6. Comparison study

In the previous chapters, successful synthesis, characterization and application of transition metal grafted GO supported heterogeneous catalysts in various oxidation reactions are discussed. This sub-chapter is intended to:

- Execute a comparative analysis of heterogeneous catalysts synthesized by sequential modification of –OH and –COOH functional groups of GO.
- Recognize the best suited catalyst based on the comparative analysis.
- Conclusion.

6.1. Comparative analysis of heterogeneous catalysts synthesized by sequential modification of –OH and –COOH functional groups of GO

As stated in the research objectives pertaining to the application of as-synthesized heterogeneous catalysts in the catalytic studies (See chapter 4 and 5), the heterogeneous catalysts synthesized by modifying two different functional groups of GO have comparable profiles and application that supports the validity of this comparative analysis.

The catalytic studies presented in chapter 4 and 5 are analyzed comparatively in this chapter. As there is no linear correlation between conversion or selectivity and the parameters like diverse catalysts and types of solvents, the other parameters considered for comparison are:

- Different catalyst amounts
- Varying mole ratios of substrate to oxidant
- Diverse solvents amount
- Varying Time
- Diverse temperature
- Oxidant and
- Recyclability

6.1.1. Different catalyst amount

It is apparent from the Table 6.1 that for oxidation of benzyl alcohol similar amount of catalyst is required but the catalyst synthesized by modifying –COOH groups has need of precursor to obtain desirable conversion and yield. For epoxidation of styrene, comparable amount of catalyst needed, but the conversion in –OH modified catalysts is high. However, in the epoxidation of norbornene, catalyst synthesized by modifying –COOH groups is needed in higher amount; while for glucose oxidation catalyst amount required for –OH modified catalyst is high. At the end of all this discussion, in the oxidation reactions of catalyst synthesized by modifying –COOH groups, mole ratio of substrate to oxidant is higher than catalyst synthesized by modifying –OH groups except norbornene. But in the norbornene oxidation, catalyst amount required is also high. Hence, if we take the overall series of developments into consideration, one can say that catalysts synthesized by modifying –OH groups are more productive.

Table 6.1

Comparison of varying catalyst amount

Catalytic oxidation reaction	**Catalysts synthesized by modifying –OH groups**	**Catalysts synthesized by modifying –COOH groups**	**Best suited functional groups to be modified (as per discussion in chapter 4 & 5)**
	Catalyst amount (mg)	**Catalyst amount (mg)**	
Benzyl alcohol	50	50	–OH
Styrene	10	10	–OH
Norbornene	10	30	–OH
Glucose	30	10	–COOH

6.1.2. Varying mole ratios of substrate to oxidant

As can be seen from the Table 6.2 that in the catalytic evaluation of catalyst synthesized by modifying –OH groups, mole ratio of substrate to oxidant required is 1:1, however, for the catalyst synthesized by modifying –COOH groups different mole ratios of substrate to oxidant are essential, which is relatively higher, except for norbornene. Conversely, for the oxidation of norbornene, higher conversion is obtained in case of –COOH modified catalyst. Hence, eventually –COOH group modified catalyst has proven the best in case of norbornene oxidation.

Table 6.2

Comparison of various mole ratios of substrate to oxidant

Catalytic oxidation reaction	**Catalyst synthesized by modifying –OH groups**	**Catalyst synthesized by modifying –COOH groups**	**Best suited functional groups to be modified (as per discussion in chapter 4 & 5)**
	Mole ratio	**Mole ratio**	
Benzyl alcohol	1:1	1:2.5	–OH
Styrene	1:1	1:2.5	–OH
Norbornene	1:1	1:1	–COOH
Glucose	1:1	1:2	–OH

6.1.3. Diverse solvent amount

Extent of solvent is crucial parameter as its disposal process is laborious and requires considerable efforts and time. Hence, we have analyzed this parameter and results are tabulated in Table 6.3. It is obvious from the table that solvent amount required in both –OH and –COOH groups modified catalysts are identical except in the oxidation of glucose. But the conversion in oxidation of benzyl alcohol and styrene is higher in case of catalyst synthesized by modifying –OH groups. However, in case of epoxidation of norbornene, higher conversion is obtained with the catalsyst synthesized by modifying –COOH groups. In glucose oxidation, lesser amount of solvent (2 mL) is sufficient for achieving higher conversion.

Table 6.3

Comparison of diverse solvents amount

Catalytic oxidation reaction	**Catalyst synthesized by modifying –OH groups**	**Catalyst synthesized by modifying –COOH groups**	**Best suited functional groups to be modified (as per discussion in chapter 4 & 5)**
	Solvent amount (mL)	**Solvent amount (mL)**	
Benzyl alcohol	5	5	–OH
Styrene	5	5	–OH
Norbornene	5	5	–COOH
Glucose	5	2	–COOH

6.1.4. Varying Time

The results divulge that for the oxidation of benzyl alcohol and glucose, the time required to achieve higher conversion is lower for the –OH modified catalytic systems. It is apparent for Table 6.4 that in case of styrene, higher conversion of 99.22% is obtained with catalyst synthesized by modifying –OH groups, but the time rewuired to achieve such conversion is 3 h which is higher thatn the in case of catalyst synthesized by modifying –COOH groups. For glucose oxidation, almost similar conversion is obtained (99.30% in case of catalyst synthesized by modifying –OH groups and 98.52% in case of catalyst synthesized by modifying –COOH groups) but the time required for achieving for such higher conversion is higher in case of catalyst synthesized by modifying –COOH groups.

Table 6.4

Comparison of varying time

Catalytic oxidation reaction	**Catalyst synthesized by modifying –OH groups**	**Catalyst synthesized by modifying –COOH groups**	**Best suited functional groups to be modified (as per discussion in chapter 4 & 5)**
	Time (h)	**Time (h)**	
Benzyl alcohol	20 min	1	–OH
Styrene	3	1	–COOH
Norbornene	1	0.5	–COOH
Glucose	1	2	–OH

6.1.5. Diverse temperatures

Temperature is one of the essential factors that have been taken into account as a crucial parameter in the development of greener synthesis. Table 6.5 represents the temperatures required for both catalytic systems in diverse oxidation reactions. As can be seen, temperature required for all the oxidation reactions are more or less analogous. In case of oxidation of benzyl alcohol, for the catalyst synthesized by modifying –COOH groups precoursor is needed; while for the epoxidation of styrene, highest conversion of 9.22% is obtained with the catalyst synthesized by modifying –OH groups. For the epoxidation of norbornene, lowest temperature (60°C) is required in –OH group modified catalyst. However, for oxidation of glucose higher conversion of 99.81% is experienced with the catalyst synthesized by modifying –COOH groups.

Table 6.5

Comparison of diverse temperatures

Catalytic oxidation reaction	**Catalyst synthesized by modifying –OH groups**	**Catalyst synthesized by modifying –COOH groups**	**Best suited functional groups to be modified (as per discussion in chapter 4 & 5)**
	Temperature (°C)	**Temperature (°C)**	
Benzyl alcohol	90	90	–OH
Styrene	80	80	–OH
Norbornene	60	80	–OH
Glucose	70	70	–COOH

6.1.6. Oxidant

Generally we have preferred to use 30% H_2O_2 as an oxidant owing to its greener approach. But we have also checked other oxidant viz. TBHP for all the oxidation of reactions. However, as per expectation, 30% H_2O_2 has proven to be desired oxidant. Besides this, in view of other advantages of 30% H_2O_2 as discussed in the preceding chapters, it is come up as the oxidant of choice. For the comparison point of view, we need to consider the concentration of 30% H_2O_2 used for oxidation and the results prove the –OH modified catalysts are admirable.

6.1.7. Recyclability

Similar to all studies and parameters that are in linear relationship with conversion and selectivity, in this case if all these parameters have been taken into consideration, –OH modified catalysts are proven best suited catalyst.

6.2. Recognize the best suited catalyst

The synthetic approach for the modification of both –OH and –COOH groups and fabrication of transition metal grafted GO supported heterogeneous catalysts is described in the chapter 2. Successful synthesis is evidently corroborated in the chapter 3. The purpose for which these catalysts are fabricated is accomplished by evaluating it in diverse catalytic reaction discussed in chapter 4 and 5. As a result of these catalytic inspections, we are able find the best suited functional groups for the modification and at the end best suited catalyst in terms of quality, reliability, vitality and recyclability.

The possible reason for the differences between these two catalytic systems may be as given below:

- C-NH_2 in –OH modification is relatively stronger than C-Cl bond in –COOH modification. This clearly reflects characterization and catalytic results.
- The presence of –COOH groups is responsible for more acidic characteristic in –OH modified catalyst than the catalysts synthesized by modifying –COOH groups.
- Fracture edges functional groups in –COOH modification forms more staked packing arrangement of GO nanosheets which may decrease the catalytically active sites compare to –OH modified catalysts.

6.3. Conclusion

After the successful synthesis and characterization of the transition metal grafted GO supported heterogeneous catalysts, it was applied for the catalytic aptitude study. As a result of this study and data summarised in this chapter, we can evidently enunciate the –OH modified catalysts as the preferred and best suited catalysts and –OH debris as the “site of a choice for modification”.