Many homogeneous catalytic systems have been tried in the title reaction. Since heterogeneous catalysis has a lot of advantages of an easier catalyst separation and recycling, various research groups were focused on the development of a heterogeneous catalyst for cyclohexene oxidation with environmentally friendly oxidants. Heterogeneous catalysis has also found to be very effective in enhancing selectivity. Most of the mesoporous materials have been successfully used in the selective oxidation of various aromatics. Supported, site-isolated metal oxide materials are considered as an important class of heterogeneous, selective oxidation catalysts. High-surface-area supports like SBA-15 afford highly dispersed metal oxide species which are the key parameter in the rather difficult oxidation of cycloalkenes. Cyclohexene oxidation has been the subject of extensive studies as the products obtained are important synthetic intermediates for the production of fine chemicals and can also be utilized in polyether polymer synthesis. In the present chapter the oxidation of cyclohexene was applied to examine the properties of prepared catalysts in liquid phase reactions. Optimization of various reaction conditions leads to the formation of products with high selectivity and yields. The use of present heterogeneous catalysis has afforded good to excellent conversions with good selectivity to cyclohexene oxide and cyclohexane-1, 2-diol. The adopted procedure was simple, greener and more efficient to cyclohexene oxidation. The use of a clean oxidant such as H_2O_2 is an important feature of a green chemical reaction since it produces water, the only by-product. The mesoporous structure of transition metals incorporated SBA-15 materials enabled a better accessibility of active sites to bulky substrate molecules which is reflected in the high conversions of cyclohexene and better selectivity to the epoxide or diol over these novel catalysts.
4.1 Introduction

Olefin oxidation is an important transformation in synthetic organic chemistry because the products obtained are valuable and resourceful commercial intermediates, and undergo further reactions [1, 2]. There are a large number of ways available for the olefin oxidation and most of them are utilizing the peroxide moiety which generally involves the addition of other reagents to activate the peroxide compound. Epoxidation of alkenes using peroxycarboxylic acids was established nearly a century ago [3]. Recently metal-catalyzed epoxidation of olefins has been reported. The systems with high valence compounds such as Mo (VI), W (VI), and Re (VII) complexes were used as epoxidation catalysts in the presence of organic peroxides [4-8]. Studies reveal that the large positive charge of the metals make these compounds capable of accepting electron pairs in vacant d orbitals and form stable complexes with organic peroxides. This complex formation results in, the peroxidic oxygen atom to be more electrophilic and, therefore, readily attacked by an olefinic double bond [4]. Various studies have been conducted on oxidation of olefins using metal oxide based catalysts for both reactivity [5, 9-12] and mechanistic studies.

Specifically, the selective oxidation of cyclohexene is widely used as a possible alternative route for the production of adipic acid, which is a key intermediate in the manufacture of Nylon-66 polymer [13]. Various oxometal reagents, including permanganate [14] and ruthenium tetroxide [15], were reported as catalysts for this reaction. By the addition of various oxygen donors, such as NaOCl [16], NaIO₄ [17] and peracetic acid [18] the activity of these catalysts can be increased. Peroxotungstates were found to be effective catalysts for the selective oxidative cleavage of cyclohexene under phase-transfer conditions with lipophilic quaternary ammonium salts [19, 20]. Adipic acid is traditionally prepared through a two-step process involving cyclohexane oxidation with dioxygen to -ol/-one mixture followed by the
catalytic oxidation with HNO₃ [14, 21–22]. But this process results in the formation of nitrous oxide, a greenhouse gas that has to be decomposed. Thus the heterogeneous oxidation of cyclohexene in the presence of hydroperoxides has much more advantages in the field of synthetic chemistry [23]. The development of green practical procedures for the oxidation of six-carbon feedstock is highly desirable—particularly for the medium and large-scale synthesis of various intermediates and fine chemicals [24].

The area of catalytic oxidation of cycloalkenes has been widely investigated but several fundamental problems still remain. A search for a simple procedure to obtain high yield and selectivity, combining favourable economic and environmental concerns among other factors, is still a goal for current research field [25] and the establishment of a more efficient and selective catalyst for these reactions is an active area of research. Many researchers are interested in designing such a catalyst for the oxidation of cycloalkenes and the reaction system involved only the catalyst, substrate, and H₂O₂ [26]. More activated oxygen atoms are required if a direct oxygen transfer mechanism is operative in the oxidation reaction [27]. Aqueous hydrogen peroxide is the most attractive oxidant (after dioxygen) since it is green, quite cheap and easy to handle [14, 22, 28, 29]. Many researchers have reported the cyclohexene epoxidation using H₂O₂ over various micro and mesoporous catalysts [30–35]. Epoxidation catalysts developed and utilizing the H₂O₂ system is constructive for the environment also [27]. The catalytic performance of Ti-MCM-41 catalysts was studied in the oxidation reaction of cyclohexene, but resulting a low catalytic activity and product selectivity [36–40]. In recent years a lot of research was carried out on cyclohexene...
oxidation reaction to test the catalytic activity of transition metal modified mesoporous materials [13, 24, 41-50].

The mesoporous materials have attracted considerable attention in the area of catalysis in recent years. Remarkably large surface area and narrow pore size distributions make them ideal candidates for catalysis [51]. The use of high surface area mesoporous SBA-15 materials as a support for transition metals has some beneficial effects in the area of catalysis. The transition metal incorporated SBA-15 materials would give rise to well dispersed metal nano particles and show an improved catalytic efficiency especially in various oxidation reactions. Selectivity control is also a key issue in various chemical reactions and selective processes are always superior to non-selective ones to purify the target compound for its use in further application by minimizing the difficulties in the separation of the product/s from the reaction mixture. Thus the selectivity in oxidation catalysis has been thoroughly reviewed for conventional catalysts employed in oxidations [52-54].

In the present study we have demonstrated that the different physicochemical techniques indicate that the transition metals were incorporated into the silica framework in all the samples prepared and these framework metal species are the effective active sites for the selective oxidation of cyclohexene with aqueous hydrogen peroxide.

Oxidation of cyclohexene was chosen as a model reaction for the present work. In cyclohexene, oxidation of the carbon–carbon double bond undergo oxidation by aq. H₂O₂ yields cyclohexene oxide (epoxide) which upon further reaction with water produces 1,2-cyclohexanediol (diol). Oxidation of the allylic C–H bond results in 2-cyclohexene-1-ol which is further oxidized to 2-cyclohexene-1-one. Selective epoxidations over transition metals incorporated SBA-15 systems occur via heterolytic cleavage of the O–O bond.
Oxidation of Cyclohexene

by hydroperoxy/superoxo-metal species. Allylic C–H bond oxidations proceed via homolytic O–O bond cleavage. Due to differences in electronic structure, tetrapodal metal in the metallosilicates (M(OSi)$_4$) facilitate heterolytic O–O bond cleavage while the tripodal M sites (M(OH)(OSi)$_3$) facilitate homolytic cleavage of the O–O bond [41].

By an appropriate choice of oxidant and solvent, high conversions and, importantly, selectivity in oxidation reactions of bulky molecules over transition metal incorporated mesoporous SBA-15 catalysts could be obtained. The mesoporous structure of the prepared catalysts enabled a better accessibility of active sites to bulky substrate molecules which is reflected in the high conversions of cyclohexene and selectivity to the epoxide/diol over these novel catalysts. Special attention is drawn to the questions of the catalysts stability under the reaction conditions and their recyclability, both crucial for heterogeneous liquid-phase oxidations.

4.2 Influence of Reaction Parameters

The initial screening of the reaction systems provided very good conversions of the starting material with high selectivities to epoxide/diol. Blank reactions of the mesoporous SBA-15 material provided no cyclohexene conversions. We then decided to investigate the different parameters that could influence the conversion and selectivity in the present cyclohexene oxidation reaction.
4.2.1 Effect of Temperature

Effect of temperature in the oxidation of cyclohexene was initially assayed in a non optimized condition with SBW2 as the catalyst. The reaction was carried out in a range of temperatures from 308-338 K. The results obtained are presented in the Figure 4.1. Oxidation of cyclohexene with the catalyst SBW2 using H\textsubscript{2}O\textsubscript{2} in acetonitrile produced cyclohexane diol as the major product. Cyclohexene epoxide and small quantities of allylic oxidation products are also formed. The percentage distribution of products varied interestingly with reaction temperature. As the temperature rises there is an increase in conversion. The cyclohexene conversion reached a value of 98% at a temperature of 338 K. The selectivity to diol increases from 57 to 75% as the temperature rises from 308 to 338 K and that of epoxide decreases from 35 to 7%. From this it is clear that the oxidation of epoxide to diol occurs at higher temperature. To study the effect of other reaction parameters in the oxidation of cyclohexene we chose the temperature 328 K by considering both the conversion and selectivity.
4.2.2 Effect of Catalyst Amount

The present oxidation reaction of cyclohexene was not observed in the absence of catalyst indicating that H₂O₂ alone is unable to oxidize the substrate cyclohexene. The effect of the quantity of the catalyst in the oxidation of cyclohexene was studied by varying the amount of catalyst and the results are presented in Figure 4.2. A gradual increase in conversion was observed with the increase of catalyst amount. It was observed that the conversion rate reaches 100 % when the catalyst amount is 0.09 g. Further increase of catalyst weight to 0.1 g causes an increase in the percentage of diol, which is due to the oxidation of epoxide initially formed. At all catalyst concentration, diol is the major product. A clear correlation of the catalyst weight with the product distribution cannot be established. At moderate conversions only the epoxide formation observed. An optimum catalyst amount of 0.05 g is selected for further reactions.
4.2.3 Effect of Amount of Solvent

The effect of concentration of the solvent on the oxidation of cyclohexene is shown in Figure 4.3. The reaction conducted with various concentration of acetonitrile shows that the solvent concentration affects the conversion and selectivity in the present liquid phase oxidation reaction. No reaction was observed in the absence of solvent and no detectable conversion was observed up to a solvent amount 10 ml. The same conversion of 73% was obtained with solvent amounts of 10 and 15 ml. Further increase in solvent amount causes a large decrease in conversion. This can be attributed to the fact that excess amount of solvent may cause a reduction in the substrate and catalyst concentration at the interface, which results in a decrease in conversion. The selectivity of diol increases with increase in solvent amount. The solvent amount selected was 10 ml for further studies.

Figure 4.3. Reaction conditions: Temperature-328K, H₂O₂-45 mmol, SBW2-0.05 g, Cyclohexene-40 mmol, Time-6 h
4.2.4 Effect of the concentration of H$_2$O$_2$

The concentration of H$_2$O$_2$ has also a critical effect in the reaction. The effect of the amount of H$_2$O$_2$ on the oxidation of cyclohexene was investigated and the results are presented in Figure 4.4. Low H$_2$O$_2$ concentrations (22.5–45 mmol) gave relatively similar conversion of cyclohexene and selectivity to cyclohexanediol. Higher H$_2$O$_2$ concentrations (67.5 mmol) results in an increase in conversion but the selectivity remains the same. Further increase in concentration of H$_2$O$_2$ did not lead to a considerable increase of activity and selectivity in the reaction. A 67.5 mmol H$_2$O$_2$ concentration is selected as optimum in further oxidation of the cycloalkene. Interestingly, an increase in the H$_2$O$_2$ content in the systems did not significantly vary the activity and selectivity of the catalyst under the reaction conditions.
4.2.5 Effect of Substrate Amount

![Figure 4.5. Reaction conditions: Temperature-328K, SBW2-0.05g, Acetonitrile-10ml, H₂O₂-67.5mmol, Time-6h](image)

The effect of substrate concentration in the oxidation of cyclohexene is shown in Figure 4.5. No significant change in conversion and selectivity to diol was observed at 25 and 40 mmol of cyclohexene. The conversion rate and diol selectivity decrease with increase in cyclohexene volume from 40 mmol to 75 mmol. An increase in substrate to catalyst ratio can cause unavailability of active sites for the reaction, which reduces the activity and selectivity [55]. Further reactions were carried out with a substrate amount 25 mmol.
4.2.6 Effect of Oxidants

The oxidants tested were H₂O₂ (30% in water) and TBHP for cyclohexene oxidation reaction. The results obtained are presented in Figure 4.6. It was observed that the suitable oxidant for the present oxidation reaction is H₂O₂. Hydrogen peroxide is a very attractive green oxidant [56] for various organic compounds, as H₂O is the by product [57, 58]. The development of oxidation catalysts utilizing the H₂O₂ system is constructive for the environment [27]. H₂O₂ efficiency was also affected by the solvent and the catalyst structure [59].

Figure 4.6. Reaction conditions: Temperature-328K, Acetonitrile-10ml, SBW2-0.05g, Cyclohexene-25mmol, Oxidant-67.5mmol, Time-6h
4.2.7 Effect of Solvents

The effect of solvent on catalytic performance is a quite complicated but important area in studies of heterogeneous catalytic systems involving metallo silicate catalysts. Various solvent systems have been investigated; and acetonitrile is the most suitable solvent for the \( \text{H}_2\text{O}_2 \) system. However, with respect to the oxidation of cyclohexene, a converse solvent effect was observed (Figure 4.7); when acetonitrile was used as the solvent, the conversion was nearly fourfold greater than that obtained with isopropanol as solvent. A major influence of solvents on product selectivity was also observed. Isopropanol favoured the formation of epoxide. Epoxide selectivity of only 15-30% was observed in solvents acetonitrile, methanol and acetone. However, reactions in acetonitrile showed 93% cyclohexene conversion and 79% diol selectivity.

Figure 4.7. Reaction conditions: Temperature-328K, Solvent-10ml, \( \text{H}_2\text{O}_2 \)-67.5mmol, Cyclohexene-25mmol, SBW2-0.05g, Time-6h
4.2.8 Effect of Time

![Distribution of Products](image)

Figure 4.8. Reaction conditions: Temperature-328K, SBW2-0.05g, Cyclohexene-25mmol, Acetonitrile-10ml, H₂O₂-67.5mmol.

Figure 4.8 shows the cyclohexene conversion profiles versus the reaction time for the catalyst SBW2. In the cyclohexene oxidation the activity systematically increased with the reaction time and it was accompanied by a significant decrease in epoxide and an increase in diol formation. After 7 h of the reaction, the main product observed was diol. The conversion increased strongly up to 6th hour of the reaction (1-6 h) and then a dramatic slope change was observed. Cyclohexene epoxide was the main product during the initial stages of the reaction. On the other hand, Figure 4.8 shows the amount of H₂O₂ consumed (mmol) as a function of reaction time for the oxidation of cyclohexene.

4.3 Cyclohexene oxidation over prepared systems.

The cyclohexene oxidation reaction was carried out with all the prepared transition metal incorporated SBA-15 materials under the optimized reaction condition shown in Table 4.1.
Table 4.1. Optimized reaction condition for cyclohexene oxidation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>328K</td>
</tr>
<tr>
<td>Solvent Amount (Acetonitrile)</td>
<td>10ml</td>
</tr>
<tr>
<td>Oxidant Amount ($H_2O_2$)</td>
<td>67.5mmol</td>
</tr>
<tr>
<td>Substrate Amount (Cyclohexene)</td>
<td>25mmol</td>
</tr>
<tr>
<td>Catalyst Amount (Cyclohexene)</td>
<td>0.05g</td>
</tr>
<tr>
<td>Time</td>
<td>6h</td>
</tr>
</tbody>
</table>

Table 4.2. Effect of catalysts in cyclohexene oxidation reaction

Reaction conditions: Temperature-328K, Acetonitrile-10ml, Time-6h, Cyclohexene-25mmol, Oxidant-67.5mmol, Catalyst-0.05g

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of Cyclohexene (%)</th>
<th>Distribution of Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cyclohexane Diol</td>
</tr>
<tr>
<td>Nil</td>
<td>Nil</td>
<td>-</td>
</tr>
<tr>
<td>SBA-15</td>
<td>19</td>
<td>35</td>
</tr>
<tr>
<td>SBW1</td>
<td>99</td>
<td>83</td>
</tr>
<tr>
<td>SBW2</td>
<td>93</td>
<td>79</td>
</tr>
<tr>
<td>SBW3</td>
<td>85</td>
<td>58</td>
</tr>
<tr>
<td>SBTi1</td>
<td>86</td>
<td>59</td>
</tr>
<tr>
<td>SBTi2</td>
<td>64</td>
<td>54</td>
</tr>
<tr>
<td>SBTi3</td>
<td>49</td>
<td>29</td>
</tr>
<tr>
<td>SBZr1</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>SBZr2</td>
<td>89</td>
<td>2</td>
</tr>
<tr>
<td>SBZr3</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>SBV1</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>SBV2</td>
<td>78</td>
<td>9</td>
</tr>
<tr>
<td>SBV3</td>
<td>69</td>
<td>3</td>
</tr>
<tr>
<td>SBMo1</td>
<td>94</td>
<td>9</td>
</tr>
<tr>
<td>SBMo2</td>
<td>79</td>
<td>7</td>
</tr>
<tr>
<td>SBMo3</td>
<td>69</td>
<td>4</td>
</tr>
<tr>
<td>SBCo1</td>
<td>80</td>
<td>13</td>
</tr>
<tr>
<td>SBCo2</td>
<td>52</td>
<td>7</td>
</tr>
<tr>
<td>SBCo3</td>
<td>41</td>
<td>3</td>
</tr>
<tr>
<td>SBCr1</td>
<td>89</td>
<td>28</td>
</tr>
<tr>
<td>SBCr2</td>
<td>73</td>
<td>11</td>
</tr>
<tr>
<td>SBCr3</td>
<td>42</td>
<td>8</td>
</tr>
</tbody>
</table>
Oxidation of Cyclohexene

The oxidation of cyclohexene using hydrogen peroxide is frequently used as a test reaction for the catalytic evaluation of different transition metal incorporated SBA-15 materials. The cyclohexene oxide generated by the heterolytic epoxidation of the cyclohexene double bond, and the 1,2-cyclohexanediol side product, formed by hydrolysis of the epoxide ring. The allylic oxidation side products, 2- cyclohexen-1-one and 2-cyclohexen-1-ol are often ascribed to a homolytic radical pathway and are presented here as others. The oxidation products were identified by comparison with authentic samples (retention times in GC). The blank reaction conducted in the absence of catalyst did not result any reaction and the mesostructured silica support has a little activity. The modified catalysts synthesized here showed a very good activity for the oxidation of cyclohexene. Cyclohexene epoxide was the main reaction product in almost the whole range of metal incorporated SBA-15 catalysts studied. The formation of 1, 2- cyclohexane diol was observed from epoxide ring opening in the case of W and Ti incorporated catalysts. The tungsten analogues displayed very high catalytic activity. The conversion of cyclohexene is in direct relation with the concentration of the active metal sites in the materials. For the present catalytic systems, the major product was cyclohexene oxide or diol and the secondary products were mostly 2-cyclohexene-1-ol and possibly 2-cyclohexene-1-one. In all cases, the selectivity for major product was around 90%. A maximum conversion of 99% was obtained for SBW1. For samples synthesized by varying the metal content, decreasing cyclohexene conversions was observed with decrease in metal content. This result indicates a decrease in the density of metal species that are active for the oxidation of cyclohexene. As reported in Table 4.2, the W and Ti based catalysts were more selective towards cyclohexane diol however the other catalysts produced epoxide. A maximum selectivity value of 99 % epoxide was observed using the
SBZr3. The Zr incorporated SBA15 catalysts exhibited an inherently higher selectivity for epoxide. The results show acceptable catalytic activity and selectivity compared to reported literatures [60, 61]. The epoxide formation did not depend only on the metal species in the samples but also on the surface acidity. In the presence of acid centres, epoxide can react further with another molecule of hydrogen peroxide or water to form a diol. Therefore, this factor is also important for considering the catalyst selectivity [62].

4.4 Cyclohexene Conversion and Si/M mole ratio

As expected, the activity decreased with decreasing metal content because of the number of active sites decreased. Figure 4.9 illustrates the role of active metal sites in the oxidation of cyclohexene. From the figure it is clear that the conversion increases with decrease in Si/M mole ratio of each transition metal incorporated SBA-15 systems.

![Figure 4.9 Cyclohexene Conversion and Si/M mole ratio](image-url)
4.5 Effect of Substrates

The oxidation reaction was also carried out for various cyclo alkenes using the catalyst SBW2 under the optimized reaction condition of cyclohexene for comparative studies. The results obtained are presented in Table 4.3.

Table 4.3. Effect of substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Glutaraldehyde (%)</th>
<th>Diol (%)</th>
<th>Epoxide (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentene</td>
<td>96</td>
<td>56</td>
<td>31</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>93</td>
<td></td>
<td></td>
<td>79</td>
<td>10</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td>90</td>
<td></td>
<td></td>
<td>93</td>
<td>7</td>
</tr>
</tbody>
</table>

Oxidation of cyclopentene occurs with a high conversion of 96%. The major products obtained are glutaraldehyde (56%) and diol (31%). Cyclooctene, an even bulkier substrate, was converted (90%) to epoxide with 93% selectivity, over SBW2 under similar conditions using aq. H₂O₂ as the oxidant. All the substrates were converted above 90 % but there is a difference in product distribution observed.
4.6 Leaching Studies

Table 4.4. Temperature-328K, Acetonitrile-10ml, Catalyst-0.05g, Cyclohexene-25mmol, Oxidant-67.5mmol.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Time (h)</th>
<th>Conversion of cyclohexene (%)</th>
<th>Distribution of Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cyclohexane Diol</td>
</tr>
<tr>
<td>SBW2</td>
<td>1</td>
<td>24.00</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>25.20</td>
<td>56</td>
</tr>
<tr>
<td>SBZr2</td>
<td>1</td>
<td>22.64</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>23.27</td>
<td>58</td>
</tr>
<tr>
<td>SBT2</td>
<td>1</td>
<td>11.32</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>11.73</td>
<td>47</td>
</tr>
</tbody>
</table>

A very important factor in processes carried out in liquid phase is the stability of the catalyst, i.e. their resistance to leaching of the active species. The catalyst was filtered out after one hour of the reaction while hot and analysed. The filtrate was kept under the same condition for 6h and then subjected to GC analysis. It was found that the conversion of cyclohexene remain practically constant within experimental error. There was no significant oxidation of cyclohexene after the hot filtration, suggesting that leaching of catalytically active, soluble titanium species was limited under these experimental conditions. Elemental analysis after the test confirm that the metal concentrations in the catalyst vary little; proving that leaching of these atoms is negligible, due to the strong anchoring of metal species in the lattice of SBA-15. The mixture was heterogeneous before and after the reaction and the catalysis nature was also proved to be true heterogeneous.
4.7 Recycling Studies

![Conversion and Distribution of Products](image)

**Figure 4.10.** Reaction conditions: Temperature-328K, SBW2-0.05g, Cyclohexene-25mmol, Acetonitrile-10ml, H₂O₂-67.5mmol.

The stability of the materials was also tested. In the case of materials possessing the highest amount of metal, the oxidation of cyclohexene was also carried out after catalyst regeneration under the same experimental conditions. The results of these experiments are shown in Figure 4.10. Special tests were performed to assess the catalyst stability and activity after recycling. After each operation cycle, the catalyst was separated, washed with H₂O/MeOH, dried, calcined at 540°C for 6h and used in the next run. Moreover, recycling of the material showed that the activity is maintained over four runs, proving there is no leaching of active metal species. The material was therefore found to be highly reusable, preserving up to 95% of its initial catalytic activity after four reuses. It was established that the catalytic activity with respect to diol formation decreased significantly after each run although the conversion of cyclohexene was still attained. The formation of epoxide was faster after regeneration of the catalyst, which was attributed to the modification of the
catalyst surface during the first run of the process. Interestingly, the second run of the reaction gave rise to a higher initial activity.

4.8 Discussions

Cyclohexene oxidation catalysts are of particular interest, due to the potential uses of the products that can be obtained, including cyclohexene oxide, cyclohexane diol and 2-cyclohexene-1-one. From the product distribution it was observed that the oxidation of cyclohexene seems to proceed via two different and competitive reaction pathways. The substrate can be oxidised to the epoxide and ring cleavage takes place to give cyclohexanediol in the case of some prepared catalysts. A competitive reaction gives the 2-cyclohexene-1-ol which then undergoes further oxidation to 2-cyclohexen-1-one. The mesoporous structure of transition metals incorporated SBA-15 materials enabled a better accessibility of active sites to bulky substrate molecules which is reflected in the high conversions of cycloalkenes and better selectivity to the epoxide over these novel catalysts [41, 63].

The proposed mechanism suggests that the oxygen atom (from a metal-bonded peroxo activated entity) is transferred to the olefin through a direct pathway [64]. According to recent theoretical predictions for the epoxidation mechanism of olefins with supported metal oxide catalysts, an electron-poor metal center would increase the electrophilicity of the activated oxygen in the M-OOH hydroperoxy complex, thereby making the catalyst a more efficient oxygen-transfer agent. [65-67]. A more active oxygen transfer reaction would increase the amount of epoxide formed relative to allylic oxidation. The observed increase in selectivity for epoxidation over allylic oxidation is not sufficiently explained, however, by the hydrophilicity/ hydrophobicity of the surface [68]. Additionally, not a lot of research has gone into understanding this observation from a mechanistic standpoint [69].
The nucleophilic attack of the double bond of the alkene on an oxygen atom of hydroperoxy complex leads to the epoxide formation. For higher metal content, the epoxide selectivity decreases steadily due to an opening of side reaction of epoxide ring with water, probably catalyzed by the acid character of the metallosilicates. It should be taken into account that, as it has been observed by the broadening of the main UV–vis band of the catalyst at higher metal contents [70], H$_2$O has a strong tendency to coordinate with the four coordinated metal species. Moreover, the Lewis acid sites of catalyst, being the active species for the epoxidation [70], can also coordinate to water molecules which may react with the formed epoxide via epoxide ring-opening reactions leading to the formation of 1, 2-cyclohexanediol as side product [36].

![Scheme of the epoxidation reaction.]

It is possible to suggest that the metal sites remain active and available even though high contents of the metals are incorporated into SBA-15. The main oxidation product was the cyclohexene oxide for almost of the prepared catalysts, indicating that the direct epoxidation mechanism which takes place through the formation of the metal-hydroperoxo intermediate is being favoured [36]. It was believed that the homogeneous distribution of tetrahedral transition metal entities within the channel walls is vital for the success of this catalytic process. Different metal loadings in the catalyst may induce changes in the surface species and may modify, sometimes noticeably, the catalytic features.
Little research has been done for elucidating the effect of varying the metal content on the catalytic effectiveness of the active sites [36].

The catalysts synthesized here showed a very good activity for the oxidation of cyclohexene, the cyclohexene oxide being the main reaction product in most of the catalysts studied. The formation of 1, 2- cyclohexanediol as by-product arising from epoxide ring opening was also observed for some catalysts. The density of silanol groups on the support greatly influences the retention and coordination number of the grafted metal species. This characteristic of the mesoporous silica supports also has an influence on the catalytic activity of the resulting metallosilicate materials. The metal center is able to activate the oxidant and then to control the oxygen atom transfer from the metal-oxo species to the substrate [71–74].

4.9 Conclusions

- As a catalytic test reaction, the activity, selectivity, and catalyst regenerability were studied in the oxidation of cyclohexene.
- Reaction parameters such as temperature, catalyst weight, time, amount of substrate, \( \text{H}_2\text{O}_2 \) and solvent, effect of various solvents and oxidants were studied in detail and reaction conditions were optimized.
- By an appropriate choice of oxidant and solvent, high conversions and, importantly, selectivity in oxidation reaction of cyclohexene over the prepared transition metals incorporated SBA-15 catalysts could be obtained.
- It was demonstrated that these catalysts do not significantly leach under the reaction conditions.
Highly dispersed tetrahedrally coordinated metal species evidenced by various spectroscopic techniques are highly active and selective for the oxidation reactions.

The catalytic activity of the different grafted metal-SBA-15 materials was mainly influenced by the accessibility of the reactants to the active sites.

References


Chapter-4


Oxidation of Cyclohexene


Oxidation of Cyclohexene


