5. Catalytic aptitude of –COOH functionalized catalysts

Amongst all the carbonaceous solid catalysts[1-9], GO has been now trustworthy heterogeneous solid catalyst for an extensive range of transformation i.e. oxidation, reduction, hydration and hydrgenolysis reactions. Predominantly it has been adapted for the oxidation of various olefins[10], numerous alcohols[11,12] and sulphides[13] due to the presence of acidic oxidative groups, for instance, -COOH groups on its surface. However the shortcomings arising from using GO in these oxidation reactions and why it has to be modified are discussed in the chapter - 4. GO offers selective modification of the available oxidative functional groups and we have selectively modified sole –OH groups in chapter - 4 retaining the carboxyl groups as it is which provide the more acidic site to the catalyst. Here, in this chapter, we have selectively modified the carboxylic acid (-COOH) groups by thionyl chloride. This depletes the number of free carboxyl groups and thereby decreasing the acidic site on the catalysts. This truth is corroborated by NH_3-TPD analysis of GO and Cl-*f*-GO which shows two acidic sites on the GO, however, it is seen to be decreased in Cl-*f*-GO.

A variety of chlorinating agents are accessible to activate the -COOH groups of GO, for instance, pivaloyl chloride, phthaloyl dichloride, oxalyl chloride and thionyl chloride[14-17]. However, $SOCl_2$ became the most appropriate chlorinating agent owing to being cheaper, easily vaporous at normal temperatures, highly reactive and excess quantity can be removed simply by the distillation[18]. S. Niyogi and his research group[19] have functionalized carboxylic acid groups by refluxing GO in $SOCl_2$ and reacted with octadecylamine and the yield of the reaction was 20 wt% of oxidized graphite. Y. Xu et al.[20] had refluxed GO with $SOCl_2$ and reacted with TPP-NH_2 the final product was subjected to nylon membrane filtration and re-suspension in THF to produce TPP-NHCO-SPFGraphene. Z. B. Liu et al.[21] and X. Zhang et al.[22] used $SOCl_2$ to activate the carboxyl groups of GO to prepare graphene nanohybrid with porphyrin and fullerene, respectively via coupling reaction of the carboxyl groups of GO with -NH_2 group of porphyrin and -OH group of pyrrolidine fullerene.

We have fabricated heterogeneous catalysts by grafting of metal-salen ligand on to the Cl-*f*-GO [M(L)-*f*-GO] (Cu-*f*-GO, VO-*f*-GO and Co-*f*-GO) and compared its catalytic competency against the oxidation of benzyl alcohol, epoxidation of styrene, epoxidation of norbornene and oxidation of glucose as tested over the –OH functionalized catalysts.

5.1. Selective oxidation of benzyl alcohol

The catalytic aptitude in terms of quality, reliability and vitality is inspected over selective oxidation of BzA using 30% H_2O_2 as an oxidant. Diverse parameters like mole ratio, temperature, amount of catalyst, solvent effect, solvent amount, oxidant and time have been optimized. In a typical reaction condition, a catalyst was dispersed in a solvent and allowed to stir for 10 min. For complete activation of the substrate, it was added and stirred for 10 min. followed by the drop wise addition of oxidant and the final mixture is stirred for experimentally pre-decided time.

For this transformation, 40 mmol BzA, 40 mmol 30% H_2O_2, ethylene glycol as a solvent (5 mL) and 50 mg of catalyst are feed to 50 mL three-neck round bottom flask and equilibrated at 90 ºC for 3 h. The reaction progress is analyzed by GC by ejecting aliquots at different time intervals.

5.1.1. Impact of catalysts

Very little or no conversion is observed with pristine graphite and Cl-*f*-GO. GO exhibites 3.44% conversion of BzA. However, amongst neat metal-salen complexes (viz. Co-salen, VO-salen and Cu-salen), Co-salen give negligible conversion, while VO-salen complex demonstrates 9.57% conversion of BzA with 93.11% selectivity of BzH and Cu-salen achieved 6.17% conversion of BzA. Now, looking towards the catalysts performance, it exhibits very poor performance, for instance, Co-*f*-GO offers 1.99% conversion, VO-*f*-GO shows 5.15% conversion and Cu-*f*-GO exhibites 3.6% conversion of BzA. This worst performance of the catalysts is believed to be due to the absence of carboxylic acid groups which provides acidity, an enormously life-sustaining factor for the catalyst particularly in the oxidation reactions. Hence, we have decided to perform this reaction in presence of precursor. As our main focus is on the selective product BzH, we have chosen Cu-*f*-GO catalyst for further reaction. We employed 2-3 drops of conc. sulphuric acid and as per our expectation; the conversion is shoot to 92.38%

with 93.21% selectivity of BzH (Fig. 5.1). As a consequence, Cu-*f*-GO is chosen as preferred catalyst with precursor aid for further exploration on the influence of other experimental variables.

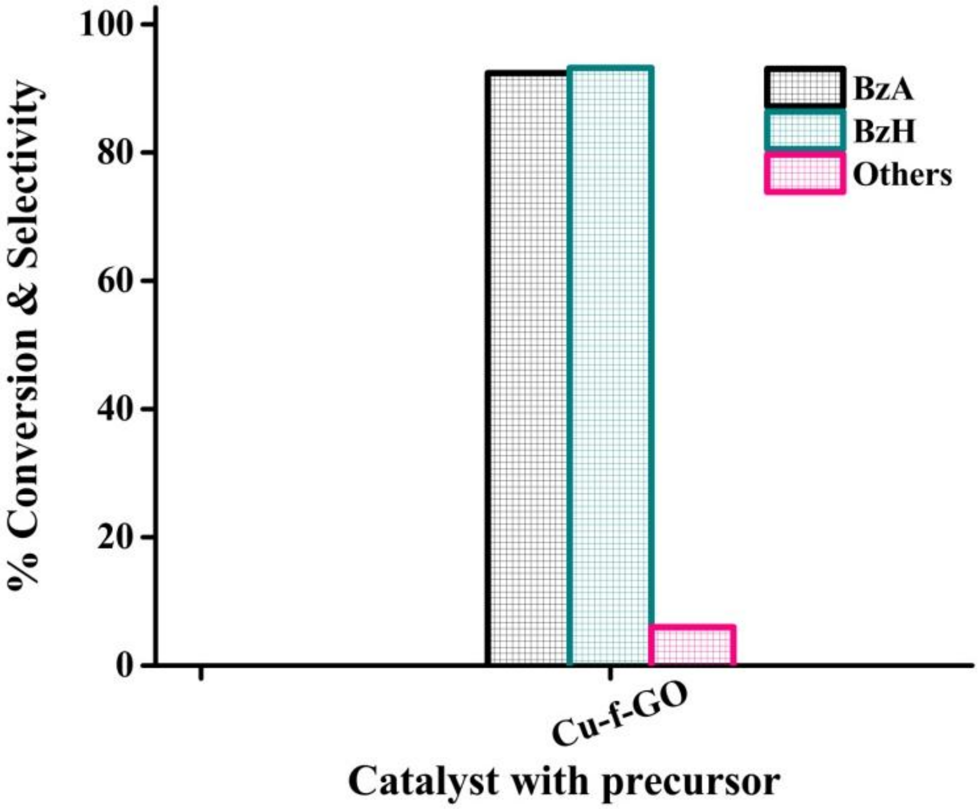

Fig. 5.1. Impact of catalyst with precursor on oxidation of BzA.
Reaction condition: BzA (40 mmol), 30% H_2O_2 (40 mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (5 mL), 3 h.

5.1.2. Impact of solvent

A choice of solvent may affect the conversion, selectivity, stability of the desired product and whole catalytic reaction[23]. This study is also aimed to assess the practicability of solvent effect on the conversion of BzA and selectivity of BzH. Hence, diverse solvents like methanol, acetonitrile, N,N-dimethylformamide (DMF), 1,4-dioxane, toluene, and ethylene glycol are scheduled and studied their effect on conversion and selectivity. As shown in Fig. 5.2, methanol, acetonitrile, DMF and toluene gives 2.77%, 3.66%, 3.88% and 6.96%, conversion, respectively. On the other hand, 1,4-dioxane exhibits

87.97% conversion of BzA with 98.76% BzH selectivity and ethylene glycol, as per expectation, proved to be a model solvent for this transformation by giving 92.38% conversion of BzA with 93.21% selectivity of BzH. As a result, ethylene glycol is chosen as the preferred solvent for this transformation.

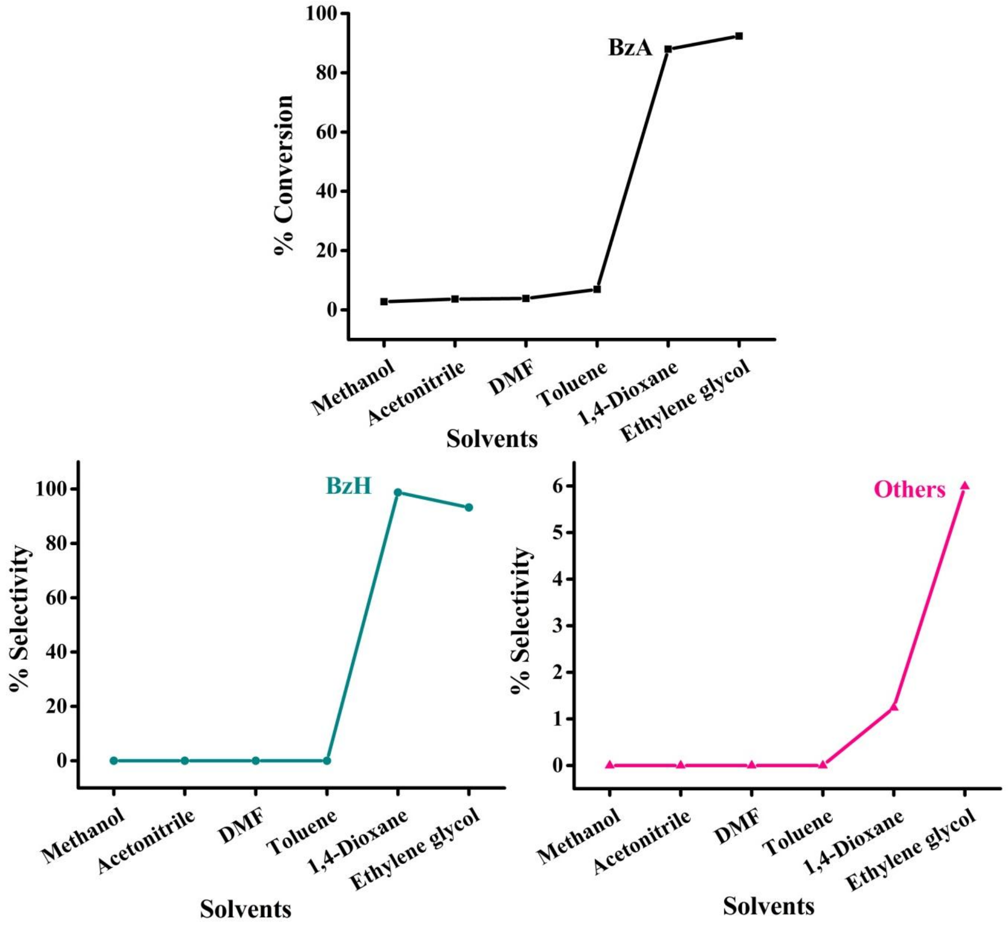

Fig. 5.2. Impact of varying solvents on the oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (40 mmol), Cu-*f*-GO (50 mg), 90 °C, solvent (5 mL), 3 h.

5.1.3. Impact of mole ratio

To determine the impact of varying mole ratios of a substrate to oxidant, four different mole ratios viz. 1:1, 1:1.5, 1:2, 1:2.5 are examined. As shown in Fig. 5.3, it can be seen that H_2O_2 has played a crucial role in the degradation of benzyl alcohol; 1:1 mole ratio gives 92.38% conversion of BzA with 93.21% BzH selectivity. While increase in mole ratio (1:1.5) has resulted in rise in the conversion of BZA (97.01%) but selectivity of BzH is seen to decreased (21.28%). Further increase in the mole ratio of substrate to H_2O_2 (1:1.5) exhibits 97.99% conversion of BzA with 25.33% BzH selectivity. On the other hand, selectivity of other products is increased in both these cases. A higher concentration of H_2O_2 (1:2.5) has extended the conversion to 100% with 98.64% BzH selectivity. Here, conversion and selectivity both increased with increasing in mole ratio. So as to attain higher yield with a higher rate of conversion, we have taken 1:2.5 as a preferred mole ratio to investigate the impact of other parameters.

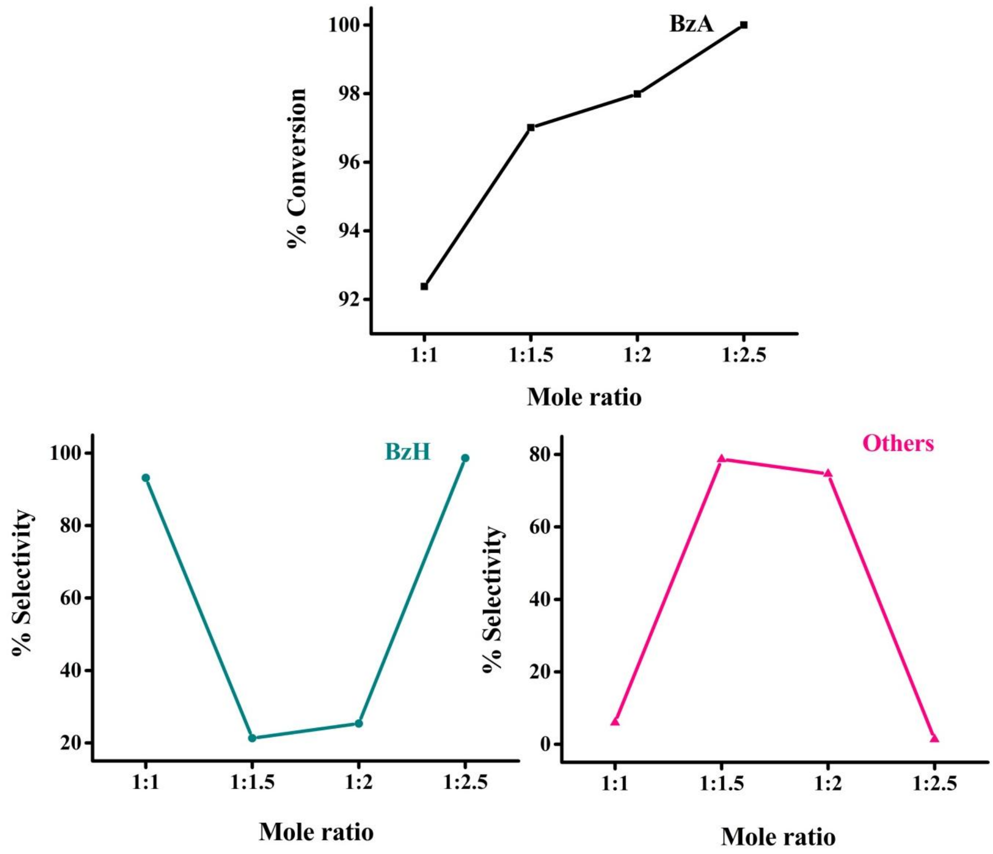

Fig. 5.3. Impact of varying mole ratio on oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (5 mL), 3 h.

5.1.4. Impact of amount of catalyst

In this selective oxidation of BzA, we have inspected four different amounts of catalyst i.e. 10, 20, 40 and 50 mg of catalyst (Fig. 5.4). After obtaining the desired conversion of BzA with 50 mg of catalyst, we have tested 40 mg of catalyst amount and very poor conversion of BzA (16.02%) is observed with petite selectivity of BzH (59.08%). On changing the catalyst amount to 20 mg, it shows further decrease in conversion of BzA (5.01%). Lowest conversion of BzA is achieved with 10 mg of catalyst amount that is 4.23%. Therefore, we have chosen 50 mg as preferred catalyst amount for further investigation of other parameters.

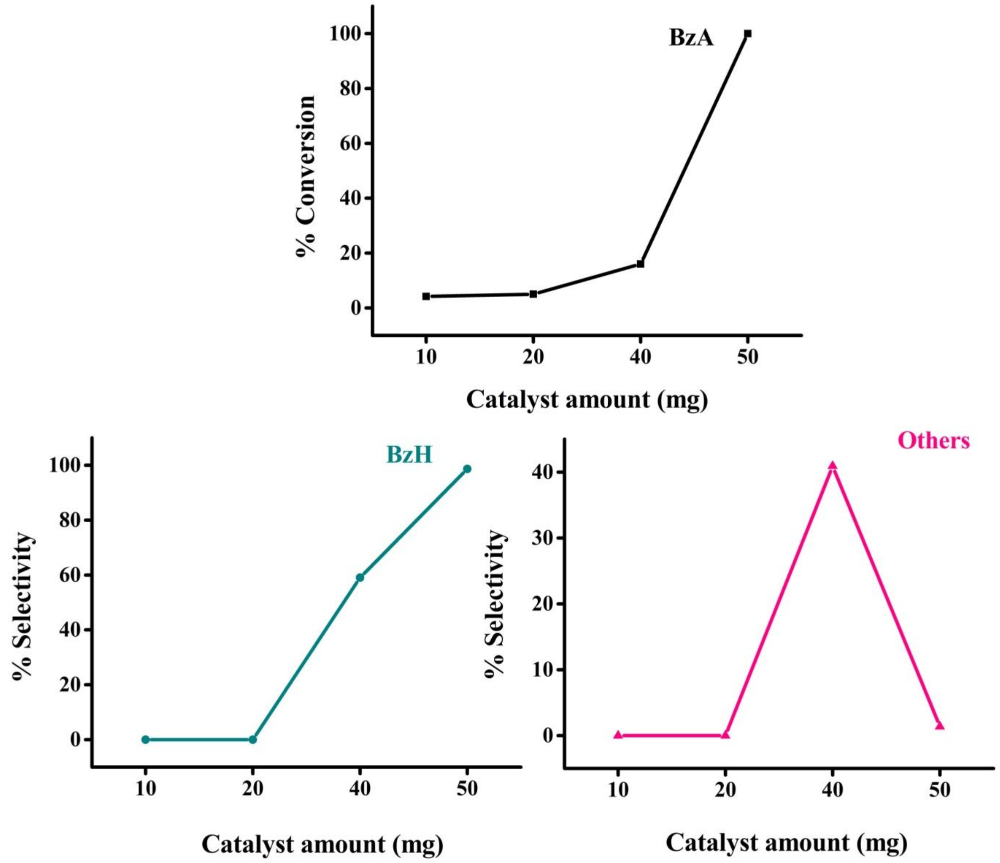

Fig. 5.4. Impact of varying amount of catalyst on the oxidation of BzA. Reaction condition: BzA (40 mmol), 30% H_2O_2 (100 mmol), Cu-*f*-GO (mg), 90 °C, ethylene glycol (5 mL), 3 h.

5.1.5. Impact of time

It is pretty essential to terminate this reaction at the correct time to succeed in achieving selected yield (BzH) with higher selectivity. For this intend, we have executed this reaction at different time intervals, viz. 0.5, 1 and 2 h (Fig. 5.5). At 0.5 h, 4.82% conversion of BzA is achieved. After the examination of the reaction mixture drawn at 1 h, it is observed that conversion attained 100% with 98.64% selectivity of BzH. However, on further continuing the reaction for 2 h, the conversion falls to 6.97%. Hence, it is noticed that the conversion and selectivity both increased with time and achieve maximum at 1 h. For this reason, we have decided to set the reaction time for 1 h for further exploration.

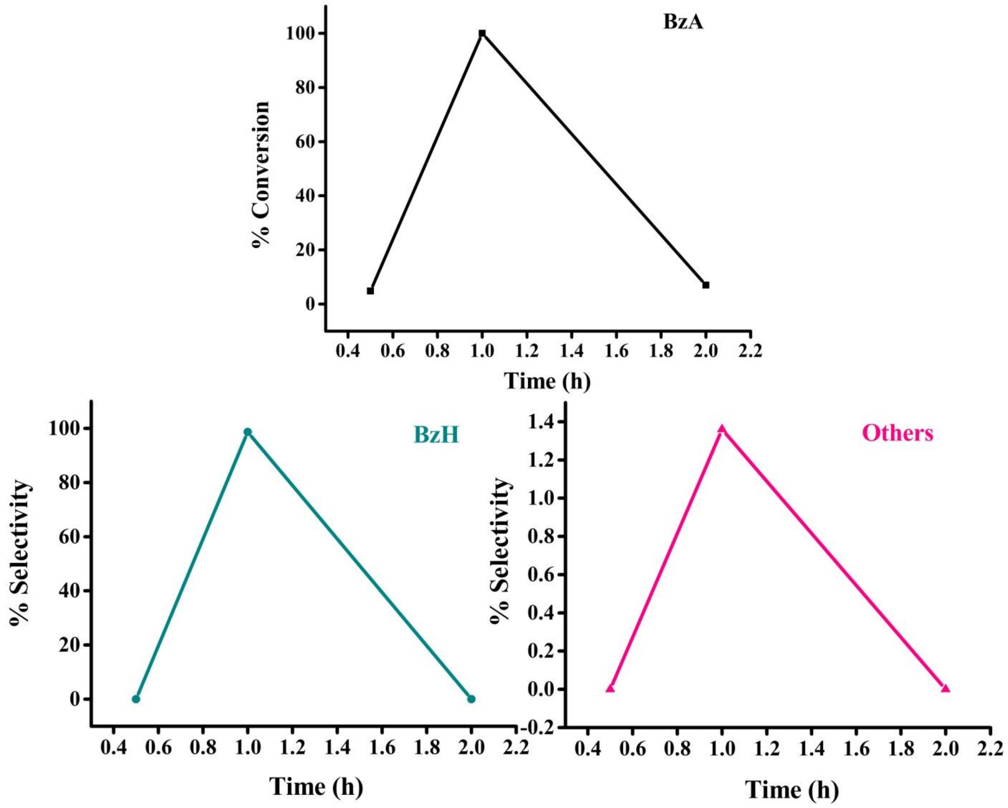

Fig. 5.5. Impact of varying time on the oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (100 mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (5 mL), time (h).

5.1.6. Impact of solvent amount

We have examined the reaction by employing 2, 5 and 10 mL of solvent amount. As shown in Fig. 5.6, poor conversion of BzA (4.83%) is obtained with 2 mL of solvent amount. If the amount of ethylene glycol is increased to 5 mL, BzA exhibits extreme conversion of 100% with 98.64% selectivity of BzH. Further rise in the amount of solvent (10 mL) decreases the conversion to 93.15%, but the selectivity lessened dramatically to 52.34%; while on the other hand the selectivity of other product has grown appreciably

(47.66%). The explanation for this reduction is given by dilution of the reaction mixture to a great extent with 10 mL of solvent amount[24]. Accordingly, we have chosen 5 mL as the preferred solvent amount for further optimization of reaction parameters.

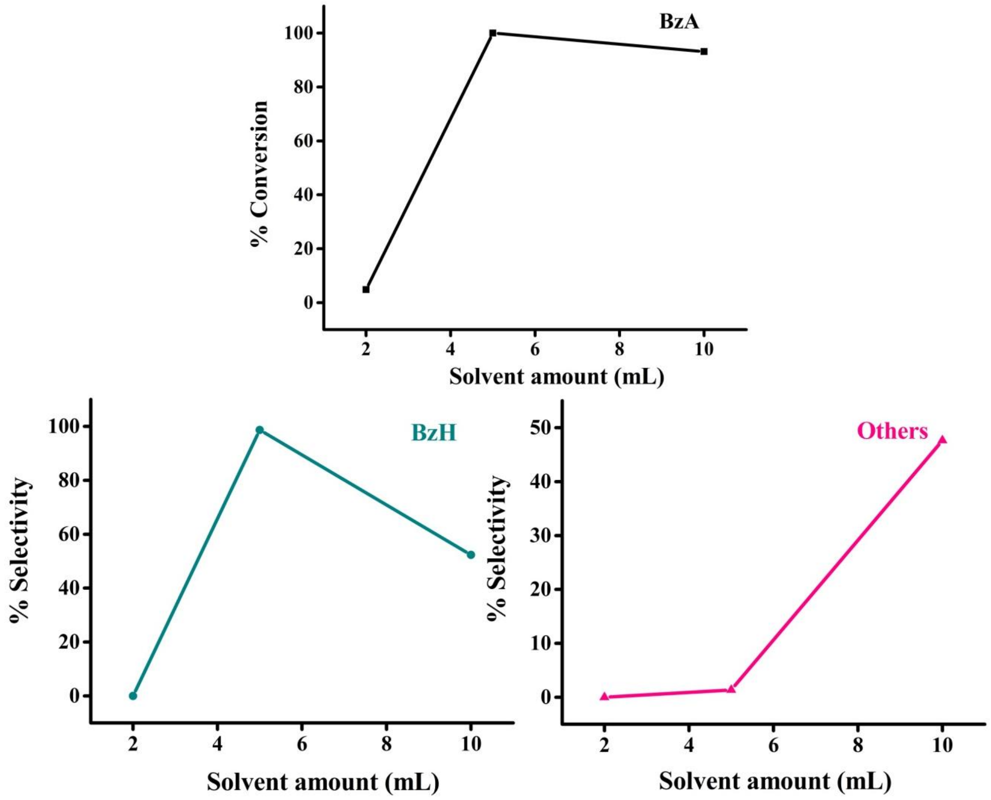

Fig. 5.6. Impact of varying amount of solvent on the oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (100 mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (mL), 1 h.

5.1.7. Impact of oxidant

Different oxidants such as 70% TBHP and 30% H_2O_2 on the oxidation of BzA (Fig. 5.7) are examined under an experimentally obtained reaction parameters. The data divulges that TBHP as an oxidant is proved to be sub-standard for this reaction as it exhibits only 16.02% conversion of BzA with 59.08% selectivity of BzH. However, higher conversion of BzA (100%) alongwith higher selectivity of BzH (98.64%) is achieved with 30% H_2O_2 as an oxidant. Therefore, 30% H_2O_2 is chosen as the preferred oxidant for further the catalytic investigation.

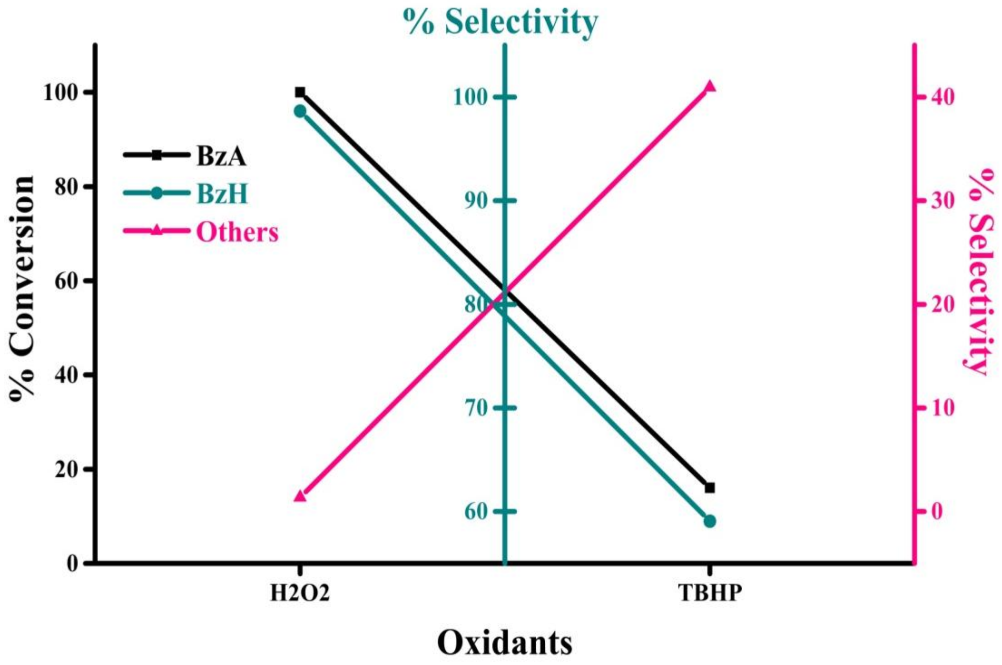

Fig. 5.7. Impact of oxidants on the oxidation of BzA.

Reaction condition: BzA (40 mmol), oxidant (100 mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (5 mL), 1 h.

5.1.8. Impact of temperature

Effect of four different reaction temperatures such as 70, 80, 90 and 100 °C on the oxidation of BzA is demonstrated in Fig. 5.8. It is visible from the figure that 8.37% conversion of BzA is achieved at 70 °C. When temperature rises to 80 °C, conversion also increased to 15.65% with 90.75% BzH selectivity. Moreover, maximum conversion of 100% of BzA is monitored together with 98.64% BzH selectivity at 90 °C. However, further rise in the temperature (100 °C) has resulted in decrease in conversion (5.08%). This decrease might be due to bulk degradation of H_2O_2 at higher temperature. Subsequently, 90 °C is chosen as representative temperature.

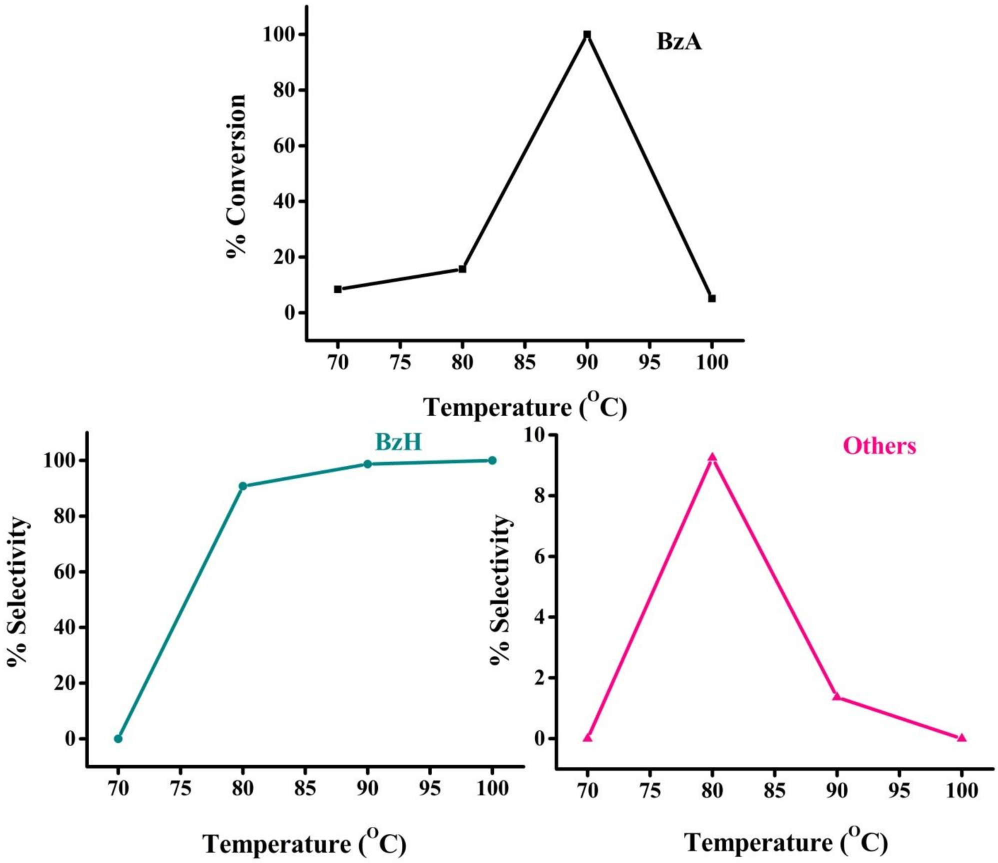

Fig. 5.8. Impact of varying temperature on the oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (100 mmol), Cu-*f*-GO (50 mg), temperature (°C), ethylene glycol (5 mL), 1 h.

5.1.9. Recyclability test

To inspect the recyclability of the as-prepared heterogeneous catalyst for this transformation, the catalyst is recovered by filtration from the reaction mixture and washed with solvent followed by oven drying prior to employing for further catalytic test. The reaction mixture of each catalytic experiment is analyzed by GC under the same conditions as employed for the previous catalytic experiments. The results of recyclability study are demonstrated in Fig. 5.9. It is apparent form the figure that this catalyst is recycled for three times and conversion in first to 3rd recycle is 97.46%, 92.32%, 85.12% and selectivity of BzH is 93.11%, 89.79% and 78.97%, respectively. This lower recyclability of the catalysts is might be due to leaching of metal ion.

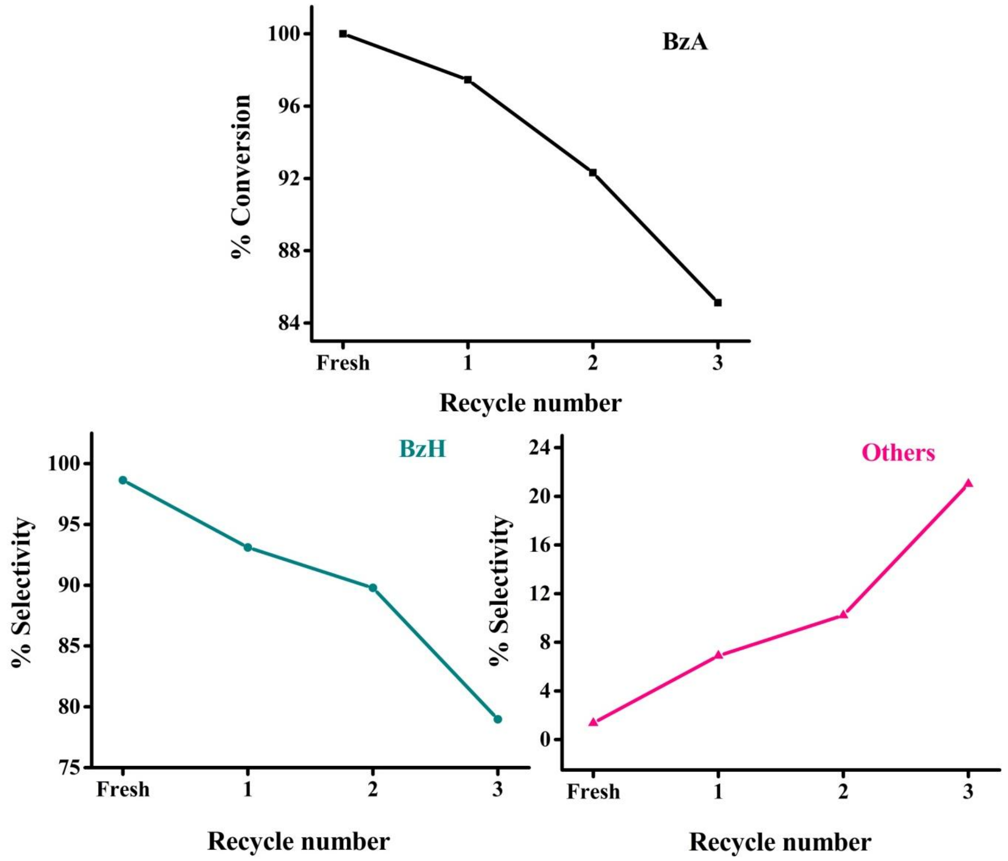

Fig. 5.9. Recyclability test of the oxidation of BzA.

Reaction condition: BzA (40 mmol), 30% H_2O_2 (100 mmol), Cu-*f*-GO (50 mg), 90 °C, ethylene glycol (5 mL), 1 h.

5.1.10. Conclusion

In concluding remarks, this sub-chapter executed the catalytic aptitude of the catalysts prepared by functionalization on the carboxylic acid groups of GO. The result of catalytic activity implies the poor performance of as-prepared catalysts. Amongst all synthesized catalyst, Cu-*f*-GO is seen to be appropriate and productive catalyst for this selective oxidation of benzyl alcohol showing 100% conversion and 98.64% BzH selectivity, but in presence of precursor. The influences of different parameters like different mole ratio, temperature, time, catalyst amount, solvents, amount of solvent and oxidant have also been studied and observed that solvents and presence of acidic sites on the surface of catalyst plays vital role in this catalytic transformation. This catalyst can be recycled three times. This deprived performance of the catalysts is might be due to the absence of carboxylic acid groups on the surface of GO which provides acidity to the catalysts.

5.2. Selective epoxidation of styrene

Here, in this sub-chapter, we assess the catalytic competency of the as-synthesized catalysts over the selective epoxidation of styrene using 30% H_2O_2 as a greener oxidant. It is carried out in a 50 mL two-necked round-bottom-flask furnished with water condenser in an oil bath with a magnetic stirrer. In a standard reaction condition to choose the best-suited catalyst, a typical reaction was performed with 10 mg of catalyst at 80°C, using acetonitrile as a solvent and 30% H_2O_2 as an oxidant and continued for 1 h. A series of experiments is executed to obtain the optimized reaction condition by investigating various parameters such as impact of the various mole ratio, temperature, oxidants, catalytic amount, solvents, solvent amount and time on this transformation.

First, the catalyst was dispersed in acetonitrile and stirred for 10 min followed by the addition of a substrate molecule. It was followed by the dropwise addition of oxidant in order to avoid the bulk decomposition of H_2O_2. The final reaction mixture was then stirred for an experimentally pre-decided time with the aim of achieving maximum conversion and selectivity of the product. The product formation was substantiated through GC analysis by taking aliquots of the reaction mixture at different time intervals.

For the pilot reaction, 20 mmol of styrene, 20 mmol of 30% H_2O_2, 5 mL acetonitrile as a solvent and 10 mg of catalyst (graphite, GO, Cl-*f*-GO, neat complexes i.e. Cu-salen, Co-salen, VO-salen, Cu-*f*-GO, Co-*f*-GO and VO-*f*-GO) is feed to a reaction vessel and equilibrated at 80 °C for 1 h. As a result of this heterogeneous catalyst driven epoxidation reaction, SO and BzH was obtained as major key products alongwith by-products like benzoic acid (BA) and phenylacetaldehyde (PAC) in little amount.

5.2.1. Impact of catalysts

The effect of diverse heterogeneous catalysts on styrene conversion and distinct product selectivity are tabulated in Table 5.1. The result divulges that under the identical conditions, extremely little or no conversion is achieved with pristine graphite and GO. While Cl-*f*-GO exhibits 9.52% conversion of styrene with 100% SO selectivity. Amongst neat complexes, Co-salen shows poor conversion of styrene (7.81%), while VO-salen complex demonstrats 13.25% conversion of styrene with 90.01% SO selectivity alongwith 9.99% formation of BzH. Cu-salen complex exhibits highest conversion of 51.65% among all neat complexes but the selectivity of SO is very petite (15.21%). It favours the formation of BzH with 84.79% selectivity. Contrarily, on employing the respective catalyst of neat complexes, conversion and selectivity decreased. Co-*f*-GO shows only 4.92% conversion of styrene, whereas VO-*f*-GO is able increas this lower conversion of styrene up to 10.25% with 100% selectivity of SO. At the same time, Cu-*f*-GO is found to be superior to convert the 44.26% styrene with lower selectivity of SO (7.71%) and higher BzH selectivity (92.27%). Hence, the conversion of styrene is found to be increased with catalyst from Co-*f*-GO to Cu-*f*-GO, but the selectivity of SO exhibited inverted trend. Hence, Cu-*f*-GO was chosen as the preferred catalyst for further investigation of other experimental variables.

Table 5.1

Impact of varying catalysts on the epoxidation of styrene.

Systems	**Styrene Conversion (%)**	**SO Selectivity (%)**	**BzH Selectivity (%)**	**TOF[a] (h^{-1})**
Graphite	0	-	-	-
GO	0.3	-	-	-
Cl-*f*-GO	9.52	-	-	-
Co-salen	7.81	-	-	28.41
VO-salen	13.25	90.01	9.99	38.15
Cu-salen	51.65	15.21	84.79	138.21
Co-*f*-GO	4.92	-	-	17.90
VO-*f*-GO	10.25	100	-	29.50
Cu-*f*-GO	44.26	7.71	92.27	118.43

Reaction condition: styrene (20 mmol), 30% H_2O_2 (20 mmol), catalyst (10 mg), 80 °C, acetonitrile (5 mL), 1 h.

[a] TOF: Moles of styrene converted per mole of metal per hour.

5.2.2. Impact of mole ratio

Impact of mole ratio of styrene to H_2O_2 on the styrene conversion, product distribution and selectivity over the catalyst Cu-*f*-GO is depicted in Fig. 5.10. On increasing the mole ratio from 1:1 to 1:1.5, styrene conversion is also demonstrated increasing trend, with increasing SO selectivity. On employing 1:1 mole ratio, 44.26% conversion of styrene is achieved with 7.71% selectivity of SO. Further rising the mole ratio (1:1.5) has resulted in 57.6% styrene conversion with 5.57% SO selectivity and 94.42% BzH selectivity. In order to achieve highest SO selectivity, mole ratio is raised to 1:2 which offers further rise in conversion (69.98%) of styrene but SO selectivity showed slight rise (9.11%) and BzH selectivity exhibits little downtrend (90.89%). With the hope of still increase in the SO selectivity, 1:2.5 mole ratio is studied and obtained result is beyond belief. Styrene conversion shows increasing trend (73.84%) but the selectivity of SO felt immense shortfall and exhibits no SO in the product and BzH selectivity hiked to 100%. The justification for this reverse trend observed with aforesaid mole ratio might be given by solvent effect on the product selectivity and it may switch by finding proper solvent for this transformation to yield SO as major product. Therefore, we have chosen 1:2.5 as a preferred mole ratio for further investigation.

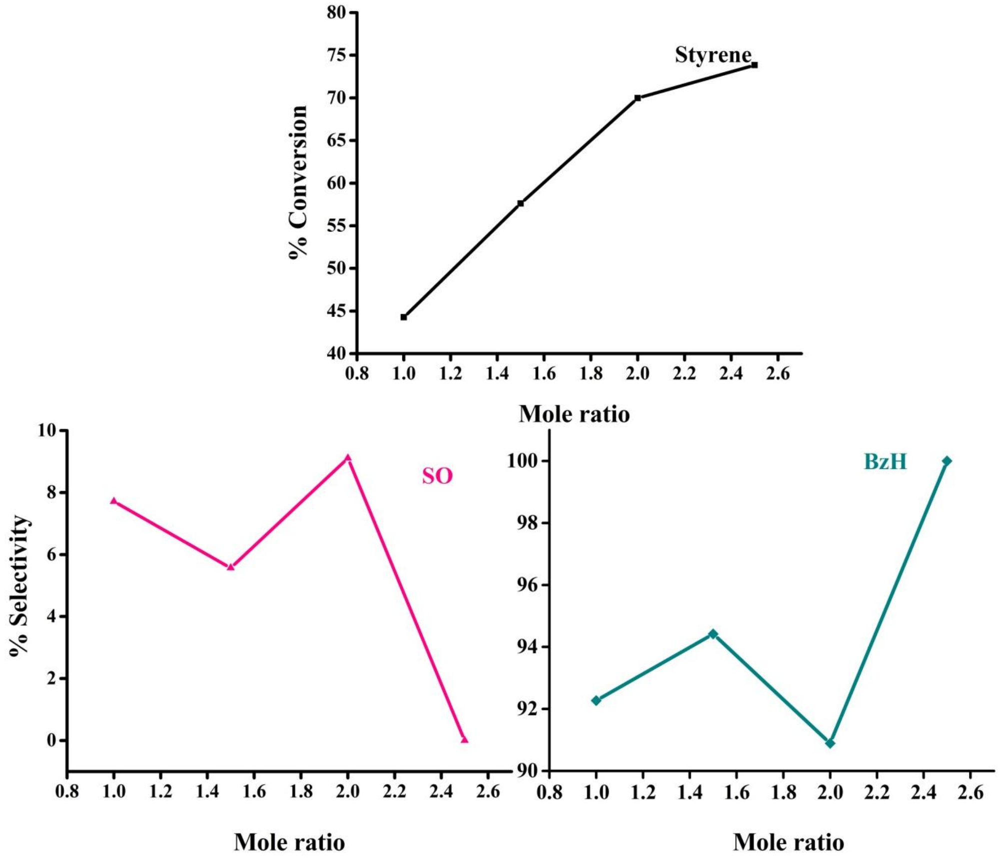

Fig. 5.10. Impact of varying mole ratio on the epoxidation of styrene.
Reaction condition: styrene (20 mmol), 30% H_2O_2 (mmol), Cu-*f*-GO (10 mg), 80°C, acetonitrile (5 mL), 1h.

5.2.3. Impact of solvent

As our main focus on achieving SO as sole key product, we have conducted this experiment to study the effect of different solvents such as toluene, DMF, ethylene glycol, acetonitrile, methanol and 1,4-dioxane on the epoxidation of styrene. This study is intended to diminish the formation of minor and/or by-product(s) and to enhance the key product. By using toluene, DMF and ethylene glycol as a solvent very little conversion of styrene i.e. 1.77%, 2.21% and 4.20%, respectively, is observed (Fig. 5.11). While employing acetonitrile, the conversion is raised to 73.84% but with 100% BzH selectivity. Here, the concern point is non selectivity for key product SO and absolute utilization of styrene molecule. Hence, in order to increase % conversion alongwith SO selectivity, we thought of using methanol as a very useful hygroscopic agent[25]. This lucrative quality of methanol was being very useful in increasing the conversion of styrene but not in increasing the selectivity of SO.

In spite of achieving a high conversion (82.54%) with methanol, the selectivity for key product (SO) is very less merely 10.7%. Hence, from our experience, another hygroscopic solvent, 1,4-dioxane is thought to employed for this transformation. It is well miscible with water at standard temperature and pressure forming an azeotrope that boils at 87.6 °C. With the aim of taking more advantage of this characteristic of 1,4-dioxane, tactically we injected H_2O_2 at much lower rate so that the produced water promptly get absorbed. As per our expectation, high conversion of 85.93% is achieved with 90.44% SO selectivity. Therefore, we have chosen 1,4-dioxane as the preferred solvent for further investigation of other experimental variables.

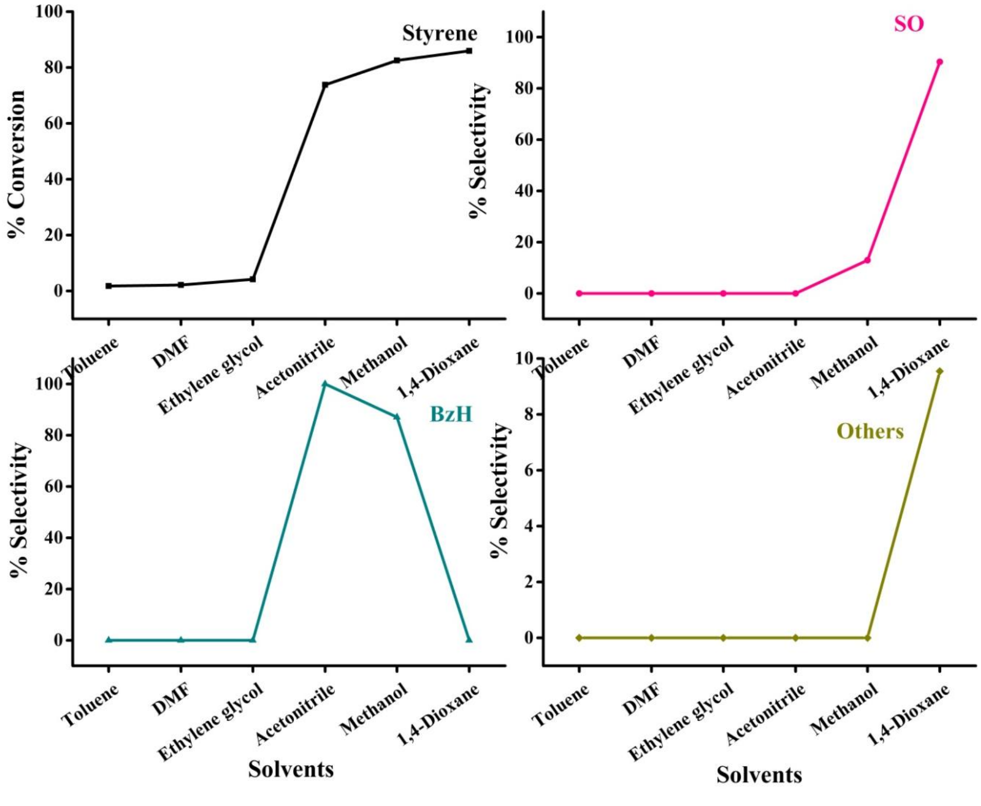

Fig. 5.11. Impact of varying solvents on the epoxidation of styrene.

Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (10 mg), 80 °C, solvents (5 mL), 1 h.

5.2.4. Impact of amount of catalyst

Three concentrations viz. 10, 20 and 30 mg of the representative catalyst are studied for the epoxidation of styrene over 30% H_2O_2 as an oxidant with 1,4-dioxane as a product selective solvent. The result is portrayed in Fig. 5.12. At lower concentration of catalyst (10 mg), higher conversion of styrene (85.93%) with 90.44% SO selectivity is observed. However, on increasing catalyst amount such as 20 and 30 mg, conversion is decreased to 78.06% and 63.51% with 98.35% and 67.17% SO selectivity, respectively. This higher styrene conversion at lower concentration is might be due to high rate of epoxidation of styrene and the explanation for the upside-down trend can be given by higher rate of degradation of H_2O_2 at higher catalyst amount. Subsequently, we have chosen 10 mg catalyst as preferred amount for further investigation of other experimental variables.

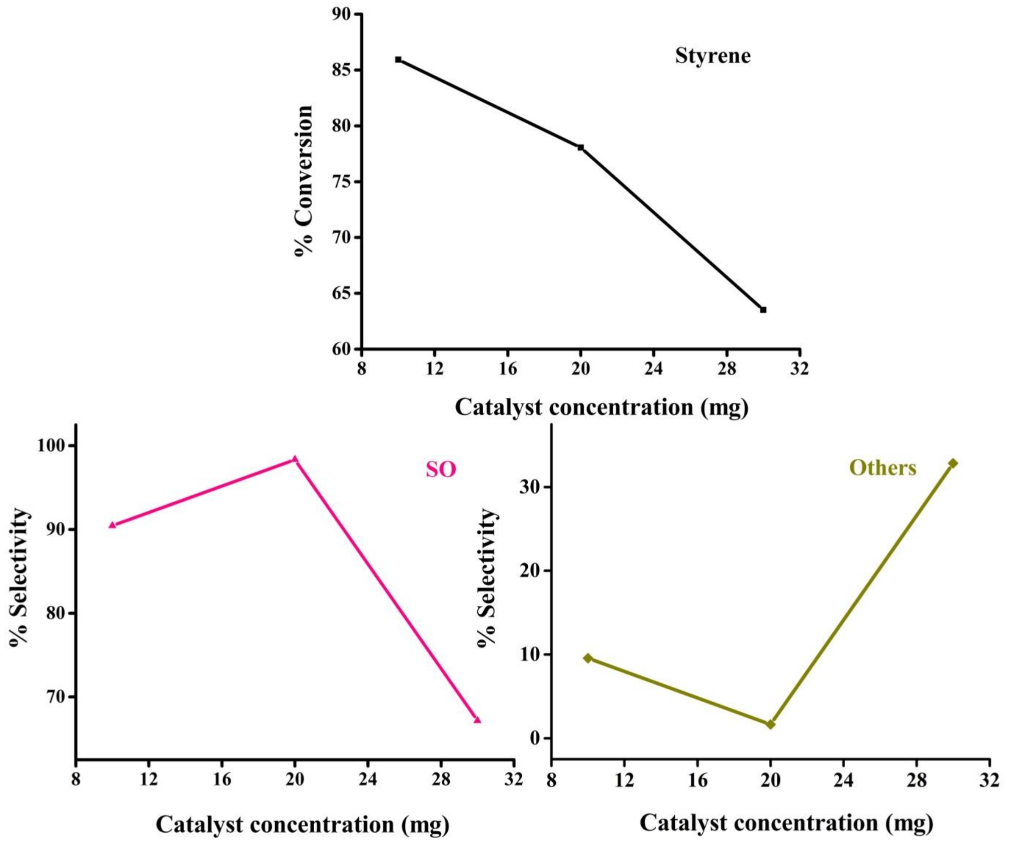

Fig. 5.12. Impact of varying amount of catalyst on the epoxidation of styrene. Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (mg), 80 °C, 1,4-dioxane (5 mL), 1h.

5.2.5. Impact of time

To analyze the impact of time on this transformation, this reaction has been conducted up to 3 h by keeping other parameters fixed. The conversion of styrene as a function of time is exhibited in Fig. 5.13. It divulges that at 1 h, higher styrene conversion of 85.93% is seen with 90.44% SO selectivity. On increasing the reaction time to 2 h, styrene conversion is seen to be decreased to 44.30% with immense decline in the selectivity of SO (35.78%). However, at 3 h, it continues to experience the down trend and diminutive conversion of styrene is observed (10.84%) with 34.39% SO selectivity. As a result, we have chosen 1 h as the preferred time for further investigation of other experimental variables.

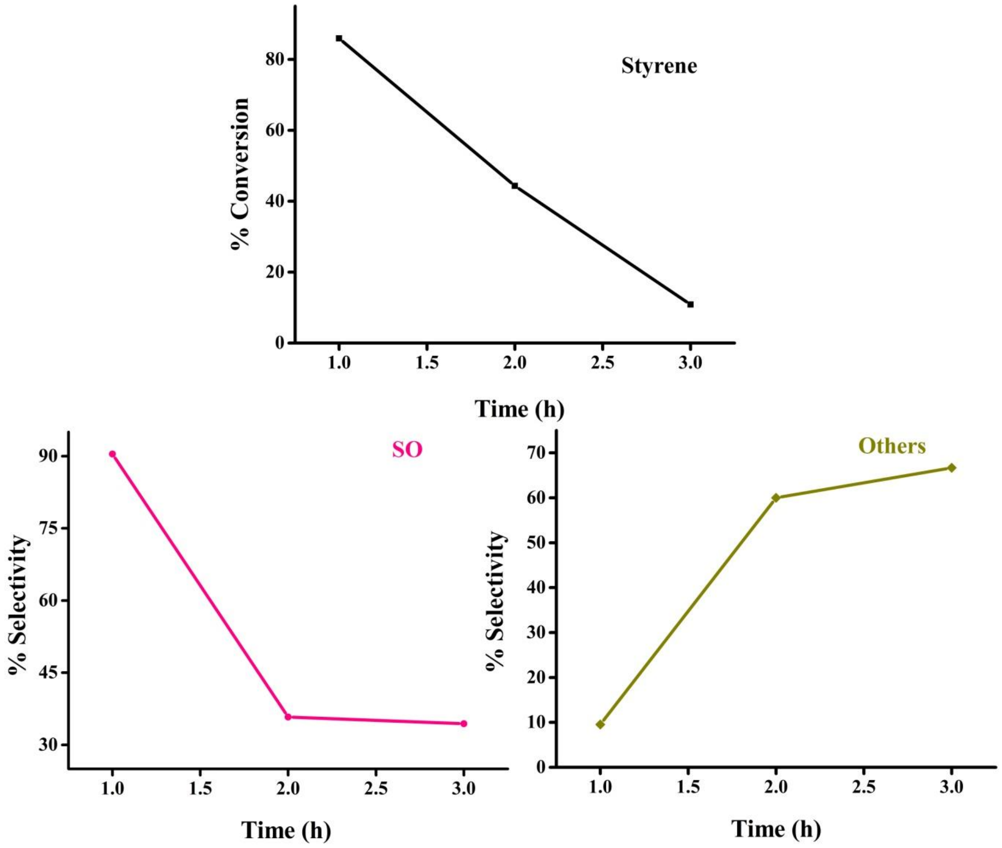

Fig. 5.13. Impact of varying time on the epoxidation of styrene.

Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (10 mg), 80 °C, 1,4-dioxane (5 mL), time (h).

5.2.6. Impact of temperature

Effect of reaction temperature on epoxidation of styrene is demonstrated in Fig. 5.14. As can be seen, 9.68% conversion of styrene is obtained with 92.37% SO selectivity at 70 °C. While on increasing the temperature to 80 °C, highest conversion of 85.93% of styrene is achieved with 90.44% SO selectivity. Moreover, on further rising the temperature to 90 °C, 27.55% conversion of styrene is experienced with 67.75% SO selectivity. After that, at 100 °C, polymerisation of styrene is observed as gel formation takes place. Therefore, we have chosen 80 °C as a preferred reaction temperature for further investigation.

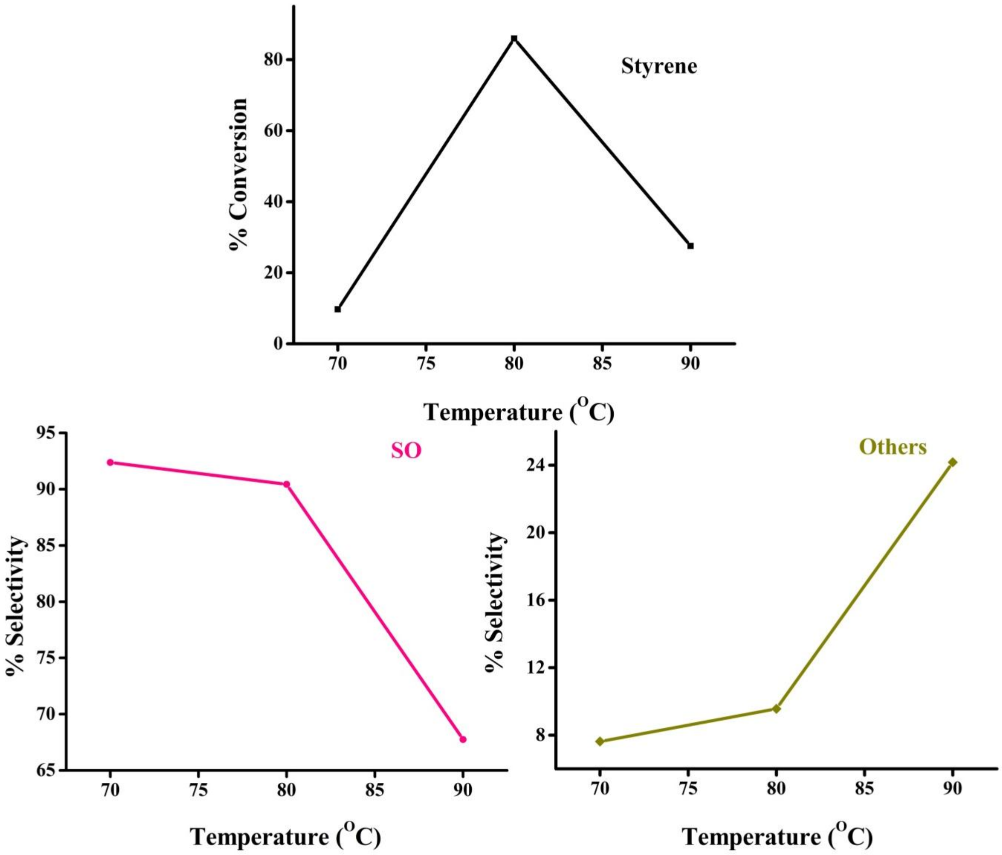

Fig. 5.14. Impact of temperature on the epoxidation of styrene.

Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (10 mg), temperature (°C), 1,4-dioxane (5 mL), 1 h.

5.2.7. Impact of oxidant

To examine the effect of oxidant on styrene conversion, 70% TBHP is employed as an oxidant other than H_2O_2. Fig. 5.15 has been demonstrated the result of this transformation. TBHP is proved substandard as an oxidant as it shows only 38.08% conversion of styrene and product distribution alongwith selectivity of the key product SO (50.30%) is also suffered. It shows inverted trend of SO and BzH selectivity. Selectivity of SO is seen to be deteriorating, alternatively, selectivity of BzH is found to be increased with same rate. In addition, though, by-product formation is very less (2.7%) with TBHP, we have preferred H_2O_2 as a greener and environmentally benign oxidant as we have intended mainly with sole key product SO.

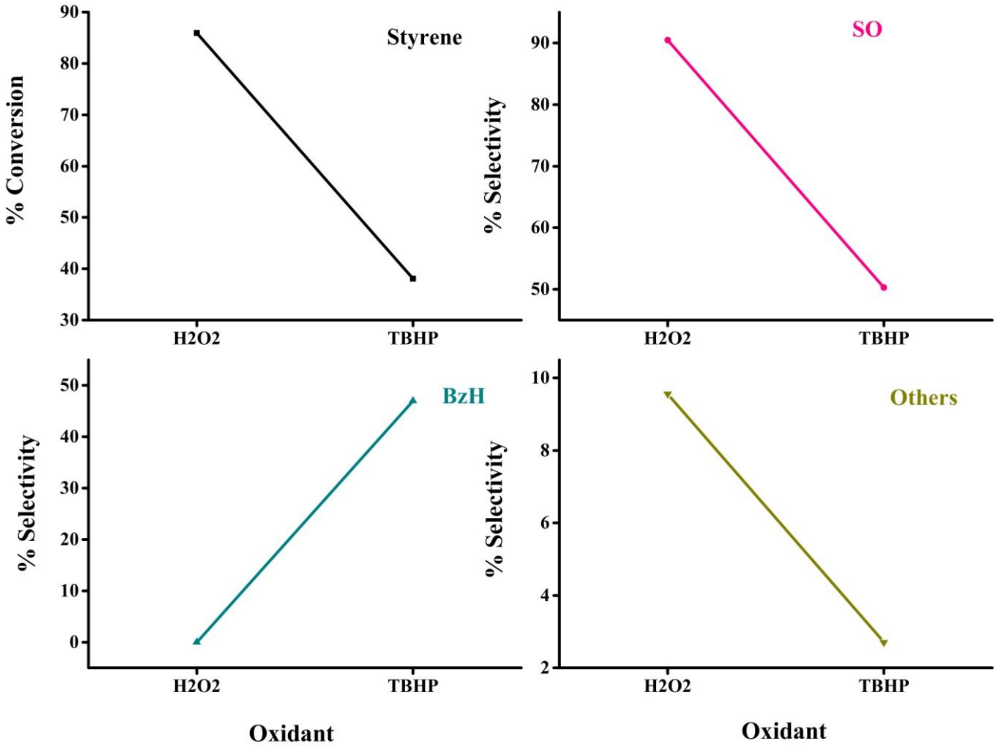

Fig. 5.15. Impact of oxidant on the epoxidation of styrene.

Reaction condition: styrene (20 mmol), oxidant (50 mmol), Cu-*f*-GO (10 mg), 80 °C, 1,4-dioxane (5 mL), 1 h.

5.2.8. Impact of solvent amount

After getting desired results with 1,4-dioxane as a solvent, we have inspected the effect solvent amount on this transformation. From Fig. 5.16, on employing 2 mL of solvent, relatively lower conversion (45.89%) is observed with 100% SO selectivity. This poor conversion is might be due to insufficient amount of solvent for the dissolution of styrene molecule. However, on increasing the amount of solvent from 2 to 5 mL, this transformation is switched to expected high conversion and selectivity of SO. The conversion is increased up to 85.93% with higher selectivity obtained for SO is 90.44%. This result has increased our eagerness to study more effect of solvent amount. Subsequently, by employing further excessive amount of solvent (10 mL), we observed surprising results that by increasing solvent amount, conversion reached to 96.92% but the selectivity of SO drop down to 44.18% with 21.29% by-product formation. It is believed that 10 mL might be required amount of solvent for the absolute dissolution of styrene, but it may causes over oxidation as well leading to formation of by-product. For this reason, 5 mL is chosen as the preferred amount of solvent for further investigation.

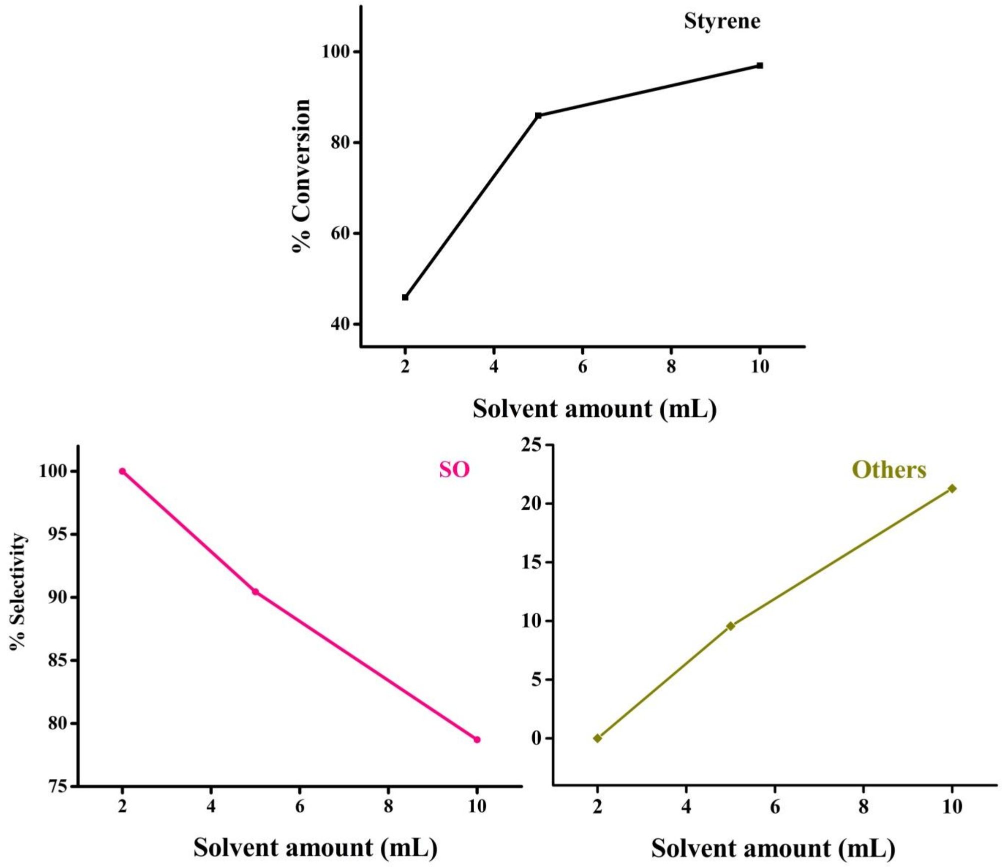

Fig. 5.16. Impact of varying amount of solvent on the epoxidation of styrene. Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (10 mg), 80 °C, 1,4-dioxane (mL), 1 h.

5.2.9. Recyclability test

To study the recyclability of the as-prepared heterogeneous catalyst for this transformation, the catalyst is recovered by filtration from the reaction mixture and washed with solvent followed by oven drying prior to employing for further catalytic test.The reaction mixture of each catalytic experiment is analyzed by GC under the same conditions as employed for the previous catalytic experiments. The results of recyclability study are demonstrated in Fig. 5.17. It is apparent form the figure that this catalyst can be recycled for three times and in 3rd recycles activity, conversion in first to 3rd recycle is 83.17%, 79.56%, 74.91% and selectivity of SO is 88.56%, 85.13% and 79.79%, respectively. This lower recyclability of the catalysts is might be due to leaching of metal ions.

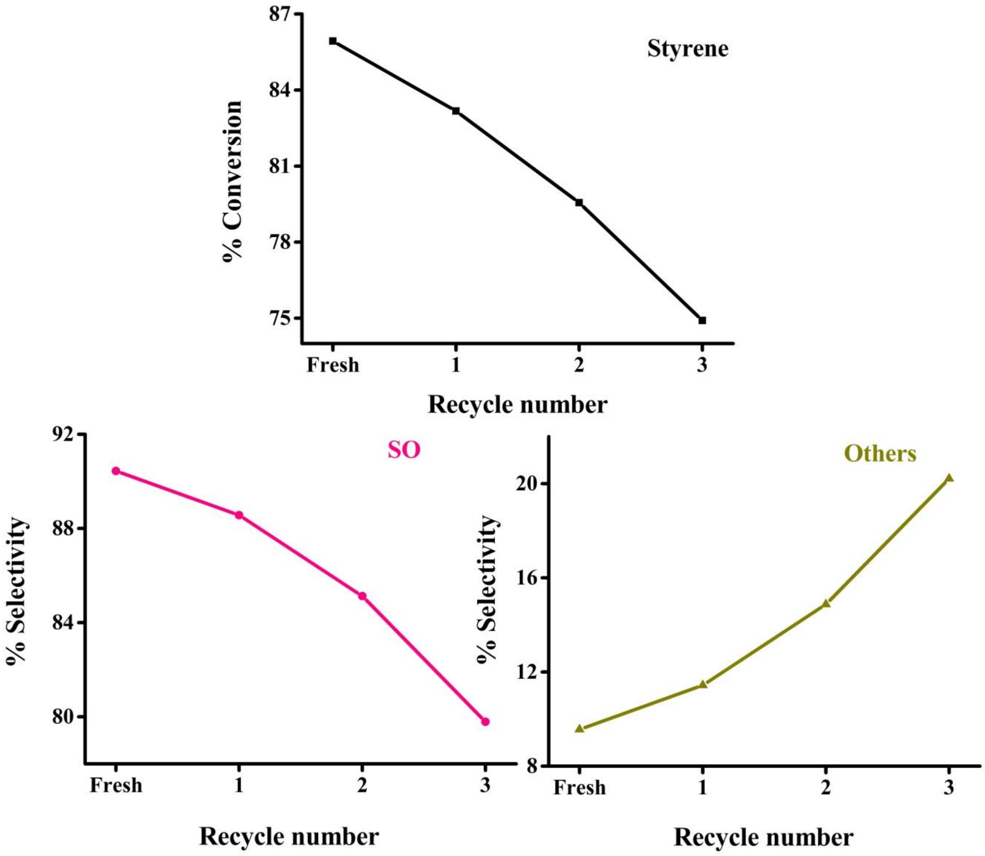

Fig. 5.17. Recyclability test of the epoxidation of styrene.

Reaction condition: styrene (20 mmol), 30% H_2O_2 (50 mmol), Cu-*f*-GO (10 mg), 80 °C, 1,4-dioxane (5 mL), 1 h.

5.2.10. Conclusion

The catalysts synthesized by modifying carboxylic acid groups have been evaluated over the selective epoxidation of styrene. The results of catalytic activity of the as-prepared catalyst demonstrate deprived activity of theses catalysts. Amongst all synthesized catalysts, Cu-*f*-GO is seen to be appropriate and productive catalyst for this selective epoxidation of norbornene with 85.93% conversion and 90.44% SO selectivity. The influences of different parameters like different mole ratio of oxidant to substrate, temperature, time, catalyst amount, solvents, amount of solvent, oxidant have also been studied. This catalyst can be recycled three times. This deprived performance of the catalysts is might be due to the absence of carboxylic acid groups on the surface of GO which provides acidity to the catalysts.

5.3. Selective epoxidation of norbornene

Herein, this sub-chapter express the epoxidation of norbornene over M-*f*-GO (M = Cu^{2+}, Co^{2+} and VO^{4+}) using 30% H_2O_2 as an oxidant. The catalytic epoxidation of norbornene over the transition metal grafted chloro-functionalized GO nanosheet as heterogeneous catalysts is carried out in a 50 mL two-necked round-bottom-flask equipped with a water condenser in an oil bath with a magnetic stirrer. To obtain the pertinent catalyst for this transformation, a typical reaction is conducted using 10 mg of catalyst in acetonitrile as a solvent and 30% H_2O_2 as an oxidant at 60°C for 1 h. The influence of the various parameters, for instance, mole ratio of substrate to oxidant, diverse temperature, oxidants, catalytic amount, solvent, solvent amount and time are also inspected in order to acquire the optimized reaction condition.

To commence, the catalyst is dispersed in 5 mL of solvent and stirred for 10 min. followed by addition of reactant molecule and kept for stirring for another 10 min afterwards oxidant is added. Here, H_2O_2 is strategically added dropwise in order to avoid the bulk decomposition of an oxidant. A small aliquot is taken at pre-decided time intervals to evaluate the formation of yield subjected to GC analysis equipped with a flame ionization detector (FID). Typically, reaction flask is feed with 10 mmol of norbornene, 10 mmol of

30% H_2O_2, 5 mL of acetonitrile as a solvent and 10 mg of catalyst, such as, graphite, GO, Cl-*f*-GO, neat complxes like Co-salen, VO-salen, VO-salen, Co-*f*-GO, VO-*f*-GO and Cu-*f*-GO and equilibrated at 60 °C for 1 h.

As a result of this heterogeneous epoxidation of nornornene, in addition to the formation of 2,3-epoxy norbornane as major product, exo/endo norborneols and 2-norbornanone as by-products are also identified in small amount.

5.3.1. Impact of catalysts

The results of this catalytic reaction have been recapitulated in Table 5.2. A quick look of Table 5.2 divulges the significance of the catalyst. Very little conversion of norbornene is observed with pristine graphite (1.55%). GO and Cl-*f*-GO exhibits 3.67% and 6.76% conversion of norbornene, respectively. However, neat Co-salen, VO-salen and Cu-salen demonstrates 3.12%, 41.93% conversion of with 73.78% epoxide selectivity and 14.02% conversion with 25.33% epoxide selectivity, respectively. If we look for the catalysts function, Co-*f*-GO gives 1.59% conversion; Cu-*f*-GO offers 10.32% conversion with 19.11% selectivity and VO-*f*-GO attains 35.14% conversion of norbornene with 64.45% epoxide selectivity. As a result of achieving higher conversion with VO-*f*-GO, we have chosen this catalyst for further exploration on the influence of other experimental variables.

Table 5.2

Impact of varying catalysts on epoxidation of norbornene.

Systems	Norbornene Conversion (%)	Epoxide Selectivity (%)	Others Selectivity (%)	TOF[a] (h^{-1})
Graphite	1.55	-	-	-
GO	3.67	-	-	-
Cl-*f*-GO	6.76	-	-	-
Co-salen	3.12	-	-	6.00
Cu-salen	14.02	25.33	74.67	18.75
VO-salen	41.93	73.78	26.22	60.36
Co-*f*-GO	1.59	100	0	2.89
Cu-*f*-GO	10.32	19.11	80.89	13.81
VO-*f*-GO	35.14	64.45	35.55	50.58

Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), catalyst (10 mg), 60 °C, acetonitrile (5 mL), 1 h.

[a]TOF: Moles of norbornene converted per mole of metal per hour.

5.3.2. Impact of mole ratio

To determine the impact of varying mole ratios of a substrate to the oxidant, this oxidation reaction of norbornene is conducted with four different mole ratios viz. 1:1, 1:1.5, 1:2 and 1:2.5 by keeping all other parameters fixed. As can be seen Fig. 5.18, 1:1 concentration of H_2O_2 offers 35.14% norbornene conversion and 64.45% epoxides selectivity. On the other hand, inverted trend has been found on increasing mole ratio. 1:1.5 mole ratio has resulted in 17% conversion and sole epoxides product (100%). Further increase in mole ratio (1:2) lowers the conversion of norbornene to 16% with 100% epoxide selectivity. A higher concentration of H_2O_2 (1:2.5) prolongs downward trend and conversion meet the number 10.93% with 100% single product selectivity. Here, conversion and selectivity both are decreased with increasing mole ratio. Hence, in an attempt to reach higher conversion with maximum epoxide yield, we have chosen 1:1 as a preferred mole ratio to probe the impact of other parameters.

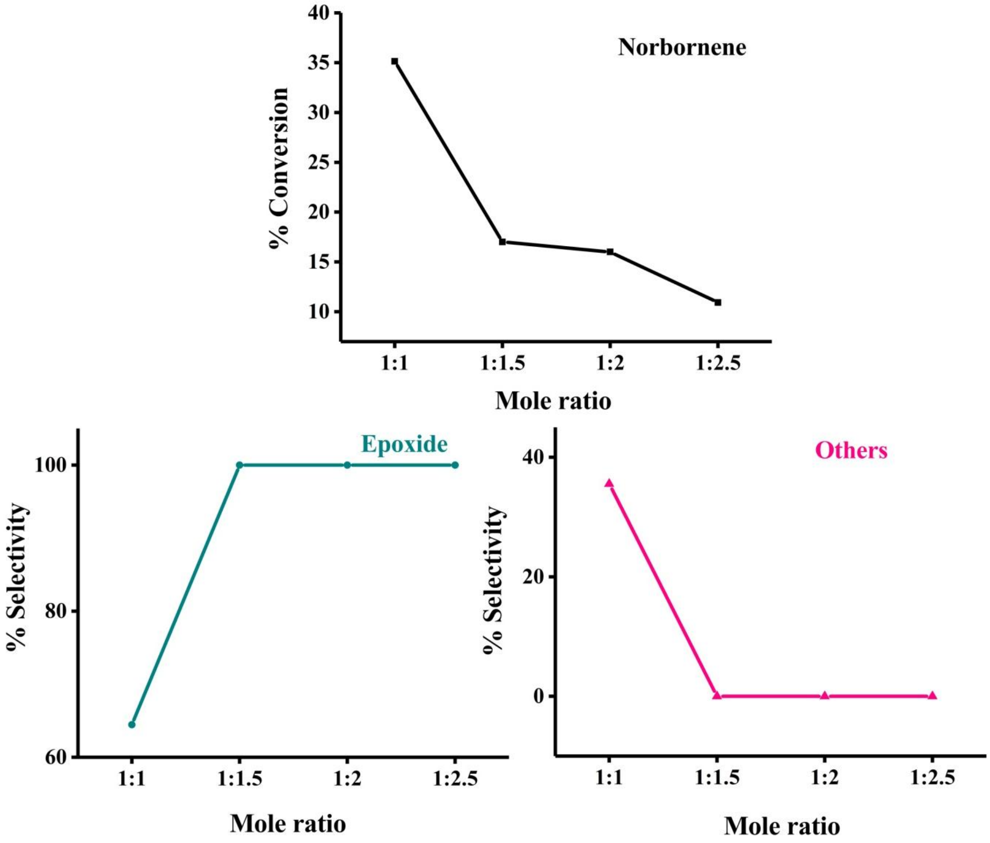

Fig. 5.18. Impact of varying mole ratio on the epoxidation of norbornene. Reaction condition: norbornene (10 mmol), 30% H_2O_2 (mmol), VO-*f*-GO (10 mg), 60 °C, acetonitrile (5 mL), 1 h.

5.3.3. Impact of solvent

As discussed in the previous sub-chapter, solvent properties affect the conversion and selectivity of the desired product[23]. This study is intended to probe the effect of various solvents, for instance, N,N-dimethylformamide (DMF), toluene, methanol, acetonitrile, 1,4-dioxane, and ethylene glycol on the epoxidation of norbornene. As shown in Fig. 5.19, DMF gives very inferior norbornene conversion of 2.4%; while 10.04% conversion of norbornene with 100% epoxide selectivity is observed with toluene. Methanol presents 27.73% conversion of norbornene and 28.21% epoxide selectivity; however, acetonitrile offers 35.14% conversion of norbornene with 64.45% epoxide selectivity. In contrast to this, 1,4-dioxane promotes the reaction with 89.49% conversion of norbornene with 45.83% epoxide selectivity. As per expectation, ethylene glycol, being a model solvent, offers 99.89% conversion of norbornene with 96.4% selectivity of epoxide. Consequently, ethylene glycol is chosen as the preferred solvent for further exploration.

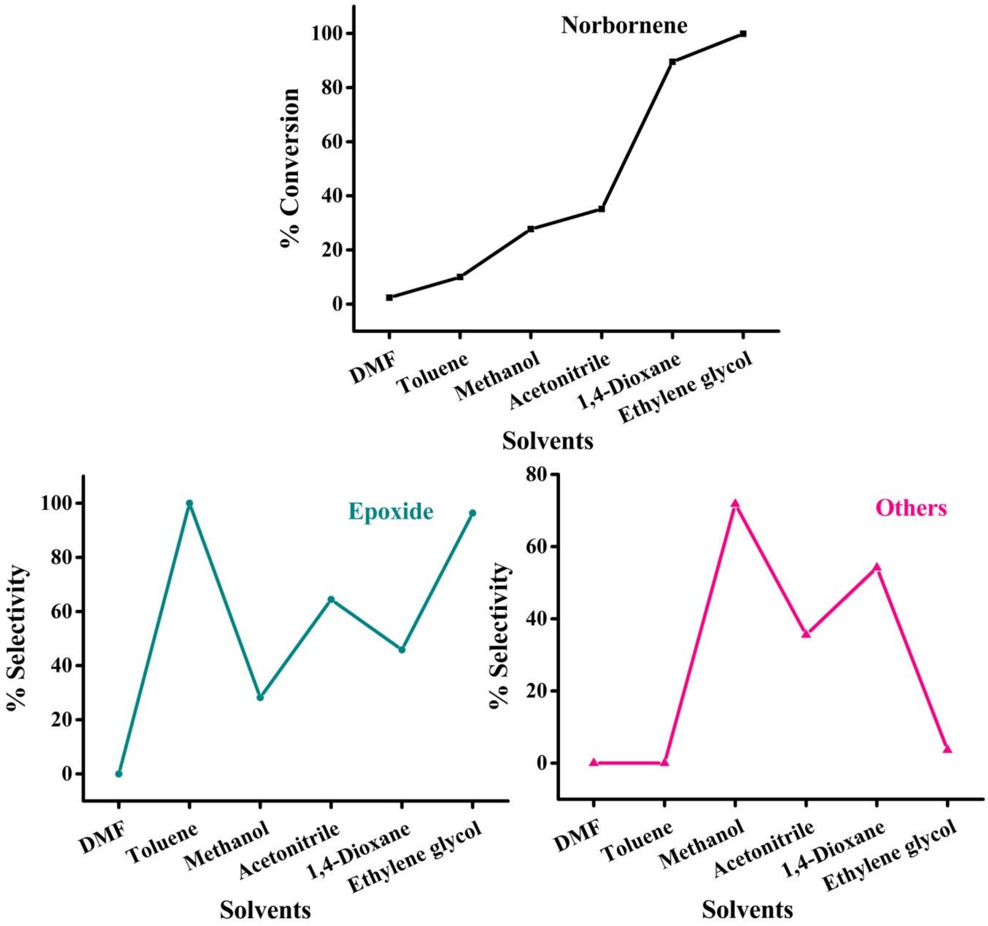

Fig. 5.19. Impact of varying solvent on the epoxidation of norbornene. Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (10 mg), 60 °C, solvent (5 mL), 1 h.

5.3.4. Impact of solvent amount

We have inspected the reaction by changing the amount of solvent as 2, 5 and 10 mL, to get the insight of solvent amount on this transformation. As shown in Fig. 5.20, pathetic conversion of norbornene (3.77%) is obtained with 2 mL of solvent. On increasing the amount of ethylene glycol from 2 to 5 mL, conversion also exhibits the similar trend and reaches to the 99.82% along with 96.38% epoxide selectivity. On further rising in the amount of solvent (10 mL), conversion remains almost same (99.45%), however, epoxide selectivity decreased by 3.4% and found to be 93.16%. The explanation for this reduction may be given as dilution can causes side reaction which results in lowering of selectivity of key product and increase in by-products[26]. Therefore, we have chosen 5 mL as the preferred solvent amount for further optimization of reaction parameters.

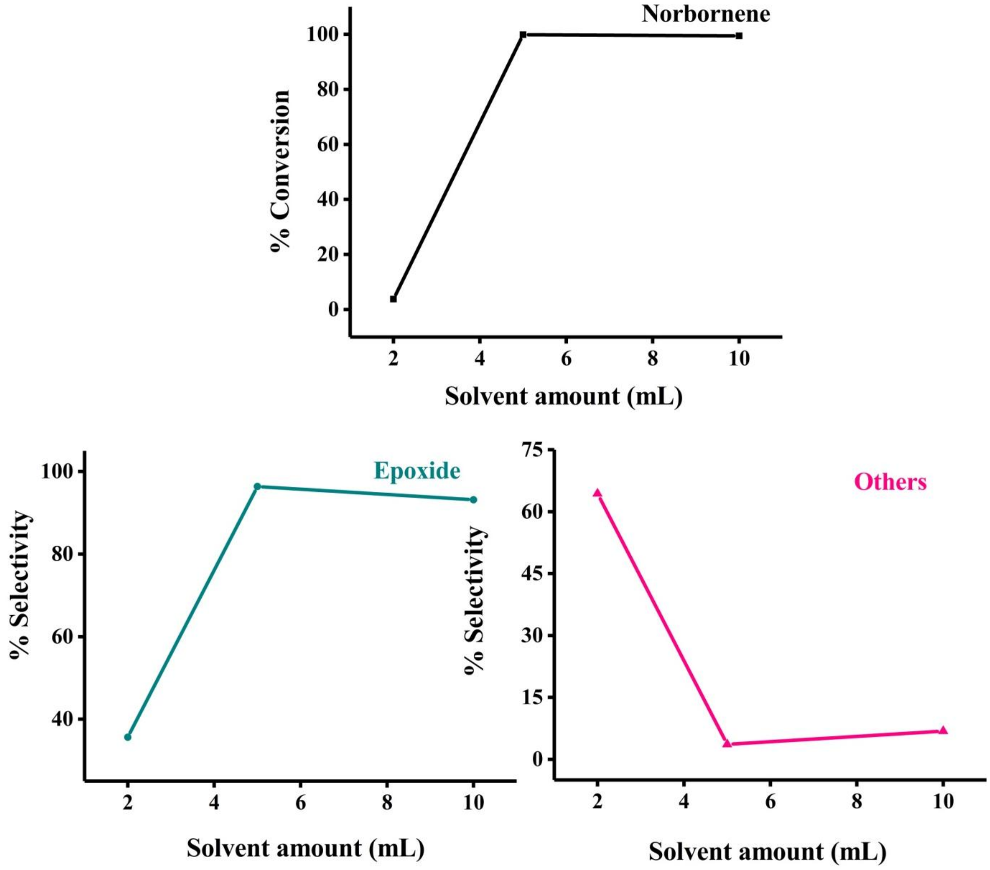

Fig. 5.20. Impact of varying solvent amount on the epoxidation of norbornene. Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (10 mg), 60 °C, ethylene glycol (mL), 1 h.

5.3.5. Impact of time

To determine the correct time for this chemical transformation, four different times viz. 0.5, 1, 2 and 3 h is exercised with keeping other parameters fixed. The conversion of norbornene as a function of time is portrayed in Fig. 5.21. As can be seen, 99.89% norbornene conversion is achieved at 0.5 h with 96.4% epoxide selectivity; while on continuing the reaction to 1 h, no change is observed in the conversion (99.86%) and selectivity (96.32%). To explore the effect of more reaction time, it continues to 2 and 3 h. Aliquot of the reaction mixture of 2 h examined by GC analysis, demonstrates 99.6% conversion with 96.1% selectivity and sample at 3 h exhibits same 99.6% conversion with little decreased (94.97%) in epoxide selectivity. Accordingly, we have chosen 0.5 h as the preferred reaction time for further investigation.

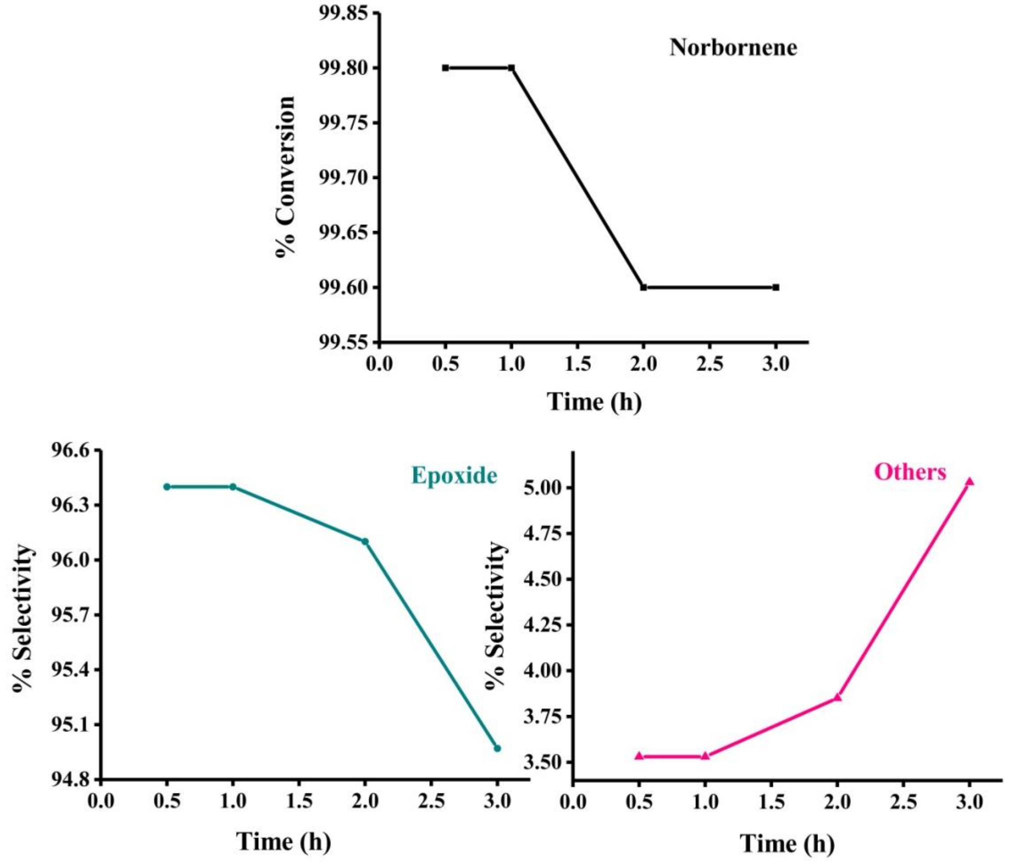

Fig. 5.21. Impact of varying time on the epoxidation of norbornene.

Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (10 mg), 60 °C, ethylene glycol (5 mL), time (h).

5.3.6. Impact of oxidant

Besides 30% H_2O_2, effect of another oxidant, TBHP, also inspected for this transformation. The data of this study is screened in Fig. 5.22. It has been observed form the figure that conversion of norbornene increased with TBHP and achieves maximum 98.94% with 98.15% epoxide selectivity. This result is found to be inferior to that of 30% H_2O_2 which offers 99.89% conversion and 96.4% epoxide selectivity. Although epoxide selectivity in TBHP is higher, we have preferred 30% H_2O_2 due to its environmentally benign nature and decided to explore other parameters with 30% H_2O_2.

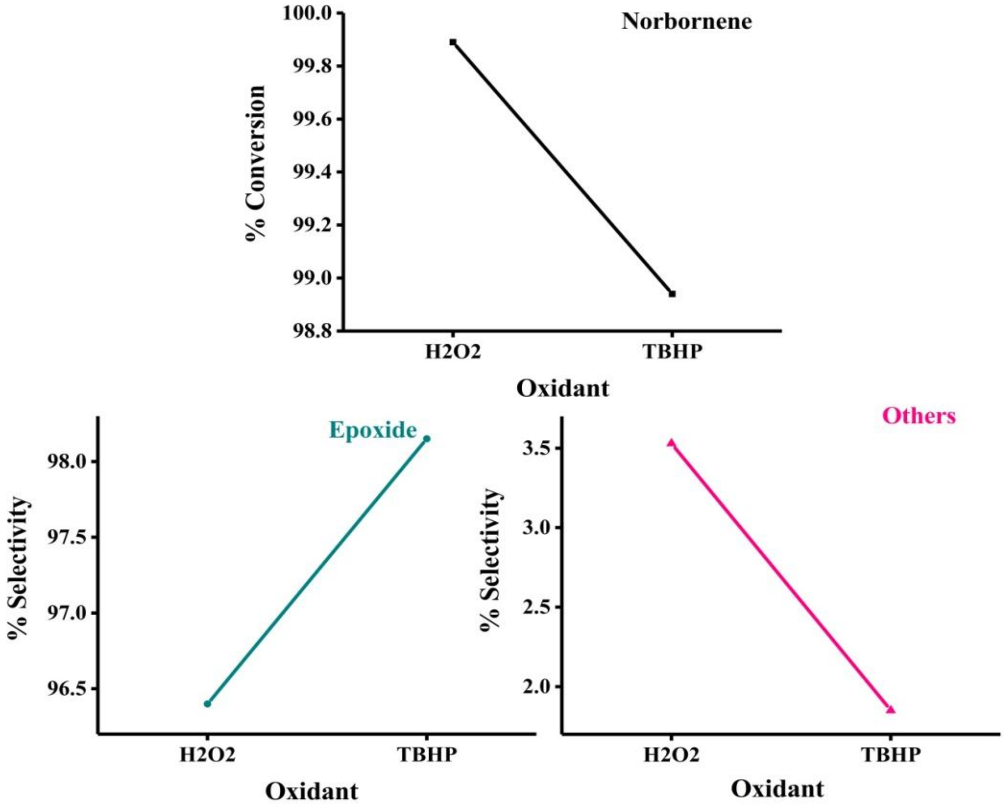

Fig. 5.22. Impact of oxidant on the epoxidation of norbornene.

Reaction condition: norbornene (10 mmol), oxidant (10 mmol), VO-*f*-GO (10 mg), 60 °C, ethylene glycol (5 mL), 0.5 h.

5.3.7. Impact of amount of catalyst

To determine the precise quantity of VO-*f*-GO, three different concentrations viz. 10, 20 and 30 mg of catalyst is studied for the epoxidation of norbornene over 30% H_2O_2 as an oxidant using ethylene glycol as a solvent. The outcome of the reaction is represented in Fig. 5.23. Higher norbornene conversion of 99.89% with 96.4% epoxide selectivity is monitored at lower catalyst concentration (10 mg) and at higher concentration of catalyst no significant change is seen in to conversion. As can be seen from the figure, once achieved maximum conversion of norbornene with 10 mg, it remains almost constant on exercising higher loading of catalyst amount. Higher catalyst concentration viz. 20 and 30 mg offers 99.17% and 99.64%

norbornene conversion with 98.07% and 99.15% epoxide selectivity, respectively. As we have attained higher norbornene conversion with superior product selectivity with 30 mg of catalyst, it is chosen as the preferred catalyst loading.

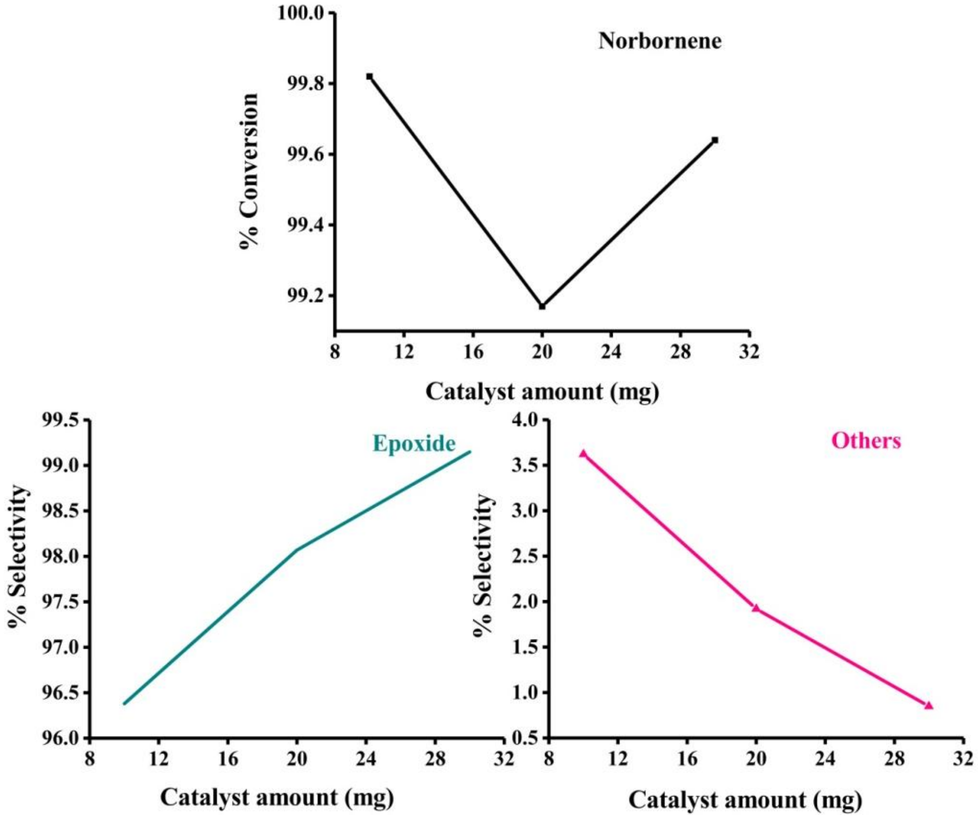

Fig. 5.23. Impact of carrying catalyst amount on the epoxidation of norbornene. Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (mg), 60 °C, ethylene glycol (5 mL), 0.5 h.

5.3.8. Impact of temperature

Effect of four different reaction temperatures such as 50, 60, 70 and 80 °C on the epoxidation of norbornene is demonstrated in Fig. 5.24. It is visible from the figure that 99.17% conversion of norbornene is achieved with 97.6% epoxide selectivity at 50 °C. When temperature rises to 60 °C, maximum conversion of 99.64% of norbornene is monitored together with 99.15% epoxide selectivity. Moreover, on further increasing the temperature up to 70 °C, conversion follows the parallel increasing trend and achieves the figure of 99.93% with 97.87% epoxide selectivity. With the desire of achieving absolute conversion and selectivity, it is decided to perform the reaction with another temperature 80 °C. As per expectation, absolute (100%) conversion of norbornene is seen with 98.84% epoxide selectivity. Subsequently, 80 °C is chosen as representative temperature.

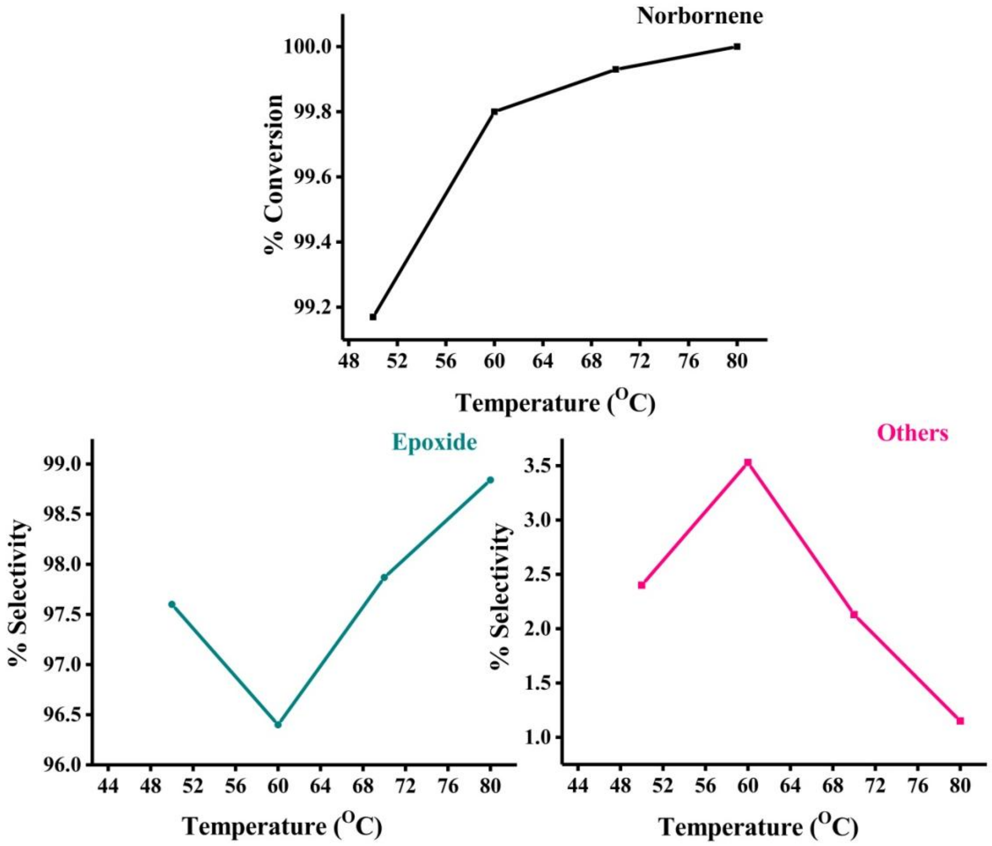

Fig. 5.24. Impact of varying temperature on the epoxidation of norbornene. Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (30 mg), temperature (°C), ethylene glycol (5 mL), 0.5 h.

5.3.9. Recyclability

To inspect the recyclability of the as-prepared heterogeneous catalyst for this transformation, the catalyst is recovered by filtration from the reaction mixture and washed with solvent followed by oven drying prior to employing for further catalytic test. The reaction mixture of each catalytic experiment is analyzed by GC under the same conditions as employed for the previous catalytic experiments for determining the optimized reaction parameters. The results of recyclability study are demonstrated in Fig. 5.25. It is apparent form the figure that this catalyst is recycled for three times and conversion in the first to 3rd recycle is 98.15%, 94.05%, 89.53% and selectivity is 97.01%, 92.89% and 89.98%, respectively. This lower recyclability of the catalysts is might be due to leaching of metal ions.

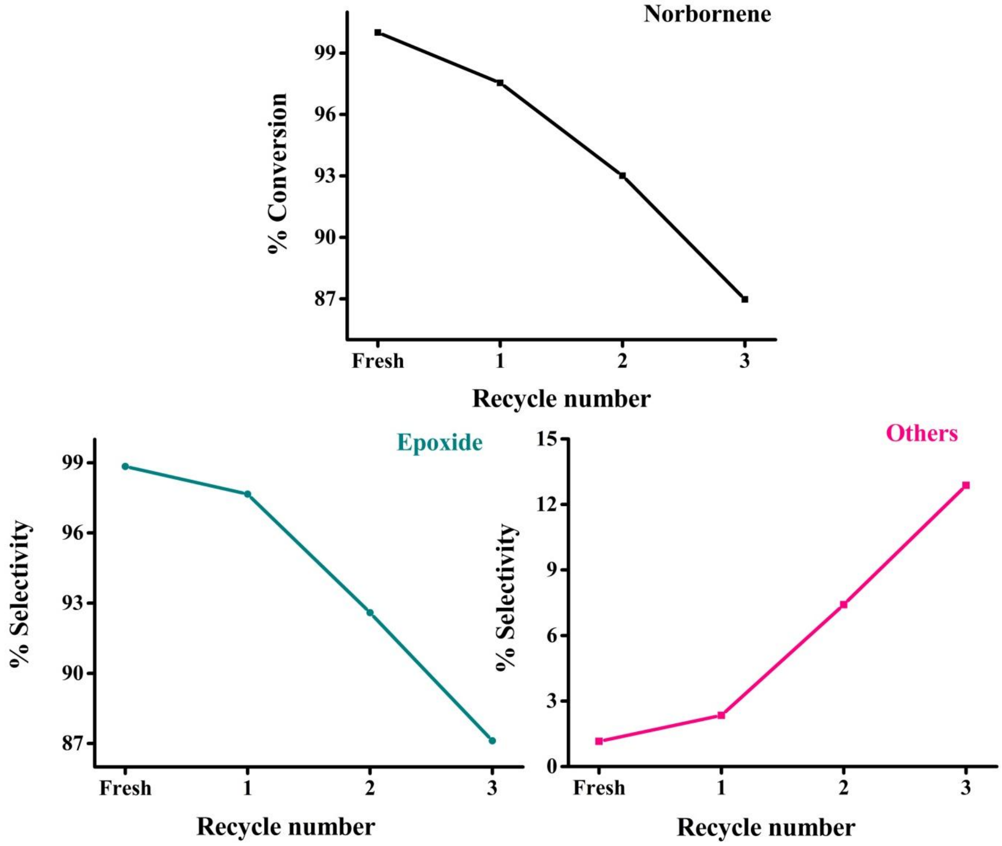

Fig. 5.25. Recyclability test on the epoxidation of norbornene.

Reaction condition: norbornene (10 mmol), 30% H_2O_2 (10 mmol), VO-*f*-GO (30 mg), 80 °C, ethylene glycol (5 mL), 0.5 h.

5.3.10. Conclusion

The catalytic activity of the catalysts prepared by functionalization on the carboxylic acid groups of GO has been studied over selective epoxidation of norbornene. Amongst all synthesized catalysts, VO-*f*-GO is seen to be appropriate and productive catalyst for this selective epoxidation of norbornene with 100% conversion and 98.84% epoxide selectivity. The influences of different parameters like different mole ratio of oxidant to substrate, temperature, time, catalyst amount, solvents, amount of solvent, oxidant have also been studied. This catalyst can be recycled three times.

5.4. Selective oxidation of glucose

In this sub-chapter we have tested the aptitude of as-prepared heterogeneous catalysts for the selective oxidation of glucose to gluconic acid using H_2O_2 as a greener oxidant. The effect of water as a greener solvent for this transformation also analyzed. The catalytic oxidation of glucose over the fabricated catalysts is carried out in a 50 mL two-necked round-bottom-flask furnished with water condenser in an oil bath with a magnetic stirrer. In a standard reaction condition to discover the best-suited catalyst for this transformation, a typical reaction is carried out with arbitrary catalyst amount (10 mg), temperature (80°C), ethylene glycol as a solvent and 30% H_2O_2 as an oxidant for 3 h. Diverse reaction parameters, for instance, impact of the varying mole ratio of substrate to oxidant, temperature, oxidant, amount of catalyst, solvent, solvent amount and time are inspected to acquire the optimized reaction condition.

First, catalyst is stirred in ethylene glycol for 10 min. followed by the substrate addition and stirred again for 10 min. Then add oxidant drop-wise and this final reaction mixture is then stirred for an experimentally pre-decided time to achieve the maximum conversion and selectivity. Formation of the product is analyzed by GC analysis of aliquots of the reaction mixture drawn at diverse time intervals.

For the pilot reaction, 6 mmol of glucose, 6 mmol of 30% H_2O_2, 5 mL ethylene glycol and 10 mg of catalyst (graphite, GO, Cl-*f*-GO, Cu-salen, VO-salen, Cu-salen, Co-*f*-GO, VO-*f*-GO and Cu-*f*-GO) is fed to a reaction container and equilibrated at 80 °C for 3 h. As a result of heterogeneous oxidation, gluconic acid (GA) is found to be the main product.

5.4.1. Impact of catalysts

The assessment of assorted heterogeneous catalysts and its effect on the glucose conversion and product selectivity are tabulated in Table 5.3. As can be seen, little or no conversion is achieved with pristine graphite, GO and Cl-*f*-GO. However, Co-salen, VO-salen and Cu-salen shows almost comparable conversion of 98.50%, 99.46% and 99.83%, respectively of glucose with 99.36%, 100% and 100% GA selectivity, respectively is observed. While Co-*f*-GO offers 93.54% conversion with 97.42% selectivity, VO-*f*-GO exhibits 94.76% conversion with 100% selectivity and Cu-*f*-GO shows 96.98% conversion of glucose with 100% selectivity of GA. Higher conversion of glucose is observed with Cu-*f*-GO, hence, we have chosen it as preferred catalyst for the optimization of other reaction parameters.

Table 5.3

Impact of varying catalysts on the oxidation of glucose.

Systems	**Glucose Conversion (%)**	**GA Selectivity (%)**	**TOF[a] (h^{-1})**
Graphite	0.30	-	-
GO	0.40	-	-
Cl-*f*-GO	23.04	100	-
Co-salen	98.50	99.36	107.51
VO-salen	99.46	100	85.90
Cu-salen	99.83	100	80.14
Co-*f*-GO	93.54	97.42	102.09
VO-*f*-GO	94.76	100	81.84
Cu-*f*-GO	96.98	100	77.85

Reaction condition: glucose (6 mmol), 30% H_2O_2 (6 mmol), catalyst (10 mg), 80 °C, ethylene glycol (5 mL), 3 h.

[a] TOF: Moles of glucose converted per mole of metal per hour.

5.4.2. Impact of time

To determine the correct time for this heterogeneous oxidation of glucose, three different time periods such as 1, 2 and 3 h (Fig. 5.26) are employed. After 1 hour, 97.90% conversion of glucose is obtained with 100% selectivity of GA. However, if we continue the reaction for 2 h, conversion is seen to be decreased to 98.52% with no change in selectivity. At this point, inverted trend of glucose conversion with time is seen. To corroborate this down trend propensity with time, the reaction mixture is analyzed at 3 h and the similar trend is observed. After 3 h, conversion falls to 96.98% while GA selectivity is found to be 100%. The possible justification for this decline in conversion with time may be due to reversible nature of the reaction. Consequently, we have determined to set the reaction time 2 h for further exploration of other parameters.

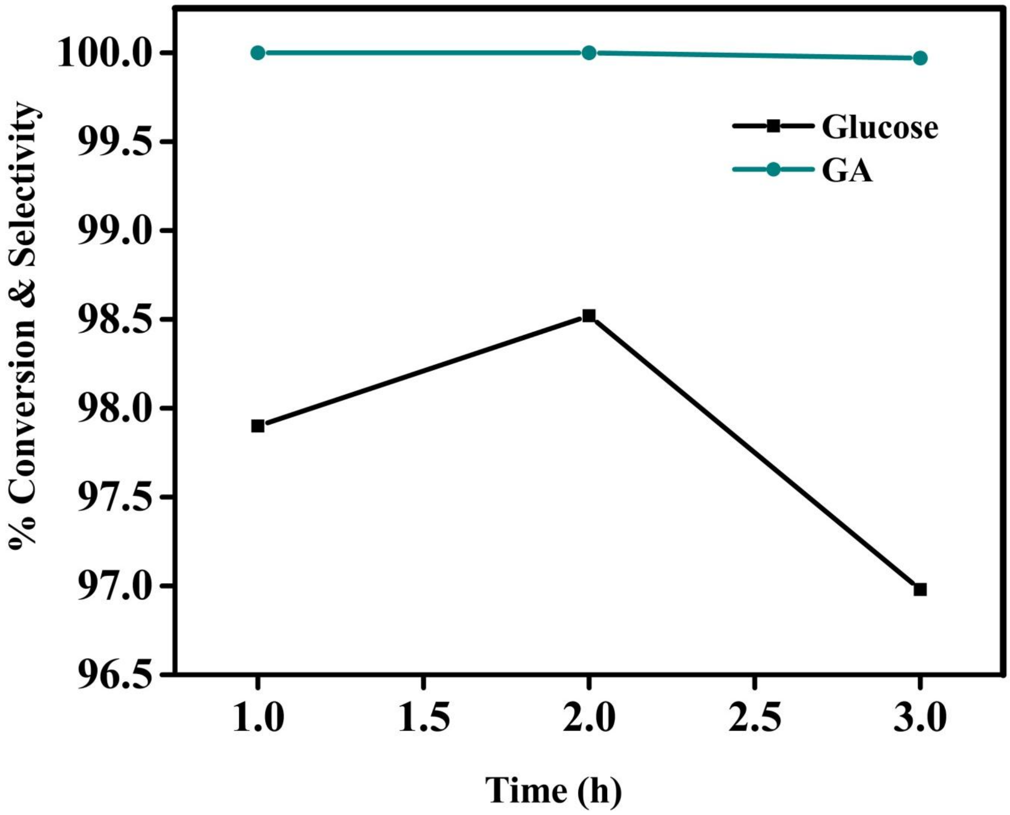

Fig. 5.26. Impact of varying time on the oxidation of glucose.
Reaction condition: glucose (6 mmol), 30% H_2O_2 (6 mmol), Cu-*f*-GO (10 mg), 80 °C, ethylene glycol (5 mL), time (h).

5.4.3. Impact of mole ratio

Different mole ratios of a substrate to the oxidant such as 1:1, 1:1.5, 1:2, 1:2.5 are exercised to inspect their effect on the oxidation of glucose by keeping all other parameters fixed and the results are depicted in Fig. 5.27. Lower mole ratio (1:1) offers 98.52% glucose conversion with 100% GA selectivity. On increasing mole ratio to 1:1.5, conversion also shows increasing trend and achieved 98.81% with 99.69% GA selectivity. Further increasing mole ratio to 1:2, glucose conversion reached maximum to 99.07% with 100% selectivity of GA. However, higher mole ratio of H_2O_2 (1:2.5), lowers the glucose conversion to 96.98% but selectivity does not affect and remains 100%. This lowering of conversion with higher ratio of H_2O_2 may be explained as reversible nature of the reaction. Hence, we have chosen 1:2 as preferred mole ratio for the investigation of other reaction parameters.

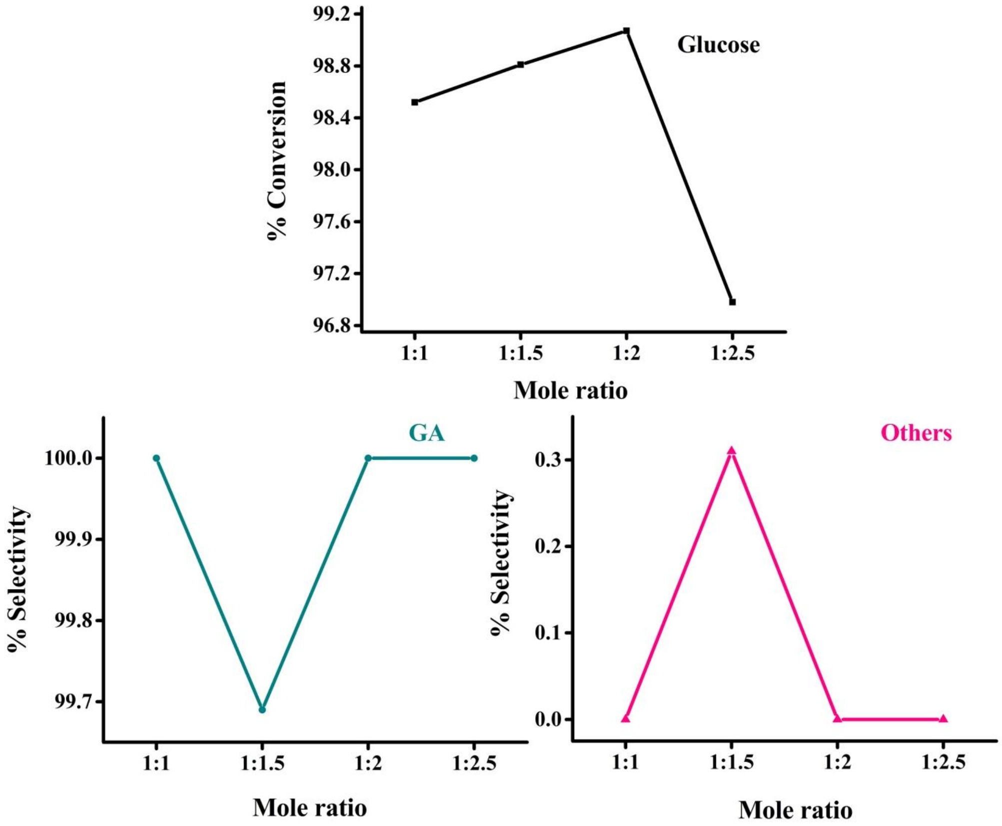

Fig. 5.27. Impact of varying mole ratio on the oxidation of glucose.
Reaction condition: glucose (6 mmol), 30% H_2O_2 (mmol), Cu-*f*-GO (10 mg), 80 °C, ethylene glycol (5 mL), 2 h.

5.4.4. Impact of solvent

Solvent may have an effect on the conversion, stability and selectivity of the desired product[23]. This study is intended to test the practicality of solvent effect on the conversion of glucose and selectivity of GA. Since, glucose is soluble in water, N,N- dimethylformamide (DMF) and ethylene glycol, these solvents are opted to study their effect on this transformation. As shown in Fig. 5.28, DMF offers almost no conversion of glucose (0.28%), while 10.1% conversion of glucose with 82.87% selectivity of GA is observed with water. In order to further increase the conversion, ethylene glycol is studied for this transformation. It is proved to be a model solvent for this transformation by giving 99.07% conversion of glucose with 100% selectivity of GA. As a result, ethylene glycol is chosen as the preferred solvent for this transformation.

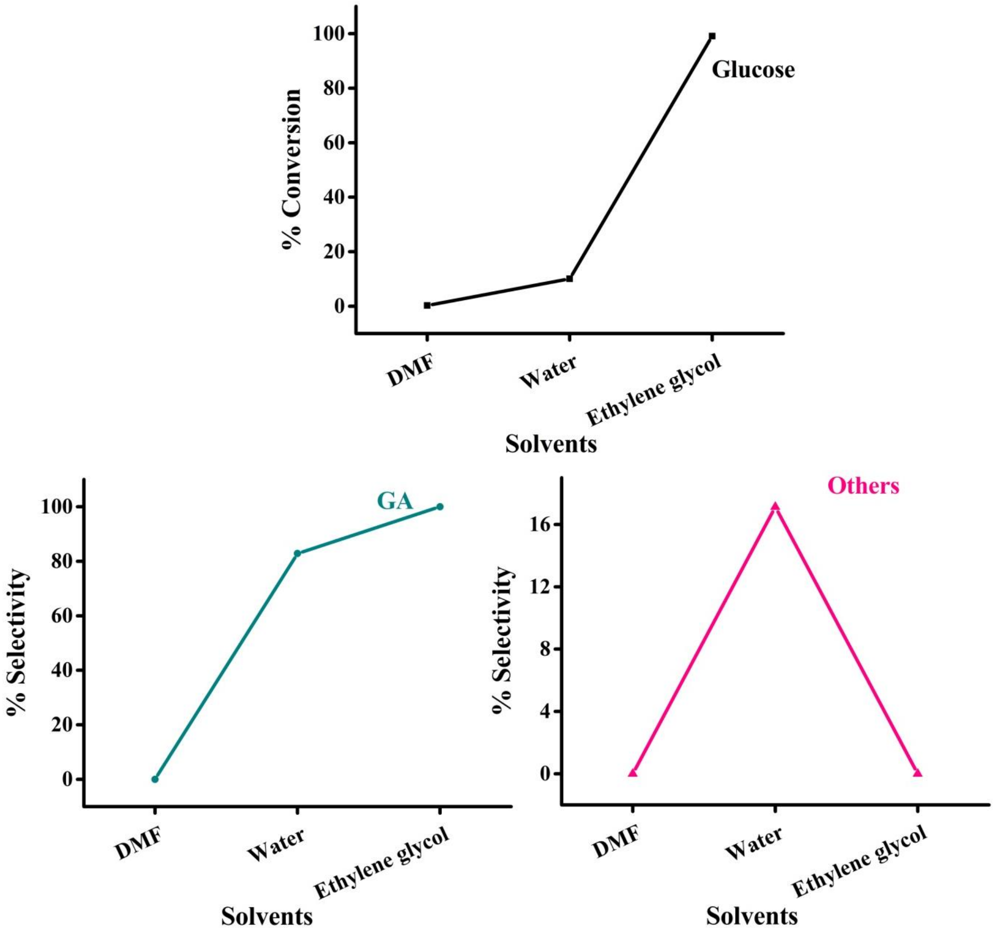

Fig. 5.28. Impact of varying solvents on the oxidation of glucose.

Reaction condition: glucose (6 mmol), 30% H_2O_2 (12 mmol), Cu-*f*-GO (10 mg), 80 °C, solvent (5 mL), 2 h.

5.4.5. Impact of solvent amount

Different solvent amounts viz. 2, 5 and 10 mL are taken to check their effects for oxidation of glucose and their results are shown in Fig. 5.29. It is apparent from the figure that 2 mL quantity of solvent offers highest conversion of glucose (99.8%) with 100% selectivity of GA. However, on increasing solvent amount to 5 mL, it shows nearly similar conversion of 99.07% with 100% GA selectivity. Furthermore, increase in solvent amount

(10 mL), it lowers the conversion to 97.96% while selectivity of GA is not affected and remains 100%. The explanation for this reduction may be 10 mL of solvent amount dilutes the reaction mixture to a great extent[24]. Therefore, we have chosen 2 mL as the preferred solvent amount for further optimization of reaction parameters.

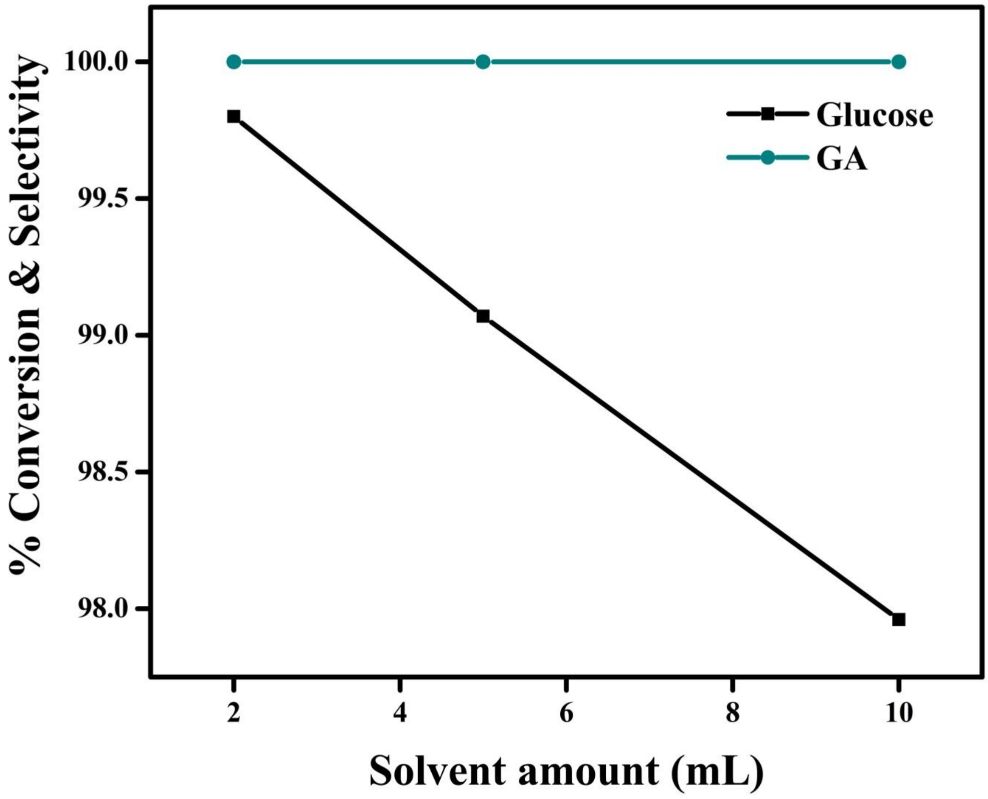

Fig. 5.29. Impact of varying solvent amount on the oxidation of glucose. Reaction condition: glucose (6 mmol), 30% H_2O_2 (12 mmol), Cu-*f*-GO (10 mg), 80 °C, ethylene glycol (mL), 2 h.

5.4.6. Impact of oxidant

Another oxidant 70% TBHP, in addition to 30% H_2O_2 is used to investigate its effect on this transformation. The results of this analysis are depicted in Fig. 5.30. The data divulges that TBHP is able to offer the absolute conversion of glucose with 100% selectivity of GA; while with 30% H_2O_2, 99.8% conversion is obtained with sole selectivity of GA. In this case, both the conversion and selectivity are more or less comparable. However, 30% H_2O_2 is chosen as preferred oxidant for further the catalytic investigation.

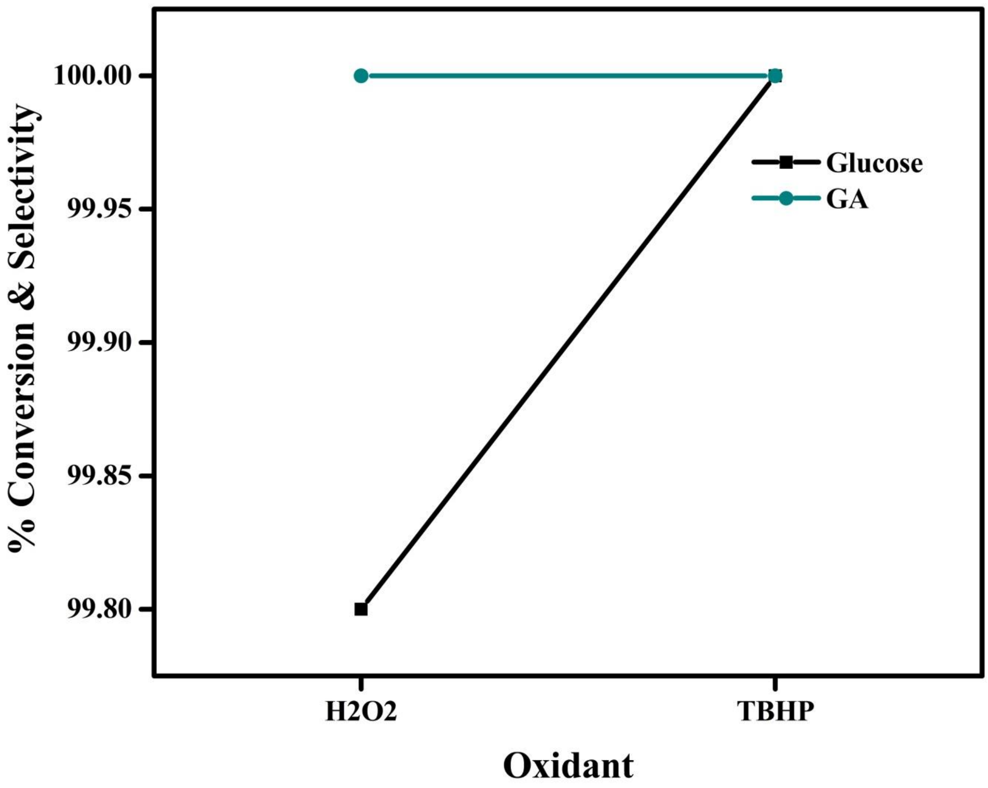

Fig. 5.30. Impact of oxidant on the oxidation of glucose.

Reaction condition: glucose (6 mmol), oxidant (12 mmol), Cu-*f*-GO (10 mg), 80 °C, ethylene glycol (2 mL), 2 h.

5.4.7. Impact of temperature

Effect of three different reaction temperatures like 70, 80 and 90 °C on this transformation is shown in Fig. 5.31. It is clear from the figure that 99.81% conversion of glucose is achieved with 100% GA selectivity at 70 °C. On increasing the temperature to 80 °C, no change in the conversion and selectivity is found. Observed conversion with 80 °C is 99.80% and selectivity of GA is 100%. Further rising temperature to 90 °C, short-fall of 2.38% in the conversion of glucose (i.e. 97.34%) is observed. This drop in the conversion may be due to faster catalytic decomposition of H_2O_2 at higher temperature. As a result, 70 °C is chosen as preferred reaction temperature.

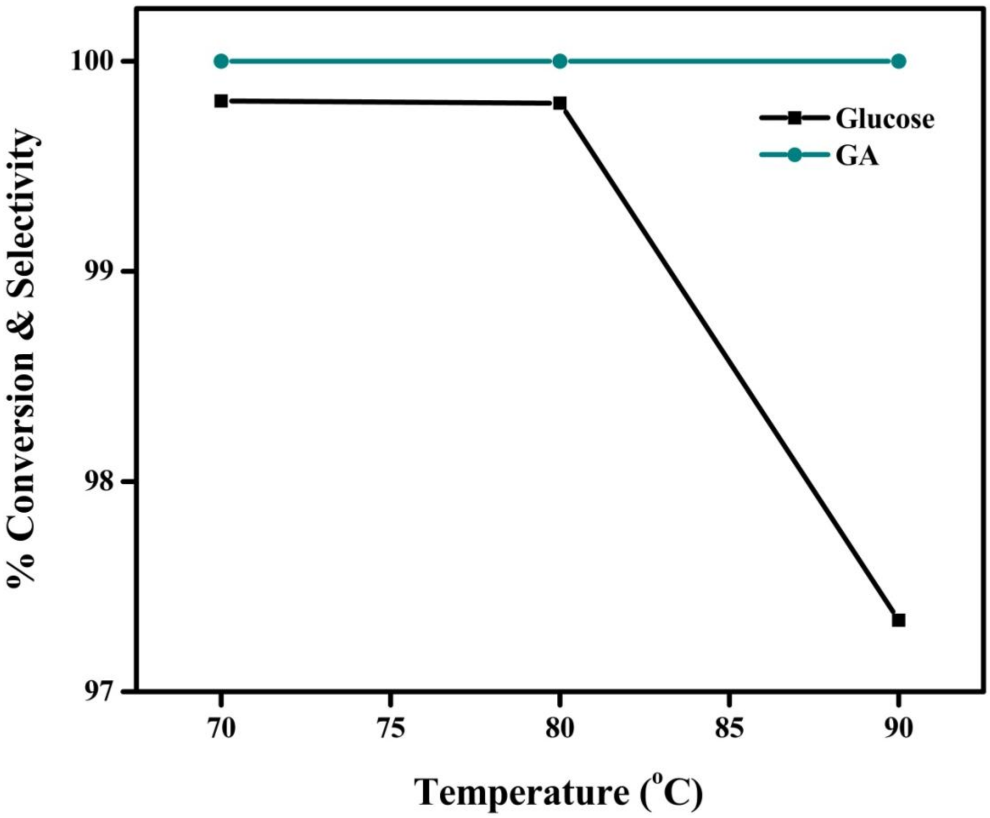

Fig. 5.31. Impact of varying temperature on the oxidation of glucose.
Reaction condition: glucose (6 mmol), 30% H_2O_2 (12 mmol), Cu-*f*-GO (10 mg), temperature (°C), ethylene glycol (2 mL), 2 h.

5.4.8. Impact of amount of catalyst

The effect of three different amounts of catalyst i.e. 10, 20 and 30 mg has been studied on this transformation (Fig. 5.32). 10 mg of catalyst amount exhibits 99.81% conversion of glucose with 100% GA selectivity. Further increase in catalyst amount to 20 mg, 99.4% conversion is obtained with 100% GA selectivity. It is apparent from the figure that with higher loading of catalyst conversion does not altered. We have further increased the catalyst amount to 30 mg and identical conversion of 99.4% is achieved with similar 100% GA selectivity. It can be said that once on achieving the equilibrium no change in the conversion is seen, hence, we have chosen lowest catalyst loading of 10 mg as preferred catalyst amount for this transformation.

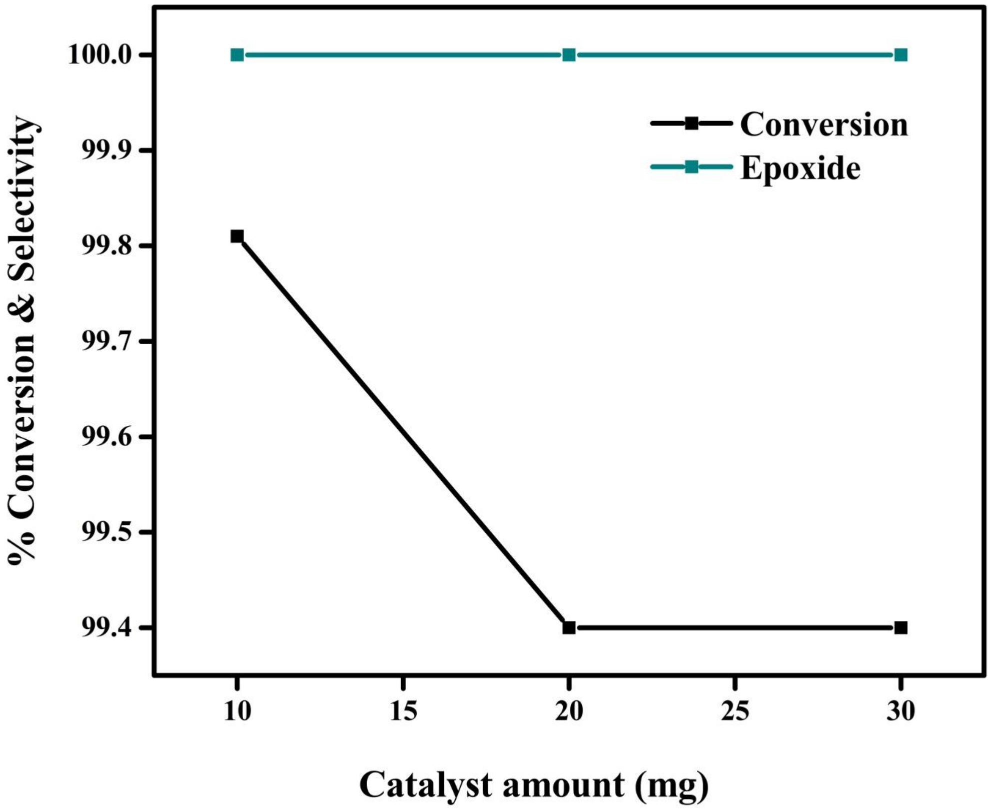

Fig. 5.32. Impact of varying amount of catalyst on the oxidation of glucose. Reaction condition: glucose (6 mmol), 30% H_2O_2 (12 mmol), Cu-*f*-GO (mg), 70 °C, ethylene glycol (2 mL), 2 h.

5.4.9. Recyclability test

To inspect the recyclability of the as-prepared heterogeneous catalyst for this transformation, the catalyst is recovered by filtration from the reaction mixture and washed with solvent followed by oven drying prior to employing for further catalytic test.The reaction mixture of each catalytic experiment is analyzed by GC under the same conditions as employed for the previous catalytic experiments for determining the optimized reaction parameters. Data screening the results of each recycle tests are depicted in Fig. 5.33. As can be seen, catalyst is recycled three times and the conversion in first to 3rd recycle is 96.29%, 92.51%, 87.49% and selectivity of GA is 98.95%, 96.76% and 94.23%, respectively.

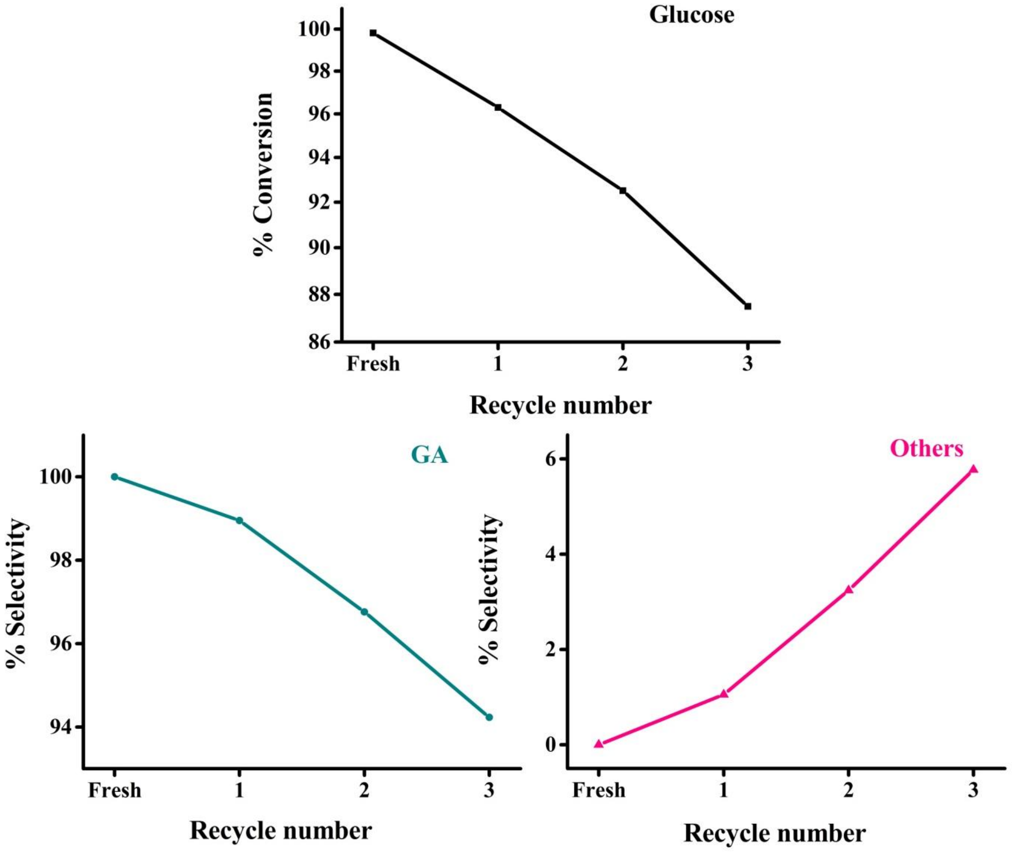

Fig. 5.33. Recyclability test of oxidation of glucose.

Reaction condition: glucose (6 mmol), 30% H_2O_2 (12 mmol), Cu-*f*-GO (10 mg), 70 °C, ethylene glycol (2 mL), 2 h.

5.4.10. Conclusion

This sub-chapter executed to inspect the catalytic aptitude of as-prepared catalysts by modifying the surface carboxylic acid groups of GOagainst the selective oxidation of glucose. Among them, Cu-*f*-GO is found to be highly effective and fruitful catalyst for this selective oxidation of glucose with 99.81% conversion and 100% GA selectivity. The influences of distinct parameters like mole ratio of oxidant to substrate, temperature, time, catalyst amount, solvents, amount of solvent and oxidant have also been studied. This catalyst can be reused three times.

5.5. References

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