [35].

In a recent study, Chen et al. (2019), synthesised microporous Titania-Silicalite (TS-1) with three different Si/Ti molar ratios (40, 70 and 80), anatase Titania (TiO_2) and mesoporous Titania-Silicate (MTS-1) with Si/Ti molar ratio 40. The catalysts were used in soybean oil epoxidation utilizing H_2O_2 as oxidant for 24 h. Preliminarily, they carried out epoxidation reactions with using the catalysts at 60 ºC in order to find most active catalyst. Obtained results with the catalysts are given in Table 3.6. When TS-1-70 and TS-1-80 was compared with TS-1-40, TS-1-40 gave higher soybean oil conversion (40.93 %) and selectivity to epoxides (88.21 %). This was attributed to existence of more Ti in the framework of TS-1-40. On the other hand, MTS-1-40 was gave similar selectivity

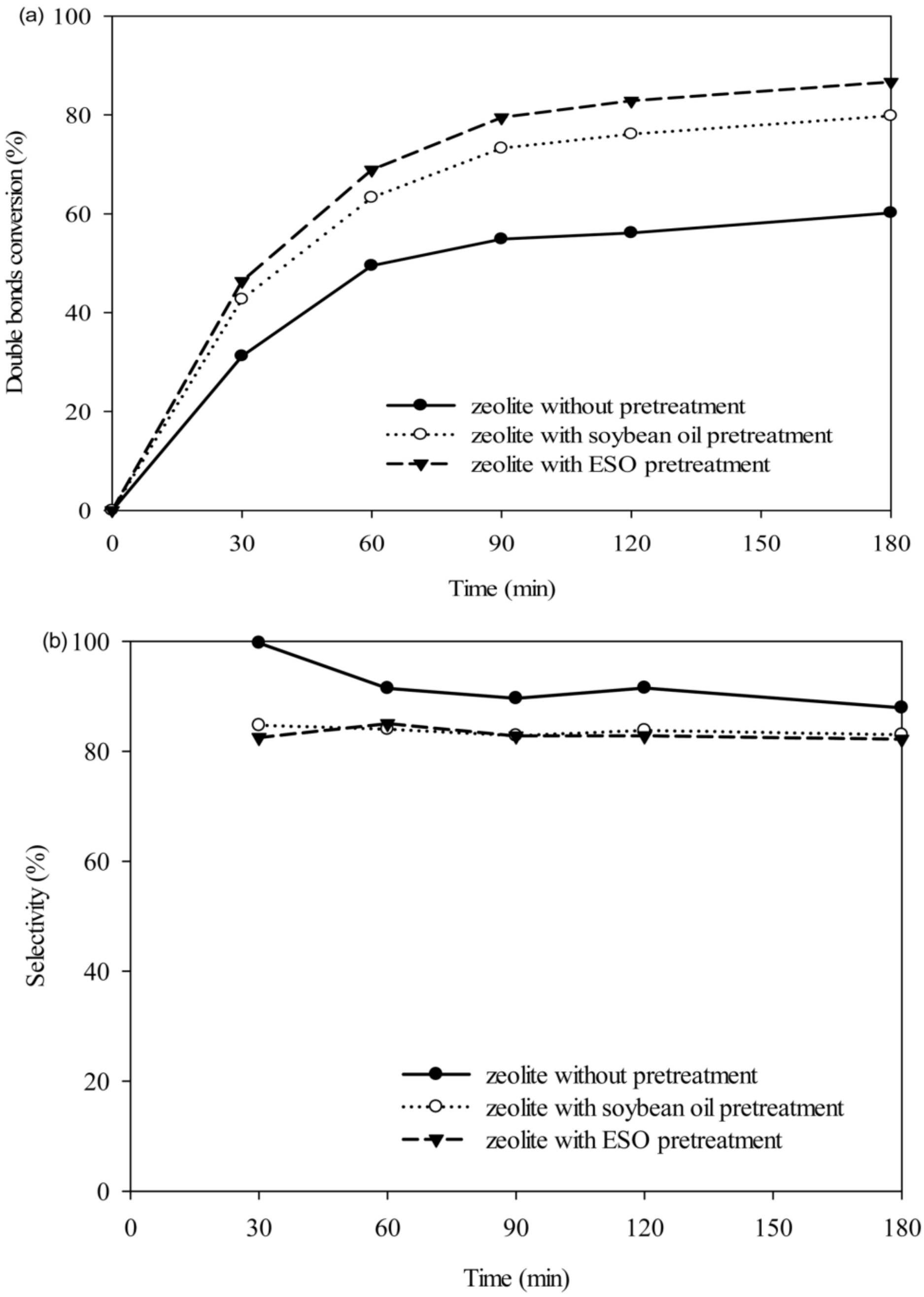


Figure 3.3. Effect of treatment of H-Y zeolite with soybean oil and epoxidized soybean oil before the use in epoxidation reaction: (a) double bonds conversion; (b) selectivity to oxirane. [35].

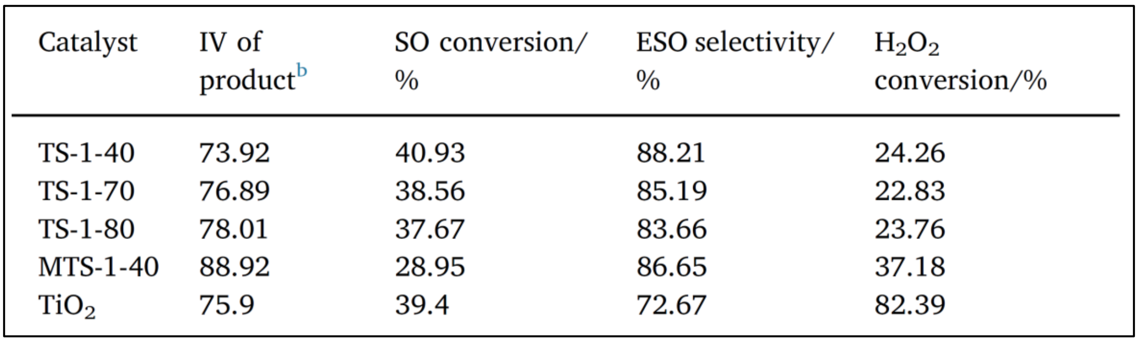
value to epoxides (86.65 %) as TS-1 catalysts, however soybean oil conversion (28.95 %) was found low and also it promoted much decomposition (about 50 % higher than TS-1 catalysts) of H_2O_2. And for anatase TiO_2, soybean oil conversion (39.4 %) was found high however epoxide selectivity (72.67 %) was found low and it was suffered from severe H_2O_2 decomposition (82.39 %).

Thereafter, they investigated many reaction parameters which were H_2O_2 to double bond molar ratio, solvent polarity, catalyst amount, temperature and catalyst reusability and regeneration by using TS-1-40 as catalyst. Firstly, they changed H_2O_2 to double bond molar ratio from 2.4 to 6. It was found that increasing H_2O_2 to double bond molar ratio from 2.4 to 4 increased conversion (40.93 % to 62.7 %) while selectivity (88 %) remain unchanged. However, further increasing H_2O_2 to double bond molar ratio from 4 to 6 caused decrease of conversion due to higher amount of water content in the reaction which was promoted by H_2O_2.

After that, they investigated effect of temperature on epoxidation reaction in the range between 50 to 80 ºC. Soybean oil conversion and decomposition of H_2O_2 increased with increasing temperature from 50 to 80 ºC whereas selectivity was increased rapidly at first and then remained constant with increasing temperature. In order to investigate effect of solvent polarity, they tested five different solvents in the reaction and found that strong polar solvent (Methanol) and weak polar (Acetone and Hexane) solvents promoted very little conversion (close to 0) whereas middle polar solvents (Ethyl acetate and Tertbutanol) promoted higher conversion. At these conditions, tertbutanol was promoted better conversion of soybean oil and selectivity to epoxides than ethyl acetate.

Furthermore, they used TS-1-40 catalyst three times in epoxidation reactions and found that catalytic activity of catalyst significantly decreased at second use (promoted around 5 % conversion and 70 % selectivity) and there was no conversion at third use. On the other hand, regeneration of catalyst after first use provided 28.7 % conversion and 73.1 % selectivity [19].

Table 3.6. Effect of the catalyst on the epoxidation of SO[a] [19].



Catalyst	IV of product[b]	SO conversion/ %	ESO selectivity/ %	H_2O_2 conversion/%
TS-1-40	73.92	40.93	88.21	24.26
TS-1-70	76.89	38.56	85.19	22.83
TS-1-80	78.01	37.67	83.66	23.76
MTS-1-40	88.92	28.95	86.65	37.18
TiO_2	75.9	39.4	72.67	82.39

[a] Reaction conditions: 5 g SO, 4 g t-butanol, 0.1 g catalyst, 6.8 g H_2O_2 (30 wt %), 333 K, 700 rpm, 24 h.

[b] IV stands for Iodine Value (Initial iodine value of SO was 125.16)

CHAPTER 4

EXPERIMENTAL STUDY

In previous section many articles related about vegetable oil epoxidation were explained briefly. Experimental study was performed according to information gathered from these studies. With this information, it was decided to synthesise 8 catalysts totally. The catalysts were Ti-SBA-15 with two SiO_2/TiO_2 molar ratios (10 and 20), MoO_3 loaded on Ti-SBA-15 catalysts with two weight percentages (8 wt % and 12 wt %) and Nb-SBA-15 with two SiO_2/Nb_2O_5 molar ratios (10 and 20). For simplicity, throughout this study SiO_2/TiO_2 and SiO_2/Nb_2O_5 molar ratios were denoted as Si/Ti and Si/Nb, respectively.

4.1. Reagents

Chemicals, that used for catalyst synthesis, epoxidation reactions and product separation and analysis, are tabulated in Table 4.1. All chemicals were purchased and used without any further purification. Refined soybean oil was kindly provided by Balsarı Oil Industry and Trade Limited Company. The fatty acid composition and some properties of soybean oil are given in Table 4.2 and Table 4.3, respectively. The main constituents of soybean oil were 10.55 wt % palmitic acid, 3.87 wt % stearic acid, 25.14 wt % oleic acid, 54.28 wt % linoleic acid, 4.50 wt % linolenic acid and rest contains traces of other fatty acids.

4.2. Catalyst Preparation

4.2.1. Preparation of Ti-SBA-15 Catalysts

Titanium was incorporated into SBA-15 structure by using sol gel method, according to procedure reported in the literature [36]. In a typical synthesis, 9.28 g Pluronic P123 was weighed in a bottle then 228.6 g water was added. After 2 h mixing and complete dissolution of Pluronic P123 at 40 °C, 4.54 g of HCI (37 %) was added and solution left stirring for 2 h. Subsequently, 20.83 g tetraethyl orthosilicate (TEOS) and 2.84 g titanium isopropoxide (TISOP) was added to the solution. After complete addition

Table 4.1. Chemicals used in the experimental study

Chemical	**Brand/Purity/Code**
Pluronic P123	Sigma Aldrich (435465)
Titanium isopropoxide	Sigma Aldrich, 97 %
Tetraethyl orthosilicate	Merck, ≥ 99.0 %
Niobium chloride	Sigma Aldrich, 99 %
Ammonium heptamolydate tetrahydrate	Merck, ≥ 99.3 %
Ammonium hydroxide solution	Sigma Aldrich, 28-30 %
Hydrochloric acid	Sigma-Aldrich, 37 %
Sulphuric acid	Merck, 95-97 %
Soybean oil	Balsarı Oil Industry
Acetic acid	Merck, glacial (100 %)
Hydrogen peroxide solution	Sigma Aldrich, 35 %
Tertbuthanol	Merck, ≥ 99.5 %
Ethyl acetate	Merck, ≥ 99.5 %
Sodium sulfate	Merck, ≥ 99.8 %
Wij’s solution	Merck (109163)
Potassium iodide	Merck, ≥ 99.5 %
Sodium thiosulfate	Sigma-Aldrich, anhydrous, ≥ 98.0 %
Chloroform	Sigma-Aldrich, ≥ 99 %
Starch solution indicator	Fluka (34117)
HBr solution	Sigma-Aldrich, 33 wt % in acetic acid
Methyl violet indicator	Sigma-Aldrich (69710)
Deuterated chloroform	Merck, 99.8 %
Sodium bicarbonate	Sigma-Aldrich, ≥ 99.8 %
Potassium hydrogen pthalate	Merck, ≥ 99.5 %
Potassium bromide	Merck (1049070)

Table 4.2. Fatty acid composition of soybean oil.

Fatty acid	**Charbon chain length: double bonds**	**wt % in oil**	**Range**
Miristic acid	C 14:0	0.05	Max 0.2
Palmitic acid	C 16:0	10.55	8.0-13.5
Palmitoleic acid	C 16:1	0.11	Max 0.2
Heptadecanoic acid	C 17:0	0.06	Max 0.1
Heptadecenoic acid	C 17:1	0.07	Max 0.1
Stearic acid	C 18:0	3.87	2.0-5.4
Oleic acid	C 18:1	25.14	17.0-30.0
Linoleic acid	C 18:2	54.28	48.0-59.0
Linolenic acid	C 18:3	4.50	4.5-11.0
Aracidic acid	C 20:0	0.48	0.1-0.6
Gadoleic acid	C 20:1	0.32	Max 0.5
Behenic acid	C 22:0	0.38	Max 0.7
Lignoseric acid	C 24:0	0.19	Max 0.5

Table 4.3. Some properties of soybean oil.

Property	**Value**	**Range**
FFA (Based on oleic acid)	0.15	max 0.3
Refraction	1.1751	1.4700-1.4760
Iodine value	136.0	125-143
color	3	max 3

of TEOS and TISOP, mixture was stirred at 40 ºC for 24 h. Resulting solution was placed in an autoclave at 100 ºC for 24 h. Resulting gel separated from solution by centrifugation and then, obtained solids washed with water 3 times to remove any remaining impurities.

Thereafter, moisture solids were dried for 12 h in a furnace at 100 ºC. Finally, dried solids were calcined at 550 ºC for 6 h to remove Pluronic P123. The resulting solid was denoted as Ti-SBA-15 (10) where the number in the bracket indicate Si/Ti molar ratio in that catalyst. Another catalyst with Si/Ti molar ratio 20 was synthesized by following the same steps using of 1.42 g of TISOP. The synthesized catalyst was denoted as Ti-SBA-15 (20). Lastly, pure SBA-15 was synthesised according to above procedure without adding Titanium precursor (TISOP) into synthesis mixture.

4.2.2. Preparation of MoO_3 Loaded Ti-SBA-15 Catalysts

MoO_3 was loaded on parent Ti-SBA-15 catalysts with different weight percentages with a slight modification of a method given in literature [37]. In a typical run, 0.1067 g or 0.16 g ammonium heptamolydate tetrahydrate (AMT) was dissolved in 250 ml water with stirring at 50 ºC for 1 h. Thereafter, 1 g of Ti-SBA-15 (10) catalyst was added into the solution. Meanwhile, a few drops of ammonium hydroxide solution was added to set pH 8 and it was allowed to stir for 1 h. The obtained colloidal solution was poured in a beaker and water was evaporated at 50 ºC in fume cupboard. Subsequently, moist solids were dried overnight at 100 ºC in a furnace then dried solids were calcined at 550 ºC for 3 h. The synthesized catalysts were denoted as $8MoO_3$/Ti-SBA-15 (10) or $12MoO_3$/Ti-SBA-15 (10) with respect to amount of AMT used. The same procedure was followed for catalyst having Si/Ti molar ratio of 20 (Ti-SBA-15 (20)). In this case, synthesised catalysts were denoted as $8MoO_3$/Ti-SBA-15 (20) and $12MoO_3$/Ti-SBA-15 (20).

4.2.3. Preparation of Nb-SBA-15 Catalysts

Niobium was incorporated into SBA-15 structure for two Si/Nb molar ratios (10 and 20) by using sol gel method. The synthesis was carried out according to a literature method [38]. Firstly, 4 g of Pluronic P123 and 30 g water was weighed and placed in a bottle and stirred for 4 h at 40 ºC. After dissolution of Pluronic P123, 70 ml (0.29 M) of hydrogen chloride solution was added to set pH of the solution to 2.2 and solution was further stirred for 2 h. Then, 9 g of TEOS and respective amount of niobium chloride ($NbCI_5$), which was 2.34 g and 1.17 g $NbCI_5$ for Si/Nb molar ratio 10 and 20 respectively, were added to above solution and mixture was stirred for 24 h at 40 ºC. Thereafter, obtained solution was poured into a Teflon bottle and kept in autoclave at 100 ºC for 48 h. After separation of solids from solution by centrifugation and washing three times with water, solids were dried at 100 ºC for 12 h. Obtained powder were crashed and finally calcined at 550 ºC for 6 h. The synthesised catalysts were denoted as Nb-SBA-15 (10) and Nb-SBA-15 (20) for Si/Nb molar ratios 10 and 20, respectively.

4.3. Catalyst Characterization

4.3.1. X-Ray Diffraction (XRD)

XRD analysis was carried out by a Philips X'Pert diffractometer with CuKα radiation. The scattering angle (2θ) was varied from 5 º to 100 º, with a step length of 0.08.

4.3.2. N_2 Adsorption/Desorption (BET)

BET analysis was carried out with a Micromeritics ASAP 2010 model static volumetric adsorption instrument. Firstly, catalysts were degassed at 200 ºC for 2 h. Analysis was performed at – 196 ºC.

4.3.3. X-Ray Fluorescence Spectroscopy (XRF)

In order to determine elemental composition of catalysts, XRF analysis was carried out by using Spectro IQ II instrument with CuKα radiation.

4.3.4. Skeletal FTIR Spectroscopy

Framework vibrations of catalysts was determined by using an infrared spectrometer type Schimadzu FTIR 8400S with a resolution of 4 cm^{-1} and wavenumber between 400 – 4000 cm^{-1}.

4.3.5. Temperature Programmed Desorption of Ammonia (NH_3-TPD)

Acidic strength and total acidity of catalysts were determined by using Micromeritics AutoChem II Chemisorption Analyzer instrument. Initially, catalysts were heated up to 500 ºC with a 5 ºC/min step ramp. Subsequently, catalysts were kept under 70 ml/min He flow for 1 h at 500 ºC. Then, temperature was dropped to 90 ºC with a step ramp of 5 ºC/min under 30 ml/min He flow. Thereafter, 70 ml/min of a mixture NH_3/He was applied to the sample at 90 ºC for 30 min and followed by 70 ml/min He flow for 150 min. Finally, desorption of ammonia was carried out by heating the sample from 90 ºC to 550 ºC with a step ramp of 10 ºC/min.

4.4. Catalytic Tests

4.4.1. Homogenous Epoxidation Reactions

Epoxidation of soybean oil was carried out in a 100 ml jacketed glass batch reactor equipped with a condenser at 75 ºC for 6 h. Experimental set up is demonstrated in Figure 4.1. Typical run was performed as follows. Firstly, 36.24 ml of soybean oil, 5.1 ml of acetic acid and 0.2 ml of sulphuric acid (18 M) was added to flask at once and temperature was set to desired value with stirring at 550 rpm. Molar ratio of H_2O_2/Acetic acid/double bonds was set to 2:0.5:1. When temperature reached 65 ºC, 28.8 ml of hydrogen peroxide added slowly dropwise over 50 min to prevent side reactions and sudden fluctuations in temperature. First addition of H_2O_2 was taken as starting point of reaction. In every 2 h, 10 ml of sample was taken from the reaction mixture during 6 h of reaction time. Thereafter, organic phase was separated from reaction mixture with common applied method in the literature [23]. Ethyl acetate was added to samples to separate organic phase from the mixture in a separating funnel. After separation of organic phase, 100 ml of sodium bicarbonate solution (0.5 wt %) was added to quench remaining acids. Then, organic phase washed with water (100 ml) three times until pH of the mixture reached 7. Subsequently, sodium sulphate was added to remove any remaining water in the organic phase. Sodium sulphate was then separated from organic phase by filtration. Finally, to remove any remaining impurities, organic phase was put into a rotary evaporator at 55 ºC for 1.5 h. The collected samples were kept at 4 ºC in a refrigerator for analysis.

4.4.2. Heterogenous Epoxidation Reactions

Heterogenous epoxidation reactions were carried out within Radley reactor system in 100 ml two necked round bottom flasks with condenser at 75 ºC for 6 h with stirring at 900 rpm. Experimental set up is demonstrated in Figure 4.2. Initially, 13.0 ml of soybean oil, 0.3 g catalyst and 51.8 ml of tertbutanol were added to flasks at one pot and temperature was set to 75 ºC. Molar ratio of H_2O_2/double bonds was set to 0.95:1. When temperature reached 65 ºC, addition of 4.8 ml of H_2O_2 was initiated and it took over 20 min for complete addition. First addition time of H_2O_2 was taken as starting point for the reaction. During the reaction time of 6 h, samples were taken in every 2 h for product analysis. Separation of organic phase from samples was carried out with same method as in the homogenous one except in heterogenous samples, at initial stage separation of solid catalysts was carried out by centrifugation and no ethyl acetate and no sodium bicarbonate solution were added to organic phase.

4.5. Product Analysis

4.5.1. Analytical Methods

4.5.1.1. Determination of Iodine Value

Determination of iodine value (IV) was carried out according to wijs method as follows. 0.2 g of sample was weighed in a flask and then, 15 ml of chloroform was added to flask to dissolve the oil. Subsequently, 25 ml of wijs solution was added to flask. Flask was then placed in a dark cupboard approximately 1 h to allow completion of the reaction. Thereafter, formerly prepared 20 ml of 10 wt % potassium iodide solution and 150 ml of water were added to flask meanwhile 0.5 ml of starch indicator was also added. Finally, solution was titrated with 0.1 M sodium thiosulphate solution until color of mixture was became lucent. The same procedure was followed with a blank flask without oil sample in order to determine iodine value. Iodine value can be calculated by using equation (4.1) [29].

$$\text{Iodine Value} = \frac{(\text{Vblank} - \text{Vsample}) * \text{C} * 12.69}{\text{Weight of sample}} \tag{4.1}$$

Where:

Vblank: Titrant volume used for blank (ml)

Vsample: Titrant volume used for the oil sample (ml)

C: Titrant molarity

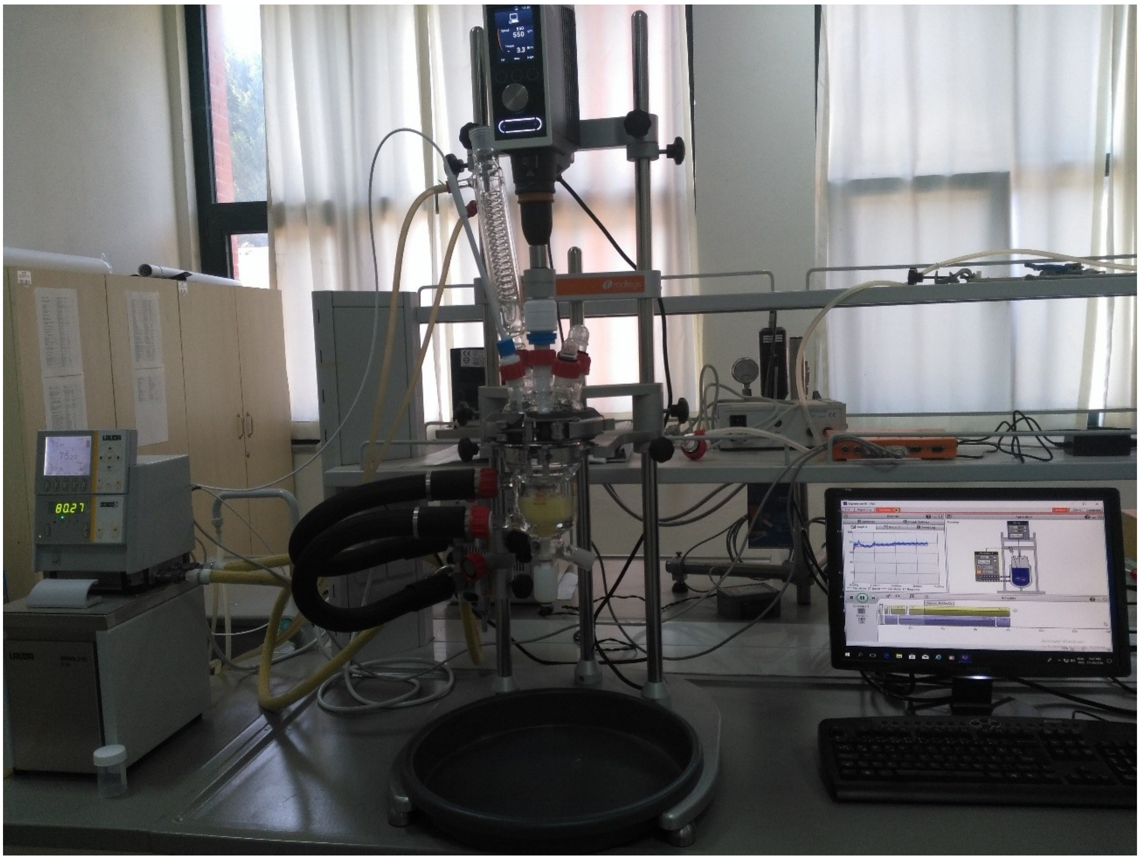


Figure 4.1. Experimental set up for homogenous catalytic reaction.

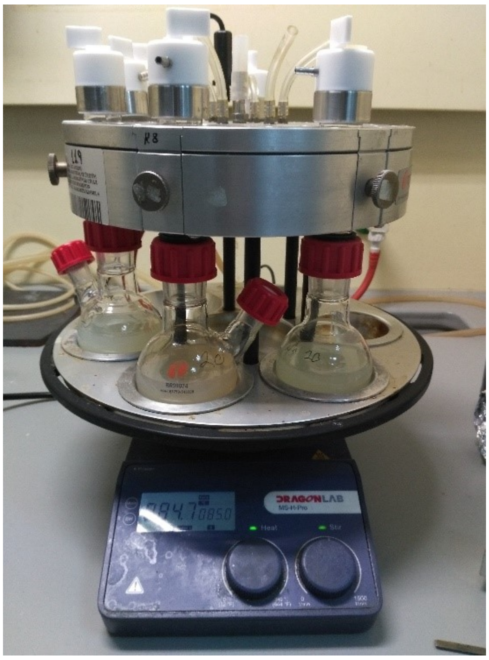


Figure 4.2. Experimental set up for heterogenous catalytic reactions

Relative double bond conversion can be calculated by using equation (4.2) [29].

$$\text{Conversion (\%)} = \frac{\text{IV (blank) } - \text{IV(sample)}}{\text{IV(blank)}} * 100 \tag{4.2}$$

Where:
IV(blank): Iodine value of virgin soybean oil
IV(sample): Iodine value of epoxidized soybean oil sample

Iodine value of soybean oil was calculated by using equation (4.1) as 124.57 ± 2.95 within 95 % confidence interval.

4.5.1.2. Determination of Oxirane Oxygen Content

Oxirane oxygen content of epoxidized oil samples were determined according to AOCS method (Cd 9-57) as follows; 0.4 g of sample was weighed in a flask and diluted with 10 ml of acetic acid. Thereafter, 2 drops of methyl violet indicator were added and then, solution was titrated with formerly prepared 0.1 N HBr solution until color changed from purple to blue. Oxirane oxygen content was calculated by using equation (4.3) [39].

$$\text{Oxirane oxygen (\%)} = \frac{\text{V} \times \text{N} \times 1.6}{\text{weight of sample(g)}} \tag{4.3}$$

Where:
V: Volume of titrant (ml)
N: Normality of titrant

Relative epoxy yield can be determined by using equation (4.4) [23].

$$\text{Yield} = \frac{\text{OO(exp)}}{\text{OO(the)}} * 100 \tag{4.4}$$

Where:
OO (exp): Oxirane oxygen determined experimentally
OO (the): Maximum oxirane oxygen determined theoretically

Maximum theoretical oxirane oxygen content can be determined by the following equation [23].

$$\mathrm{OO(the)} = \left[\frac{\frac{\mathrm{IV}}{\mathrm{MW(I2)}}}{100 + \frac{\mathrm{IV}}{\mathrm{MW(I2)}} * \mathrm{MW(O)}}\right] * \mathrm{MW(O)} * 100 \qquad (4.5)$$

Where:

IV: Iodine value of virgin soybean oil

MW (I2): Molecular weight of molecular iodine

MW (O): Molecular weight of atomic oxygen

Maximum theoretical oxirane oxygen content of soybean oil was calculated by equation (4.5) as 7.28 %.

In addition, epoxide selectivity can be calculated by dividing equation (4.4) by equation (4.2) as follows [3];

$$\text{Selectivity (\%)} = \frac{\text{Yield}}{\text{Conversion}} * 100 \qquad (4.6)$$

4.5.2. Instrumental Methods

4.5.2.1. Proton Nuclear Magnetic Resonance Spectroscopy (H-NMR)

H-NMR can be used to analyse soybean oil and discern epoxide peaks. H-NMR spectrum of samples were carried out by using Varian Inova 300 MHz spectrometer instrument. For analysis, 0.06 ml of sample was dissolved in 0.5 ml of deuterated chloroform. Resultant solution was put into a 5 mm diameter NMR tube. Following acquisition parameters were applied for analysis: Spectral width, 6410 Hz; relaxation delay, 1 s; number of scans, 32; acquisition time, 2.56 s and with total acquisition time of 2.94 min. H-NMR spectrum of virgin soybean oil was carried out and result is demonstrated in Figure 4.3. Considering shift of peaks, peak assignment of spectrum was carried out according to literature and tabulated in Table 4.4. The peaks between 2.85 to 3.20 ppm are epoxides peaks and as demonstrated in Figure 4. 3 soybean oil had none of the peaks associated with epoxides.

4.5.2.2. FTIR Spectroscopy

For qualitative analysis of epoxidized soybean oil samples FTIR spectroscopy was used. The peak assignment of FTIR spectrum are given in Table 4.5. Samples were prepared for analysis as follows; 150 mg KBr pellet was pressed and 0.005 ml of oil sample was poured and dispersed on the pellet. Analysis was carried out by using an infrared spectrometer type Schimadzu FTIR 8400S with a resolution of 4 cm^{-1} and wavenumber between 400 – 4000 cm^{-1}.

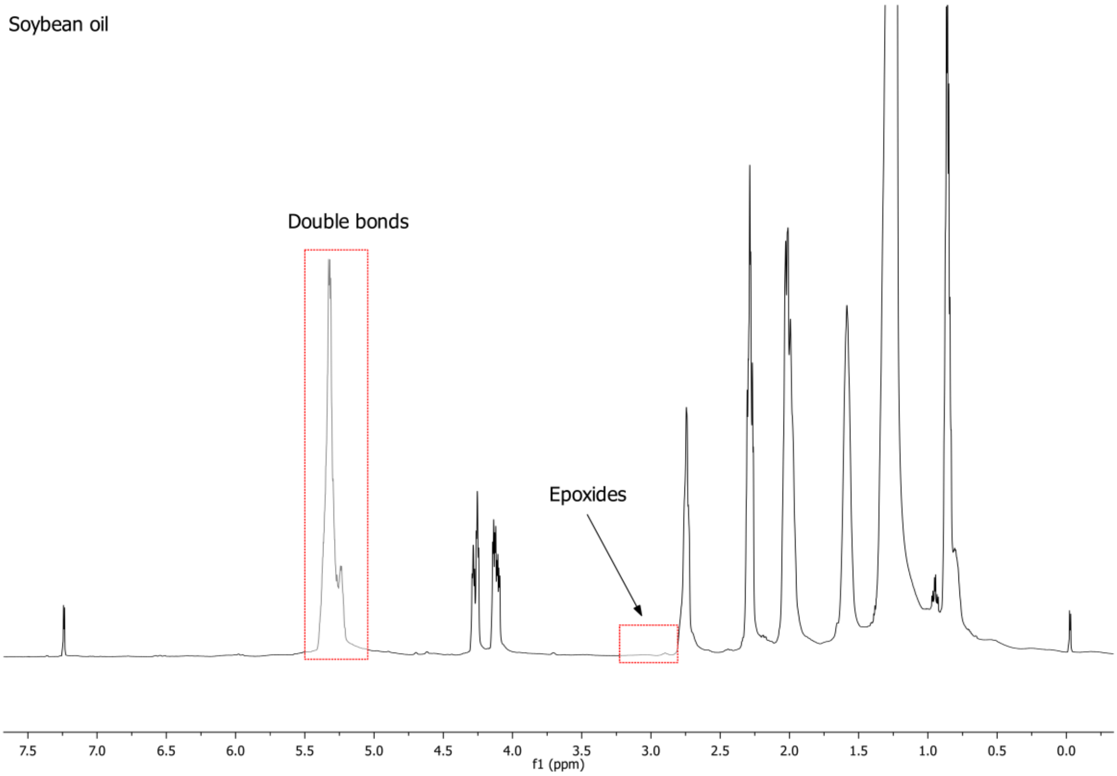


Figure 4.3. H-NMR spectrum of virgin soybean oil.

Table 4.4. Peak assignment of H-NMR spectrum for soybean oil and epoxidized soybean oil [40, 41].

Chemical Name/Functional group	**Peak signals (ppm)**
$-CH_3$ (acyl group)	~0.75 – 0.90
$-(CH_2)_n-$ (acyl group)	~1.05 – 1.40
$-OCO-CH_2-CH_2-$ (acyl group)	~1.50 – 1.75
$-CH_2-CH=CH-$ (acyl groups)	~1.78 – 2.12
$-OCO-CH_2-$ (acyl group)	~2.12 – 2.40
$=HC-CH_2-CH=$ (acyl groups)	~2.62 – 2.84
Monoepoxides	~2.85 – 2.95
Diepoxides	~2.95 – 3.15
Triepoxides	~3.15 – 3.20
Alcohols	~3.43 – 3.62
sn 1,3 glycerol protons	~3.97 – 4.40
sn 2 glycerol proton	~5.15 – 5.26
Olefinic protons ($-CH=CH-$)	~5.26 – 5.40
Conjugated dienes	~5.40 – 6.58
Double bonds conjugated with carbonyls	~6.08. – 6.82
Solvent ($CDCI_3$)	~7.24

Table 4.5. FTIR band frequencies of soybean oil and epoxidized soybean oil [1, 24].

Frequency (cm^{-1})	**Oil associated band**
3500	−OH Glycols (by products)
3009	−C−H (next to double bonds) band stretching
2926	$-CH_2$ asymmetric stretching
2855	$-CH_3$ symmetric stretching
1746	−CH=O stretching
1655	−CH=C stretching
1465	$-CH_2$ stretching
1418	−CH=C−H deformational
1378	$-CH_3$ symmetric deformational
843	−C−O−C− epoxy group stretching
723	$-CH_2$ oscillating

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1. Characterization of Catalysts

Wide angle XRD spectra of SBA-15, Ti-SBA-15 and Nb-SBA-15 catalysts were carried out. Obtained spectra results for SBA-15 and Ti-SBA-15 catalysts are demonstrated in Figure 5.1. Pure SBA-15 only demonstrated characteristic peak of amorphous silica (wide peak centered at 22.0 θ) [42, 43]. For Ti-SBA-15 catalysts the peaks, as denoted by arrows, at 2θ of 25.5, 37.4, 48 and 53 indicated existence of anatase Titanium (TiO_2) [36]. Intensity of the peaks decreased with decreasing Titanium content which indicated more homogenous distribution of Titanium into structure for Ti-SBA-15 (20). On the contrary, XRD spectra of SBA-15 and Nb-SBA-15 catalysts are demonstrated in Figure 5.2. Nb-SBA-15 catalysts exhibited characteristic peak of amorphous silica. There was no visible peaks associated with crystalline Nb_2O_5 aggregates which indicated that all niobium was incorporated into SBA-15 structure or amorphously dispersed on its surface [44]. Intensity of peak at 22 θ decreased for Nb-SBA-15 (10) which could be due to amorphous distribution of extra framework Nb_2O_5 on the surface. Literature studies reported that both incorporation and loading of Niobium into a silica structure provided same XRD results as in this study [45, 46].

Moreover, even successful synthesis and characterization of MoO_3/SBA-15 catalysts were performed, their characterization data was not given due to severe leaching of the catalysts.

N_2 adsorption/desorption isotherms of the catalysts are demonstrated in Figure 5.3 and Figure 5.4. The catalysts demonstrated IUPAC type 4 adsorption/desorption isotherms with hysteresis loop which indicate the existence of mesoporous structure. However, only SBA-15 and Nb-SBA-15 (20) demonstrated a good H1 hysteresis loop which indicate regular ordered mesopore structure.

Textural properties of SBA-15, Ti-SBA-15 and Nb-SBA-15 catalysts are summarized in Table 5.1. The actual Si/Ti and Si/Nb molar ratios found to be higher or lower than theoretical ratio but they were in acceptable error range hence it could be

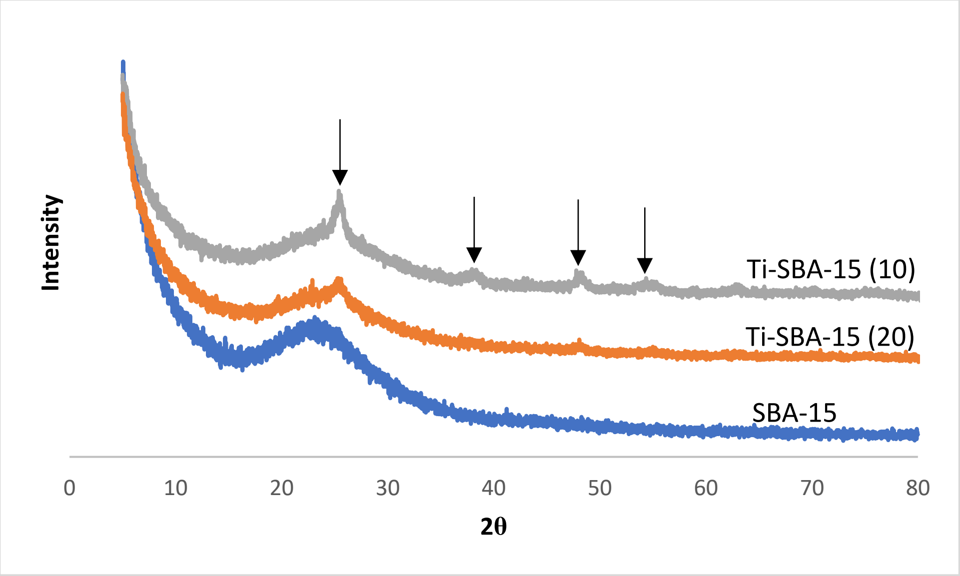


Figure 5.1. Wide angle XRD spectra of SBA-15 and Ti-SBA-15 catalysts

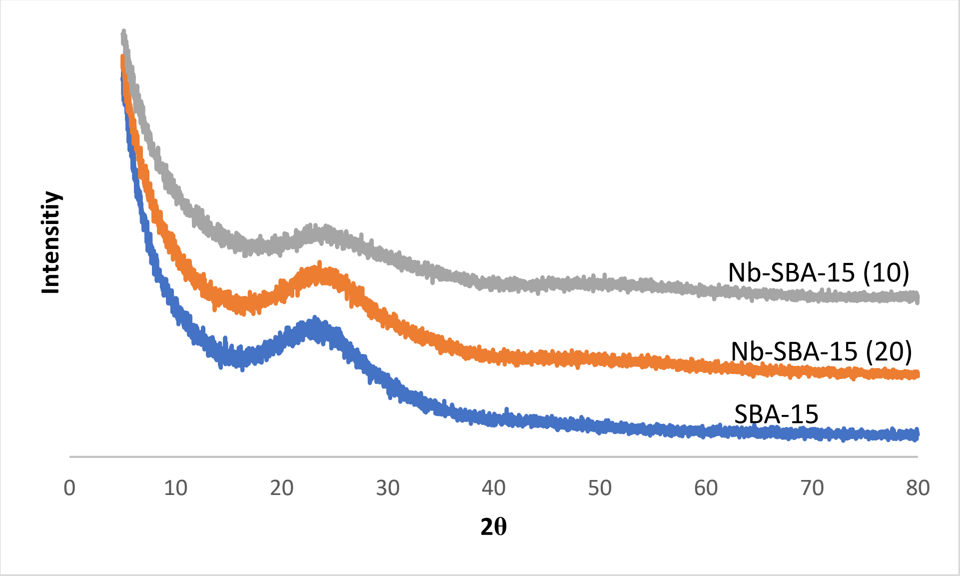


Figure 5.2. Wide angle XRD spectra of SBA-15 and Nb-SBA-15 catalysts

concluded that incorporation of Ti and Nb into SBA-15 structure carried out successfully.

Surface area mean pore diameter and mean pore volume of the catalysts determined by BET and N_2 adsorption/desorption analysis. Surface area mean pore diameter and mean pore volume of SBA-15 found as 877.3 m^2/g, 48.7 Å and 0.720 cm^3/g, respectively. Incorporation of Ti into SBA-15 caused some increase in surface area and decrease of pore diameter which was in accordance with the literature result [47]. On the other hand, Nb incorporation caused decrease of surface area. Both types of the catalysts possessed very high surface area which ranged between 668 and 935 m^2/g. Ti-SBA-15 catalysts had larger surface area than Nb-SBA-15 catalysts which ascribed that Niobium is a bigger molecule than Titanium. Thus, it occupied more area and blocked more pores in the support structure. On the other hand, mean pore diameter of Nb-SBA-15 catalysts were larger than Ti-SBA-15 catalysts which could be due to longer synthesis time. For Ti-SBA-15 and Nb-SBA-15 catalysts, surface area, mean pore diameter and mean pore volume decreased with increasing Ti and Nb content. The decrease of these values with increasing Ti and Nb content may attributed to occurrence of TiO_2 and Nb_2O_5 nanoclusters in the pores of SBA-15 structure.

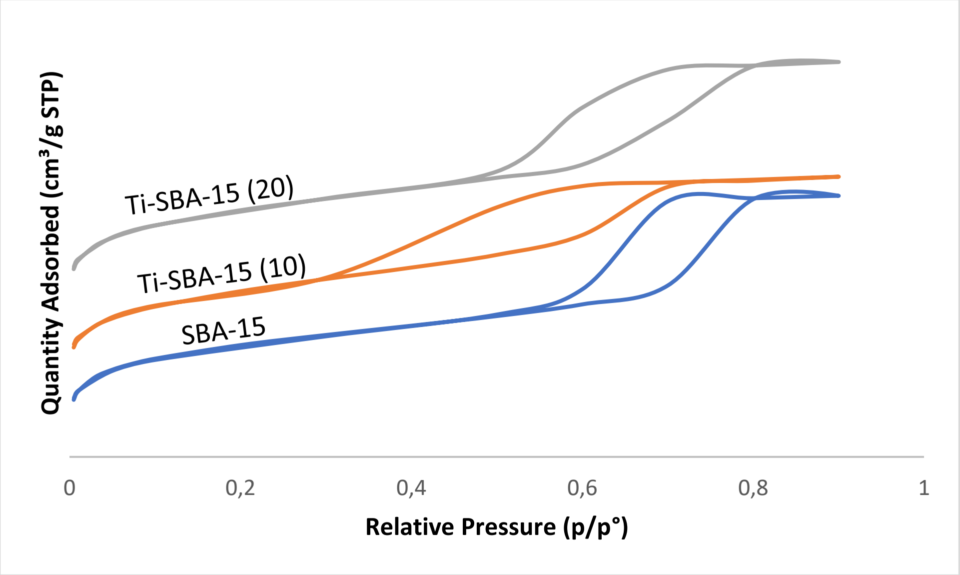


Figure 5.3. N_2 Adsorption/Desorption isotherms of SBA-15 and Ti-SBA-15 catalysts

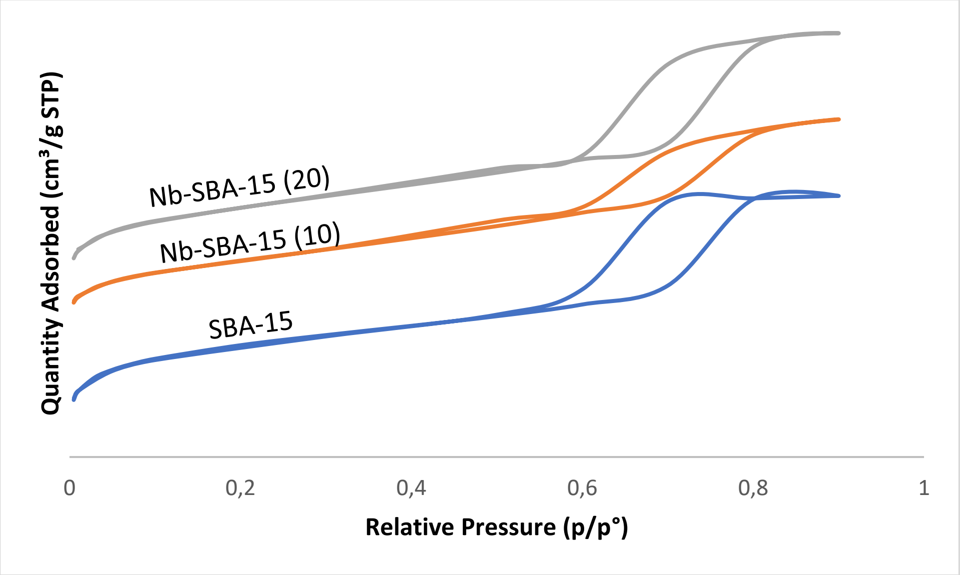


Figure 5.4. N_2 Adsorption/Desorption isotherms of SBA-15 and Nb-SBA-15 catalysts

Table 5.1. Textural properties and total acidity of SBA-15, Ti-SBA-15 and Nb-SBA-15 catalysts

Catalyst	**Actual Molar Ratio (Si/Ti or Si/Nb)**	**Surface Area (m^2/g)**	**Pore Diameter (Å)**	**Pore Volume (cm^3/g)**	**Total Acidity (mmol/g)**
SBA-15	-	877.3	48.7	0.72	0.04
Ti-SBA-15 (10)*	10.02	885.8	30.3	0.64	0.44
Ti-SBA-15 (20)*	22.15	935.7	42.6	0.73	0.27
Nb-SBA-15 (10)*	9.39	668.4	45.6	0.62	0.76
Nb-SBA-15 (20)*	27.67	803.8	50.7	0.80	0.53

*Numbers in the brackets refers to Si/Ti or Si/Nb ratio in the synthesis mixture

Total acidity of the catalysts determined by temperature programmed NH_3 desorption analysis. Obtained TCD signals with temperature are demonstrated in Figure 5.5 and Figure 5.6. Figure 5.5 demonstrates acidic nature of SBA-15 and Ti-SBA-15 catalysts. Pure SBA-15 exhibited some acidic nature at some temperature range but peak intensities of this sites were low. Aside that, Ti-SBA-15 catalysts possessed weak and moderate acidic sites between 100 and 350 ºC and they also demonstrate strong acidic sites between 400 and 550 ºC. Acidic strength of Ti-SBA-15 (10) was higher than Ti-SBA-15 (20) due to presence of more Ti content in the structure.

On the other hand, as demonstrated in Figure 5.6, Nb-SBA-15 catalysts demonstrated weak to strong acid sites between 100 – 500 ºC. The acidic sites of Nb-SBA-15 catalysts increased with increasing niobium content which was due to presence of more Nb in the structure of SBA-15. Total acidity of the catalysts were calculated by integrating area under TCD signals in the Figures and given in Table 5.1. Total acidity of pure SBA-15 found very low. Incorporation of Ti and Nb into SBA-15 structure increased acidity significantly. Total acidity of Nb-SBA-15 catalysts found to be higher than Ti-SBA-15 catalysts.

FTIR spectra of Ti-SBA-15 catalysts are given in Figure 5.7. The bands at 800, 1069 and 1228 cm^{-1} indicate existence of Si–O bonds [48]. The band at 966 cm^{-1} demonstrated the presence of Si-O-Ti vibrations [36]. And the broad bands at between 3300 and 3700 cm^{-1} attributed to surface hydroxy group and physisorbed water [36]. The peaks at 1085 cm^{-1} and 1195 cm^{-1} attributed to the asymmetric stretching of framework Si-O-Si vibrations [44]. Figure 5.8 demonstrates FTIR spectra of Nb-SBA-15 catalysts. Peak assignment carried out same as Ti-SBA-15 catalysts. But this time, the peak at

960 cm^{-1} interpreted as isomorphous substitution of Si by Nb atoms [44, 49].

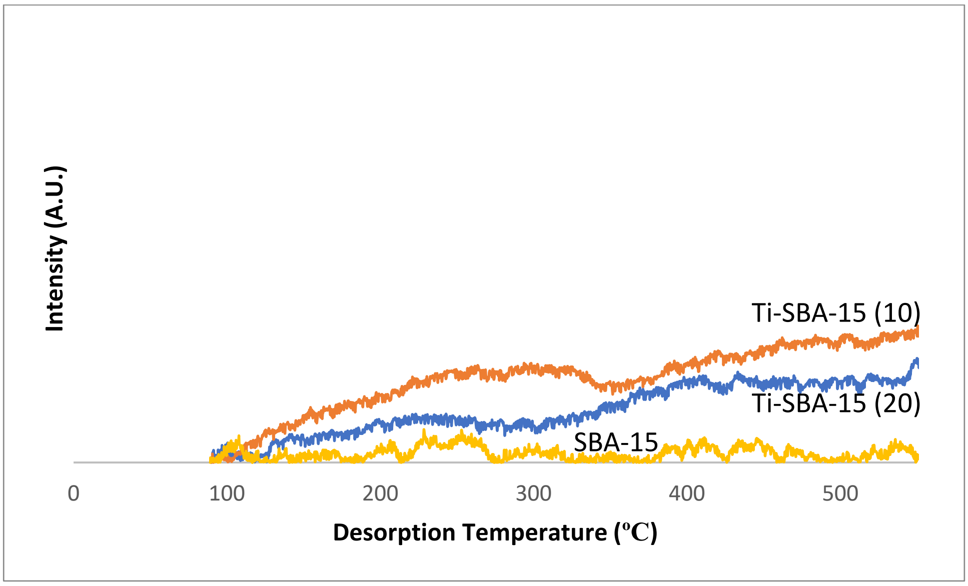


Figure 5.5. NH_3 desorption with temperature for SBA-15 and Ti-SBA-15 catalysts

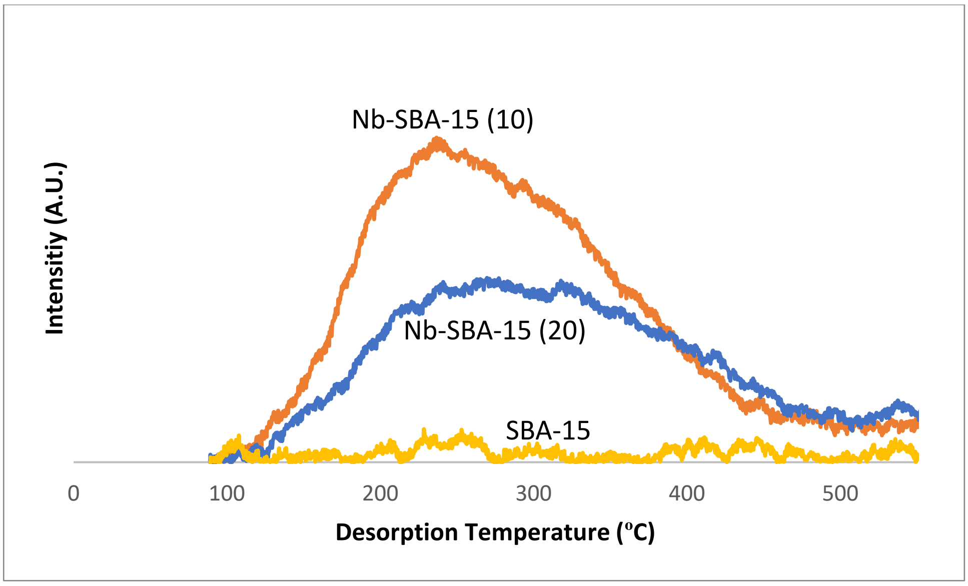


Figure 5.6. NH_3 desorption with temperature for SBA-15 and Nb-SBA-15 catalysts

Surface morphology of the catalysts analysed with SEM and given in Figure 5.9. Pure SBA-15 particles demonstrated mostly rod-like and twisted rod-like (semi-circular and circular) structure and it also contained some bold irregular particles. Throughout literature rod-like particle structure is the most encountered one for SBA-15 [38, 47] but different morphologies can be obtained by changing synthesis parameters [50]. Consequently, considering synthesis conditions of this catalyst was different, obtained particle morphologies were reasonable. Ti and Nb incorporation did not affect morphology of particles for Nb-SBA-15 (10), Nb-SBA-15 (20) and Ti-SBA-15 (10) catalysts. However, different particle morphology obtained with Ti-SBA-15 (20) catalyst (spherical and irregular shapes) which may be due to varying synthesis conditions or lower titanium content of the catalyst.

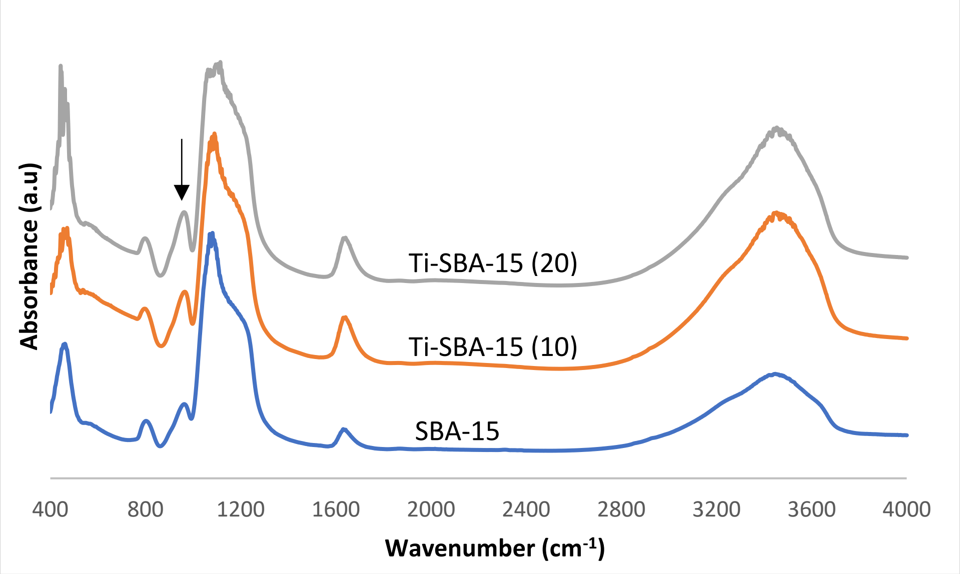


Figure 5.7. FTIR spectra of SBA-15 and Ti-SBA-15 catalysts

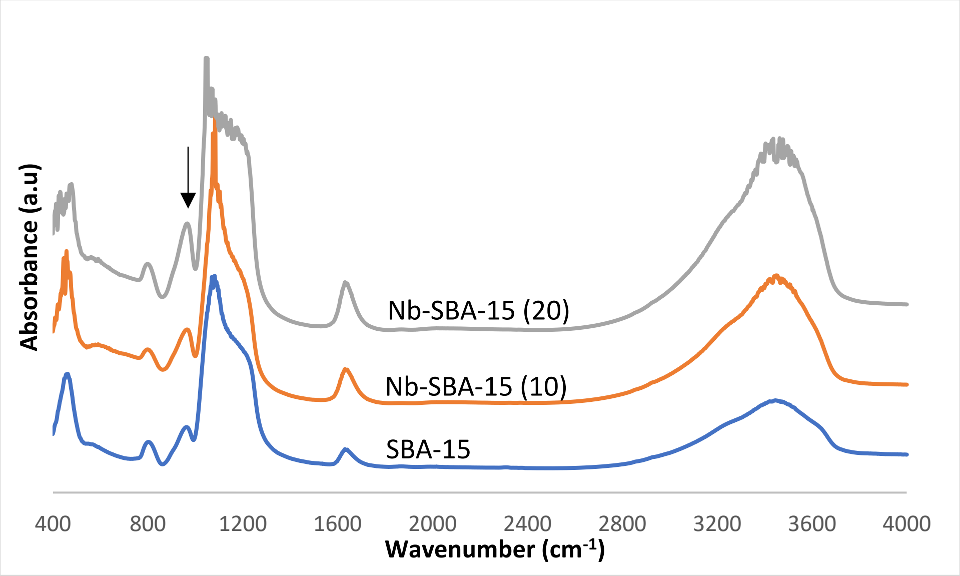


Figure 5.8. FTIR spectra of SBA-15 and Nb-SBA-15 catalysts

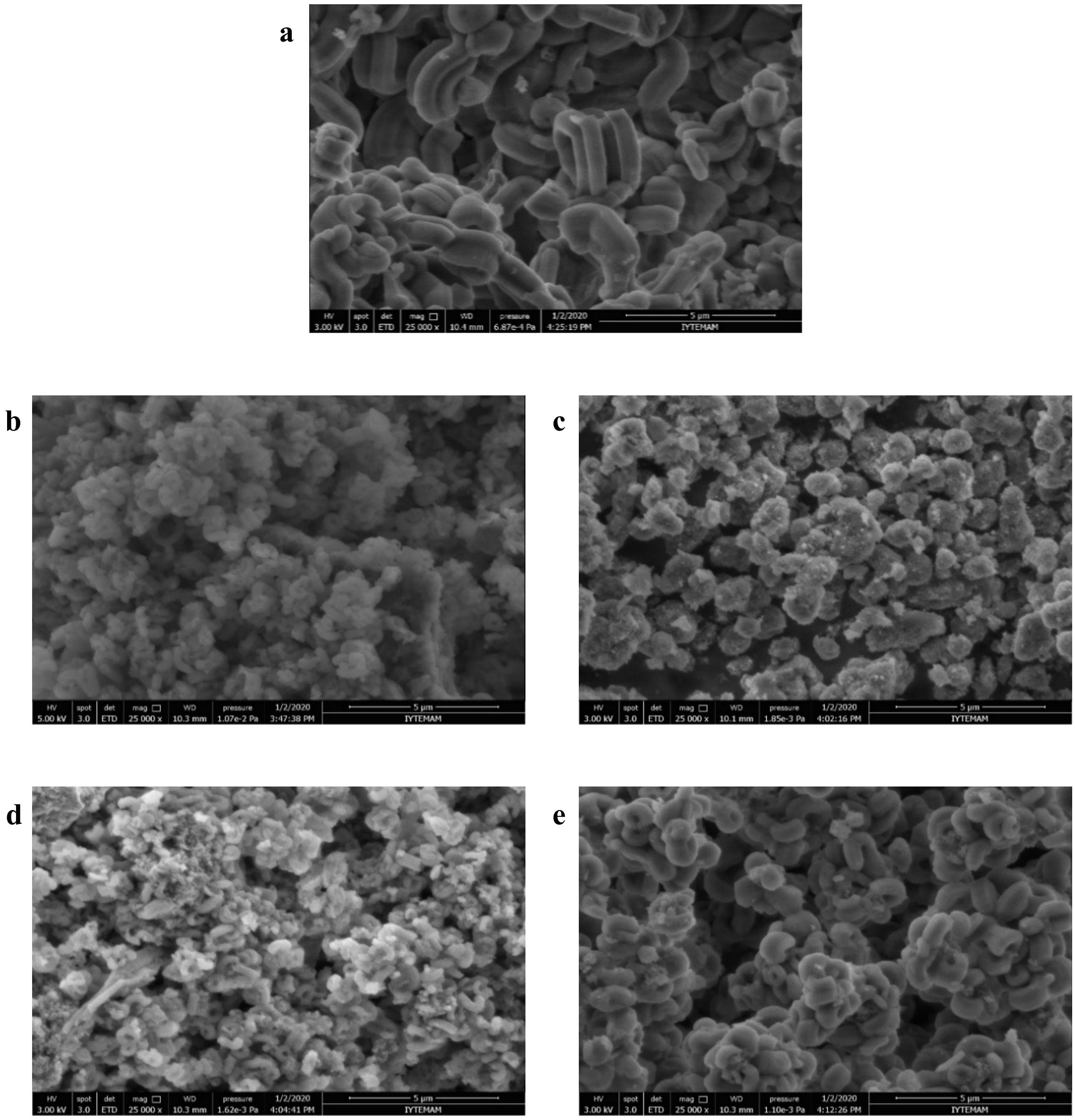


Figure 5.9. SEM micrographs of the catalysts a) SBA-15 b) Ti-SBA-15 (10) c) Ti-SBA-15 (20) d) Nb-SBA-15 (10) e) Nb-SBA-15 (20)

5.2. Catalytic Test Results

Products obtained in homogenous and heterogenous catalytic reactions were analysed by H-NMR, FTIR and analytical methods. The results obtained by analytical method were given with standard deviation. For double bond conversion standard deviation was calculated by performing one sample triplicate for each catalyst whereas for yield standard deviation was calculated by analysing samples two or more times.

5.2.1. Homogenous Catalysis Test Results

In order to compare with heterogenous catalytic reaction results, homogenous reaction was carried out at 75 ºC. Results calculated by analytical methods for homogenous system are demonstrated in Table 5.2. At initial reaction time of 2 h, double bond conversion, yield and epoxide selectivity was found as 65.37 %, 49.85 % and 76.26 % respectively. Conversion increased with increasing time from 65.37 % to 98.65 %. However, epoxide selectivity decreased to 65.77 % at 6 h. The decrease of selectivity attributed to high reaction temperature, since in the literature it pointed out that ideal working temperature for this system was between 65 and 70 ºC [29]. And due to high temperature, more side reactions occurred and therefore caused decrease of epoxide selectivity. On the other hand, epoxide yield initially increased with time from 49.85 % to 65.97 % and then decreased to 64.89 %.

Table 5.2. Double bond conversion, yield and epoxide selectivity for homogenous catalytic system determined by analytical methods.

Time	**Double Bond Conversion (%)**	**Epoxide Yield (%)**	**Epoxide Selectivity (%)**
2 h	65.37 ± 0.54	49.85 ± 0.06	76.26
4 h	90.95 ± 0.54	65.97 ± 0.18	72.53
6 h	98.65 ± 0.54	64.89 ± 0.75	65.77

Figure 5.10 shows FTIR spectra results obtained for homogenous catalyst. For comparison FTIR spectrum of virgin soybean oil (SO) and epoxidized soybean oil (ESO) are also given in the figure. The peaks at 1656 cm^{-1} and 3009 cm^{-1} are responsible for double bonds whereas epoxidized oil peak appears at 843 cm^{-1}. Double bond peaks were slightly visible for sample obtained at 2 h and disappeared after that time. Epoxidized oil peak quite visible for all samples. These results indicate conversion of soybean oil and formation of epoxides. Also, the peak at around 3500 cm^{-1} associated with by products were became apparent for all samples. This showed that more by product formation with reaction time. This was in accordance with analytical measurement.

H-NMR spectrum of homogenous samples obtained at 2 h, 4 h and 6 h are given in Figure 5.11, Figure 5.12 and Figure 5.13, respectively. The peaks between 5.26 and 5.40 ppm are characteristic peaks of double bonds. The intensity of the peaks decreased with time and disappeared at 6 h. The peaks associated with epoxides appeared at between 2.85 and 3.15 ppm. Intensity of the peaks increased until for 4 h and after remained constant. These results were also in accordance with analytical measurements.

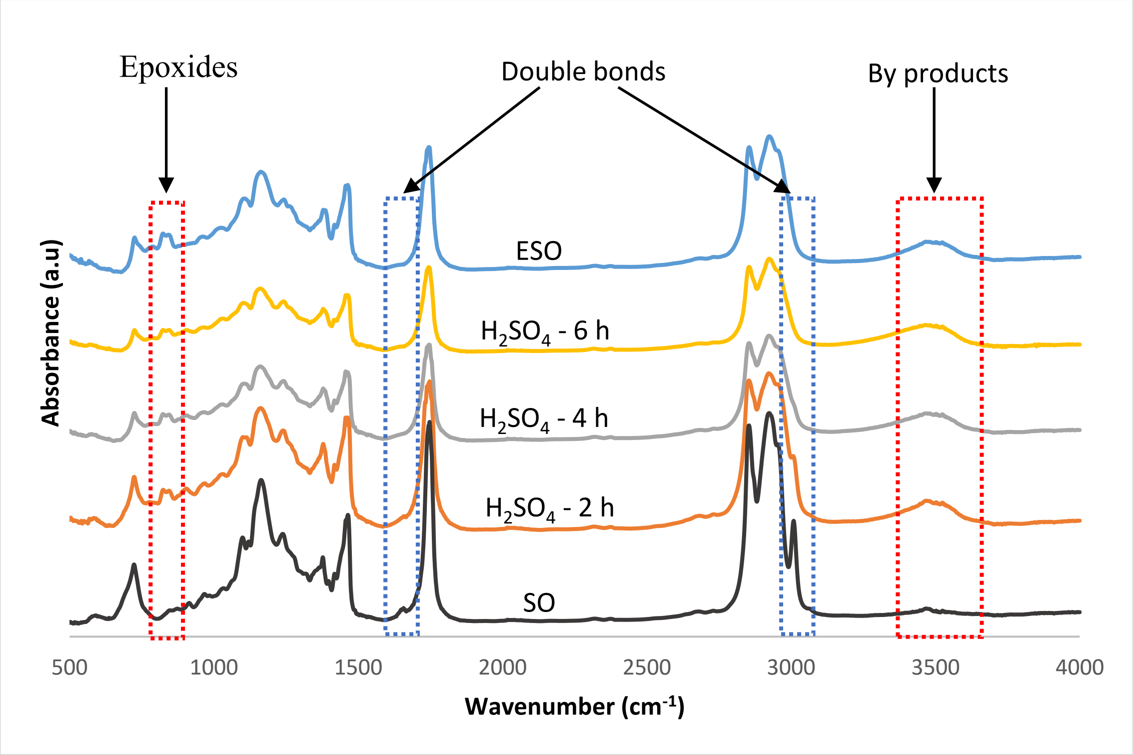


Figure 5.10. FTIR spectra obtained with homogenous catalyst at different reaction times

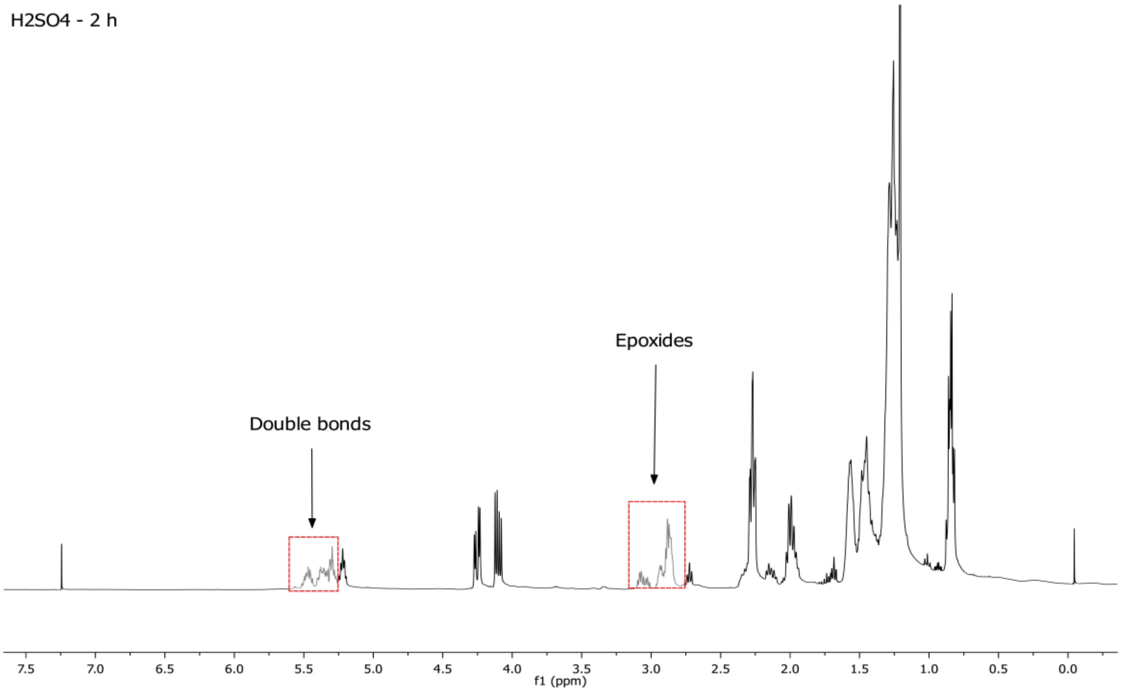


Figure 5.11. H-NMR spectrum of homogenous catalyst sample obtained at 2 h.

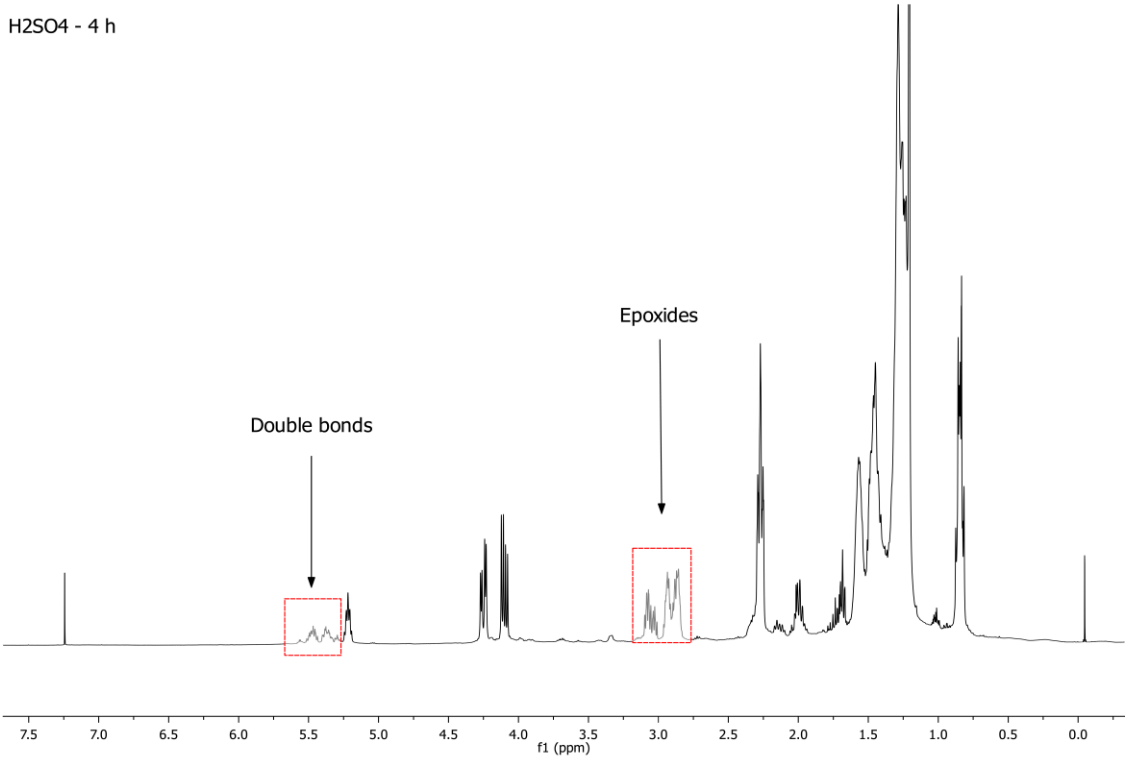


Figure 5.12. H-NMR spectrum of homogenous catalyst sample obtained at 4 h.

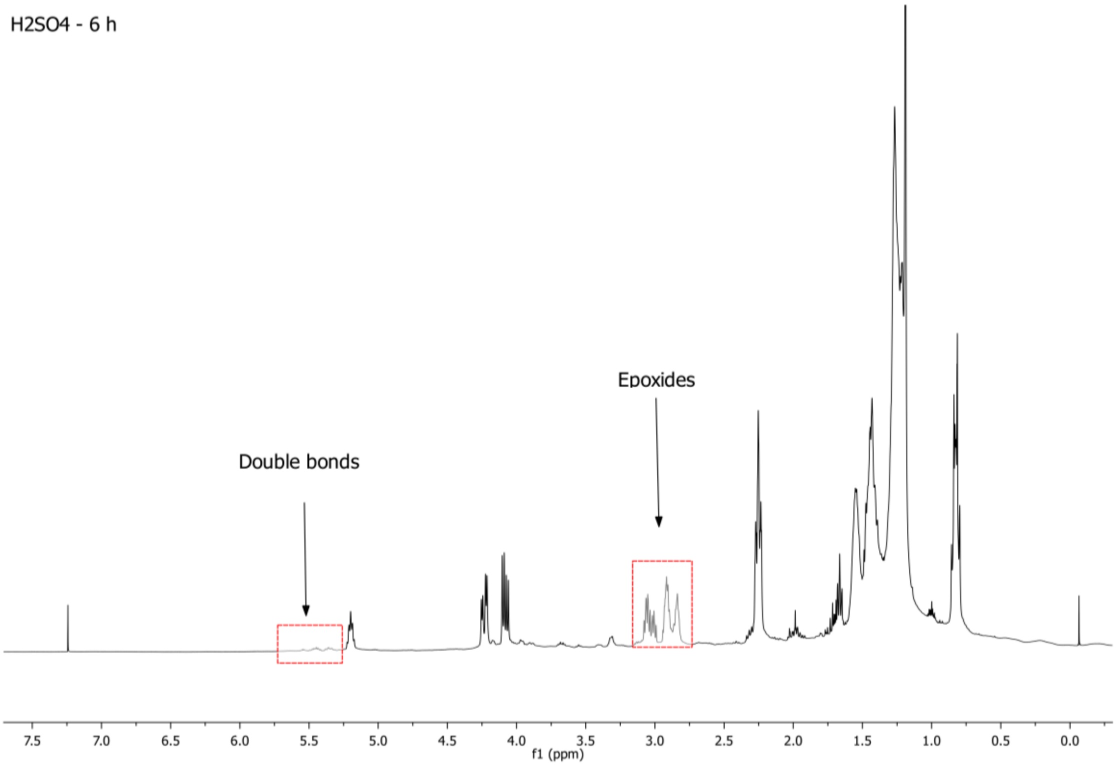


Figure 5.13. H-NMR spectrum of homogenous catalyst sample obtained at 6 h.

5.2.2. Heterogenous Catalysis Test Results

Initially, epoxidation reactions were carried out by SBA-15. Obtained products analysed analytically and results indicated no double bond conversion which was due to low acidity of catalyst. Results obtained with Ti-SBA-15 catalysts are given in Table 5.3. For Ti-SBA-15 (10) catalyst double bond conversion, epoxide yield and epoxide selectivity increased with reaction time. But activity of the catalyst was found low. On the contrary, despite the increase of double bond conversion and epoxide yield with time, Ti-SBA-15 (20) catalyst also showed low activity. It gave 6 % conversion after 6 h.

Double bond conversion, epoxide yield and epoxide selectivity results obtained with Nb-SBA-15 catalysts are given in Table 5.4. Nb-SBA-15 (10) catalyst promoted 28 % conversion, 6.49 % yield and 22.97 % selectivity after 6 h. However, despite the increase of double bond conversion, yield and epoxide selectivity did not change significantly with increasing time. On the other hand, for Nb-SBA-15 (20) catalyst double bond conversion and epoxide yield increased with time whereas epoxide selectivity increased up to 4 h and then decreased.

When compared to Ti-SBA-15 catalysts, Nb-SBA-15 catalysts demonstrated higher activity. However, epoxide selectivity with Nb-SBA-15 catalysts found lower than Ti-SBA-15 catalysts. Overall, yield obtained from Ti-SBA-15 (10) and Nb-SBA-15 catalysts found similar.

Table 5.3. Double bond conversion, yield and epoxide selectivity for Ti-SBA-15 (10) and Ti-SBA-15 (20) catalysts determined by analytical methods

Catalyst	Time	Double Bond Conversion (%)	Epoxide Yield (%)	Epoxide Selectivity (%)
Ti-SBA-15 (10)	2 h	6.77 ± 1.53	2.04 ± 0.21	30.20
	4 h	9.51 ± 1.53	3.79 ± 0.31	39.79
	6 h	10.48 ± 1.53	4.87 ± 0.32	46.45
Ti-SBA-15 (20)	2 h	3.10 ± 0.09	1.52 ± 0.01	49.26
	4 h	4.75 ± 0.09	2.15 ± 0.21	45.33
	6 h	6.08 ± 0.09	2.84 ± 0.17	46.78

In the literature, it was stated that increasing H_2O_2 concentration would promote double bond conversion [25]. Campanella et al. (2004) studied soybean oil epoxidation using different H_2O_2 to double bond molar ratios ranging from 0.6:1 to 5.5:1 by using Ti/SiO_2 as catalysts. 65.95 % conversion obtained after 31 h when H_2O_2 to double bond molar ratio was 5.5:1. Also, 72.03 % conversion obtained after 48 h when H_2O_2 to double bond molar ratio was 1.1:1 [4]. Chen et al. (2019) used 2.4:1 H_2O_2 to double bond molar ratio by using Titanium silicalite-1 catalysts. Epoxidation reactions were carried out 24 h where 40.93 % conversion obtained [19]. Di serio et al. (2012) used 4.8:1 H_2O_2 to double bond molar ratio by using Nb_2O_5-SiO_2 catalysts and obtained 30 % conversion after 5 h [33]. Considering this findings and test conditions of the present study, (H_2O_2 to double bond molar ratio set to 0.95:1 to effectively utilize H_2O_2 and reactions carried out for 6 h) it can be concluded that conversion results obtained with Nb-SBA-15 catalysts were reasonable even using low H_2O_2 concentration. Utilizing concentrated H_2O_2 and increasing reaction time would promote higher conversion and yield. Further studies are required to explain results obtained.

Table 5.4. Double bond conversion, yield and epoxide selectivity for Nb-SBA-15 (10) and Nb-SBA-15 (20) catalysts determined by analytical methods.

Catalyst	**Time**	**Double Bond Conversion (%)**	**Epoxide Yield (%)**	**Epoxide Selectivity (%)**
Nb-SBA-15 (10)	2 h	17.48 ± 1.35	3.95 ± 1.05	22.58
	4 h	23.02 ± 1.35	5.59 ± 1.12	24.30
	6 h	28.24 ± 1.35	6.49 ± 1.90	22.97
Nb-SBA-15 (20)	2 h	15.11 ± 0.1	4.13 ± 0.06	27.32
	4 h	17.72 ± 0.1	5.51 ± 0.67	31.11
	6 h	28.94 ± 0.1	6.22 ± 0.48	21.51

FTIR spectra of samples obtained by Nb-SBA-15 and Ti-SBA-15 catalysts after 6 h of reaction time are given in Figure 5.14. Spectrum of soybean oil (SO) and epoxidized soybean oil (ESO) also given. It was hard to recognize any difference between soybean oil spectrum and spectra obtained from Ti-SBA-15 samples. The characteristic peaks of double bonds at 1556 cm^{-1} and 3009 cm^{-1} were found almost same for Ti-SBA-

15 samples and soybean oil. This indicated low activity of these catalysts. On the contrary, intensity of double bonds peaks decreased for Nb-SBA-15 samples which indicated some activity of this catalysts.

On the other hand, the peak associated with epoxidized oil at 843 cm^{-1} was not visible for Ti-SBA-15 and Nb-SBA-15 catalysts samples due to lower yield of the catalysts. The wide peak at around 3500 cm^{-1} associated with glycols was observed for all samples which indicated formation of by-products. It was known that temperature, solvent, catalyst concentration, stirring speed, concentration of reactants and type of catalyst influence epoxidation reactions [3]. Bearing these findings in mind, and homogenous reactions literature studies, presence of the acids in the reaction medium caused ring opening reactions thus decreased epoxide selectivity [5, 34]. Considering low epoxide yield obtained in this study and formation of by products, it can be concluded that acidity of the catalysts should be examined for better activities. Further research is needed.

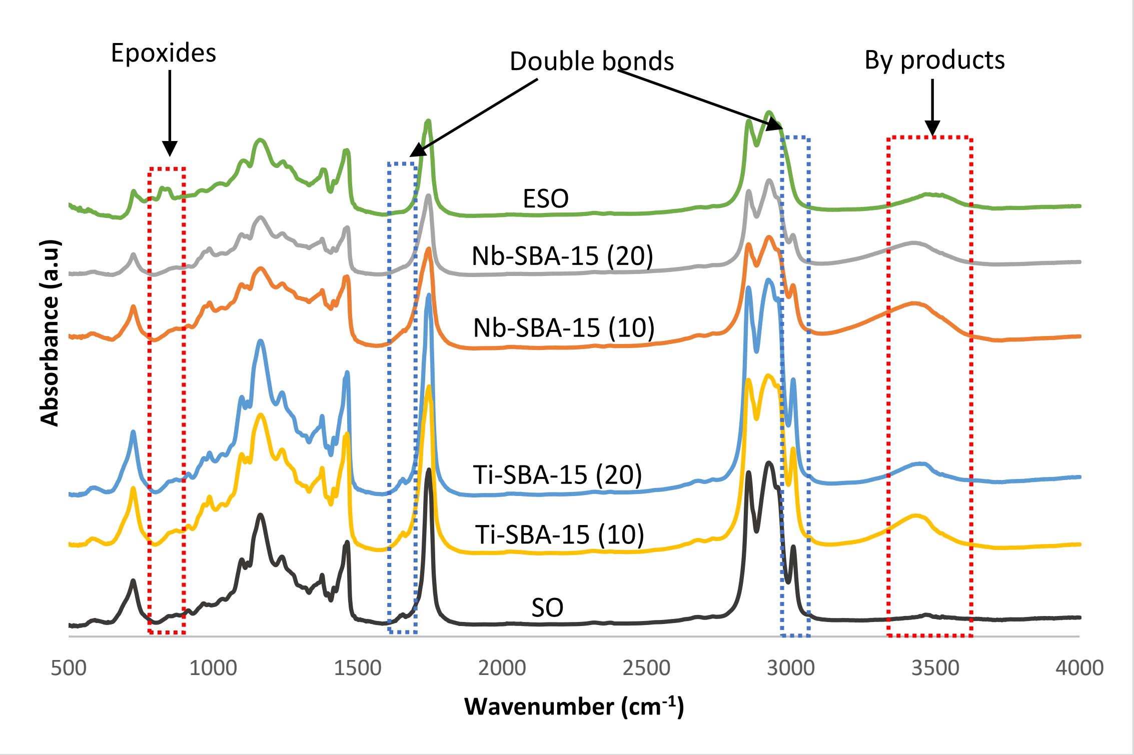


Figure 5.14. FTIR spectra of Ti-SBA-15 and Nb-SBA-15 samples obtained at 6 h.

H-NMR spectrum of samples obtained from Ti-SBA-15 (10) and Nb-SBA-15 (10) catalysts at 6 h reaction time are given in Figure 5.15 and Figure 5.16, respectively. The peaks responsible for epoxides were between 2.85 ppm and 3.15 ppm. Their intensity for both samples were found low which indicated lower epoxide selectivity. However, the peak intensity of sample obtained from Nb-SBA-15 (10) was found higher than sample obtained from Ti-SBA-15 (10) catalyst. H-NMR spectrum of the catalyst's samples obtained for different reaction times and other catalysts are given in appendix A. The results obtained by H-NMR and FTIR confirmed the analytical findings.

5.2.2.1. Effect of Solvent

Two solvents were tested for heterogenous catalytic system which were tert-butanol and ethyl acetate. Firstly, epoxidation reactions carried out in the presence of ethyl acetate. The system was running normally until addition of H_2O_2. After complete addition of H_2O_2 and following 30 min, some problems encountered such as gelation, precipitation, aggregation and unproper mixing of catalysts. No further investigation was carried out to explain this problem. However, in chapter 3 the study carried out by Turco et al. [34] reported that ethyl acetate decomposed to its components in the presence of γ-alumina at 80 ºC by using aqueous H_2O_2. Considering reaction conditions in this study were similar to their conditions, one can assess that, ethyl acetate is decomposed to its components in the presence of some metal oxides in the presence of aqueous H_2O_2 at around 80 ºC. But that fact needs to be further investigated and proved. Consequently, ethyl acetate did not find suitable under test conditions used in present study. On the other hand, no problems encountered when tertbutanol was used as solvent. Therefore, all the studies were performed by tertbutanol.

5.2.2.2. Catalyst Stability Tests

After performing epoxidation reactions, the stability of catalysts was investigated. For this purpose, samples obtained from Ti-SBA-15 (20) and Nb-SBA-15 (20) catalysts were analysed by elemental analysis (ICP-OES). It was not easy to give precise leaching values for both metals due to low concentration of Ti and Nb in the mixture. However, it was clear that leaching of both catalysts were lower than 1 wt %. Aside that, it was found that Ti was more stable than Nb against leaching. On the other hand, when MoO_3/Ti-SBA-15 catalysts subjected to epoxidation reactions, a strong color change was observed in the reaction medium. Figure 5.17 shows color change of reaction mixture between

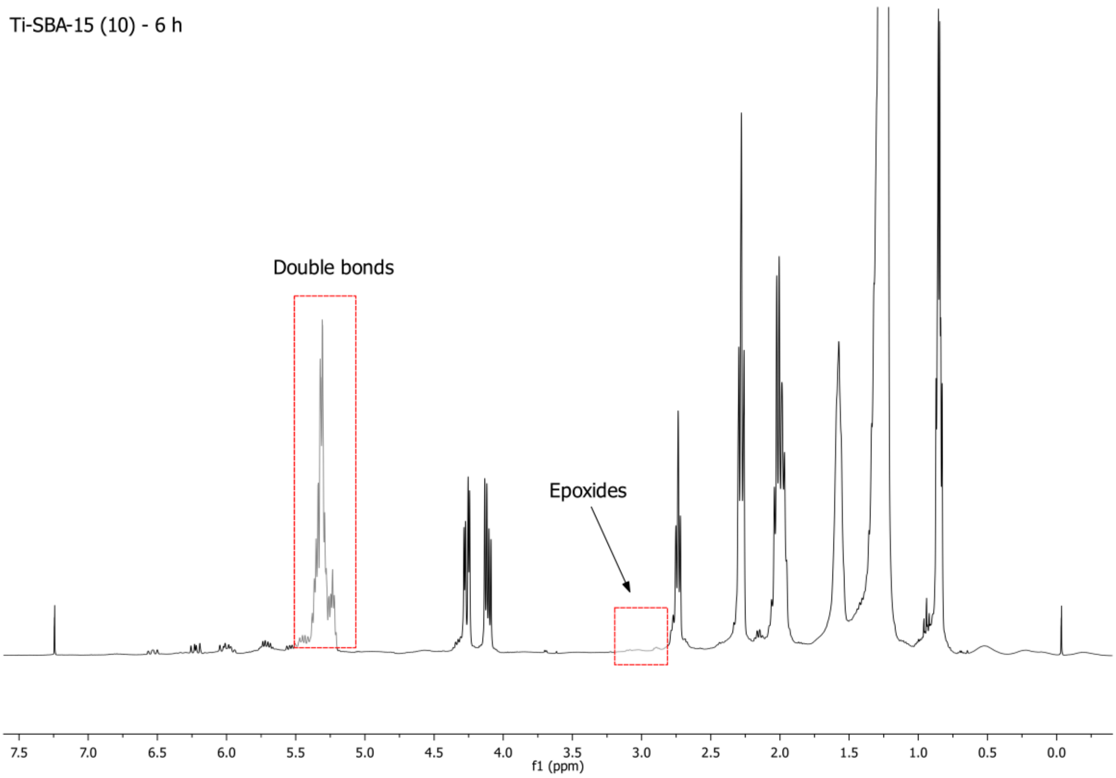


Figure 5.15. H-NMR spectrum of Ti-SBA-15 (10) catalyst sample obtained at 6 h

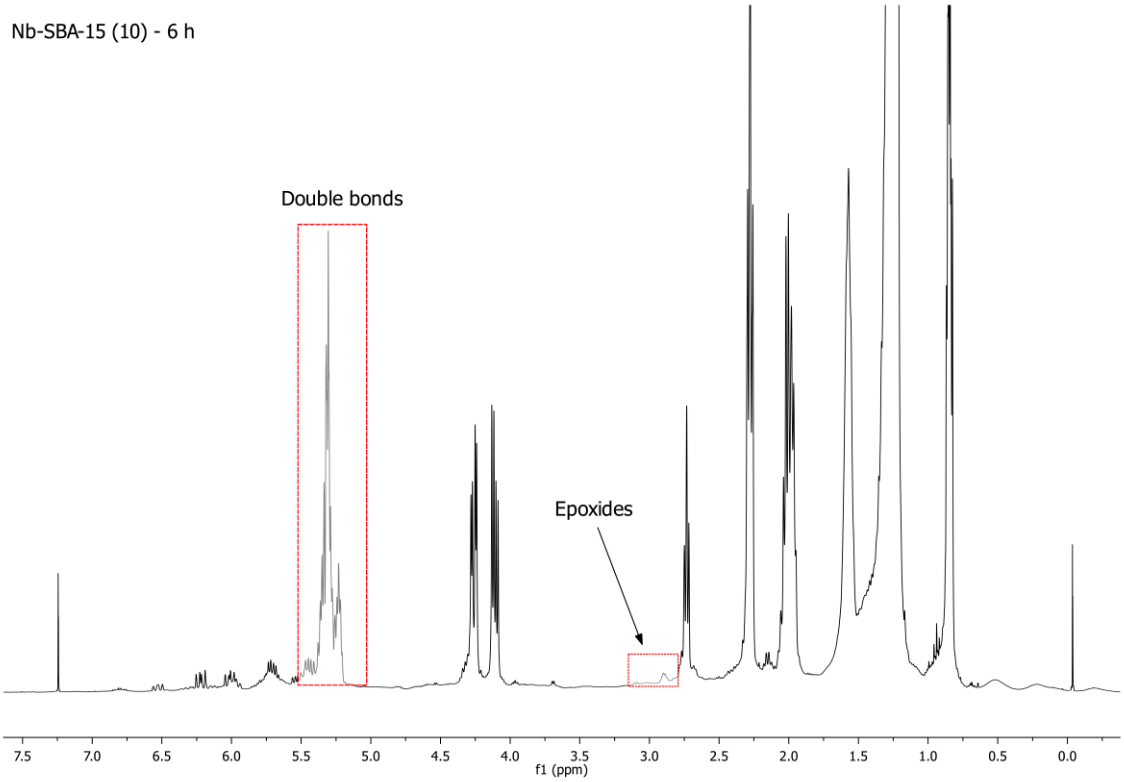


Figure 5.16. H-NMR spectrum of Nb-SBA-15 (10) catalyst sample obtained at 6 h.

reaction at the beginning and after 6 h. Severe leaching of Molybdenum was suspected. To investigate that, only tertbutanol and MoO_3/Ti-SBA-15 catalysts were put into reactor and allowed to mix 6 h at 75 ºC. Even under that conditions, color change of mixture was very apparent. After 6 h, catalyst separated from the mixture and dried for 12 h. Thereafter, elemental composition of catalyst analysed with XRF and reaction mixture was analysed with ICP-OES analysis. Both analyses indicated about 80 wt % of Mo leaching. Consequently, MoO_3/Ti-SBA-15 catalysts were not investigated further and no characterization results for these catalysts were given in this study.

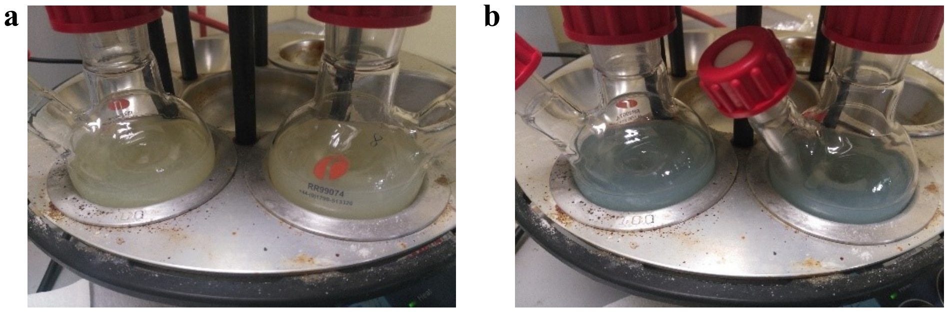


Figure 5.17. Color change during the reaction with MoO_3/Ti-SBA-15 catalysts a) At the beginning of reaction b) After 6 h of reaction time.

Moreover, in order to further investigate catalysts properties after epoxidation reactions, BET and XRD analysis carried out on spent catalysts. For this purpose, after epoxidation reactions catalysts separated from reaction mixture by filtration. Obtained solids washed several times with ethanol and one time with ethyl acetate. Subsequently, catalysts dried at 100 ºC for 12 h. Figure 5.18 are demonstrated XRD spectra of fresh and spent catalysts. Spectra obtained from spent catalyst found almost same as fresh catalysts spectra. However, in some cases peak intensities decreased for spent catalysts which can be ascribed to adsorbed species on the surface. Therefore, adsorbed species caused increase of amorphous structure. Aside that, spent catalysts did not demonstrate any crystalline peak associated with agglomeration of Niobium or Titanium species.

Figure 5.19 demonstrates N_2 adsorption/desorption isotherms of spent and fresh Ti-SBA-15 and Nb-SBA-15 (20) catalysts. Even there were slight difference between spent and fresh catalysts isotherms which was caused probably by adsorption of species on the surface, isotherms obtained from spent catalysts still demonstrated type 4 adsorption/desorption isotherms with hysteresis. This indicated preservation of the mesoporous structure.

Textural properties of spent catalysts are tabulated in Table 5.5. For all three catalysts, surface areas and pore volumes were decreased slightly. This was probably due to chemically adsorbed species on the catalysts surface. On the other hand, pore diameter slightly decreased for Ti-SBA-15 (20) and Nb-SBA-15 (20) catalysts but unexpectedly increased for Ti-SBA-15 (10) catalyst. Increase of pore diameter could be attributed to desorption of chemically adsorbed water on the catalyst pores which was removed during epoxidation reaction or during washing process.

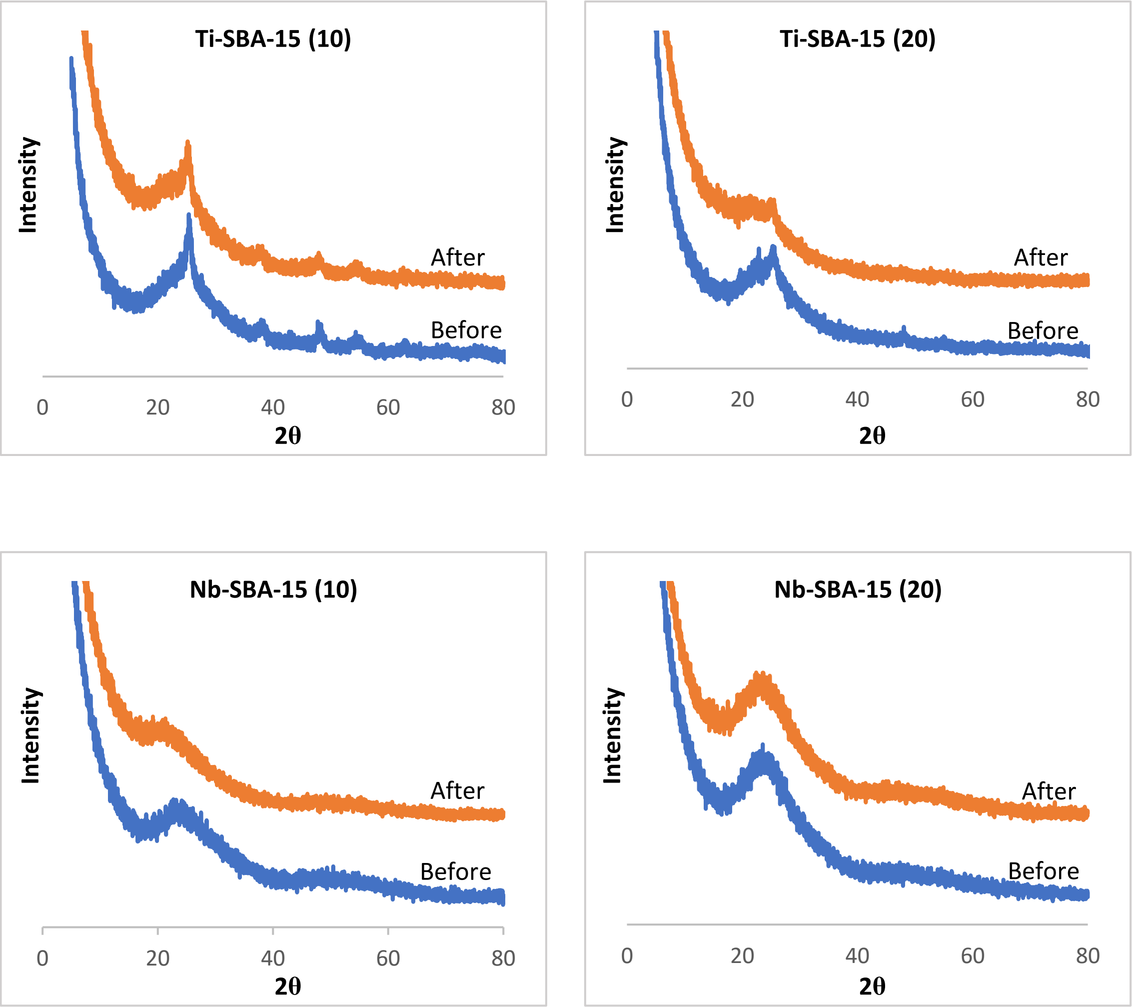


Figure 5.18. XRD spectra of fresh and spent Ti-SBA-15 and Nb-SBA-15 catalysts

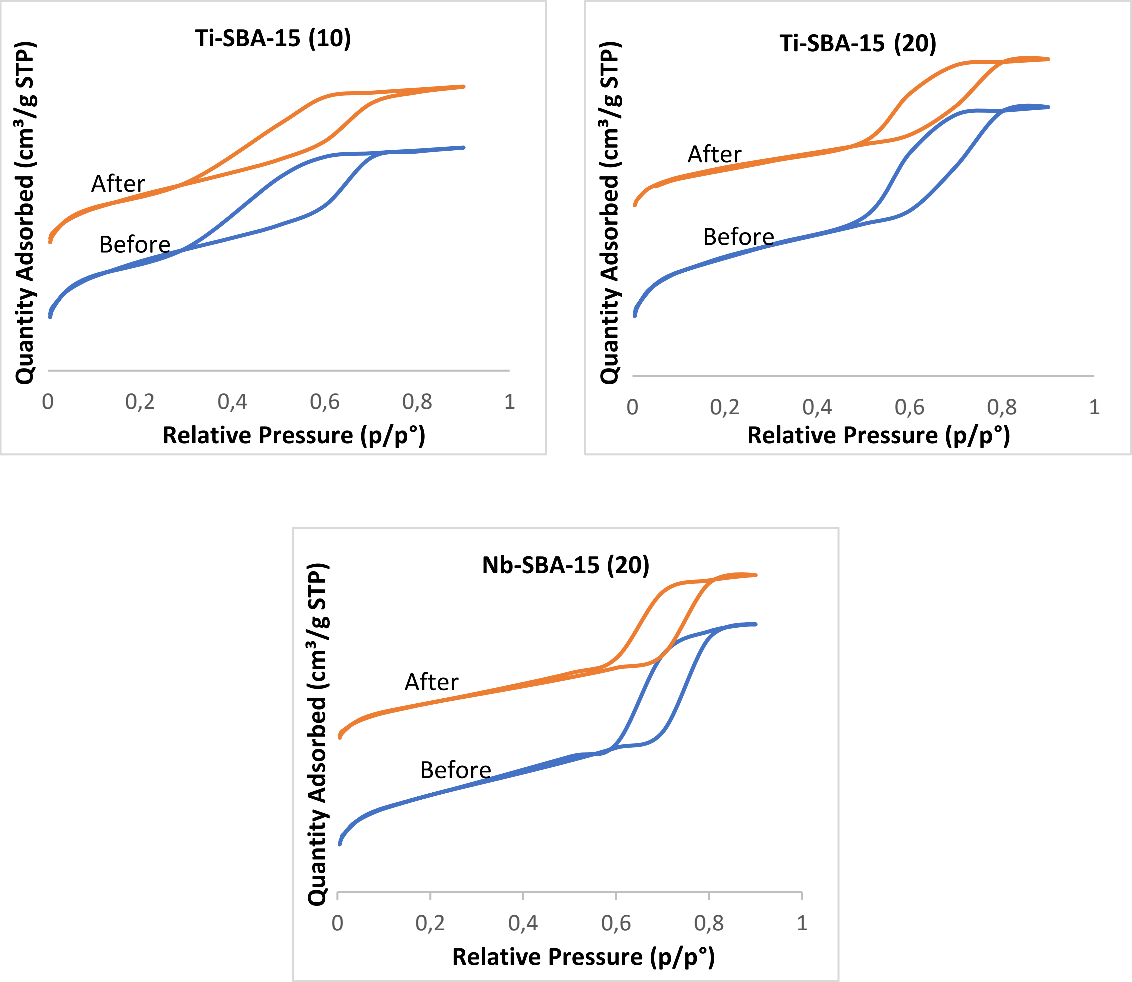


Figure 5.19. N_2 adsorption/desorption isotherms of spent and fresh Ti-SBA-15 and Nb-SBA-15 (20) catalysts.

Table 5.5. Textural properties of spent Ti-SBA-15 and Nb-SBA-15 (20) catalysts

Catalyst	**Surface Area (m^2/g)**	**Pore Diameter (Å)**	**Pore Volume (cm^3/g)**
Ti-SBA-15 (10)	743.7 (885.8*)	31.6 (30.3*)	0.60 (0.64*)
Ti-SBA-15 (20)	618.8 (935.7*)	40.6 (42.6*)	0.66 (0.73*)
Nb-SBA-15 (20)	537.1 (803.8*)	48.1 (50.7*)	0.59 (0.80*)

Numbers in the brackets with a star refers to value before epoxidation

CHAPTER 6

CONCLUSION

Ordered mesoporous Ti-SBA-15 and Nb-SBA-15 catalysts were prepared by hydrothermal synthesis. The catalysts had mesopore structure with high surface area. Ti and Nb were incorporated into SBA-15 structure succesfully. In addition, MoO_3-Ti-SBA-15 catalyst was prepared by impregnation. Nb-SBA-15 catalysts were more acidic than Ti-SBA-15 catalysts. The catalysts showed lower activity in soybean oil conversion. Higher conversion were obtained for the more acidic Nb-SBA-15 catalysts, which also provided higher epoxide yield. Utilization of ethyl acetate as solvent caused precipition, agglomeration and unproper mixing of the catalysts. Catalysts stability tests indicated preservation of mesoporous structure and robustness of Nb and Ti against leaching whereas Mo showed poor stability. Further studies are required to improve and understand findings obtained in the present study.

REFERENCES

1. Sienkiewicz, A.M. and P. Czub, The unique activity of catalyst in the epoxidation of soybean oil and following reaction of epoxidized product with bisphenol A. Industrial Crops and Products, **2016**. 83: p. 755-773.

2. Zhang, H., et al., Solvent-free selective epoxidation of soybean oil catalyzed by peroxophosphotungstate supported on palygorskite. Applied Clay Science, **2014**. 90: p. 175-180.

3. Janković, M., et al., KINETICS OF SOYBEAN OIL EPOXIDATION WITH PERACETIC ACID FORMED IN SITU IN THE PRESENCE OF AN ION EXCHANGE RESIN: PSEUDO-HOMOGENEOUS MODEL. Chemical Industry & Chemical Engineering Quarterly, **2017**. 23(1).

4. Campanella, A., et al., Soybean oil epoxidation with hydrogen peroxide using an amorphous Ti/SiO2catalyst. Green Chem., **2004**. 6(7): p. 330-334.

5. Di Serio, M., et al., Liquid–Liquid–Solid Model for the Epoxidation of Soybean Oil Catalyzed by Amberlyst-16. Industrial & Engineering Chemistry Research, **2017**. 56(45): p. 12963-12971.

6. Cheng, W., et al., Kinetics of the epoxidation of soybean oil with H2O2catalyzed by phosphotungstic heteropoly acid in the presence of polyethylene glycol. European Journal of Lipid Science and Technology, **2015**. 117(8): p. 1185-1191.

7. Wei, Y., et al., Epoxidation of Methyl Oleate and Unsaturated Fatty Acid Methyl Esters Obtained from Vegetable Source over Ti-Containing Silica Catalysts. Industrial & Engineering Chemistry Research, **2018**. 57(48): p. 16284-16294.

8. Sinadinović-Fišer, S., M. Janković, and O. Borota, Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion exchange resin. Chemical Engineering and Processing: Process Intensification, **2012**. 62: p. 106-113.

9. Ivanchikova, I.D., et al., Toward understanding the unusual reactivity of mesoporous niobium silicates in epoxidation of C C bonds with hydrogen peroxide. Journal of Catalysis, **2017**. 356: p. 85-99.

10. Ramanathan, A., et al., Remarkable epoxidation activity of neat and carbonized niobium silicates prepared by evaporation-induced self-assembly. Microporous and Mesoporous Materials, **2018**. 261: p. 158-163.

11. Zhang, X., et al., Catalytic performance of surface-silylated and phenyl-bridged Ti-containing mesoporous silica for epoxidation of propylene. Microporous and Mesoporous Materials, **2018**. 262: p. 251-257.

12. Yan, W., et al., Liquid-Phase Epoxidation of Light Olefins over W and Nb Nanocatalysts. ACS Sustainable Chemistry & Engineering, **2018**. 6(4): p. 4423-4452.

13. Fukuda, M., et al., Highly active and selective Ti-incorporated porous silica catalysts derived from grafting of titanium(iv)acetylacetonate. Journal of Materials Chemistry A, **2015**. 3(29): p. 15280-15291.

14. Yang, X.-L. and Y. Zhang, Lyophilization-based synthesis of HKUST-1 encapsulated molybdenyl acetylacetonate nanocrystals: An effective soybean oil epoxidation catalyst. Catalysis Communications, **2017**. 94: p. 9-12.

15. Farias, M., M. Martinelli, and G.K. Rolim, Immobilized molybdenum acetylacetonate complex on montmorillonite K-10 as catalyst for epoxidation of vegetable oils. Applied Catalysis A: General, **2011**. 403(1-2): p. 119-127.

16. Farias, M., M. Martinelli, and D.P. Bottega, Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex. Applied Catalysis A: General, **2010**. 384(1-2): p. 213-219.

17. Rios, L.A., D.A. Echeverri, and A. Franco, Epoxidation of jatropha oil using heterogeneous catalysts suitable for the Prileschajew reaction: Acidic resins and immobilized lipase. Applied Catalysis A: General, **2011**. 394(1-2): p. 132-137.

18. Guidotti, M., et al., Epoxidation of unsaturated FAMEs obtained from vegetable source over Ti(IV)-grafted silica catalysts: A comparison between ordered and non-ordered mesoporous materials. Journal of Molecular Catalysis A: Chemical, **2006**. 250(1-2): p. 218-225.

19. Chen, C., et al., Heterogeneous and non-acid process for production of epoxidized soybean oil from soybean oil using hydrogen peroxide as clean oxidant over TS-1 catalysts. Microporous and Mesoporous Materials, **2019**. 276: p. 89-97.

20. Feliczak, A., et al., The use of mesoporous molecular sieves containing niobium for the synthesis of vegetable oil-based products. Catalysis Today, **2009**. 140(1-2): p. 23-29.

21. Chua, S.-C., X. Xu, and Z. Guo, Emerging sustainable technology for epoxidation directed toward plant oil-based plasticizers. Process Biochemistry, **2012**. 47(10): p. 1439-1451.

22. Fan, W., et al., Mo Schiff base-tungstate ionic hybrid with enhanced heterogeneous catalytic activity for epoxidation reactions. Applied Catalysis A: General, **2015**. 506: p. 173-179.

23. Piccolo, D., et al., Epoxidation of soybean oil enhanced by microwave radiation. Chemical Engineering Journal, **2019**. 377: p. 120113.

24. Vianello, C., et al., Study of Soybean Oil Epoxidation: Effects of Sulfuric Acid and the Mixing Program. Industrial & Engineering Chemistry Research, **2018**. 57(34): p. 11517-11525.

25. Danov, S.M., et al., Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: a review and perspective. Catalysis Science & Technology, **2017**. 7(17): p. 3659-3675.

26. Zhang, C., et al., Recent advances in vegetable oil-based polymers and their composites. Progress in Polymer Science, **2017**. 71: p. 91-143.

27. Casson Moreno, V., et al., Thermal risk in semi-batch reactors: The epoxidation of soybean oil. Process Safety and Environmental Protection, **2017**. 109: p. 529-537.

28. Hammond, E.G., et al., Soybean oil. Bailey's industrial oil and fat products, **2005**.

29. Turco, R., Industrial catalytic processes intensification through the use of microreactors. **2010**, PhD dissertation, The University of Naples Federico II, Naples.

30. Liao, C.-H., Evaluation of assays for epoxides in oxidized lipids. **2013**, Rutgers University-Graduate School-New Brunswick.

31. He, W., et al., Epoxidation of Soybean Oil by Continuous Micro-Flow System with Continuous Separation. Organic Process Research & Development, **2013**. 17(9): p. 1137-1141.

32. Wang, J., et al., Epoxidation of Soybean Oil Catalyzed by Deep Eutectic Solvents Based on the Choline Chloride–Carboxylic Acid Bifunctional Catalytic System. Industrial & Engineering Chemistry Research, **2017**. 56(29): p. 8224-8234.

33. Di Serio, M., et al., Valuation of Nb2O5–SiO2 catalysts in soybean oil epoxidation. Catalysis Today, **2012**. 192(1): p. 112-116.

34. Turco, R., et al., New findings on soybean and methylester epoxidation with alumina as the catalyst. RSC Advances, **2016**. 6(38): p. 31647-31652.

35. Turco, R., et al., Selective Epoxidation of Soybean Oil in the Presence of H–Y Zeolite. Industrial & Engineering Chemistry Research, **2017**. 56(28): p. 7930-7936.

36. Sharma, R.V., K.K. Soni, and A.K. Dalai, Preparation, characterization and application of sulfated Ti-SBA-15 catalyst for oxidation of benzyl alcohol to benzaldehyde. Catalysis Communications, **2012**. 29: p. 87-91.

37. Huang, Z., et al., The modification of MoO3 nanoparticles supported on mesoporous SBA-15: characterization using X-ray scattering, N2 physisorption, transmission electron microscopy, high-angle annular darkfield technique, Raman and XAFS spectroscopy. Journal of Materials Science, **2007**. 43(1): p. 244-253.

38. Srinivasu, P., et al., Direct Synthesis and the Morphological Control of Highly Ordered Two-Dimensional P 6 mm Mesoporous Niobium Silicates with High Niobium Content. The Journal of Physical Chemistry C, **2008**. 112(27): p. 10130-10140.

39. Firestone, D., Official methods and recommended practices of the AOCS. **2009**: AOCS.

40. Xia, W., S.M. Budge, and M.D. Lumsden, New 1H NMR-based technique to determine epoxide concentrations in oxidized oil. Journal of agricultural and food chemistry, **2015**. 63(24): p. 5780-5786.

41. Guillén, M.D. and P.S. Uriarte, Contribution to further understanding of the evolution of sunflower oil submitted to frying temperature in a domestic fryer: study by 1H nuclear magnetic resonance. Journal of agricultural and food chemistry, **2009**. 57(17): p. 7790-7799.

42. Tiozzo, C., et al., Niobium–silica catalysts for the selective epoxidation of cyclic alkenes: the generation of the active site by grafting niobocene dichloride. Physical Chemistry Chemical Physics, **2013**. 15(32): p. 13354-13362.

43. Turco, R., et al., Influence of preparation methods and structure of niobium oxide-based catalysts in the epoxidation reaction. Catalysis Today, **2015**. 254: p. 99-103.

44. Mandal, S., et al., Niobium doped hexagonal mesoporous silica (HMS-X) catalyst for vapor phase Beckmann rearrangement reaction. RSC Advances, **2014**. 4(2): p. 845-854.

45. García-Sancho, C., et al., Influence of pore size and loading for Nb2O5/SBA-15 catalysts on synthetic ester production from free fatty acids of castor oil. Molecular Catalysis, **2017**. 436: p. 267-275.

46. Palcheva, R., et al., NiMo catalysts supported on the Nb modified mesoporous SBA-15 and HMS: Effect of thioglycolic acid addition on HDS. Applied Catalysis A: General, **2016**. 520: p. 24-34.

47. Devi, P., U. Das, and A.K. Dalai, Production of glycerol carbonate using a novel Ti-SBA-15 catalyst. Chemical Engineering Journal, **2018**. 346: p. 477-488.

48. Sharma, R.V. and A.K. Dalai, Synthesis of bio-lubricant from epoxy canola oil using sulfated Ti-SBA-15 catalyst. Applied Catalysis B: Environmental, **2013**. 142: p. 604-614.

49. Ziolek, M. and I. Sobczak, The role of niobium component in heterogeneous catalysts. Catalysis Today, **2017**. 285: p. 211-225.

50. Chaudhary, V. and S. Sharma, An overview of ordered mesoporous material SBA-15: synthesis, functionalization and application in oxidation reactions. Journal of Porous Materials, **2017**. 24(3): p. 741-749.

APPENDIX A

H-NMR SPECTRUM RESULTS OF PRODUCTS OBTAINED BY HETEROGENOUS CATALYSTS

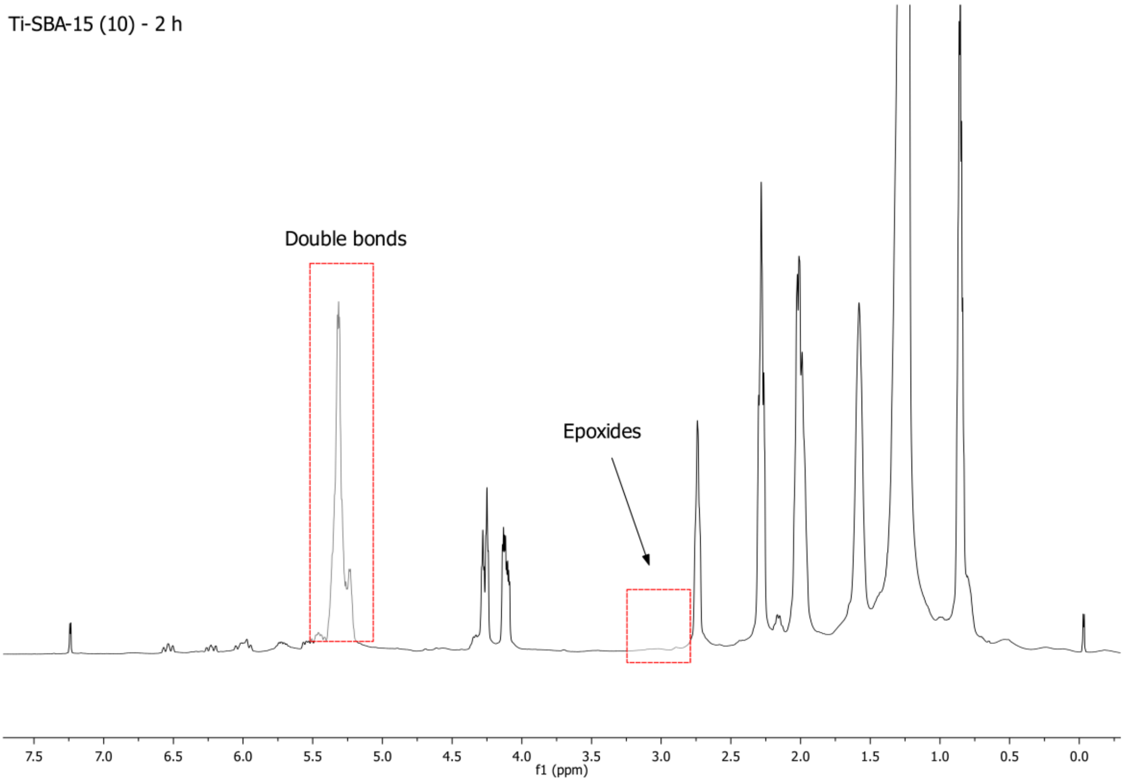


Figure A.1. H-NMR spectrum of Ti-SBA-15 (10) catalyst sample obtained at 2 h.

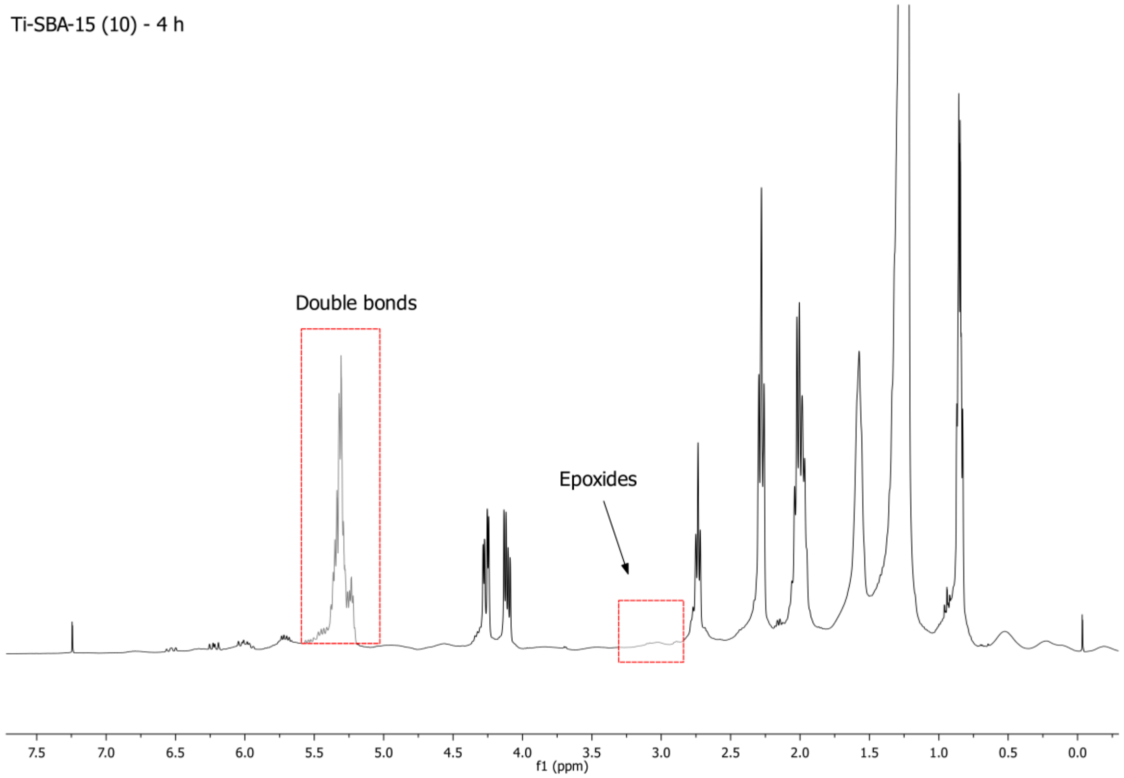


Figure A.2. H-NMR spectrum of Ti-SBA-15 (10) catalyst sample obtained at 4 h.

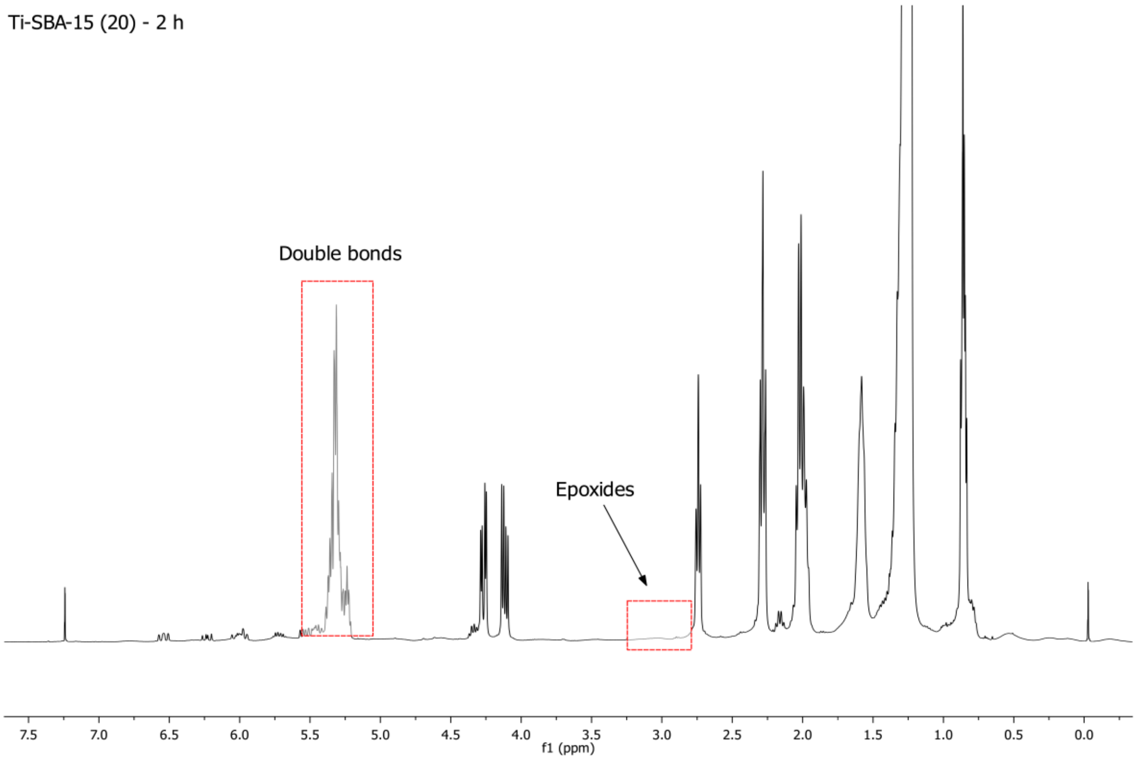


Figure A.3. H-NMR spectrum of Ti-SBA-15 (20) catalyst sample obtained at 2 h.

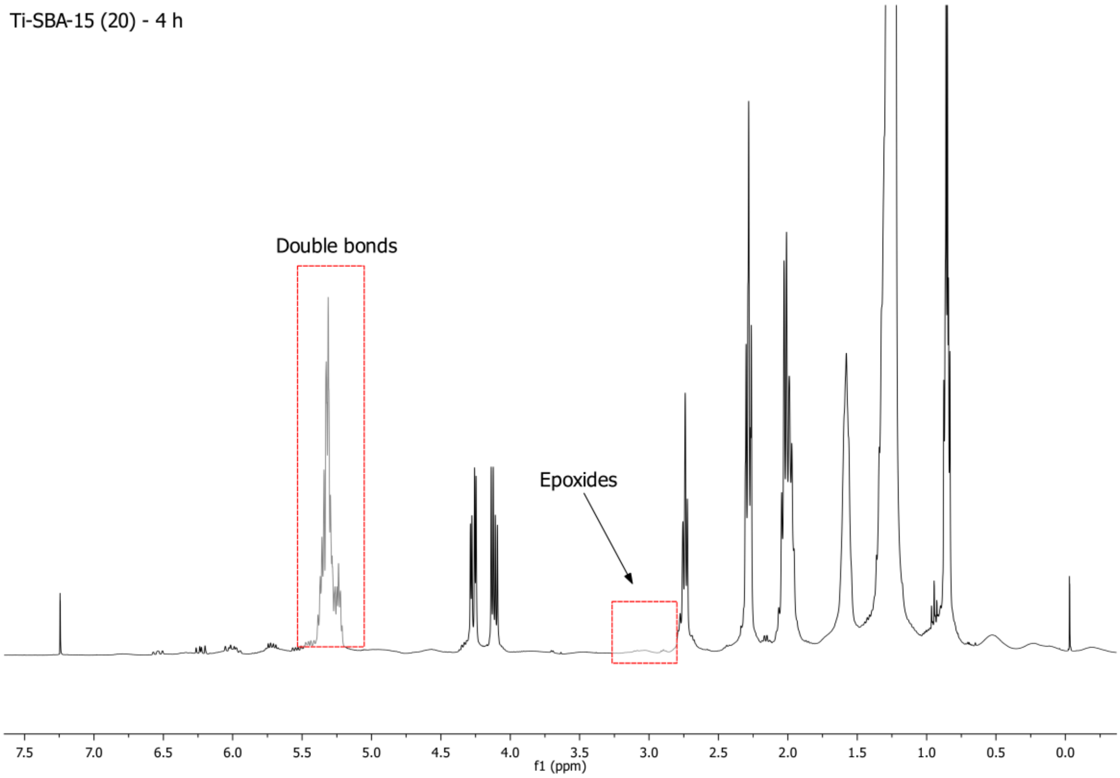


Figure A.4. H-NMR spectrum of Ti-SBA-15 (20) catalyst sample obtained at 4 h.

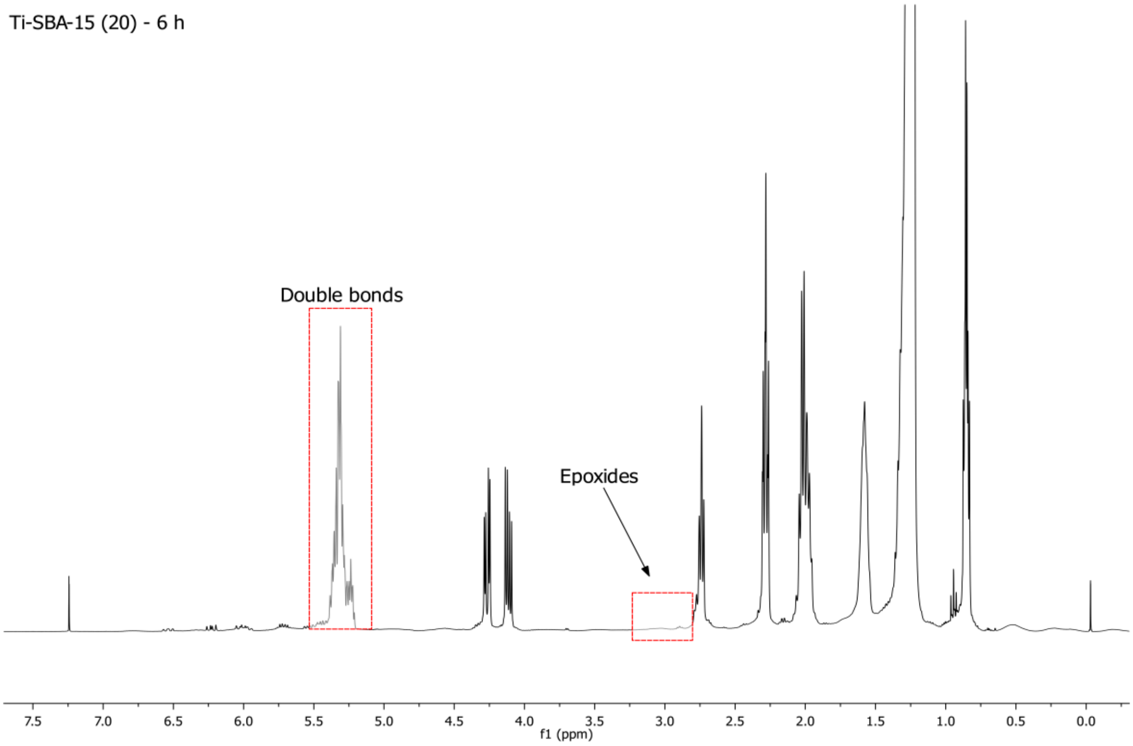


Figure A.5. H-NMR spectrum of Ti-SBA-15 (20) catalyst sample obtained at 6 h.

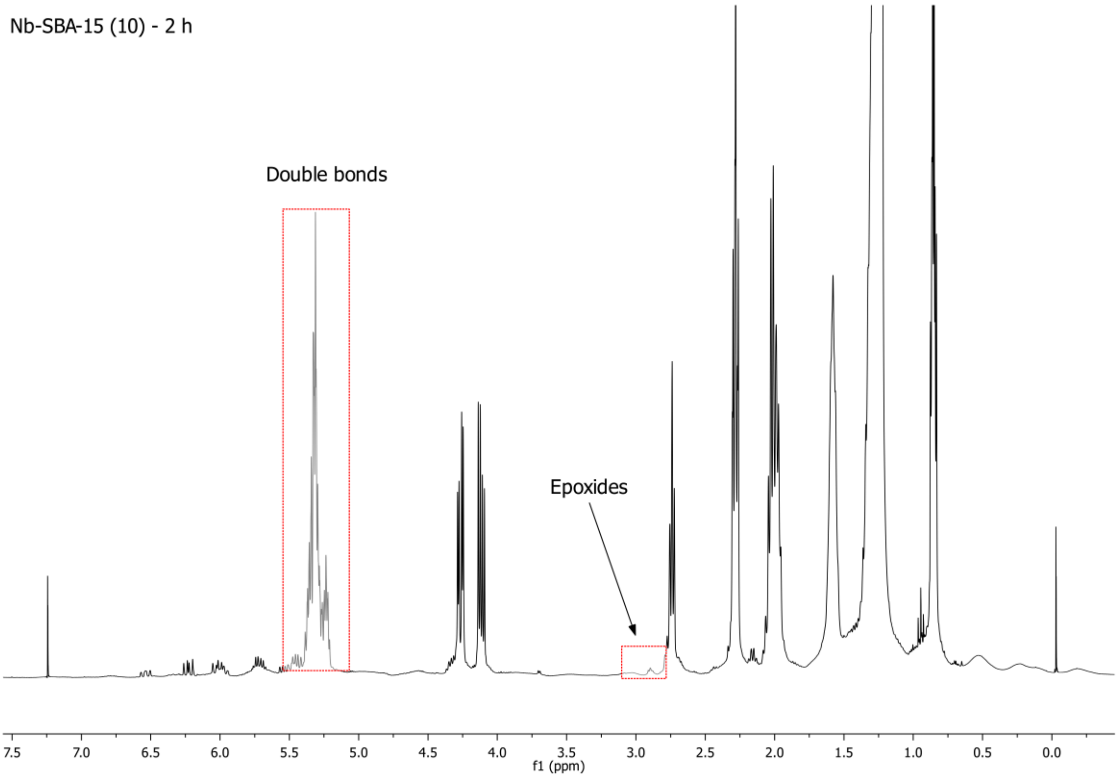


Figure A.6. H-NMR spectrum of Nb-SBA-15 (10) catalyst sample obtained at 2 h.

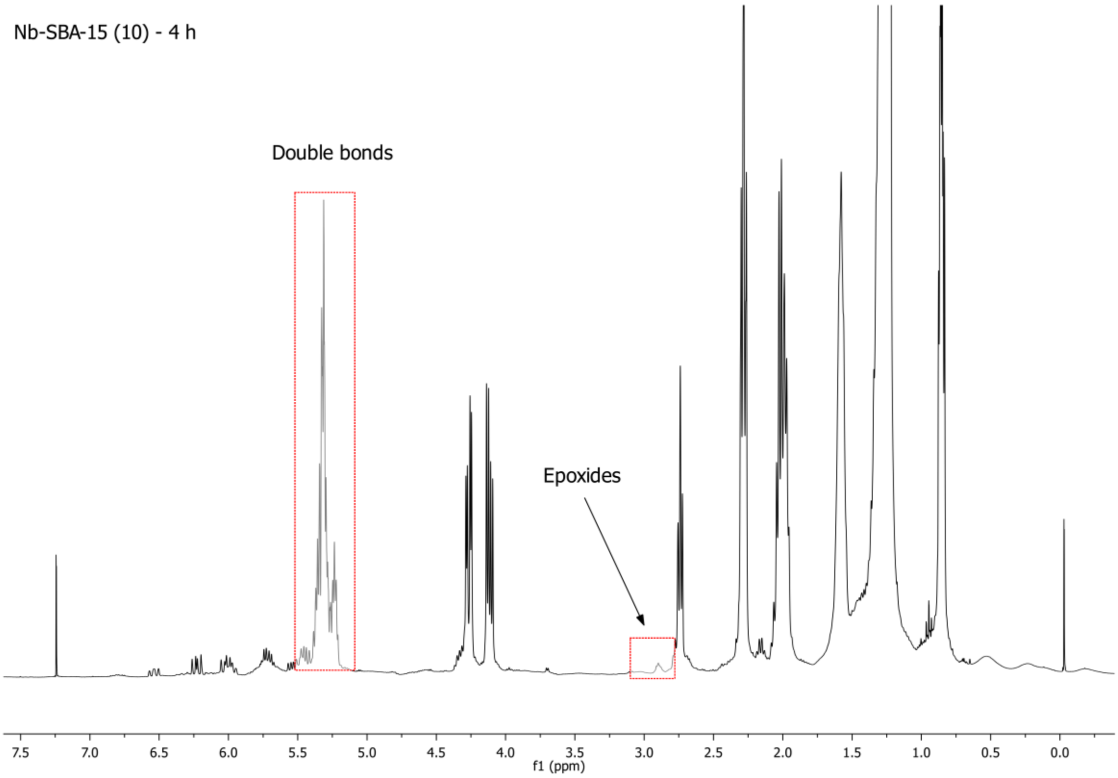


Figure A.7. H-NMR spectrum of Nb-SBA-15 (10) catalyst sample obtained at 4 h.

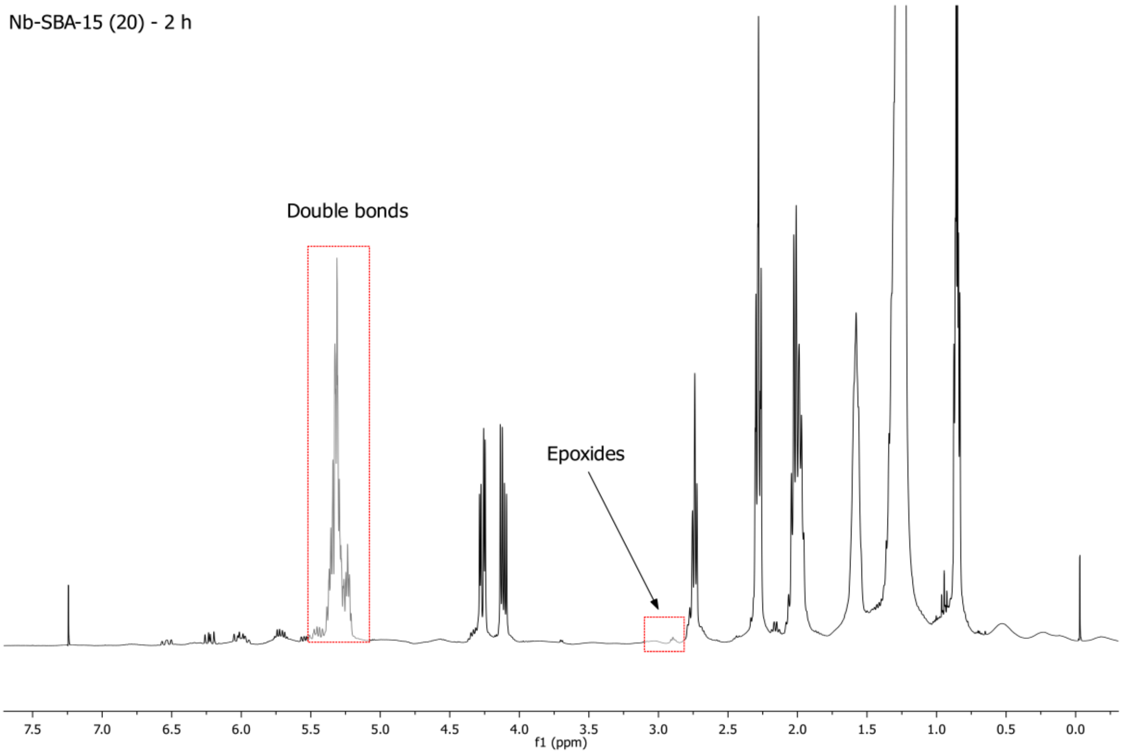


Figure A.8. H-NMR spectrum of Nb-SBA-15 (20) catalyst sample obtained at 2 h.

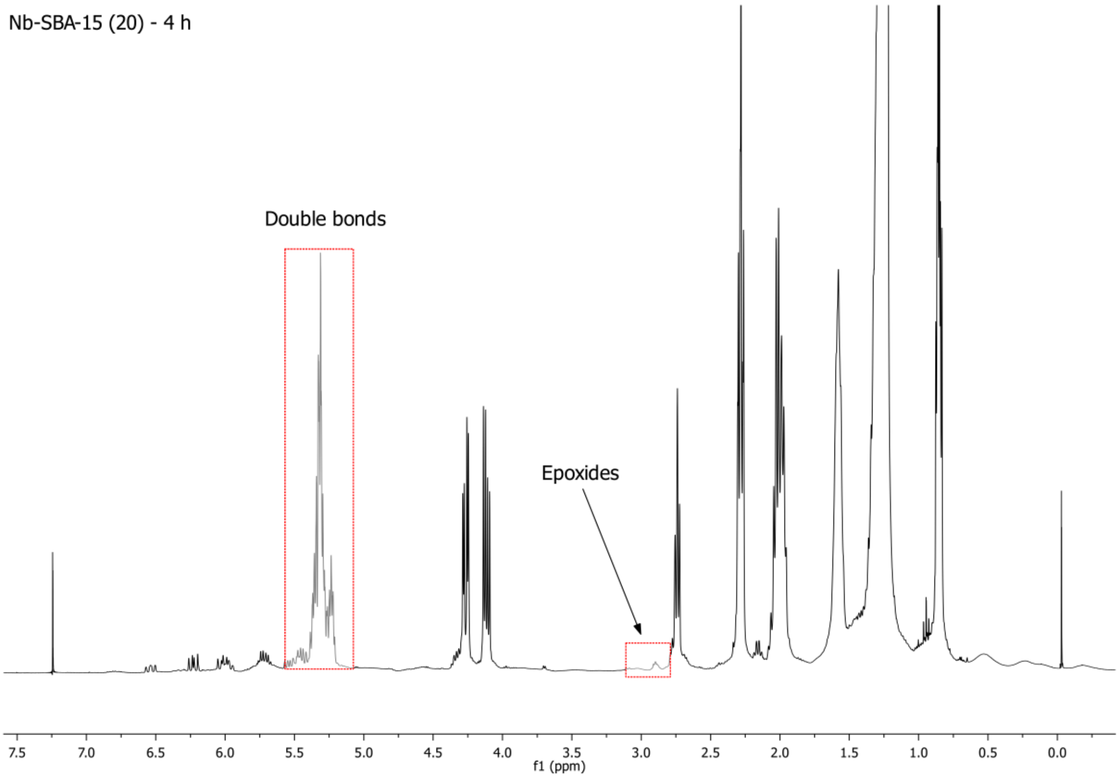


Figure A.9. H-NMR spectrum of Nb-SBA-15 (20) catalyst sample obtained at 4 h.

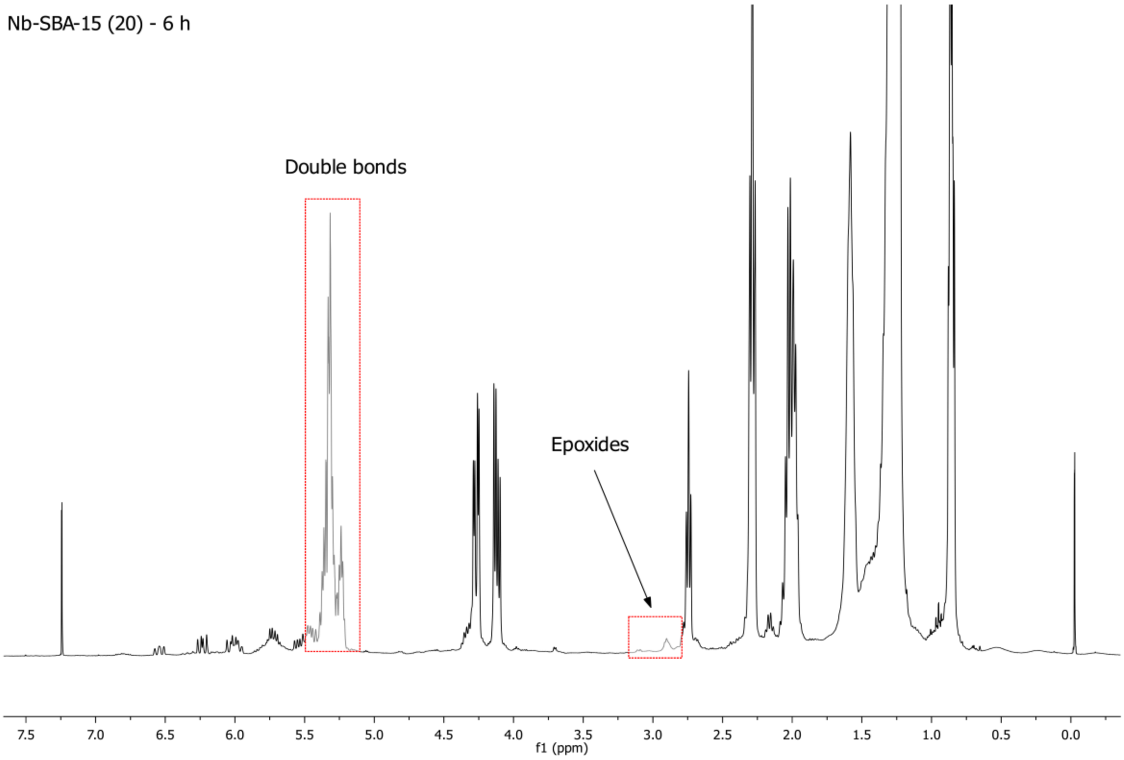


Figure A.10. H-NMR spectrum of Nb-SBA-15 (20) catalyst sample obtained at 6 h.