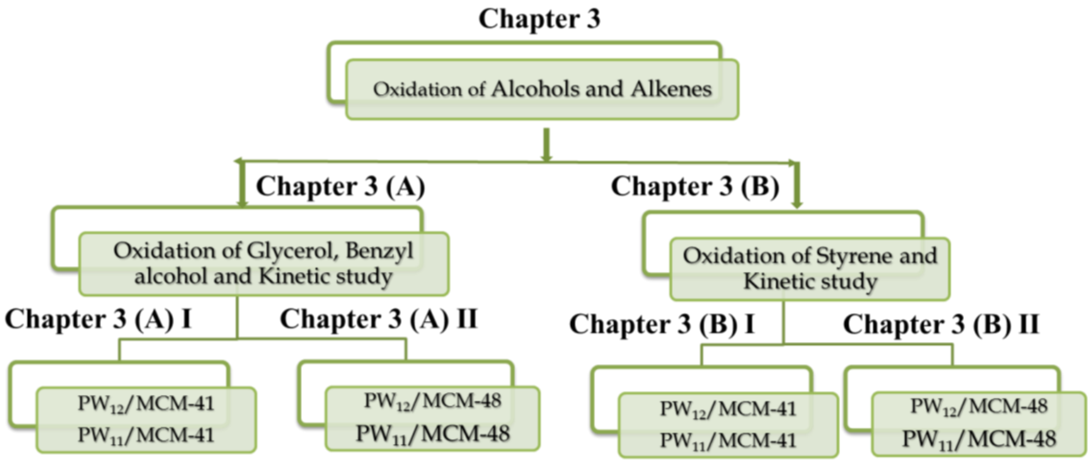
Chapter 3

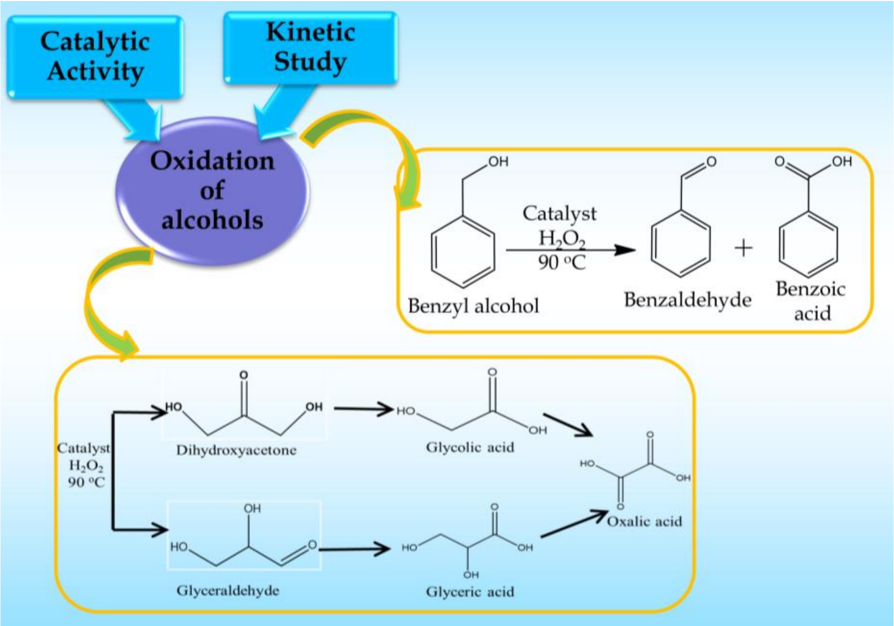
Oxidation reactions……

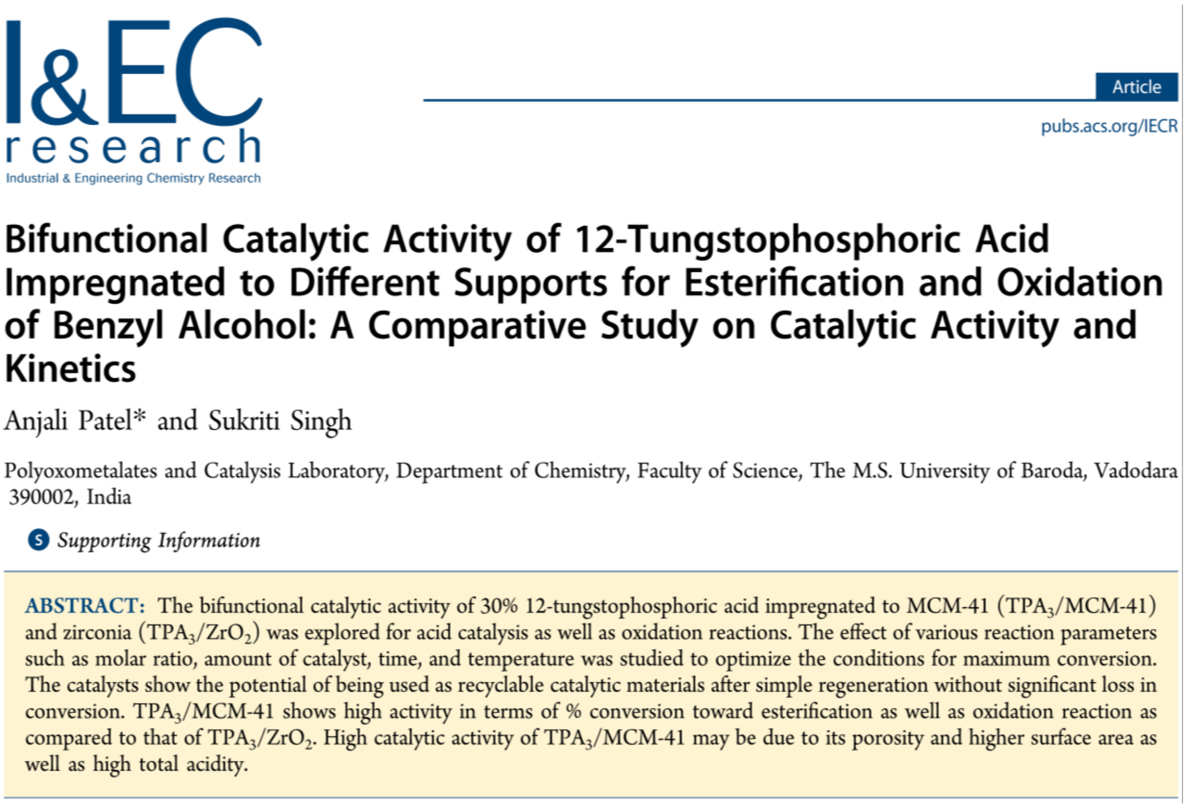


CHAPTER 3A

Oxidation of Alcohols…..

1) Glycerol
2) Benzyl Alcohol





I&EC research
Industrial & Engineering Chemistry Research
Article
pubs.acs.org/IECR

Bifunctional Catalytic Activity of 12-Tungstophosphoric Acid Impregnated to Different Supports for Esterification and Oxidation of Benzyl Alcohol: A Comparative Study on Catalytic Activity and Kinetics

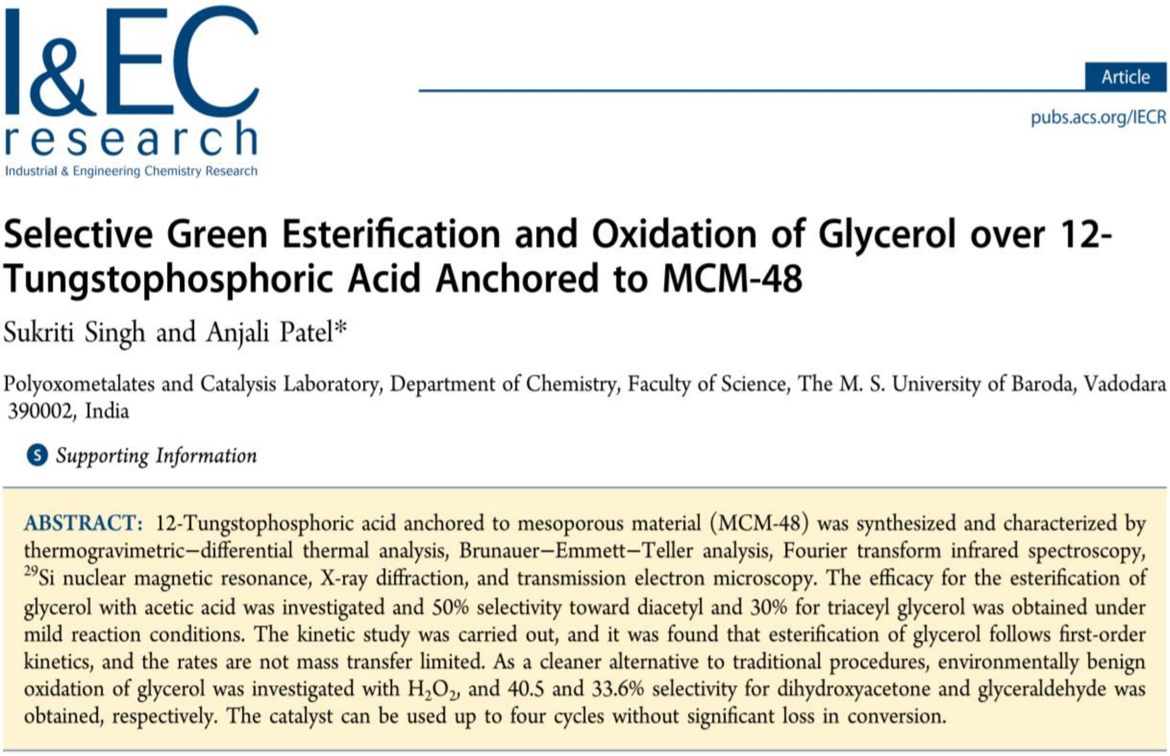
Anjali Patel* and Sukriti Singh

Polyoxometalates and Catalysis Laboratory, Department of Chemistry, Faculty of Science, The M.S. University of Baroda, Vadodara 390002, India

Supporting Information

ABSTRACT: The bifunctional catalytic activity of 30% 12-tungstophosphoric acid impregnated to MCM-41 (TPA_3/MCM-41) and zirconia (TPA_3/ZrO_2) was explored for acid catalysis as well as oxidation reactions. The effect of various reaction parameters such as molar ratio, amount of catalyst, time, and temperature was studied to optimize the conditions for maximum conversion. The catalysts show the potential of being used as recyclable catalytic materials after simple regeneration without significant loss in conversion. TPA_3/MCM-41 shows high activity in terms of % conversion toward esterification as well as oxidation reaction as compared to that of TPA_3/ZrO_2. High catalytic activity of TPA_3/MCM-41 may be due to its porosity and higher surface area as well as high total acidity.

Ind. Eng. Chem. Res. 2013, 52, 10896−10904



I&EC research
Industrial & Engineering Chemistry Research
Article
pubs.acs.org/IECR

Selective Green Esterification and Oxidation of Glycerol over 12-Tungstophosphoric Acid Anchored to MCM-48

Sukriti Singh and Anjali Patel*

Polyoxometalates and Catalysis Laboratory, Department of Chemistry, Faculty of Science, The M. S. University of Baroda, Vadodara 390002, India

Supporting Information

ABSTRACT: 12-Tungstophosphoric acid anchored to mesoporous material (MCM-48) was synthesized and characterized by thermogravimetric−differential thermal analysis, Brunauer−Emmett−Teller analysis, Fourier transform infrared spectroscopy, ^{29}Si nuclear magnetic resonance, X-ray diffraction, and transmission electron microscopy. The efficacy for the esterification of glycerol with acetic acid was investigated and 50% selectivity toward diacetyl and 30% for triaceyl glycerol was obtained under mild reaction conditions. The kinetic study was carried out, and it was found that esterification of glycerol follows first-order kinetics, and the rates are not mass transfer limited. As a cleaner alternative to traditional procedures, environmentally benign oxidation of glycerol was investigated with H_2O_2, and 40.5 and 33.6% selectivity for dihydroxyacetone and glyceraldehyde was obtained, respectively. The catalyst can be used up to four cycles without significant loss in conversion.

Ind. Eng. Chem. Res. 2014, 53, 14592−14600

Microporous and Mesoporous Materials 195 (2014) 240–249

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Undecatungstophosphate anchored to MCM-41: An ecofriendly and efficient bifunctional solid catalyst for non-solvent liquid-phase oxidation as well as esterification of benzyl alcohol

Anjali Patel*, Sukriti Singh

Polyoxometalates and Catalysis Laboratory, Department of Chemistry, Faculty of Science, The M.S. University of Baroda, Vadodara 390002, India

ARTICLE INFO

Article history:
Received 12 July 2013
Received in revised form 14 April 2014
Accepted 19 April 2014
Available online 26 April 2014

Keywords:
Undecatungstophosphate
Bifuctional catalyst
MCM-41
Oxidation
Esterification

ABSTRACT

Undecatungstophosphate anchored to MCM-41 was synthesized and characterized by various physico-chemical techniques. The bifunctional catalytic activity was evaluated for esterification as well oxidation reactions of benzyl alcohol. The influence of different parameters such as molar ratio, amount of catalyst, reaction time and reaction temperature on oxidation as well as esterification of benzyl alcohol was investigated for maximum conversion. Detailed kinetic studies reveal that the reactions follow first order kinetics and the low values of activation energy for esterification and oxidation indicates that the reaction rate is truly governed by the chemical step. The present bifunctional catalyst can be recycled without any significant difference in % conversion for both reactions. Further, oxidation and esterification of various alcohols were also carried out under optimized conditions to see the effect of chain length and type of alcohols.

Catal Lett (2016) 146:1059–1072
DOI 10.1007/s10562-016-1732-7

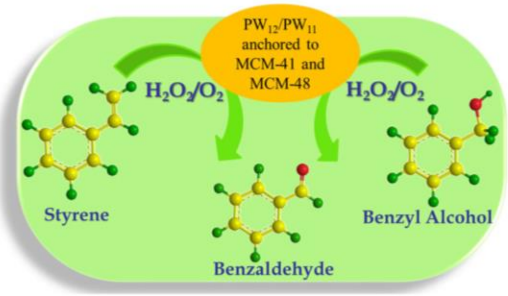
Environmentally Benign Oxidations of Alkenes and Alcohols to Corresponding Aldehydes over Anchored Phosphotungstates: Effect of Supports as Well as Oxidants

Sukriti Singh[1] · **Anjali Patel**[1]

Received: 5 March 2016 / Accepted: 13 March 2016

Abstract Series of catalysts comprising of parent phosphotungstate (PW_{12}) and mono lacunary phosphotungstate (PW_{11}) anchored to different mesoporous materials (MCM-41 and MCM-48) were prepared. Environmentally benign oxidation of alkenes and alcohols were carried out with H_2O_2 and molecular oxygen as oxidants. The influence of different parameters on the conversion as well as the selectivity was investigated. Comparative study was ascertained over anchored parent, lacunary phosphotungstates as active species and the supports. The kinetic and thermodynamic studies were correlated with the effect of support as well as active species. Moreover, the catalysts could be recovered and reused four times without significant loss in their activity and selectivity.

Graphical Abstract



Keywords 12-Tungstophosphoric acid · Mono lacunary phosphotungstate · Mesoporous supports · Environmental benign · Oxidation

Selective oxidation of alcohol is widely recognized as one of the most fundamental transformations in both laboratory and industrial synthetic chemistry, as resulting carbonyl compounds serve as important and versatile intermediates for synthesis of fine chemicals [1]. Many oxidizing reagents, including permanganate and dichromate, have been traditionally employed to achieve this transformation. These stoichiometric oxidants, have serious drawbacks as they are expensive and/or toxic, produce large amounts of waste and require solvents (as acetone, acetonitrile, and hexane) as well as phase transfer catalyst (PTC) [2-4]. Increasing environmental concerns have directed much attention towards development of promising catalytic protocols. Catalytic liquid phase oxidations employ soluble metal salts or complexes in combination with clean, inexpensive oxidants such as O_2, H_2O_2, or RO_2H. Among these, reactions catalyzed by high valent d^0 transition metals using H_2O_2 are the most studied [5]. O_2 is the most attractive oxidant, since it is cheap, abundant in atmosphere and it presents highest active. In this respect, POMs are suitable candidates for activation of H_2O_2 and they have been used as heterogeneous catalysts for oxidation reactions using H_2O_2 and O_2 [6-9].

Oxidation of Glycerol (Gly)

As discussed in *Chapter 2B,* oxidation of glycerol also gives variety of value added products (Table 1).

Table 1. Applications of products derived from glycerol esterification.

Products	Application
Dihydroxyacetone (DHA)	Synthon in organic chemistry, starting material in D, L-serin synthesis, tanning agent in cosmetics
Glyceraldehyde (GLYALD)	Cosmetic ingredient, pharmaceutical precursors and chemical intermediates.
Glyceric acid (GLYAC)	Intermediate for synthesis of tartronic acid and mesoxalic acid
Glycolic acid (GLYCAC)	Chemical peels performed by a dermatologist, skin care products
Oxalic acid (OA)	Cleaning or bleaching, removal of dust, mordant in dyeing processes, baking powder

One of the key problems in this transformation is the potential complexity of the products and hence careful design of catalyst to control selectivity toward the desired product is required.

Most previous studies dealing with the chemo-selective catalytic oxidation of glycerol reports the use of supported noble metals (palladium, platinum, gold) as catalysts in basic medium [11-24]. In a basic pH medium, mainly sodium glycerate is formed, and the reaction mixture needs additional neutralization and acidification in order to get the free glycerol acid. Apart from the cost of noble metals, the other disadvantage of supported Pt and Pd catalysts is the deactivation with increasing reaction time. Accordingly, in most of the reported work, DHA is not even detected in the reaction medium. The reaction optimization can be initiated by a careful literature investigation on type of catalyst, oxidant and reaction temperature. The reaction mechanism in basic conditions is based on the oxidation of a primary hydroxyl group and the corresponding GLYALD is then transformed into DHA by base-catalysed interconversion [25-26].

The selective oxidation of glycerol to DHA can be achieved by two different types of catalytic systems and similar pH dependent conversions have been studied earlier [26]. Few groups have explored the glycerol oxidation reactions under base free conditions in presence of H_2O_2 as oxidant. Silicalite containing Ti, Fe, V catalysts [27] in base free conditions gives 34.8, 31.9, and 33.9% conversion, respectively, with only selectivity toward formate ester, hydroxyethanoic acid, and acetals. Ti containing catalysts TS-1, Ti-MCM-41 also give 10-35% conversion but with a higher catalyst amount and selectivity was obtained for GLYALD, formate ester. DHA as well as other acid products were obtained in trace amounts.

Luque et al. reported that the oxidation of glycerol on supported Pd catalyst in base-free conditions with hydrogen peroxide (30%, v/v) under microwave irradiation produced mainly glycolic acid and oxalic acid [28]. Shulpin et al. [29] reported the oxidation of glycerol in the homogeneous manganese complex-H_2O_2-oxalic acid-acetonitrile system, whereas the yield of DHA did not surpass 15%. Villa et al. [12] reported that, AuPt nanoparticles supported on the zeolite H-Mordenite were found to be selectively oxidize glycerol directly to glyceric acid without the use of basic conditions.

Sulphonato-salen-chromium(II) intercalated LDH in base free oxidation with 3% H_2O_2 shows 71.3% conversion with 43.5% and 20.9% selectivity for DHA and GLYALD, respectively [30]. In a separate investigation, Nunes and Guerreiro [31] reported chemometric study of effects of the catalyst preparation method and reaction conditions on the efficiency of glycerol oxidation catalyzed by Au nanoparticles supported on activated carbon using H_2O_2 as oxidant, however they obtained higher glycolate. Recently, Crotti and Farnetti [32] synthesised Iron complexes with the polydentate ligand bis(2-pyridinylmethyl)amine (BPA) as catalysts and employed for oxidation of glycerol using H_2O_2. The only observed reaction products were DHA and formic acid. It was shown that although the overall conversion in all cases was lower than 50%, by accurate choice of the experimental conditions selectivities in DHA up to 100% could be obtained.

One can figure out that the reaction mechanisms that end up in DHA formation in basic and acidic media are completely different. One of the main advantages for working in acid media is the prevention of salt formation (otherwise formed due to addition of NaOH in the reaction mixture) from neutralisation reactions, which eventually eliminates/reduces the cost issue in the design of industrial processes. Even though POMs based catalysts have gained promising results for oxidation of variety of alcohols, till date there are no reports on oxidation of glycerol with these catalysts.

Oxidation of Benzyl Alcohol (BA)

BA is a promising molecule in organic chemistry as number of organic transformations are possible. The huge amount of applications of alcohols has recently increased the interest in the synthesis of a various aldehydes, ketones, and acids via selective catalytic oxidation processes. Especially, benzaldehyde is very valuable chemical that has widespread applications in perfumery, dyestuff, and agro chemical industries [33]. Among carbonyl compounds, benzaldehyde is the second most important aromatic molecule (after vanillin) used in the cosmetics and flavor industries. Production of benzaldehyde is the first step in oxidation of BA and further oxidation leads to the production of benzoic acid with side reactions leading to the other products like toluene, dibenzyl acetal, and benzyl benzoate [34]. Benzaldehyde is commercially produced as a byproduct from the benzoic acid industry, oxidation of toluene in organic solvents, and hydrolysis of benzyl chloride which often contains traces of chlorine impurities, and copious waste is generated in this process. Most of these procedures suffer from a lack of selectivity, high temperature, use of organic solvents, toxicity of the reagents, and waste production.

Especially, for heterogeneous POM based catalysts, there are only few reports for oxidation of BA. An active and reusable zirconia-ceria mixed oxide supported $H_3PMo_{12}O_{40}$ (PMA) catalyst was developed for the selective oxidation of benzyl alcohol to benzaldehyde using H_2O_2 [35]. POM catalysts based on the Keggin structured $H_4PMo_{11}VO_{40}$ functionalized by the cationic surfactants have been prepared and characterized by different techniques. These catalysts were applied in the liquid-phase oxidation of BA to benzaldehyde with H_2O_2 under organic solvent-free conditions [36].

Patel and group have efficiently carried out oxidation of BA with H_2O_2 or O_2 over lacunary phosphomolybdate (PMo_{11}) supported onto Al_2O_3 [37], ZrO_2 [38-39], MCM-41 [40] and Hβ [41]. They have found moderate conversion (22-26%), high TONs (> 9000) and excellent selectivity towards benzaldehyde

(>90%) under solvent free mild conditions. However, further investigation shows that there are no reports on the oxidation of either Gly or BA over anchored lacunary phosphotungstates (PW_{11}).

In the present chapter, oxidation of Gly (with H_2O_2) and BA (with H_2O_2 and O_2) was carried out using anchored PW_{12} and PW_{11}. In order to optimize the conditions, detailed study was carried out by varying different parameters such as % loading, mole ratio of substrate to H_2O_2, catalyst amount, time and temperature.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Gly, BA, cyclopentanol, cyclohexanol, 1-butanol, 1-hexanol, 30% aq. H_2O_2, *tert*-butylhydroperoxide (70% aq. TBHP), ethyl acetate and dichloromethane were obtained from Merck and used as received.

Catalytic reactions

Oxidation with H_2O_2

Oxidation of Gly and BA was carried out in a 50 mL batch reactor provided with a double-walled condenser, alcohol (10 mmol), and 30% aq. H_2O_2 (30 mmol) with constant stirring at 90 ^{o}C. After completion of reaction, the products were extraction with ethyl acetate (Gly), dichloromethane (BA), dried with magnesium sulphate and analysed on a gas chromatograph (GC) using Rtx-5 capillary column (30 m, 0.25 mm id).

Oxidation with O_2

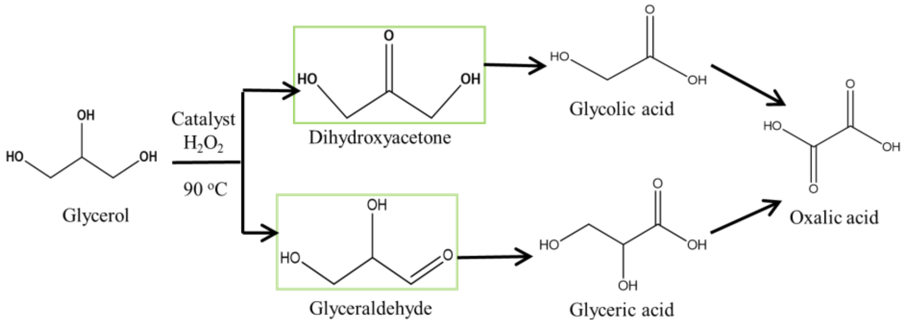
Oxidation of BA was performed in a batch-type reactor under atmospheric pressure. In a typical reaction appropriate amount of catalyst was added in a 50 mL two-necked flask containing alcohol (100 mmol) and 0.2 mmol TBHP was added in order to initiate the reaction. Reaction was maintained at 90 °C on REMI magnetic stirrer equipped with preheated oil bath at 600 rpm. The reaction was started by bubbling O_2 (analytical grade) into the liquid. After completion of reaction, catalyst was removed by simple centrifugation. Products were analysed on a GC using Rtx-5 capillary column by diluting with dichloromethane and drying with magnesium sulphate. GC programming parameters: Injector temperature= 240 ^{o}C, Detector temperature= 250 ^{o}C, Column temperature= 80- 220 ^{o}C with rate 10 ^{o}C/min. Identification of product was carried out by comparing it with authentic samples and then by GC-MS.

RESULTS AND DISCUSSION

3A (I) Oxidation of Gly and BA over PW_{12}/MCM-41 and PW_{11}/MCM-41.

- ***Oxidation of Gly with H_2O_2***

Study was carried out to obtain maximum Gly conversion and selectivity for desired C3 oxidised products from oxidation of the secondary alcohol- DHA and of the primary alcohol- GLYALD (Scheme 1).



Scheme 1. Oxidation of glycerol with H_2O_2.

To ensure the catalytic activity, all reactions were carried out without a catalyst and it was found that no auto-oxidation reaction takes place. As discussed in the introduction of this chapter, adjusting the solution pH of reaction medium seems to be a reasonably adequate way to stabilize the target compound, DHA/GLYALD. In the present work, the final pH of the reaction mixture (substrate + H_2O_2 + catalyst) was found to be mild acidic (around 4-5).

Effect of % loading of PW_{12}/PW_{11}

To study the effect of % loading oxidation reaction was carried out with 10-40% loading (Figure 1). It was observed that with an increase in the % loading of PW_{12}/PW_{11}, % conversion also increases same as other systems. For 30% PW_{12}/PW_{11} loading, maximum conversion was obtained. On increasing the % loading to 40%, no significant increase in conversion was observed which might be due to the blocking of the active sites due to formation of multilayer on the support. Also, along with the conversion optimum selectivity for DHA was obtained at 30% loading. Hence, 30% of PW_{12}/PW_{11} anchored to MCM-41 was considered for further studies.

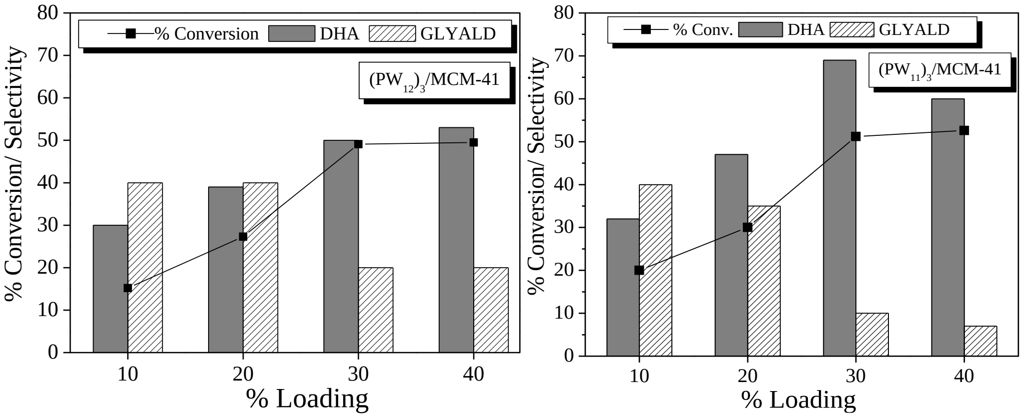


Figure 1. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Gly: H_2O_2- 1:3, amount of catalyst- 25 mg, temperature- 90 ^{o}C, time- 20 h.

Effect of mole ratio of Gly: H_2O_2

Figure 2 shows that with an increase in molar ratio (Gly to H_2O_2) from 1:1 to 1:3, the conversion increases linearly, due to the increase in H_2O_2 concentration. On further increase in the mole ratio from 1:3 to 1:4, no significant increase in conversion was observed. Therefore, 1:3 mole ratio was found to be optimum in terms of conversion. $(PW_{12})_3$/MCM-41 shows 49.1% conversion with 49% selectivity for DHA, $(PW_{11})_3$/MCM-41 shows 51.2% conversion with 60% selectivity for DHA.

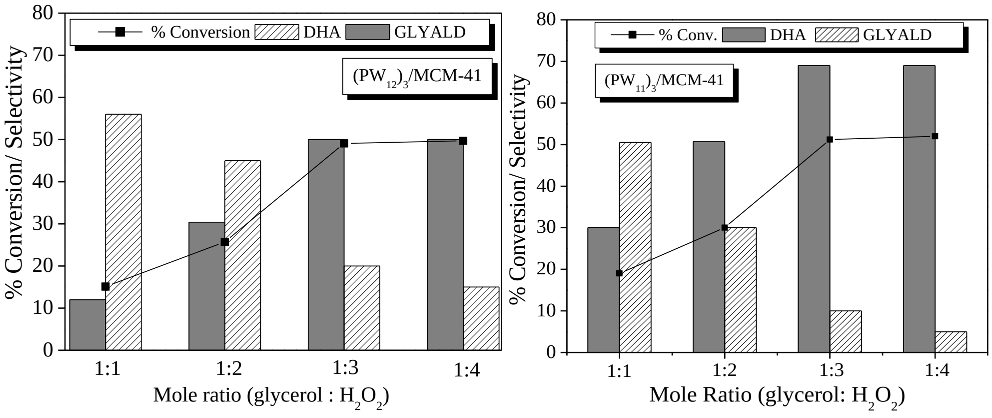


Figure 2. Effect of mole ratio Gly/H_2O_2: amount of catalyst- 25 mg, temperature- 90 °C, time- 20 h.

Effect of amount of catalyst

It is observed from Figure 3 that % conversion increases as the active species increases; i.e., the catalyst amount increases, which is as expected. Mild acidic pH assists oxidation of the secondary hydroxyl group, giving selectivity toward DHA [30], similar effect was observed in the present work. Under the conditions; 1:3 molar ratio, 25 mg of catalyst, conversion was 49.1% for $(PW_{12})_3$/MCM-41 and 51.2% for $(PW_{11})_3$/MCM-41, and the product selectivity for DHA was 49%, 60% respectively. It was important to note that on changing the active species for PW_{12} to PW_{11} there was greater selectivity towards DHA. This may be due to acidity of the reaction medium as well as lacunary environment in PW_{11}.

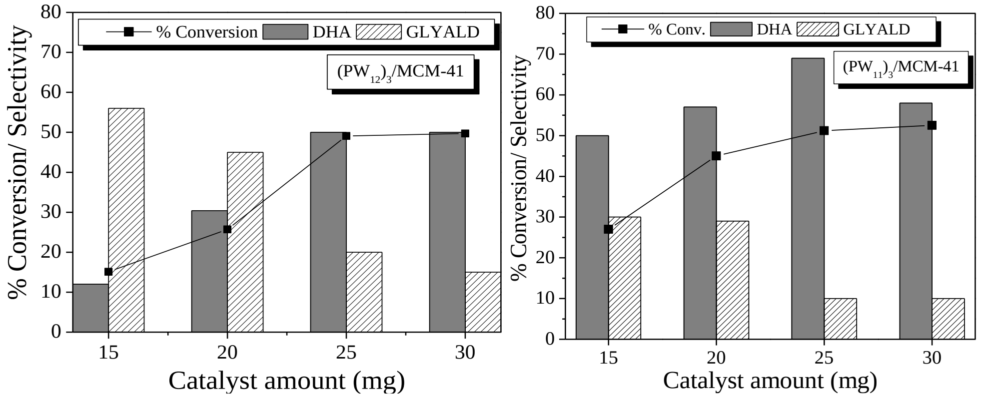


Figure 3. Effect of catalyst amount: mole ratio of Gly: H_2O_2- 1:3, temperature- 90 °C, time- 20 h.

Effect of reaction time

The effect of reaction time on conversion of Gly was studied (Figure 4). It was observed that with an increase in the reaction time, % conversion also increases. This may be due to the reason that more induction time is required for the formation of a reactive intermediate species (substrate + catalyst), which finally converts to the products. Highest conversion and selectivity of DHA is obtained at 20 h for both the catalysts. Also, no significant increase in conversion was observed after 20 h, however formation of over-oxidation acid products were detected at 24 h for both the catalysts.

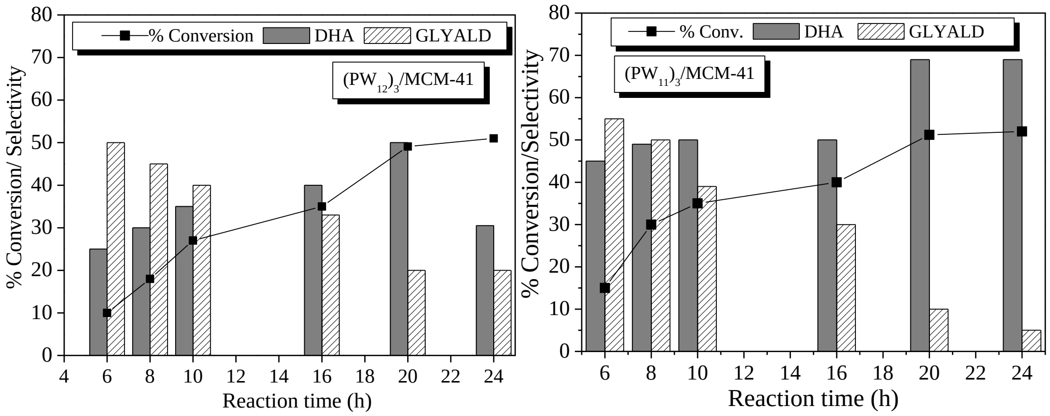


Figure 4. Effect of reaction time: mole ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C.

Effect of temperature

The effect of temperature on reaction activity was investigated at different temperatures (70-100 °C) (Figure 5).

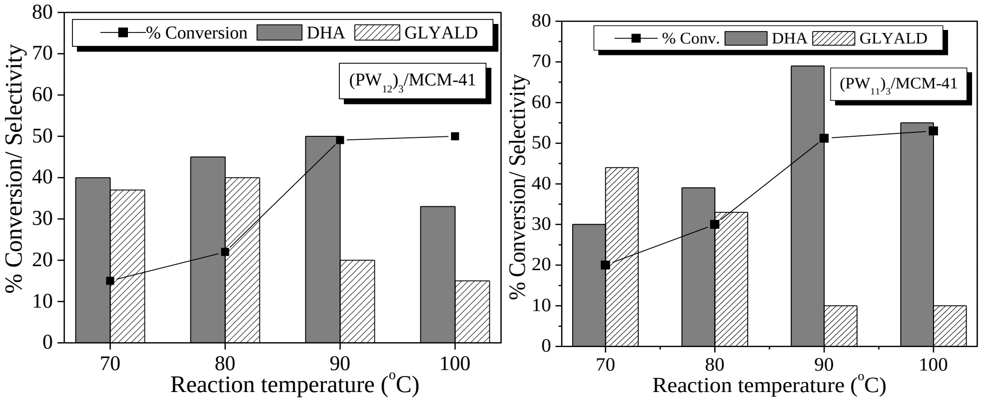


Figure 5. Effect of reaction temperature: mole ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h.

The results show that conversion increases on increasing the temperature from 70 to 90 °C. There was no significant increase in conversion on increasing the temperature from 90 to 100 °C, due to attainment of equilibrium, however a decrease in selectivity for DHA and GLYALD was observed due to further over-oxidation of these products to acids. So, 90 °C was optimized in order to obtain maximum Gly conversion and selectivity towards DHA/GLYALD.

Optimized conditions: [49.1% conversion, 50% DHA, 20% GLYALD-$(PW_{12})_3$/MCM-41; 51.2% conversion, 69% DHA, 10% GLYALD-$(PW_{12})_3$/MCM-41] mole ratio Gly: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h, and temperature- 90 °C.

Kinetic study

A detailed study on the kinetic behaviour was carried out over $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41. Plot of log Co/C (Figure 6) for oxidation with H_2O_2 shows that with an increase in reaction time, there was a gradual and linear decrease in the glycerol concentration over both the catalysts. These observations indicates that the reactions follows first-order dependence with respect to time.

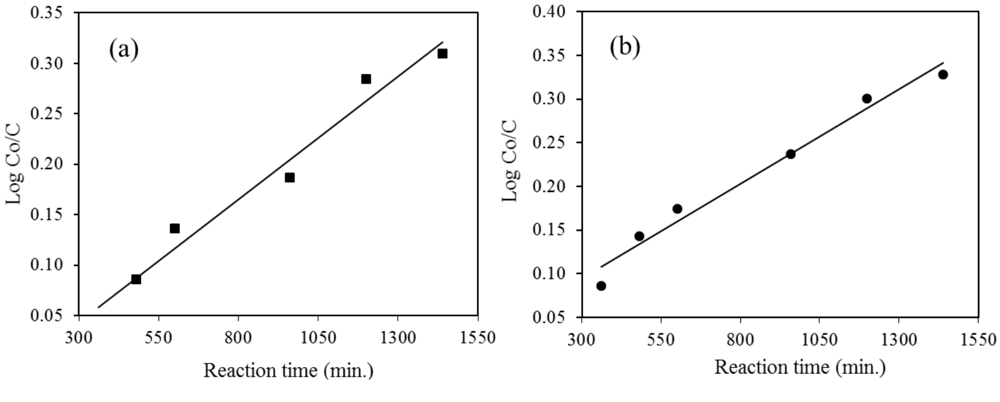


Figure 6. First-order plot for oxidation over, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

The catalyst concentration was varied (Figure 7) at a fixed substrate concentration of 10 mmol and 90 °C temperature. The rate of reaction increases with an increase in the catalyst concentration.

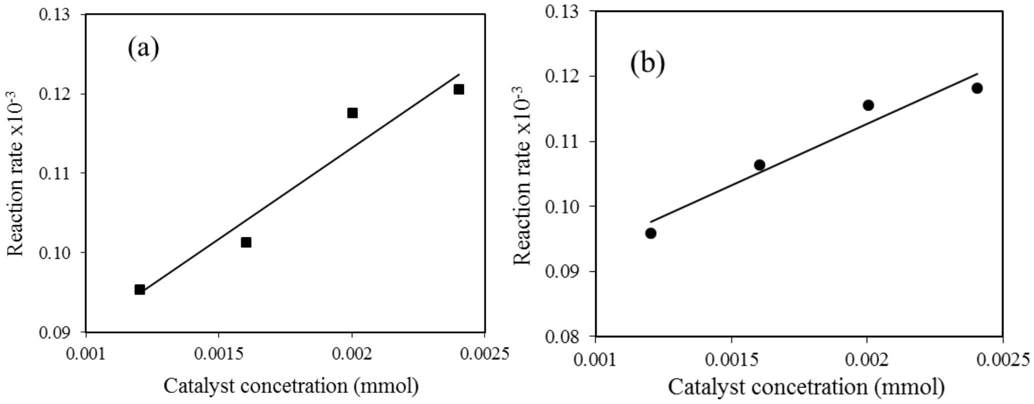


Figure 7. Plot of reaction rate vs catalyst concentrations for oxidation over a) $(PW_{12})_3$/MCM-41 and b) $(PW_{11})_3$/MCM-41.

The graph of ln k versus 1/T was plotted (Figure 8), and value of Ea was determined from the plot. The details are same as discussed in *chapter 2A.* Ea for $(PW_{12})_3$/MCM-41 was found to be 50.5 kJ mol^{-1} and for $(PW_{11})_3$/MCM-41 it was 46.5 kJ mol^{-1} indicating that the rate is truly governed by the chemical step.

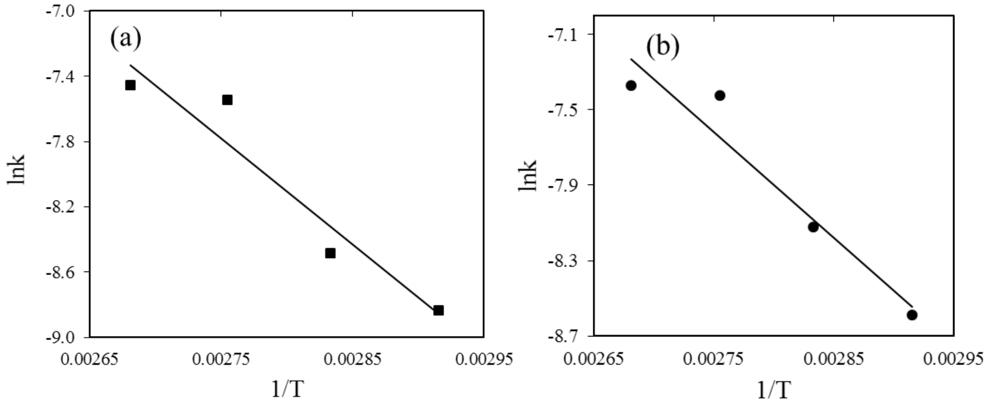
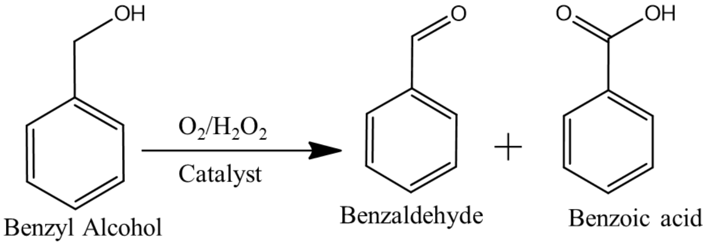


Figure 8. Arrhenius plots for determination of Ea, a) $(PW_{12})_3$/MCM-41 and b) $(PW_{11})_3$/MCM-41.

From the value of Ea, the order of catalysts was found out to be, $(PW_{11})_3$/MCM-41 > $(PW_{12})_3$/MCM-41.

- ***Oxidation of BA with H_2O_2***

Detail study was carried out for oxidation of BA using $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41 as catalysts (Scheme 2).



Scheme 2. Oxidation of BA with different oxidants.

Effect of % loading of PW_{12}/PW_{11}

The effect of % loading (10-40%) of PW_{12}/PW_{11} on MCM-41 was carried out using H_2O_2 (1:3 molar ratio, 25 mg catalyst, 90 °C for 24 h). The results are presented in Figure 9, which shows an increase in the conversion with increase in the % loading of active species from 10% to 20%. A significant increase in the conversion was observed on increasing the loading from 20% to 30%. The 30% loaded catalyst showed highest conversion, however further increasing the loading to 40% did not show significant change. Hence 30% loaded catalysts were used for further studies for both the catalysts.

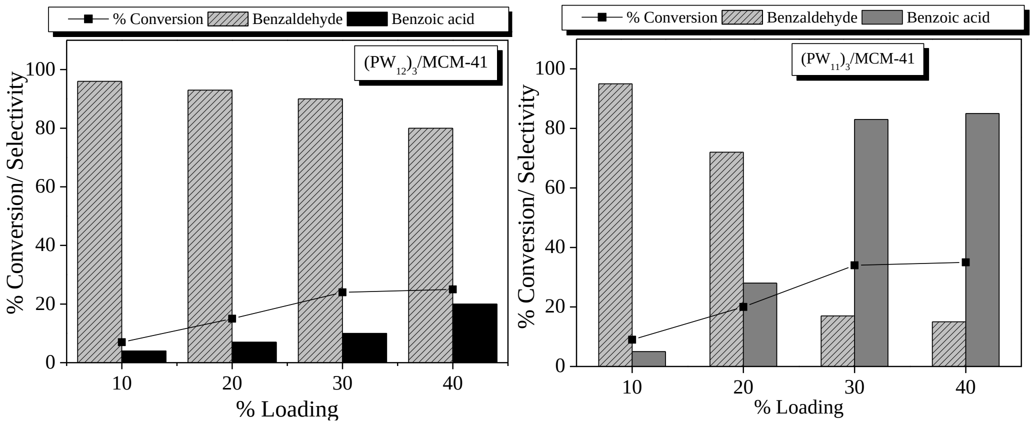


Figure 9. Effect of % loading: mole ratio of BA: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C, time- 24 h.

Effect of mole ratio of BA to H_2O_2

Reaction was carried out by changing molar ratio of BA to H_2O_2, as shown in Figure 10 with 25 mg catalyst for 24 h at 90 °C, over both catalysts. With increase in concentration of H_2O_2, an increase in conversion was observed. Maximum 24% and 34% conversion was obtained for $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41 respectively, with 1:3 molar ratio. Hence, further optimization of conditions were carried out with 1:3 molar ratio of BA: H_2O_2.

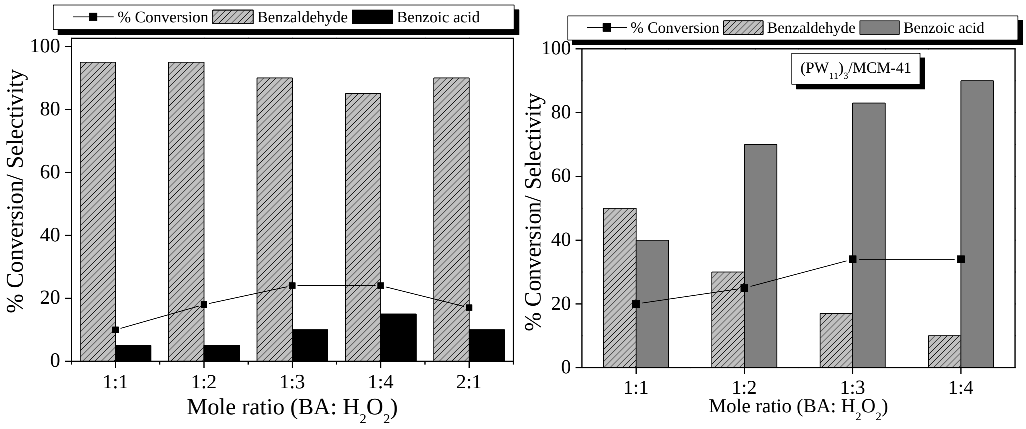


Figure 10. Effect of mole ratio: amount of catalyst- 25 mg, temperature- 90 °C, time- 24 h.

Effect of catalyst amount

The catalyst amount was varied in the range 10 mg- 40 mg (Figure 11) while keeping the other parameters constant.

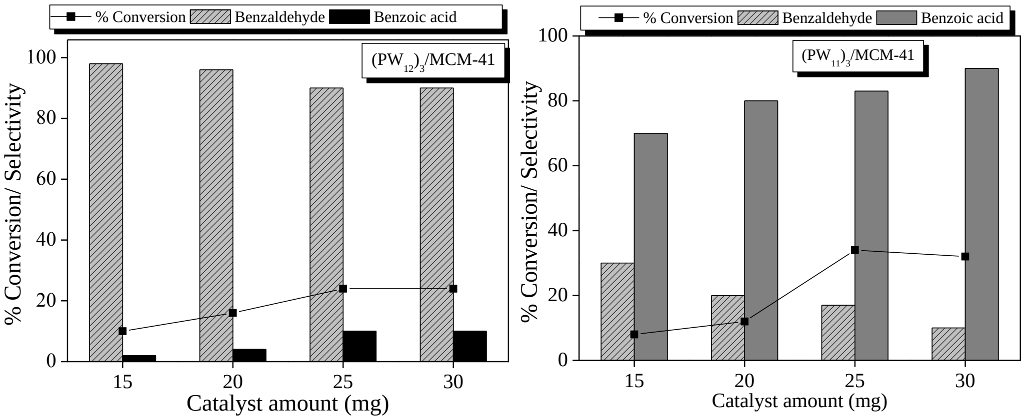


Figure 11. Effect of catalyst amount: mole ratio BA: H_2O_2- 1:3, temperature- 90 °C, time- 24 h.

It can be observed from Figure 11 that the catalytic activity increases initially up to 25 mg and then becomes constant with a further increase in catalyst amount. It is known that in the company of polar molecules, heteropolyacids display pseudoliquid behaviour [42] in which catalytic activity is directly proportional to the active species in the catalyst. Additionally, no significant increase in conversion after 25 mg was observed. As we take a total of 10 mmol of alcohol in reaction (which is fixed each time) and the amount of catalyst is increased, so it might be possible that with the increase in amount of catalyst, new active sites might not be available for attack of the reactants. A possibility may arise that the active sites (PW_{12}/PW_{11}) might not get rid of the product molecules. Therefore, 25 mg catalyst amount was taken to be optimal.

Effect of reaction time

The time dependence oxidation (Figure 12) was studied by performing the reaction of BA with H_2O_2 in presence of 25 mg catalyst at 90 ^{o}C with constant stirring. The % conversion was monitored at different reaction times.

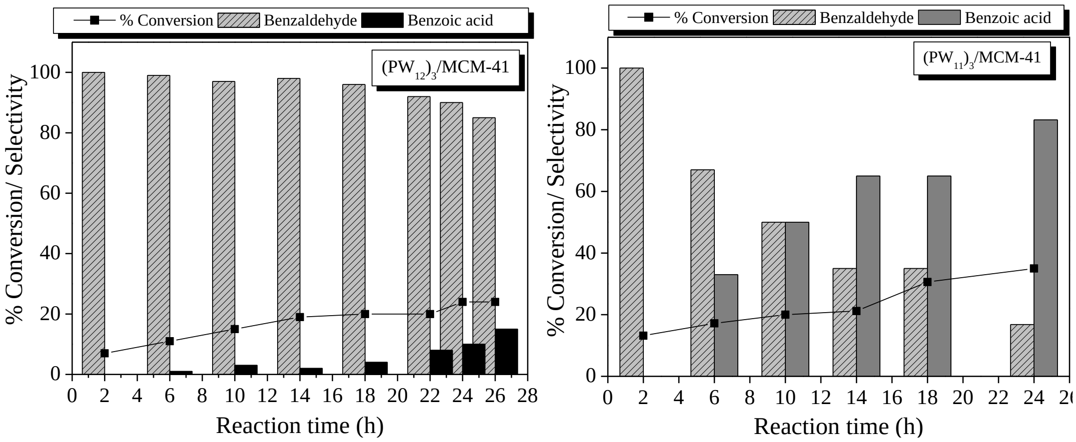


Figure 12. Effect of reaction time: mole ratio BA: H_2O_2- 1:3, catalyst amount- 25 mg, temp.- 90 °C.

At 2 h, 12% conversion was achieved with 100% selectivity towards benzaldehyde. It was observed that there is an increase in conversion with an increase in reaction time and maximum selectivity towards benzoic acid is achieved in 24 h. $(PW_{11})_3$/MCM-41 showed higher conversion (34%) in 24 h as compared to $(PW_{12})_3$/MCM-41 (24%) in 24 h, however due to high oxidizing properties of the lacunary catalyst higher selectivity was obtained for benzoic acid instead of benzaldehyde.

Effect of reaction temperature

It was also found that as the reaction temperature increases, conversion of alcohol also increases (Figure 13). But the selectivity increases towards benzoic acid. This drastic change in selectivity might be due to further oxidation of benzaldehyde to benzoic acid, which may arise due to acidity of the catalyst as well as the effect of support.

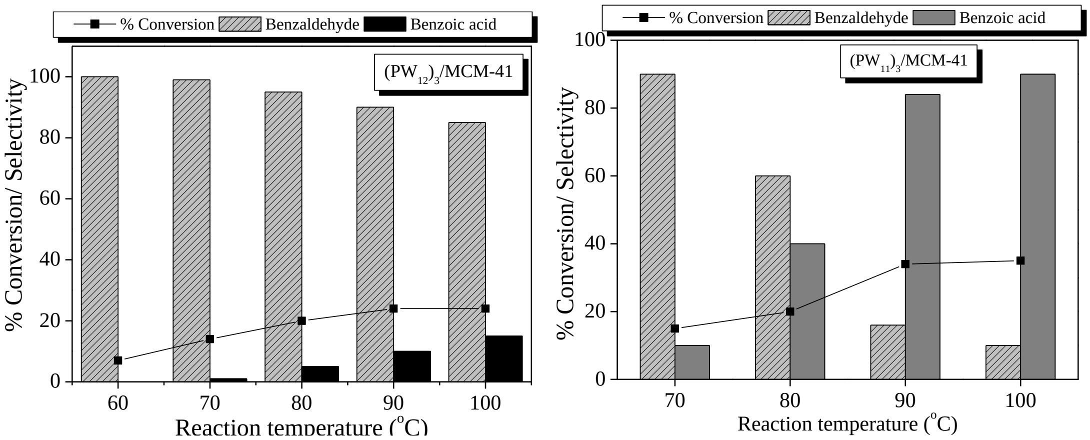


Figure 13. Effect of temperature: mole ratio BA: H_2O_2- 1:3, catalyst amount- 25 mg, time- 24 h for $(PW_{12})_3$/MCM-41 and 20 h for $(PW_{11})_3$/MCM-41.

Optimised conditions: [24% conversion, 90% selectivity for benzaldehyde- $(PW_{12})_3$/MCM-41; 34% conversion, 16% benzaldehyde and 84% benzoic acid $(PW_{11})_3$/MCM-41] mole ratio BA: H_2O_2- 1:3, amount of catalyst- 25 mg, temperature- 90 °C, time- 24 h.

Kinetics study

A detailed kinetic study was carried out over $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41. In all the experiments, reaction mixtures were analysed at fixed interval of time using GC. The plot of log Co/C versus time (Figure 14) shows a linear relationship of BA consumption with respect to time. With increase in reaction time there was gradual and linear decrease in BA concentration over both the catalysts indicating first order kinetics.

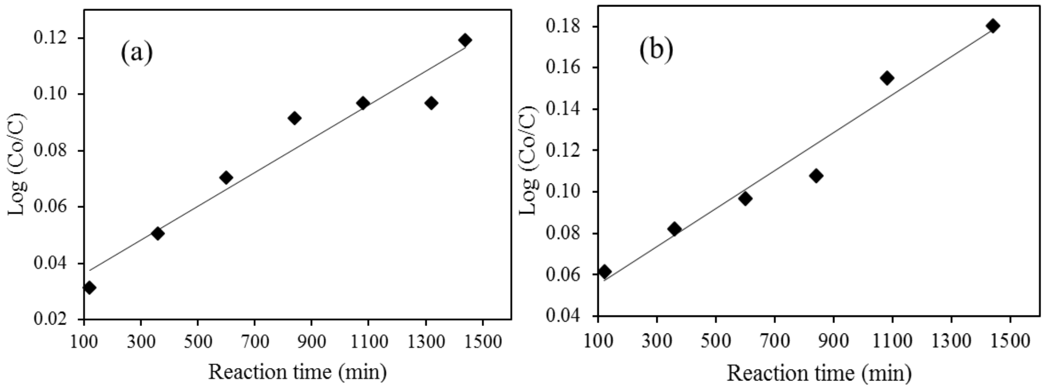


Figure 14. First-order plot for oxidation of BA over, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

The catalyst concentration was varied at 90 ^{o}C temperature. The plot of reaction rate versus catalyst concentration (Figure 15) shows that rate of reaction increases linearly with an increase in the catalyst concentration for both the reactions.

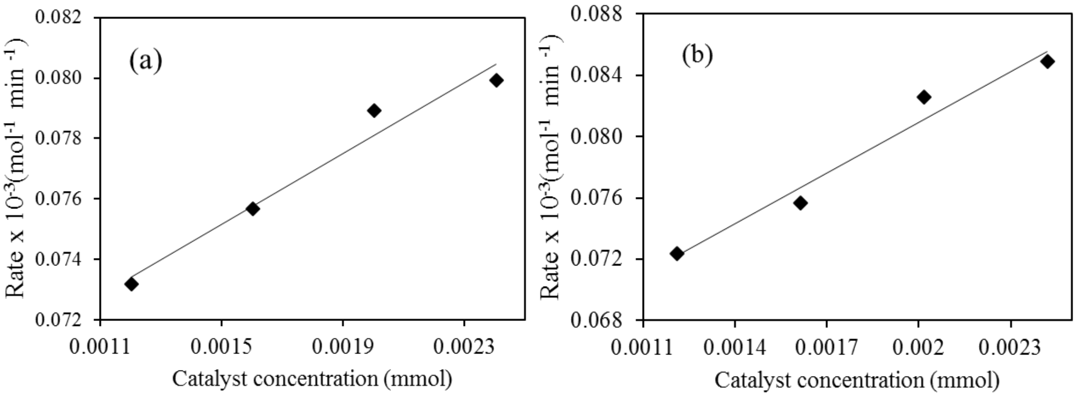


Figure 15. Plot of reaction rate versus catalyst concentrations over, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

The graph of ln k versus 1/T was plotted (Figure 16) and Ea was found to be 49.2 kJ mol^{-1} $(PW_{12})_3$/MCM-41 and 44.6 kJ mol^{-1} $(PW_{11})_3$/MCM-41 respectively, indicating that the rate is truly governed by chemical step and there was no diffusion limitation over both the reactions.

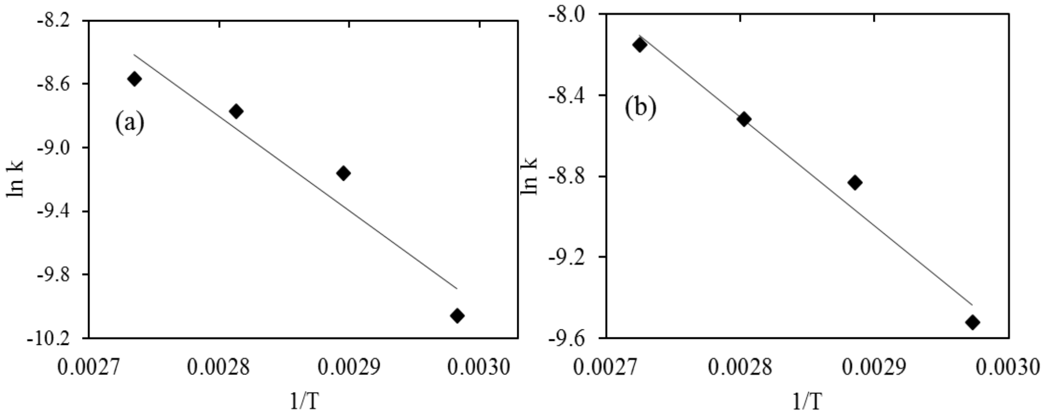


Figure 16. Arrhenius plot for determination of Ea over, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

The Ea value for $(PW_{11})_3$/MCM-41 was found to be low as compared to $(PW_{12})_3$/MCM-41 suggesting the following order of activity,

- $(PW_{11})_3$/MCM-41 > $(PW_{12})_3$/MCM-41.

- ***Oxidation of BA with O_2***

For oxidation with O_2 it is essential to check whether the reaction is just auto-oxidation or not. Control experiment without catalysts and no conversion of substrates indicates that the reaction does not proceed through auto-oxidation.

Effect of catalyst amount

Reaction was carried out by varying catalysts amount (10 mg- 30 mg) (Figure 17). Initially, on increasing catalyst amount from 10 mg to 25 mg, the conversion increases sharply. Further increase in catalyst amount does not increase the conversion very significantly. This may be due to the combined effect of the surface adsorption phenomenon which stabilizes the distribution of products. Therefore, 25 mg was considered optimum for obtaining maximum conversion.

Effect of reaction time

The effect of reaction time on the selective oxidation was carried out by monitoring % conversion at different time intervals (Figure 17). Initially with increase in reaction time up to 20 h, the % conversion increases slowly. The catalyst initially takes an induction period to accelerate the reaction. The maximum conversion was achieved at 24 h. On further increasing reaction time, there was no significant increase in the conversion. However, decrease in % selectivity for benzaldehyde was also observed due to over-oxidation. 24 h reaction time was optimised for obtaining maximum conversion of BA for both the catalysts.

Effect of reaction temperature

To determine the optimum aerobic oxidation temperature the reaction was investigated at temperatures 60-100 ^{o}C (Figure 17) keeping other parameters fixed (25 mg catalyst amount, reaction time 24 h). The results show that conversion increases with increase in temperature which is as expected. Similarly, on increasing temperature from 90 to 100 ^{o}C, conversion increases but at the same time selectivity of benzaldehyde. This result is attributed to further oxidation of benzaldehyde to benzoic acid at higher temperature. So temperature of 90 ^{o}C was found optimal for the maximum conversion.

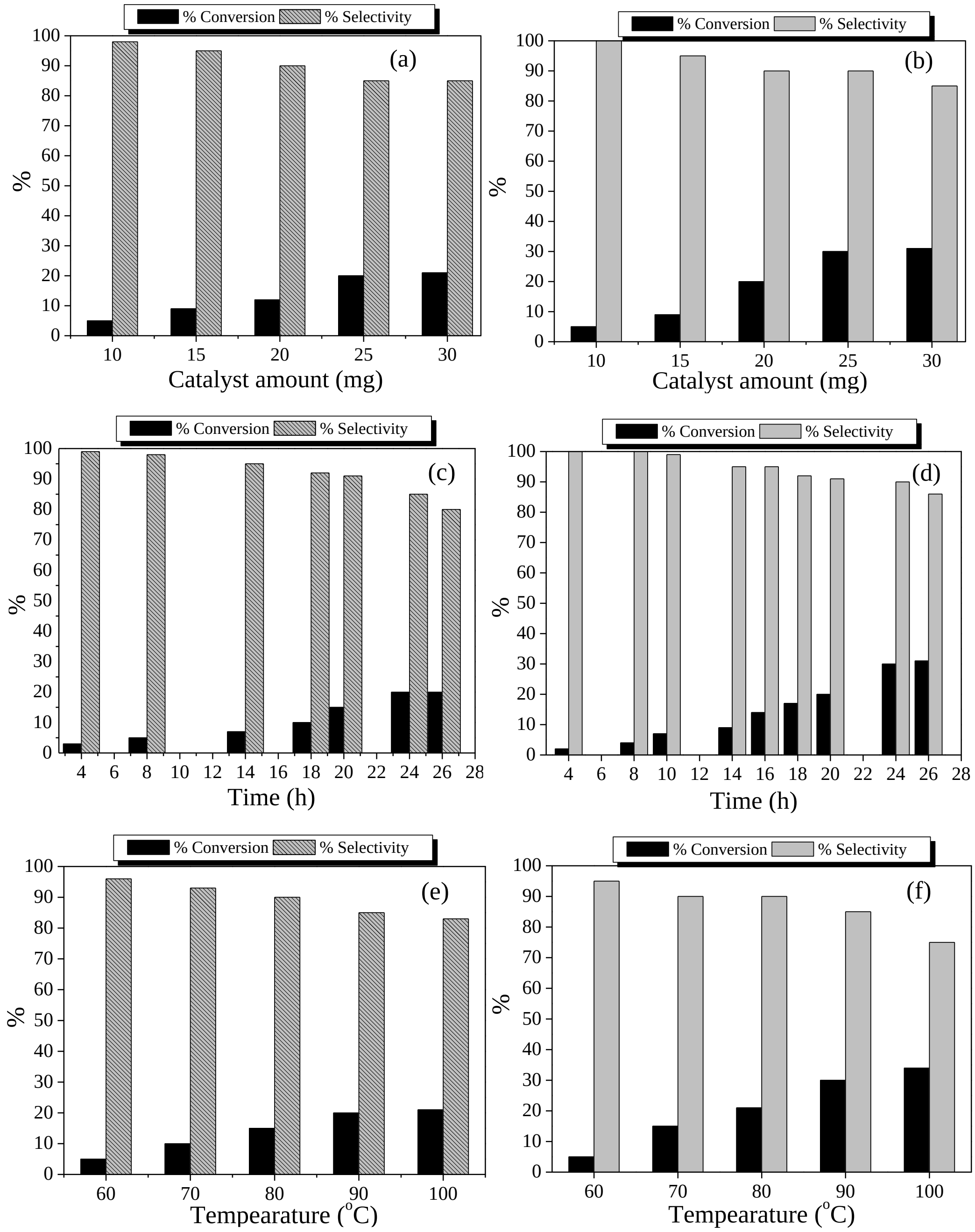


Figure 17. Effect of catalyst amount (a) $(PW_{12})_3$/MCM-41, (b) $(PW_{12})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, time- 24 h, temperature- 90 °C; Effect of reaction time (c) $(PW_{12})_3$/MCM-41, (d) $(PW_{12})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 25 mg, temperature- 90 °C; Effect of reaction temperature (e) $(PW_{12})_3$/MCM-41, (f) $(PW_{12})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 25 mg, time- 24 h.

***Optimised conditions*:** [20% conversion, 85% benzaldehyde- $(PW_{12})_3$/MCM-41; 30% conversion, 90% benzaldehyde $(PW_{11})_3$/MCM-41] catalyst amount - 25 mg, temperature- 90 °C, time- 24 h. Comparison of optimised conditions with both the oxidants are given in Table 2.

Table 2. Optimized conditions for both the oxidants.

Conditions	Oxidants	
	H_2O_2	O_2
Mole ratio of substrate	1:3	-
Substrate Concentration	10 mmol	100 mmol
Reaction time	24 h	24 h
Catalyst amount	25 mg	25 mg
Reaction temperature	90 °C	90 °C

Role of oxidants

It is seen from Table 3 that for both the catalysts order of activity of oxidant was $O_2 > H_2O_2$ i.e. high mole conversion of substrate and TON was observed with O_2 as compared to that of H_2O_2. The reason for difference in conversion can be explained as follows. In case of H_2O_2 the activation of the metal center takes place through the formation of $[XO_4\{MO(O_2)_2\}_4]^{3-}$ intermediate *in situ* from $XM_{11}O_{39}$ [44]. The formed active peroxo intermediate oxidizes the alcohols. However, in the case of TBHP as an initiator and O_2 as a main oxidant, initiation of TBHP forms species BuO*/*OH and hence activates O_2 to form the superoxo-species [44].

Table 3. Comparison of catalytic activity of both the catalysts.

Catalyst	Oxidant	% Conv.	% Sel.	TON
$(PW_{12})_3$/MCM-41	H_2O_2[a]	24	82	1200
	O_2[b]	20	85	10000
$(PW_{11})_3$/MCM-41	H_2O_2[a]	34	35	1673
	O_2[b]	30	90	16862

% Conversion based on substrate: [a] Reaction with H_2O_2, substrate: H_2O_2- 1:3, catalyst amount- 25 mg, time- 24 h, temperature- 90 °C; [b] Reaction with O_2, TBHP- 0.2 mmol, substrate- 100 mmol, catalyst amount- 25 mg, time- 24 h, temperature- 90 °C, Selectivity for Benzaldehyde.

Three different oxidation processes were studied to explain the role of TBHP and O_2, (1) TBHP as the sole oxidant showed no conversion for BA, (2) using O_2 as the sole oxidant gives less conversion (<5%) for BA at 10-14 h, and (3) employing O_2 as the oxidant with 0.2 mmol TBHP as the initiator gives highest conversion. It is observed that the conversion increase significantly in the case of reaction (3). This can also be explained on the bases of plot of kinetic curve (% conversion vs time) (Figure 18), where O_2 as the only oxidant requires a longer time for activation, i.e. a larger induction period, whereas in the case of TBHP + O_2, TBHP acts as radical initiator by reducing the induction period. Hence, O_2 proved to be better oxidant as compared to H_2O_2 based on the high TONs.

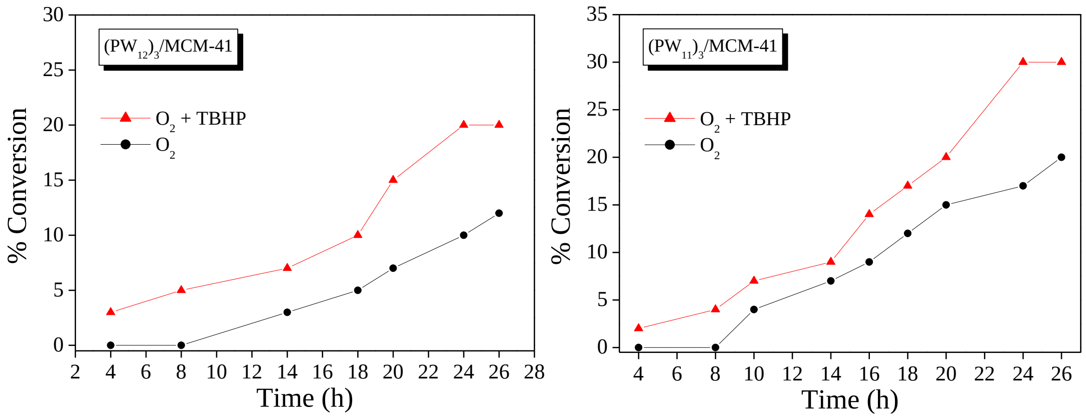


Figure 18. Role of TBHP in promoting the oxidation over both the catalysts.

Control experiments and Heterogeneity test

Control experiments for oxidation of Gly and BA (Table 4) shows that that catalytic activities of PW_{12}/PW_{11} have been retained in the respective catalysts indicating that PW_{12}/PW_{11} behaves as real active species.

Table 4. Control experiments for oxidation of Gly and BA with H_2O_2.

Catalyst	% Conv. $^{a/b}$	% Sel. $^{a/b}$	TON $^{a/b}$
No catalyst	-/-		-
MCM-41	<1/<1	50/100	-
PW_{12}	20.5/20	61/98	1050/1000
$(PW_{12})_3$/MCM-41	49.0/24	50/82	2000/1200
PW_{11}	30.0/30	68/80	1476/1476
$(PW_{11})_3$/MCM-41	51.2/34	69/16	2250/1673

^{a} *Oxidation of Gly: amount of* PW_{12}/PW_{11}*- 5.7 mg, selectivity for DHA,* ^{b} *Oxidation of BA: amount of* PW_{12}/PW_{11}*- 5.7 mg, catalyst- 25 mg, selectivity for benzaldehyde.*

Heterogeneity test [43] was carried out for both the catalysts (Figure 19). The reaction mixture after filtration does not show any increase in conversion or selectivity indicating that there was no leaching of active species (PW_{12}/PW_{11}) from the support and catalysts are truly heterogeneous in nature.

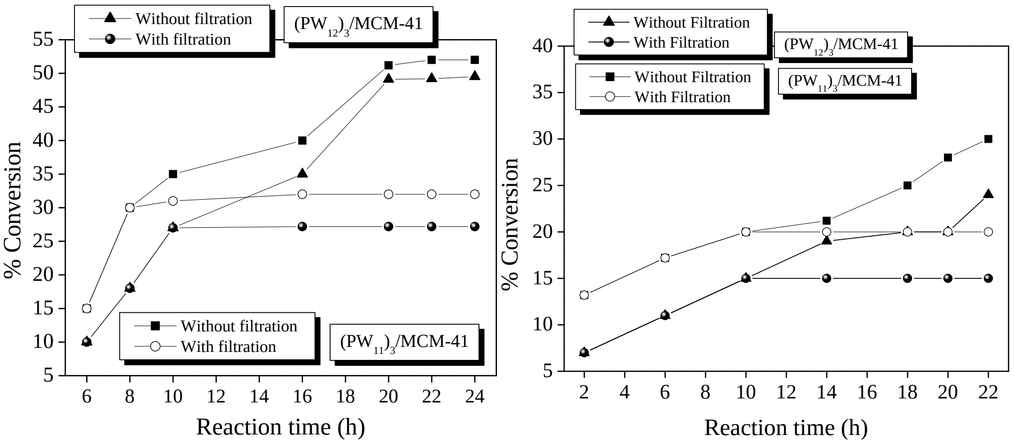


Figure 19. Heterogeneity test for Gly oxidation (Left), BA oxidation (Right) with H_2O_2.

Recycling and regeneration of catalysts

The catalysts were recycled up to four times in order to test their activity in successive runs for oxidation of Gly (Figure 20) and BA (Figure 21). The procedure for recycling was same as explained in *chapter 2*. From Figure 20, 21 it was observed that no significant difference in the % conversion and selectivity even after four cycles. Thus, the catalysts can be reused up to four cycles with minimal loss in the activity. Recycled catalysts were characterized by different techniques and results are previously presented in *Chapter 2a,* hence they are not included here again.

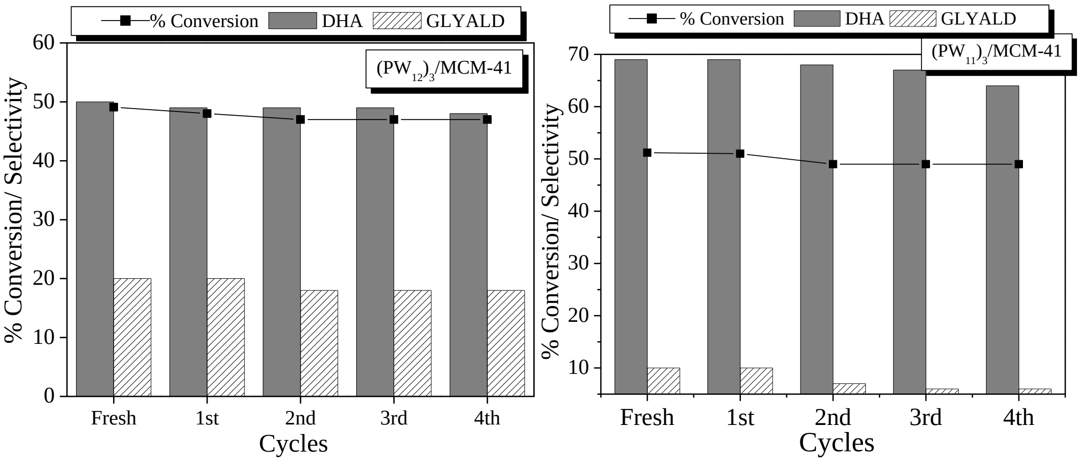


Figure 20. Recycling study for oxidation of Gly: molar ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h and temperature- 90 °C.

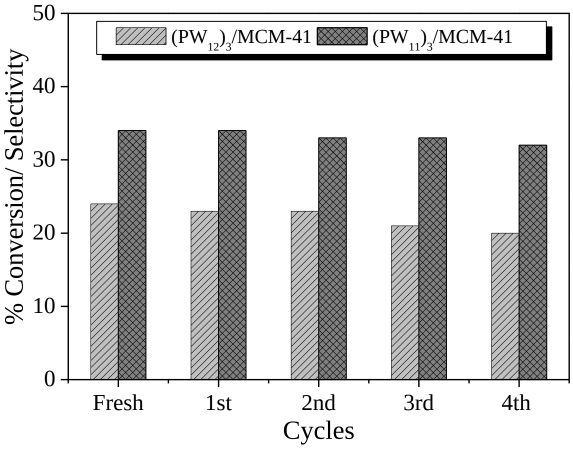


Figure 21. Recycling study for oxidation of BA: molar ratio of BA: H_2O_2- 1:3, catalyst amount- 25 mg, time- 24 h and temperature- 90 °C.

3A (II) Oxidation of Gly and BA over PW_{12}/MCM-48 and PW_{11}/MCM-48.

- ***Oxidation of Gly with H_2O_2***

Optimisation studies over $(PW_{12})_3$/MCM-48 and $(PW_{11})_3$/MCM-48 was carried out similar to the *previous section (I).*

Effect of % loading of PW_{12}/PW_{11}

The effect of % loading of PW_{12}/PW_{11}, on reaction was carried out with 10 to 40% loadings (Figure 22). It was observed that with increase in the % loading of PW_{12}/PW_{11}, % conversion also increases till 30%. On further increasing the loading to 40% there was no significant change in % conversion/selectivity. Hence, 30% loading of PW_{12}/PW_{11} were selected for further catalytic studies.

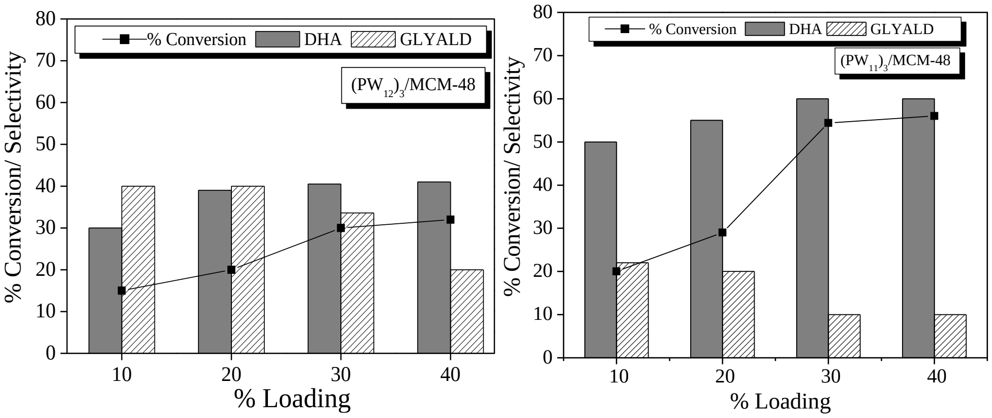


Figure 22. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C, time- 20 h.

Effect of mole ratio of Gly: H_2O_2

It can be observed from Figure 23 that, with an increase in mole ratio of Gly to H_2O_2 from 1:1 to 1:3, there was an increase in the conversion, which may be due to increase in concentration of H_2O_2, which assists in further oxidation of the primary and secondary hydroxyl group of Gly. On further increasing the mole ratio to 1:4, no significant increase in conversion was observed. Therefore, 1:3 mole ratio was found to be optimum in terms of conversion.

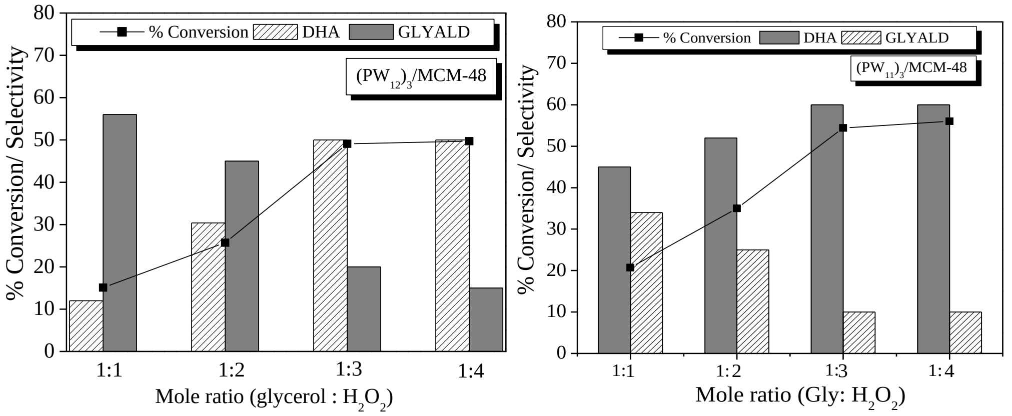


Figure 23. Effect of mole ratio: catalyst amount- 25 mg, temperature- 90 °C, time- 20 h.

Effect of catalyst amount

From Figure 24, it was observed that % conversion increases as the active species (PW_{12}/PW_{11}) increases from 15 to 25 mg, i.e., the catalyst amount increases, which is as expected (acidic pH assists oxidation of secondary hydroxyl group, giving selectivity toward DHA). After 25 mg there was no significant increase in conversion. Under the optimized conditions at 1:3 molar ratio, 25 mg catalyst, conversion was 30%, and the product selectivity for DHA, GLYALD was 40.5, 33.6%, respectively for $(PW_{12})_3$/MCM-48.

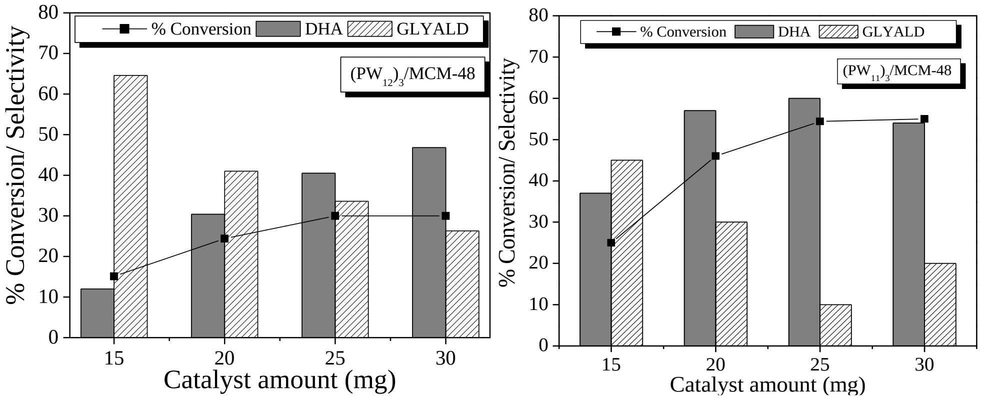


Figure 24. Effect of catalyst amount: mole ratio Gly:H_2O_2- 1:3, temperature- 90 °C, time- 20 h.

Effect of reaction time

It was observed from Figure 25 that with an increase in time, % conversion also increases. This may be due to the reason that more time is required for the formation of a reactive intermediate species (substrate + catalyst), which finally gets converted into products. Highest conversion (30%) and selectivity of DHA (46.8%) is obtained at 20 h. No significant change in % conversion and % selectivity was observed after 20 h.

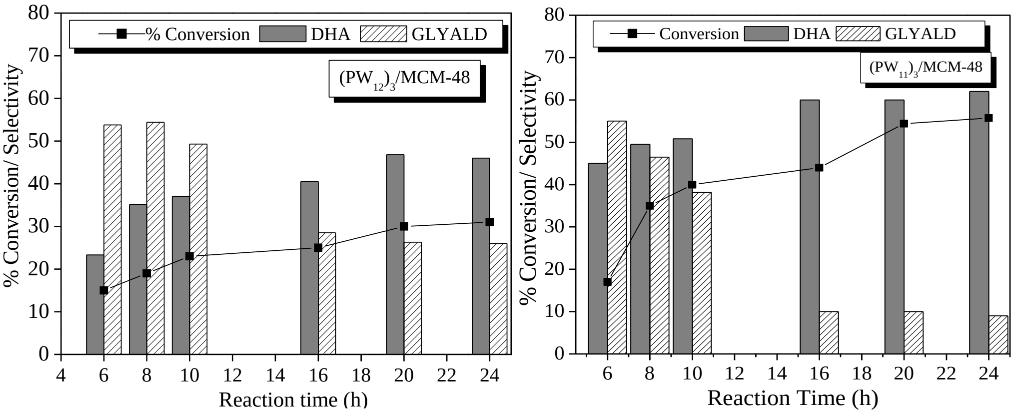


Figure 25. Effect of time: mole ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C.

Effect of reaction temperature

In order to determine the optimum temperature, the reaction was investigated at four different temperatures 70-100 °C (Figure 26), keeping other parameters fixed (25 mg catalyst amount, reaction time 24 h).

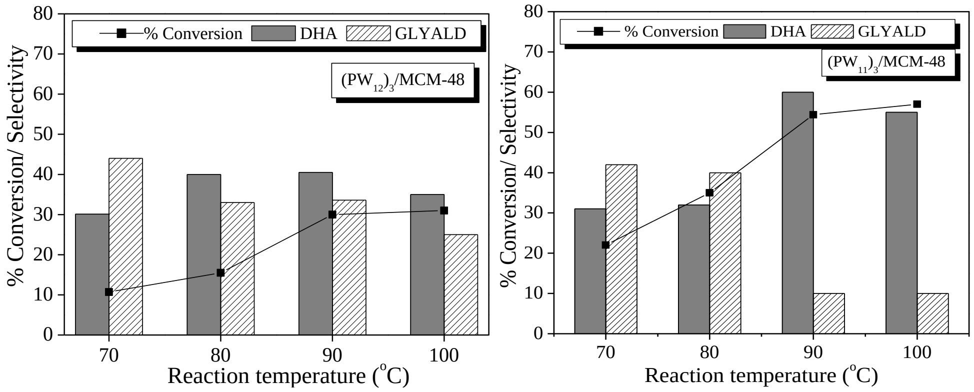


Figure 26. Effect of reaction temperature: mole ratio Gly: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C, time- 20 h.

The results show that conversion increased for $(PW_{12})_3$/MCM-48, on increasing the temperature from 70 to 90 °C (10.7-30.0% conversion and 30-40% selectivity for DHA, 44-33% selectivity for GLYALD). On increasing the temperature from 90 to 100 °C, there is no significant increase in conversion, but a decrease in selectivity for DHA and GLYALD (at 90 °C - 40.5, 33.6%, at 100 °C - 35, 25%, respectively) was observed due to further oxidation of these products to acid. So, 90 °C was optimized for further studies. Similar trend was observed for $(PW_{11})_3$/MCM-48.

Optimized conditions: [30% conversion $(PW_{12})_3$/MCM-48 and 54.4% $(PW_{11})_3$/MCM-48] mole ratio Gly:H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h and temperature- 90 ^{o}C.

Kinetic study

The plot of log C_o/C versus time (Figure 27) shows a linear relationship of glycerol consumption with respect to time and follows first order kinetics. It was observed from Figure 28 that rate of reaction increases with increase in the catalyst concentration (at fixed substrate concentration of 10 mmol and temperature 90 °C) and the plot of reaction rate vs catalyst concentration also show a linear relationship.

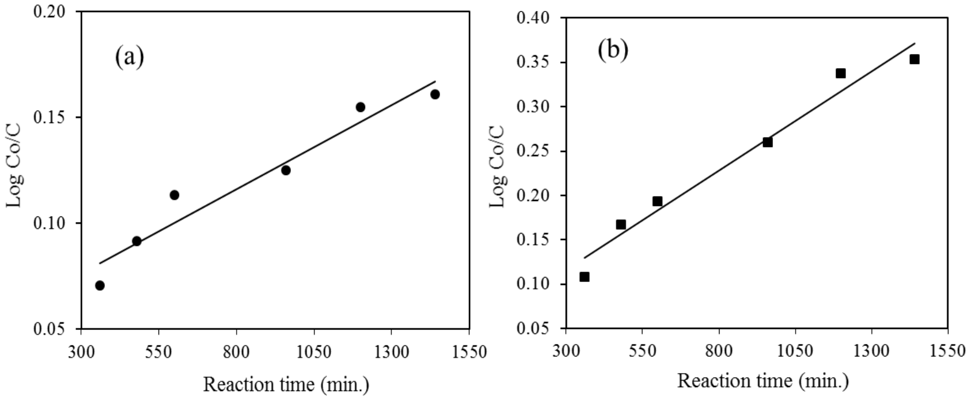


Figure 27. First-order plot for oxidation of Gly over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

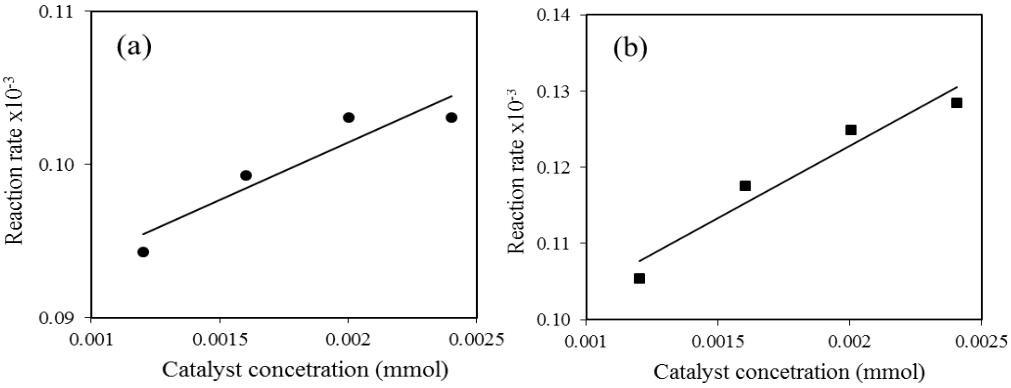


Figure 28. Rate of reaction versus catalyst concentration over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

The graph of ln k versus 1/T was plotted (Figure 29), and the value of Ea was determined from the plot. Activation Energy (Ea) for $(PW_{12})_3$/MCM-48 was found to be 46.1 kJ mol^{-1} and for $(PW_{11})_3$/MCM-48 it was 42.2 kJ mol^{-1} indicating that the rate is truly governed by the chemical step.

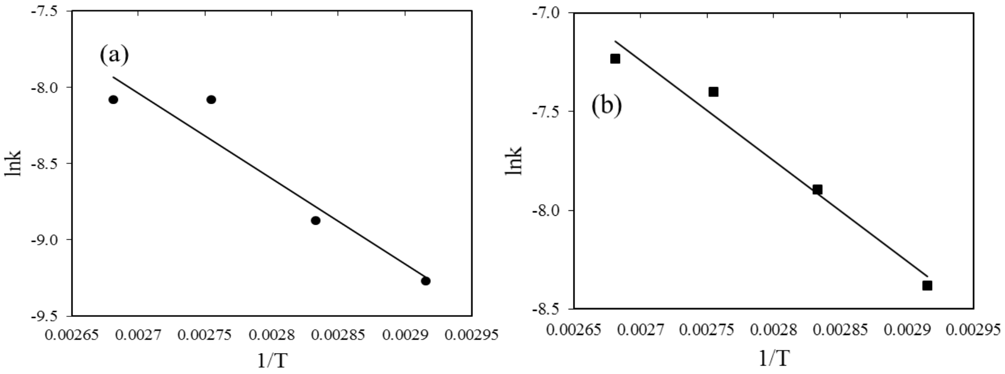


Figure 29. Arrhenius plot for determination of Ea, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

From the Ea value, order of activity for catalysts are; $(PW_{11})_3$/MCM-48 > $(PW_{12})_3$/MCM-48.

- ***Oxidation of BA with H_2O_2***

Effect of % loading PW_{12}/PW_{11}

As discussed in all the previous chapters systematic % loading variation suggested that 30% loading was best for obtaining maximum conversion (Figure 30).

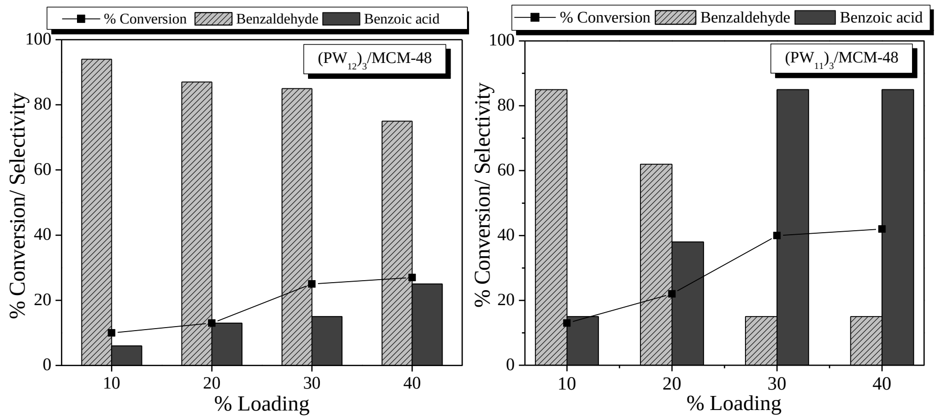


Figure 30. Effect of % loading of PW_{12}/PW_{11}: mole ratio of BA: H_2O_2- 1:3, catalyst amount- 25 mg, temperature- 90 °C, time- 24 h.

Effect of mole ratio

Study on effect of mole ratio (1:1 to 1:4) was carried out (Figure 31) and it was found that 1:3 molar ratio gives maximum conversion (40% for $(PW_{11})_3$/MCM-48), however with a very poor selectivity for benzaldehyde (15%- $(PW_{11})_3$/MCM-48) in 24 h. Further increase in molar ratio does not improve the conversion, hence 1:3 molar ratio was optimized for further reactions.

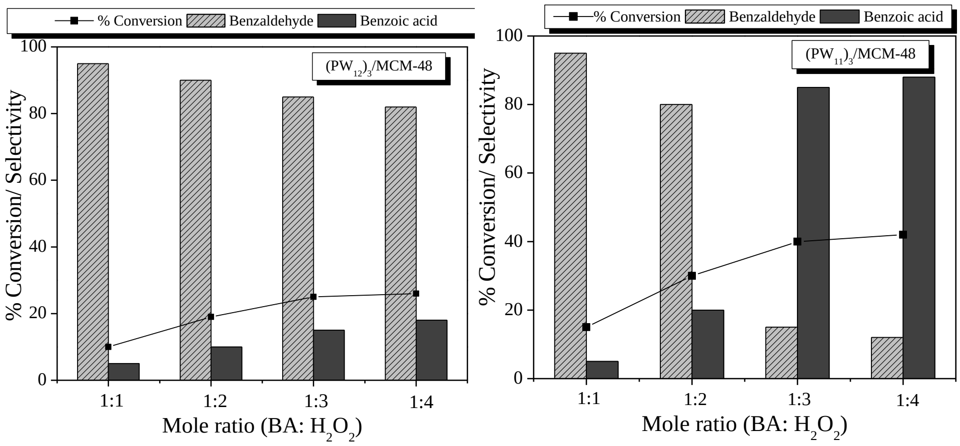


Figure 31. Effect of mole ratio: catalyst amount- 25 mg, temperature- 100 °C, time- 24 h.

A drastic difference in selectivity of benzaldehyde was observed between $(PW_{12})_3$/MCM-48 and $(PW_{11})_3$/MCM-48 due to nature of active species which will be discussed in further sections.

Effect of reaction time

Our main aim was to obtain benzaldehyde as the major product by avoiding it's over oxidation to benzoic acid, hence effect of reaction time was investigated (Figure 32). The % conversion was monitored at different reaction time (from 2-24 h). At 2 h, 7% conversion was achieved with 90% selectivity towards benzaldehyde. Increase in conversion with an increase in reaction time was observed and maximum conversion was achieved in 20 h with 60 % selectivity for benzaldehyde. On further increasing the time to 24 h there was no significant change in conversion, however over oxidation of benzaldehyde to acid was observed. Hence, 20 h was optimised for further reactions.

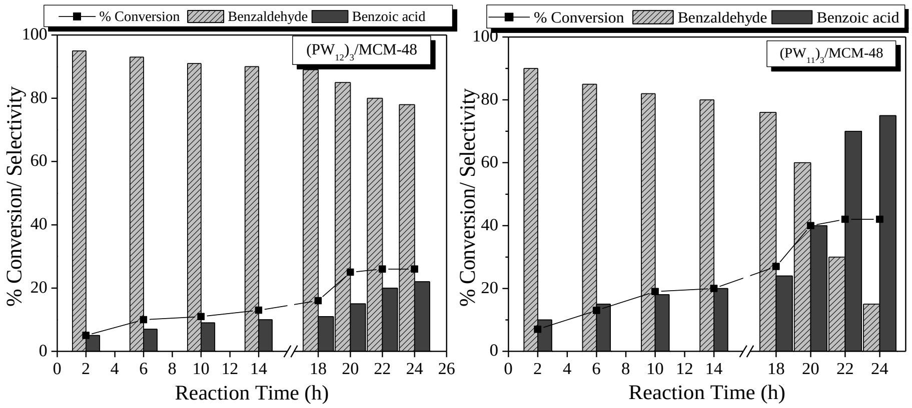


Figure 32. Effect of reaction time: mole ratio- 1:3, catalyst amount - 25 mg, temperature- 90 °C.

Effect of catalyst amount

Amount of catalyst has substantial effect on oxidation of BA (Figure 33) as increase in conversion is directly proportional to the increase in amount of catalyst from 15 to 25 mg. Lower conversion of alcohol with 15-20 mg catalyst may be due to fewer catalytic sites. Maximum % conversion was observed with 25 mg catalyst, however there was no remarkable difference in the progress of reaction when catalyst amount was increased from 25 to 30 mg.

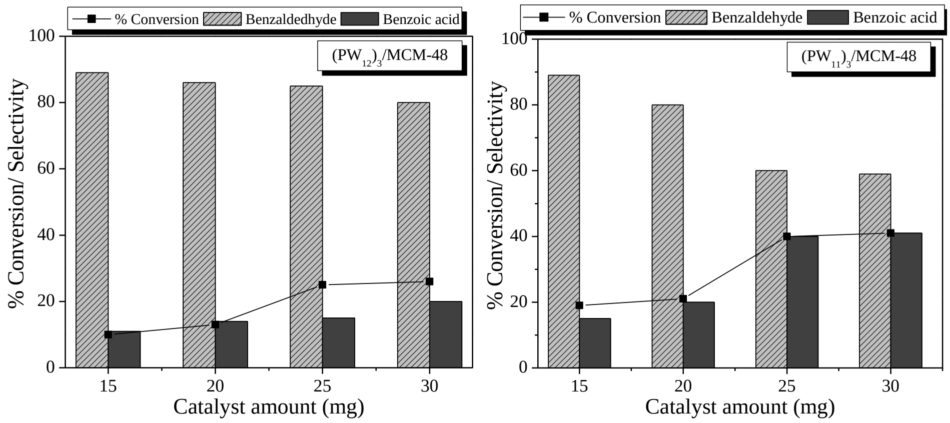


Figure 33. Effect of catalyst amount: mole ratio- 1:3, time- 20 h, temperature- 90 °C.

Effect of reaction temperature

It was also found that as the temperature increases (70-90 °C), conversion of alcohol also increases (Figure 34). But selectivity decreases drastically on increasing the temperature. This drastic change in selectivity might be due to further oxidation of benzaldehyde to benzoic acid, which may also arise due to acidity of catalyst as well as the effect of support. 90°C was found to be optimum for obtaining maximum conversion.

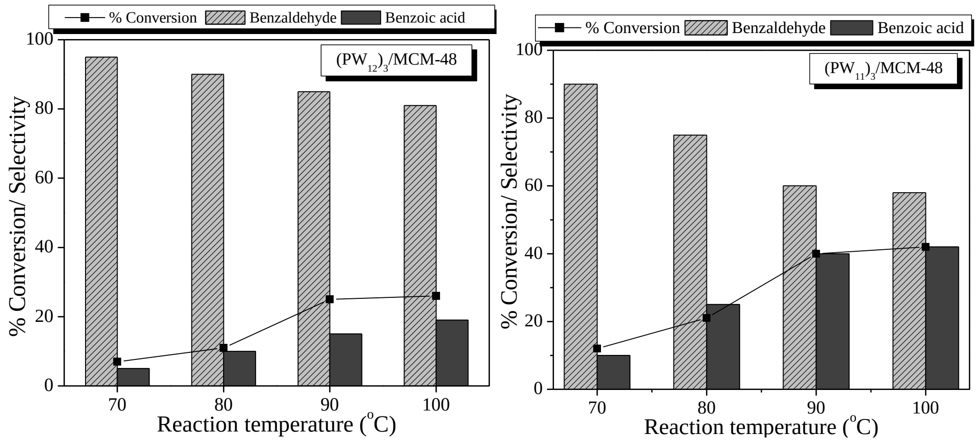


Figure 34. Effect of temperature: mole ratio- 1:3, catalyst amount- 25 mg and time- 20 h.

Optimized conditions: [25% conversion for $(PW_{12})_3$/MCM-48 and 40% conversion for $(PW_{11})_3$/MCM-48] mole ratio BA:H_2O_2- 1:3; catalyst amount- 25 mg, time- 20 h and temperature- 90 °C.

Kinetic study

A detailed study on the kinetic behavior was carried out. The plot of log C_o/C versus time (Figure 35) shows a linear relationship of alcohol consumption with respect to time and follows first order kinetics. It was observed from Figure 36 that rate of reaction increases with increase in the catalyst concentration (at fixed substrate concentration of 10 mmol and temperature 90 °C) and the plot of reaction rate vs catalyst concentration also show a linear relationship.

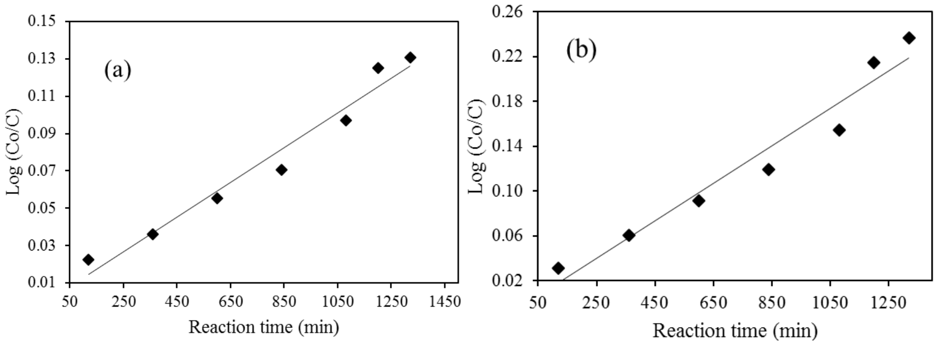


Figure 35. First-order plot for oxidation of BA over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

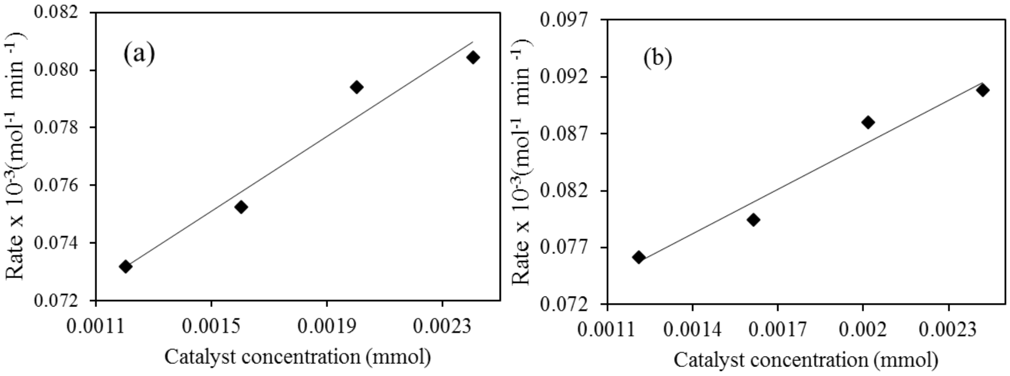


Figure 36. Rate of reaction versus catalyst concentration over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

The graph of ln k versus 1/T was plotted (Figure 37), and the value of Ea was determined from the plot. Ea for $(PW_{12})_3$/MCM-48 and $(PW_{11})_3$/MCM-48 was found to be 46.5 kJmol^{-1} and 41.0 kJ mol^{-1} respectively, indicating that the rate is truly governed by the chemical step, without any mass transport/diffusion limitations.

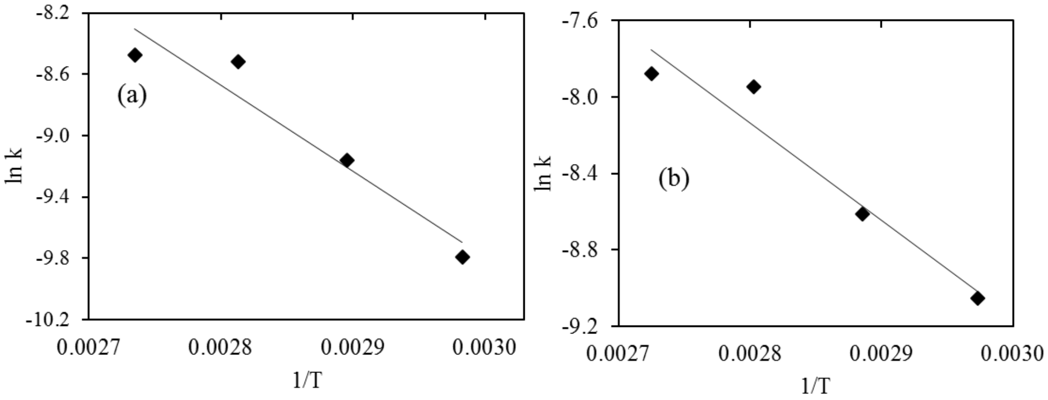


Figure 37. Arrhenius plot for determination of Ea, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

The order of activity based on the Ea value was found to be, $(PW_{11})_3$/MCM-48 > $(PW_{12})_3$/MCM-48.

- ***Oxidation of BA with O_2***

Optimisation studies for maximum conversion was carried out similar to the *previous section (I).*

Effect of catalyst amount

Reaction was carried out by varying catalysts amount (10 mg- 30 mg) (Figure 38 a, b). Initially, on increasing catalyst amount from 10 mg to 25 mg, the conversion increases sharply. Further increase in the catalyst amount does not increase the conversion very significantly. Therefore, 25 mg for BA was considered optimum for obtaining maximum conversion.

Effect of reaction time

The effect of reaction time on the selective oxidation was carried out by monitoring % conversion at different time intervals (Figure 38 c, d). Initially with increase in reaction time up to 20 h, the % conversion increases slowly. The catalyst initially takes an induction period to accelerate the reaction. The maximum conversion was achieved at 24 h. On further increasing the reaction time, there was no significant increase in the conversion. However, a decrease in % selectivity for benzaldehyde was observed, hence 24 h reaction time was optimised.

Effect of reaction temperature

Temperature was varied from 60-100 ^{o}C (Figure 38 e, f) keeping other parameters fixed. The results show that conversion increases with increase in temperature which is as expected. Similarly, on increasing temperature from 90 to 100 ^{o}C, conversion increases but at the same time selectivity of benzaldehyde. This result is attributed to further oxidation of benzaldehyde to benzoic acid at higher temperature. So temperature of 90 ^{o}C was found optimal for the maximum conversion.

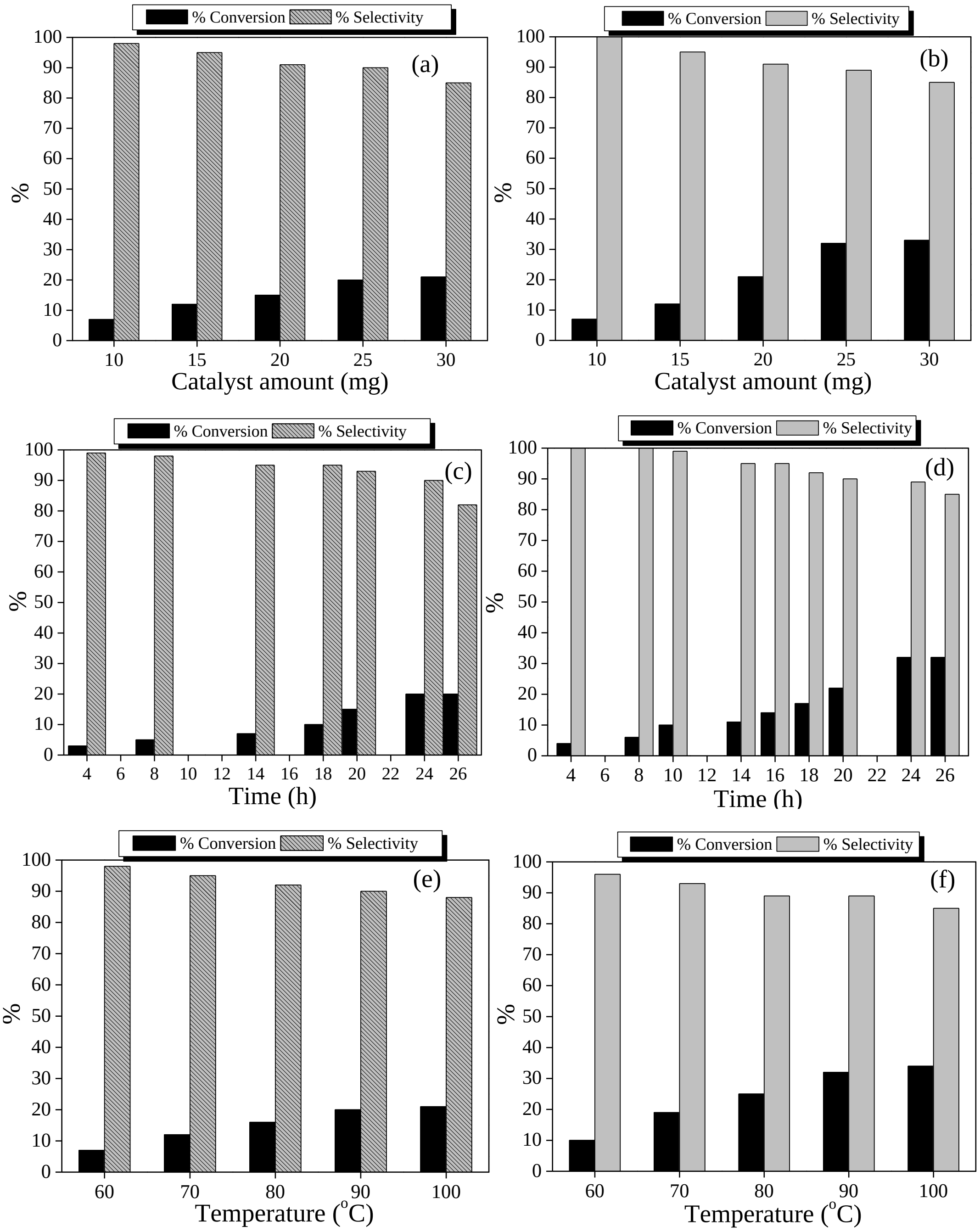


Figure 38. Effect of catalyst amount (a) $(PW_{12})_3$/MCM-48, (b) $(PW_{11})_3$/MCM-48: substrate- 100 mmol, TBHP- 0.2 mmol, time- 24 h, temperature- 90 ^{o}C; Effect of reaction time (c) $(PW_{12})_3$/MCM-48, (d) $(PW_{11})_3$/MCM-48: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 25 mg, temperature- 90 ^{o}C; Effect of reaction temperature (e) $(PW_{12})_3$/MCM-48, (f) $(PW_{11})_3$/MCM-48: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 25 mg, time- 24 h.

Optimised conditions: [20% conversion $(PW_{12})_3$/MCM-48, 32% conversion $(PW_{11})_3$/MCM-48] catalyst amount- 25 mg, TBHP- 0.2 mmol, temperature- 90 °C, time- 24 h. Comparison of optimised conditions with both the oxidants is given in Table 5.

Table 5. Optimized conditions with both the oxidants.

Conditions	Oxidants	
	H_2O_2	O_2
Mole ratio of substrate to H_2O_2	1:3	-
Substrate Concentration	10 mmol	100 mmol
Reaction time	20 h	24 h
Catalyst amount	25 mg	25 mg
Reaction temperature	90 °C	90 °C

It is seen from Table 6 that for both the catalysts order of activity of oxidant was $O_2 > H_2O_2$ i.e. high mole conversion of substrate and TON was observed with O_2 as compared to that of H_2O_2. As discussed in *section 3A (I)* similar explanation can be given for role of oxidant.

Table 6. Comparison of catalytic activity of both the catalysts.

Catalyst	Oxidant	% Conv.	% Sel.	TON
$(PW_{12})_3$/MCM-48	H_2O_2[a]	25	85	1250
	O_2[b]	20	90	10000
$(PW_{11})_3$/MCM-48	H_2O_2[a]	40	60	2000
	O_2[b]	32	89	17986

[a] *Reaction with H_2O_2, BA: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h, temp.- 90 °C;* [b] *Reaction with O_2, BA- 100 mmol, TBHP- 0.2 mmol, catalyst amount-25 mg, time- 24 h, temperature- 90 °C, Selectivity for Benzaldehyde.*

Plot of kinetic curve (% conversion vs time) (Figure 39), suggested that O_2 was the only oxidant and it requires a longer time for activation, and TBHP acts as an radical initiator, as discussed in *section 3B (I)*.

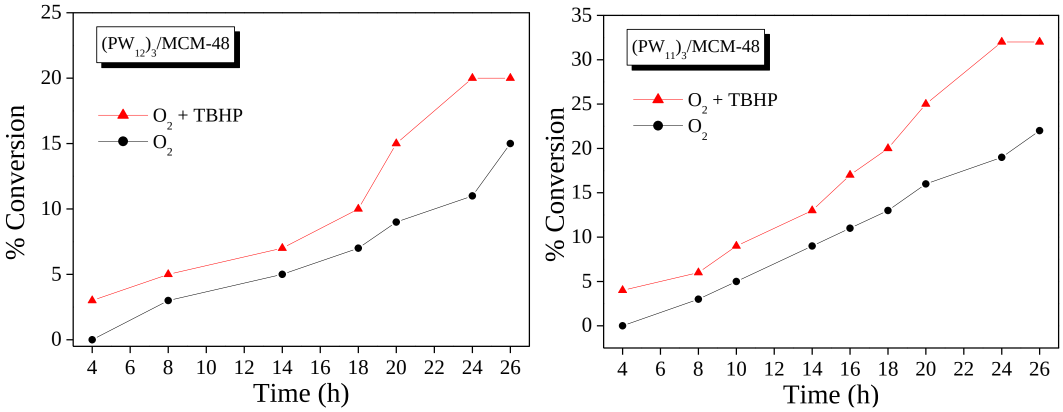


Figure 39. Role of TBHP in promoting the oxidation over both the catalysts.

Control experiments and Heterogeneity test

Control experiments for oxidation of Gly and BA (Table 7) shows that that catalytic activities of PW_{12}/PW_{11} have been retained in the respective catalysts indicating that PW_{12}/PW_{11} behaves as real active species.

Table 7. Control experiments for oxidation of Gly and BA with H_2O_2.

Catalyst	% Conv. $^{a/b}$	% Sel. $^{a/b}$	TON $^{a/b}$
No catalyst	-/-		-
MCM-48	<1/<1	50/100	-
PW_{12}	20.5/20	61/98	1050/1000
$(PW_{12})_3$/MCM-48	30.0/25	41/85	1500/1250
PW_{11}	30.0/30	68/80	1476/1476
$(PW_{11})_3$/MCM-48	54.4/40	60/60	2540/2000

[a] *Oxidation of Gly: mole ratio 1:3, amount of PW_{12}/PW_{11}- 5.7 mg, catalyst- 25 mg, selectivity for DHA;* [b] *Oxidation of BA: mole ratio- 1:3, amount of PW_{12}/PW_{11}- 5.7 mg, catalyst- 25 mg, selectivity for benzaldehyde.*

Heterogeneity test (Figure 40) shows that reaction mixture after filtration does not show any increase in the conversion or % selectivity, indicating that there was no leaching of active species (PW_{12}/PW_{11}) from the support and catalysts are truly heterogeneous in nature.

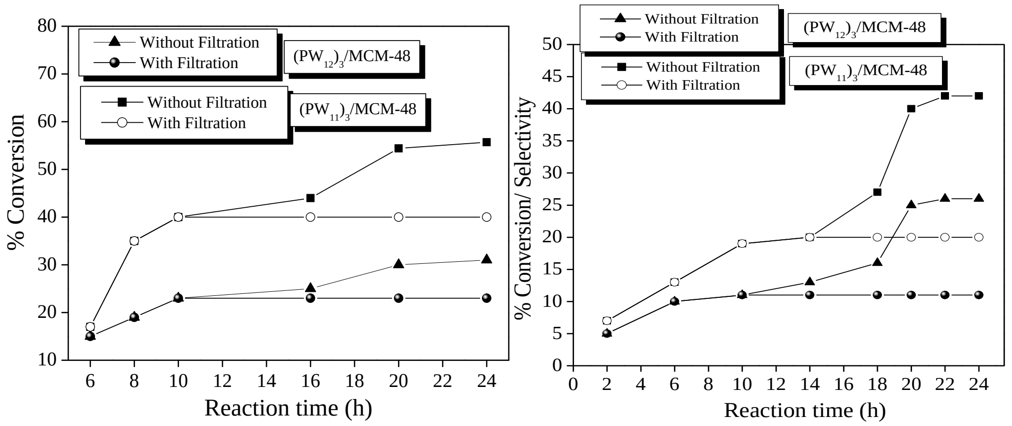


Figure 40. Heterogeneity test for oxidation of Gly (Left) and BA (Right) with H_2O_2.

Recycling and regeneration of catalysts

The catalysts were recycled up to four times in order to test their activity in successive runs for oxidation of Gly (Figure 41) and BA (Figure 42). The procedure for recycling was same as explained in *chapter 2*. No significant difference in the % conversion and selectivity was observed even after four cycles. Thus, catalysts could be reused up to four cycles without minimal loss in the activity.

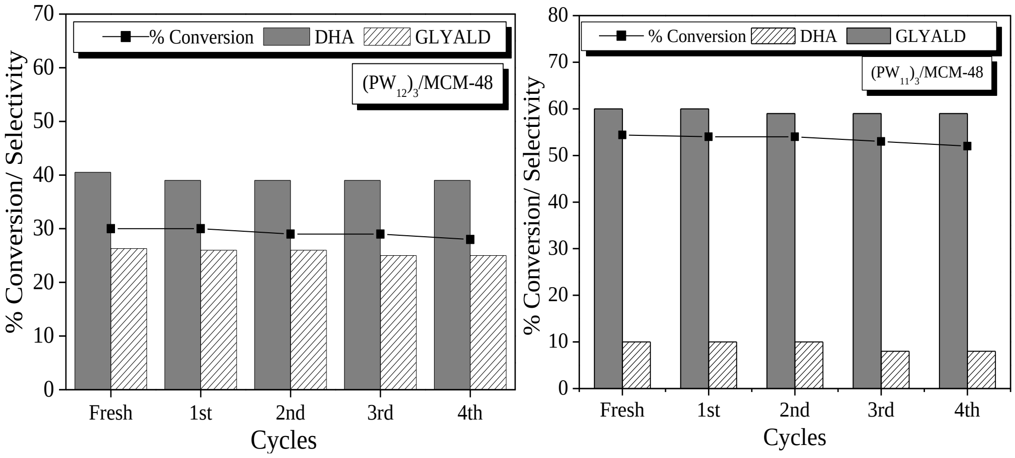


Figure 41. Recycling study for oxidation of Gly: mole ratio of Gly: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h and temperature- 90 °C.

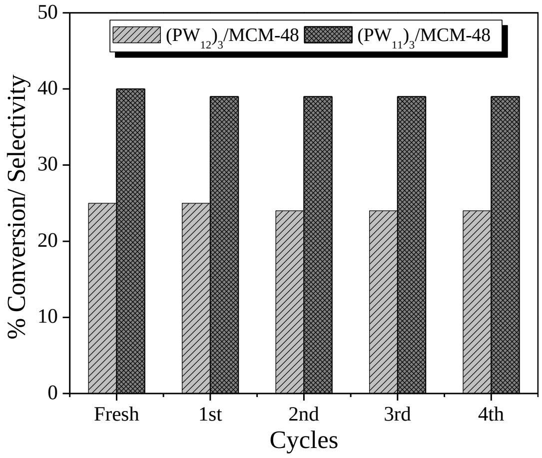
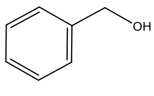
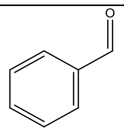
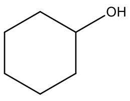
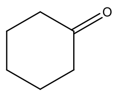
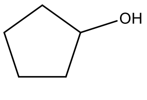
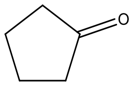
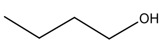
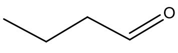
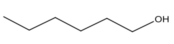
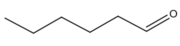


Figure 42. Recycling study for oxidation of BA: molar ratio of BA: H_2O_2- 1:3, catalyst amount- 25 mg, time- 20 h and temperature- 90 °C.

Substrate scope for oxidation of different alcohols over all the catalysts

Different substrate scope was carried out under optimized conditions (Table 8). Oxidation of secondary alcohol was easier as compared to primary alcohols, which is as expected. It was observed that as compared to cyclohexanol, cyclopentanol gives less conversion. It was also observed that, long chain primary alcohol (1-hexanol) was less reactive. In all cases, very high TON was observed.

Table 8. Scope of different alcohol substrate under optimised conditions.

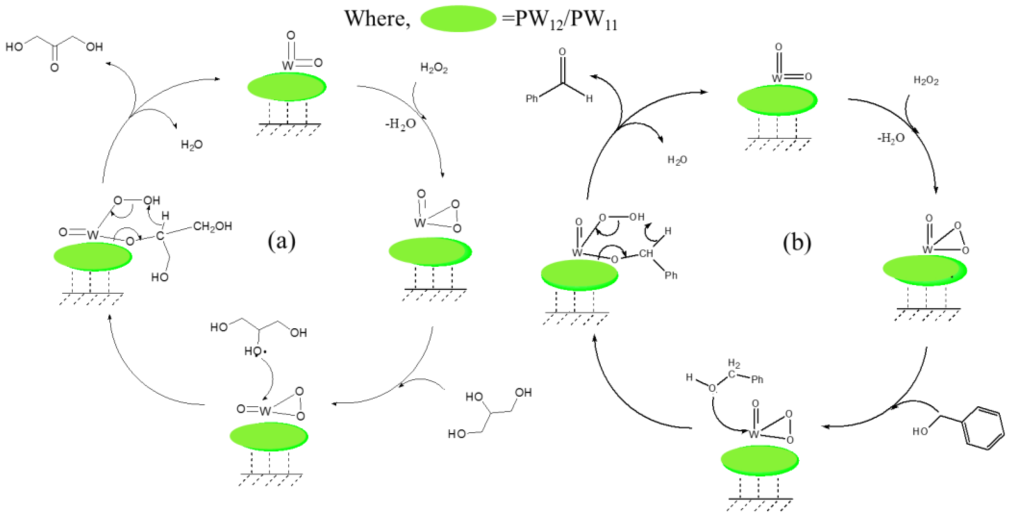
Substrate	% Conv. a/b/c/d	Products	% Sel. a/b/c/d	TON a/b/c/d
	24/34/25/40		82/16/60/60	1200/1673/2000/ 2139
	18/30/20/30		91/90/92/90	900/1476/1600/ 1604
	15/23/17/25		90/89/92/90	750/984/1360/ 1337
	16/32/20/30		86/91/88/90	800/1369/1529/ 1604
	16/30/19/18		92/90/90/95	800/1476/1452/ 962

[a] $(PW_{12})_3$/MCM-41, [b] $(PW_{11})_3$/MCM-41, [c] $(PW_{12})_3$/MCM-48 and [d] $(PW_{12})_3$/MCM-48.

Probable reaction mechanism for oxidation of Gly and BA

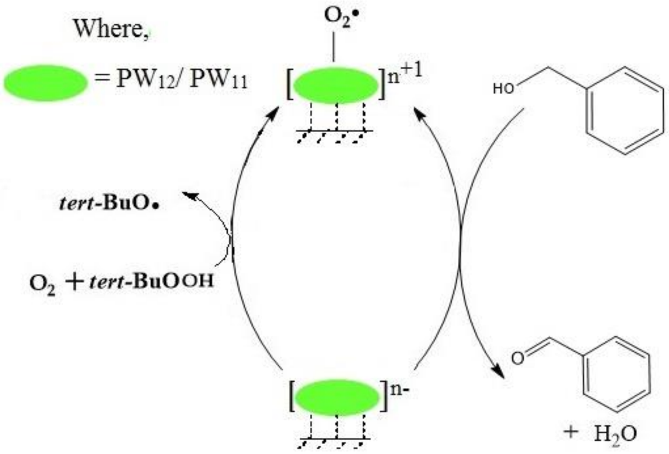
In order to study the reaction mechanism, set of reactions were carried out at different stages (oxidation of Gly and BA). The pore geometry of support to some extent also influences the conversion and product selectivity for Gly oxidation as reported by Rodrigues et al. for gold supported MWCNT and activated carbon [45]. They have shown different selectivities for DHA or GLYALD depending on the pore geometry in the support. In the present case also due to three dimensional pore network of MCM-48 and hexagonal pore network of MCM-41, the reaction as well as selectivity for DHA is much favoured.

It is known for oxidation reactions with transition metal atoms, especially POMs, that H_2O_2 first binds to the metal centre and then transfers an oxygen atom to the alcohol. Thus, the activation of the metal center results via. generation of active species which may be hydroperoxo or bridging peroxo species [44]. In the present case, the catalysts are also expected to follow the same mechanism via. formation of an active tungsten-peroxo or hydroperoxo intermediate (Scheme 3 a, b).



Scheme 3. Probable reaction mechanism for liquid phase oxidation of (a) Gly and (b) BA with H_2O_2.

Also for investigations of mechanism of BA with O_2, different sets of experimental studies proposed that the reaction appears to be a radical mechanism and activation of catalyst was necessary for initiating the reaction (Scheme 4), where TBHP acts as a radical initiator only. The experimental data and studies in previous section (role of oxidants) also suggest the following mechanism with O_2.



Scheme 4. Proposed mechanism for oxidation of BA with O_2.

Conclusions

- Selective oxidation of glycerol with *environmatally benign H_2O_2* to give value added products (*DHA* and *GLYALD*) under solvent free mild conditions was achieved for the first time.
- Oxidation of *benzyl alcohol* with *H_2O_2* and *O_2* was also explored under solvent free green conditions.
- *Kinetic studies* for both the reactions follow *first order rate law* with absence of any mass transfer/ diffusion limitation.
- A probable *mechanism* for both the alcohols were proposed based on various experimental conditions.
- *Environmatal* and *economic benefits* were achieved as glycerol, a byproduct of biodiesel, was utilized to give value added products.
- From catalytic activity and kinetic studies the order of catalysts are: *$(PW_{11})_3$/MCM-48* > *$(PW_{11})_3$/MCM-41*> *$(PW_{12})_3$/MCM-48*> *$(PW_{12})_3$/MCM-41*.

References

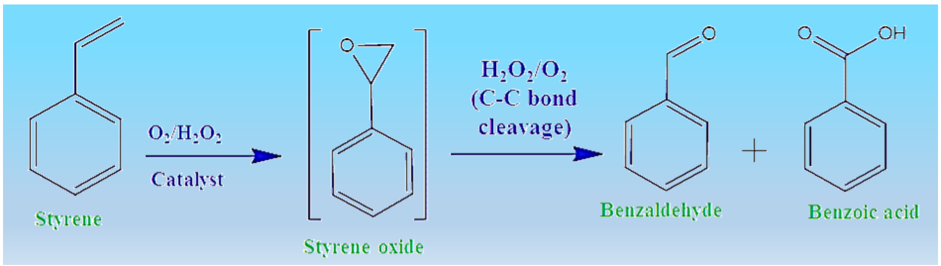
1. N. Mizuno, K. Kamata, S. Uchida, K. Yamaguchi, *Modern Heterogeneous Oxidation Catalysis- Design, Reactions and Characterization* (Ed. N. Mizuno), Wiley-VCH, Verlog, Ch.- 6, 2009.
2. A. C. Dengel, W. P. Griffith, B. C. Parkin, J. Chem. Soc. Dalton Trans., 2683, (1993).
3. S. G. Casuscelli, M. E. Crivello, C. F. Perez, G. Ghione, E. R. Herrero, L. R. Pizzio, P. G. Vazquez, M. N. Blanco, Appl. Catal. A: Gen., 274, 115, (2004).
4. M. Naik, S. Samantaray, B. Mishra, A. Dubey, Reac. Kin. Catal. Lett., 98, 125, (2009).
5. B.S. Lane, K. Burgess, Chem. Rev., 103, 2457, (2003).
6. R. Neumann, M. Levin, J. Org. Chem. 56, 5707, (1991).
7. S. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, J. Mol. Catal. A: Chem., 110, 105, (1996).
8. A. Bordoloi, S. Sahoo, F. Lefebvre, S.B. Halligudi, J. Catal. 259, 232, (2008).
9. Y. M. A. Yamada, C. K. Jin, Y. Uozumi, Organic Lett., 12, 4540 (2010).
10. M. Pagliaro, M. Rossi, *The Future of Glycerol- New Uses of a Versatile Raw Material*, RSC Green Chemistry Series, 2nd Edition, (2010).
11. S. Gil, M. Marchena, C. M. Fernandez, L. S. Silva, A. Romero, J. L. Valverde, Appl. Catal. A: Gen., 450, 189, (2013).
12. A. Villa, G. M. Veith, L. Prati, Angew. Chem., Int. Ed. 49, 4499, (2010).
13. S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nakagawa, K. Tomishige, J. Catal. 300, 205, (2013).
14. H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, Appl. Catal. A: Gen., 96, 217, (1993).
15. H. Kimura, Appl. Catal. A: Gen., 105, 147, (1993).
16. R. Garcia, M. Besson, P. Gallezot, Appl. Catal. A: Gen., 127, 165 (1995).
17. A. Abbadi, H. van Bekkum, Appl. Catal. A: Gen., 124, 409, (1995).
18. H. Kimura, Polym. Adv. Technol., 12, 697, (2001).

19. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G. J. Hutchings, Chem. Commun., 7, 696, (2002).
20. S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G. J. Hutchings, C. J. Kielly, Phys. Chem. Chem. Phys., 5, 1329, (2003).
21. N. Dimitratos, F. Porta, L. Prati, Appl. Catal. A: Gen., 291, 210, (2005).
22. D. I. Enache, J. K. Edwards, P. Landon, B. S. Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, Science, 311, 362, (2006).
23. W. Hu, B. Lowry, A. Varma, Appl. Catal. B: Env., 106, 123, (2011).
24. G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzing, M. Conte, J. A. L. Sanchez, C. J. Kiely, D. W. Knight, S. H. Taylor, G. J. Hutchings,. Angew. Chem. Int. Ed., 50, 10136, (2011).
25. C. H (Clayton) Zhou, J. N. Beltramini, Y. X. Fan, G. Q. (Max) Lu, Chem. Soc. Rev., 37, 527, (2008).
26. B. Katryniok, H. Kimura, E. Skrzynska, J. S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul, F. Dumeignil, Green Chem. 13, 1960, (2011).
27. P. McMorn, G. Roberts, G. J. Hutchings, Catal. Lett., 63, 193, (1999).
28. R. Luque, V. Budarin, J. H. Clark, D.J. Macquarrie, Appl. Catal. B: Env., 82 157, (2008).
29. G. B. Shulpin, Y. N. Kozlow, L.S. Shulpin, T.V. Strelkova, D. Mandelli, Catal. Lett., 138, 193, (2010).
30. X. Wang, G. Wu, F. Wang, K. Ding, F. Zhang, X. Liu, Y. Xue, Catal. Commun., 28, 73, (2012).
31. C. A. Nunes, M. C. Guerreiro, J. Mol. Catal. A: Chem., 370, 145 (2013).
32. C. Crotti, E. Farnetti, J. Mol. Catal. A: Chem., 396, 353, (2015).
33. *Ulmann's Encyclopedia of Industrial Chemistry*, 5th ed. VCH: Weinheim, p 469, (1985).
34. G. Li, D. I. Enache, J. K. Edwards, A. F. Carley, D. W. Knight, G. J. Hutchings, Catal. Lett., 110, 7, (2006).

35. S. Mallick, S. Rana, K. Parida, Ind. Eng. Chem. Res., 51, 7859, (2012).
36. L. Jing, J. Shi, F. Zhang, Y. Zhong, W. Zhu, Ind. Eng. Chem. Res., 52, 10095, (2013).
37. A. Patel, S. Pathan, Ind. Eng. Chem. Res., 51, 737, (2012).
38. S. Pathan, A. Patel, Chem. Eng. J., 243, 183, (2014).
39. S. Pathan, A. Patel, *Environmentally Benign Catalysts for Clean Organic Reactions*, (Ed. A. Patel), Springer publications, Chapter- 10, (2013).
40. N. Narkhede, A. Patel, S. Singh, Dalton Trans., 43, 2512, (2014).
41. S. Singh, N. Narkhede, A. Patel, RSC Adv., 5, 36270, (2015).
42. S. Shanmugam, B. Viswanathan, T. K. Varadarajan, J. Mol. Catal. A: Chem., 223, 143, (2004).
43. A. Sheldon, M. Walau, I. W. C. E. Arends, U. Schuchurdt, Acc. Chem. Res. 31, 485, (1998).
44. N. Mizuno, *Mechanisms in homogeneous and heterogeneous epoxidation catalysts.* S. T. Oyama (Ed), Ch.- 4, Elsevier, New York, (2008).
45. E. G, Rodrigues, M. F. R, Pereira, J. J. Delgado, X. Chen, J. J. M. Orfao, Catal. Commun., 16, 64, (2011).

CHAPTER 3B

Oxidation of Alkene…..



Catal Lett (2016) 146:1059–1072
DOI 10.1007/s10562-016-1732-7

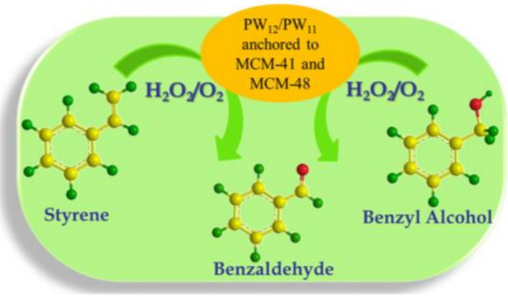
Environmentally Benign Oxidations of Alkenes and Alcohols to Corresponding Aldehydes over Anchored Phosphotungstates: Effect of Supports as Well as Oxidants

Sukriti Singh[1] · **Anjali Patel**[1]

Received: 5 March 2016 / Accepted: 13 March 2016

Abstract Series of catalysts comprising of parent phosphotungstate (PW_{12}) and mono lacunary phosphotungstate (PW_{11}) anchored to different mesoporous materials (MCM-41 and MCM-48) were prepared. Environmentally benign oxidation of alkenes and alcohols were carried out with H_2O_2 and molecular oxygen as oxidants. The influence of different parameters on the conversion as well as the selectivity was investigated. Comparative study was ascertained over anchored parent, lacunary phosphotungstates as active species and the supports. The kinetic and thermodynamic studies were correlated with the effect of support as well as active species. Moreover, the catalysts could be recovered and reused four times without significant loss in their activity and selectivity.

Graphical Abstract



Keywords 12-Tungstophosphoric acid · Mono lacunary phosphotungstate · Mesoporous supports · Environmental benign · Oxidation

Oxidation of alkenes

The products of oxidative cleavage of C-C bond to aldehydes or ketones, is widely recognized as one of the most fundamental transformations in organic chemistry and especially benzaldehyde is very valuable and demanding chemical. As the traditional procedures suffer from a lack of selectivity, the use of organic solvents, toxicity of the reagents, and waste production, it is a challenge for chemists to develop new environmentally benign and non-polluting oxidation procedures [1]. Therefore, the development of eco-sustainable catalytic systems would contribute in launching green and sustainable chemical processes.

In this regard, since past few years, heterogeneous catalysts based on POMs have gained much attention. Incorporation of POMs, specifically 12-tungstophosphoric acid (PW_{12}) or lacunary PW_{11}, into amorphous or structured silicates in oxidative catalysis are well-known [2-6]. There are number of reports on oxidation of alkene/olefin by heterogeneous POMs with H_2O_2/molecular oxygen [7-11]. For the synthesis of benzaldehyde one synthetic route was already discussed in *Chapter 3A* via. oxidation of BA and in the present chapter we will be discussing it synthesis via oxidation of styrene.

Johnstone and group [12] demonstrated C-C bond oxidative cleavage reaction of alkenes using H_2O_2 over $H_3PW_{12}O_{40}$ supported to aluminium oxide. For oxidation of styrene they obtained 90% yield for benzoic acid using 2-methylpropan-2-ol as solvent in 24 h.

Parida and Malik [13] investigated liquid phase epoxidation of trans-stilbene using *tert*-butylhydroperoxide as an oxidant using Zirconia-alumina mixed oxide supported $H_3PW_{12}O_{40}$. They obtained 46% conversion and 89% of selectivity towards trans-stilbene oxide other product being benzaldehyde.

Mesoporous $H_3PMo_{12}O_{40}/ZrO_2$ was found to be active in oxidation of various alkenes using H_2O_2 in acetonitrile as solvent [14]. Especially, styrene oxidation shows 30% conversion with 95% selectivity for benzaldehyde in presence of H_2O_2 and CH_3CN as solvent.

Mao et al. [15] reported pore expanded silica pillared clay (SPC) as the supports for $H_3PW_{12}O_{40}$ (PW) loading and carried out oxidation reaction of cyclohexene using H_2O_2 as oxidant and acetonitrile as solvent. 40% loaded catalyst, $H_3PW_{12}O_{40}$ (40)-SPC, gives 95% conversion in 4 h at 80 °C.

Recently, Sun and Hu [16], synthesised $H_3PW_{12}O_{40}$/SBA-15 catalyst and utilised it for styrene oxidation at 343 K in acetonitrile for 24 h under the reactant ratio (styrene: H_2O_2= 1:4) due to its suitable textural and structural characteristics. The yield of benzaldehyde, conversion of H_2O_2, and selectivity for benzaldehyde reached 22.6, 98.6, and 100%. Farsani and group, [17] investigated epoxidation of olefins in water with H_2O_2 catalyzed by $H_3PMo_{12}O_{40}$ in nanocapsule (Keplerates). For styrene they obtained 90% yield towards epoxide and other product being benzaldehyde.

In terms of lacunary counterparts, Patel and group have efficiently carried out oxidation of styrene with H_2O_2 or O_2 over PW_{11}/PMo_{11} supported onto different supports [18-24]. They have found excellent conversions and selectivity as well as high TONs under solvent free mild conditions. Granadeiro et al. [25] reported liquid phase oxidation of cis-cyclooctene, geraniol and R-(+)-limonene over PW_{11}@MIL-101 and SiW_{11}@MIL-101 using the H_2O_2 as oxidant. Apart from these, to the best of our knowledge there are no reports on oxidation of styrene over lacunary PW_{11}. In the present chapter we have carried out oxidation of styrene with H_2O_2 (liquid phase) and O_2 (aerobic) over PW_{12}/PW_{11} anchored to MCM-41/MCM-48. Detail optimization study was carried varying different parameters such as % loading, mole ratio of substrate to H_2O_2, catalyst amount, time and temperature.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Styrene, substituted alkenes, 30% aq. H_2O_2, *tert*-butylhydroperoxide (70% aq. TBHP) and dichloromethane were obtained from Merck and used as received.

Catalytic reactions

Oxidation with H_2O_2 and O_2

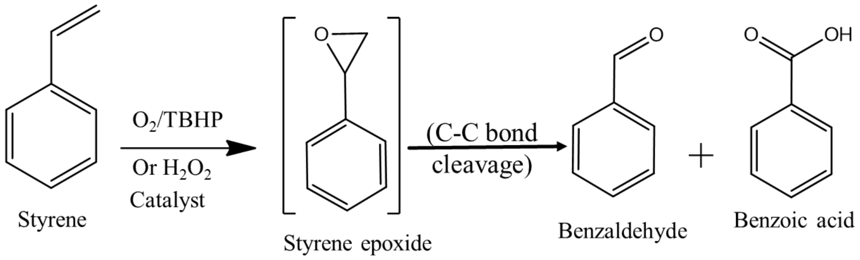
Similar procedure (as described in ***Chapter 3A***) for catalytic oxidation using H_2O_2 and O_2 as well as GC programming conditions were followed in the present chapter.

RESULTS AND DISCUSSION

3B (I) Oxidation of styrene (Sty) over PW_{12}/MCM-41 and PW_{11}/MCM-41.

- ***Oxidation of Sty with H_2O_2***

Oxidation of Sty with different oxidants are presented in Scheme 1. In order to ensure the catalytic activity, all reactions were carried out without catalyst and it was found that no oxidation takes place.



Scheme 1. Oxidation of Sty with different oxidants.

Effect of % loading of PW_{12}/PW_{11}

The effect of % loading (10-40%) (Figure 1) of PW_{12}/PW_{11} on MCM-41 was carried out for oxidation of Sty using H_2O_2 (1:3 molar ratio, 25 mg catalyst, 80 ^{o}C for 18 h). Increase in the conversion with increase in % loading of active species from 10% to 20% was observed. A significant increase in conversion was observed on increasing the loading from 20% to 30%. The 30% loaded catalyst showed highest conversion, however further increasing the loading to

40% did not show significant change, but decrease in selectivity towards benzaldehyde was observed. Hence 30% loaded catalysts were used for further studies for both the catalysts.

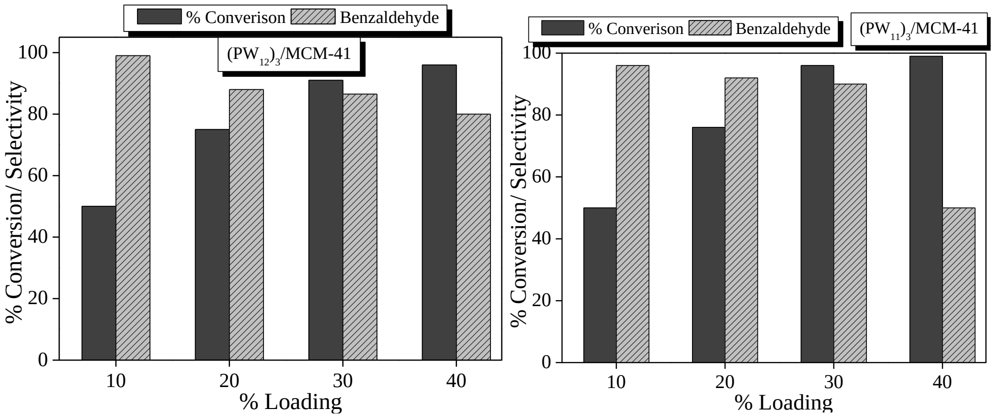


Figure 1. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Sty: H_2O_2- 1:3, catalyst amount - 25 mg, temperature- 80 °C, time- 18 h.

Effect of mole ratio of Sty: H_2O_2

Change in mole ratio also significantly affects conversion as well as selectivity towards the products (Figure 2). The study shows linear increase in the conversion for both the catalysts on increasing the molar ratio from 1:1 to 1:3. Increasing the mole ratio of Sty (ie. 2:1) also did not improve the reaction significantly. It was observed that 1:3 molar ratio gives maximum conversion.

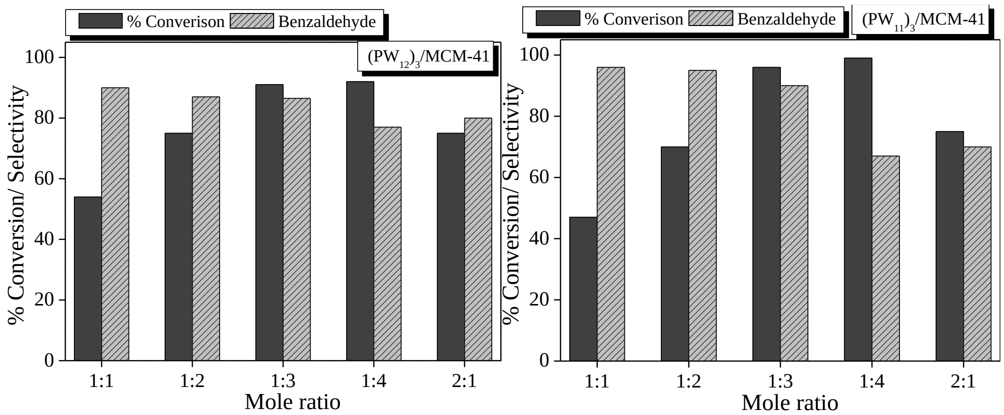


Figure 2. Effect of mole ratio Sty/H_2O_2: catalyst amount - 25 mg, temperature- 80 °C, time- 18 h.

Effect of catalyst amount

The catalyst amount has a significant effect on the reaction hence, catalyst amount was increased from 15 mg to 25 mg (Figure 3). Initially a sharp increase in conversion was observed on increasing the catalyst amount from 15 mg to 20-25 mg. On further, increasing the catalyst amount the conversion does not increase significantly. However, selectivity for benzaldehyde decreased on increasing the catalyst amount from 25 mg to 30 mg. This may be due to further oxidation of benzaldehyde to benzoic acid in presence of higher loading of active species. Therefore, 25 mg catalyst amount, was found optimum for obtaining maximum conversion in the case of $(PW_{12})_3$/MCM-41. However, a marked difference is observed in the catalytic activity with 20 mg $(PW_{11})_3$/MCM-41, which demonstrated best activity. This effect can be well explained by better oxidative property of the lacunary species due to formation of lacuna.

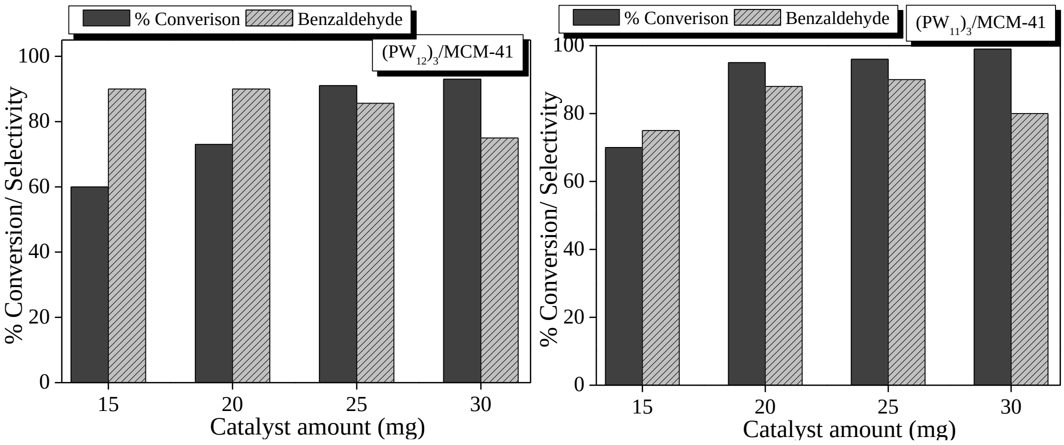


Figure 3. Effect of catalyst amount: mole ratio of Sty: H_2O_2- 1:3, temperature- 80 °C, time- 18 h.

Effect of reaction time

The effect of reaction time was carried out by observing change in % conversion at different time intervals. It was observed that on increasing the reaction time, the % conversion also increases significantly (Figure 4). It is known that more reaction time is necessary to form a reactive intermediate (substrate + catalyst) which subsequently leads to the products. Maximum 95% conversion for $(PW_{11})_3$/MCM-41 was observed at 18 h. However, when the reaction was allowed to continue till 20 h no significant increase in conversion was observed, however selectivity of benzaldehyde decreases drastically.

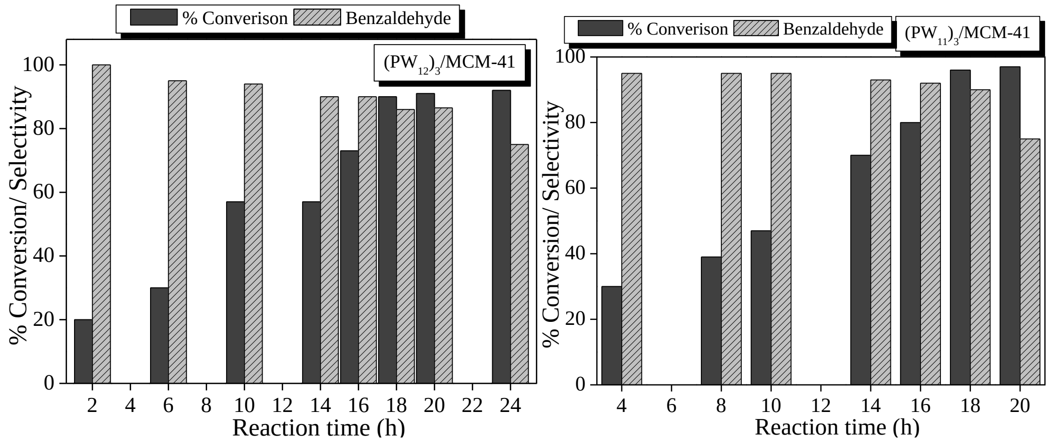


Figure 4. Effect of time: mole ratio of Sty: H_2O_2- 1:3, catalyst amount- 25 mg for $(PW_{12})_3$/MCM-41 and 20 mg for $(PW_{11})_3$/MCM-41, temperature- 80 °C.

Effect of temperature

The effect of temperature was investigated in the range 60-90 °C (Figure 5).

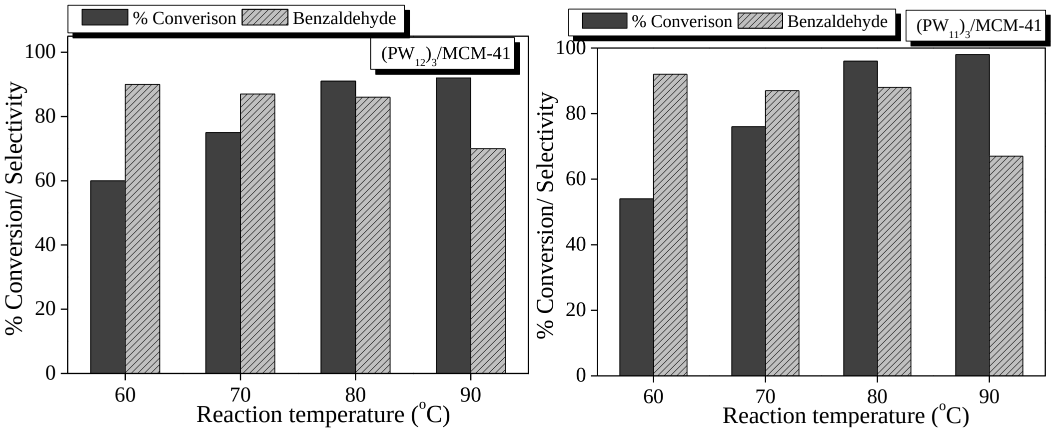


Figure 5. Effect of temperature: mole ratio of Sty: H_2O_2- 1:3, catalyst amount- 25 mg for $(PW_{12})_3$/MCM-41 and 20 mg for $(PW_{11})_3$/MCM-41, time- 18 h.

At 80 °C highest conversion was achieved. On increasing the temperature to 90 °C, there was no significant increase in the conversion. Thus, 80 °C was considered optimised temperature for obtaining maximum conversion as well as selectivity for benzaldehyde.

***Optimized conditions**:* [85% conversion $(PW_{12})_3$/MCM-41 and 95% conversion $(PW_{11})_3$/MCM-41] mole ratio of Sty: H_2O_2- 1:3, catalyst amount- 20 mg, time- 18 h, and temperature- 80 °C.

Kinetic study

A detailed study on kinetic behaviour was carried out. Plot of log Co/C (Figure 6) shows that with an increase in reaction time, there was a gradual and linear decrease in the Sty concentration over both the catalysts. These observations indicate oxidation reactions follows first-order dependence with respect to time. The catalyst concentration was varied (Figure 7) at fixed substrate concentration of 10 mmol and 80 °C temperature. The rate of reaction increases with an increase in the catalyst concentration.

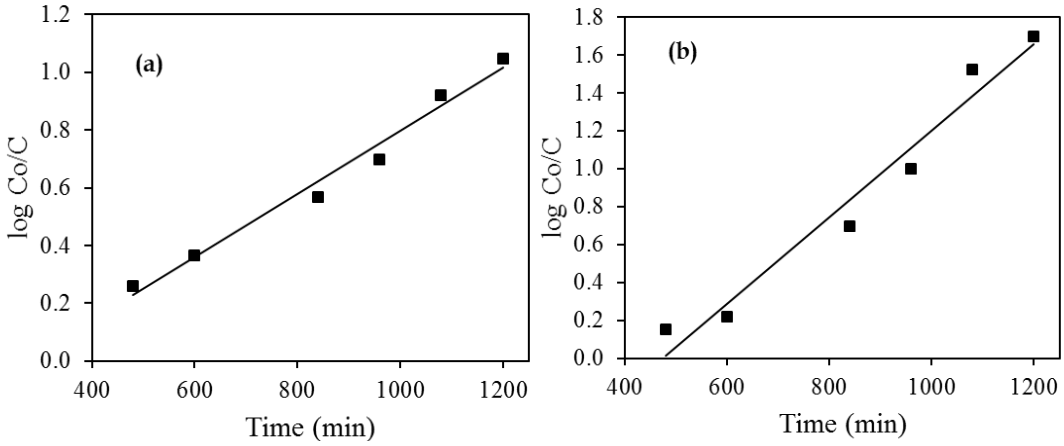


Figure 6. First-order plot over, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

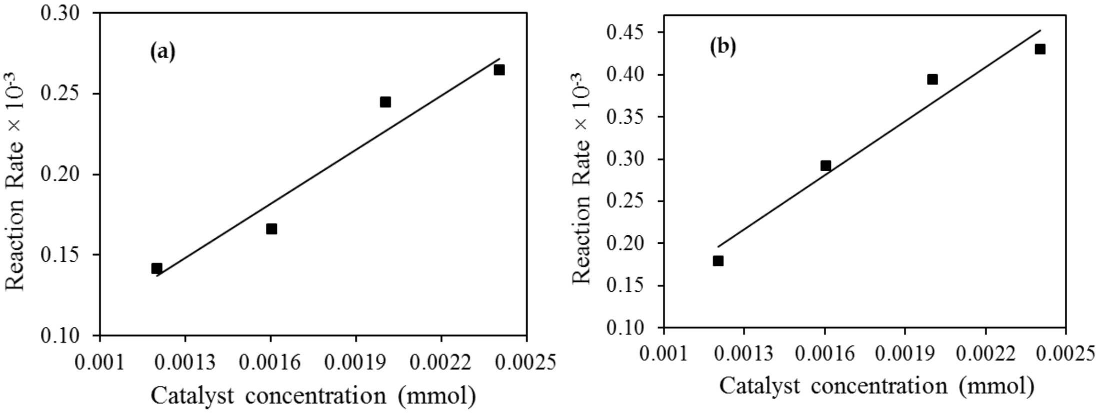


Figure 7. Plot of reaction rate vs catalyst concentrations over (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

The graph of ln k versus 1/T was plotted (Figure 8), and the value of Ea was determined from the plot. Ea for $(PW_{12})_3$/MCM-41 was found to be 53.5 kJ mol^{-1} and for $(PW_{11})_3$/MCM-41 it was 46.9 kJ mol^{-1} indicating that the rate is truly governed by the chemical step.

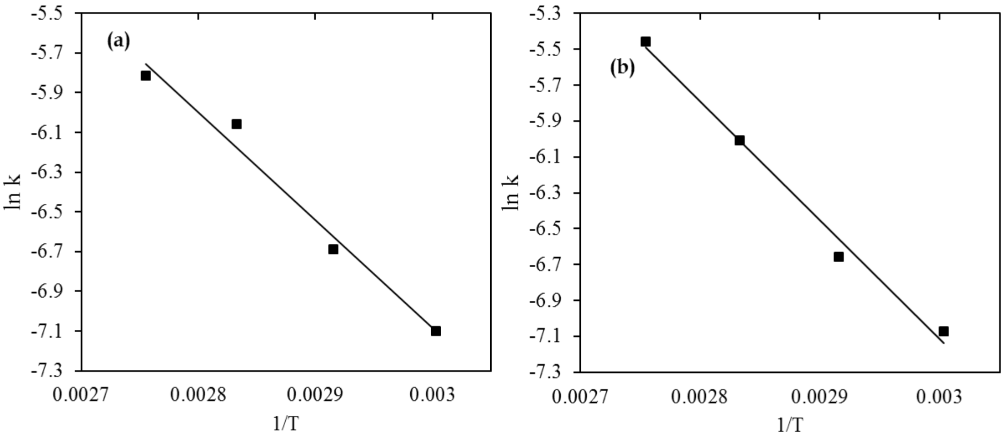


Figure 8. Arrhenius plots for determination of Ea, (a) $(PW_{12})_3$/MCM-41 and (b) $(PW_{11})_3$/MCM-41.

In terms of Ea, $(PW_{11})_3$/MCM-41 was found to be more active as compared to $(PW_{12})_3$/MCM-41.

- ***Oxidation of styrene with O_2***

For carrying out oxidation reaction with O_2 it is essential to check whether the reaction is just auto-oxidation or not. We have carried out control experiment without catalysts and no conversion of substrates indicates that the reaction does not proceed through auto-oxidation.

Effect of catalyst amount

The oxidation of styrene was carried out by varying catalysts amount (10 mg-30 mg) (Figure 9 a, b). Initially, on increasing catalyst amount from 10 mg to 20 mg, the conversion increases sharply. Further increase in the catalyst amount does not increase the conversion very significantly, but there was gradual decrease in the selectivity of benzaldehyde. Therefore, 20 mg catalyst amount was considered optimum for obtaining maximum conversion.

Effect of reaction time

The effect of reaction time on the selective oxidation of styrene was carried out by monitoring % conversion at different time intervals (Figure 9 c, d). Initially with increase in reaction time up to 6 h, % conversion increases slowly. The catalyst initially takes an induction period to accelerate the reaction. The maximum conversion was achieved in 8 h. On further increasing the reaction time, polymer formation is initiated and selectivity towards desired benzaldehyde decreases.

Effect of reaction temperature

To determine the optimum aerobic oxidation temperature the reaction was investigated at temperatures 60-90 ^oC (Figure 9 e, f) keeping other parameters fixed (20 mg catalyst amount, time 8 h). The results show that conversion increases with increase in temperature which is as expected. Similarly, on increasing temperature from 80 to 90 ^oC, conversion increases but at the same time selectivity of benzaldehyde decreases. This result is attributed to further oxidation of benzaldehyde to benzoic acid at higher temperature. So 80 ^oC temperature was found optimal for maximum conversion.

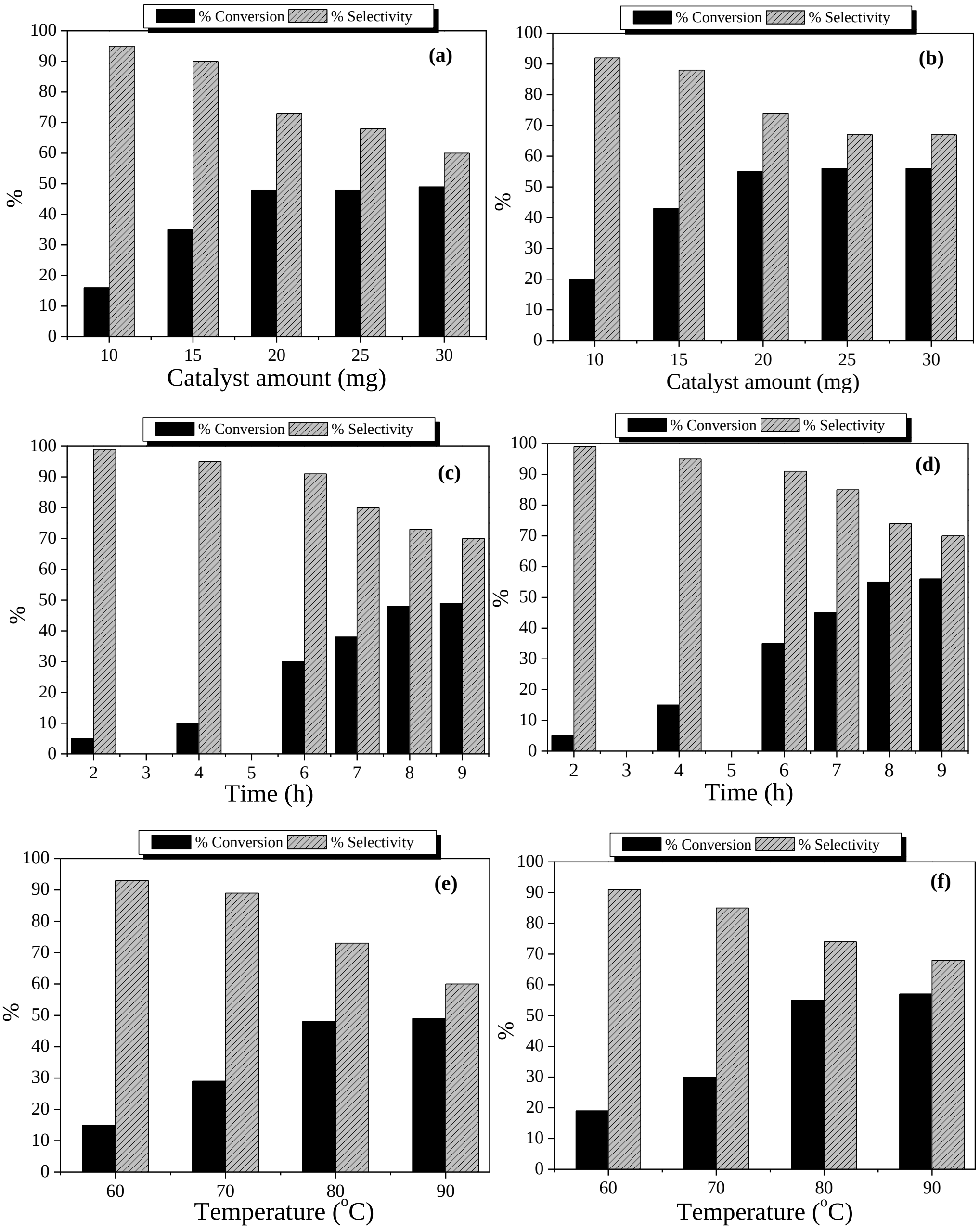


Figure 9. Effect of catalyst amount (a) $(PW_{12})_3$/MCM-41, (b) $(PW_{11})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, temperature- 80 ^{o}C, time- 8 h; Effect of catalyst amount (c) $(PW_{12})_3$/MCM-41, (d) $(PW_{11})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, temperature- 80 ^{o}C, time- 8 h; Effect of reaction temperature (e) $(PW_{12})_3$/MCM-41, (f) $(PW_{11})_3$/MCM-41: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 20 mg, time- 8 h.

Optimised conditions: [48% conversion $(PW_{12})_3$/MCM-41 and 55% conversion $(PW_{11})_3$/MCM-41] catalyst amount- 20 mg, temperature- 80 °C, time- 8 h. Table 1 presents comparison of optimised conditions with H_2O_2 and O_2.

Table 1. Optimized conditions with both the oxidants.

Conditions	Oxidants	
	H_2O_2	O_2
Mole ratio of substrate	1:3	-
Substrate concentration	10 mmol	100 mmol
Reaction time	18 h	8 h
Catalyst amount	25 mg [a]/20 mg [b]	20 mg
Reaction temperature	80 °C	80 °C

Where, [a] *$(PW_{12})_3$/MCM-41 and* [b] *$(PW_{11})_3$/MCM-41.*

It can be observed from Table 2, that for both the catalysts order of activity of oxidant was $O_2 > H_2O_2$ and explanation was already discussed in *chapter 3A.*

Table 2. Comparison of catalytic activity of both the catalysts.

Catalyst	Oxidant	% Conv.	% Sel.	TON
$(PW_{12})_3$/MCM-41	H_2O_2[a]	85	86	4250
	O_2[b]	48	73	24000
$(PW_{11})_3$/MCM-41	H_2O_2[a]	95	89	4522
	O_2[b]	55	74	30914

% Conversion based on substrate: [a] *Reaction with H_2O_2, substrate: H_2O_2 1:3, catalyst amount- 25 mg $(PW_{12})_3$/MCM-41, 20 mg $(PW_{11})_3$/MCM-41, time- 18 h, temp.- 80 °C;* [b] *Reaction with O_2: substrate 100 mmol, TBHP- 0.2 mmol, catalyst amount-20 mg, time- 8 h, temp.- 80 °C.*

Plot of kinetic curve (% conversion vs time) (Figure 10), suggested that O_2 was the only oxidant and it requires a longer time for activation and TBHP acts as an radical initiator by reducing the induction period as discussed in *section 3A (I)*.

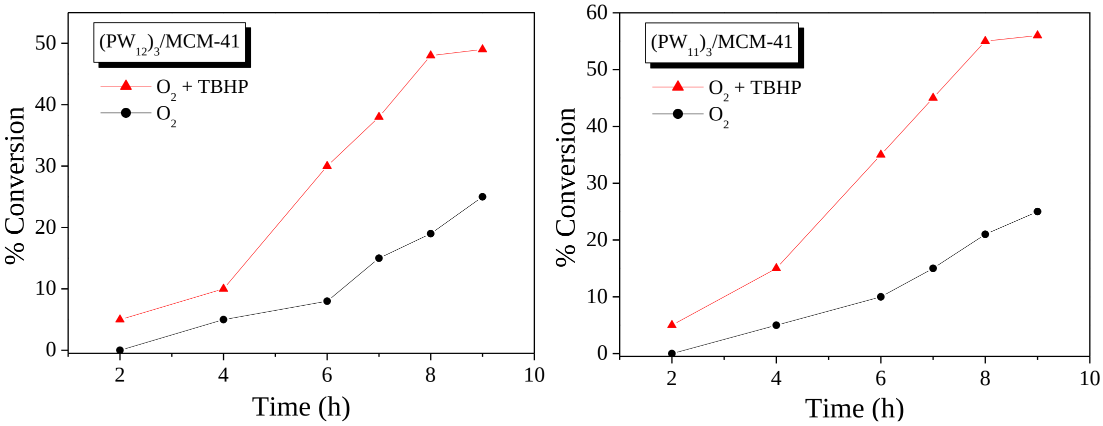


Figure 10. Role of TBHP in promoting the oxidation over both the catalysts.

3B (II) Oxidation of Sty over PW_{12}/MCM-48 and PW_{11}/MCM-48.

- ***Oxidation of Sty with H_2O_2***

As discussed in the previous *section 3B (I)* similar optimisation studies were carried out over $(PW_{12})_3$/MCM-48 and $(PW_{11})_3$/MCM-48.

Effect of % loading of PW_{12}/PW_{11}

On increasing the % loading (Figure 11) from 10 to 30% there was increase in the conversion. Further, increase in % loading from 30% to 40%, results in decrease in conversion. Thus, loading of PW_{12}/PW_{11} on the supports was fixed at 30% and detail studies were carried out over 30% loaded catalysts.

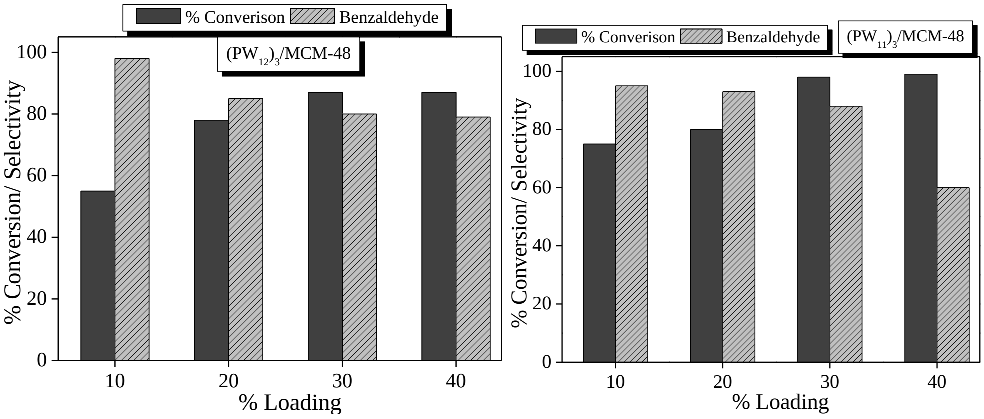


Figure 11. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Sty: H_2O_2- 1:3, amount of catalyst- 20 mg, temperature- 80 °C, time- 18 h.

Effect of mole ratio Sty: H_2O_2

Conversion increases with increase in Sty to H_2O_2 mole ratio (Figure 12) from 1:1 to 1:3.

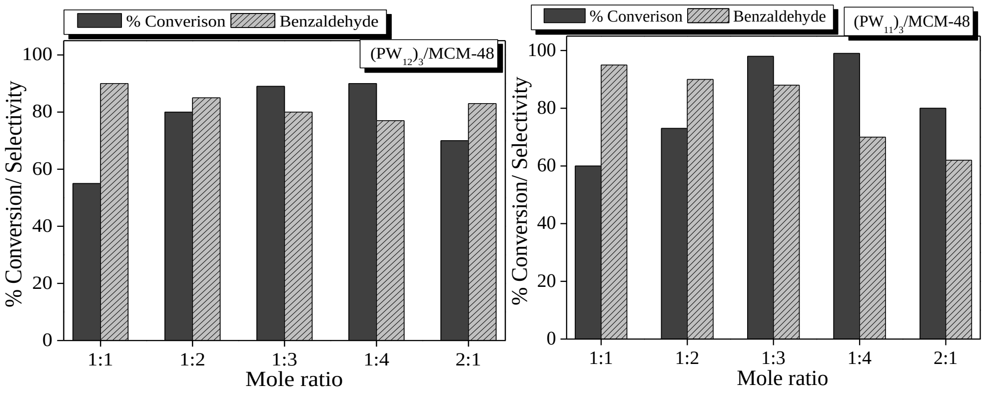


Figure 12. Effect of mole ratio: catalyst amount- 20 mg, temperature- 80 °C, time- 18 h.

However, conversion was found to be almost same when the molar ratio was further changed to 1:4. At this stage, selectivity for benzaldehyde decreases significantly. This may be due to oxidation of benzaldehyde to benzoic acid in presence of excess H_2O_2. Therefore, 1:3 mole ratio was found to be the optimum in terms of conversion as well as selectivity for both the catalysts.

Effect of catalyst amount

The catalyst amount was increased from 15 mg to 30 mg (Figure 13). Initially a sharp increase in conversion was observed on increasing the catalyst amount from 15 mg to 25 mg for $(PW_{12})_3$/MCM-48 and 20 mg for $(PW_{11})_3$/MCM-48. On further, increasing the catalyst amount the conversion does not increase significantly. However, selectivity for benzaldehyde decreased on increasing the catalyst amount further. This may be due to further oxidation of benzaldehyde to benzoic acid in presence of higher loading of active species. Therefore, as discussed in section 3B (I), similar trend was observed for MCM-48 based catalysts. Hence, 25 mg catalyst amount for $(PW_{12})_3$/MCM-48 and 20 mg for $(PW_{11})_3$/MCM-48 showed highest conversion.

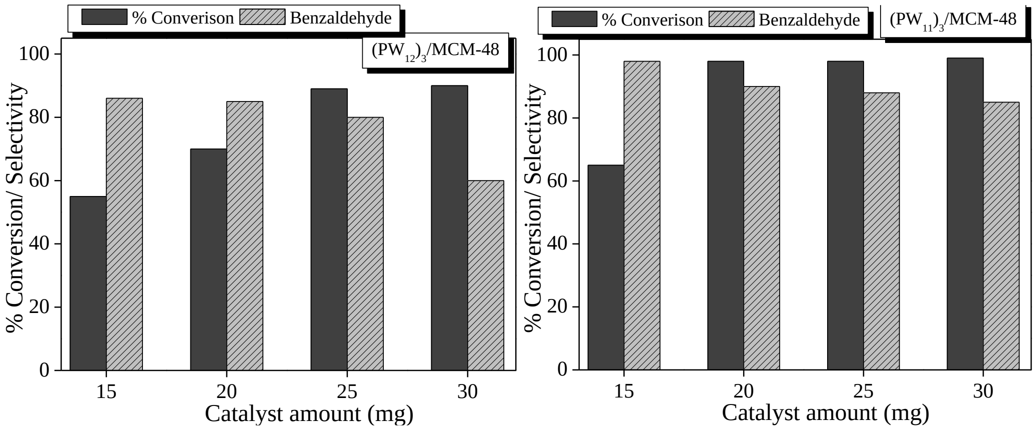


Figure 13. Effect of catalyst amount: mole ratio Sty: H_2O_2- 1:3, temperature- 80 °C, time- 18 h.

Effect of reaction time

The catalytic activity was monitored at different reaction times. It was seen from Figure 14, that with increase in reaction time, the % conversion also increases. Initially conversion increased with the reaction time. This was due to the reason that more time is required for the formation of reactive intermediate (substrate + catalyst) which finally converts to products. It was seen that almost similar conversion was observed for 18 h and 20 h in case of $(PW_{11})_3$/MCM-48, but at the same time, because of over oxidation, selectivity of benzaldehyde decreases. Hence, 18 h was optimized for further reaction for both the catalysts.

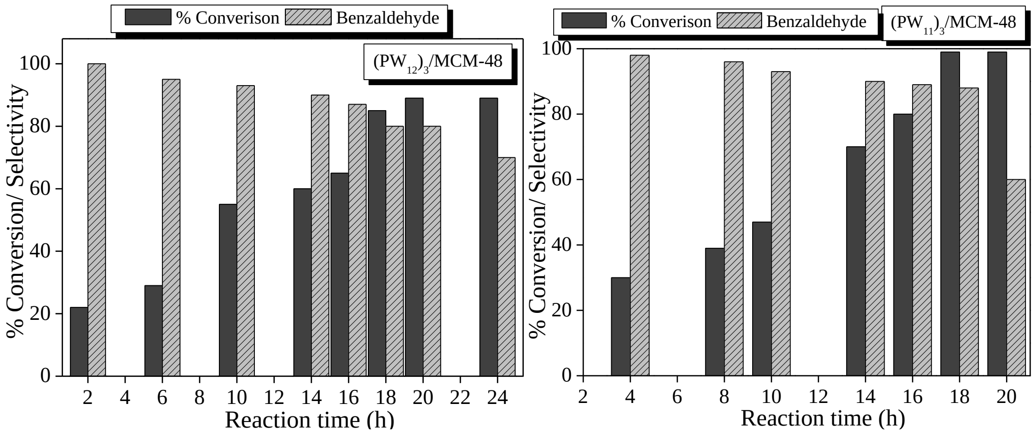


Figure 14. Effect of reaction time: mole ratio of Sty: H_2O_2- 1:3, catalyst amount- 25 mg $(PW_{12})_3$/MCM-48 and 20 mg for $(PW_{11})_3$/MCM-48, temperature- 80 °C.

Effect of reaction temperature

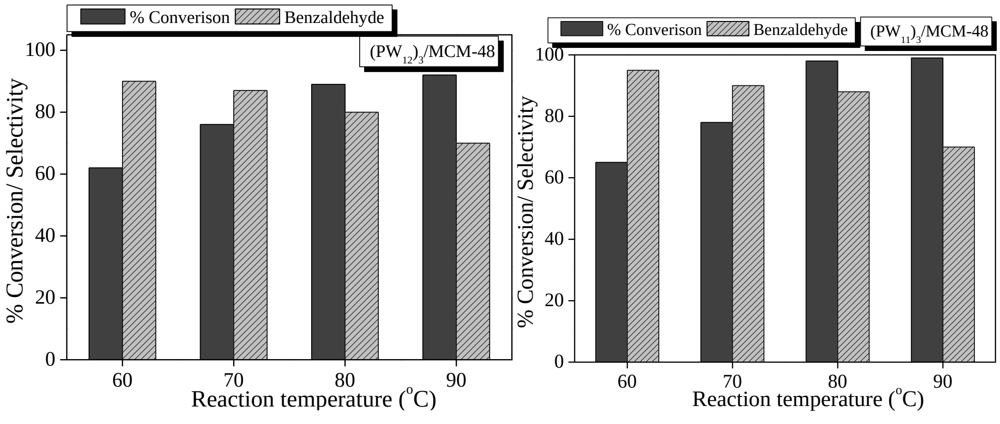


Figure 15. Effect of reaction temperature: mole ratio of Sty: H_2O_2- 1:3, temperature- 80 °C, time- 18 h.

On increasing the temperature (Figure 15) from 60 to 80 °C, improvement in conversion was observed, however on increasing the temperature to 90 °C selectivity for benzaldehyde decreases drastically. This may be due to oxidation of benzaldehyde to benzoic acid at elevated temperature. Hence, 80 °C temperature was selected as optimization condition.

Optimized conditions: [90% conversion for $(PW_{12})_3$/MCM-48, 98% conversion for $(PW_{11})_3$/MCM-48] mole ratio Sty: H_2O_2- 1:3, catalyst amount- 25 mg $(PW_{12})_3$/MCM-48, 20 mg $(PW_{11})_3$/MCM-48, time- 18 h and temperature- 80 °C.

Kinetic study

Plot of log C_o/C versus time (Figure 16) shows a linear relationship of styrene consumption with respect to time and follows first order kinetics. It was observed from Figure 17 that rate of reaction increases with increase in the catalyst concentration (at fixed substrate concentration of 10 mmol and temperature 80 °C) and the plot of reaction rate vs catalyst concentration also show a linear relationship.

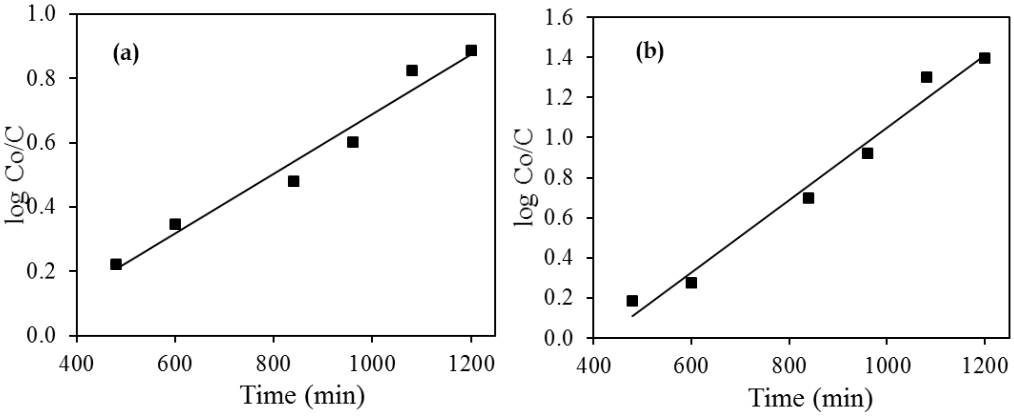


Figure 16. First-order plot for oxidation of Sty over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

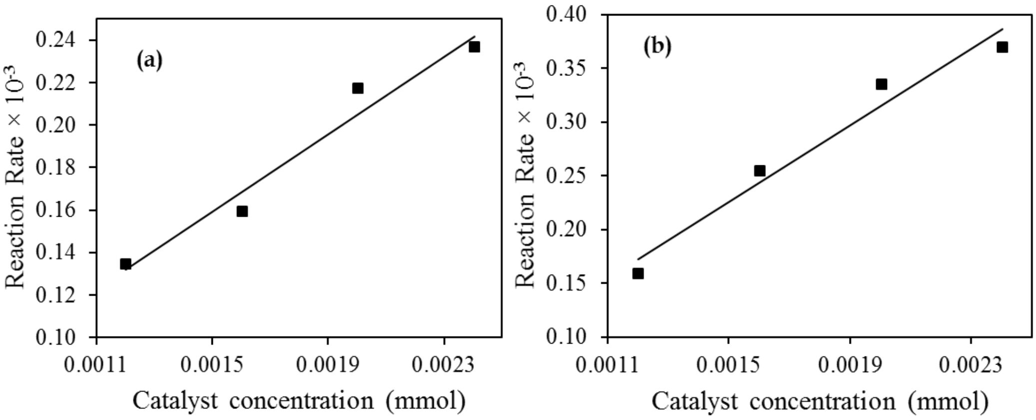


Figure 17. Rate of reaction versus catalyst concentration over, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

The graph of ln k versus 1/T was plotted (Figure 18), and the value of activation energy (Ea) was determined from the plot. Ea for $(PW_{12})_3$/MCM-48 was found to be 50.8 kJ mol^{-1} and for $(PW_{11})_3$/MCM-48 it was 44.1 kJ mol^{-1} indicating that the rate is truly governed by the chemical step without any mass transport or diffusion limitation.

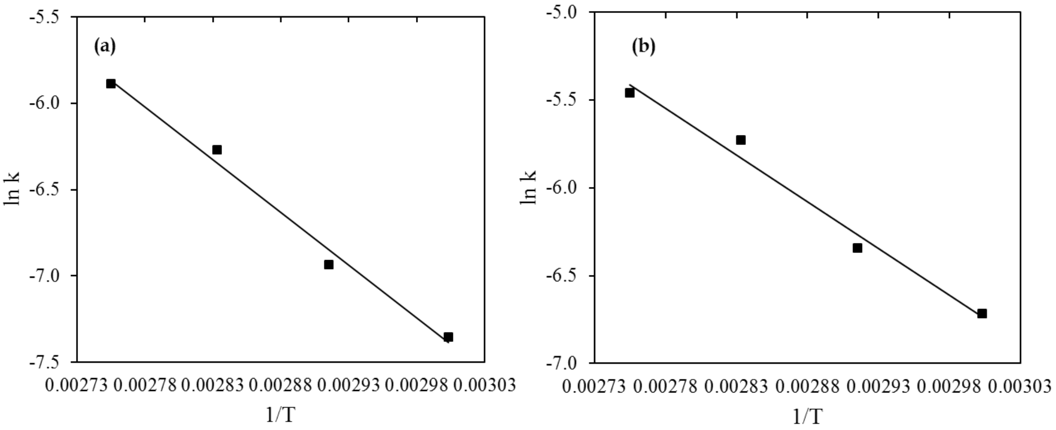


Figure 18. Arrhenius plot for determination of Ea, (a) $(PW_{12})_3$/MCM-48 and (b) $(PW_{11})_3$/MCM-48.

The Ea value for $(PW_{11})_3$/MCM-48 was found to be low as compared to $(PW_{12})_3$/MCM-48 suggesting the following order of activity,

- $(PW_{11})_3$/MCM-48 > $(PW_{12})_3$/MCM-48.

- ***Oxidation of Sty with O_2***

As discussed in *previous section* similar trend in catalytic activity was observed over $(PW_{12})_3$/MCM-48 and $(PW_{11})_3$/MCM-48.

Effect of catalyst amount

Reaction was carried out by varying catalysts amount (10 mg- 30 mg) (Figure 19 a, b). Initially, on increasing catalyst amount from 10 mg to 20 mg, the conversion increases sharply. Further increase in the catalyst amount does not increase the conversion very significantly. Therefore, 20 mg was considered optimum for obtaining maximum conversion.

Effect of reaction time

The effect of time was carried out by monitoring % conversion at different time intervals (Figure 19 c, d). Initially with increase in time up to 8 h, the % conversion increases slowly. The catalyst initially takes an induction period to accelerate the reaction. The maximum conversion was achieved at 8 h. On further increasing the time, there was no significant increase in the conversion, however, a decrease in % selectivity for benzaldehyde was observed.

Effect of reaction temperature

Temperature was varied from 60-90 ^{o}C (Figure 19 e, f) keeping other parameters fixed. The results show that conversion increases with increase in temperature which is as expected. Similarly, on increasing temperature from 80 to 90 ^{o}C, there was no significant increase in conversion. So temperature of 80 ^{o}C was found optimal for the maximum conversion.

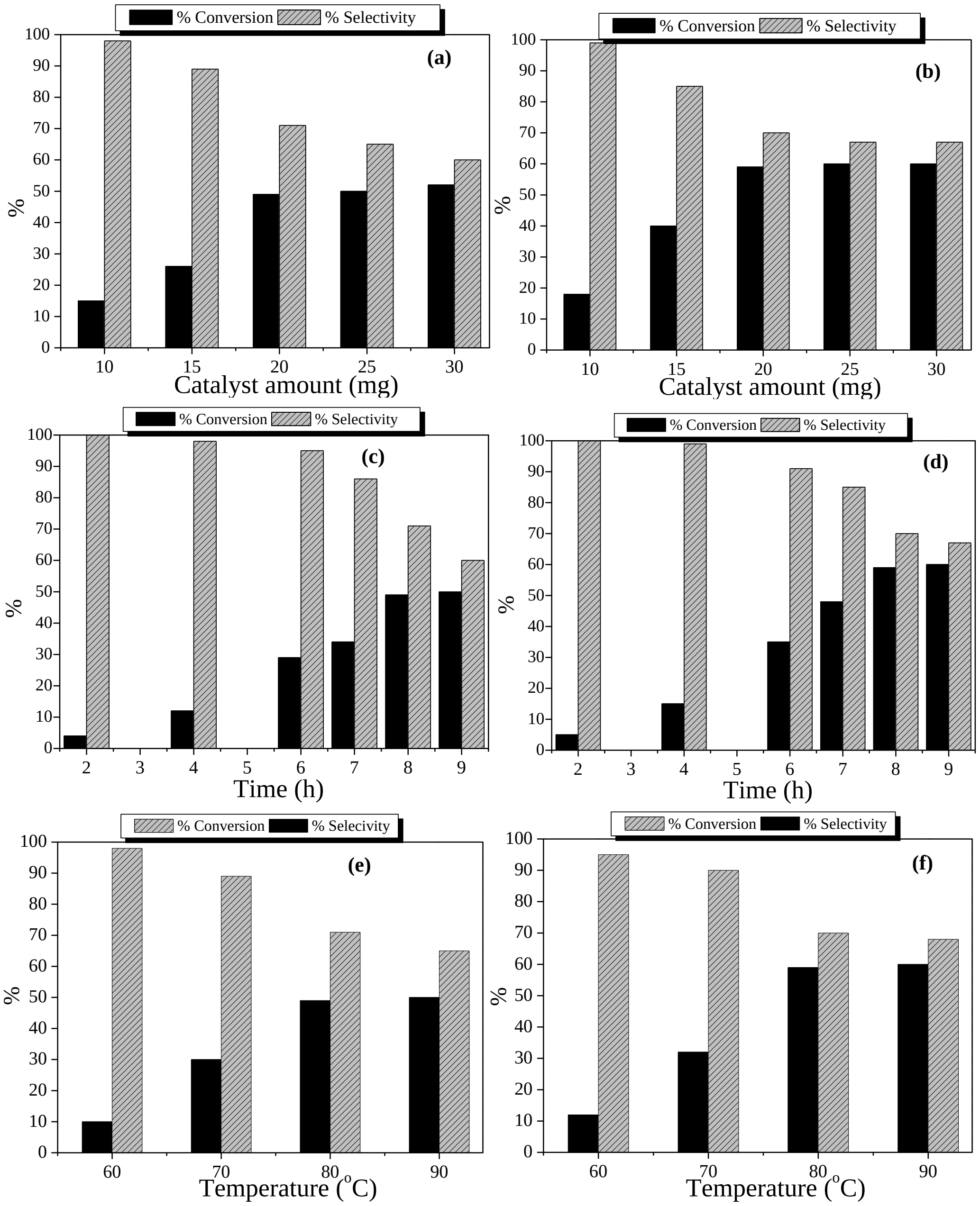


Figure 19. Effect of catalyst amount (a) (PW$_{12}$)$_3$/MCM-48, (b) (PW$_{11}$)$_3$/MCM-48 : substrate- 100 mmol, TBHP- 0.2 mmol, temperature- 80 ^{o}C, time- 8 h; Effect of catalyst amount (c) (PW$_{12}$)$_3$/MCM-48, (d) (PW$_{11}$)$_3$/MCM-48: substrate- 100 mmol, TBHP- 0.2 mmol, temperature- 80 ^{o}C, time- 8 h; Effect of reaction temperature (e) (PW$_{12}$)$_3$/MCM-48, (f) (PW$_{11}$)$_3$/MCM-48: substrate- 100 mmol, TBHP- 0.2 mmol, catalyst amount- 20 mg, time- 8 h. Selectivity for Benzaldehyde in all cases.

Optimised condition: [49% conversion $(PW_{12})_3$/MCM-48 and 59% conversion $(PW_{12})_3$/MCM-48] catalyst amount- 20 mg, TBHP- 0.2 mmol, temperature- 80 °C, time- 8 h. Table 3 shows the optimised conditions for both the catalysts as well as both the oxidants.

Table 3. Optimized conditions with both the oxidants.

Conditions	Oxidants	
	H_2O_2	O_2
Mole ratio of substrate	1:3	-
Substrate concentration	10 mmol	100 mmol
Reaction time	18 h	8 h
Catalyst amount	20 mg	20 mg
Reaction temperature	80 °C	80 °C

It is seen from Table 4 that for both the catalysts order of activity of oxidant was O_2>H_2O_2 i.e. high mole conversion of substrate and TON was observed with O_2 as compared to that of H_2O_2 and similar explanation can be given for role of oxidant, as discussed in *Chapter 3A, section 3A (I).*

Table 4. Comparison of catalytic activity of both the catalysts.

Catalyst	Oxidant	% Conv.	% Sel.	TON
$(PW_{12})_3$/MCM-48	$H_2O_2{}^a$	90	85	4500
	$O_2{}^b$	49	71	24500
$(PW_{11})_3$/MCM-48	$H_2O_2{}^a$	98	88	4384
	$O_2{}^b$	59	70	31476

% Conversion based on substrate: [a] *Reaction with H_2O_2, substrate: H_2O_2- 1:3, catalyst amount- 25 mg $(PW_{12})_3$/MCM-48, 20 mg $(PW_{11})_3$/MCM-48, time- 18 h, temp. 80 °C;* [b] *Reaction with O_2, substrate 100 mmol, TBHP- 0.2 mmol, catalyst amount- 20 mg, time- 8 h, temperature- 80 °C, Selectivity for Benzaldehyde.*

Plot of kinetic curve (% conversion vs time) (Figure 20), suggested that O_2 was the only oxidant and it requires a longer time for activation and TBHP acts as an radical initiator, as discussed in *section 3A (I)*.

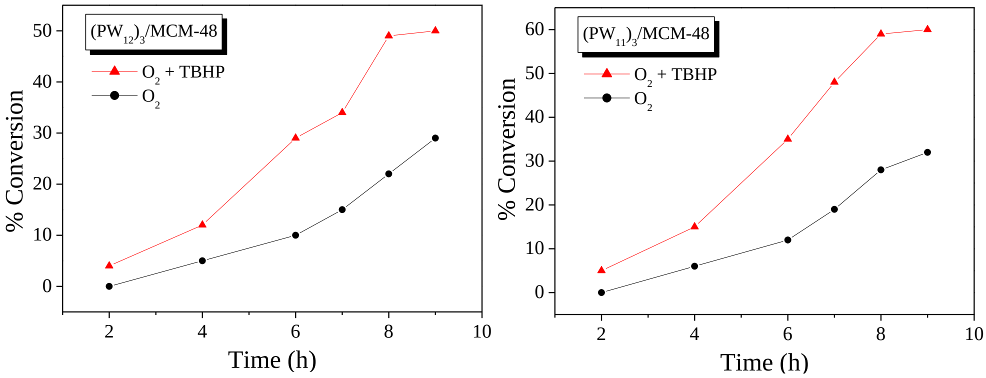


Figure 20. Role of TBHP in promoting the oxidation over both the catalysts.

Control experiments and Heterogeneity tests

Control experiments for oxidation of styrene with H_2O_2 (Table 5) shows that catalytic activities of PW_{12}/PW_{11} have been retained in the respective catalysts indicating that PW_{12}/PW_{11} behaves as real active species.

Table 5. Control experiments for oxidation with H_2O_2^{a} and ^{b} O_2.

Catalyst	% Conv. $^{a/b}$	% Sel. $^{a/b}$	TON $^{a/b}$
No catalyst	-	-	-
MCM-41	<1	100	-
MCM-48	<1	100	-
PW_{12}	85/45	95/90	4250/22500
$(PW_{12})_3$/MCM-41	85/48	86/73	4250/24000
$(PW_{12})_3$/MCM-48	90/49	85/71	4384/24500
PW_{11}	92/48	92/88	4379/26979
$(PW_{11})_3$/MCM-41	95/55	89/74	4522/30914
$(PW_{11})_3$/MCM-48	98/59	88/70	4665/31476

^{a} *Oxidation with H_2O_2; amount of PW_{12}- 5.7 mg, PW_{11}- 4.6 mg, time- 18 h, temp.- 80 °C,* ^{b} *Oxidation with O_2: amount of PW_{12}/PW_{11}- 4.6 mg, time- 8 h, temp.- 80 °C.*

Heterogeneity test was carried out by for both the catalysts (Figure 21). The reaction mixture of after filtration does not show any increase in the conversion or % selectivity indicating that there was no leaching of active species (PW_{12}/PW_{11}) from the support and catalysts are truly heterogeneous in nature.

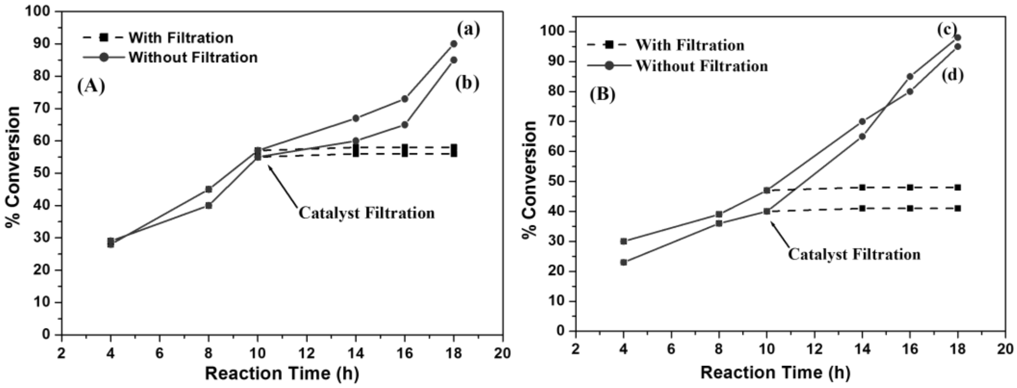


Figure 21. Heterogeneity study with H_2O_2 over (a) $(PW_{12})_3$/MCM-41, (b) $(PW_{12})_3$/MCM-48, (c) $(PW_{11})_3$/MCM-41 and (d) $(PW_{11})_3$/MCM-48.

Recycling and regeneration of catalysts

The catalysts were recycled up to four times in order to test their activity in successive runs (Figure 22). The procedure for recycling was same as explained in *chapter 2*. It was observed that there was no significant difference in the % conversion and selectivity even after four cycles. Thus, the catalysts could be reused up to four cycles with minimal loss in the activity. Recycling study for oxidation with O_2 also suggests the similar observation.

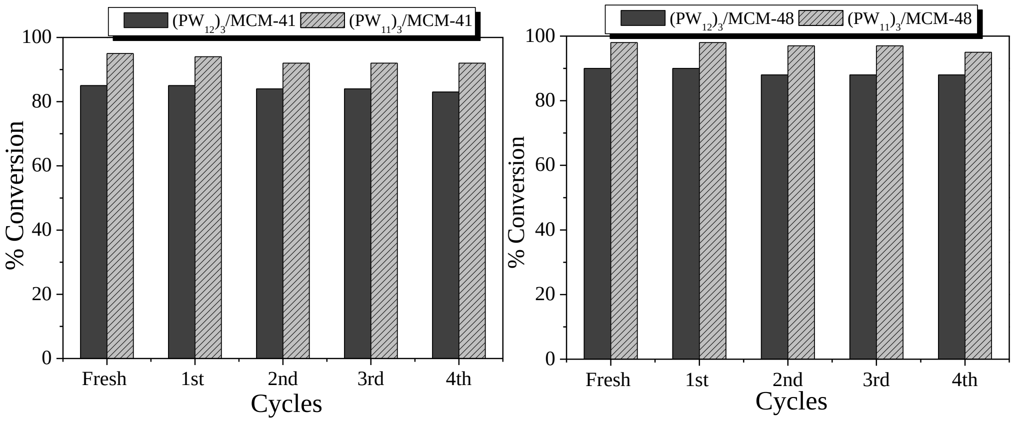
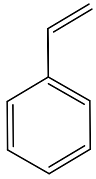
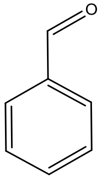
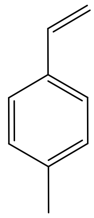
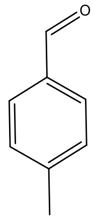
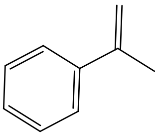
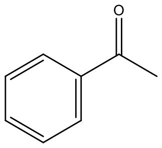


Figure 22. Recycling study under optimized conditions with H_2O_2.

Substrate scope for oxidation of different alkenes with H_2O_2

The scope of oxidation reaction were extended over different alkene substrates (Table 6). Generally, oxidation of styrene gives styrene oxide as an intermediate product. However, in the present case, stable product benzaldehyde was observed as major product via i) direct oxidative cleavage of C=C of styrene and ii) fast conversion of styrene oxide to benzaldehyde. In all cases, excellent conversion of desired product with very high selectivity is obtained for H_2O_2 and O_2 systems. Present catalytic systems are not applicable for oxidation of cyclic olefins.

Table 6. Oxidation of various alkenes over supported catalysts.

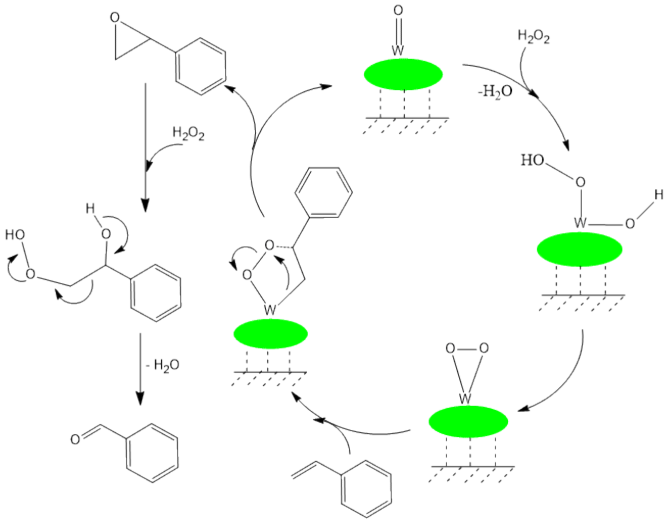
Substrate	Products	% Conv. a/b/c/d	% Sel. a/b/c/d
		85/95/90/98	86/89/85/88
		80/89/88/95	90/90/85/92
		78/86/86/92	100/100/100/100

^{a} *$(PW_{12})_3$/MCM-41,* ^{b} *$(PW_{11})_3$/MCM-41,* ^{c} *$(PW_{12})_3$/MCM-48 and* ^{d} *$(PW_{11})_3$/MCM-48.*

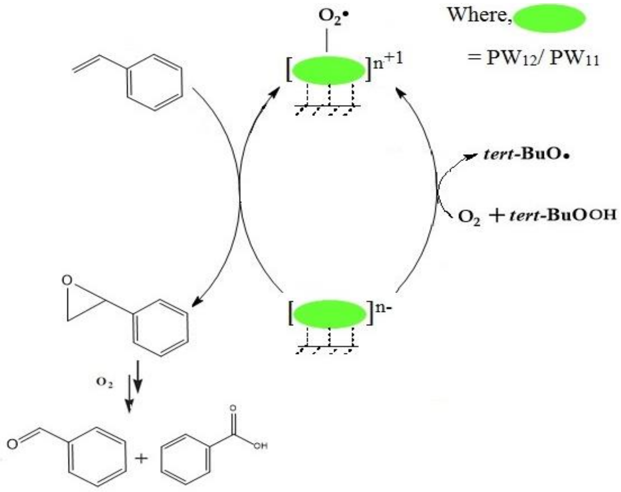
Probable reaction mechanism

In order to study the reaction mechanism, sets of reactions were carried out at different stages of the reactions. It is known for oxidation reactions with transition metal atoms, especially polyoxometalates, that H_2O_2 first binds to the metal centre and then transfers an oxygen atom to the olefin/alcohol. Thus, the activation of the metal center results via. the generation of the active species which may be hydroperoxo or bridging peroxo species [26]. In the present case, the catalysts are also expected to follow the same mechanism via. formation of an active tungsten-peroxo or hydroperoxo intermediate (Scheme 2).

Also for investigations of mechanism of styrene with O_2, different sets of experimental studies proposed that the reaction appears to be a radical mechanism and activation of catalyst was necessary for initiating the reaction (Scheme 3), where TBHP acts as a radical initiator only. The experimental data and studies in previous section (role of oxidants) also suggest the following mechanism with O_2.



Scheme 2. Proposed reaction mechanism for liquid phase oxidation of styrene with H_2O_2.



Scheme 3. Proposed reaction mechanism for aerobic oxidation of styrene with O_2.

Comparison of active species and supports for oxidation reactions

Effect of active species (PW_{12}/PW_{11})

The effect of lacunary PW_{11} was more pronounced for oxidation reactions on comparing the difference in the catalytic activity between all the catalysts. $(PW_{11})_3$/MCM-48 showed higher oxidative conversions (Table 7, 8) as compared to $(PW_{12})_3$/MCM-48 due to higher redox activity of PW_{11} than the parent PW_{12}.

Table 7. Comparison of activity of PW_{12}/PW_{11} and MCM-41 based catalysts.

Substrate	Catalyst	Surface area (m^2/g)	% Conv.	TON	Ea (kJ/mol)
BA	$(PW_{12})_3$/MCM-41	360	24.0	1200	49.2
	$(PW_{11})_3$/MCM-41	252	34.0	1673	44.6
Gly	$(PW_{12})_3$/MCM-41	360	49.0	2000	50.5
	$(PW_{11})_3$/MCM-41	252	51.2	2250	46.5
Sty	$(PW_{12})_3$/MCM-41	360	85.0	4250	53.5
	$(PW_{11})_3$/MCM-41	252	95.0	4522	46.9

Table 8. Comparison of activity of PW_{12}/PW_{11} and MCM-48 based catalysts.

Substrate	Catalyst	Surface area (m^2/g)	% Conv.	TON	Ea (kJ/mol)
BA	$(PW_{12})_3$/MCM-48	286	25.0	1250	46.5
	$(PW_{11})_3$/MCM-48	319	40.0	2000	41.0
Gly	$(PW_{12})_3$/MCM-48	286	30.0	1500	46.1
	$(PW_{11})_3$/MCM-48	319	54.4	2540	42.2
Sty	$(PW_{12})_3$/MCM-48	286	90.0	4384	50.8
	$(PW_{11})_3$/MCM-48	319	98.0	4665	44.1

It is well known that lacunary PW_{11} have commendable catalytic activity because of removal of tungsten-oxygen octahedral moiety from saturated PW_{12} framework (as lacunary core has a greater negative charge than the parent PW_{12}) [27-29]. In PW_{12} the negative charge is delocalized over the entire structure. However, in PW_{11} the nucleophilic properties of the oxygen atoms increases and become localized at the surface of the lacuna, ultimately rendering these oxygen atoms more reactive toward electrophilic groups. Overall, this leads to an increase and localization of anionic charge, the resulting lacunary anion becomes highly nucleophilic and reacts easily with electrophilic groups [27]. Also, it has been reported by Yoshida et al. [30] that in the lacunary species the surface $W(=O)_2$ atoms are active enough to catalyse the reaction as lacunary core has a greater negative charge than the parent PW_{12} [27-29]. Hence, comparatively higher activity, higher TONs and low Ea for lacunary PW_{11} anchored to MCM-48, goes well in agreement with the above explanations.

Effect of support

A comparative study was carried out to evaluate the effect of support by studying kinetic parameters and having a correlation between them. In almost all the reactions, $(PW_{12})_3$/MCM-48 exhibited excellent activity as compared to that of $(PW_{12})_3$/MCM-41. Similarly activity of $(PW_{11})_3$/MCM-48 was better than that of $(PW_{11})_3$/MCM-41 (Table 9).

Table 9. Effect of supports on different oxidation reactions with H_2O_2.

Catalyst	Surface area (m^2/g)	Pore width (Å)	Parameters	Substrates		
				BA	Gly	Sty
$(PW_{12})_3$/MCM-41	360	30.1	% Conv.	24.0	49.0	85.0
			Ea	49.2	50.5	53.5
$(PW_{12})_3$/MCM-48	286	20.2	% Conv.	25.0	30.0	90.0
			Ea	46.5	46.1	50.8
$(PW_{11})_3$/MCM-41	252	30.0	% Conv.	34.0	51.2	95.0
			Ea	44.6	46.5	46.9
$(PW_{11})_3$/MCM-48	318	27.5	% Conv.	40.0	54.4	98.0
			Ea	41.0	42.2	44.1

Among both the supports MCM-48 was the best in terms of conversion as well as high TON. The reason for this effect can be derived from the fact that the support allows high degree of dispersion of active species (PW_{12}/PW_{11}) and relatively higher surface area of $(PW_{11})_3$/MCM-48 (319 m^2/g) as compared to $(PW_{11})_3$/MCM-41 (252 m^2/g) (Chapter 1).

It is known that MCM-48 has well ordered three dimensional pore network which allows better dispersion of the active species inside the channels and provide feasible catalytic active sites for the reaction. This high dispersion leads to better mass transfer which allows the product and reactant molecules to move in the channels of the support. For example, it was observed that for oxidation of reaction of styrene, $(PW_{11})_3$/MCM-48 gives lower activation energy- Ea (44.1 kJ mol^{-1}) as compared to $(PW_{11})_3$/MCM-41 (46.9 kJ mol^{-1}) (Table 9). Similar trend in activation energy was observed for glycerol and benzyl alcohol (*Chapter 3A*). The selection of MCM-48 as best support was thus performed, taking into account the kinetic studies, surface area and pore geometry (3D for MCM-48 and 2D for MCM-41).

Conclusions

- A *green* and *environmentally benign* approach, has been executed for *liquid phase oxidation* of styrene as a model reaction using H_2O_2 and O_2.
- All the synthesised catalysts exhibits *excellent catalytic activity* with more than 85% conversion and good selectivity towards desired benzaldehyde under *solvent free mild conditions*.
- Kinetic study suggests that the reactions follow *first order kinetics* and reaction rate is truly governed by the *chemical step* with no mass/diffusion limitation.
- O_2 proved to be a better oxidant as compared to H_2O_2 based on the catalytic activities and TON.
- The *recycling studies* showed that all the catalysts can be reused several times without any significant loss in the activity.
- Probable reaction mechanism was suggested based on *different experimental setups*.
- The current *heterogeneous catalysts* are promising *sustainable* alternative to the traditional catalysts for solvent free oxidation of alkenes.
- The order of catalytic activity for oxidation reaction:
    - In terms of support **MCM-48 > MCM-41.**
    - In terms of catalysts **$(PW_{11})_3$/MCM-48 > $(PW_{11})_3$/MCM-41 > $(PW_{12})_3$/MCM-48 > $(PW_{12})_3$/MCM-41.**

References

1. D. V. McGrath, R. H. Grubbs, J. W. Ziller, J. Am. Chem. Soc. 113, 3611, (1991).
2. C. L. Hill, O. A. Kholdeeva, *Liquid Phase Oxidation via Heterogeneous Catalysis,* (Eds.) M. G. Clerici, O. A. Kholdeeva, Ch. 6, Wiley (2013).
3. N. Mizuno, K. Kamata, S. Uchida, K. Yamaguchi, *Modern Heterogeneous Oxidation Catalysis*, (Eds.) N. Mizuno, Ch. 6, Wiley-VCH (2009).
4. F. Lefebvre, J. Chem. Soc. Chem. Commun., 756, (1992).
5. I. V. Kozhevnikov, K. R. Kloetstra, A. Sinnema, H. W. Zandbergen, H. van Bekkum, J. Mol. Catal. A: Chem., 114, 287, (1996).
6. H. Zhao, L. Zeng, Y. Li, C. Liu, B. Hou, D. Wu, N. Feng, A. Zheng, X. Xie, S. Su, N. Yu, Microporous Mesoporous Mater., 172, 67, (2013).
7. N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, Inorg. Chem. 49, 2920, (2010).
8. I. Tamiolakis, I. N. Lykakis, A. P. Katsoulidis, C. D. Malliakas, G. S. Armatas J. Mater. Chem., 22, 6919 (2012).
9. L. Y. Meng, S. R. Zhai, S. Li, B. Zhai, Q. D. An, X. W. Song, Eur. J. Inorg. Chem., 2337, (2014).
10. E. Skliri, I. N. Lykakis, G. S. Armatas, RSC Adv., 4, 8402, (2014).
11. B. Wang, J. Zhang, X. Zou, H. Dong, P. Yao, Chem. Eng. J., 260, 172, (2015).
12. C. D. Brooks, L. Huang, M. McCarron, R. A. W. Johnstone, Chem. Commun., 37, (1999).
13. K. M. Parida, S. Mallick, Catal. Commun., 11, 51, (2009).
14. G. S. Armatas, G. Bilis, M. Louloudi, J. Mater. Chem., 21, 2997, (2011).
15. H. Mao, K. Zhu, X. Lu, G. Zhang, C. Yao, Y. Kong, J. Liu, J. Colloid Interface Sci., 446, 141, (2015).
16. W. Sun, J. Hu, Reac. Kinet. Mech. Cat., DOI 10.1007/s11144-016-1024-7, (2016).
17. R. F. Alamdari, S. M. Hafshejani, H. Taghiyar, B. Yadollahi, M. R. Farsani, Catal. Commun., 78, 64, (2016).

18. A. Patel, S. Pathan, Ind. Eng. Chem. Res., 51, 737 (2012).
19. S. Pathan, A. Patel, Chem. Eng. J, 243, 183, (2014).
20. P. Shringarpure, A. Patel, Dalton Trans., 39, 2615, (2010).
21. P. Shringarpure, A. Patel, Ind. Eng. Chem. Res., 50, 9069, (2011).
22. P. Shringarpure, A. Patel, Chem. Eng. J., 173 612, (2011).
23. N. Narkhede, A. Patel, S. Singh, Dalton Trans., 43, 2512, (2014).
24. S. Singh, N. Narkhede, A. Patel, RSC Adv., 5, 36270, (2015).
25. C. M. Granadeiro, A. D.S. Barbosa, P. Silva, F. A. A. Paz, V.K. Saini, J. Pires, B. de Castro, S. S. Balula, L. C. Silva, Appl. Catal. A: Gen., 453, 316, (2013).
26. N Mizuno, *Mechanisms in homogeneous and heterogeneous epoxidation catalysts.* S. T. Oyama (ed), Chapter- 4, Elseiver, New York, (2008).
27. Y. Guo, Y. Yang, C. Hu, C. Guo, E. Wang, Y. Zou, S. Feng, J. Mater. Chem. 12, 3046, (2002).
28. M. I. Khan, L. S Swenson, *New and Future Developments in Catalysis, Hybrid Materials, Composites, and Organocatalysts*, (Ed.) S. L. Suib, Elsevier, Chapter-2, (2013).
29. L. C. W. Baker, D. C. Glick, Chem. Rev., 98, 3, (1998).
30. A. Yoshida, S. Hikichi, N. Mizuno, J. Organomet. Chem., 692, 455, (2007).