

**VAPOR PHASE DEHYDRATION OF GLYCEROL  
OVER MESOPOROUS SILICA SUPPORTED IRON  
(III) PHOSPHATE CATALYSTS**

A DISSERTATION

Submitted in partial fulfillment of the  
requirements for the award of the degree

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**MASTER OF TECHNOLOGY**

in

**CHEMICAL ENGINEERING**

(with Specialization in Industrial Safety and Hazards Management)

by

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## **Declaration**

I hereby declare that the work presented in this dissertation entitled “**VAPOR PHASE DEHYDRATION OF GLYCEROL OVER MESOPOROUS SILICA SUPPORTED IRON (III) PHOSPHATE CATALYSTS**” submitted towards partial fulfillment for the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Safety and Hazards Management at the Indian Institute of Technology, Roorkee is an authentic record of my original work carried out under the supervision of **Dr.Prakash Biswas** Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee. I have not submitted this work embodied in this dissertation for the award of any other degree.

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## **Certificate**

This is to certify that Mr. Shubhradeep Moitra (Enrol. No.11516014) has completed the dissertation entitled “**VAPOR PHASE DEHYDRATION OF GLYCEROL OVER MESOPOROUS SILICA SUPPORTED IRON (III) PHOSPHATE CATALYSTS**” under my supervision.

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## ABSTRACT

Surplus glycerol produced during the production of biodiesel is having a detrimental effect on the production of biodiesel which is due to lack of commercial utilities of glycerol which is a major by-product. Conversion of glycerol into value added products can further improve the economics of biodiesel production. Catalytic conversion of glycerol to acrolein and acetol by vapor phase dehydration of glycerol with the help of various solid acid catalysts has been an area of research for commercial utilization of glycerol. In previous studies, several solid acid catalysts have been proposed for these reactions. Dehydration study with mesoporous silica as support are very limited. Here in this study a series of Iron (III) phosphate impregnated on mesoporous silica MCM-41 with varying iron (III) phosphate loading were prepared by incipient wetness impregnation methods. The physiochemical properties of the catalysts such as acidity and morphologies were characterized by N<sub>2</sub> adsorption/desorption, surface areas, NH<sub>3</sub>-temperature programmed desorption (TPD), X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDX). Surface area of mesoporous silica was found to be 1141 m<sup>2</sup>/g. With increase in weight percentage of FePO<sub>4</sub>, it was found that the surface area of the impregnated catalysts got reduced significantly. The XRD results confirmed the presence well dispersed FePO<sub>4</sub> on MCM-41. The TPD results revealed that, the presence of moderate acid sites on the catalysts. The catalytic tests were carried out in a continuous flow reactor. Dehydration of glycerol was carried out at 300°C and atmospheric pressure. 20% wt% aqueous solution of glycerol was used for the dehydration reaction. The catalysts amount was kept constant at 1.0 g for all the experiments. The effect of support and various weight per cent of FePO<sub>4</sub> loading on vapour phase reaction was studied. Among all the catalysts tested, FePO<sub>4</sub> on MCM-41 with Si to Fe ratio 5:1 and P to Fe ratio 1.3:1 showed superior performance for dehydration reactions. FePO<sub>4</sub>/MCM-41(Si: Fe=5:1) catalyst showed the highest conversion of glycerol along with highest acrolein selectivity. For dehydration of glycerol, the maximum selectivity to acrolein of 82% was obtained with a glycerol conversion of 99% after a reaction time of 5h. Acetol selectivity increased with increase in time for all the catalysts tested reaching maxima of 72%.

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### INTRODUCTION

In the 21<sup>st</sup> century biomass has emerged as an economic and sustainable source of energy. The great resourcefulness of biomass as starting material is due to a large range of materials that can be produced from it using biological and thermo-chemical conversion processes. Presently, biomass energy is the principal renewable energy source, signifying 10.4% of the world's total prime energy supply or around 80% of the global energy production [1].

With an increase in the crude oil prices and environmental concerns, the demands for the supply of biofuels in the energy market have witnessed a rapid increase in the production of bio-diesels from vegetable oil. Because of this reason chemical market has been flooded with cheap and surplus glycerol. Glycerol is the main by-product (10 wt%) in production of biodiesel by the process of natural tri-glyceride methanolysis and trans esterification of vegetable oils. With the production of 10 gallons of biodiesel 7 pounds of crude glycerol is generated.

The national biodiesel board of US has predicted a growth in the production of bio-diesel over the next decade. Present production scenario of bio-diesel is in the range of 395 million gallons and in the near future the biodiesel industry is expected to increase the capacity to more than 1.1 billion gallon. This in turn will generate more than 800 million pounds of glycerol in an annual manner. In the last decade the increase in the use and production of Bio-Diesel has in turn resulted in a sharp increase in glycerol production. Because of the surplus production of glycerol the price of this chemical has significantly reduced. This particular reason has made glycerol a cheap and easily available building block molecule for the synthesis of other valuable chemical products. Large increase in bio-diesel production has been influenced by several Government policies to reduce carbon emission and protect environment.

Glycerol is a sweet tasting viscous liquid having properties which makes it colourless and odourless. Other names of glycerol include Propane 1, 2, 3 triol, glycerine and glycyol alcohol. By definition Glycerol is an alcohol containing sugar. Because of its humectant properties, number of carbon atoms, high solubility index in water and most importantly high energy content, glycerol is widely utilized in pharmaceutical, food and cosmetic industries.



With constant increase in the number of bio-fuel industries including the processing of soyabean and Jatropha oil to produce bio-diesel fuel, there is a large untapped source of unrefined glycerol which although being a by-product is a valuable energy source for renewable energy production. In the present scenario, glycerol uses are mainly confined to pharmaceuticals and cosmetic industry which has kept glycerol uses in a limited direction. With the increase in availability of huge amount of cheap glycerol, researchers have been drawn to develop new processes for its utilization in producing a wide variety of high value products and fine chemicals. Converting glycerol to high value products also improve the economic viability of Bio-Diesel production and bio-fuel marketing.

Glycerol with three Carbon atoms can be used to manufacture attractive chemicals such as acrolein, propanediols, ethylene glycols and acetols. Of all the products derived from glycerol, propanediols are used for manufacturing cosmetics and drugs for the pharmaceutical industry. Ethylene glycol is marketed as an anti-freeze and a building block material for the production of polyesters. Acrolein is an important chemical in the industry which is largely used as the building block for the production of acrylic acid ester. It also acts as a super absorber polymer and detergent. Because of these reasons acrolein is an important chemical intermediate for the agro industry.

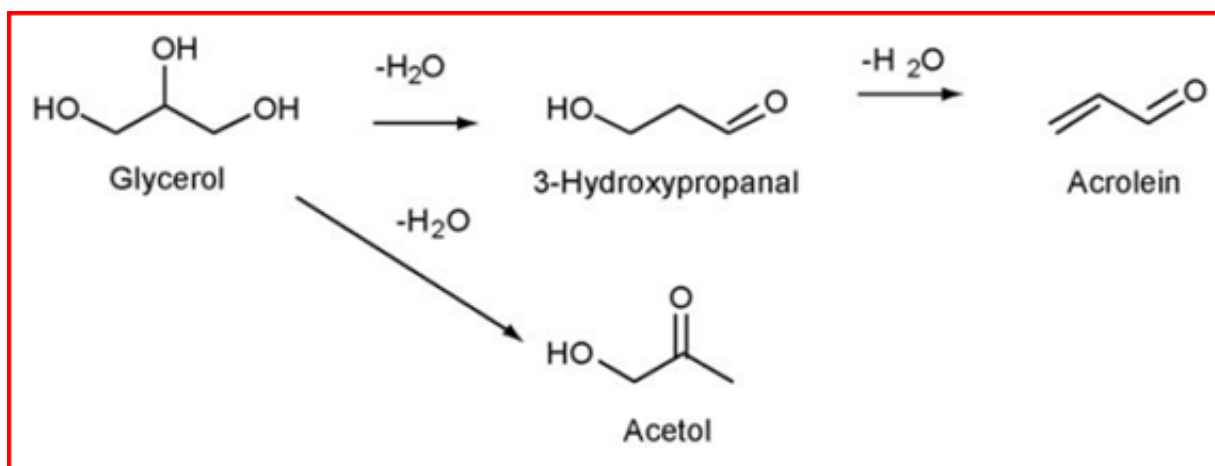
The basic problem in the conversion of glycerol is the occurrence of primary and secondary hydroxyl groups with dissimilar reactivity that create problems involving selectivity in redox as well as acid base reactions [4]. Commercially glycerol is oxidised with the help of  $H_2O_2$  which produces glyceraldehyde and di hydroxyacetone as an intermediate of glyceric acid and syringic acid in the liquid phase. Researchers have solved the reactivity problem by the production of derivatives of glycerol i.e. acetals or esters that allow the corresponding oxidation of only a single type of carbon atom. Presently the formation of acrolein by catalytic conversion of glycerol is in high demand.

Acrolein is a highly inflammable and toxic material with extreme lacrimatory properties. Acrolein is liquid at room temperature with volatility and flammability analogous to acetone but unlike acetone it is less soluble in water. Acrolein has been formed commercially since 1978. In 1995, acrolein was being produced at a rate of about 1,13,000 tonnes/year throughout the globe. It has anti-microbial properties, as a result of which it has found usage as an instrument to control the development of microbes in process feed lines thereby controlling plugging and corrosion.

At a concentration of less than 500 ppm of acrolein it is used to protect liquid fuels against micro-organisms [5]. The commercial production of acrolein is presently done via the gas phase selective oxidation of petroleum product propylene using bulk metal oxides. (Bi-Mo-O, Fe-Sb-Ti-O, Mo-Te-O, Sn-Sb-O, U-Sb-O, and cuprous oxide) as catalysts [5]. The source of propylene is non-renewable petroleum crude. Glycerol being a C-3 Carbon source has the potential to replace propylene as feedstock for acrolein production. This would mean better economic conditions for biodiesel production and also utilization of a waste by-product from a natural source to produce acrolein. Propylene can be used instead for LPG production. Acrolein would be a biomass based transitional and a CO<sub>2</sub> neutral fabrication would be provided. In comparison with the commercial processes glycerol dehydration to acrolein would be more environments friendly as well as a non-petroleum based product. Since the reaction is acid – catalysed, crude glycerol which contains lots of water and the high catalyst acidity makes the water tolerance of the catalyst an important factor to obtain high conversion of glycerol as well as high selectivity for acrolein.

In the past decade a number of research papers have been published on the conversion of glycerol by catalytic routes involving reforming, oxidation, hydrogenolysis, and etherification and esterification reactions [6]. Acrolein production by dehydration of glycerol is key route for economic utilization of the growing glycerol resources. This might as well be a sustainable substitute to the present commercially produced acrolein from crude petroleum using propylene as feed. This glycerol dehydration thereby yielding acrolein is in the leading list of acid catalysed reactions (Scheme 1). This reaction pathway is widely used for the fabrication of acrylic super absorber polymers, acid esters and detergents. Sulphates, Phosphates, Zeolite, solid phosphoric acid and other acid catalysts have been tested for glycerol dehydration to acrolein in both liquid and gaseous phases. Besides the solid acid catalysts, salts and liquid acids were also used as catalysts to determine the glycerol dehydration in sub supercritical and supercritical environments.

Though commercialization of acrolein production from glycerol has yet not been possible because of its limited economic stability as compared to an out dated fabrication route based on the oxidation of propylene with bi metallic metal oxide based multi metal oxide catalyst. The 21<sup>st</sup> century has seen a steep increase in crude oil prices and consequently propylene prices which has again made conversion of glycerol an economic pathway for acrolein production.



Scheme 1. Reaction pathway for dehydration of glycerol [4].

### LITERATURE REVIEW

The most widely used acid catalysed reactions using glycerol are

- i. condensation to form oligomers and linear or cyclic glycerol dimers
- ii. Dehydration to form acrolein along with other compounds such as acetol.

Since the 1900s, numerous solid-acid catalysts have been considered for the dehydration of glycerol in both the gaseous or liquid-phase. Biocatalysts, homogeneous and heterogeneous acid catalysts have been used for this reaction. Environmentally and technically, heterogeneous catalysts are more attractive than homogeneous catalysts. To convert glycerol to acrolein by dehydration, heavy-duty catalyst acidity is essential. However, initially the glycerol conversion was restricted to 10–30%. In liquid phase there is excessive loss of selectivity and thus to overcome the low catalytic activity for the fabrication of acrolein in liquid phase reaction, vapour phase reactions started creating more interests among researchers.

Degussa et al. [7] in the mid-nineties carried out reactions in liquid phase at 180<sup>0</sup>C – 340<sup>0</sup>C and in gas phase at 250<sup>0</sup>C – 340<sup>0</sup>C with many acidic catalysts but these catalysts did not show a good conversion and selectivity. Very recently, Tsukuda et al. [7] carried out the same reactions with heteropolyacids supported over SiO<sub>2</sub> and establish that the introduction of mesopores in silica support considerably increased the catalytic activity. As a matter of anomaly such strongly acidic catalysts becomes neutralised quickly. Such incidents took place because of carbon deposits in the mesopores and on the surface of the catalyst.

Till now, the major findings have shown that the acidic sites which are the most efficient for acrolein production are the sites having highest acid strengths in the variety of  $-8.2 < H_0 \leq -3.0$  ( $H_0$  being the Hammett acidity function [3]), and thus Bronsted acid sites are showed to be more in effect to Lewis acid sites [10]. Hydrated niobium oxide (Nb<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O), tungstated zirconia (WO<sub>3</sub>/ZrO<sub>2</sub>), solid phosphoric acid as well as supported heteropolyacids [8] surfaced as the new acid catalysts over which the selectivity of acrolein was found to be more than about 68 mol% at 300<sup>0</sup>C when the concentration of aqueous Glycerol was kept at 20 wt% . Higher acrolein selectivity was observed using low concentration of glycerol in the aqueous reaction feed.

Although most of the studies appear to agree with the fact that Bronsted acid sites are more effective than Lewis acid sites. One study reported that the catalyst's competence in

acrolein synthesis was boosted by medium acidity; simultaneously another study concluded that weak acidity was more suitable and yet an additional research reported that the best selectivity to acrolein was attained with strong acidic catalysts. Given these inconsistencies, it is likely that other restrictions, such as the quantity and dispersal of acid sites at the surface of the catalysts, may be the critical to the catalyst's properties. Tolerance to water has also been suggested as a key factor in the instance of heteropolyacids.

The production of acrolein is an endothermic reaction along with a standard enthalpy of  $19.8 \text{ kJ mol}^{-1}$  for a gas-phase reaction process. Characteristically, the reaction is carried out in the temperature array of  $260^{\circ}\text{C}$  –  $350^{\circ}\text{C}$  by means of an aqueous glycerol as a feedstock. Since much steam is existing in the gas flow, the catalyst should have decent water lenience. The catalyst effectiveness in acrolein synthesis is enriched with growing catalyst acidity. Supported Keggin heteropoly acids, holding very strong Brønsted acidity, have been found as the most capable catalysts for glycerol to acrolein transformation in the gas phase. In particular, with 12- tungstosilicic acid,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , is detected possessing a higher water tolerance compared to other Keggin heteropoly acids, acrolein yields of 80% have been attained at an optimal temperature of  $275^{\circ}\text{C}$ [11].

The gas-phase reaction is more appropriate for the production of acrolein than the liquid-phase reaction because, the glycerol conversion and the selectivity for acrolein can be modified in the gas-phase reaction system. Although a liquid-phase medium, together with sub and supercritical water, has been projected to run the reaction, the gas-phase remains the most economically practical method, even though a diluted aqueous solution of glycerol has to be used as preliminary material, and vaporized exceeding  $250^{\circ}\text{C}$ . Numerous acidic catalysts have been suggested in recent years, for the gas-phase selective conversion of glycerol into acrolein. . However, in the case of solid catalysts, supplementary to the acidity, the textural properties also play an essential role in this process. The selectivity and deactivation may be strongly affected by diffusion restrictions due to coke development.

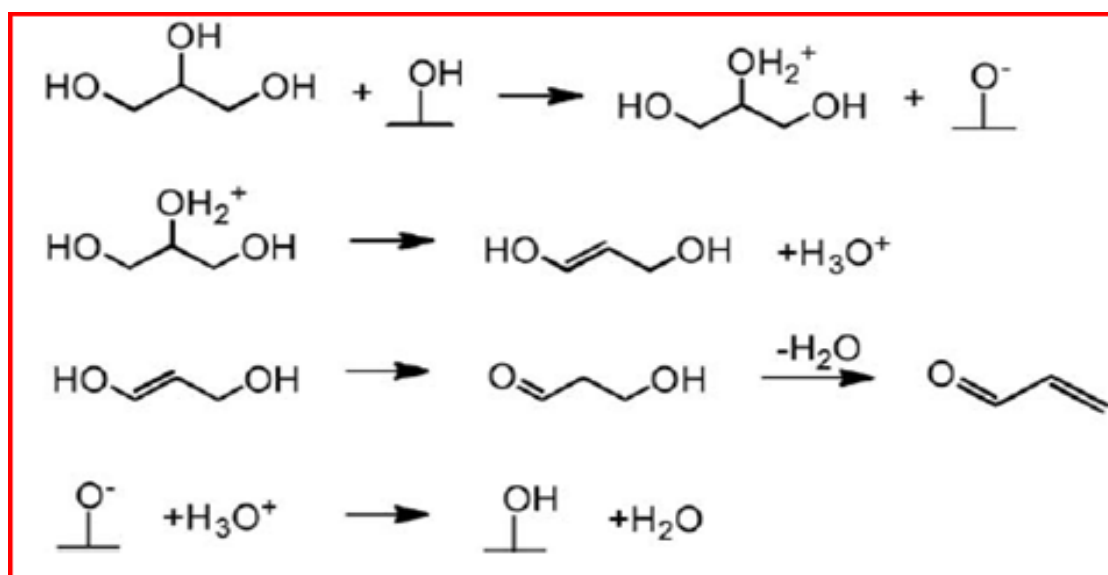
Three types of catalyst allow the reaction to run positively are

- i. heteropolyacids supported or unsupported
- ii. Supported oxides and
- iii. zeolites

All of these display great catalytic properties, at temperatures in the range amid  $260^{\circ}\text{C}$  and  $350^{\circ}\text{C}$ , with an acrolein selectivity extending from 70% and 80% at total glycerol conversion.

There are also various other solid-acid catalysts for instance metal sulfates, metal phosphates which have previously been studied. In the case of solid-acid catalysts, it has been seen that the catalytic performance for the dehydration of glycerol is related to the acid properties. Although the gas-phase reaction with several solid-acid catalysts could obtain extraordinary conversion of glycerol, the selectivity for acrolein and lasting steadiness are still unsatisfactory because of carbon deposition. To burn off the coke on the catalyst, its thermal stability is vital.

As far as the reaction mechanism is concerned, the dehydration of glycerol on acid catalysts is proposed to advance via the creation of 3-hydroxypropanal, with 1-hydroxyacetone (acetol) formed as a fairly stable by-product. Acrolein is the chief product (>90% selectivity) in the gas-phase dehydration of glycerol on mixed oxide catalysts, for instance copper chromite, and supported metal catalysts. This may show that Lewis acid sites and metal sites are vital for the formation of acetol, whereas the formation of 3-hydroxypropanal trailed by its dehydration to acrolein is preferred in the presence of strong Bronsted acid sites (Scheme 2). The foremost drawback to the gas-phase dehydration of glycerol on acid catalysts is catalyst deactivation due to widespread coke deposition on the catalyst surface as well as the strain of direct usage of the crude glycerol acquired from biodiesel production.



Scheme 2. Reaction mechanism of glycerol dehydration over solid acid catalyst.[4]

If all the diverse solid-acid catalysts are taken in account, protonic zeolites are engaged for the acid-catalyzation of the reaction due to the heat opposition they offer and their selectivity of shape. Till date, low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio zeolites have been used to dehydrate glycol to acrolein in the gasiform state so as to attain a high fabrication of acrolein. For H-ZSM-5, the addition of molecular oxygen and moving bed reactor were examined to cope with the coke gathering. FTIR spectroscopy was also engaged to study the reaction mechanism over H-ZSM-5.

Sulfates, phosphates, zeolites, and solid phosphoric acid (SPA) are some solid catalysts that have been examining for glycerol dehydration in either gas or liquid states. Glycerol dehydration was also examined in sub-supercritical and supercritical water at the range of conditions: 270–400 °C and 27–40 MPa in the presence of low concentrated liquid acids or salts. Glycerol dehydration was performed in supercritical water at a temperature of  $T > 374$  °C,  $p > 221$  bar with  $\text{H}_2\text{SO}_4$  having an acrolein selectivity of 88% at 50% conversion, or with  $\text{ZnSO}_4$  catalyst with 80% selectivity at 56% conversion. The selectivity of Acrolein in the range of 83% at 91% conversion was recorded with  $\text{H}_2\text{SO}_4$  catalyst at 450 °C. Glycerol is generally obtained as a mixture with water. The direct glycerol application in water is beneficial over pure glycerol for the manufacture of acrolein, but for that a highly water-tolerant solid acid catalyst is needed.

12-tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , HPW) loaded on an inert  $\alpha\text{-Al}_2\text{O}_3$  support possessed a high acrolein selectivity, but this HPW/ $\alpha\text{-Al}_2\text{O}_3$  catalyst deactivated swiftly due to the low surface area it possessed. Additionally, low resistivity to heat of HPW can be also a prospective hurdle for its realistic use since renewal of the coked catalyst generally needs a process temp higher than 510 °C. Nevertheless it is worthwhile to mention that it is required to pursue for other support materials that has to keep both the high selectivity for acrolein and also remarkably improve the thermal and catalytic stability of the active structure of HPW catalyst in glycerol dehydration. Silica gel are frequently used as the support materials because they have large surfaces, but their interaction with HPW is very less thereby resulting in comparatively poor scattering and thermal constancy of the supported HPW. Initially impregnating a hydrogel-derived zirconyl hydroxide [ $\text{ZrO}(\text{OH})_2\text{-CP}$ ] with HPW in solution,  $\text{ZrO}_2$  has been off late observed to be better than  $\text{SiO}_2$  as a support solid for HPW because the extraordinary dispersion of HPW on  $\text{ZrO}_2$  was able to keep its Keggin structure at high temp of around 770 °C. HPW/ $\text{ZrO}_2$  catalysts also showed higher catalytic activity than HPW/ $\text{SiO}_2$  for a number of acid catalyzed reactions.

Even if many catalytic systems have a high selectivity towards acrolein at total glycerol conversion, very few are able to keep their catalytic properties for more than 5–10 h. The catalyst deactivation is due to continuous coke deposition on its surface. The degree of coking has been curbed by adding O<sub>2</sub> or H<sub>2</sub> in the gas phase and altering the catalysts, have not been emphatically effective. Catalyst regeneration by burning coke has been attempted, either in situ regularly or ex situ in fixed time periods, here also there has been inadequate success. Glycerol dehydration by means of fluidised catalyst bed with catalyst rotation between the reactor and regenerator comparable to the fluidised catalytic cracking process has been studied. Regeneration of heteropoly acid catalysts by incineration of coke is problematic because of moderately low resistance to heat of heteropoly acids.

Alhanash et al. [9] stated that the acidic heteropoly salt, caesium 12-tungstophosphate Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> (CsPW), is an effective catalyst for the dehydration of glycerol to acrolein in the gas phase. It was insoluble in water and had a strong Bronsted acid and it was also an efficient solid acid catalyst which had high thermal stability (530 °C) and water tolerance. The working life of the catalyst was augmented and the coke deposition was reduced by doping the catalyst with platinum cluster metals (PGM) such as Ru, Pd and Pt, and co-feeding hydrogen to the reaction scheme.

Caesium 12-tungstophosphate, Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> (CsPW), exhibited strong Bronsted acid sites which acted as an dynamic catalyst for the dehydration of glycerol to acrolein in the gas-phase process at 280 °C and 1.1 bar pressure. To start with, glycerol conversion was 100% at 98% acrolein selectivity, but it lessened considerably with time (40% after 6 h) due to catalyst coking, without disturbing acrolein selectivity. When CsPW was doped with platinum group metals (PGM) (0.3–0.5%) along with co-feeding hydrogen augmented catalyst stability, whereas it kept a high selectivity of acrolein. The augmenting effect of PGM was found to surge in the order: Ru < Pt < Pd. The catalyst containing 0.5%Pd in CsPW gave 96% acrolein selectivity at 79% glycerol conversion, with a specific rate of acrolein manufacture of 23 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> at 275 °C and 5 h time on stream, which is better than what had been stated before for supported heteropoly acids (5–11 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> per total catalyst mass).

The catalyst Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> (CsPW) was produced from H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and Cs<sub>2</sub>CO<sub>3</sub> as a white crystalline powder. Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> and Cs<sub>3.5</sub>H<sub>0.5</sub>SiW<sub>12</sub>O<sub>40</sub> were prepared likewise. PGM-doped CsPW catalysts were prepared by permeating CsPW with a solution of suitable metal precursor. All the catalysts were kept in desiccators over P<sub>2</sub>O<sub>5</sub>.



Jia et al. [10] has studied catalytic conduct of nanocrystalline HZSM-5 with high Si/Al molar ratio as catalyst for the vapour phase dehydration of aqueous glycerol. When the results were matched with bulk HZSM-5, the matching nanocrystalline constituents possessed enhanced catalytic performance in glycerol dehydration. Besides the size effect, the impact of Si/Al ratio and the proton interchange degree of  $H_xNa_{1-x}ZSM-5$  on the catalytic behaviour of the catalyst were also been examined. Author was able to summarize that small-sized HZSM-5 with high Al per cent was a capable catalyst for gas phase dehydration of glycerol.

Zeolites are crystalline microporous aluminosilicates constituting of tetrahedral  $SiO_4$  and  $AlO_4$  units which are linked via shared oxygen sites to form exposed framework assemblies. This produces a system of pores and voids with molecular magnitudes. Zeolite constituents are widely used in applications, such as catalysis and chemical segregations. The moderate pore size zeolite ZSM-5 is industrially vital member of this class of materials. HZSM-5 has also been used as catalyst for glycerol dehydration. Neher et al. [15] performed this reaction in liquid state at 280–320 °C and 80 bar using HZSM-5 as the catalyst. At low conversion of glycerol (15–19 mol%), they observed extraordinary selectivity (71–75 mol%) to acrolein. Chai et al. [17] mentioned for gas phase dehydration (GHSV = 80 h<sup>-1</sup>) with a fixed bed reactor at 315 °C, using HZSM-5 as catalyst, a reasonably low glycerol conversion (23 mol%), and acrolein selectivity (52 mol%) at TOS = 9–10 h was observed. This was uncertainly attributed to micropore logjam by carbon deposits during the reaction. In the other hand, no facts on particle size and Si/Al ratio of the HZSM-5 catalyst were revealed in these two reports. Recently, Corma et al. explored the dehydration of glycerol on zeolite-based catalyst in a moving bed reactor analogous to a FCC type reactor. High acrolein yield (55–61%) was obtained at 350 °C with a HZSM-5-based catalyst (Si/Al = 100, particle size 40–120 nm). Nanocrystalline zeolites (<100 nm) could deliver large outer surface areas and shorten the dispersion distances in the networks of the particles, thereby enabling access to the active sites and decreasing deactivation. There has been some information on the better catalytic properties of Nano crystal-like ZSM-5, such as amplified selectivity in toluene conversion to cresol and diminished coke formation relative to conventional ZSM-5 materials. However, up to now, research on the performance of nano crystalline HZSM-5 catalyst in glycerol dehydration are deficient, although one can expect superior properties as related to materials with grander crystal sizes.

Chai et al. [12] has investigated on the catalytic behaviour of Nb<sub>2</sub>O<sub>5</sub> catalysts which were manufactured by fluctuating the calcination temperature of a hydrated niobium oxide (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) for the vapour-phase dehydration of aqueous glycerol. The data that has been provided in this paper gives us a base for equating the catalyst acidity with the catalytic performance in case of glycerol dehydration. Niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) had previously been used as a water-resistant solid acid catalyst for numerous water-involving reactions, such as dehydration, hydration, esterification and hydrolysis. A key to the acidic and catalytic properties of Nb<sub>2</sub>O<sub>5</sub> is its calcinations or pre-treatment temperature.

The gas-phase dehydration of glycerol to harvest acrolein was observed at 315 °C over Nb<sub>2</sub>O<sub>5</sub> catalysts calcined in the temperature assortment of 350<sup>0</sup>C –700<sup>0</sup>C. Calcination at 350 and 400 °C created amorphous Nb<sub>2</sub>O<sub>5</sub> catalysts with good properties to carry out the dehydration reaction.

- i. It possessed considerably higher sections of tough acid sites at  $-8.2 < H_0 < -3.0$  ( $H_0$  is the Hammett acidity function [3]) than the crystallized Nb<sub>2</sub>O<sub>5</sub> samples acquired by calcination at or above 500 °C.
- ii. Glycerol conversion and acrolein selectivity of the Nb<sub>2</sub>O<sub>5</sub> catalysts were based on the division of strong acid sites ( $-8.2 < H_0 < -3.0$ ).
- iii. The amorphous catalyst that was produced by the calcinations at 400 °C, having the maximum portion of acid sites at  $-8.2 < H_0 < -3.0$ , showed the highest mass specific action and acrolein selectivity (51 mol %). The new samples, having an augmented fraction of one or the other stronger ( $H_0 < -8.2$ ) or weaker acid sites ( $-3.0 < H_0 < 6.8$ ), were less effective for glycerol dehydration and production of the acrolein.

Nb<sub>2</sub>O<sub>5</sub> catalysts were produced by calcination of a hydrous niobium oxide (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O), which was purchased. The calcination was completed under flowing air (80 ml min<sup>-1</sup>) in a horizontal tubular oven (50 mm i.d.) using 3.0 g of Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O dispersed in a quartz boat positioned in the central of the oven. The heating speed was 8<sup>0</sup>C/min, and the calcinations were sustained for 4 h at each of the selected temperatures (350–700 °C).

Lourenco et al. [13] has investigated a series of methodical mesoporous SBA-15 functionalized with an alkanesulfonic group, prepared by a one-pot (co-condensation) technique, in order to receive acclaim for both high acidity of the sulfonic group and the large pore diameter of SBA-15. These features combined with the occurrence of only one type of acid sites are accountable for a high performance of the catalyst in terms of selectivity and activity. The co-condensation process for inclusion of functional species in this type of

materials is advantageous because it allows a high degree of organic moieties dispersion and the inclusion of thermally-stable covalent Si—C anchoring bonds.

A comparative study of the above discussed catalyst has been done here which cover the operating conditions of the reaction, characterization of the catalyst and the results obtained from those catalysts in terms of conversion and selectivity.

**Table 1.** Literature review in tabular form.

CATALYST	OPERATING CONDITIONS	CATALYST CHARACTERIZATION	RESULTS	REFERENCE
Acidic binary metal oxide catalysts (SnO <sub>2</sub> –TiO <sub>2</sub> , SnO <sub>2</sub> –ZrO <sub>2</sub> , TiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> –TiO <sub>2</sub> , ZrO <sub>2</sub> –SiO <sub>2</sub> , ZnO–TiO <sub>2</sub> and TiO <sub>2</sub> –ZrO <sub>2</sub> )	<b>Pressure:</b> atm <b>Temperature:</b> 315°C <b>Feed:</b> 10 mole% or 36.2 wt% of glycerol in water <b>Reaction Time:</b> 9-10h <b>Vapor Phase Amount of Catalyst:</b> 0.63 ml volume of catalyst	<b>BET:</b> surface area, <b>XRD, n-butylamine titration method using Hammett Indicators:</b> for catalyst acidity	<b>Selectivity:</b> 45-52 mole% <b>Conversion:</b> 10 mol% TiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> calcined at 600°C and 50 mol% TiO <sub>2</sub> –ZrO <sub>2</sub> calcined at 550°C exhibited the best catalytic performance for acrolein production from aqueous glycerol.	[20]
Caesium 12-tungstophosphate, Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> (CsPW), <b>Metal added:</b> Ru, Pt and Pd	<b>Pressure:</b> 1 bar <b>Temperature:</b> 275°C <b>Feed:</b> glycerol–water (10:90, w/w) solution <b>Reaction Time:</b> 6 h	<b>BET:</b> surface area and porosity <b>XRD, FTIR, DRIFT TPD, TPR:</b> acidity	<b>Conversion:</b> 100% <b>Selectivity:</b> 98% Decreases with time (6h=40%) Metal doping also affect the conversion and selectivity (Ru, Pt and Pd), CsPW is	[9]

	<p><b>Vapor Phase Catalyst loading:</b></p> <p><b>Amount of Catalyst:</b> 0.30 g of catalyst (45–180 <math>\mu\text{m}</math> particle size).</p>		<p>very thermally stable and water resistance</p> <p>solid acid catalyst,</p> <p>Deactivation mainly due to coke deposition</p>	
Nb <sub>2</sub> O <sub>5</sub> catalysts	<p><b>Pressure:</b> atm</p> <p><b>Temperature:</b> 315°C</p> <p><b>Feed:</b> 36.2 wt% glycerol (molar ratio glycerol/water = 1/9)</p> <p><b>Reaction Time:</b> 10h</p> <p><b>Vapor Phase Amount of Catalyst:</b> 0.63 ml of catalyst, catalyst mass in the reactor varied with the catalyst calcinations temperature (<math>T</math>) and were 0.56 g (<math>T = 350</math> °C), 0.57 g (400 °C), 0.61 g (500 °C),</p>	<p><b>BET:</b> surface areas, pore volumes, and average pore diameters</p> <p><b>XRD:</b> catalyst structure</p> <p><b>Acidity:</b> <i>n</i>-butylamine titration method using various Hammett indicators, including anthraquinone (<math>\text{p}K_a = -8.2</math>), dicinnamalacetone (<math>\text{p}K_a = -3.0</math>), and neutral red (<math>\text{p}K_a = 6.8</math>)</p> <p><b>TPO:</b> oxidation state of oxide form in catalyst</p>	<p><b>Conversion:</b> 100% at 400°C</p> <p><b>Selectivity:</b> 51% at 400°C calcinations temp</p> <p>calcination temp, 40% at 700°C calcination temp</p>	[12]

	0.73 g (600°C), and 0.84 g (700 °C).			
SiO <sub>2</sub> , Si <sub>0.95</sub> Al <sub>0.05</sub> O <sub>x</sub> , Si <sub>0.9</sub> Al <sub>0.1</sub> O <sub>x</sub> , Si <sub>0.8</sub> Al <sub>0.2</sub> O <sub>x</sub> , Si <sub>0.6</sub> Al <sub>0.4</sub> O <sub>x</sub> , Si <sub>0.4</sub> Al <sub>0.6</sub> O <sub>x</sub> , Si <sub>0.2</sub> Al <sub>0.8</sub> O <sub>x</sub> , and η-Al <sub>2</sub> O <sub>3</sub>	<b>Pressure:</b> atm <b>Temperature:</b> 300°C <b>Feed:</b> Glycerol+water (concentration unknown) 23.4 mmol/h <b>Reaction Time:</b> 177h (selectivity: 82%) <b>Vapor Phase Amount of Catalyst:</b> 0.10 g	<b>BET:</b> surface area, N <sub>2</sub> - <b>adsorption,</b> <b>XRD, NH<sub>3</sub>-TPD,</b> <b>FT-IR, IR</b> <b>spectra,</b> <b>MAS/NMR,</b> <b>TPO and Raman</b> <b>spectra</b>	<b>Conversion:</b> decreasing in following order Si <sub>0.6</sub> Al <sub>0.4</sub> O <sub>x</sub> ~ Si <sub>0.8</sub> Al <sub>0.2</sub> O <sub>x</sub> > Si <sub>0.9</sub> Al <sub>0.1</sub> O <sub>x</sub> > Si <sub>0.4</sub> Al <sub>0.6</sub> O <sub>x</sub> > Si <sub>0.2</sub> Al <sub>0.8</sub> O <sub>x</sub> > Si <sub>0.95</sub> Al <sub>0.05</sub> O <sub>x</sub> > η - Al <sub>2</sub> O <sub>3</sub> from 50-15% <b>Selectivity:</b> decreasing in following order Si <sub>0.8</sub> Al <sub>0.2</sub> O <sub>x</sub> > Si <sub>0.6</sub> Al <sub>0.4</sub> O <sub>x</sub> > Si <sub>0.9</sub> Al <sub>0.1</sub> O <sub>x</sub> > Si <sub>0.4</sub> Al <sub>0.6</sub> O <sub>x</sub> > Si <sub>0.95</sub> Al <sub>0.05</sub> O <sub>x</sub> ~ Si <sub>0.2</sub> Al <sub>0.8</sub> O <sub>x</sub> > η - Al <sub>2</sub> O <sub>3</sub> from 17-4%	[14]
WO <sub>3</sub> /TiO <sub>2</sub> based catalyst	<b>Pressure:</b> atm <b>Temperature:</b> 260-340°C <b>Feed:</b> 20 wt% aqueous Glycerol (23 g/h) <b>Reaction Time:</b> 8h	<b>BET:</b> surface area, pore volume and average pore diameter <b>TPD:</b> basicity and acidity <b>XRD</b>	<b>Conversion:</b> 100% <b>Selectivity:</b> 75% at 280°C Effect of temperature, WO <sub>3</sub> amount, oxygen content etc	[15]

	<b>Vapor Phase</b> <b>WO<sub>3</sub> loading:</b> <b>0.0-27.6%</b> <b>Amount of</b> <b>Catalyst:</b> unknown			
WO <sub>3</sub> /ZrO <sub>2</sub> catalysts Doped with SiO <sub>2</sub>	<b>Pressure:</b> atm <b>Temperature:</b> 300°C <b>Feed:</b> 20 wt% of glycerol solution (3.8 g/h) <b>Reaction Time:</b> 177h (selectivity: 82%) <b>Vapor Phase</b> <b>Amount of</b> <b>Catalyst:</b>	<b>BET:</b> surface area, pore size, pore volume <b>BJH, XRD,</b> <b>Raman spectra,</b> <b>NH<sub>3</sub> TPD:</b> acidity	<b>Conversion:</b> 100% (82% after 177h) <b>Selectivity:</b> 78% SiO <sub>2</sub> on ZrO <sub>2</sub> favored the formation of larger mesoporous pores and reduces the support basicity which limits formation of by- products that can be coke precursors.	[16]
zirconia- supported 12- tungstophosp horic acid	<b>Pressure:</b> atm <b>Temperature:</b> 315°C <b>Feed:</b> 36.2 % Glycerol (GSHV 400h <sup>-1</sup> ) <b>Reaction Time:</b> 10h <b>Vapor Phase</b> <b>Catalyst</b> <b>loading</b>	<b>BET:</b> surface area <b>XRD, Raman</b> <b>spectra</b>	<b>Conversion:</b> <b>Selectivity:</b> 70 mole % At 315°C and 36.2 wt% glycerol feed	[17]

Zirconium and niobium mixed oxides catalyst (ZrNbO)	<b>Pressure:</b> atm <b>Temperature:</b> 280, 290, 300°C <b>Feed:</b> 20 wt% of glycerol solution (3.8 g/h) <b>Reaction Time:</b> 177h (selectivity: 82%) <b>Vapor Phase Amount of Catalyst:</b> 4.5 ml	<b>atomic absorption (ICP):</b> metal content of oxide <b>BET:</b> surface area <b>XRD, Raman spectra, XPS, CPMAS NMR</b> <b>TPD:</b> acidity	<b>Conversion:</b> 100% <b>Selectivity:</b> 82% after 177h (at 300°C) Prepared catalyst is compare with other catalyst, some studies on the active site inactive sites was also done in this paper	[18]
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## CHAPTER 3

### OBJECTIVE

The main objective of this work is to design and synthesis of suitable catalysts system for the gas phase dehydration of glycerol to acrolein.

Catalyst preparation by precipitation and wet impregnation method.

Catalyst characterization includes:

- i. BET Surface Area measurement.
- ii. TPR (temperature program reduction) measurement.
- iii. X-Ray Diffraction (XRD).
- iv. Temperature- programmed desorption (TPD) measurement.
- v. Scanning electron microscopy (SEM).

The catalyst systems prepared included  $\text{FePO}_4$  doped mesoporous silica with different mole per cent ratio of Silica to Iron and Phosphate to Iron.

These catalysts were tested for 8 hour time on stream data and the major products were identified and their selectivity is calculated with the help of calibration charts.

Finally the best catalyst is chosen for further experiments.



## CHAPTER 4

### EXPERIMENTAL DETAILS

#### 4.1. Reagents

Iron nitrate nonahydrate  $[\text{Fe}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  (RFCL Private Ltd., purity 98%, India) was used as metal precursors. (1-Hexadecyl)trimethyl-ammonium bromide  $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}]$  (Alfa Aesar, purity 98%, United Kingdom), Tetraethoxysilane  $[\text{C}_8\text{H}_{20}\text{O}_4\text{Si}]$  (Alfa Aesar, purity 99.9%, United Kingdom) and 35% aqueous ammonia  $[\text{NH}_3]$  (Thomas Baker, India) was used as precursors for synthesis of MCM-41 used as support of the catalyst.

#### 4.2. Support Synthesis

The synthesis of MCM – 41 was carried out using 55 ml of  $\text{NH}_4\text{OH}$  diluted in 210 ml of distilled water under vigorous stirring and at a temperature of  $40^\circ\text{C}$ . After the attainment of  $40^\circ\text{C}$ , 1 gram of hexadecyltrimethylammonium bromide (CTAB) is added to the solution which acts as a cationic surfactant. The temperature is further raised to  $70^\circ\text{C}$  and maintained throughout the preparation of the catalyst. After attaining the temperature of  $70^\circ\text{C}$ , 5 ml of tetraethyl orthosilicate (TEOS) serving as silica source is added drop wise to the solution. The solution can be seen as turning white cause of formation of white slurry. The temperature along with vigorous stirring is maintained for the next 3 hours. The resultant slurry for filtered and washed repeatedly with distilled water and kept for drying at  $90^\circ\text{C}$  in the oven for 12 hours. After drying the residue is kept for calcination at  $450^\circ\text{C}$  for 6 hours. The product obtained is white in colour.

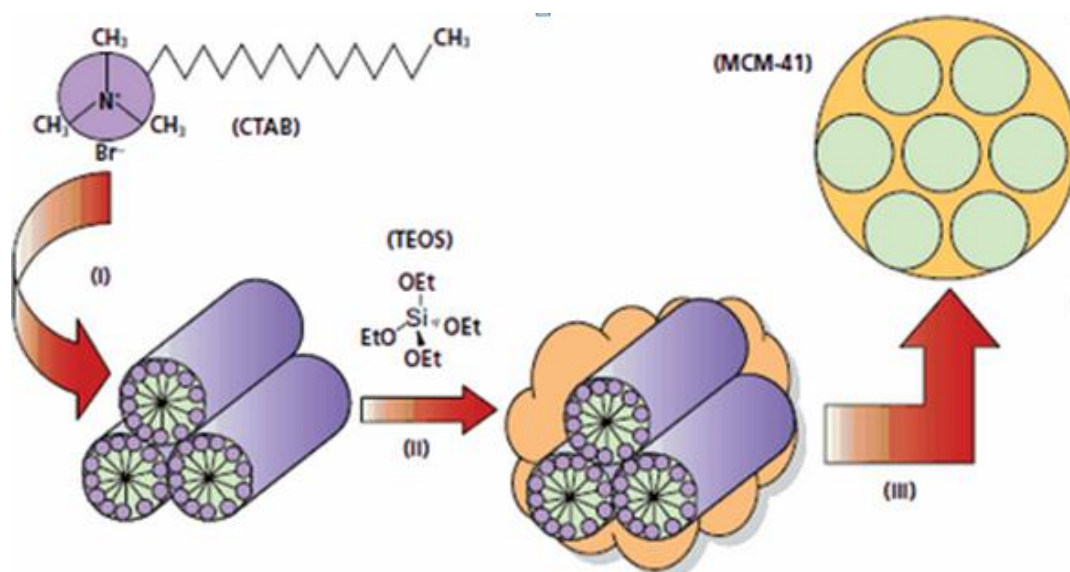


Fig. 1. Internal Structure of MCM-41[3].

### 4.3 Catalysts Synthesis

MCM -41 supported FePO<sub>4</sub> catalysts were prepared by an impregnation method. A set of catalyst of different mole ratio of iron to phosphate and iron to silica was prepared. Iron (III) nitrate is dissolved in 50 ml of distilled water. Adequate amount of ortho phosphoric acid is added to the aqueous solution such that quantity the phosphate to iron ratio is maintained at 1.15. (P/Fe = 1.15). Pre calculated amount of MCM-41 is added to the aqueous solution such that the silica to iron ratio is varied from 1 to 5. (Si/Fe = 1,2,3,4,5). The aqueous solution is stirred at room temperature for 12 hours. The resultant slurry is kept for drying in the oven for 12 hours and then calcined at 550<sup>0</sup>C for 6 hours.

### 4.4. Catalysts characterization

#### 4.4.1. BET Surface Area measurement

The BET surface area of the catalysts were calculated by the dynamic pulsing technique on a Micromeritics Pulse Chemisorb 2720 instrument, employing nitrogen physio-sorption at liquid nitrogen temperature. Nitrogen was used as the adsorbate. Before measuring the area all the samples were degassed at 300 °C for 1 h with helium flow of 20cc/min. The total gas flow rate (30% N<sub>2</sub> in He) was maintained at 20 cc/min.

#### 4.4.2. X-Ray Diffraction (XRD)

Powder X-ray diffraction (XRD) was carried out using a Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation with  $\lambda = 1.5406 \text{ \AA}$  between 0.5° and 4° (2 $\theta$ ) also between 10° and 40° (2 $\theta$ ), at a scanning speed of 0.02°/min with radiation source at 40 KV and 40 mA.

The average crystallite can be determined using the Scherrer equation (eqn-1) from the half-widths of the XRD peaks corrected for instrumental broadening:

$$D = \frac{0.90\lambda}{B \cdot \cos\theta} \quad \text{eqn-1.}$$

Where  $\theta$  is diffraction angle, B is a full width at half-maximum of diffraction peak in radians.

#### 4.4.3. Temperature-programmed desorption (TPD) measurement

The acidity of samples were determined by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) on micromeritics. 0.1 gram of sample was introduced into a quartz glass tube and preheated at 150<sup>0</sup>C under the flow of nitrogen at 20cc/min to carry out degassing of

the sample. The sample is again weighed with the apparatus (i.e. quartz glass). The weight loss is deducted from the sample. It is the actual weight of the catalyst taken for calculations. The sample is then kept at 100<sup>0</sup>C and saturated ammonia for 30 minutes at 20cc/min. After saturation, the weakly absorbed ammonia is eliminated with the help of dry Helium at same rate and temperature. Subsequently, the temperature is increased to 800<sup>0</sup>C at a linear rate of 10<sup>0</sup>C/min. the amount of NH<sub>3</sub> evolving from the sample is determined with a TCD detector keeping the Helium flow rate constant

#### **4.4.4. Scanning electron microscopy (SEM)**

The morphology of the synthesized catalysts were examined by scanning electron microscopy (SEM) on a microscope, coupled with energy-dispersive X-ray analysis (EDX) for local elemental composition determination. Field emission scanning electron microscopy (FE-SEM) was performed on a JSM-7400F (JEOL). The samples for SEM were dusted on an adhesive conductive carbon paper attached to a brass mount. Then the sample is sputtered with gold dust before being placed into the FE-SEM.

### **4.5 Catalysts testing**

#### **4.5.1. Experimental apparatus and procedure**

Glycerol hydrogenolysis reactions were carried out in a steel continuous flow reactor (Chemito, India). The reactor was equipped with a HPLC pump, mass flow controllers, ATS furnace, a condenser and an outlet for liquid sampling. Glycerol was diluted with deionised water to give a 20% (wt.) aqueous glycerol solution. The dehydration of glycerol was performed at 300 °C under atmospheric pressure in a fixed-bed vertical stainless steel tubular reactor (12.7 mm OD x 8.48 mm ID x 530 mm L.), using 1 g of catalyst. The temperature was controlled by a thermocouple placed near the catalyst bed. Before each test, the catalyst was heated at 300 °C under a flux of dry nitrogen (32 mL min<sup>-1</sup>) for 1 hour. The reaction feed, an aqueous solution containing 20 wt. % of glycerol, was introduced in the reactor by a HPLC syringe pump at a rate of 0.2 mL/min in presence of dry nitrogen (32 mL min<sup>-1</sup>). Prior to a run, the reactor was flushed with N<sub>2</sub> for 1 hour, after that reactor was heated to the reaction temperature of 300°C at the heating rate of 50<sup>0</sup>C/min. After attainment of steady state (5h) samples were collected and weighed at an interval of 1h. They were analysed by Gas Chromatography (GC).

#### 4.5.2. Product analysis

The samples were taken a time interval of 1h, the reaction products were condensed with a cold trap kept at  $2^{\circ}\text{C}$ ., filtered using whatman 42 filter paper to eliminate the catalyst. These samples were examined by gas chromatography (Newchrom 6800 gas chromatograph equipped with a 50 m capillary column and a FID detector, India). The gas chromatography equipped with a flame ionisation detector. A Chmorsorb-101 column was used for separation of major products such as acrolein and acetol. Nitrogen (30cc/min) was used as the carrier gas. Analyses were carried out according to the following temperature program: initially, the oven temperature was at  $100^{\circ}\text{C}$ . The temperature increased from  $100^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , with a slope of  $10^{\circ}\text{C}/\text{min}^{-1}$  again from  $150^{\circ}\text{C}$  to  $180^{\circ}\text{C}$ , with a slope of  $3^{\circ}\text{C}/\text{min}^{-1}$  then from  $180^{\circ}\text{C}$  to  $240^{\circ}\text{C}$ , with a slope of  $10^{\circ}\text{C}/\text{min}^{-1}$  finally it was kept on hold at  $240^{\circ}\text{C}$  for 4 min. The temperature of injector was maintained at  $260^{\circ}\text{C}$ , while the detector temperature was maintained at  $280^{\circ}\text{C}$ . To calculate the product selectivity the calibration charts were prepared for the main products.

## Results and Discussions

### 5.1 Catalyst Characterization

#### 5.1.1 Effect of physic-chemical properties

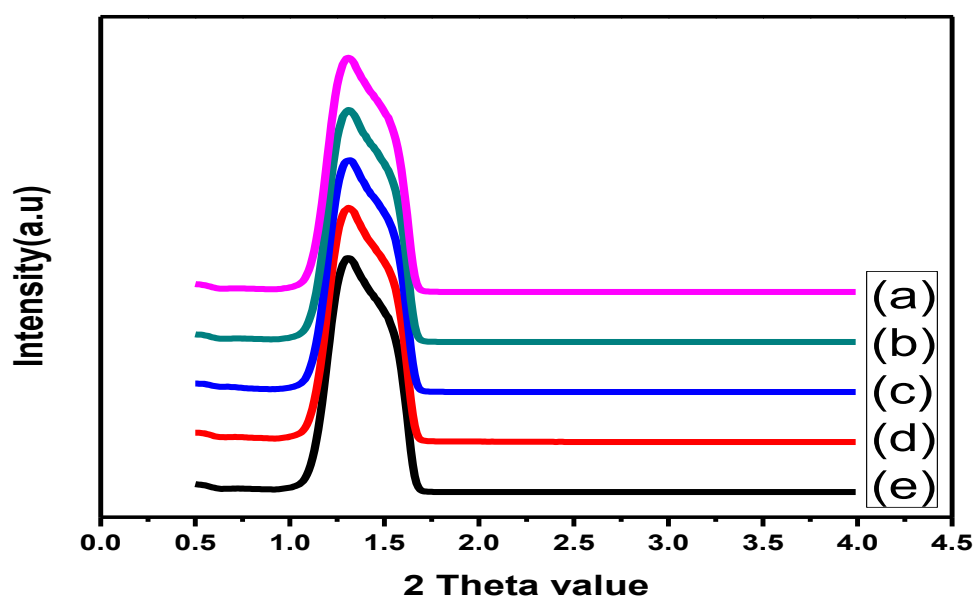
In this project, a series of iron (III) phosphate doped mesoporous silica has been tested in the gas phase dehydration of glycerol. Mesoporous characteristics of these catalysts have been performed by the analysis of the adsorption- desorption isotherms of N<sub>2</sub> at -196<sup>0</sup>C. The catalysts have been seen to possess high specific surface areas, pore volumes and pore sizes thus revealing the mesopous nature of iron (III) phosphate doped mesoporous silica. The surface area of pure MCM-41 and FePO<sub>4</sub> was found to be 1153m<sup>2</sup>/g and 42.5 m<sup>2</sup>/g respectively. The results showed that the surface area of the support constantly decreased with increase in FePO<sub>4</sub> impregnation.

**Table 2.** Surface area, pore volume and average pore diameter of Si-FePO<sub>4</sub> catalysts

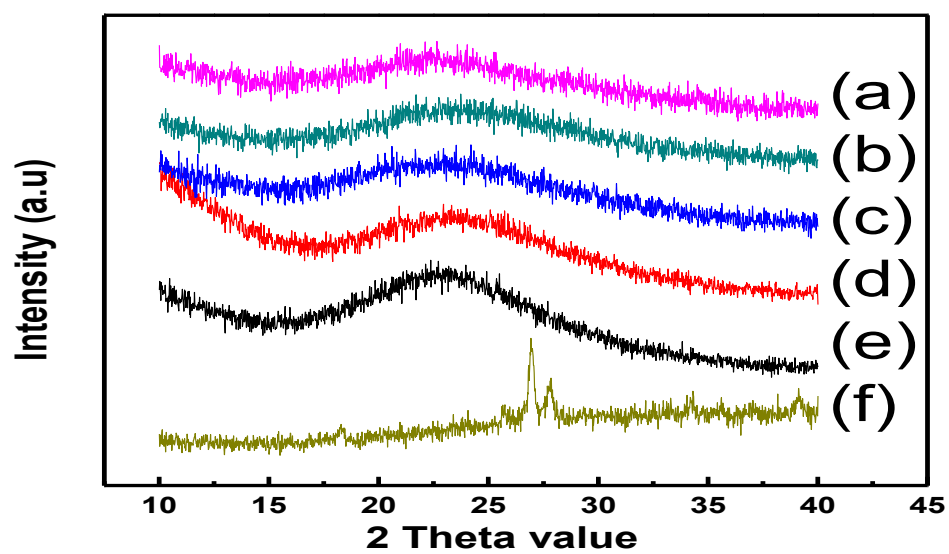
<b>Catalyst</b>	<b>Surface Area (m<sup>2</sup>/g)</b>	<b>Pore Volume (cm<sup>3</sup>/g)</b>	<b>Average Pore Diameter(nm)</b>
<b>MCM-41</b>	1153	1.04	3.3
<b>MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	989	0.71	3.1
<b>MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	723	0.59	3.0
<b>MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	601	0.47	2.9
<b>MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	471	0.32	2.7
<b>MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	324	.25	2.6
<b>FePO<sub>4</sub></b>	43.5	-	-

### 5.1.2 XRD

XRD patterns in the high angle region range between ( $10^{\circ}$  to  $40^{\circ}$ ) did not show any kind of evidence of the characteristics relations of crystalline phases of  $\text{FePO}_4$ , thus helping us to emphasise on the fact that  $\text{FePO}_4$  is evenly distributed in the pores of Mesoporous Silica and stuck to the silica walls. The low angle XRD ( $0.5^{\circ}$  to  $5^{\circ}$ ) provides us with a sharp peak at  $1.2^{\circ}$  as reported by Sancho et al. (Fig. 3 and 4).



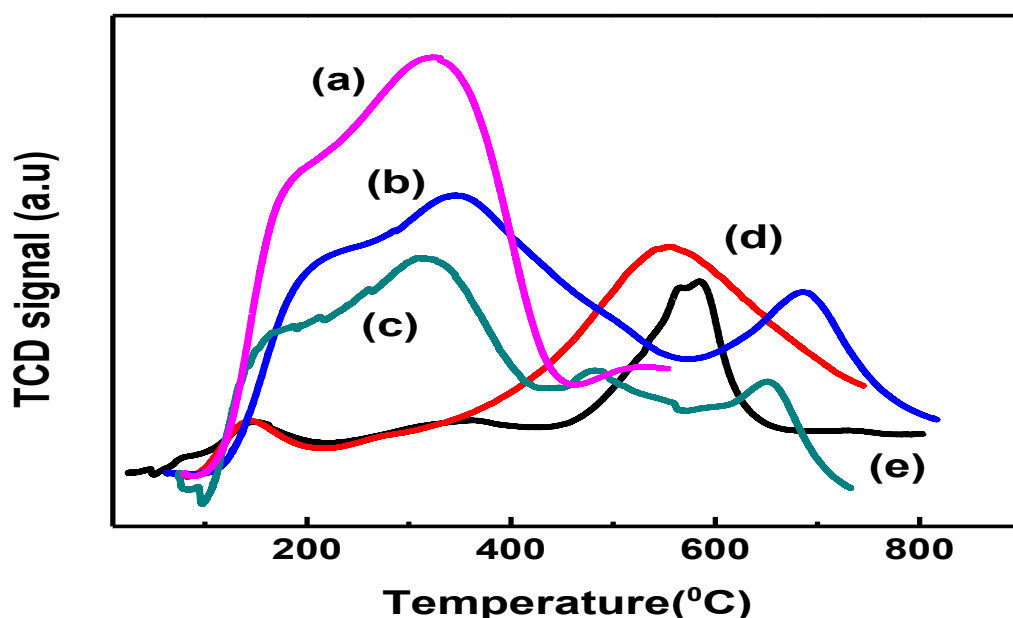
**Fig. 2.** Low angle XRD patterns of Si/Fe catalysts: (a) Si:Fe=5:1; (b) Si:Fe=5:2; (c) Si:Fe=5:3; (d) Si:Fe=5:4; (e) Si:Fe=1:1.



**Fig. 3.** XRD patterns of Si/Fe catalysts: (a) Si:Fe=5:1; (b) Si:Fe=5:2; (c) Si:Fe=5:3; (d) Si:Fe=5:4; (e) Si:Fe=1:1; (f) FePO<sub>4</sub>

### 5.1.3 TPD

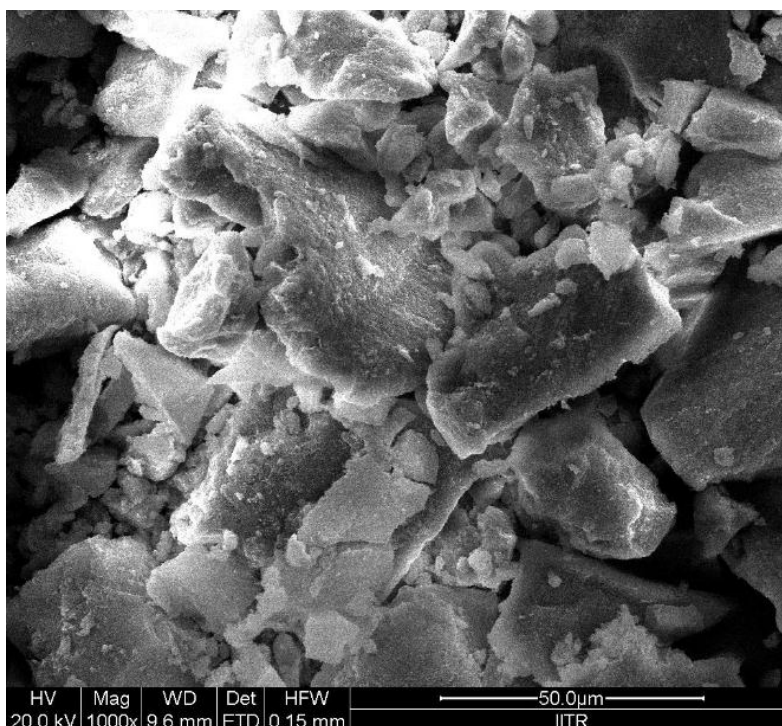
It has been stated that the acidity of the catalyst is a prevalent factor which affect the performance of the catalyst in glycerol conversion to acrolein.[12-14]. The concentration at the surface of acid sites has been calculated with the help of  $\text{NH}_3$  –TPD. In general it can be stated that the acid strength is highly dependent on the desorption temperature of ammonia: weak (100-200), medium (200-400), high (>400). [16]. These curves are broad and the complete desorption of ammonia was observed to take place within 400 °C. with a small peak at 600 °C. which shows the presence of a few strong acidic sites there by indicating a heterogeneous distribution of acid strengths; whereas, the weak- medium sites of acid are predominant as the majority of ammonia get dissolved in the range 100-400 °C. Iron (III) phosphate doped mesoporous silica catalyst display a total acidity higher than that of pure mesoporous silica[13]. It can also be inferred that with increase in the amount of  $\text{FePO}_4$  in the framework, the acidity of the catalyst increases equivalently,  $\text{FePO}_4$  doped silica in the ratio of 1:1 catalyst being the most acidic among the Iron (III) phosphate doped mesoporous silica catalysts. The acid sites are mainly due to the presence of  $\text{FePO}_4$  into the mesoporous network.



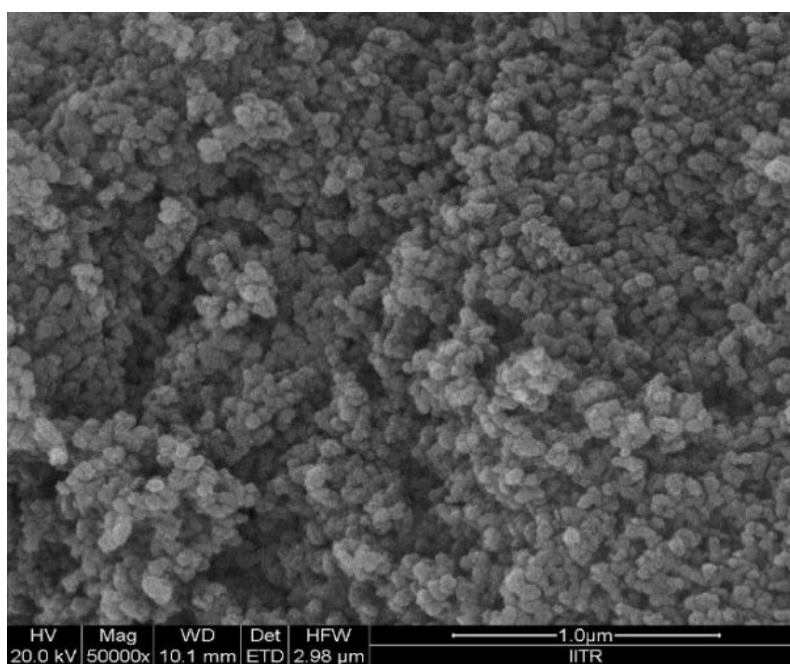
**Fig. 4.** TPD profiles of Si/Fe catalysts: (a) Si:Fe=5:1; (b) Si:Fe=5:2; (c) Si:Fe=5:3; (d) Si:Fe=5:4; (e) Si:Fe=1:1; (f)  $\text{FePO}_4$



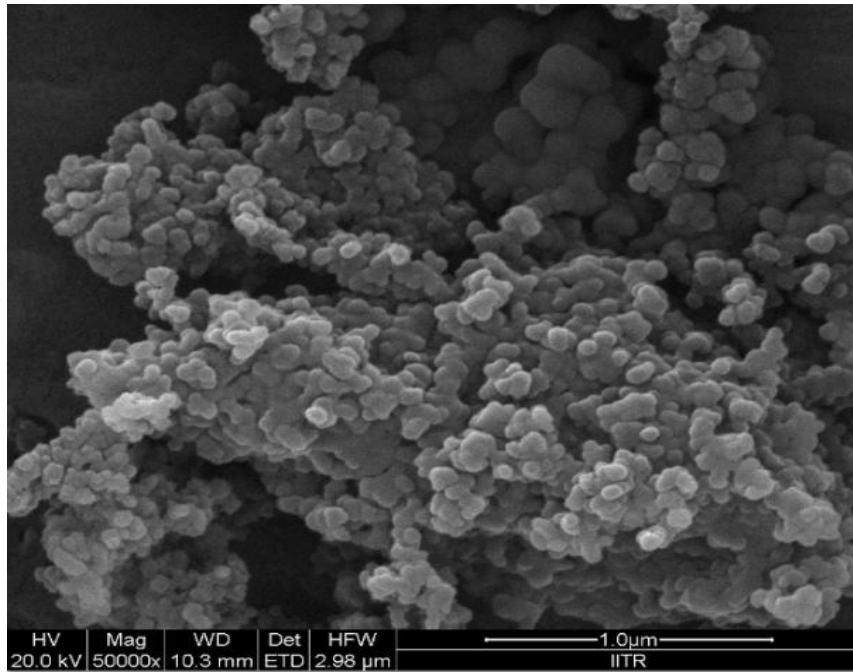
#### 5.1.4 Scanning electron microscopy



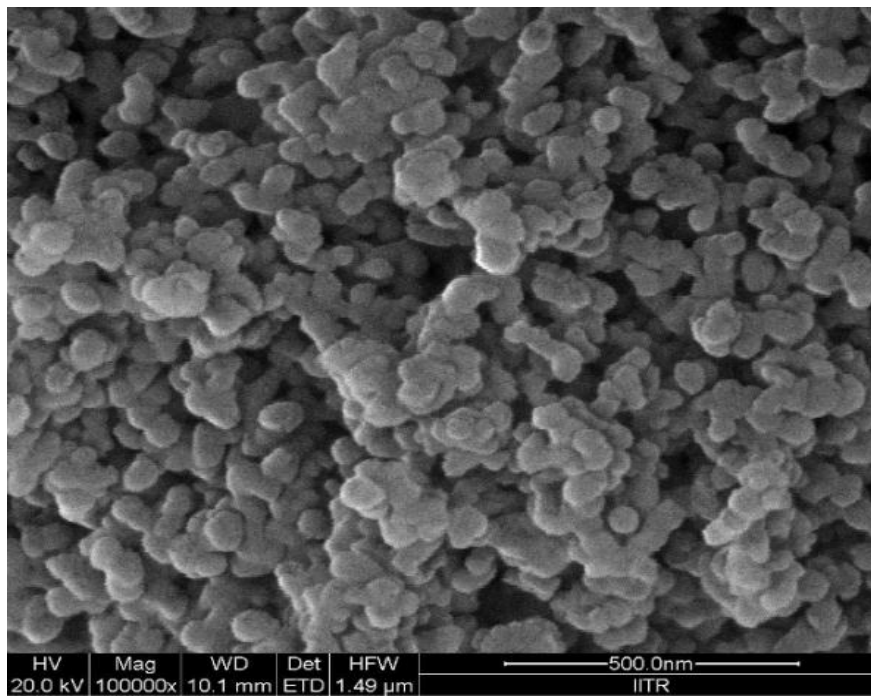
**Fig. 5.** SEM image of FePO<sub>4</sub> on MCM-41(Si:Fe= 5:1) in 50µm range



**Fig. 6.** SEM image of FePO<sub>4</sub> on MCM-41(Si:Fe= 5:1) in 1.0µm range



**Fig. 7.** SEM image of FePO<sub>4</sub> on MCM-41(Si:Fe= 1:1) in 1.0µm range



**Fig. 8.** SEM image of FePO<sub>4</sub> on MCM-41(Si:Fe= 5:1) in 500nm range

## 5.2 Catalytic activity results

The analysis of liquid product collected on an hourly basis after an initial time lag of 5 hours has been performed to obtain a steady state for 8 hrs at a temp of 300<sup>0</sup>C. The products reveal the formation of acrolein, propionaldehyde, allyl alcohol, 2, 3 butanedione and hydroxyacetone. Small concentration of acetone, acetaldehyde, acrylic acid were also detected. These minor components were identified along with others in GC-MS. The major products are listed along with their selectivity in Table 3 first hour of data collection and Table 4 shows us the selectivity of the products after being 8 hrs. on stream.

Table 3. Glycerol conversion (%) and product selectivity (%) at the start of the reaction.

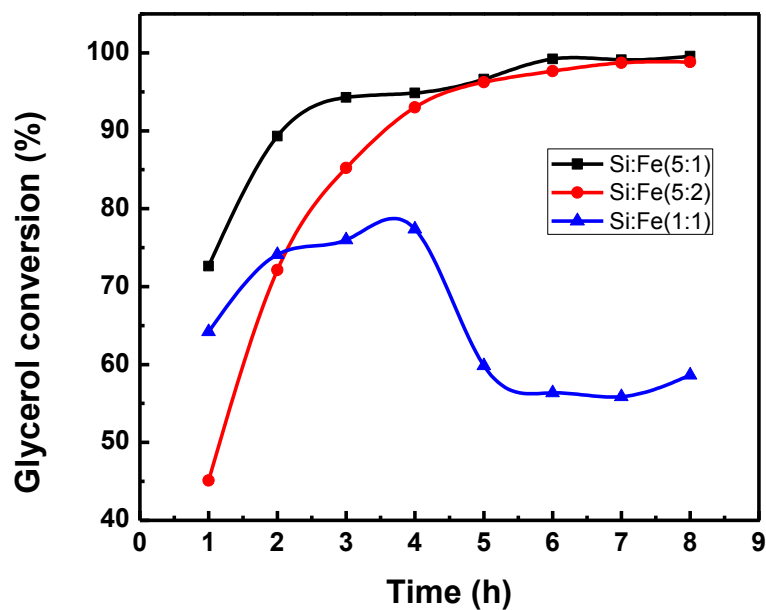
<b>Catalyst</b>	Glycerol Conversion	Propionaldehyde	Acrolein	Allyl alcohol	2,3 Butanedione	Acetol
MCM-41-FePO <sub>4</sub> (Si/Fe:5/1)	72	0.1	58	8	2.6	20
MCM-41-FePO <sub>4</sub> (Si/Fe:5/2)	45	.03	73	5.6	2.5	16
MCM-41-FePO <sub>4</sub> (Si/Fe:1/1)	64	0.017	83	14	2.7	11
MCM-41-FePO <sub>4</sub> (P/Fe:1.15)	29	0	49	44	2.9	44
MCM-41-FePO <sub>4</sub> (P/Fe:1.3)	72	0.1	58	8	2.6	20
MCM-41-FePO <sub>4</sub> (P/Fe:1.45)	83	0	72	8.2	5.7	14

**Table 4.** Glycerol conversion (%) and product selectivity (%) at the end of 17 h

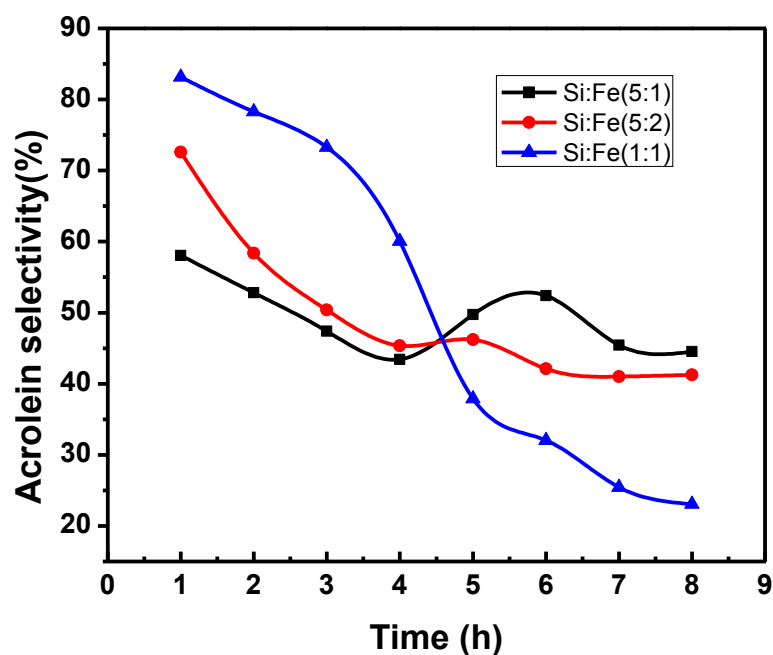
<b>Catalyst</b>	<b>Glycerol Conversion</b>	<b>Propionaldehyde</b>	<b>Acrolein</b>	<b>Allyl alcohol</b>	<b>2,3 Butanedione</b>	<b>Acetol</b>
<b>1.MCM-41-FePO<sub>4</sub> (Si/Fe:5/1)</b>	99	.05	33	7.5	3.8	51
<b>2. MCM-41-FePO<sub>4</sub> (Si/Fe:5/2)</b>	98	0.012	41	1.5	1.7	54
<b>3.MCM-41-FePO<sub>4</sub> (Si/Fe:1/1)</b>	58	0.013	23	1.2	2.8	72
<b>4.MCM-41-FePO<sub>4</sub> (P/Fe:1.15)</b>	49	0	45	2.6	2.3	51
<b>5. MCM-41-FePO<sub>4</sub> (P/Fe:1.3)</b>	99	.05	33	7.5	3.8	51
<b>6. MCM-41-FePO<sub>4</sub> (P/Fe:1.45)</b>	47	0.04	31	3.1	5.5	57

The products which could not be identified were formed possibly due to secondary reactions among products or between products and Glycerol, together with gases like CO and CO<sub>2</sub> which has been formed as expected. In spite of the unidentified products the carbon balance was usually found to be above 80% except for the catalyst with P:Fe=1.15 and 1.45. Almost a complete conversion of glycerol is observed with all the catalysts after 10 hours into the reaction except for the catalyst numbered 3,4,6. However, initially for the first 5hrs the glycerol conversion was observed to be only about 65%. The glycerol conversion increased with acidity, but no significant increase was observed. Contrarily, after 17 hours of time on stream, all the catalysts which were tested showed excellent glycerol conversion except catalyst number 3 which possessed some degree of deactivation. Catalyst numbered 1 and 2 maintained a glycerol conversion of 99.9% (Fig 9). The catalyst having Si to Fe ratio

(5:1) is found to be the most active and stable catalyst but not the most selective to acrolein (table 3), its selectivity to acrolein is 33% of time on stream at the end of 17 hrs(Fig 10 & Fig 11). Catalyst with Si to Fe ratio equal to 1 is the most selective to acrolein with the maximum of 83%. Along with acrolein, acetol is the major by product of the reaction which is formed due to the presence of lewis acid sites on the catalyst.

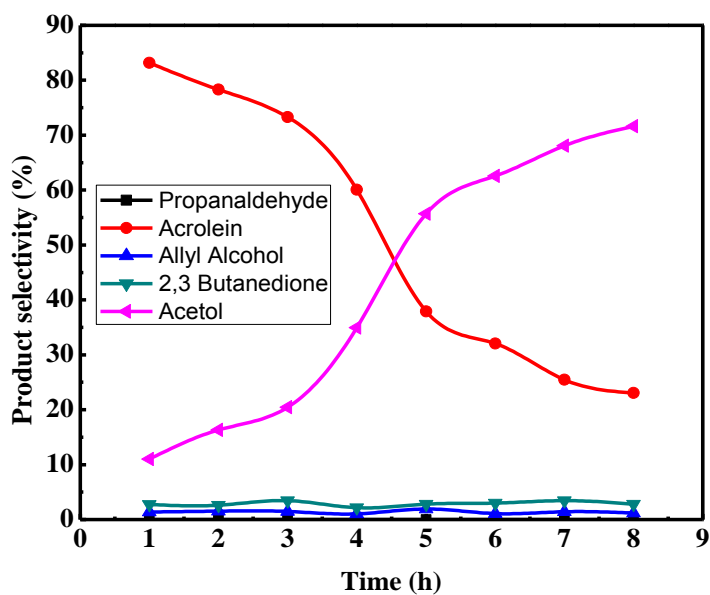


**Fig. 9.** Variation of conversion of glycerol with time for different Si/Fe ratio.



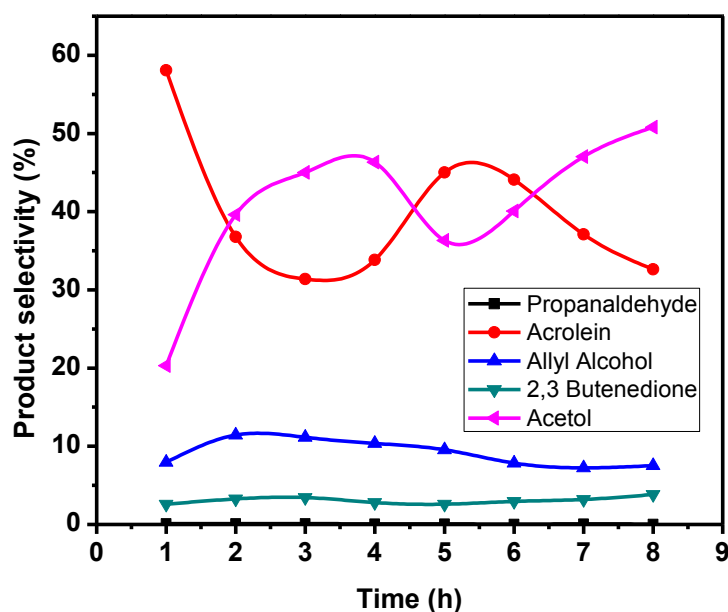
**Fig. 10.** Variation of acrolein selectivity with time for different Si/Fe ratio.

Allyl alcohol has also been detected as dehydration product of glycerol (table 4). In fact for the case of the 3<sup>rd</sup> catalyst, the major constituent in the reaction product is Acetol which reaches upto 72% of selectivity after a time on stream of 12 hours (Fig 11).



**Fig. 11.** Variation of products selectivity with time for Si/Fe (1:1) ratio.

The selectivity of acrolein after a time on stream of 17 hours is noticeably decreasing in all the catalysts (Fig10). This pattern of selectivity has also been observed for the case of acetol obtained at 300 °C, which is the second main reaction product. In contrast, the selectivity to acetol for catalyst with Si:Fe ratio 5:1 was observed to reach a minimum value (Fig 11).



**Fig. 12.** Variation of products selectivity with time for Si/Fe (1:1) ratio.

These FePO<sub>4</sub> impregnated silica catalysts depict a reaction product distribution quite different to that which has been reported in the bibliography. There by Deleplanque et al. has stated that the acrolein selectivity is higher than 90% for FePO<sub>4</sub> thereby producing acetol as the main by-product. Mixed alumina FePO<sub>4</sub> was observed to show an acrolein selectivity of 15% by Suprun et al. after a time on stream of 10 hours. Similar to the results reported by Deleplanque et al. in this particular case also acetol was found to be the main by product with propionaldehyde selectivity as low as 5%. It is already known that Iron Phosphate is a typical Lewis acid solid thereby highlighting the fact that there is formation of acrolein in the dehydration reaction of glycerol. However at a later stage of the reaction there is a significant presence of acetol for 99% glycerol conversion (Fig 11).

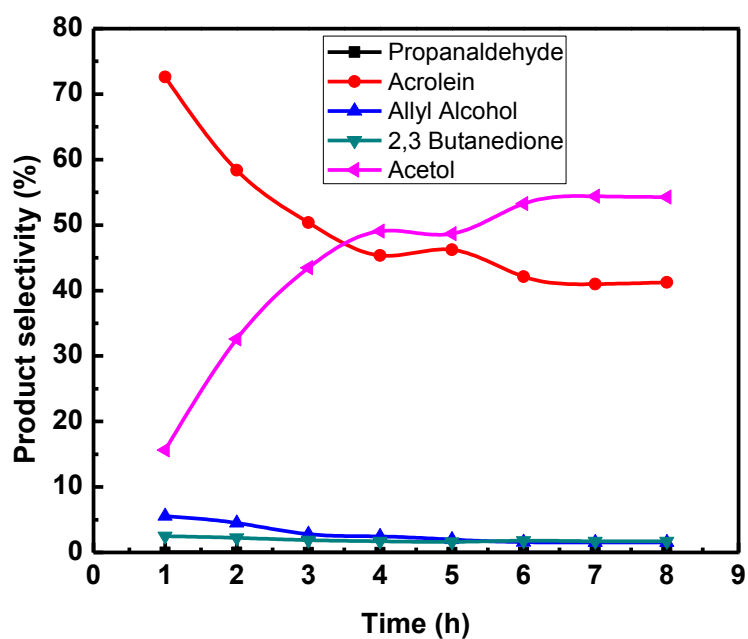


Fig. 13. Variation of products selectivity with time for P/Fe (1.3:1) and Si/Fe (5:1) ratio.

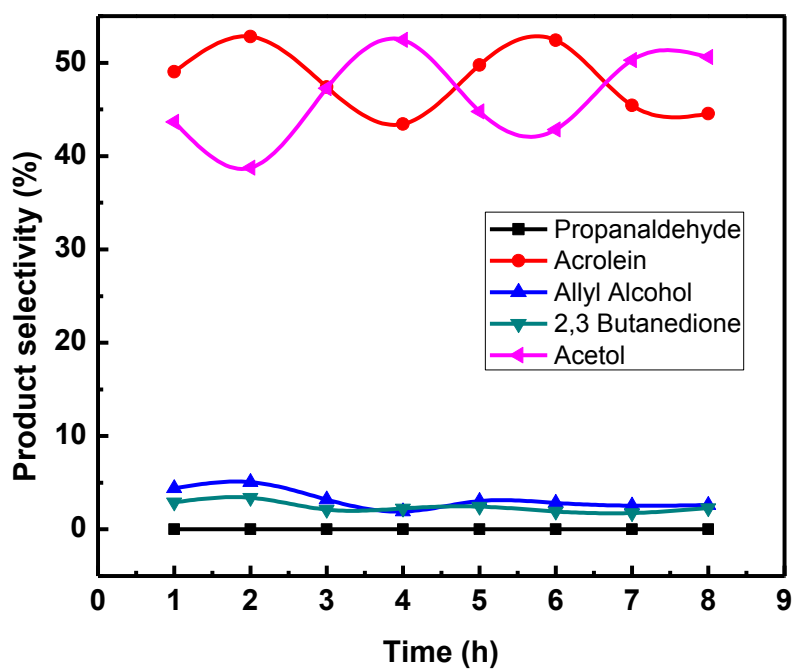


Fig. 14. Variation of products selectivity with time for P/Fe (1.45:1) ratio.



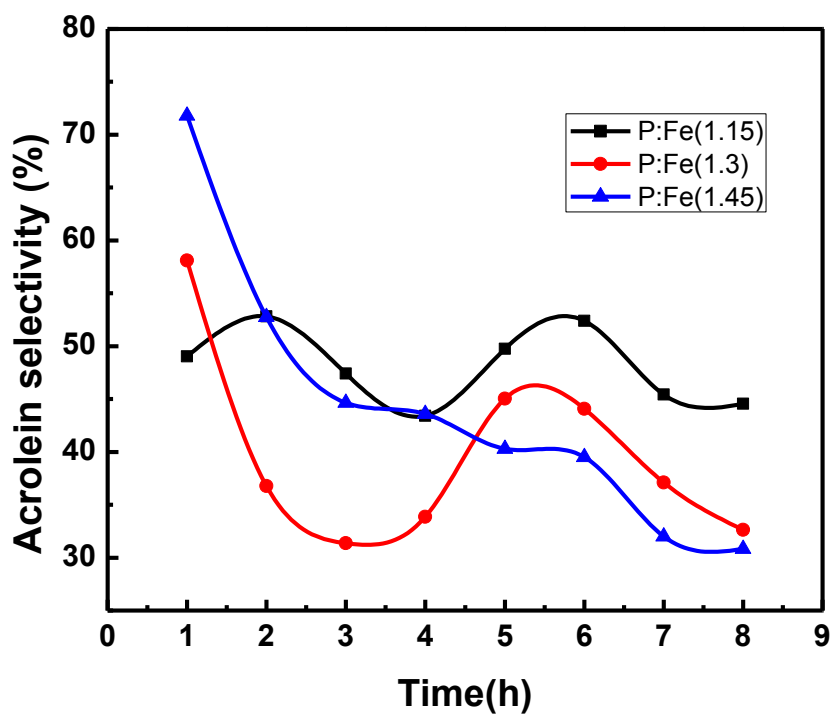


Fig. 15. Variation of acrolein selectivity with time for different P/Fe ratio.

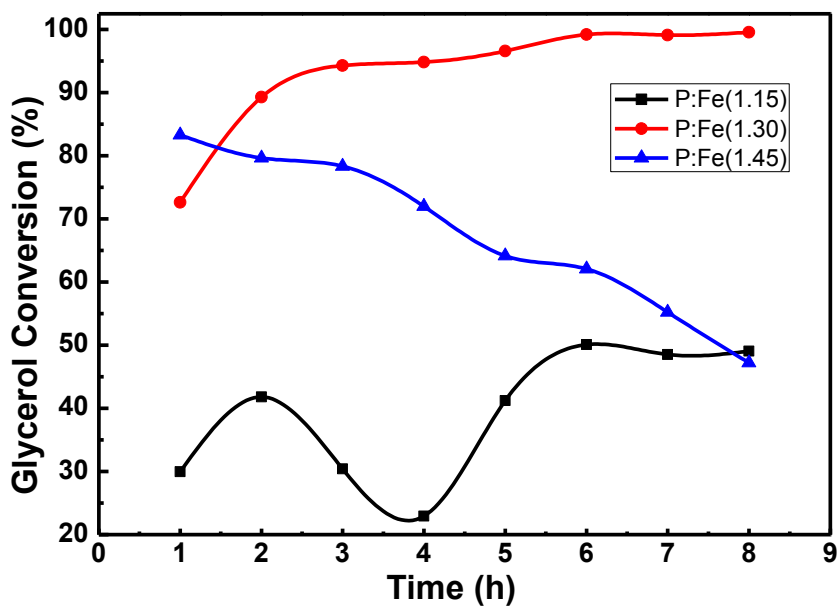


Fig. 16. Variation of glycerol conversion with time for different P/Fe ratio.

It is also worthwhile to mention that these catalysts have a much higher catalytic performance than those based on bulk or mixed oxides of  $\text{FePO}_4$  [11,17, 18,19]. Generally the mechanisms which are proposed to explain large variety of products coming from this reaction gives rise to main methods for the activation of glycerol. Alternatively on lewis acid sites the glycerol OH terminal gets activated yielding acetol. Whereas on the sites of bronsted acids, the protonation of secondary OH evolves towards the formation of acrolein [4,9,17]. Since both the products are getting formed, so the two reaction pathways cannot be ruled out.

The formation of Acrolein indicates protonation based mechanism of the secondary alcohol of glycerol to form unstable 3 hydroxy propionaldehyde intermediate which gets dehydrated to acrolein. Acetol byproduct is formed when glycerol gets in contact with the lewis acid sites present on the catalyst surface. An empirical relationship between the the yield of acetol and lewis acid sites concentration has been established by kim et al. Lewis acid sites can be converted into bronsted sites in presence of steam, which is followed by an increase in the acrolein selectivity. The transformation of lewis acid sites into bronsted ones can be carried out by pretreating the catalyst in a nitrogen flow saturated with steam water at a temperature of  $300^\circ\text{C}$  for 1 hour. This pre-treatment of the catalysts increase the concentration of bronsted acid sites. Due to the conversion of lewis acid sites into bronsted sites, the stability of the catalysts increase and the deactivation rate decreases. Glycerol conversion is in excess of 99% even after 12 hrs into the reaction is obtained and the acrolein selectivity is increased to 50%. The selectivity of acetol constantly increases after 10 hrs on stream revealing that a fraction of bronsted acid sites is getting converted into lewis acid sites after a certain time into the reaction. After 17 hrs the selectivity to acetol and of acrolein is almost similar for all the catalysts. The reaction were carried out at an optimal temperature of  $300^\circ\text{C}$  as conversion of glycerol increases noticeably with the increase in reaction temperature from  $270^\circ\text{C}$  to  $325^\circ\text{C}$ , which is evident from the conclusion inferred by Ulgen et al. who stated that the intermolecular dehydration is favourable at temperatures below  $280^\circ\text{C}$  there by producing glycerol oligomers instead of the acrolein formation due to intra molecular dehydration. They deemed that the selectivity of acrolein is affected by these oligomers at low temperatures.

The productivity of acrolein shows a slight increase than reported, which goes upto a value of 33% at  $300^\circ\text{C}$ . As per the literature if the reaction temperature is increased there is a significant decrease in the selectivity of the by-products. However, at higher temperature the stability of the catalyst decreases due increase in the amount of coke formation. This

behaviour of catalyst is in line with Corma et al. They denoted an increase in the deposition of coke on the catalysts when the temperature of the reaction decreased from 300<sup>0</sup>C to 280<sup>0</sup>C. They also reported that a lower production of by-products exists which is in contrast with the production of acrolein which remains unchanged throughout the tested range of temperatures.

Nevertheless the the selectivity of acrolein also depends on the Phosphate to Iron ratio in the catalysts. The optimum ratio for best selectivity towards acrolein as well as conversion of glycerol was found to be 1.3 for phosphate to Iron(III) ratio (Fig 14,15,16).

The results thus inferred in the glycerol dehydration process at 300<sup>0</sup>C after 17 hrs of catalytic tests of the five FePO<sub>4</sub> catalysts have been represented in table 3 and 4. The samples obtained in the initial 5 hours were not considered since steady state was not reached during the formation of products. The complete conversion of glycerol has been observed in most cases with acrolein being the main product. Five catalysts perform similarly with very few differences. The amount of by products is slightly different for these catalysts. The acrolein yield reaches a high value of 70% in each case and more than 90% in iron phosphate having a ratio of S:Fe =5. Consequently the catalyst by-products very low with acetol being the primary one. Exception occurs for the case of Si:Fe (1:1) catalyst which leads to the formation of more acetol after 12hrs of reaction. The main differences between those catalysts are the amount of by-products formed. GS- MS analysis and mass spectral data base were required for the identification of some compounds. Fig 9, 16 represents the evolution of glycerol conversion and the product distribution for the five iron phosphate catalyst with TOS. The stability of catalysts depends on the amount of FePO<sub>4</sub> doped into the mesoporous silica. With high wt% of iron phosphate the stability of catalysts decreases due to coke formation in micropores, resulting in blocking and deactivation of the acid sites. Due to which there is a drop in the glycerol conversion followed by decrease in selectivity towards acrolein.

The change in the product distribution hints on an alteration of the mechanism and the catalyst deactivation. Development of the mechanism can be illustrated by an increasing amount of by-products such as acetol and Allyl Alcohol. It can be assumed that there is a development of active sites during a reaction imbibing other pathways of obtaining those by-products. The decrease in the carbon balance can also implicate deactivation of the catalyst. Missing carbon is actually due to an increase in the amount of unknown molecules and carbon deposition on the surface of catalysts. It can also be stated from Fig 13,14,15,16 that

the catalyst stability significantly depends on the wt% of FePO<sub>4</sub> in the catalyst system. A few parameters were examined in order to illustrate catalyst performances out of which acidity and texture were elaborated [7-11,14,15]. In particular the comparison of acid based catalysts and their classification in different groups depending on their acidity has been made by Chai et al. it was proved that very strong acid catalysts ( $H_0 \leq -8.2$ ) are more active than strong acid catalysts ( $-8.2 \leq H_0 \leq -3$ ) but less selective toward acrolein due to the severe coking of the catalysts. Weak acid catalysts ( $-3 \leq H_0 \leq +6.8$ ) presented the lowest yields in acrolein whereas solid base catalysts are not effective for the dehydration of glycerol into acrolein. Highly porous catalysts for instance Al<sub>2</sub>O<sub>3</sub>-PO<sub>4</sub> or TiO<sub>2</sub>-PO<sub>4</sub> possess high activity in glycerol dehydration but limited selectivity to acrolein. Contrarily small micropores were more selective but not as highly active.[14]. Similar inference has been stated by Tsukuda et al.[7]. Thus the glycerol dehydration activity and acrolein selectivity depends on both the acid strengths and pore size.

### 5.3 Influence of acidity and textural properties

Iron phosphate being a weak and strong bronsted acid and having a hammet acidity  $H_0 \leq 12$  has comparatively a low specific surface area. ( $5 \text{ m}^2 / \text{gram}$ ). In order to increase this property, mesoporous silica doped with iron phosphate has been prepared by impregnating iron phosphate on mcm-41. In comparison with the bulk, iron phosphate stability can have a significant enhancement using silica support, since deactivation is deciphered after 10-15 hrs of the test. A selectivity of around 65% with a carbon balance of 72 % was observed for acrolein after 17 hrs of test. Though stability is higher than those obtained with iron phosphate catalysts.

FePO<sub>4</sub> catalysts are not as famous in the list of strength of acidic catalysts. The results of NH<sub>3</sub>- TPD imply on the weak acidity of the catalyst with a temperature range of 150-170<sup>0</sup>C for maximum desorption. SiFe(1:1) density records to be the highest deactivation of acid sites which explains the acetol presence after only five hours of the test and a faster conversion drop. SiFe1 is the strongest acid catalyst with the highest density of acid site resulting in quick deactivation. The most concrete proof of deactivation is nothing but an abrupt carbon balance drop and acrolein yield, which indicates a high deposition of coke on the catalyst surface thereby leading to the production of hydrogen which may get into reaction of acrolein yielding propanal or 2- propan-1-ol. In the first 5 hrs strength of acidity is high enough to negate the acetol formation but not that high so as to hinder the formation of coke.

In contrast even weak acidic catalysts can help in the performance of the reaction with the advantage of avoiding or decreasing the formation of coke on the catalyst surface.

20wt% solution of glycerol was maintained during the reaction. The feed contained added nitrogen which helped to maintain the following composition vol% (N<sub>2</sub>/H<sub>2</sub>O/GLY) = (78/20/2) with a gas hourly space velocity of 2800h<sup>-1</sup>. The results obtained with these catalysts after 17 hours TOS has been shown in table 4. A carbon balance of around 80% – 105% was observed. Glycerol conversion is partially or totally complete as perceived in the anaerobic experiment. Reactions at high temperatures and high valences metal centres identify glycerol as a strong reductant.

## **CHAPTER 6**

### **CONCLUSION**

The primary objective of the study was to develop suitable catalyst is for conversion of glycerol and increase selectivity towards acrolein with high stability. For this study a series of FePO<sub>4</sub> doped mesoporous silica, with different Si/Fe molar ratios, has been synthesized and tested in the vapour phase dehydration of glycerol. NH<sub>3</sub>-TPD and XRD, SEM, BET surface area has revealed the presence of well dispersed acid sites, mainly of Lewis type, associated to iron (III) Phosphate species. These active sites are located on the pore walls of the siliceous framework. The glycerol conversion increases with the FePO<sub>4</sub> content, reaching values higher than 99 mol% for a Si/Fe molar ratio of 5:1, at 300<sup>0</sup>C after 5 h of reaction. However, the catalysts suffer from deactivation after a certain period of time. Carbon deposits are taking place which in turn is reducing glycerol conversion as well as acrolein selectivity. The selectivity towards acrolein and acetol can be explained by considering the influence of the nature of active sites. The acrolein selectivity reduced from 82% to 33% and the acetol selectivity increased from 14% to 72%. Selectivity towards other products remained almost constant throughout the reaction time.

## **Future recommendations**

1. Performance of catalysts synthesised by different synthesis methods and the changes in their physical and textural properties.
2. Gather more details with the help of more characterization study such as high transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM) etc.
3. More elaborate study based on the following points is highly desirable to comments on a particular different set of catalysts:
  - (i) Effect of catalysts amount
  - (ii) Effect of temperature
  - (iii) Effect of reaction time
  - (iv) Catalysts deactivation study
  - (v) Characterization of used catalysts
4. More experimental data is required for kinetic study.

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