CHAPTER 4

DEVELOPMENT OF NOVEL SOLID ACID CATALYST MUICAT-5 FOR GAS PHASE DEHYDRATION OF GLYCEROL
4.1 INTRODUCTION

Comprehensive literature survey on glycerol conversion and use of heteropolyacid as catalysts was presented in Chapter 3. In reported literature so far on dehydration of glycerol to acrolein the problem was catalyst deactivation due to formation of coke during reaction, and also reusability of catalyst was not discussed. Thus, there is a tremendous scope to develop new robust and reusable catalysts for production of acrolein from glycerol.

The current investigation deals with a novel solid acid catalyst MUICaT-5 for dehydration of glycerol to acrolein in gas phase (Yadav et al. 2012; Yadav et al. 2013). Scheme 4.1 shows glycerol dehydration processes leading to acrolein along with associated products due to consecutive and parallel reactions.

![Scheme 4.1: Dehydration of glycerol to acrolein](image-url)
4.2. EXPERIMENTAL

4.2.1 Chemicals

The following chemicals were procured from firms of repute and used without further purification: Glycerol (LR), aluminium nitrate, tungstic acid, ethanol (s.d. Fine Chem., Mumbai, India), zirconium oxychloride (LR), tetraethyl orthosilicate (TEOS) (Fluka, Germany), dodecyl amine (Spectrochem Ltd., Mumbai, India).

4.2.2 Catalyst preparation

HMS: The ordered hexagonal mesoporous silica (HMS) was prepared using the following procedure. 5 g Dodecyl amine was dissolved in 41.8 g of ethanol and 29.6 g of distilled water. 20.8 g of tetraethyl orthosilicate was added under vigorous stirring. The addition of ethanol improved the solubility of the template. The reaction mixture was aged for 18 h at 30°C. The clear liquid above the white colored precipitate was decanted and the precipitate HMS was dried on a glass plate. The template was removed by calcining the resulting material at 650°C in air for 3 h.

MUICaT-5: 2.39 g of zirconium oxychloride and 0.11 g of aluminum nitrate were dissolved in aqueous solution and added to 5 g of precalcined HMS by incipient wetness technique. After addition, the solid was dried in an oven at 110°C for 3 h. The dried material was hydrolyzed by ammonia gas and washed with deionized water until a neutral filtrate was obtained and the absence of chlorine ion in the filtrate was detected by phenolphthalein and silver nitrate tests. A material balance on chlorine before and after precipitation and washing showed no retention on the solid. It was then dried in oven for 24 h at 110°C. The generation of super acidic centers into this material was made possible by grinding tungstic acid (0.1078 g) with 0.9 g of zirconium hydroxide and aluminum hydroxide on HMS followed by hydrothermal treatment and then it was calcined at 750°C for 3 h.

4.2.3 Selection of Lewis acid based catalyst supported on HMS

In our laboratory, we have been working in the preparation on supported solid acid catalyst. In chapter 3 study it was reported that hexagonal mesoporous silica (HMS)
acts as better support for acrolein selectivity. In this chapter, investigation of a new MUICaT-5 catalyst based on HMS as support is presented. It was used as moderate Lewis acid catalyst for the dehydration of glycerol to acrolein in vapor phase under milder conditions in comparison with other reported catalysts. The moderate acid strength was confirmed by NH$_3$-TPD profile. MUICaT-5 catalyst has W-Zr-Al/HMS catalyst composition and the elemental composition is discussed in this chapter. It was reported that zirconium and tungsten based catalyst has more Lewis acid character (Mohamed et al. 2001; Kim et al. 2012; Massa et al. 2013). The exact catalytic reaction mechanism of MUICaT-5 to convert glycerol to acrolein is not known; however some reports mentioned that tungsten oxide is converted into tungsten hydroxide at elevated temperature in presence of steam, which could provide Bronsted acidity (Massa et al. 2013). Typical reaction conditions were: 1.0 g of catalyst loading, 275 °C of reactor bed temperature, 275 °C of preheater temperature, 20% (w/w) of glycerol solution, 10.2 ml/h of feed flow rate (glycerol solution), 1.5 L/h of N$_2$ flow rate, 4 h, and 10.74 h$^{-1}$ of WHSV. The various solid acid catalysts such as UDCaT-1, UDCaT-4, UDCaT-6, and MUICaT-5 were screened for glycerol dehydration reaction. The catalyst compositions, percentage conversion of glycerol and acrolein selectivity are mentioned in Table 4.1. It was observed that MUICaT-5 catalyst showed the highest glycerol conversion and highest acrolein selectivity as compared to other studied HMS based catalysts. It can be due to the presence of moderate acid site on MUICaT-5 catalyst which was confirmed by NH$_3$-TPD profile. Hence, further studies have been carried out by using MUICaT-5 catalyst. This enhanced activity of MUCaT-5 catalyst was further co-related to NH$_3$-TPD profile, BET surface area, pore volume, and EDX elemental analysis for better understanding.
Table 4.1 Lewis acid based catalyst screening (catalyst composition, percentage conversion of glycerol, and acrolein selectivity)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst composition</th>
<th>% Conv. Glycerol</th>
<th>% Selectivity Acrolein</th>
<th>% Selectivity Hydroxyacetone</th>
<th>% Selectivity Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>UDCaT-1</td>
<td>Sulfuric acid treated - Zr/HMS</td>
<td>60</td>
<td>28</td>
<td>15</td>
<td>57</td>
</tr>
<tr>
<td>UDCaT-4</td>
<td>Persulfated Zr-Al/HMS</td>
<td>68</td>
<td>38</td>
<td>16</td>
<td>46</td>
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<tr>
<td>UDCaT-6</td>
<td>Chlorosulfonic acid treated - Zr/HMS</td>
<td>71</td>
<td>29</td>
<td>14</td>
<td>57</td>
</tr>
<tr>
<td>MUICaT-5</td>
<td>W-Zr-Al/HMS</td>
<td>86</td>
<td>60</td>
<td>10</td>
<td>30</td>
</tr>
</tbody>
</table>

*acetaldehyde, propionaldehyde, acetone, allyl alcohol

Reaction conditions: 20% (w/w) glycerol solution, 1.0 g of catalyst weight, 275 °C, 1.5 L/h of N₂ flow rate, 10.2 ml/h of feed flow rate 10.74 h⁻¹ WHSV, 10 h.

4.2.4 Catalyst Characterization

Acidic sites of the MUICaT-5 catalyst were determined with temperature programmed desorption (TPD) by using Autochem II 2910 (Micromeritics, USA) with ammonia as probe molecules. The specific surface area, pore volume and pore diameter of catalyst were obtained from nitrogen adsorption-desorption isotherms measured in ASAP 2010 (Micromeritics, USA) automated instrument and specific surface area of prepared catalyst was calculated by using BET model. Images of the surface morphology of the catalyst samples were captured with scanning electron microscope (SEM) (Camera...
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SU 30 microscope, JEOL, Japan). The chemical composition of the catalyst (average of three data points at different locations of the solid) was determined by energy dispersive X-ray spectroscopy (EDXS) (KEVEX X-ray spectrometer JED-2300, JEOL, Japan). Fourier transform infrared (FTIR) spectra of catalyst in the range of 400 to 4000 cm$^{-1}$ were collected on a Perkin Elmer Spectrophotometer using a sample disk of 5% catalyst weight in KBr powder.

4.2.5. Experimental set up and analytical method

Gas-phase dehydration of glycerol to produce acrolein was investigated at 250 to 325°C, on fixed bed catalytic reactor with solid acid catalysts. The vapor phase fixed bed reactor consisting of a down flow fixed bed haste alloy HC-276 reactor having 25.4mm ID and 300mm length, equipped with an upstream vaporizer and downstream condenser. The liquid feed was passed by a double piston (Well Chrom HPLC-pump K-120) pump to the vaporizer by using N$_2$ as a carrier gas. A known amount of catalyst was sandwiched in the middle of the reactor with quartz wool and remaining volume of the reactor was filled by glass beads. Before starting the reaction the catalyst was pretreated at reaction temperature for 2 h in presence of flowing nitrogen (30 ml min$^{-1}$). The reaction feed of an aqueous solution of glycerol in distilled water was passed continuously in to the preheater to vaporize the glycerol/water mixture and then in to the reactor from top position by using HPLC-pump. The catalytic performance of the solid acid catalyst was evaluated at a weight hourly space velocity (WHSV) by glycerol feed.

The analysis of reaction products was carried out using GC (Chemito 1000) equipped with a BPX-50 capillary column (length: 30m, ID: 0.25mm) and with FID detector. Before analysis, reaction products were condensed in an ice-water trap on hourly basis and then analyzed. Further confirmation of products was done by GC-MS using same capillary column.
4.3. RESULTS AND DISCUSSION

4.3.1 Catalyst characterization

4.3.1.1 NH$_3$-TPD

Acidic sites of the catalyst were determined with temperature programmed desorption (TPD) analysis by using Autochem II 2910 (Micromeritics, USA) with ammonia as probe molecules. A quantity of 30 mg of the catalyst was taken in a quartz tube and degassed up to 600°C in the presence of nitrogen flow. Then ammonia was passed for 30 min to adsorb the ammonia over the surface of the catalysts at room temperature. Physisorbed gas was removed by passing inert nitrogen at room temperature. Chemisorbed ammonia was desorbed by using temperature programmed desorption and detected by TCD.

Figures 4.1 and 4.2 show NH$_3$-TPD data of fresh and regenerated MUICaT-5 catalyst. NH$_3$-TPD data confirmed that the acidity of the used catalyst was regained after calcinations and that provides evidence for reusability shown by MUICaT-5 catalyst.

![Figure 4.1 NH$_3$-TPD of fresh MUICaT-5 catalyst](image)

Figure 4.1 NH$_3$-TPD of fresh MUICaT-5 catalyst
4.3.1.2 BET Surface area analysis

The surface area and pore size distribution study of fresh, used and regenerated catalyst were measured by the Brunauer–Emmett–Teller (BET) method using ASAP 2010 (Micromeritics, USA) instrument. The catalyst samples were degassed under vacuum at 300°C for 3 h. The measurements were made using N₂ gas as the adsorbent and with a multipoint method. Isotherms were measured at liquid nitrogen temperature. Surface area and pore volume were calculated from N₂-adsorption–desorption isotherms using conventional BET method. Data were represented in Table 4.2. Figures 4.3, 4.4 and 4.5 show the N₂ adsorption and desorption results of fresh, used and regenerated catalyst. The surface area and the pore volume of the fresh and regenerated catalyst were found to be nearly same. Hence it was concluded that coke was completely removed from the catalyst after calcinations.
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Figure 4.3 BET of Fresh MUICaT-5 catalyst

Figure 4.4 BET of Used MUICaT-5 catalysts

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Figure 4.5 BET of Regenerated MUICaT-5 catalyst

Table 4.2: Nitrogen adsorption-desorption data of fresh, used and Regenerated MUICaT-5 catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Pore Volume (cm²/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh MUICaT-5</td>
<td>143.93</td>
<td>0.144</td>
<td>4.013</td>
</tr>
<tr>
<td>Used MUICaT-5</td>
<td>25.19</td>
<td>0.055</td>
<td>8.572</td>
</tr>
<tr>
<td>Regenerated MUICaT-5</td>
<td>138.01</td>
<td>0.140</td>
<td>4.029</td>
</tr>
</tbody>
</table>

4.3.1.3 SEM and EDXS analysis

Surface morphology of the catalyst samples was determined with Scanning Electron Microscope (SEM) (JEOL 6380LA instrument, Japan). The dried samples were coated with thin film of platinum and then mounted on specimen chamber for further analysis. The platinum coated surface was then scanned at various magnifications by
using SEM. The chemical composition of the catalysts (average of three data points at different locations of the solid) was determined by Energy Dispersive X-ray spectroscopy (EDXS) using same instrument. Figures 4.6, 4.7, and 4.8 represent the external morphology of the fresh, used and regenerated MUICaT-5 catalyst. The elemental analysis of fresh, used and regenerated catalyst was represented in the Table 4.3.

Figure 4.6 SEM image of fresh MUICaT-5 catalyst
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Figure 4.7 SEM image of used MUICaT-5 catalyst

Figure 4.8 SEM image of regenerated MUICaT-5 catalyst

Table 4.3 Elemental analysis by EDXS
<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass (%) of fresh MUICaT-5</th>
<th>Mass (%) of used MUICaT-5</th>
<th>Mass (%) of regenerated MUICaT-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-----</td>
<td>4.19</td>
<td>------</td>
</tr>
<tr>
<td>O</td>
<td>45.26</td>
<td>44.51</td>
<td>45.26</td>
</tr>
<tr>
<td>Al</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Si</td>
<td>34.12</td>
<td>33.70</td>
<td>34.12</td>
</tr>
<tr>
<td>Zr</td>
<td>9.79</td>
<td>9.20</td>
<td>9.79</td>
</tr>
<tr>
<td>W</td>
<td>10.63</td>
<td>8.20</td>
<td>10.63</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

4.3.1.4 FT-IR studies

Fourier transforms infrared (FTIR) spectra of catalyst samples were collected on a Perkin Elmer Spectrophotometer (Figure 4.9). Catalyst samples were shaped into disks by mixing 5% catalyst weight in KBr powder, and form a Pilate by applying 10 ton pressure, catalyst samples were scanning in the range of 400 to 4000 cm\(^{-1}\). The IR spectra for hexagonal mesoporous silica (HMS) and MUICaT-5 catalyst shows the characteristics peaks at different wave numbers and giving the information at 3451 cm\(^{-1}\) = H-bonding stretching vibrations of OH group, 1637 cm\(^{-1}\) = characteristic bands of H\(_2\)O molecules due to – OH bending frequency, and 1088,804,462 cm\(^{-1}\) = evidence of silica presence in the materials. It can conclude that catalyst compositions were uniformly supported on the support hexagonal mesoporous silica (HMS).
4.3.2 Effect of Temperature

The glycerol dehydration reaction was carried out at four different temperatures of 250, 275, 300 and 325 °C under otherwise similar reaction conditions. Figure 4.10 (A), (B) shows that with increasing the temperature from 250 to 325 °C, the conversion of glycerol also increases, but selectivity of acrolein decreases and formation of byproducts increases. However, at 275 °C, MUICaT-5 catalyst gave 86% glycerol conversion and high acrolein selectivity of 60% vis-vis other temperatures and hence 275 °C was chosen for further study.
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![Graph showing glycerol conversion (%)](image)

- **A**

Glycerol conversion (%)

TOS (h)

- 250 C
- 275 C
- 300 C
- 325 C

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Figure 4.10 Effect of temperature (A) glycerol conversion and (B) acrolein selectivity.

Reaction conditions: 20% (w/w) glycerol solution, 1.0 g catalyst, 1.5 lit/h, N₂ flow rate, 10.2 ml/h feed flow rate, 10.74 h⁻¹ WHSV, 4 h reaction time.

4.3.3 Effect of glycerol concentration

Glycerol is a co-product of biodiesel process and is obtained in different concentration depending on the workup procedure used. Hence, different concentrations of glycerol such as 10%, 20% and 50% (w/w) were used to evaluate the activity of the catalyst. It was observed that 10% and 20% (w/w) of glycerol solution gave almost similar results. However, 50% (w/w) of glycerol solution resulted into a decrease in glycerol conversion as well as acrolein selectivity. This is a complex reaction network.
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strongly dependent on reaction temperature and concentration (partial pressure). As the concentration of glycerol increases on sites, it leads to cracking and coking. Some pore channels become inaccessible due to deposition of carbeneous (viscous) material. Even if a few junctions are blocked, the number networks become less reducing the number of active sites. Hence there is decrease in selectivity and conversion. Hence, 20% w/w of glycerol solution was used for further optimization (Figure 4.11).

![Figure 4.11 Effect of glycerol concentration](image)

**Figure 4.11 Effect of glycerol concentration**

Reaction conditions: 10-50% (w/w) glycerol solution, 1.0 g catalyst weight, 275°C bed temperature, 1.5 lit/h N₂ flow rate, 10.2 ml/h feed flow rate, 4 h reaction time.
4.3.4 Effect of feed flow rate

Three different feed flow rates 5.1, 10.2, and 20.4 ml/h were selected to establish the catalyst activity. WHSV of the four different reactions were 5.37, 10.74, and 21.48 h\(^{-1}\), respectively. It was observed that with increasing the feed flow rate from 10.2 to 20.4 ml/h conversion and selectivity both decreased. The decrease in catalyst activity is due to increase in WHSV values; and hence the residence time of glycerol is decreased. Also, as the catalyst to substrate weight ratio decreases with the increase in feed flow rate, less number of catalyst active sites is available to convert glycerol to acrolein. Therefore, 10.2 ml/h of glycerol flow rate was chosen for further studies (Figure 4.12).

![Figure 4.12 Effect of feed flow rate](image)

**Figure 4.12 Effect of feed flow rate**

Reaction conditions: 20% (w/w) glycerol solution, 1.0 g catalyst weight, 275°C temperature, 1.5 L/h N\(_2\) flow rate, 5.1-20.4 ml/h feed flow rate, 4 h reaction time.
4.3.5 Effect of nitrogen flow rate

Effect of N\textsubscript{2} flow rate was studied at 0.72, 1.5, and 3.0 L/h. With increasing N\textsubscript{2} flow rate from 0.72 to 3.0 L/h, the selectivity of acrolein decreased. This could be because at higher N\textsubscript{2} flow rate, the partial pressure of glycerol decreases and the residence time decreases which affects selectivity of acrolein, but it does not affect on conversion of glycerol, in all cases conversion was nearly same. This would suggest zero order dependence on glycerol partial pressure but acrolein selectivity is dependent on partial pressure. The escaped gases were collected by bubbling it through 250 ml distilled water and confirm presence of acrolein by injecting in GC. The total carbon balance was obtained in the range of 89-93% for all liquid products by GC analysis. The remaining was gaseous phase and carbon deposited on the catalyst pores (Figure 4.13).

![Figure 4.13 Effect of nitrogen flow rate](image)

Reaction conditions: 20\% (w/w) glycerol solution, 1.0 g catalyst weight, 275 °C temperature, 10.2 ml/h feed flow rate, 4 h.
4.3.6 Effect of catalyst loading

It was predictable that with increase in catalyst loading, the life of catalyst can also be increased due to proportional increase in catalyst active sites. Hence, the effect of catalyst loading with the conversion of glycerol was evaluated by loading the reactor with 0.5, 1.0, and 2.0 g of MUICaT-5 catalyst with WHSV value 5.37, 10.74 and 21.48 h\(^{-1}\), respectively, by using 20% w/w of glycerol solution. It shows that with increase in catalyst loading from 0.5 to 2.0 g, catalyst life increased from 6 to 15 h without affecting the selectivity of acrolein (Figure 4.14 (A), (B))
Figure 4.14 (A), (B) Effect of catalyst loading on glycerol conversion and acrolein selectivity.

Reaction conditions: 20% (w/w) glycerol solution, 275 °C temperature 1.5 lit/h, N₂ flow rate, 10.2 ml/h feed flow rate.

4.3.7 Product selectivity profile

The product selectivity profile of dehydration of glycerol to acrolein over MUICaT-5 catalyst using all optimized reaction parameters includes, 20% (w/w) glycerol solution, 1.0 g catalyst loading, 1.5 L/h, N₂ flow rate, 10.2 mL/h feed flow rate, 4 h reaction time. Table 4.4 shows conversion of glycerol and selectivity of acrolein and other products at different temperatures.
Table 4.4 Product selectivity profile at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>(%) Glycerol conv.</th>
<th>(%) Acrolein selectivity</th>
<th>(%) Acetaldehyde selectivity</th>
<th>(%) Hydroxypropanal selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1</td>
<td>64</td>
<td>59</td>
<td>25</td>
<td>16</td>
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<td></td>
<td>2</td>
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<td>47</td>
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</table>

4.3.8 Time on stream study

The stability and activity of the catalyst were evaluated by time on stream (TOS) data. Figure 4.15 (A), (B) shows that the catalyst MUICaT-5 was stable and active for initial 12 h without any appreciable loss in activity and selectivity for acrolein. After that it undergoes gradual deactivation. The deactivation was due to coke deposition occurs on the active site of the catalyst.
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![Graph showing conversion and selectivity over TOS (h)]
4.3.9 Regeneration and reusability of catalyst

After completion of the reaction under given conditions, the catalyst was removed from the reactor and washed with methanol to remove the adsorbed polymerized material from the catalyst. Then catalyst was subjected to calcinations under air flow at 550 °C for
3 h to burn off coke present on the catalyst. The coke formed was responsible for deactivation of the catalyst. There was an inevitable loss of catalyst particles during these operations. Hence, actual amount of catalyst used in the next batch was almost 10% less than the previous batch. The loss of the catalyst was made up with fresh catalyst. Catalyst reusability was verified by performing reaction under standard condition for 4 h. The catalyst was activated under the flow of N₂ at the reaction temperature for 2 h before reusing. Figure 4.16 shows that there is no appreciable decrease in the activity of the catalyst even after 6th reuse of the catalyst. The catalyst shows very good reusability and is stable. The fresh and regenerated catalysts were subjected to characterization to correlate the activity of the fresh and regenerated catalyst.

![Graph showing catalyst reusability](image)

**Figure 4.16 Catalyst reusability study**

Reaction conditions: 20% (w/w) glycerol solution, 1.0 g catalyst weight, 275 °C temperature, 1.5 lit/h N₂ flow rate, 10.2 ml/h feed flow rate, 4 h reaction time.
4.3.10 Reaction with O₂ as premix gas

To avoid catalyst coking and in situ regeneration of the catalyst, small amount of oxygen in nitrogen was used (5% O₂ + nitrogen balance) to decrease the rate of deactivation of catalyst and in situ regeneration of the catalyst. The emphasis of this study was to remove coke from the catalyst by passing premix gas during the reaction and remove the carbon in the form of CO₂. Hence reactions were carried out using premix gas 5% O₂ + nitrogen balance as carrier gas with similar reaction conditions. The results confirmed that there is decrease in acrolein selectivity while glycerol conversion was almost same as compared to above results. This may be due to oxidation of acrolein had occurred forming acrylic acid in addition with other by products (Figure 4.17).

![Figure 4.17 Reaction with O₂ as premix gas](image)

**Figure 4.17 Reaction with O₂ as premix gas**
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Reaction conditions: 20% (w/w) glycerol solution, 1.0 g catalyst weight, 275 °C temperature, 1.5 L/h O$_2$+N$_2$ flow rate, 10.2 ml/h feed flow rate, 4 h reaction time.

4.4 CONCLUSION

In this chapter selection and preparation of moderate Lewis acid based catalyst MUICaT-5 and its effects on glycerol dehydration and acrolein selectivity were studied. It was found that the catalyst also undergoes deactivation due to coke deposition inside the pores of the catalyst. However, the used catalyst regains its activity after calcination at 550 °C. The catalytic activity of regenerated catalyst was confirmed by NH$_3$-TPD data, BET surface area, BJH pore volume, SEM image and EDX elemental analysis. Hence, MUCaT-5 catalyst which has moderate acid site has good activity and reusability for glycerol dehydration reaction to get acrolein in good yield. At optimized reaction conditions it gave 86% of glycerol conversion and 60% of acrolein selectivity at 275 °C, which is lower than temperatures used by others. The catalyst was recycled up to 6 times without affecting the activity of catalyst and selectivity of acrolein.

The global market for biodiesel is estimated to reach 180 million tons by 2016 and to grow at the rate of 42% per year (Zhou et al. 2008). This will make huge amount of glycerol available as a cheap feedstock to produce several chemicals. Glycerol can also be chemically converted to acrylic acid by dehydration of glycerol to acrolein followed by oxidation to acrylic acid which is an important chemical building block, and used in production of polyacrylates and commodity acrylates. The global market for acrylic acid was worth US$8 billion in 2011 and growing at 3 to 4 percentage per year. Hence, the proposed route can also be useful to meet the acrylic acid market demand. Overall this work has added useful new knowledge to dehydration of glycerol to acrolein.