Synthesis of Phosphate based Magnetic Catalyst for Glycerol Acetylation with Acetic Acid to produce Triacetin

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Submitted By

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PATIALA-147004

2019

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis of phosphate based magnetic catalyst for glycerol acetylation with acetic acid to produce triacetin**" submitted by **Ms. Ritika Jindal** in the partial fulfilment of the requirements for the degree of **Master of Science in Chemistry** from **Thapar Institute of Engineering and Technology, Patiala** is a bonafide piece of work carried out under the guidance and supervision of **Dr. Amjad Ali**, *Professor and Head*, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala and no part of this project has been submitted for award of any other degree in this or any other university.

Ritika

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This is to certify that the above statement made by student concerned is correct and true to the best of my knowledge.

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SELF DECLARATION

I hereby declare the work embodied in the project entitled "**Synthesis of phosphate based magnetic catalyst for glycerol acetylation with acetic acid to produce triacetin** " has been done by me in the partial fulfilment of the requirements for the award of degree of **Master of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala** is an authentic record of my own work carried out under the guidance and supervision of **Dr. Amjad Ali,** *Professor and Head,* School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala. All the ideas and references have been duly acknowledged.

Date: 15/7/19

Ritika

Place: Patiala **(RITIKA JINDAL)**

I also confirm that, the thesis is only for my academic requirement not for any other purpose.

…..Ritika Jindal

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The dissertation project I had was a great chance for learning and professional development. Therefore, I consider myself as a very lucky individual as I was provided with an opportunity to be a part of it.

I would like to use this opportunity to express my deepest gratitude **Dr. Amjad Ali**, *Professor and Head*, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, who in spite of being busy with his duties took time out to hear and guide me. I am thankful for their valuable suggestions and constructive criticism until the completion of my project.

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I would like to express my gratitude towards my parents for their kind co-operation and encouragement which help me in completion of this project.

I perceive this opportunity as a big milestone in my career development. I will strive to use gained skills and knowledge in the best possible way and I will continue to work on their improvement, in order to attain desired career objectives.

…..Ritika Jindal

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ABSTRACT

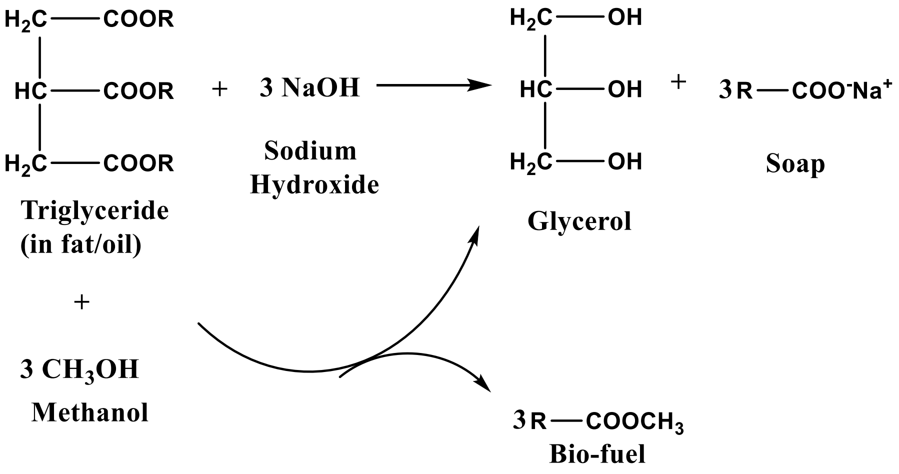
The efficient acetylation of glycerol with acetic acid to produce triacetin selectively is achieved using phosphate based magnetic catalyst. The $Fe_3O_4@SiO_2-PO_4^{3-}$ MNPs were prepared successfully and employed in the glycerol acetylation. As a result, 92.3% selectivity for triacetin was acquired in the presence of catalytic amount of $Fe_3O_4@SiO_2-PO_4^{3-}$-600 °C catalyst at 80 °C for 80 min, exhibiting higher catalytic activity than that of sulphate based magnetic catalyst. The magnetic catalytic was characterized by XRD, FT-IR and SEM-EDX techniques. Moreover, the effects of reactant ratio, catalyst amount, reaction time and reaction temperature in the glycerol acetylation are studied in detail. Finally, a reusability experiment is also performed indicating low activity of the prepared catalyst after 4 runs of experiment.

CHAPTER 1

1. INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Biodiesel (BD), also known as FAME (fatty acid methyl ester), is rapidly replacing fossil fuel as there is limited reserve of fossil fuel which cannot respond to the increasing demand of energy. BD is a much cheaper and greener alternative as it is produced from renewable sources such as animal fats and vegetable oil. It is much cleaner, biodegradable and generates an acceptable amount of emission gases [1]. Glycerol (GL), also known as glycerin, is the principal byproduct in BD manufacturing process. It is colourless, odourless liquid with a sweet taste. It is also produced from saponification or transesterification reaction as shown in **Scheme 1**.



Scheme 1. Saponification reaction

In general, approximately 10 litre of crude GL is produced for every 100 litre of biodiesel produced [2]. Excess of GL may pose a threat to the environment. Hence, the efficient utilization of surplus of GL has become a hot research topic nowadays [3]. The crude GL possesses very low value because of the impurities contained and purification of this GL is quite expensive for utilization in various industries as shown in pie chart **(Fig. 1)** [4].

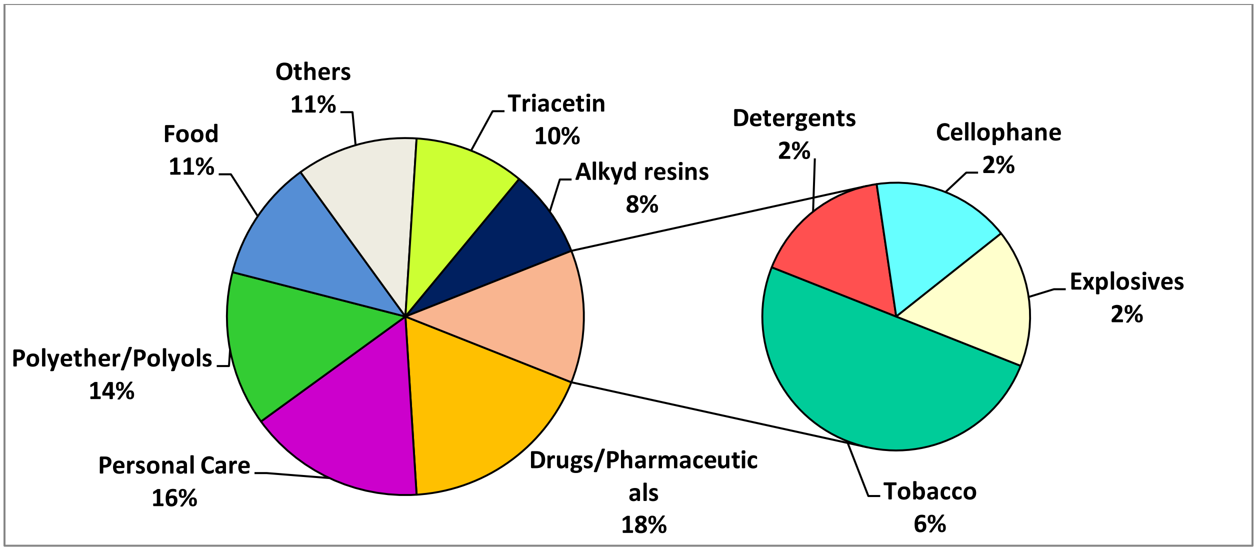


Fig. 1 Industrial uses of glycerol

Therefore, biodiesel producers must look for alternative methods for the utilization of excess of GL. However, researchers found that some very valuable products namely monoacetyl glycerol (monoacetin, MAG), diacetyl glycerol (diacetin, DAG), triacetyl glycerol (triacetin, TAG), dihydroxyacetone (DHA), ketomalonic acid, fuels oxygenate, acrolein and glycerol carbonate could be produced employing various reactions using crude GL as a starting material as shown in **Fig. 2** [2].

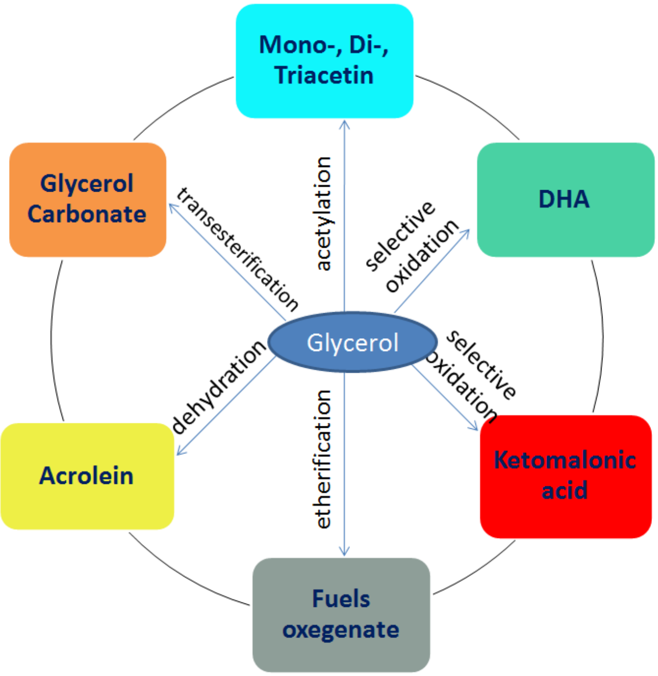


Fig. 2 Various valuable products obtained from glycerol

Acetins are widely used in various types of industries as shown in **Fig. 3**. MAG and DAG are desired as raw material for the production of biodegradable polyesters and in cryogenics [4]. MAG is also used as a food additive and due to its explosive properties it is also used in the manufacture of dynamite. DAG is used as a solvent for variety of dyes and presents great properties as a plasticizer. TAG is used for gasoline as an anti-knock additive in biodiesel industry and it also improves the cold and viscous properties of biodiesel [5]. TAG is also used as an additive in cosmetics, pharmaceutical compounds and tobacco and as a gelatinizing agent and plasticizer in polymers and explosives. Thus, TAG is the most widely used product due to its numerous applications in various industries [6]. In this work, we aim to achieve maximum (more than 90%) selectivity for TAG by optimization of various reaction parameters in acetylation reaction because the low selectivity of TAG at mild conditions has always been the greatest challenge [7].

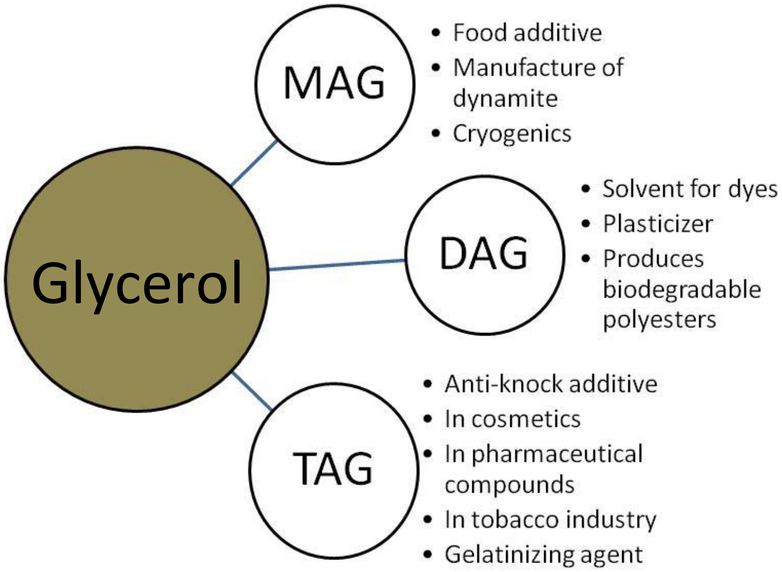


Fig. 3 Uses of MAG, DAG and TAG

1.2 Literature Review

The acetylation of glycerol with acetylation agents such as acetic acid/acetic anhydride/methyl acetate produces mainly the esters of mono, di and triacetin. Traditionally, homogeneous catalysts (HCl, HF, H_3PO_4, $HClO_4$ and H_2SO_4) were commonly used in the industrial applications as they are highly reactive and give higher conversion of GL. But these catalysts require longer reaction time up to 5 h and high reaction temperature up to 120 ˚C. Also, for large scale industrial processes, the use of homogeneous acid catalyst is considered as very unpractical because it leads to serious environmental contamination, hard catalyst separation and corrosion of equipment [6,8]. Homogeneous catalysts are corrosive and hazardous in nature while the use of heterogeneous catalysts is quite advantageous as it involves easy purification of product, simple catalyst separation, reusability and eco-friendly nature [8,9]. Hence, heterogeneous catalysts are rapidly replacing homogeneous catalysts nowadays and utilization of homogeneous catalysts in industrial processes has decreased to less than 20% [10].

To facilitate the fast and simple separation of the catalysts particle, magnetic core could be embedded to avoid the problems like oxidation of catalyst, need for extra solvent, loss of catalyst and time-consuming centrifugation and filtration steps. Hence, magnetic nanoparticles (MNPs) came as a “double green dream” in the history of Nanoscience [11].

Bare Fe_3O_4 MNPs have a tendency of agglomerating into large clusters and losing their catalyst loading capacity [12]. Also, when the surface of particles is oxidized, the surface properties of MNPs change dramatically [11]. So, the modification and surface coating of MNPs is essential to prevent the oxidation of MNPs [13]. Thus, coating of an appropriate material such as a polymer, carbon or silica has to be there on the surface of Fe_3O_4 MNPs [12]. Silica is a metal oxide which is commonly employed for coating the surface of MNPs as it delivers classic applications of heterogeneous catalysis like it possess high specific surface area, inertness, chemical and thermal stability under the normal conditions where the catalysts operate, non-toxicity and low cost [11,14]. Silica also brings various key advantages in catalyst fabrication as shown in **Fig. 4** and **Fig. 5.**

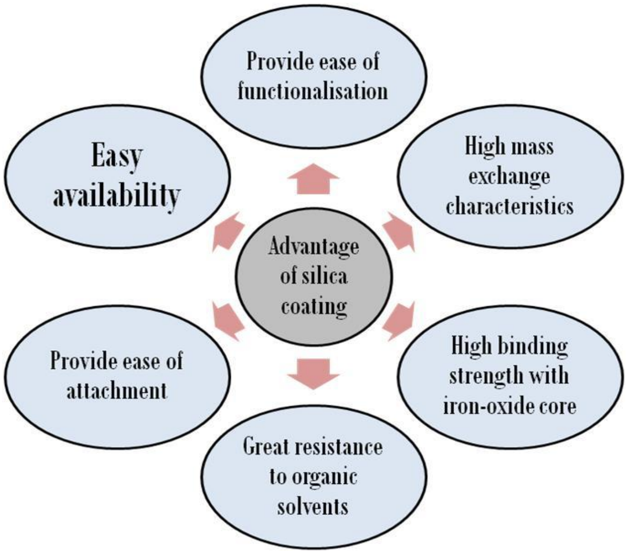


Fig. 4 Advantages of silica coating

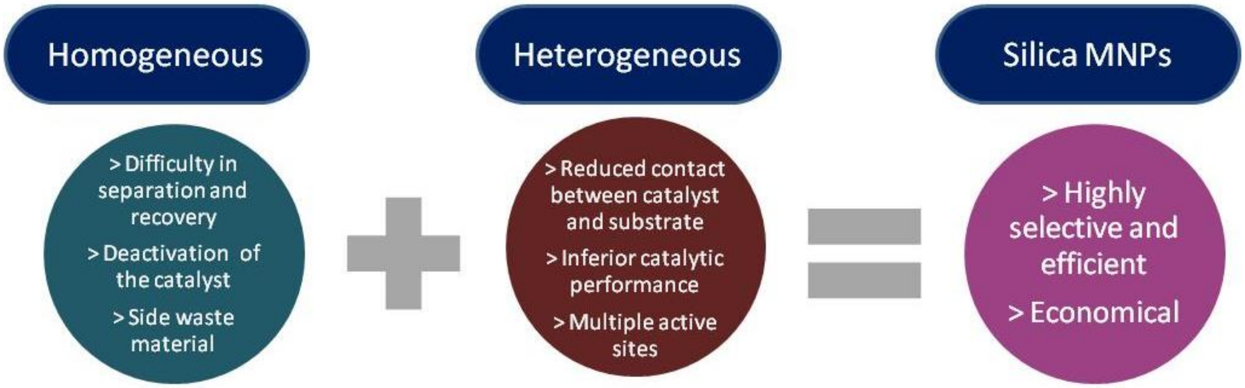


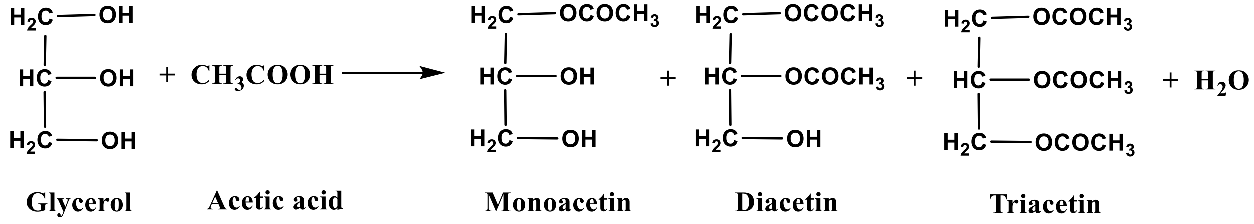
Fig. 5 Advantages of Si-MNPs over simple homogeneous and heterogeneous catalysts

Initiation of acetylation reaction takes place when a proton from catalyst is transferred to the carboxylic acid group of the acetic acid [15,16]. Therefore, to carry out the acetylation reaction, various proton providing catalysts can be used such as H_2SO_4, H_3PO_4, HCl etc. and the solid catalyst having metal oxide as support could be modified with the Bronsted acids such as SO_4^{2-}, PO_4^{3-}, WO_4^{2-}, etc. Acid strength of phosphated catalysts was found to be as good as sulphated one although phosphoric acid is a weaker acid than sulphuric acid [17,18]. The density of Lewis acidic sites is higher in phosphated silica materials than that of sulphated samples [19]. Moreover, when sulphated catalysts are calcined at higher temperatures (700 °C), they tend to decompose easily in comparison to the phosphated catalysts [17,18,20].

For carrying out GL acetylation, a few number of heterogeneous solid acid catalysts having improved activity after impregnation of phosphate are reported in literature. It was reported that mesoporous Al-MCM-41 and zirconia have improved stability after they get post-treatment with phosphoric acid. Also, mesoporous titania framework gets stabilized by impregnation of phosphorous from H_3PO_4 to produce phosphated mesoporous titania with high surface area, small crystallite size and very high thermal stability [21].

Acetylation of glycerol with acetic acid

The most attractive acetylating agent for the acetylation of glycerol to get acetins is acetic acid owing to its lower cost as compared to that of acetic anhydride and higher activity than that of methyl/ethyl esters [15,22]. Moreover, acetic acid has self-catalyzing property as it can furnish the proton in the absence of a catalyst [15]. Acetylation of glycerol with acetic acid (**Scheme 2**) over Amberlyst-70 gives selectivity of 85.4% towards TAG after 10 h of reaction at temperature of 105 °C and glycerol to acetic acid molar ratio of 1:6 with 5 wt% of catalyst [23].



Scheme 2 Acetylation of glycerol with acetic acid

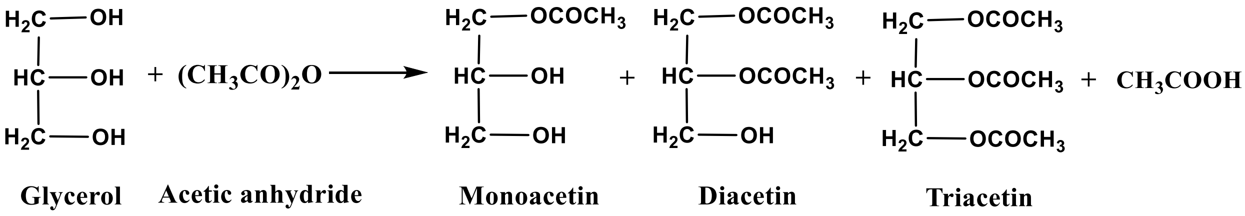
The use of acetic acid (AcA) to prepare triacetin from glycerol in presence of various catalysts at optimized reaction conditions is shown in **Table 1**.

Table 1 Different solid acid catalysts used for glycerol acetylation to produce triacetin

S. No.	Catalyst	Temp. (°C)	GL/AcA ratio	Catalyst Amt. (wt%)	Time (h)	TAG yield (%)	Reference
1.	Amberlyst-70	105	1:6	5	10	85.4	[23]
2.	PTA	100	1:8	8	3	73	[24]
3.	Amberlyst-15	110	1:9	NR	5	44.5	[25]
4.	SO_4^{2-}- AC	120	1:8	8	3	34	[26]
5.	$PrSO_3H$-SBA15	80	1:6	NR	8	19.6	[27]
6.	Amberlyst-35	105	1:6	5	4	25.9	[28]
7.	HY	105	1:6	5	4	3.2	[28]
8.	HZSM-5	105	1:6	5	4	2.5	[28]

Acetylation of glycerol with acetic anhydride

Acetylation of glycerol with acetic anhydride (AA) (**Scheme 3**) using niobium phosphate as catalyst produces triacetin with 47% selectivity at 60 °C and glycerol to acetic anhydride molar ratio of 1:4 within 2 h of reaction [5].



Scheme 3 Acetylation of glycerol with acetic anhydride

The reaction of acetic anhydride and glycerol to produce triacetin over different catalysts is shown in **Table 2** where K-10 has maximum selectivity of 78% towards triacetin.

Table 2 Acetylation of glycerol with acetic anhydride over several catalysts to produce triacetin

S. No.	Catalyst	Temp. (°C)	GL/AA ratio	Time (h)	TAG yield (%)	Reference
1.	Nb Phosphate	60	1:4	2	47	[29]
2.	H-Beta	60	1:3	2	62	[29]
3.	K-10	60	1:3	2	78	[29]

1.3 LACUNA

In literature, most of the acetylation reactions of GL have been carried out using sulphate based acidic catalysts which are non-convenient to use due to their various disadvantages like they leach out during acetylation and require higher reaction temperature upto 120 °C for glycerol conversion. However, phosphate based solid acid catalysts require low reaction temperature upto 80 °C.

To the best of our knowledge, phosphate based magnetic solid acid catalysts have not yet been studied in the field of glycerol esterification. The present work deals with the preparation of inorganic oxide catalyst modified with phosphate ions with an objective to increase Lewis and BrØnsted acid sites on the catalyst surface. During the study, various parameters such as catalyst mass, time and temperature, have also been optimized, to make the reaction more selective towards TAG.

1.4 OBJECTIVES

1. To prepare phosphate impregnated magnetic catalyst for glycerol acetylation with acetic acid.
2. To characterize the prepared catalyst by SEM-EDS, powder XRD, and FT-IR techniques.
3. To optimize the reaction conditions to make the reaction more selective towards triacetin.

2. EXPERIMENTAL METHODS

2.1 MATERIALS

Ferrous sulphate heptahydrate (99%), Ferric chloride hexahydrate (97%), sodium acetate (99%), glycerol (99%) and acetic acid (99%) were obtained from Loba Chemie Ltd. (India), polyethylene glycol supplied from HiMedia Laboratories Pvt. Lmt. (India), ethylene glycol (99%), isopropanol (HPLC grade) and hexane (HPLC grade) supplied from Spectrochem Pvt. Ltd. (India), ammonia solution (25%) procured from Merck Life Science Pvt. Ltd. (India), ethanol (95%), tetraethyl orthosilicate (98%), phosphoric acid (85%) and Deuterated water (D_2O) obtained from Sigma Aldrich (USA), dichloromethane (85%) procured from Avarice Industries

2.2 METHODS

2.2.1 Powder X–ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns of synthesized catalysts were recorded by Panalytical's X'Pert Pro Diffractometer where the radiation (λ =1.5406) used is Cu K-alpha-1 where as Nickel metal is used as beta filter. The samples were scanned in the range of $2\theta = 20 - 80°$ at the scanning speed of 2 min.

2.2.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was recorded on Perkin Elmer – Spectrum RX-IFTIR spectrophotometer in the range of 400- 4000 cm^{-1}.

2.2.3 Scanning Electron Microscopy (SEM)

To determine the surface morphology and elemental distribution of the prepared catalysts, they were characterized by scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) technique which was performed on JEOL JSM 6510LV instrument.

2.2.4 Pyridine Adsorption

The Lewis and Brønsted acidic sites of the phosphate magnetic catalyst were determined by Pyridine adsorption method. Initially, the catalyst sample under investigation was saturated with pyridine, dried at 50 °C for 2 h, further heated for 10 min at 300 °C to desorb the pyridine, and finally, subjected to the diffuse reflectance FT-IR analysis.

2.2.5 Nuclear Magnetic Resonance (H^1-NMR)

H^1-NMR spectrum of triacetin was recorded on a JEOL ECS-400 (400 MHz) spectrophotometer in D_2O solvent.

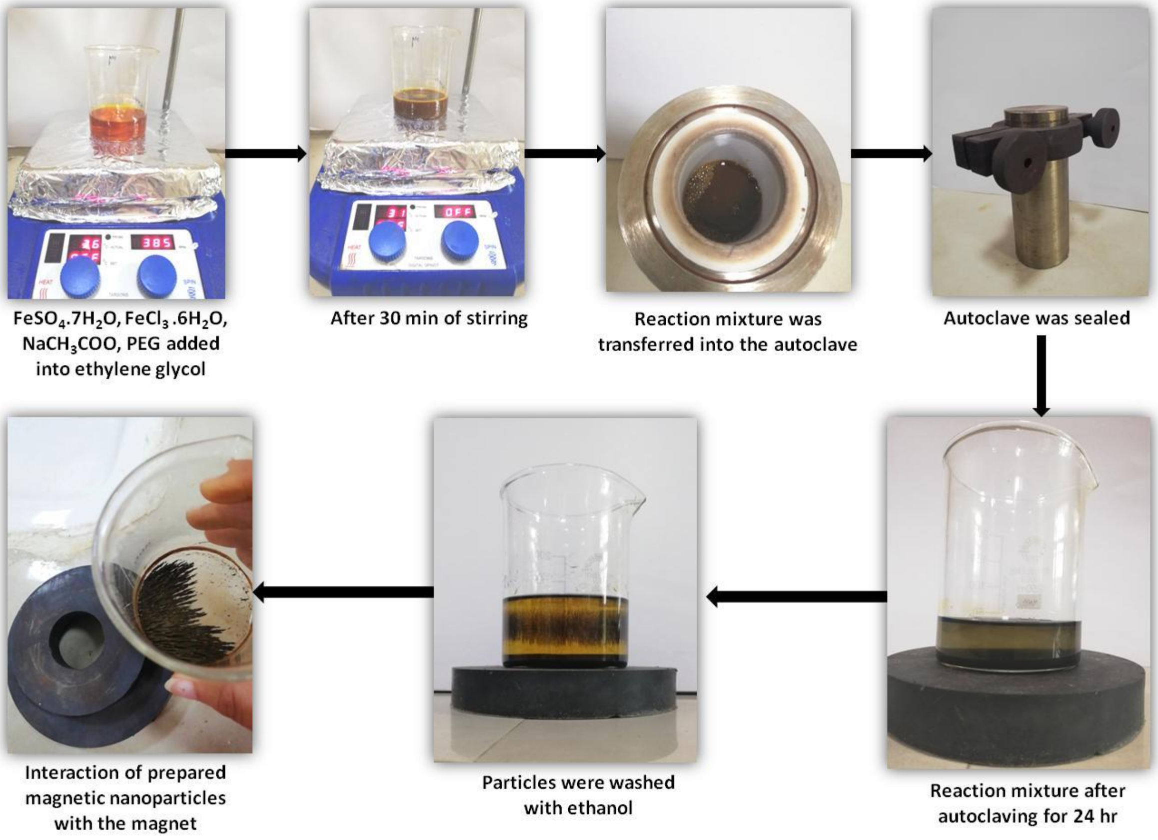
2.2.6 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) was performed over Agilent Infinity 1200 instrument to quantify the desired product. A column temperature of 35 °C was maintained and sample volume of 20 μL was injected to analyze the samples. During the analysis, hexane/isopropanol (60/40; v/v) was employed as mobile phase with a flow rate of 0.6 ml/min and RX-SIL column (250 × 4.6 mm, 5μm) as a stationary phase. The obtained peaks were identified by refractive index (RI) detector.

2.3 CATALYST PREPARATION

2.3.1 Preparation of Fe_3O_4 MNPs

Fe_3O_4 MNPs were synthesized by following the literature reported procedure with a slight modification i.e $FeSO_4.7H_2O$ is used instead of $NiCl_2.6H_2O$ and polyethylene glycol (PEG) is used as capping agent [30]. In a typical preparation as shown in **Fig. 6**, 0.6 g $FeSO_4.7H_2O$, 1.16 g $FeCl_3.6H_2O$, 1 g PEG and 2.64 g sodium acetate were added into 50 ml of ethylene glycol. The resulted colloidal solution was stirred vigorously for 30 min at room temperature. The mixture was then sealed into Teflon lined stainless-steel autoclave having capacity of 50 ml. The temperature of autoclave was maintained at 200 °C for 24 h. After the stipulated time the autoclave was allowed to cool down to room temperature, supernatant was decanted off, the Fe_3O_4 obtained in the form of black particles was washed with ethanol 4-5 times and finally dried in oven at 60 °C for 6 h.



$FeSO_4.7H_2O$, $FeCl_3.6H_2O$, $NaCH_3COO$, PEG added into ethylene glycol

After 30 min of stirring

Reaction mixture was transferred into the autoclave

Autoclave was sealed

Reaction mixture after autoclaving for 24 hr

Particles were washed with ethanol

Interaction of prepared magnetic nanoparticles with the magnet

Fig. 6 A typical preparation of magnetic nanoparticles

2.3.2 Preparation of $Fe_3O_4@SiO_2$ MNPs

The $Fe_3O_4@SiO_2$ MNPs were synthesized according to the method described earlier as shown in [8]. In a 500 ml round-bottom flask, 1 g of magnetic nanoparticles were suspended into 300 ml isopropanol (IPA) and 50 ml ammonia solution. To form nicely dispersed nanoparticles, the reaction mixture was subjected to sonication for 15 min. With vigorous stirring, 5 ml of tetraethyl orthosilicate (TEOS) in 30 ml of IPA was added drop-wise using a separatory funnel over a period of 4 h as shown in **Fig. 7**. The stirring was continued for further 3 h. The prepared silica-coated magnetic nanoparticles were collected by permanent magnet. The nanoparticles were washed with ethanol for four times after decanting off the supernatant and the final product was dried in oven at 80 °C for 24 h.

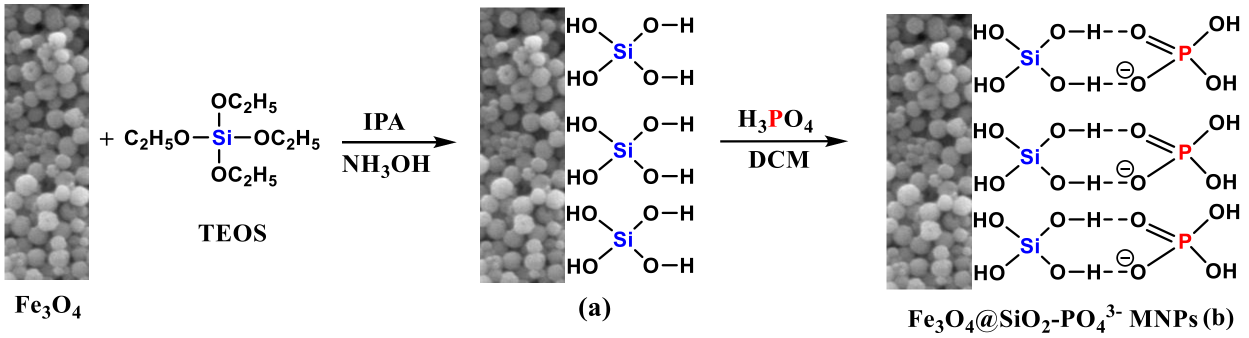
Fig. 7 Preparation of $Fe_3O_4@SiO_2$ MNPs

2.3.3 Preparation of $Fe_3O_4@SiO_2$-PO_4^{3-} MNPs

The $Fe_3O_4@SiO_2$-PO_4^{3-} MNPs were prepared according to the method reported in literature but with slight modification i.e. phosphoric acid is used instead of chlorosulphuric acid [31]. 0.5 g of

$Fe_3O_4@SiO_2$ MNPs suspended in 20 ml dichloromethane (CH_2Cl_2) was sonicated for 30 min. Then resulted suspension was stirred vigorously with the help of mechanical stirrer at room temperature as shown in **Fig. 8**, To this concentrated (85%) phosphoric acid H_3PO_4 (0.5 ml) was added dropwise using a dropper. The reaction mixture was allowed to stir for 12 h, and the resulted phosphate impregnated nanoparticles were recovered with the help of magnetic decantation. The product was then washed two times with 10 ml CH_2Cl_2 and 10 ml ethanol and finally dried in air to obtain $Fe_3O_4@SiO_2\text{-}PO_4^{3-}$ MNPs as shown in **Scheme 4**.

Fig. 8 Preparation of $Fe_3O_4@SiO_2\text{-}PO_4^{3-}$ MNPs



TEOS= Tetraethyl orthosilicate, IPA= Isopropanol, DCM= Dichloromethane

Scheme 4 Preparation steps for fabricating phosphate immobilized $Fe_3O_4@SiO_2$

2.4 General procedure for the acetylation of glycerol

The acetylation of glycerol with acetic acid was performed in a 50 ml double necked-round bottomed flask equipped with the magnetic stirrer with temperature controller. The optimum reaction conditions for the acetylation of GL was established by varying the molar ratio of AcA to GL (1-9), reaction temperature (30-100 °C) and catalyst amount (1-5 wt % with respect to GL). The products obtained were characterized by H^1-NMR and quantified by HPLC technique.

To evaluate the catalyst reusability, it was recovered from the reaction mixture by external magnetic force, washed with ethanol and finally calcined at 600, 700 and 800 °C. The catalyst was reused four times under the similar regeneration and experimental conditions.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 CATALYST CHARACTERIZATION

3.1.1 X-ray diffraction (XRD)

The structure of Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-PO_4^{3-} nanoparticles was characterized by X-ray diffraction technique as shown in **Fig. 9**. For Fe_3O_4 particles, diffraction peaks at 2θ = 30.31, 35.61, 43.27, 57.48 and 62.84 (indicated by ♣) support the cubic phase of the inverse spinel structure for Fe_3O_4, as shown in Fig. 9(a) (JCPDS card no. 01-075-0449). In reported work the diffraction peak for Fe_3O_4 spinel phase has been observed at 2θ = 35.70 [32]. After coating the magnetic particles with silica, no significant change of XRD pattern was observed as silica is amorphous in nature Fig. 9(a). Upon phosphate impregnation over the silica coated MNPs, a new peak at 2θ = 25.72 and an increase in intensity of peak at 2θ = 35.61 (indicated by ♥) was observed which corresponds to *monoclinic* silicon phosphate (SiP_2O_7; JCPDS card no. 01-070-2245).

The influence of calcination temperature over the structure of $Fe_3O_4@SiO_2$-PO_4^{3-} catalyst was studied in the range of 600-800 °C as shown in Fig. 9(b). The samples calcined at 600 and 700 °C exhibited no significant structural changes (Fig. 9(b)). Elevation of calcination temperature to 800 °C resulted in the formation of only a single diffraction peak at 2θ = 25.72 corresponding to silicon phosphate (SiP_2O_7; JCPDS card no. 00-025-0755) indicating low crystallinity. Hence, the sample calcined at 600 °C exhibited the best catalytic activity.

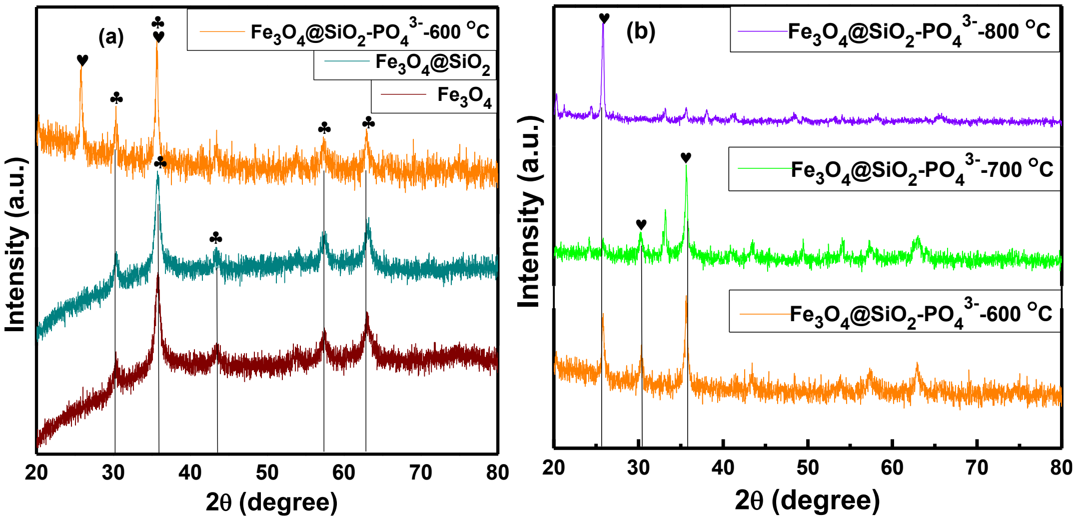


Fig. 9(a) XRD analysis of Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-PO_4^{3-}-600 °C **(b)** Comparison of XRD patterns of $Fe_3O_4@SiO_2$-PO_4^{3-} at 600, 700 and 800 °C.

3.1.2 FT-IR Analysis

The FT-IR spectrum of Fe_3O_4 particles shows a band at 562 cm^{-1} associated to Fe—O bond as shown in **Fig. 10** [14]. Incorporation of silica over these particles is supported by the appearance of a new band at 1063 cm^{-1} due to Si—O—Si stretching vibrations as indicated in Fig. 10b [19]. Incorporation of phosphate group over $Fe_3O_4@SiO_2$ is supported by the presence of the bands at 3450 cm^{-1} and 1638 cm^{-1} related to O—H deforming vibrations of P—OH group [14]. The band at 813 cm^{-1} can be ascribed to P=O vibrations while bands at 477, 600 and 636 cm^{-1} are associated with O—P—O bending vibrations [33,34].

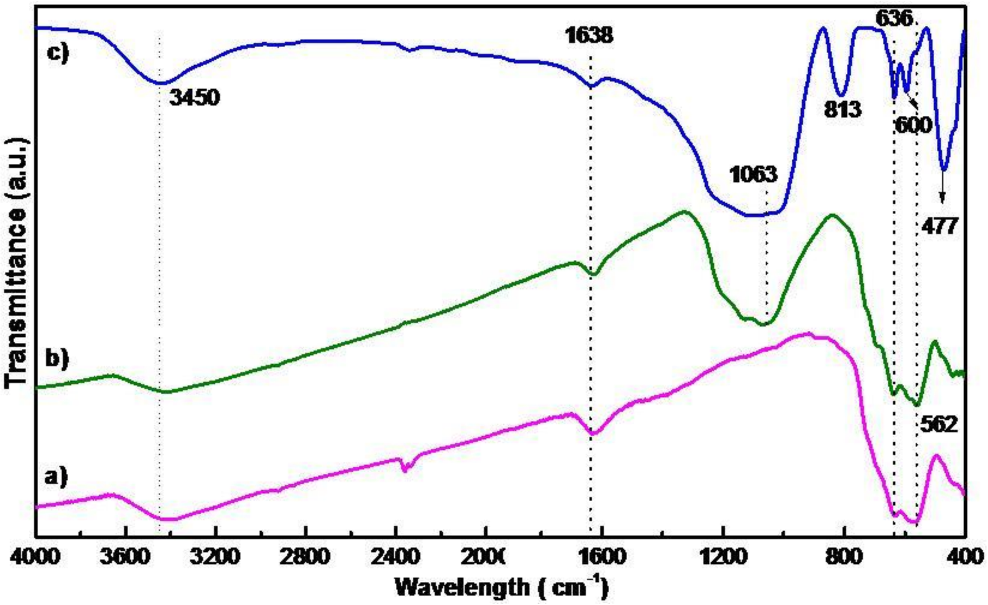


Fig. 10 The FT-IR spectra of the synthesized (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$ and (c) $Fe_3O_4@SiO_2$-PO_4^{3-}-600 catalysts

3.1.3 SEM-EDX study

The surface morphology and elemental distributions of the magnetic catalysts (Fe_3O_4 and $Fe_3O_4@SiO_2$-PO_4^{3-}) were determined by SEM-EDX technique as shown in **Fig. 11** and **Table 3** respectively. The average size of the Fe_3O_4 particles was found to be ~ 200 nm with spherical shape. Upon silica coating and phosphate group impregnation the agglomerates of $Fe_3O_4@SiO_2$-PO_4^{3-} particles had formed which consists of the particle of size 298 nm.

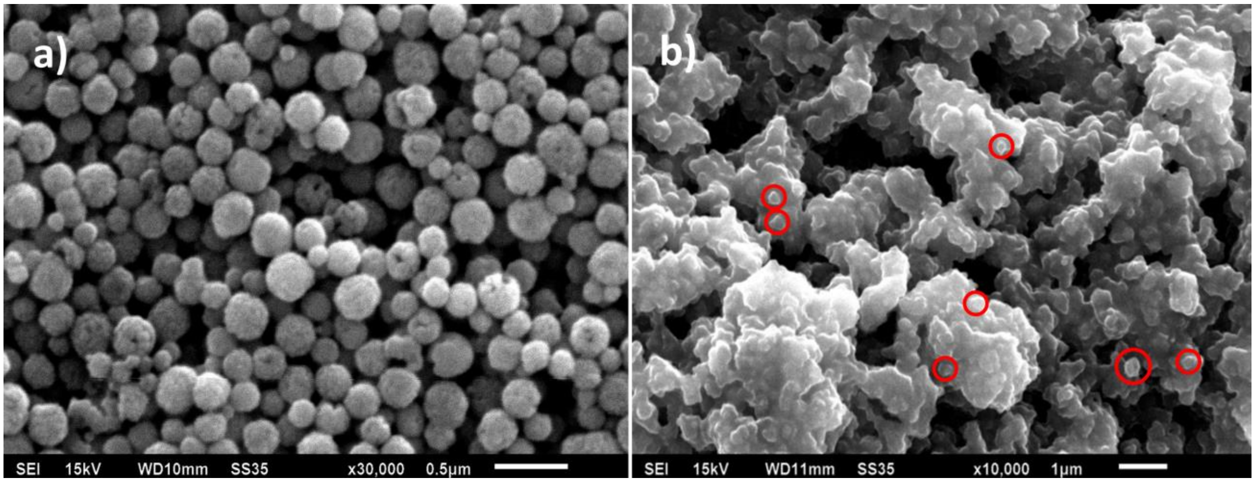


Fig. 11 SEM images of (a) Fe_3O_4 and (b) $Fe_3O_4@SiO_2$-PO_4^{3-}

Energy Dispersive X-ray Spectroscopy (EDX) analysis of the $Fe_3O_4@SiO_2-PO_4^{3-}$ particles, as shown in Table 3, also demonstrates the presence of P to support the anchoring of phosphate group over the matrix.

Table 3 EDX data of Fe_3O_4 and $Fe_3O_4@SiO_2-PO_4^{3-}$

Catalysts ↓ Elements →	**Fe (wt%)**	**O (wt%)**	**Si (wt%)**	**P (wt%)**
Fe_3O_4	64.67	35.33	-	-
$Fe_3O_4@SiO_2-PO_4^{3-}$	6.97	60.22	22.11	10.7

3.1.4 Pyridine adsorption study

In the FTIR spectra of pyridine saturated Fe_3O_4 as well as $Fe_3O_4@SiO_2$ (Fig. 12 a-b), a peak at 1627 cm^{-1} was observed to indicate the formation of Lewis (L) acidic sites. However, incorporation of phosphate group over the matrix leads to the formation of bands of Bronsted (B) sites which is characterized by the band at ~1546 cm^{-1} due to the formation of pyridinium ion, and Lewis (L) site are characterized by band at ~1627 cm^{-1} due to covalently bonded pyridine. The band at ~1490 cm^{-1} is assigned to the coordination of pyridine on B + L sites over the catalyst surface. Incorporation of phosphate group over the silica coated magnetic catalyst generates new acidic sites at 1546 cm^{-1} and 1490 cm^{-1} corresponding to B and B+L respectively.

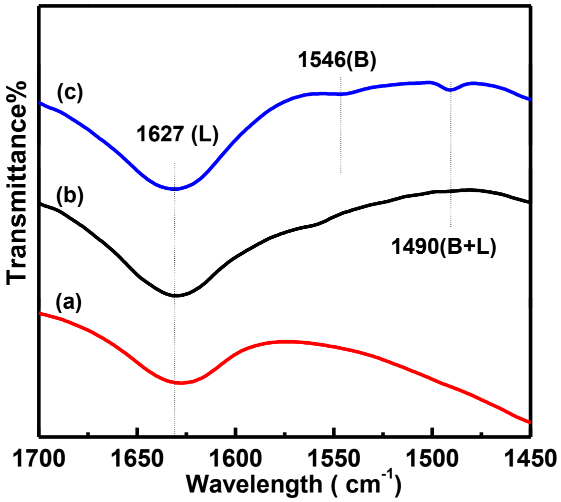


Fig. 12 FT-IR spectra of pyridine absorbed on (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$ and (c) $Fe_3O_4@SiO_2-PO_4^{3-}$

3.1.5 H^1-NMR Spectroscopy

In the H^1-NMR spectrum of glycerol (a), the peak obtained at 3.39-3.44 ppm is due to CH_2 protons, the peak at 3.59 is due to CH proton. After acetylation, a new peak is formed at 1.9 ppm corresponding to methyl ($-CH_3$) protons due to formation of product that is TAG as shown in Fig. 13 (b). There is no additional peak corresponding to MAG and DAG which supports the fact that TAG is formed exclusively.

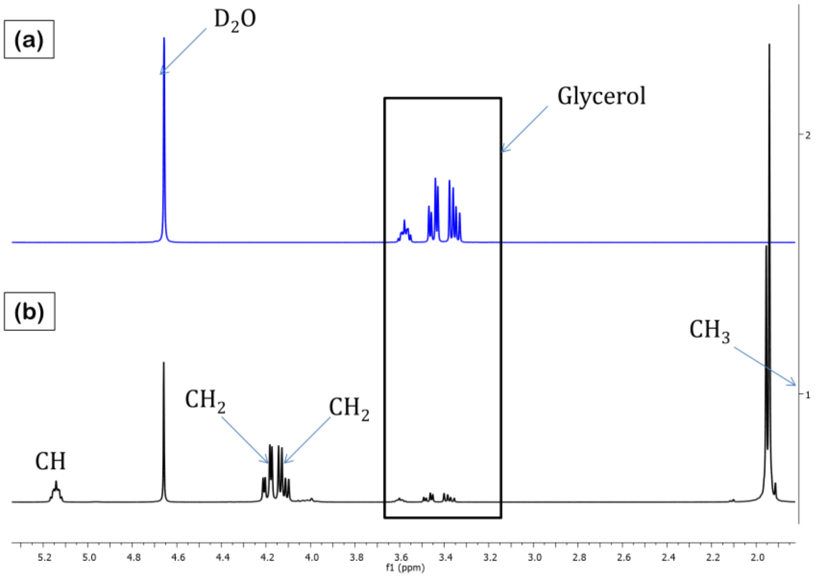


Fig. 13 H^1-NMR spectra of (a) glycerol and (b) triacetin.

3.2 CATALYTIC ACTIVITY

The catalytic activity of $Fe_3O_4@SiO_2-PO_4^{3-}$ material was investigated for the GL acetylation with AcA. Reaction parameters were screened including AcA/GL reactant ratio, reaction time, reaction temperature and catalyst weight for obtaining the best catalytic activity. During acetylation of GL with AcA, one or more -OH groups of the GL molecule can react with AcA. Therefore, up to three esters *viz.*, MAG, DAG and TAG may be formed depending on extent of acetylation.

The influence of AcA/GL ratio on the GL acetylation over the prepared catalyst was investigated by performing the reaction in the presence of 3 wt% catalyst (with respect to GL) at 80 °C, for 2 h and varying the AcA/GL molar ratio 1:1 to 9:1 (Fig. 13). It can be observed that at 3:1 acetic acid to glycerol molar ratio, MAG was found to be the main product, which gradually decreases while the TAG selectivity increases as the as the reactant ratio was increased from 3:1 to 6:1. At reactant ratio of 6:1, the observed GL conversion was as high as 97.42 % and selectivity towards TAG was found to be ~ 92.31%.

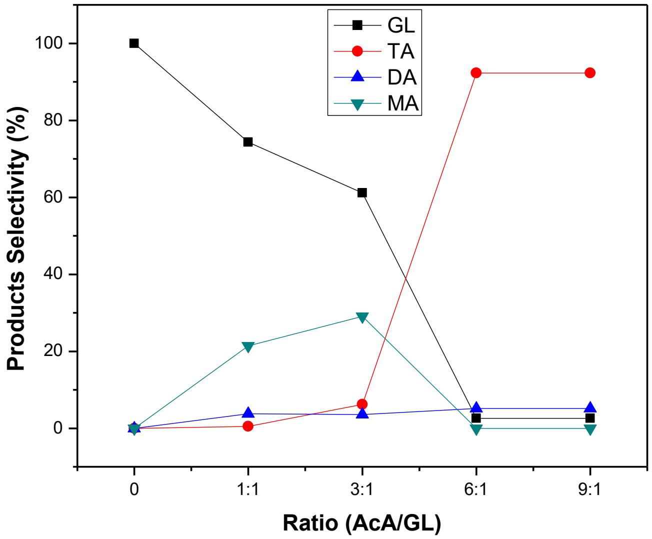


Fig. 14 Influence of reactant ratio over GL conversion and selectivity of MAG, DAG and TAG

Fig. 14 shows the influence of catalyst amount over GL conversion and selectivity towards MAG, DAG and TAG when the reaction was performed for 2 h, at AcA/GL molar ratio of 6:1, at reaction temperature 80 °C and varying the catalyst amount from 1 to 5 wt%. As a result, it was observed that GL conversion increased sharply along with catalyst amount being increased from 0 to 3 wt% and then remained constant from 3 wt% to 5 wt%. At 1 wt%, MAG was the main product which decreases gradually on increasing the catalyst amount. The triacetin selectivity increased to the highest value at 3 wt% and then decreased slowly as the amount of catalyst further increases.

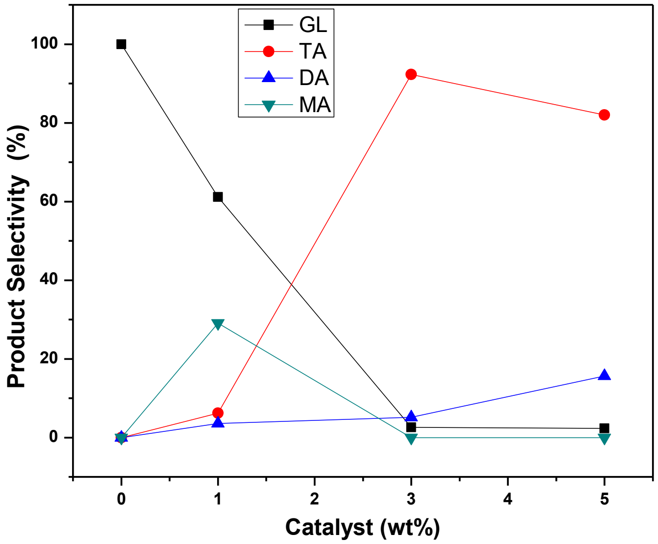


Fig. 15 Influence of catalyst amount over GL conversion and selectivity of MAG, DAG and TAG

An increase in reaction time also affected the selectivity of acetins when the reaction was performed in the presence of 3 wt% catalyst (with respect to GL) at 80 °C, employing AcA/GL molar ratio of 6:1 and varying the reaction time from 20 to 80 min as shown in Fig. 15. As expected, the conversion of GL rose steadily with the passage reaction time. On increasing the reaction time from 0 to 60 min, the selectivity of MAG and DAG increases gradually while the TAG concentration almost remains constant. After 80 min, the TAG concentration reaches to the maximum value of 92.3 % and then remains constant as we increase the reaction time to 120 min. Thus, glycerol acetylation most likely is taking place in a stepwise fashion involving the formation of MAG and DAG followed by TAG.

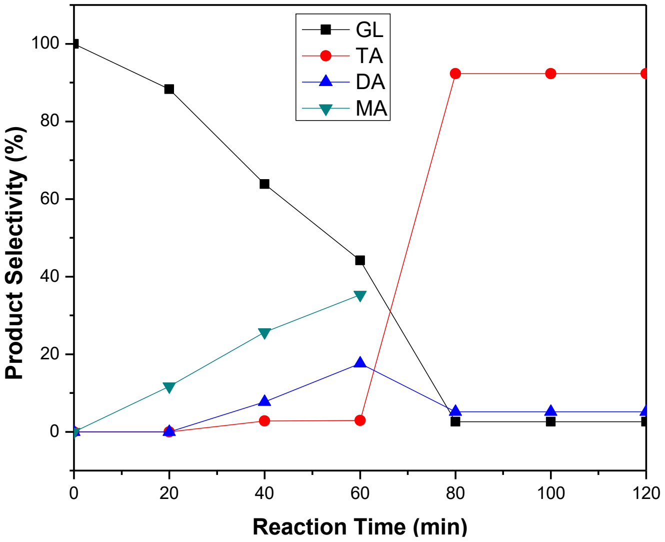


Fig. 16 Influence of reaction time over GL conversion and selectivity of MAG, DAG and TAG

The effect of increase in temperature over acetins selectivity was studied when the reaction was performed in the presence of 3 wt% catalyst (with respect to GL), AcA/GL molar ratio 6:1, at 2 h and varying the reaction temperature from 30 to 100 °C as shown in Fig. 16. At room temperature (30 °C), the major product formed was MAG which decreases on increasing temperature. As the temperature is increased to 80 °C, the selectivity to TAG touches the highest value and remained constant even at 100 °C.

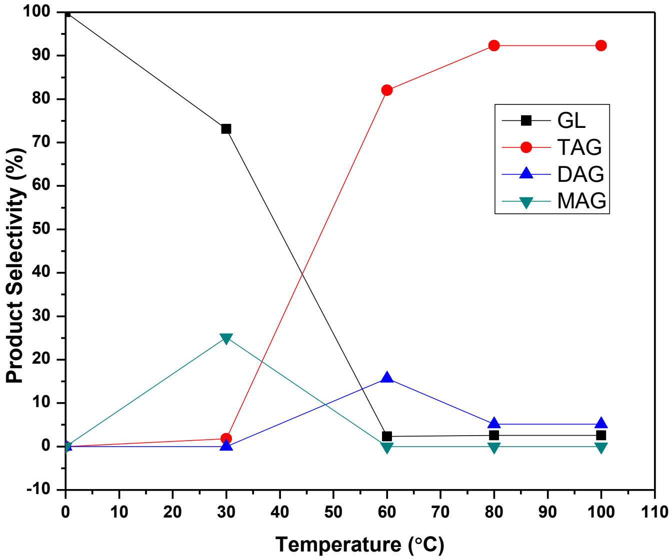


Fig. 17 Influence of reaction temperature over GL conversion and selectivity of MAG, DAG and TAG

3.3 REUSABILITY STUDY

The ease of catalyst separation and reusability are the main advantages of heterogeneous catalysts over the homogeneous one. The magnetic catalyst was employed for the GL acetylation under the optimized reaction conditions and after the completion of the reaction it was removed from the reaction mixture under the influence of external magnetic field as shown in Fig. 17. The catalyst recovered was washed with ethanol, dried and calcined 600 °C for 3 h in the muffle furnace. The regenerated catalyst was further reused during 4 reaction cycles under the similar regeneration and experimental conditions. As shown in Fig. 18, it can be noticed that the selectivity of triacetin decreased to 42.41% in the second run, 40% in the third run and remained 19.69% during the last run.

Fig. 18 Separation of catalyst with the help of magnet

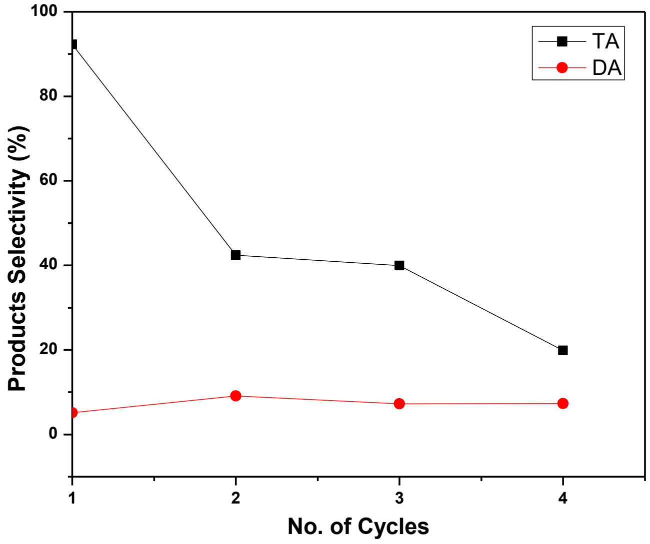


Fig. 19 Reusability experiment of $Fe_3O_4@SiO_2$-PO_4^{3-}-600 catalyst in the acetylation of glycerol

CHAPTER 4

4. CONCLUSIONS AND REFERENCES

4.1 CONCLUSIONS

The efficient and selective conversion of GL to TAG with acetic acid was successfully performed with magnetic catalyst. A 97.42% conversion of glycerol and 92.3% selectivity of triacetin is obtained using the $Fe_3O_4@SiO_2-PO_4^{3-}$-600 catalyst at 80 °C for 80 min. This indicates that the magnetic catalyst is very promising for the utilization of GL to produce TAG. Further studies such as finding out the reason behind low selectivity in reusability experiment, a possible reaction mechanism can be proposed to explain good selectivity and high conversion of acetylation reaction.

4.2 REFERENCES

[1] C.A.G. Quispe, C.J.R. Coronado, J.A. Carvalho, Glycerol: Production, Consumption, Prices, Characterization and New Trend in Combustion, Renew. Sustain. Energy Rev. 27 (2013) 475–493.

[2] M.L. Testa, V. La Parola, L.F. Liotta, A.M. Venezia, Screening of Different Solid Acid Catalysts for Glycerol Acetylation, Journal of Molecular Catalysis A, 367 (2013) 69–76.

[3] P.U. Okoye, A.Z. Abdullah, B.H. Hameed, Synthesis of Oxygenated Fuel Additives via Glycerol Esterification with Acetic Acid over Bio-Derived Carbon Catalyst, Fuel 209 (2017) 538-544.

[4] P.S. Kong, M.K. Aroua, S.E. Group, P. Cognet, Y. Peres, Catalytic Role of Solid Acid Catalysts in Glycerol Acetylation for the Production of Bio-Additives: A Review, RSC Adv. 6 (2016) 68885.

[5] M.L. Testa, V. La Parola, F. Mesrar, F. Ouanji, M. Kacimi, M. Ziyad, L.F. Liotta, Use of Zirconium Phosphate-Sulphate as Acid Catalyst for Synthesis of Glycerol-Based Fuel Additives, Catalysts 9 (2019) 148.

[6] S. Karnjanakom, P. Maneechakr, C. Samart, G. Guan, Ultrasound Assisted Acetylation of Glycerol for Triacetin Production over Green Catalyst: A Liquid Biofuel Candidate, Energy Conv. Manag. 173 (2018) 262–270.

[7] A. Casas, J.R. Ruiz, M.J. Ramos, A. Perez, Effects of Triacetin on Biodiesel Quantity,

Energy Fuels 24 (2010) 4481–4489.

[8] H. Wang, J. Covarrubias, H. Prock, X. Wu, D. Wang, S.H. Bossmann, Acid-Functionalized Magnetic Nanoparticle as Heterogeneous Catalysts for Biodiesel Synthesis, J. Phys. Chem. C 119 (2015) 26020-26028.

[9] Y. Zhou, R. Huang, F. Ding, A.D. Brittain, J. Liu, M. Zhang, M. Xiao, Y. Meng, L. Sun, Sulfonic Acid-Functionalized α-Zirconium Phosphate Single-Layer Nanosheets as a Strong Solid Acid for Heterogeneous Catalysis Applications, ACS Appl. Mater. Interfaces 6 (2014) 7417-7425.

[10] S. Shylesh, V. Schünemann, W.R. Thiel, Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis, Angew. Chem. Int. Ed. 49 (2010) 3428–3459.

[11] M.B. Gawande, Y. Monga, R. Zboril, R.K. Sharma, Silica-decorated magnetic nanocomposites for catalytic applications, Coordination Chemistry Reviews 288 (2015) 118–143.

[12] Y. Chengyuan, Z. Yan, C. Jing, Molybdenum Oxide Supported on Hydroxyapatite-Encapsulated ϒ-Fe_2O_3: A Novel Magnetically Recyclable Catalyst for Olefin Epoxidation Chinese J. Catal. 32 (2011) 1166–1172.

[13] R. Hong, J. Li, S. Zhang, H. Li, Y. Zheng, Preparation and Characterization of Silica-Coated Fe_3O_4 Nanoparticles used as Precursor of Ferrofluids, Appl. Surf. Sci. 255 (2009) 3485–3492.

[14] A. Rostami, A. Ghorbani-choghamarani, B. Tahmasbi, F. Sharifi, Y. Navasi, D. Moradi, Silica Sulfuric Acid-Coated Fe_3O_4 Nanoparticles as High Reusable Nanocatalyst for the Oxidation of Sulfides into Sulfoxides, Protection and Deprotection of Hydroxyl Groups using HMDS and Ac_2O, J. Saudi Chem. Soc. 21 (2017) 399–407.

[15] X. Liao, Y. Zhu, S. Wang, H. Chen, Y. Li, Theoretical Elucidation of Acetylating Glycerol with Acetic Acid and Acetic Anhydride, Appl. Catal. B Environ. 94 (2010) 64–70.

[16] S.R. Kirumakki, N. Nagaraju, K.V.R. Chary, Esterification of Alcohols with Acetic Acid over Zeolites Hβ, HY And HZSM5, Appl. Catal. A Gen. 299 (2006) 185–192.

[17] E. Ortiz-Islas, T. Lόpez, R. Gomez, J. Navarrete, Effect of Phosphate Ions in the Properties of Titania Sol-Gel, J. Sol-Gel Sci. Techn. 37 (2006) 165–168.

[18] M. Signoretto, F. Pinna, G. Strukul, Platinum Promoted Zirconia-Sulfate Catalysts: One-Pot Preparation, Physical Properties and Catalytic Activity, Catal. Lett. 36 (1996) 129–133.

[19] M.E. Manriquez, T. Lόpez, R. Gomez, M. Picquart, J.G. Hernández-Cortez, Sol–Gel Silica Modified with Phosphate and Sulfate Ions, Journal of Non-Crystalline Solids 346 (2004) 643–646.

[20] N. Kaur, A. Ali, Preparation and Application of Ce/$Zro_2 - Tio_2/SO_4{}^{2-}$ as Solid Catalyst for the Esterification of Fatty Acids, Renewable Energy 81 (2015) 421-431.

[21] P. Goswami, J.N. Ganguli, Synthesis, Characterization and Photocatalytic Reactions of Phosphated Mesoporous Titania, Bull. Mater. Sci. 35 (2012) 889–896.

[22] M. Aghbashlo, M. Tabatabaei, H. Jazini, H.S. Ghaziaskar, Exergoeconomic and Exergoenvironmental Co-Optimization of Continuous Fuel Additives (Acetins) Synthesis From Glycerol Esterification with Acetic Acid using Amberlyst 36 Catalyst, Energy Convers. Manag. 165 (2018) 183–194.

[23] S. Kale, S.B. Umbarkar, M.K. Dongare, R. Eckelt, U. Armbruster, A. Martin, Selective Formation of Triacetin by Glycerol Acetylation using Acidic Ion-Exchange Resins as Catalyst and Toluene as an Entrainer, Appl. Catal. A Gen. 490 (2015) 10–16.

[24] M.A. Betiha, H.M.A. Hassan, E.A. El-Sharkawy, A.M. Al-Sabagh, M.F. Menoufy, H.E.M. Abdelmoniem, A New Approach to Polymer-Supported Phosphotungstic Acid: Application for Glycerol Acetylation Using Robust Sustainable Acidic Heterogeneous-Homogenous Catalyst, Appl. Catal. B: Env. 182 (2016) 15-25.

[25] L. Zhou, T.H. Nguyen, A.A. Adesina, The Acetylation of Glycerol over Amberlyst-15: Kinetic and Product Distribution, Fuel Process. Technol. 104 (2012) 310–318.

[26] M.S. Khayoon, B.H. Hameed, Acetylation of Glycerol to Biofuel Additives over Sulfated Activated Carbon Catalyst, Bioresour. Technol. 102 (2011) 9229–9235.

[27] I. Kim, J. Kim, D. Lee, A Comparative Study on Catalytic Properties of Solid Acid Catalysts for Glycerol Acetylation at Low Temperatures, Appl. Catal. B Environ. 148–149 (2014) 295–303.

[28] X. Liao, Y. Zhu, S.G. Wang, Y. Li, Producing Triacetylglycerol with Glycerol by two Steps: Esterification and Acetylation, Fuel Process. Technol. 90 (2009) 988–993.

[29] L.N. Silva, V.L.C. Gonçalves, C.J.A. Mota, Catalytic Acetylation of Glycerol with Acetic

Anhydride, Catal. Commun. 11 (2010) 1036–1039.

[30] J. Wang, F. Ren, R. Yi, A. Yan, G. Qiu, X. Liu, Solvothermal Synthesis and Magnetic Properties of Size-Controlled Nickel Ferrite Nanoparticles, J. Alloys Compd. 479 (2009) 791–796.

[31] M. Gilanizadeh, B. Zeynizadeh, E. Gholamiyan, Green Formylation of Alcohols Catalyzed by Magnetic Nanoparticles of the Core–Shell Fe_3O_4 @SiO_2 -SO_3H, Iran. J. Sci. Technol. Trans. A Sci. 43 (2019) 819–827.

[32] O.U. Rahman, S.C. Mohapatra, S. Ahmad, Fe_3O_4 Inverse Spinal Super Paramagnetic Nanoparticles, Mater. Chem. Phys. 132 (2012) 196–202.

[33] P.R. Rout, R.R. Dash, P. Bhunia, Nutrient Removal from Binary Aqueous Phase by Dolochar: Highlighting Optimization, Single and Binary Adsorption Isotherms and Nutrient Release, Process Safety and Environmental Protection 100 (2016) 91–107.

[34] W. JastrzębskiM. Sitarz, M. Rokita, K. Bułat, Infrared Spectroscopy of Different Phosphates Structures, Spectrochimica Acta Part A 79 (2011) 722– 727.

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