Chapter 8

Epoxidation of Cyclohexene

Abstract

Epoxides are important intermediates in organic synthesis of fine chemicals and pharmaceuticals. Therefore the synthesis of an epoxide by an easier method and a low cost route is of great interest to researchers working in this field. Titanium containing catalysts showed an increased activity and epoxide selectivity. The Ce$^{3+}$/Ce$^{4+}$ and Cu$^{1+}$/Cu$^{2+}$ redox couple present in TiO$_2$-containing catalysts is known to be responsible for the intrinsic property because it acts as an oxygen buffer by storing and releasing oxygen under controlled conditions. The present chapter illustrates an exhaustive investigation on the liquid phase epoxidation of cyclohexene over the prepared catalytic systems. The influence of various reaction parameters like time, temperature, mole ratio of the reactant:oxidant, amount of the catalyst and nature of the solvent were investigated thoroughly.
8.1.0 Introduction

In recent years, several heterogeneous and homogenous catalysts have been shown to be effective in the selective oxidation of olefins[1-5]. Heterogenization of alkene epoxidation catalysts was done recently to produce an appropriate material, which would allow the obtention of epoxides with high selectivity under industrial conditions[6]. Framework Ti- substituted and Ti- grafted MCM-41 mesoporous materials have been tested as catalysts for cyclohexene oxidation[7]. The mesoporous structure of the catalyst plays an important role in the oxidation of cyclohexene, especially when bulky TBHP was used as the oxidant. The mesoporous materials with different compositions, new pore systems, and novel properties have attracted considerable attention because of their remarkably large surface areas and narrow pore size distributions, which make them ideal candidates for catalysis [8]. Recently, much attention has been directed to the synthesis of nanostructured mesoporous oxides using surfactant templating method. It has been developed for the synthesis of materials with a narrow mesopore size distribution and controlled pore structure [9-11]. It is generally anticipated that the use of a high surface area mesoporous oxide support, rather than a commercial, low surface area support, for noble metals or transition metals has some beneficial effects on the catalytic performance [12]. The mesoporous support would give rise to well dispersed and stable metal particles on the surface upon thermal treatments and as a consequence would also show an improved catalytic efficiency.

Cyclohexene epoxide is of great technical importance as it is applied in the modification of epoxy resin properties and the synthesis of new polymers, copolymers and solvents. Another very interesting
application is the preparation of cyclohexanol and pyrocatechins [13]. Special attention was paid to cyclohexene because cyclohexene epoxide could replace cyclohexenone as an intermediate in the synthesis of adipic acid, the precursor for Nylon- 66[14]. The current production of adipic acid amounts to 2 million tones/year worldwide. It involves cyclohexenone oxidation by nitric acid and those reduction products include N2O. Nitrous oxide is a strong green house gas, 200 times more potent than CO2, and is partly involved in ozone layer damage. Also the epoxide materials are largely used for the synthesis of several perfume materials, epoxy resins, plasticizers, drugs, sweeteners, etc.

Titanium containing carbon-silica composite catalysts showed an increased activity and epoxide selectivity [15]. This may be attributed to the hydrophobic nature of the carbon surface and the local environment of active titanium centers on the silica support. Peng Wu et al studied the liquid phase alkene epoxidation activity over a novel titanosilicate with the MWW topology[16]. Interaction of titanosilicates (TS-1, TiMCM-41 and Pd (n)-TS-1) with H2O2, urea- H2O2, and (H2 + O2) generates reactive Ti(IV)-superoxo and hydroperoxo/peroxo species[17]. The selectivity for epoxidation over these catalysts can be enhanced by controlling the type of Ti-oxo species. The organic modification of titania - silica catalysts by mono and bidendate functional groups enhanced the rate of epoxidation of cyclohexene remarkably[18]. A high and stable activity for ceria/titania catalysts has been established for the water-gas shift reaction. The relationship between metal loading and catalytic activity was studied over a wide temperature range for the epoxidation. It was shown that titania plays the role of an active support capable of producing oxygen. The high and
stable activity of ceria / titania catalysts could arise from the high and stable
dispersion ceria present during the catalytic operation[19, 20].

Many efforts have been made to develop new catalysts to oxidize
cyclohexene under mild conditions with high selectivity for the target
products using different oxidizing agents. A noteworthy development in
this regard was the results by K.U. Ingold et al[21]. The concepts and
informations given by Sheldon et al were of much importance in the field
of catalytic oxidations[22-24]. The activity of these catalysts in liquid phase
oxidation was generally been correlated with the redox properties of the
catalysts. In this work, titania based catalysts like CeO$_2$/TiO$_2$ and
CuO/TiO$_2$ were used. Variable valency of the ions Ce$^{3+}$/Ce$^{4+}$ and Cu$^{1+}$/Cu$^{2+}$
usually lead to the efficient catalytic activity of the reaction. There are a
variety of experimental systems capable of carrying out an oxygen transfer
to an alkene double bond to produce an epoxide. The oxygen vacancies
present in the catalysts will facilitate the adsorption of hydrogen peroxide
to form molecular oxygen for the oxidation reaction [25]. In a number of
them, the oxygen added to the olefin comes from a peroxo group, either in
the form of an organic peroxide or coordinated to a transition metal. The
use of cleaner oxidants than usual hazardous and costly organic peroxides
for epoxidation allows the development of greener reaction. Hydrogen
peroxide (H$_2$O$_2$) and tert-butyl hydroperoxide (TBHP) are more suitable
from environmental point of view of green chemistry because their
reduction products, water or alcohol can be easily recycled [26]. The
profitability of epoxidation with hydroperoxides depends on the possible
utilization of co-products, namely tert-butyl alcohol in the case of TBHP
[27].
The general reaction pathway is represented in scheme 8.1. The nature of the products demonstrates that cyclohexene can suffer either epoxidation yielding epoxy cyclohexane (cyclohexane epoxide) and glycol (cyclohexane diol) or an allylic attack forming cyclohex-2-ene-1-ol (cyclohexenol) and cyclohex-2-ene-1-one (cyclohexenone). All the catalytic systems showed considerable activity towards the reaction with high selectivity towards cyclohexene epoxide.

Scheme 8.1 Reaction Pathway of cyclohexene epoxidation
8.2.0 Mechanism of the Reaction

In the epoxidation of cyclohexene, the oxidant (TBHP) interacts with titanium centers and transfers oxygen to cyclohexene. The cyclohexene epoxidation proceeds via free alkoxy radical chemistry (i.e., O-O bond homolysis of TBHP). Upon the exposure of TiO$_2$ surface with this TBHP, tert-butyl peroxo titanium complex is formed. The peroxo titanium complex formed by the direct reaction between the prepared catalysts of titania and TBHP should have been considered as another candidate for an active species. This suggests that the Ti–OO–t-Bu is a plausible active species.

Scheme 8.2 Proposed pathway for the epoxidation of cyclohexene
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The cyclohexene epoxidation is then proceeded by oxygen transfer from the tert-butyl peroxo titanium complex to the cyclohexene double bond. The consumed complex is finally regenerated by tert-butyl hydroperoxide. The enhanced cyclohexene conversion in the case of metal modified titania systems may be attributed to the assistance of the added metal oxide to form the corresponding tetra-tert-butyl peroxo titanium complex. The additional possibility of the added metal to form the corresponding tetra-tert-butyl peroxo complex due to the ability of the metal to form a variety of high valent oxocomplex cannot be ignored. A schematic representation of the reaction mechanism is also given:

![Scheme 8.3 Schematic representation of the reaction mechanism](image)

8.3.0 Procedure of the Reaction

The epoxidation of cyclohexene with tert-butyl hydroperoxide was carried out in a 50 ml round bottomed flask having a side tube equipped with a reflux condenser and a thermometer. The reactor and oil bath were continuously stirred to ensure that the system was well mixed and isothermal. In a standard procedure 0.1g of the catalyst, TiO$_2$.Ce 6 and
reactant cyclohexene and oxidant TBHP, in the mole ratio 1:2 were added into 10ml of the solvent, acetonitrile. The mixture was heated to 313K under stirring. All the reagents were used as such without further purification. The samples were withdrawn at different reaction time and the products were separated by filtration. Then the products were analyzed by gas chromatography using a capillary column (Chemitto GC 1000, FID, SE 30 column-12m length, 0.25mm Dia,N2 carrier gas). Product identification was done by comparing the retention times with standards. Two other systems were also performed keeping the temperature at 323K and 333K respectively.

When the reaction is conducted in the absence of a catalyst (blank run) and in the presence of the catalyst (0.1g TiO2.Ce6), it is observed that in the blank run, even after 3h, the percentage conversion is only 2wt % and the number of detectable side products remained very low. When conducted in presence of 0.1g of CeO2/TiO2 catalyst under the same reaction conditions, the yield is 89 wt % with prominent selectivity for all the products formed. From this it can be concluded that in presence of the catalyst, the reaction proceeded through a different path with lower activation energy. Hence the percentage conversion is higher in the catalyzed reaction.

8.4.0 Influence of reaction conditions

The reaction is conducted by varying the reaction parameters like the time of the reaction, temperature, mole ratio of reactant and oxidant, amount of the catalyst, different solvents and compared the activity of these systems under the same reaction condition to get an favourable optimized state. This is discussed below.
8.4.1 Effect of Time

The epoxidation of cyclohexene, was carried out continuously for 6h at 323K using TBHP as the oxidant in presence of acetonitrile as solvent over the prepared catalyst systems in order to study the effect of time on the reaction. Figures 8.1,8.2 and 8.3 show the time courses for the epoxidation of cyclohexene over TiO₂, TiO₂-Ce₆, and TiO₂-Cu₆ respectively. It is observed that a common trend is followed in the activity as well as in the epoxide selectivity. During the initial stages of the reaction the percentage conversion increased and approached an almost steady value within 3h. But the selectivity towards the corresponding epoxide increased till to 3h of the reaction and thereafter it drops suddenly. This may be due to the possible side reactions. These reactions afford mostly allylic oxidation products and oligomers, and thus limit the epoxidation selectivity.

Reaction Conditions

<table>
<thead>
<tr>
<th>Catalyst chosen</th>
<th>-0.1g TiO₂, TiO₂-Ce₆, TiO₂-Cu₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene : TBHP</td>
<td>1:2</td>
</tr>
<tr>
<td>Solvent</td>
<td>-10ml Acetonitrile</td>
</tr>
<tr>
<td>Temperature</td>
<td>-323K</td>
</tr>
</tbody>
</table>
Fig 8.1 Effect of time on the reaction by TiO$_2$

Fig 8.2 Effect of time on the reaction by TiO$_2$-Ce6
8.4.2 Effect of Temperature

The epoxidation of cyclohexene depends greatly on the reaction temperature. The reaction was carried out with the oxidant TBHP at different reaction temperatures as 313, 323 and 333K respectively and the results were given in figure 8.4. Interestingly, the product distribution varied depending on reaction temperature. The percentage conversion was 60% when conducted at a temperature of 333K. The cyclohexene conversion reached about 89% when the temperature reaches 323K with a epoxide selectivity of 76%. But as the temperature is increased, the amount of allylic oxidation products increases leading to a lower selectivity of epoxide. The percentage cyclohexene conversion decreases with temperature beyond 323K. From the results it can be concluded that the epoxidation of cyclohexene proceeds with high activity and selectivity under gentle reaction temperature. The high conversion is not accompanied
by the highest selectivity of transformation to epoxide with regard to TBHP consumed. This is due to the decomposition of TBHP to alcohol and oxygen at higher temperature. \((H_3C)_3C-OOH \rightarrow (H_3C)_3C-OH + 0.5 O_2\)

**Reaction Conditions**

- Catalyst chosen: 0.1 g TiO2-Ce6
- Cyclohexene : TBHP - 1:2
- Solvent: 10 ml Acetonitrile
- Duration: 3 hrs

![Graph showing the effect of temperature on the reaction by TiO2-Ce6](image)

**Fig8.4 Effect of temperature on the reaction by TiO2-Ce6**

**8.4.3 Effect of Mole Ratio of Reactant:Oxidant**

The epoxidation reaction was carried out using oxidants like hydrogen peroxide and tert-butyl hydroperoxide. A blank run was made by conducting the reaction without the addition of an oxidant and that yields negligible conversion with a poor selectivity of cyclohexene epoxide. At 262
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333K, the corresponding epoxides are obtained with 50% selectivity though the percentage cyclohexene conversion is only 40 wt.%. Here the colour of the catalyst changed to brown. This can be due to the possible formation of hydroperoxy complexes with titanium. When the epoxidation is carried out with TBHP as oxidant, the conversion was very much higher with a percentage epoxide selectivity of 76%. Despite its outstanding interest in green chemistry, hydrogen peroxide gives poorer results and so TBHP is preferred in the epoxidation of cyclohexene. Here only the TBHP graph is shown. To investigate the effect of concentration of TBHP on the rate of cyclohexene epoxidation, a series of reactions were performed with varying concentration of the reactant: the oxidant TBHP from 1:1 to 1:3. From the figure 8.5, it is evident that an optimum mole ratio of cyclohexene : TBHP is needed for maximum activity as well as selectivity of the products. As the concentration increases, the rate of epoxidation of cyclohexene increases with a good selectivity of cyclohexene epoxide. The rate reaches a maximum value for 1:2 mole ratio and thereafter goes on decreasing. From the observation of XPS values it can be noticed that hydroxylation degree of systems prepared in the presence of TBHP appears slightly higher. This could indicate that the presence of metal could enhance the acidic properties of the surface and hence the strength of hydroxyl groups at the surface [28].

**Reaction Conditions**

- Catalyst chosen: 0.1g TiO₂·Ce₆
- Solvent: 10ml Acetonitrile
- Temperature: 323K
- Duration: 3hrs
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8.4.4 Effect of catalyst amount

In heterogeneous catalysis, the amount of the catalyst plays an important role in determining the rate of the reaction. To study this, the catalyst weight is varied by taking different amounts of CeO$_2$/TiO$_2$ catalyst under otherwise identical reaction conditions. Figure 8.6 shows the influence of amount of catalyst weight on the catalytic activity and selectivity. In the absence of a catalyst, the conversion is negligible. Addition of 0.05g catalyst changes the percentage conversion from 65 to 78 in the epoxidation of cyclohexene. An initial sharp rise in the percentage conversion is observed when the catalyst amount is increased to 0.1g. After that the percentage conversion remains almost the same even though the catalyst amount is changed to 0.15g. But the percentage conversion decreases with further increase in catalyst weight. The effect of catalyst weight is more substantial when considering the epoxidation activity, but
no clear correlation of catalyst weight with the percentage conversion can be established. A gradual change in the epoxide selectivity is also noticed with the change in catalyst weight. An optimum catalyst weight of 0.1g is chosen for the present reaction, considering the percentage conversion as well as epoxide selectivity.

**Reaction Conditions**

- **Catalyst chosen**: TiO$_2$-Ce 6
- **Cyclohexene : TBHP**: 1:2
- **Solvent**: 10ml Acetonitrile
- **Duration**: 3hrs
- **Temperature**: 323K

![Graph showing effect of catalyst amount on reaction conversion and selectivity](image)

Fig8.6 Effect of catalyst amount on the reaction by TiO$_2$-Ce6
8.4.5 Effect of Solvent

Catalytic activity depends largely on the nature of solvent used. So it is necessary to find out an ideal solvent for the epoxidation of cyclohexene using TBHP as the oxidant. K.U.Ingold et al reported in his work that the solvent suitable for olefin epoxidation is one, which is not a hydrogen bond donor (HBD) and is also only a relatively poor hydrogen bond acceptor (HBA)\cite{29}. If the solvent is a strong HBA, it would be expected to deactivate the catalyst (via any surface hydroxyl groups) and also deactivate the hydroperoxide (via ROOH...HBA hydrogen bonding).

When water is used as a solvent for epoxidation, the catalyst systems showed the least activity as well as selectivity of the epoxide. Another change noticed was the formation of a product like cyclohexene-3-(t-butyl) peroxide in appreciable amount other than this epoxide, cyclohexane diol, cyclohexenol and cyclohexenone. It has been reported that when water was added to the reaction mixture, significant amounts of cyclohexene-3- (t-butyl) peroxide was produced \cite{30}. A nice balance between these various solvent requirements is achieved for TiCe6 catalyst by using acetonitrile, which may well be the optimum solvent for these epoxidation reactions.

**Reaction Conditions**

- Catalyst chosen: 0.1gTiO₂.Ce 6
- Cyclohexene : TBHP - 1:2
- Solvent volume: - 10ml
- Duration: - 3hrs
- Temperature: - 323K

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### Table 8.1 Effect of solvent on the reaction by TiO$_2$-Ce6

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (wt %)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Epoxide</td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>89</td>
<td>76</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>

8.5.0 Catalytic activity of different systems in the reaction

**Optimized Reaction Conditions**
- Catalyst amount: 0.1 g
- Cyclohexene: TBHP - 1:2
- Solvent: 10 ml Acetonitrile
- Temperature: 323 K
- Duration: 3 hrs

### Table 8.2 Effect of the catalysts in the reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt %)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Epoxide</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>65</td>
<td>81</td>
</tr>
<tr>
<td>TiO$_2$ -Ce 3</td>
<td>82</td>
<td>65</td>
</tr>
<tr>
<td>TiO$_2$ -Ce 6</td>
<td>89</td>
<td>76</td>
</tr>
<tr>
<td>TiO$_2$ -Ce 9</td>
<td>85</td>
<td>80</td>
</tr>
<tr>
<td>TiO$_2$ -Cu 3</td>
<td>79</td>
<td>52</td>
</tr>
<tr>
<td>TiO$_2$ -Cu 6</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>TiO$_2$ -Cu 9</td>
<td>78</td>
<td>75</td>
</tr>
</tbody>
</table>
A comparative account of the catalytic activity of various metal modified titania systems in the epoxidation of cyclohexene is given in the Table 8.2. All the prepared systems were tested for activity over a reaction time of 6h under the optimized reaction conditions, temperature of 323K using 10 ml acetonitrile solvent and the reactant: oxidant mole ratio as cyclohexene : TBHP is 1:2. The results of epoxidation of cyclohexene over metal modified titania systems were presented in the table 8.2. Titania catalysts like 3,6 and 9 wt % metal incorporated systems were subjected to the study of this particular reaction. The different catalytic systems were represented- for 3wt% of the metal loaded catalyst of ceria and copper as TiO2-Ce 3, TiO2-Cu 3, for 6wt% of the metal loaded catalyst of ceria and copper as TiO2-Ce 6, TiO2-Cu 6 and TiO2-Ce 9 TiO2-Cu 9 for 9 wt% of the metal loaded catalyst of ceria and copper. Pure titania exhibited poor activity towards the epoxidation of cyclohexene. The interesting point to be noted is that in spite of its poor activity, pure titania shows a very good selectivity towards cyclohexene epoxide. Whatever be the nature of the metal incorporated, all the catalytic systems give cyclohexene epoxide as the major product. Higher conversion of cyclohexene is observed in the case of TiO2-Ce 6 and TiO2-Cu 6 catalysts. Remarkable conversion was shown by TiO2-Ce 6 catalyst among all the other systems. But the selectivity to cyclohexene epoxide is higher in the case of 9wt% incorporated metals of Ceria and Copper modified titania catalytic systems. An attempt to investigate the influence of the metal loading on catalytic activity is quite reasonable. As expected, variation in metal loading had a significant impact on the catalytic cativity. As the percentage of metal loading is increased from 3 to 6wt.%, the conversion is also increased and thereafter it decreases but the selectivity increased gradually. Reports 268
provide access to highly dispersed Lewis acidic sites, which can effectively activate the alkyl hydroperoxide oxidant[31-32]. It is concluded that Lewis acidic sites are electron acceptors and $\text{Ce}^{4+}$ state accepts electron and gets changed to $\text{Ce}^{3+}$ state. The good epoxidation activity and selectivity of modified titania systems is attributed to the presence of highly dispersed Lewis acidic titanium sites which is evident from the NH$_3$-TPD graph.

8.6.0 Reusability of the catalysts

Regeneration and stability studies of the catalysts were tested for various cycles by introducing the same catalyst in the reaction mixture and observed that the recovered catalysts are less effective as expected in comparison to fresh ones. Though pure titania exhibited poor activity towards the epoxidation of cyclohexene it can be recycled. But owing to leaching of cerium ions under the same reaction conditions the activity of the TiO$_2$-Ce 6 catalyst systems seems to diminish. This is generally observed with all liquid-phase reactions more predominantly with peroxide catalyzed reaction in acetonitrile solvent [33]. Generally, use of 30% peroxide and acetonitrile as solvent results considerable leaching[34]. But it has been found that even after four regeneration cycles the activity, i.e. both conversion as well as selectivity of TiO$_2$-Cu6 catalyst remains same as in the initial cycle, showing the efficiency of the catalysts.
References