CHAPTER TWO

LITERATURE REVIEW

2.1 Review on Ti-MCM-41 Catalyst

A considerable increase has been observed over the last decade in the number of publications dealing with synthesis, characterization and evaluation of mesoporous solids in catalysis, adsorption and separation, pollution environmental control and zeolitic reactions. Considerable progress has been made in the study of these solids in a number of disciplines, which has resulted in the appearance of a new family of molecular sieves known as M41S, which is discovered in 1992 by Mobil researchers [36-37].

This family consist of MCM-41 (hexagonal phase), MCM-48 (cubic phase) and MCM-50 (lamellar phase) [38] as shown in Figure 2.1.

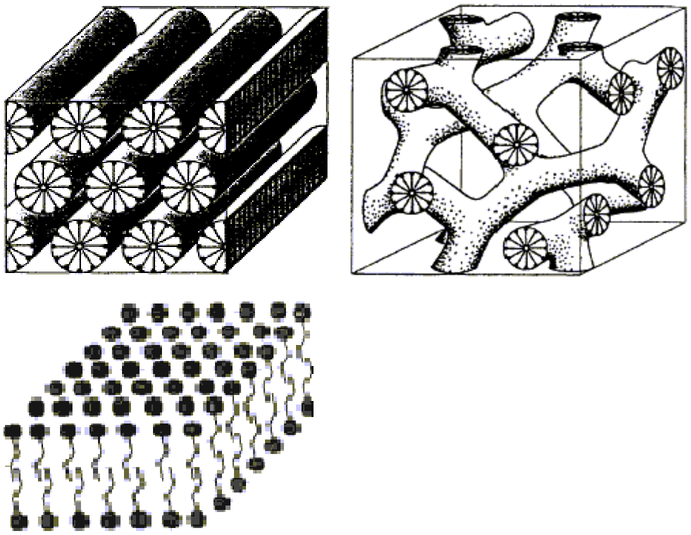

Figure 2.1: Mesoporous structure of M41S (i) MCM-41 (ii) MCM-48 (iii) MCM-50

The hexagonal phase is the result of hexagonal packing of cylindrical micelles, the lamellar phase corresponds to the formation of surfactant bilayers and the cubic phase may be regarded as a bicontinuous structure. The overall structure of MCM-41 is shown below;

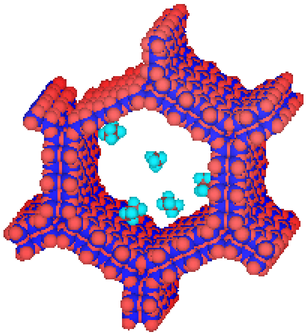

Figure 2.2: Structure of MCM-41

A great application of this novel mesoporous material is to take advantage of the highly ordered pore systems with tunable pore sizes, large specific surface area (typically >800 m^2/g), high hydrocarbon sorption capacities (>0.7 m^3/g) [39] and high density of surface silanols [40] that provide excellent opportunities in inclusion chemistry [41-42].

These properties make MCM-41 potentially useful as a selective catalyst or support material for heterogeneous catalysis and production of chemicals in a large scale, as well as for producing fine chemicals [43].

Moreover, because MCM-41 exclusively contains mesopores, it will allow the diffusion of bulky reactants and bulky products, thus minimizing unwanted consecutive reactions and catalyst decay that are usually encountered in the acid catalyzed organic reactions of fine chemicals.

This mesoporous structure of MCM-41 are controlled by proper selection of molding agent, in this case is surfactant and by adding auxiliary chemical compounds and/or modifying parameters such as gel composition, pH value, timescale, temperature and pressure [44].

Typically, uniform mesopores with the diameter in the range of 5-10 nm could be obtained using $C_nH_{2n+1}N^+(CH_3)_3$ as a template, where $8<n<16$. Size, charge and shape of surfactants are important structure-determining parameters of MCM-41 [45].

The preparation of these versatile ordered mesoporous materials has opened new possibilities in the most of the fields of catalysis. It is however, remarkable that most of the work has been done using MCM-41, even though it has a unidirectional structure.

Obviously, an explosion of research activity has occurred within a few years (Figure 2.3). This includes new investigations on different aspects such as synthesis procedures, synthesis mechanisms, heteroatom insertion, stability, physico-chemical characterization, adsorption, and catalytic applications etc. [46-49].

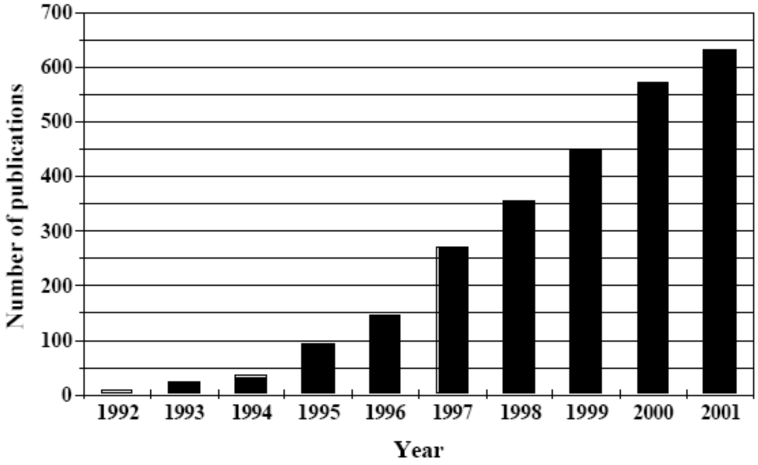

Figure 2.3: Number of publications on ordered mesoporous materials as found by Chemical Abstracts on Compact Disks (CA on CD) of the American Chemical Society using different keywords (MCM-41 or FSM-16 or SBA-15 or

mesoporous materials or ordered mesoporous oxides or ordered mesoporous materials).

2.1.1 Formation of MCM-41

The MCM-41 formation differs from that of normal zeolite crystallization principally in its timing; however, the synthesis method is exactly the same: these solids are obtained through hydrothermal reaction of silica or a silica-aluminum gel in the presence of the structure orienting agent.

A number of models have been proposed in order to explain the mechanism of formation of mesoporous materials by various synthesis routes. All these models are based on the presence and the role of surfactants in solution to guide the formation of inorganic mesostructures.

In solution, surfactants having two parts within the same molecule (hydrophilic head group and long chain hydrophobic tail group) will aggregate and self organize in such a way as to minimize contact between the incompatible ends. The type of interaction between the surfactant and the inorganic precursor under different synthesis conditions needs careful attention and is a subject of much discussion.

(a) Liquid Crystal Templating (LCT) Mechanism

In order to explain the synthesis mechanism, Mobil researchers proposed a liquid crystal templating (LCT) mechanism, based on the similarity between liquid crystalline surfactant assemblies (*i.e.* lyotropic phases) and M41S [36-37]. The mesostructure formation depends on the hydrocarbon chain length of the surfactant tail group [50], the effect of variation of the surfactant concentration and the additional organic swelling agents.

The lowest concentration at which surfactant molecules aggregate to form spherical isotropic micelles is called critical micelle concentration (CMC1). Further increase in the surfactant concentration initiates aggregation of spherical into cylindrical or rod-like micelles (CMC2).

Two mechanistic pathways were postulated for the formation of M41S type materials:

(A) The structure is defined by the organization of surfactant molecules into lyotropic liquid crystal (LC) phase, which serves as template for the formation of the MCM-41 structure. The first step of the synthesis is the formation of a micellar rod around the surfactant micelle which will produce a hexagonal array of rods, followed by incorporation of an inorganic array around the rod-like structures in the second step (Figure 2.4).

(B) Highly sensitive liquid crystal structures formed in surfactant solutions may also interact with the silicate species directly which results in the ordering of the subsequent silicate-enclatherated surfactant micelles to form MCM-41 structure.

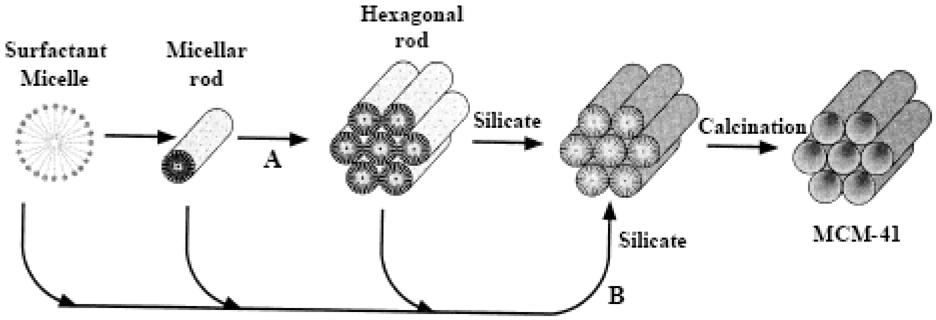

Figure 2.4: Liquid crystal templating mechanism proposed for the formation of MCM-41: (A) liquid crystal phase initiated and (B) silicate anion initated [36-37]

So, the negatively charged inorganic components preferentially interacted with the positively charged ammonium head groups of the surfactants and condensed into a solid. However, it was clearly shown [51] that pathway A (Figure 2.4) did not take place because the surfactant concentrations used were far below the critical micelle concentration (CMC2) required for hexagonal LC formation.

However, once MCM-41 has been formed, its pores are filled with template and in order to obtain a completely mesoporous support material, the micelles must be removed. The solution to this demand is removal by means of calcination.

(b) Silicate Rod Assembly

Davis and co-workers [52] proposed that the liquid crystalline phase is not present in the synthesis medium during the formation of MCM-41, and consequently, this phase cannot be the structure-directing agent for the synthesis of the mesoporous materials (Figure 2.5).

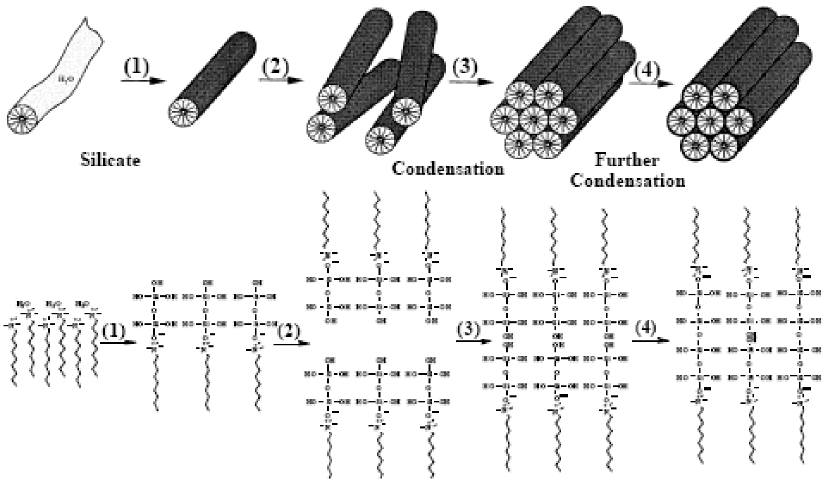

Figure 2.5: Silicate rod assembly proposed for the formation of MCM-41; (1) and (2) involve the random ordering of rod-like micelles and interaction with silicate species; (3) represents the spontaneous packing of the rods and (4) is the remaining condensation of silicate species upon final heating of the organic/inorganic composites [52].

2.1.2 Titanium substituted MCM-41

Due to inactive property of MCM-41 synthesized with only pure silicon, some modification to the synthesis procedure is possible; particularly the incorporation of hetero-elements inside the pore walls of MCM-41 structure. The most frequently incorporated elements are aluminum (Al) and titanium (Ti) which are used to take place of the silicon position to generate catalytically active centre in MCM-41 together with long range order which enabled one to use these materials in acid, base and redox catalysis, as well as high surface area supports for acids, bases, metal oxides and transition metal complexes [53].

The presence of Al inside the pore walls generates an excess negative framework charge (as in zeolites and amorphous silica-alumina).

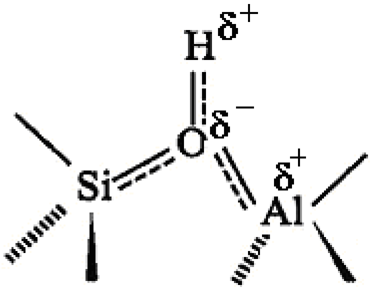

Figure 2.6: Bronsted acid sites

When this charge is compensated by protons, the resulting material is weakly Bronsted acid. Compared to all-silica MCM-41, the physical properties of materials containing Al are generally a bit less well-developed and dealumination can take place during template removal (especially in the presence of steam during calcination). Incorporation of titanium inside the silica walls as shown in Figure 2.7 results in materials displaying interesting oxidation properties based on unique shape-selective character [54] and the advantages related to the use of solid catalysts in industrial processes.

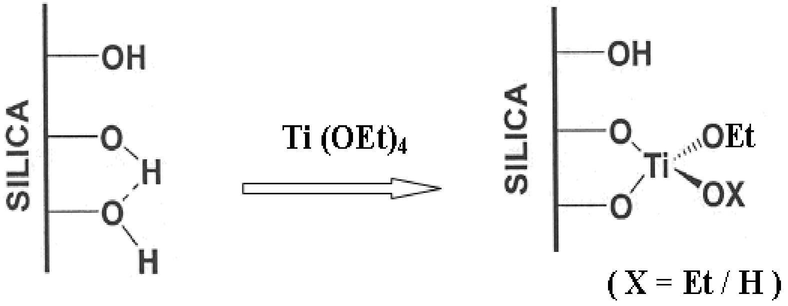

Figure 2.7: Formation of Ti(IV) tetrahedron sites onto silica walls [55].

Titanium containing mesoporous materials of the MCM-41 type are to date the most efficient heterogeneous catalyst in epoxidation of spacy olefins by TBHP [56-58]. Great efforts have therefore been recently spent to incorporate Ti(IV) in larger pore molecular sieves (larger than 0.7 nm), leading to the material, such as Ti-MCM-41 [59].

It should be mentioned that a wide variety of preparation methods for Ti-MCM-41 have been reported and details of the presented methods often dictate reproducibility and stability of the prepared MCM-41 material to a large extent. In a paper by Grun *et. al.*, a "fool proof" method for the synthesis of MCM-41 [60] has been explained. Nevertheless, Ti-MCM-41 materials for this study were synthesized according to procedures developed by Corma and co-workers [61], which yields (all-silica) MCM-41 material of good quality and reproducibility.

Ti-MCM-41 was first reported by Corma *et. al.* [62] in 1994 and has had since then great impact shown by a considerable number of papers published on its structural and catalytic characteristics. In existing industrial processes, the epoxide is produced by reacting the unsaturated compound with a peracid either preformed [63] or synthesized in situ [64] with an organic acid usually acetic or formic acid and hydrogen peroxide.

Using this procedure, the yields to epoxide are relatively low as a consequence of the low H_2O_2 selectivities. Thus, hydrogen peroxide is not an appropriate oxidant for Ti-MCM-41. Hence, it would be interesting to replace the processes based on peracids by a more desirable catalytic one [65-68]. It appears that Ti-MCM-41 has the greatest potential as an epoxidation catalyst when organic hydroperoxides are used as the oxidant *e.g.*TBHP which contains less water (>< 8 % H_2O) than aqueous H_2O_2 (70% H_2O).

2.2 Model Compounds

An inherent property of heterogeneous catalytic system is the difficulties on studies of active sites of the catalyst on bulky feedstocks. As such, smaller molecule or simple hydrocarbon which can easily diffuse in the catalyst structure is chosen as the model compound. Besides that, a model compound is also selected based on several factors; cost, molar balance and availability.

Epoxidation of alkenes is one of the most important methods of functionalizing simple hydrocarbons. In this study, the catalytic activities of Ti-MCM-41 are tested in the epoxidation of 1-octene as a model reaction using TBHP in a batch reactor. Initially, 1-hexene (C6) is used as the model compound. However, due to the problems encounter prior to the use of 1-hexene, the model compound has been changed to 1-octene (C8). This is explained in section 2.2.1.

Analysis by gas chromatography-mass spectrometry (GC-MS) indicates that epoxide (1,2-epoxyoctane) is produced by the process. This is an indirect multistage process with diol (1,2-octanediol) and ketone (2-octanone) as by-products due to Bronsted acid sites present in the samples; the former is obtained through rearrangement of alkene while the latter, through epoxide ring opening reaction.

2.2.1 1-Hexene

1-hexene is a higher olefin, or alkene, with a formula C_6H_{12}. It is an alpha-olefin, meaning that the double bond is located at the alpha (primary) position, endowing this compound with higher reactivity and thus useful chemical properties.

Figure 2.8 shows the chemical structure of 1-hexene.

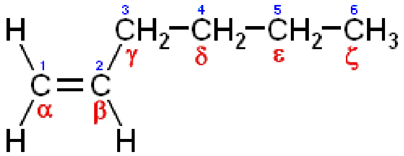

Figure 2.8: Chemical structure of 1-hexene

However, after a series of epoxidation reactions using 1-hexene as the model compound and TBHP as the oxidant, the molar balance discovered to be very low which is only 75%. This implies that not all the substrate is converted to epoxide, but being exposed to air. This proved that 1-hexene which possess low boiling point, around 63 ^{o}C is an inefficient feedstock for epoxidation reaction; due to its volatile characteristic.

Moreover, the studies also show that after a short reaction times, significantly high epoxide selectivity is obtained, with the caveat that with lower boiling point alkene substrates (1-hexene), reactivity is reduced, presumably due to limited solubility of this alkene in liquid phase at the reaction temperature.

Furthermore, due to instability of Ti-MCM-41 during epoxidation and the problems encounter prior to the use of 1-hexene as mentioned earlier, elaboration on this matter is a must towards the change of feedstock.

2.2.2 1-Octene

1-octene is also an alpha-olefin as 1-hexene but having eight carbon atoms with a double bond between the first and second carbon atoms. It is one of industrially important linear alpha olefins. With a formula of C_8H_{16} and molecular weight of 112.214 g/mol, 1-octene exhibits a higher boiling point, 121 ^{o}C compared to 63 ^{o}C for 1-hexene.

1-octene fulfils the requirement to be chosen as model substrate for its good molar balance, inexpensive and availability. Hence, it is an appropriate model compound for epoxidation reaction, whereby in this study, the molar balance has improved to 90% and above.

Several papers [69-70] and patent [71] disclose the olefin epoxidation process *e.g.* 1-octene with H_2O_2 or TBHP in the presence of titanium silicate zeolite catalyst and also catalyst-modified Pt, Pd or Cu compound. However, since the titanium silicate zeolite catalysts are acidic in nature, they also catalyze the epoxide isomerization and/or epoxide ring opening, thereby reducing the selectivity for the formation of epoxide in the epoxidation process over these catalysts.

In the work done by Lewandowski, G. and M, Eugeniusz from Technical University of Szczecin, Poland, epoxidation of 1-octene using TBHP is studied in the presence of $Mo(CO)_6$. The influence of crucial parameters on the yield of 1,2-epoxyoctane, in relation with hydroperoxide, hydroperoxide conversion, selectivity to epoxide and yield of 1,2-epoxyoctane with respect to 1-octene has been described by the use of regression functions in the form of a second order polynomial.

The optimal values of parameters: reaction time, temperature, olefin to hydroperoxide and $Mo(CO)_6$ to hydroperoxide mol ratio, ensuring the maximum values of these functions have also been determined.

On the other hand, Prasetyoko, Didik and co-worker from University Technology of Malaysia did a study on low-loaded ZrO_2/SiO_2 composite prepared by sol-gel method and exhibit promising results on the epoxidation of 1-octene using TBHP as oxidant [72-73].

Its activity is related to the structure of zirconium in the materials, *i.e.* coordinatively unsaturated configuration. Owing to this, the group has demonstrated that Titanosilicalite-1 (TS-1) in combination with sulfated zirconia efficiently catalyzes 1-octene with aqueous hydrogen peroxide in the epoxidation process. The presence of both octahedral zirconium and sulfate species in the catalysts enhances the epoxidation rates.

The proposed model of TS-1 loaded with sulfated zirconia for transformation of 1-octene to 1,2-epoxyoctane and 1,2-octanediol is shown in Figure 2.9.

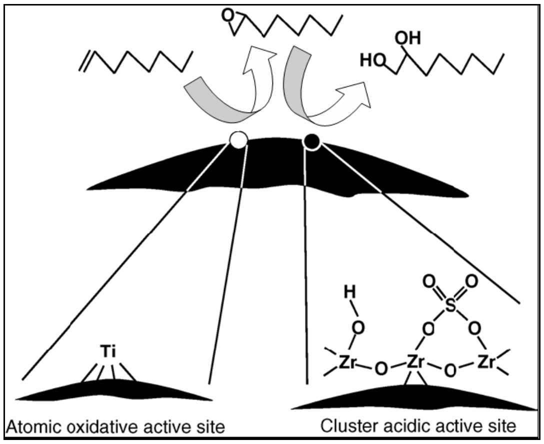

Figure 2.9: Proposed model of TS-1 loaded with sulfated zirconia for transformation of 1-octene to 1,2-epoxyoctane and 1,2-octanediol

2.3 Epoxidation of Vegetable Oils

Currently, there is a great interest in the utilization of renewable resources as an alternative to fossil and mineral raw materials. In this context, vegetable oils and fats are promising feedstocks to be extended, by varying the nature and position of substituents on the fatty acid hydrocarbon chain [74].

In particular, epoxidized fatty acid derivatives from vegetable sources can be used in several domains, *e.g.* as stabilizers and plasticizers in polymers, as additives in lubricants and as precursors of polyfunctional compounds.

Unfortunately, the severe acidic conditions, under which the industrial peracid process is commonly carried out, give rise to several drawbacks. An efficient heterogeneous catalytic process could therefore overstep such disadvantages, by using more sustainable technologies. In this goal, the epoxidation reaction of unsaturated fatty acid methyl esters (FAMEs) is a field of application, in which the use of titanium-containing heterogeneous catalyst, namely Ti-MCM-41 could bring some practical improvements [75].

Epoxidation of FAMEs is first studied in 1943 and later on it has been the subject of many studies. Several papers in recent years dealt with the setting up of catalytic processes, with the aim to improve selectivity to epoxidized product which is relatively low due to acid-catalyzed oxirane ring opening, using a more sustainable compounds and technologies [76-78].

2.3.1 Methyl Oleate (Palm Oil)

With the above aim, some heterogeneous titanium-grafted catalytic systems, already extensively tested in the epoxidation of terpenic substrates [79-80], have been applied to the selective epoxidation of C-18 unsaturated fatty acid methyl esters (FAMEs) using TBHP.

The focus of this section is epoxidation of vegetable oils, particularly palm-base (MO). Epoxidation of double bond MO with TBHP in the presence of catalyst, in this case Ti-MCM-41 with various Si/Ti ratios gave the corresponding monoepoxy derivatives [81]. Epoxy ester with oxirane group at the double bond site is the main product in the epoxidation of methyl oleate, identified as methyl-(9,10)-epoxystearate [82]. Ketone and hydroxyl esters had been reported as the reaction by-products, which is produced via epoxide rearrangement reaction [83-84]. The chemical structure of methyl oleate, epoxyester and its by-products are shown in Figure 2.10.

Epoxidation of methyl oleate

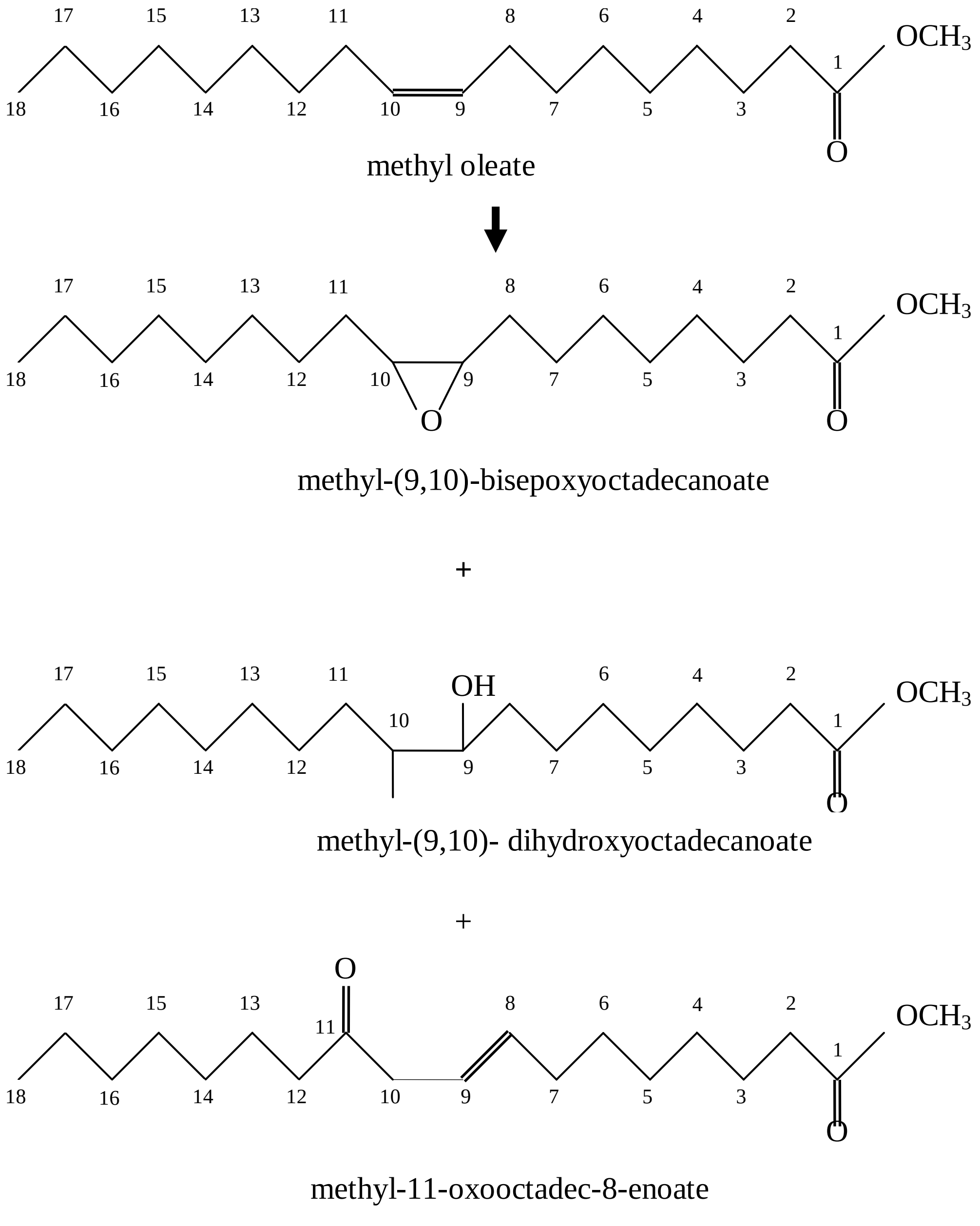

Figure 2.10: Proposed reaction scheme for epoxidation of methyl oleate to epoxide as main product and ketone and hydroxyl esters as by-products.

Reaction condition: C=C / TBHP = 4 : 1, catalyst = 0.5 g, wt. % of Ti = 1.68 %, time = 7 hrs.

Camblor *et. al.* [85] claimed the epoxidation of unsaturated fatty esters over Ti-MCM-41 using H_2O_2 or TBHP. Their main conclusions are that the ester cannot be epoxidized with Ti-MCM-41 using H_2O_2 because water inhibits the activity and stability of Ti-MCM-41. However, with TBHP as oxygen donors, high conversion and high epoxide selectivities are obtained on Ti-MCM-41.

Koyano *et. al.* [86] was also able to synthesized titanium containing MCM-41, which was applicable to the oxidation of bulky alkenes with TBHP as the oxidant, as with Camblor *et. al.* However, the stability of Ti-MCM-41 to water is low with respect to pure silica MCM-41.