

CHAPTER FIVE

CONCLUSION

MCM-41, the most investigated mesoporous molecular sieve of the M41S family is an amorphous silica or aluminosilicate structure with a honeycomb-like hexagonal array of uniform pores. Incorporation of heteroatoms, such as titanium into the framework of MCM-41 produces oxidation catalyst with unique shape-selective properties and has better resistance to hydrothermal treatment. Investigations of this titanium incorporated epoxidation catalysts support the general consensus that the most active and selective sites are isolated, mononuclear, 4-coordinate Ti(IV) centers. Mesoporous materials with the MCM-41 structure with various titanium contents have been synthesized by using hexadecyltrimethyl ammonium bromide as the template.

All calcined MCM-41 materials were subjected to nitrogen physisorption and XRD analysis. The XRD patterns of both as-synthesized and calcined MCM-41 materials show a sharp (100) peak and three higher order peaks of lesser intensity. Upon calcination, some decrease in intensity of all peaks is observed together with a shift towards higher 2θ values. The XRD patterns and the quite high BET surface areas with isotherms of type IV of all the samples are typical for hexagonal MCM-41 type ordered mesoporous materials. The crystallinity and surface area of Ti-MCM-41 both decreases with titanium content. The crystallinity was two-fold higher after calcination than that before calcination.

In addition, increasing Ti content resulted in a decrease in pore volumes and surface areas. These changes of pore parameters were expected because of the replacement of surface silanol groups by the larger Ti content, resulting in the decrease in pore size as well as surface areas and pore volumes. The pore volume is still considered small because the depth of every pore is not deep enough for reactant molecules to diffuse into the pore. The sample with Ti has lower surface area and smaller pore diameter, however, it has thicker walls.

In addition to XRD and nitrogen adsorption measurements, scanning electron microscopy (SEM) was used to obtain information about the morphology and inherent quality of MCM-41 samples. The investigations revealed the quality of the MCM-41 materials by giving an indication of the percentages of hexagonally ordered mesoporous material, disordered mesoporous material and amorphous material.

DTA-TGA and FT-IR techniques are used to follow the development of the surfactant decomposition-elimination process up. Spectroscopic studies confirmed the presence of framework titanium atoms in these silicates and the absence of bulk TiO_2 particles. The infrared spectrum of the Ti -MCM-41 sample showed an absorption band at approximately 960 cm^{-1} , which is associated to Ti-O-Si bonds and SiOH group. Diffuse Reflectance UV-visible (DRUV-vis) spectra of Ti-MCM-41 samples confirm the incorporation of titanium into the framework. Both DRUV-Vis and FTIR data demonstrate the presence of Ti-oxide species as both isolated

tetrahedral sites and complex particles present on the surface of the Ti-MCM-41 sample.

Further investigations demonstrate catalytic activities of this titanium silicate for olefin epoxidation. Here, the excellent titanium-based epoxidation procedure developed for simple alkene is extended to fatty esters as a route to the useful epoxide products. Ti-MCM-41 when properly prepared is active for selective oxidation of bulky substrates such as methyl oleate that cannot diffuse inside the titanium-silicalite channels.

For epoxidation of both 1-octene and methyl oleate, the most suitable oxidant is *tert*-butyl hydroperoxide (TBHP). From the discussion in chapter 4, it has been proposed that oxo-titanium species (superoxo- and hydroperoxo-titanium) are the reactive sites for olefin epoxidation using TBHP catalyzed by Ti-MCM-41. Theoretically, the epoxidation reaction of olefin to epoxide and the hydrolysis of epoxide to form diol are catalyzed by oxidative and acidic sites, respectively.

In this study, the optimal temperature for epoxidation of 1-octene and methyl oleate are 60 °C and 70 °C respectively. Temperature should not exceed this number to inhibit the formation of by-products (diol and ketone). One of the most important achievements is to realize that the formation of ketone from the epoxide rearrangement reaction is the main route that leads to by-products when reactions involving epoxidized alkene and palm oil are performed. The essential data are collected in Table 6.1.

Table 6.1: Summary of textural properties and catalytic performance of the studied materials.

Si/Ti	25	55	66	80	100
% of Ti	2.85	2.29	1.68	1.24	1.13
Surface Area (m ² /g)	883.32	906.9	905.03	997.26	1075.16
Pore Volume (cm ³ /g)	0.58	0.59	0.65	0.68	0.71
Pore Diameter (nm)	2.85	2.85	2.84	2.86	2.89
Wall thickness (nm)	1.68	1.65	1.62	1.59	1.49
d_{100} (nm)	3.92	3.9	3.86	3.85	3.79
C8 conversion (%)	10.3	12.2	18.1	19.3	10.9
Epoxyoctane selectivity (%)	86.5	90.0	93.5	92.4	90.9
C18 conversion (%)	41.5	43.6	57.3	48.5	33.4
Epoxyoleate selectivity (%)	90.4	91.7	95.2	93.3	88.6

In general, the model catalyst possess moderate activity in the epoxidation reaction, while showing good selectivity to 1,2-epoxyoctane based on the TBHP consumed. Based on the experimental findings presented here, it is found that 66-TiMCM41, which contains 1.68 wt% titanium, exhibits the highest 1-octene and methyl oleate conversion in all five samples. The activities of 25-TiMCM-41 and 55-TiMCM-41 were similar. The activity of Ti-MCM-41 per unit weight of catalyst increases with

titanium contents but does not present a linear relationship. Formation of nanosized TiO₂, however, was inescapable at higher Ti loadings.

Substantially high catalytic activity accompanied by high TBHP selectivity in 1-octene and methyl oleate epoxidation was obtained with 80-TiMCM41 and 66-TiMCM41 prepared, extrapolating the catalytic performances of those low ($1.24 < x < 1.68$ wt%) titanium content of Ti-MCM-41 without sacrificing oxidant efficiency. Selectivity to epoxide increases with increase in Ti loadings before reaching a limiting value of $66 \leq x \leq 80$.

Sample with high concentration of silanol groups located at the external surface of the pores of Ti-MCM-41 as in catalyst 100-TiMCM41 gives a relatively hydrophilic character; hence lower the catalytic activity and turnover. On the other hand, at high Ti content (25-TiMCM41), although the hydrophobicity is improved, catalyst deactivation will occur due to high side products.

It is observed that higher activity of 1-octene is observed earlier, in contrast to the methyl oleate, probably a manifestation of the reactant shape selectivity exhibited by Ti-MCM-41 in retarding the diffusion of bulkier methyl oleate to the active Ti centers located inside the channel system.

Further, slower diffusion of bulkier substrates results in consecutive hydrolysis of epoxides to the corresponding diols due to an increase in residence time and polarity of the former on the active sites.

In the case of smaller allylic substrates (1-octene), such diffusional limitation is expected to be very low and therefore, the desorption of the product (epoxide) from the active Ti-sites will be faster and hence, the cleavage of oxirane ring is very low leading to high epoxide selectivity. The low conversion for both the substrates may also be attributed to diffusional restriction of comparatively bulky molecules.

As expected, at low catalyst concentration, the concentration of Ti-superoxo complex is low and therefore, secondary reactions are facilitated. With the increase in the Ti loading, the concentration of Ti-superoxo complex also increases which facilitates the formation of desired 1,2-epoxyoctane inside the zeolitic pore. However, the formation of side products also increased.

On the effect of temperature, higher temperature, $T=70\text{ }^{\circ}\text{C}$ exhibit higher efficiency of titanium incorporation in the silicate matrix as compared to that at low temperature ($T=50\text{ }^{\circ}\text{C}$) for a given Si/Ti mole ratio.

However, beyond a certain temperature (above $60\text{ }^{\circ}\text{C}$ for epoxidation of 1-octene and $70\text{ }^{\circ}\text{C}$ for methyl oleate) depending upon the composition of the reactant mixture, the concentration of the anatase (TiO_2) phase starts growing, thus lower the catalytic activity of the titanium sites. In other word, a high temperature environment is not preferred for these materials because of dissolution problem with the micelles of Ti-MCM-41.

On the other hand, silylated samples exhibit higher catalytic activity and conversion as well as a threefold activity per Ti atom (TON) compared to non-silylated samples. The increase in activity observed in the silylated hydrophobic catalyst is due to the absence of water in the reaction medium as well as a decrease in catalyst deactivation.

In particular, the water concentration and the hydrophobic-hydrophilic characteristics of the samples are going to be of great importance for the global catalytic phenomena. In this regard, it is to be noted that hydrophobic titania-silica materials are reported to exhibit significant improvements and outstanding catalytic performance in liquid phase oxidation. The trimethylsilylation of Ti-MCM-41 resulted in an increase in their hydrophobicity and thus a remarkable enhancement in their catalytic activity for epoxidation of olefin with TBHP.

This is proven by much higher conversion obtained in silylated samples (more than 50% at 2 hours) compared to commercial catalyst where the conversion is only 10% after 8 hours. A selectivity of >98% for both feedstocks (model compound & methyl oleate) are obtained after only 2 hours compared to commercially available catalysts. In conclusion, hydrophobic Ti-MCM-41 has been demonstrated to be effective catalytic systems to prepare epoxidized fatty esters with high conversions and selectivities to epoxide.

Over the silylated Ti-MCM-41, the yield of epoxide is improved while the selectivity to by-products decreased. As reported above, good selectivities to epoxides were

achieved. Since the catalytic performance of Ti-MCM-41 not only were constant during the three repeated 7 hour-cycles, but rather improved, it is possible to conclude that Ti-MCM-41 is reasonably stable for this sort of reactions.

The high conversion of 1-octene and methyl oleate on Ti-MCM-41 indicates that it is a good catalyst in epoxidation. It can attribute to its hydrophobicity and large pore size. In general, the model catalysts shows good selectivity to 1,2-epoxyoctane based on the TBHP consumed. In other word, epoxide yields are based on the amount of peroxide used. For all the catalysts tested, the selectivity based on 1-octene was 95% and above. It is also proposed that the excellent performance obtained on Ti-MCM-41 is due to the presence of high Ti (IV) tetrahedral active centres, which is monitored by DRUV-Vis spectroscopy.

The work presented here motivates further research into the use of silylation agents under liquid-phase reaction conditions to modify the surface properties of mesoporous molecular sieves.

The calcined material was active and in agreement with the notion that a coordinatively unsaturated, Lewis acidic titanium centre is a pre-requisite for activation of the hydroperoxide. It is proposed that the good catalytic performances obtained on Ti-MCM-41 are due to the presence of a high surface concentration of well spaced and structurally well defined Ti(IV) isolated tetrahedral centres, as shown by DRUV-vis spectra.

In summary, these results suggest that for the epoxidation of oleic acid methyl ester with TBHP catalyzed by Ti-MCM-41, the two more important catalyst properties are titanium dispersion and external surface area, both must be high. After the important conclusion drawn from the epoxidation reactions with Ti-MCM-41 regarding the outstanding role of the external surface area, it was straight forward to reach the idea that a simple amorphous titanium-loaded silica could do also the job, provided the titanium is properly dispersed.