ESTERIFICATION OF GLYCEROL WITH ACETIC ACID OVER ALUMINA BASED CATALYSTS: REACTION KINETIC STUDY

A DISSERTATION

Submitted in partial fulfilment of the

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CHEMICAL ENGINEERING

(With Specialization in Hydrocarbon Engineering)

By

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DEPARTMENT OF CHEMICAL ENGINEERING

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DECLARATION

I hereby declare that the work being presented in this dissertation report titled "ESTERIFICATION OF GLYCEROL WITH ACETIC ACID OVER ALUMINA BASED CATALYSTS: REACTION KINETIC STUDY" in partial fulfilment of the requirements for the award of the degree of Integrated Dual Degree (B.Tech Chemical Engineering and M.Tech Hydrocarbons) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee is an authentic record of my own work carried out during the period from June 2013 to June 2014 under the supervision of Dr. Prakash Biswas, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, India.

The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute

Date-

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Enrollment.No.09210010

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Abstract

In the future, it is expected that biodiesel production will increase to meet the growing energy demands in light of declining petroleum reserves. Glycerol is a by-product of biodiesel production and the increase in glycerol production from biodiesel refining will create a surplus in the glycerol market. Converting glycerol into valuable products is important in order to make biodiesel production more economical. Esterification of glycerol to produce glycerol acetates – Monoacetyl glycerol (MAG), Diacetyl glycerol (DAG), and Triacetyl glycerol (TAG) is one such process. MAG, DAG and TAG have a variety of uses ranging from fuel additives to ingredients in cosmetics. TAG is most attractive as an antiknock agent to gasoline and additive to biodiesel due to its viscosity reducing properties.

This work studies the use of alumina based catalyst for the acetylation of glycerol. Two series of catalysts were tested; Cu/ Ni monometallic and bimetallic catalysts on γ-Al_2O_3 and sulfated alumina (SO_4^{2-} / γ- Al_2O_3) catalysts. Cu/ Ni on γ-Al_2O_3 catalysts were prepared with varying ratios of the two metals and SO_4^{2-}/ γ- Al_2O_3 catalysts were prepared with different concentrations of sulphuric acid. The catalysts were characterized using several techniques like X-ray diffraction, BET surface area, NH_3–TPD measurements and FT-IR spectra. The impregnation of the metals in case of Cu/ Ni on γ-Al_2O_3 catalysts was observed by the presence of NiO and CuO peaks in the XRD patterns. The sulfate group on alumina was identified by the corresponding peaks in the FT-IR spectra and the XRD patterns. The catalytic activity of these samples for the glycerol esterification reactions were tested under standard conditions; temperature: 110 ^{o}C, atmospheric pressure, glycerol to acetic acid molar ratio: 1:9, and catalyst loading: 0.25g. Cu-Ni/ γ-Al_2O_3 catalysts were active for the esterification reaction and activity increased with increasing Ni content. 2M SO_4^{2-} / γ- Al_2O_3 was found to be the most active catalyst resulting in a glycerol conversion of 97% within 2 hours of reaction and TAG selectivity of 23% after five hours of reaction. Stability of the catalysts was examined via leaching and reusability tests through three consecutive runs. With Ni/ γ-Al_2O_3 the glycerol conversion dropped from 97% with fresh catalyst to 88% in the third run. The loss in activity could be due to leaching of metal. With 2M SO_4^{2-} / γ-Al_2O_3, there was no loss in activity after three consecutive runs and the catalyst can be considered stable for the esterification of glycerol with acetic acid. Arrhenius equation was employed to determine rate constant, order of equation and activation energy.

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Sailee Rane

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Introduction

1.1 Biofuels scenario in India and the world

In recent years, the declining reserves of conventional fossil fuels and increased attention to environmental issues such as emission of green house gases and consequent global warming caused by the use of conventional fuels has spurred the search for alternative sources of energy. “Biomass is plant matter of non-geological origin than can be used to produce various useful chemicals and fuels” [1]. Biomass is a resource than has the potential to become a renewable and clean source of energy. Biofuels refer to fuels derived from biomass and they are emerging as a sustainable source of energy that could help several nations achieve self-sufficiency in energy and reduce dependence on imported oil and gas. Biofuels could refer to liquid fuels like ethanol and biodiesel or gaseous fuels like biogas and hydrogen, and find use mainly in transportation fuels.

Biodiesel is a fuel derived from biological sources such as animal fats and vegetable oils that has properties similar to diesel and can serve as an alternative to diesel. Biodiesel can be produced from oils and animal fats in several different ways. These include direct blending, use of microemulsions, pyrolysis and transesterification. Among all these processes, transesterification is the one most preferred currently. [2].

The emergence of biofuel as a renewable energy source offers many countries opportunities for greater energy independence. Currently, India uses petroleum derived fuels and products to meet 95% of its transportation energy needs and relies greatly on imports to meet this demand. India imports approximately 70% of its crude oil needs, mostly from the Middle East. [3]

The Government of India has been actively exploring its biofuel potential since 2001. India began a 5% ethanol blending program in 2001 [4, 5]. The Government of India adopted a biofuel policy in 2009 that envisages 20% blending of both biodiesel and bioethanol by 2017. Bioethanol is currently produced from molasses (a byproduct of sugar manufacturing) and the government is considering the possibilities of using sugarcane juice to increase bioethanol production. It also hopes to enhance India's energy security by launching one of the world's biggest non-edible oilseed-based biodiesel industries [6]. Jatropha and Pongamia are the two prominent oilseed plants undergoing experimentation for biodiesel production. Biofuels are an important option in the renewable energy mix in India and will play a significant role in helping India achieve greater energy security [7].

From a global perspective too, attention to biofuels has increased in recent years. Most countries, especially the US and EU countries support various forms of biofuel production and thus production increases every year. In 2010, the worldwide biofuel production had crossed the 105 billion liters mark. In the European Union alone, between 2010 and 2011, the annual consumption of biofuel increased by 3.1% or 14 million tonnes of oil equivalent [8].

As of 2011, mandates for biofuel blending with conventional fuels exist in 31 countries at the national level [9]. According to the International Energy Agency, by 2050, biofuels can potentially supply more than 25% of the worldwide demand for transportation fuels [10].

Table 1.1

Production and blending targets for biofuels [11]

Country	Feedstock		Production (2007) (mil litres)		Blending targets
	Biodiesel	Ethanol	Biodiesel	Ethanol	
Brazil	Castor seed	Sugarcane, palm oil	242	18,798	E25 –25% ethanol blending in gasoline (2007) B2- 2% biodiesel with diesel (2008)
China	Used vegetable oils, jatropha	Corn, wheat, cassava	113	1599	E10 - 10% ethanol blending with gasoline (5 provinces)
Canada	Animal fat	Corn, straw	96	1000	E5 – 5% Ethanol (2010) B2 - 2% biodiesel (2012)
India	Jatropha,	Molasses,	45	400	E10- 10% Ethanol (2008)

	palm oil	sugarcane			B5 -5% Biodiesel (2012)
EU	Rapeseed, sunflower, soybeans	Wheat, alcohol, wine	6555	2302	5.75% share of transportation fuel should be biofuel by 2010, 10% by 2020
USA	Soybeans, oilseeds, recycled fats	Corn	1682	24,597	7.5 billion gallons of biofuel use by 2012

1.2 Biodiesel production

Different routes of biodiesel production have been studied – direct use or blending, microemulsion, pyrolysis and finally transesterification. The viscosity of oil can be reduced by the formation of microemulsions of oil with solvents such as methanol, ethanol and butanol. The pyrolysis of fats has been studied for hundreds of years. The products of the thermal cracking of vegetable oil are similar to petroleum derived gasoline and diesel.

Transesterification refers to the reaction of a fat or oil with an alcohol to give esters and glycerol. The reaction is shown in Fig. 1.

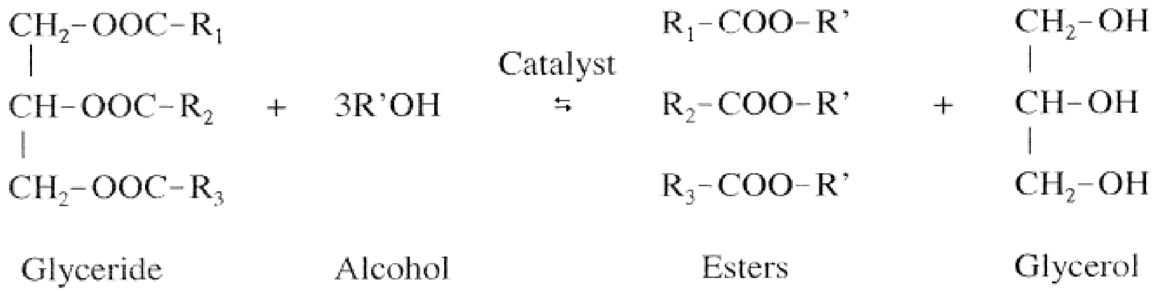

Fig. 1.1 Transesterification of triglycerides with alcohol [2]

Alcohols used for the transesterification process include methanol, ethanol, propanol and butanol. Methanol and ethanol are most commonly used because of their low cost and their physical and chemical properties that are favorable for the reaction. The reaction is reversible and hence excess alcohol is used to shift the equilibrium to the products side. Stoichiometrically, the molar ratio of alcohol to triglycerides should be 3:1 for the reaction to proceed. In practice, a higher ratio is needed to ensure maximum ester yield. Generally, a catalyst is used to improve yield. Both acids and alkalis are used to catalyze the reaction. Alkali-catalysed transesterification is faster than acid-catalysed transesterification and is preferred commercially. The transesterification reaction gives a mixture of esters, tri-, di- and monoglycerides, unreacted alcohol, glycerol and catalyst as the product. The byproduct, glycerol is a valuable industrial chemical and needs to be recovered by gravitational settling or centrifuging [2]. Transesterification consists of several consecutive, reversible reactions [12]. In the first step, the triglyceride reacts with alcohol to give a diglyceride. The diglyceride further reacts with alcohol to monoglyceride in the second step and finally the monoglyceride again reacts with alcohol to give glycerol. One mole of ester is released at each step. All reactions are reversible, with the equilibrium lying towards the production of fatty acid esters and glycerol.

$$1.\ \text{Triglyceride (TG)} + \text{R'OH} \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride (DG)} + \text{R'COOR}_1$$

$$2.\ \text{Diglyceride (DG)} + \text{R'OH} \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{Monoglyceride (MG)} + \text{R'COOR}_2$$

$$3.\ \text{Monoglyceride (MG)} + \text{R'OH} \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{Glycerol (GL)} + \text{R'COOR}_3$$

Fig. 1.2 Step- wise transesterification reactions of vegetable oil [12]

Two aspects need to be considered while thinking about the cost of the biodiesel production – the transesterification process and the utilization of by-product glycerol. Running the transesterification reaction as a continuous process lowers cost of production by shortening the reaction time and increasing production capacity. The recovery and utilization of glycerol, which is a valuable industrial chemical, is another way to lower production cost. Further, the cost of recovering biodiesel glycerol is actually lower than the cost of recovering soap glycerol as little water is present in the biodiesel production system.

1.3 Properties of glycerol

- Chemical formula - $C_3H_8O_3$
- Melting point - 17.8°C
- Boiling point - 290°C
- Other names – Glycerine, glycyl alcohol, propane-1, 2, 3-triol, 1, 2, 3-propanetriol etc.
- Odour – Odourless
- Color – Clear or colorless
- Taste - sweet

Glycerol is an organic compound that has no toxic effect on humans and the environment [13]. A hydroxyl (OH) group is attached to each carbon atom in glycerol. The hydrogen bonding in the OH groups gives rise to the high viscosity and high boiling point. The three OH groups are responsible for its solubility properties. Glycerol is completely soluble in water and alcohols and serves as a good solvent for iodine, bromine and phenol. It is a reactive molecule and is known to undergo several reactions [12].

1.4 Applications of glycerol

Glycerol has several applications in the food industry. It is used as a solvent, sweetener and a preservative. It also finds use as filler in commercially prepared low-fat foods, and as a thickening agent in liqueurs. It also finds use as a sugar substitute and is 60% as sweet as sucrose.

Glycerol is used in the medical and pharmaceutical industry and also in personal care products. It performs the function of providing lubrication and improving smoothness and is also used a as humectants. It is found in toothpaste, mouthwashes, skincare products, shaving cream, hair care products, soaps and water-based personal lubricants. Glycerol is a component of glycerin soap.

Glycerol was traditionally as an anti-freeze in cars, but it has now been replaced by ethylene glycol, with a lower freezing point. Glycerol also finds use in preparing botanical extracts.

Table 1.2

Product- wise distribution of glycerol consumption [15].

Industry	Percent consumption (%)
Cosmetics, soaps, pharmaceuticals	26
Resale	17
Polyglycerol esters	12
Esters	11
Food and drinks	8
Alkyl resins	6
Tobacco	4
Cellulose films	3
Paper	1
Other uses	12

1.5 Conversion processes of glycerol

With the expected increase in biodiesel production to meet the fuel blending mandates in different countries, glycerol production will also increase. With the current levels of demand in the glycerol market, glycerol supply will exceed demand and there will be a surplus of glycerol in the market. Therefore it is important to explore new markets and application for glycerol by converting it into value-added products [13]. Combustion of glycerol to generate heat is one way to consume large quantities of it. However, it is not desirable from an economic point of view. To make biodiesel production more economically viable, it is necessary to convert glycerol into valuable commodity chemicals that fetch a higher price and have a larger market [16]. Glycerol is a highly functionalized molecule that can undergo a number of chemical reactions, and thus produce a large number of value-added chemicals [13].

Different conversion processes of glycerol include –

1.5.1 Hydrogenolysis

Ethylene glycol or 1, 2-propanediol, 1,3-propanediol can be prepared by the selective hydrogenolysis of glycerol in the presence of hydrogen and a suitable catalyst. 1, 2-Propanediol finds use in the manufacture of polyester resins, liquid detergents, pharmaceuticals, paints, cosmetics, flavours and fragrances. 1,3-Propanediol is used in films, polyester fibers, and coatings. Ethylene glycol finds use in the production of explosives and synthetic fibers [16].

1.5.2 Etherification

Glycerol reacts with isobutylene and other olefins to form ethers. In the presence of an acid catalyst they react to form a mixture of mono-,di-, tri and tert-butyl ethers of glycerol. The ethers thus formed are used as additives for diesel fuel to improve its quality by reducing emission of particulate matter and the levels of carbonyl compounds and oxides of carbon in the exhaust gases. Glycerol ethers are also used to decrease the cloud point of diesel fuel. The mono-ether of ethylene glycol is miscible with water and is used as a solvent for paints and coatings. Glycol ethers can be used for trapping isobutylene from C-4 fraction [17].

1.5.3 Fermentation

1,3- propanediol can also be produced by fermentation of glycerol. This process takes place via two enzymatic reactions in sequence. The separation of 1, 3 – propanediol from the reaction mixture can be carried out by selective adsorbents such as activated carbons and zeolites. The effectiveness of separation depends on the components of the mixture and the sorbents involved [16].

1.5.4 Dehydration

Dehydration of glycerol in the presence of a suitable catalyst yields acrolein. Gas phase dehydration of glycerol to acrolein has been demonstrated [13].

1.5.5 Carboxylation

Glycerol carbonate can be used as a constituent of gas separation membranes, polyurethane, paints, coatings, foams and surfactants. It also finds use in the production of polycarbonates and polyurethanes. It is obtained by allowing glycerol to react with carbon-di-oxide and oxygen, under high pressure and in the presence of a suitable catalyst [19].

1.5.6 Production of hydrogen and synthesis gas

Glycerol can be used to produce hydrogen via a number of processes like steam reforming, partial oxidation, and autothermal reforming. The catalytic steam reforming of glycerol to hydrogen is a three step process. The first step is glycerol dehydrogenation, the second step involves CO getting bonded onto the catalyst surface followed by desorption and the third step is water–gas-shift reaction or methanation [13].

Glycerol being an oxygenated hydrocarbon can also be used to produce synthesis gas via pyrolysis, steam gasification and catalytic reforming reaction. Syngas can be used as fuel for the generation of electricity or as a source of hydrogen [19].

1.6 Esterification of glycerol

Esters of glycerols can be produced by the esterification of glycerol with acids or transesterification with esters and glycerides. The three OH groups attached to the three carbon atoms of glycerol are identical and thus the product of the esterification of glycerol is a mixture of mono, di and tri glycerides along with unreacted glycerol. The esterification reaction could be caalysed by acidic or basic catalysts. Esters of glycerols find applications in a wide variety of industries, particularly in foods, cosmetics and pharmaceuticals [18].

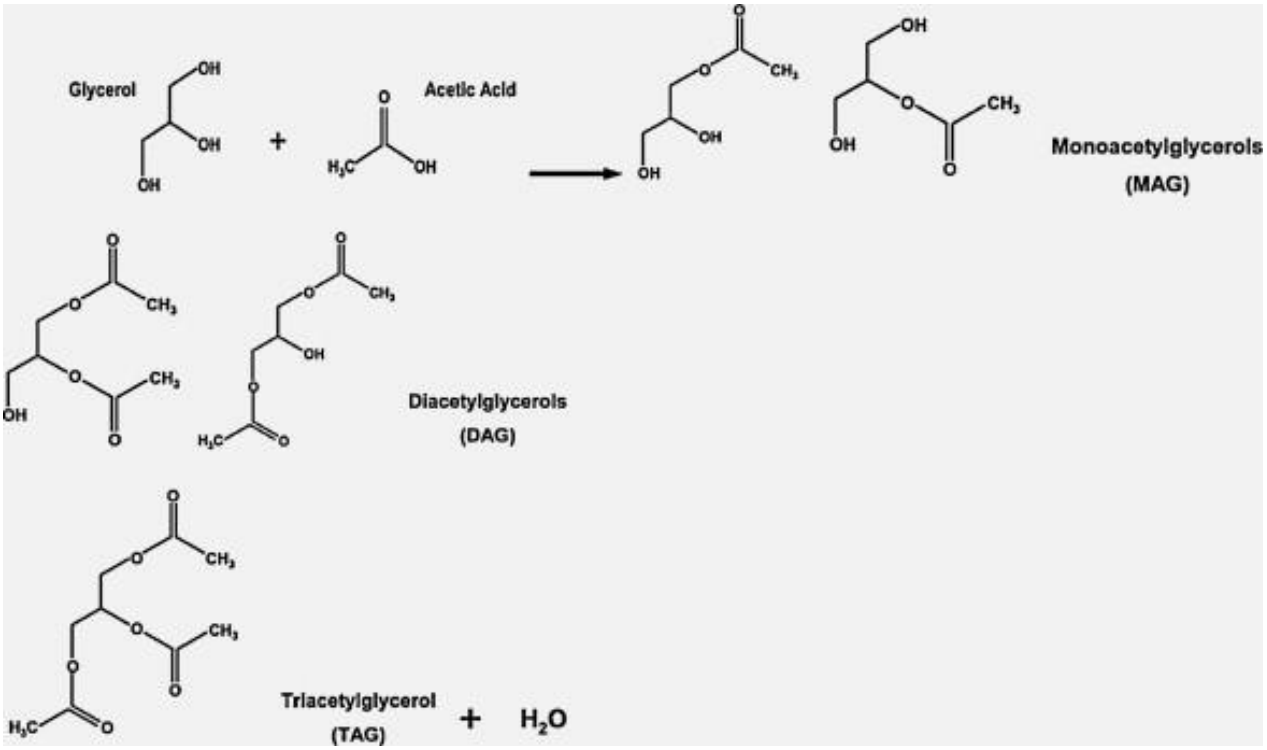

Fig. 1.3 General reaction mechanism for the esterification of glycerol with acetic acid [19]

The esterification of glycerol with acetic acid to yield glycerine acetates, such as monoacetyl glycerol (MAG), diacetyl glycerol (DAG) and triacetyl glycerol (TAG) has been studied. Glycerol acetates are widely used as fuel additives for biodiesel. They can reduce viscosity when blended with biodiesel fuel and improve anti-knocking properties when added to gasoline [18].

MAG is used as an additive in the foods industry and in the manufacture of explosives. DAG and TAG are used to manufacture inks, softening agents and plasticizers. DAG and TAG are also useful fuel additives for reducing viscosity and improving anti-knocking behaviour. TAG has the required flash point and oxidation stability. MAG, DAG and TAG are also used in cryogenics and in the biodegradable polymers industry.

2.1 Catalysts for esterification of glycerol with acetic acid

Goncalves et al. [21] purchased five different commercial solid acid catalysts. They used resins such as Amberlyst 15, zeolites such as HZSM-5 and HUSY, K-10 montmorillonite, and Niobic acid. Acidity value of Amberlyst 15 was much higher as compared to other solid acid catalysts (0.3-1.9 mmol base/g). The performance of these solid acid catalysts was tested for acetylation of glycerol with acetic acid in a round bottom flask at constant acetic acid to glycerol mole ratio of 3 at 110^{o}C. Catalysts amount was varied in such a way that the total acidity of the solid acid catalysts remained constant at 2 mmol for all the experiment. The reaction was carried out for 30 min and the product samples were collected after intervals of 5 min. Amberlyst-15 has been reported as a most active catalysts among all solid acid catalysts tested, followed by K-10 montmorillonite and niobic acid. The zeolites HZSM-5 and HUSY reported the least activities, in that order. 97% glycerol conversion with 54% selectivity to DAG, 31% to MAG and 13% to TAG has been reported over Amberlyst-15 catalyst after a reaction time of 30 min. HUSY has been reported as least active catalysts. The activity of the catalysts was not directly related to total acidy. Lower selectivity to di and tri acetylated product over zeolite catalyst was explained based on diffusion problem. The formation of diacetin and triacetin are space demanding and the pore selectivity was obtained may be because of the resistance to diffuse the di and tri acetin inside the zeolit pores. The formation of α-hydroxyacetone (acetol) was detected over all the catalysts tested. The acetol selectivity was highest (17%) over niobic acid and lowest (2%) over Amberlyst 15. Authors reported the acetol formation occurs due to the dehydration of the glycerol.

Ferreira et al. [22] took dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$) (PMo) and encapsulated it in USY zeolite, and used the PMo encaged in zeolite as catalysts for the acetylation of glycerol. The textural characterization of the catalysts was done by the aid of the nitrogen adsorption isotherm, determined at 77 K. FITR spectra and XRD patterns were also recorded. ICP analysis was used to determine the amount of acid capsulated in the zeolite by dissolving the catalysed H_2SO_4 /HF 1:1 (v/v), and then analyzing the obtained solution. The experiment was carried out in a batch reactor at reflux with 20 mL of acetic acid, 2 g of glycerol and 0.2 g catalyst loading. Stability of the prepared catalyst was tested by using the same catalyst sample for four consecutive runs. Reaction conditions were kept fixed for all runs with the catalyst separated by centrifugation and dried between experiments. It was reported that the immobilization of PMo in the NaUSY zeolite lead to a decrease in the surface area and the microporous volume. The products of the esterification observed were MAG, DAG and TAG. The effect of different HPA acid loading (0.6 to 5.4 wt %) on the initial activity of the catalyst was observed. As the HPA acid content was increased, the initial activity also increased until a maximum HPA content, which was obtained with PMo3-NaUSY (0.019 g HPA/ g zeolite) catalyst. On further increasing HPA load on zeolite, a decrease in the catalytic activity is observed. Initially, the increase of the HPA loading, causing an increase in catalytic activity may be attributed to kinetic effect. On further increasing the HPA loading, the limitations on the internal diffusion in the zeolite may be responsible for decreased activity. A decrease of BET surface area, microporous volume and accessibility to acid sites was observed as the amount of heteropolyacid on zeolite was increased. PMo3-NaUSY was reported as the most active catalyst showing the highest glycerol conversion (68% after 3 h). In the same time period PMo3-NaUSY resulted in a selectivity of 59% to DAG, 37% to MAG and 2% to TAG. The relatively high selectivity to DAG was attributed to the fact that DAG and TAG are formed through consecutive esterification reactions of MAG. The stability of the catalyst was studied by conducting consecutive experiments with the same sample and it was observed that the sampled showed stabilization of catalytic activity after second run.

Liao et al. [23] have proposed a two-step reaction to obtain high glycerol conversion rate and high selectivity to TAG, an additive of biofuel from its by-product glycerol. The esterification reaction was carried out in a round bottom flask with glycerol and acetic acid added directly along with the catalyst. After a definite period of the reaction, the catalyst was separated from the mixture. Then acetic anhydride was added drop wise to the reaction mixture till the conversion of glycerol reached 100%. Commercial resins, Amberlysts-15 (A-15) and Amberlysts-35 (A-35) and two large-pore zeolites HY and HZSM-5 were used as catalysts. The average pore diameters of the resins are 30 nm and those of the zeolites are 0.74 and 0.56 nm. The BET surface area of the resins is around $50m^2/g$ and that of the zeolites is 400 and 730 m^2/g respectively. It was reported that the reaction follows a two step procedure where first glycerol is completely converted to the mixture of MAG, DAG and TAG. On addition of anhydride, a second reaction takes place where both MAG and DAG are converted to TAG. The conversion reached 99% in 2 h with A-15 and A-35 and about 80% in 4 h with the zeolites. The conversion for the blank reaction (without catalyst) was close to 80%. In the reaction catalyzed by A-35, it was observed that the selectivity to TAG increases as the reaction progresses and reaches 25.9% after 4 h of reaction. The selectivity with A-15 is almost the same, but the selectivity with the zeolites is much lower, less than 5%. The poor selectivity may be attributed to the small pore diameters as TAG is a space demanding molecule. The reaction was optimised over A-35, which had shown best results. Optimising reactions varying molar ratio and temperature, showed that between 95 ^{o}C and 115 ^{o}C at 6:1 molar ratio a conversion of almost 100% was obtained after 4 hours however the reaction mixture becomes suspended close to 115 ^{o}C. On varying molar ratio it was observed that selectivity to TAG increases with increase in the molar ratio of acetic acid to glycerol in the reaction mixture. So the highest selectivity was obtained when the molar ratio of acetic acid to glycerol was maintained at 9:1. Adding of more catalyst did not affect the conversion and selectivity significantly. With only first step, selectivity to TAG did not rise beyond 34.8%. The authors attempted to see the effect of acetylation in a separate step by adding anhydride. The reaction mixture was divided into 3 parts after the allowing the first reaction to take place for 4 hours. 1 part was allowed to continue to react as it were. In the second part 0.2 ml acetic acid and in the third part 0.1 ml acetic anhydride was added. It was seen that the selectivity to TAG rose slightly in the second part to which acetic acid was added while in the third part to which acetic anhydride was added a sharp increase of selectivity to TAG to almost 100% in 15 min was seen. The better selectivity resulting from the acetylation step can be attributed to the acylium intermediate RCO^{+} that is generated. Therefore the two step reaction showed better results than a single step procedure in improving selectivity to TAG, however the high cost of acetic anhydride may be a hindrance.

Ferreira et al. [24] have studied the esterification of glycerol with acetic acid over dodecatungstophosphoric acid (PW) immobilized into silica matrix. They used two methods for the immobilization of dodecatungstophosphoric acid into silica matrix, sol–gel [25] and impregnation [26] methods. Characterization was done by Nitrogen adsorption isotherm, XRD-diffraction patterns, Scanning electron microscopy (SEM) and FITR. Acidity of the catalyst was measured by carrying out potentiometric titration. The catalytic runs were carried out in a batch reactor at reflux loaded with 20 ml of acetic acid, 2 g of glycerol and 0.2 g of catalyst. Stability of the best catalyst prepared by each method was also studied by conducting consecutive runs with the same samples. Analyses were carried out using GC analysis. The sol-gel method (samples labelled PW-in-S) resulted in samples with higher surface area as compared to the impregnation method (samples labelled PW-on-S). The XRD patterns of the prepared catalysts did now show any peaks corresponding to PW. This may be due to high level of dispersion of particles. The results of the potentiometric titration showed that the acidity of the catalysts increased with the amount of PW and PW-on-S3 (0.155 g HPA/ g support) showed highest acidity. The products of the acetylation reaction were MAG, DAG and TAG. The initial catalytic activity increases with the amount of PW immobilized in silica for both methods of catalyst preparation. Conversion increased with time and reaction was allowed to take place for 7 hours. After 7 h, PW-in-S2 (0.065 g HPA/ g support) showed highest glycerol conversion (87%) and selectivity of 59%, 36% and 4% to DAG, MAG and TAG respectively. DAG and TAG are formed through consecutive esterification reactions of MAG and hence the high selectivity to DAG. It was found that temperature had a positive effect on glycerol conversion. With the molar ratio of glycerol to acetic acid and temperature kept constant, on increasing catalyst loading from 0.1 g to 0.2 g a substantial increase was seen in the glycerol conversion. However, on further increasing the catalyst from 0.2 g to 0.3 g, glycerol conversion increased only marginally. Therefore, increase in catalyst loading above 0.2 g did not influence initial rate of reaction. The initial increase has been attributed to the increase in the total number of active catalytic sites for the reaction. Reactions were conducted by varying the glycerol to acetic acid molar ratio from 1:6 to 1:16. High molar ratio of glycerol to acetic acid resulted in lower selectivity to MAG and higher selectivity to DAG and TAG. Excess acetic acid in the reaction mixture pushes the equilibrium towards high conversion of glycerol and further conversion of MAG into DAG and TAG. Stability reactions showed that catalytic activity decreases from first run to second run , however remains constant from second run to third run, in case on PW-in-S2 catalyst. Stability tests on PW-on-S3 catalyst showed a decrease of the catalytic activity from the first to the fourth use. This was attributed to the leaching of PW from the catalyst surface to the reaction mixture.

Jagadeeswaraiah et al. [27] studied the acetylation of glycerol over tungstophosphoric acid (TPA) supported on Cs-containing zirconia and studied the effect of different reaction paramteres. A new support was created by doping Cs on zirconia and TPA was then dispersed on this support. The quantity of Cs was varied and the catalysts were denoted as 20%TPA/Cs_x-ZrO_2 where x = 0, 1, 2 and 3. Catalysts were characterised using XRD patterns, NH_3 – TPD and FT-IR spectra. The XRD patterns showed peaks corresponding to support zirconia and characteristic peaks of the Keggin ion structure of TPA. The FT-IR spectra further endorsed the existence of Keggin structure. TPD analysis showed three desorption peaks relating to different strength of acid sites. It was observed that the number of acidic sites depended on the amount of the Cs on zirconia. The products of the acetylation reaction were MAG, DAG and TAG. The glycerol conversion increased with time and reached a maximum within three hours of reaction. The selectivity of MAG decreased as the reaction proceeded and that of DAG and TAG decreased. The increase in selectivity for DAG and TAG with time is due to the further conversion of MAG. The authors explained the high activity of the catalysts by the presence of intact Keggin ions on the Cs – zirconia support. The doping of Cs on zirconia had a positive effect on the reaction. The catalyst without Cs showed the lowest activity and the catalyst with Cs content equal to 2 exchangeable moles showed the highest activity. This was explained based on high acid site density as indicated by the TPD analysis. Both glycerol conversion and selectivity to DAG and TAG was found to increase with an increase in temperature. On varying the molar ratio, the conversion varied marginally on changing the molar ratio from 1:4 to 1:5, but further increase did not bring any change in conversion. Selectivity of dia and triacetin increases with increase in acetic acid. Increasing the catalyst loading from 0.1 to 0.2 gm increased the conversion marginally but further increase in catalyst did not cause any increase in conversion. The selectivity does not change with catalyst loading.

Xianbing et al. [28] obtained multi-walled carbon nanotubes and used them to prepare Sulphate functionalized multiwalled carbon nanotubes (S-CNTs). Catalyst characterization was done using the FT-IR and TEM. FT-IT speactra showed that the sulphate group was successfully modified on the surface of carbon nanotubes. TEM images used to study the surface morphology of the carbon nanotubes proves that material consisted of hollow tubes and higher magnification of images showed that the material prepared consisted of multiwall tubes. The sulphate functionalised carbon nanotubes were used as a catalyst for the esterification of glycerol with acetic acid. Reaction was performed in a three neck flask with Glycerol (0.05 mol), acetic acid (0.25 mol) and catalyst (0.015 mol) mixed at room temperature. After two hours of reaction, the samples of the reaction mixture were collected and analysed using gas chromatography. The conversion of glycerol was studied without catalyst, with carbon nanotubes and with sulphate functionalised carbon nanotubes. Blank reaction and unmodified CNTs give a conversion of around 2%, while S-CNTs gave a a conversion of about 75.9 % after 2 hours. The yield of monoglyceride was 47.75%, while that of diglyceride and triglyceride was 27.65 and 0.5%, respectively. Recycling tests were carried out in order to study the stability of the S-CNTs. Only a slight deactivation was observed for recycyling the catalyst after each run.. From the results of the activity and stability of the S-CNT the authors concluded that grafting of sulphate groups onto CNTs is a suitable method to obtain active and stable catalysts for the acetylation of glycerol.

Goncalves et al. [29] studied the use of Tin Chloride ($SnCl_2.2H_2O$) as a catalyst for the esterification of glycerol and studied the effect of temperature, acetic acid: glycerol ratio, catalyst concentration on the selectivity and conversion. The use of tin chloride in place of conventional mineral acid catalyst is attempted as tin chloride can be expected to show lower corrosion and unnecessary neutralization at the end of the reaction can be prevented. Blank reactions without catalyst were also performed at the same conditions. Results of the reaction were compared with those of esterification reaction catalysed by sulfuric and p-toluene sulfonic acids. To study the reusability of the catalyst, the catalyst was collected after the reaction, by evaporating the esters and remaining reactants under reduced pressure. The collected catalyst was washed, dried and then reused in a catalytic test. At high acetic acid: glycerol molar ratios, such as 12:1 and 18:1, and temperatures in the range of 120^{o}C to 160 ^{o}C, good conversion was obtained even in the absence of a catalyst. However at 60 ^{o}C the blank reaction gave only 18% conversion, with MAG as the only product and no significant production of DAG and TAG was observed. It was observed that in the presence of catalyst, the conversion increased with increasing acetic acid: glycerol ratio. Also the DAG yield increased, which did not increase with a similar increase in the acetic acid: glycerol ration in case of a blank run. Glycerol conversion and DAG selectivity also increased with an increase in reaction temperature. On comparing the results of tin chloride catalysed reaction to that catalysed by Sulphuric acid and p-toluene sulphonic acid, it was observed that conversion in case of tin chloride is 96% compared to 98% and 85% for the two acid in that order. TAG was obtained only in traces with all three catalysts, and tin chloride gave a DAG selectivity of 48%, compared to 27% and 8% for the two acids. Recylability reaction showed that conversion was maintained at 92% even after 5 runs and catalyst recovery was 93%.

Ferreira et al. [30] studied esterification of glycerol over dodecatungstophosphoric acid (PW) immobilized on activated carbon (AC). They impregnated activated carbon with heteropolyacid-dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$) solutions of different concentrations (0.035 g acid/ g AC, 0.049 g acid/ g AC and 0.0065 g acid/ g AC). Catalyst characterization was done by using BET surface area, ICP analysis, FT- IR spectra and XRD patterns. The BET surface area was found to decrease with increasing concentration of acid. The total porous volume and the microporous volume of the catalyst also decreased with an increase in the acid concentration. FT-IR spectra showed characteristic bands of PW species. The XRD patterns showed no peaks associated with PW, which was attributed to low loading of PW or high dispersion of the acid over support. The experiments were conducted as a batch process in a round bottom flask at reflux, with 20 cm^3 of acetic acid, 2 g of glycerol and 0.2 g of catalyst. Stability of PW2-AC catalyst was studied by running four consecutive reactions with the same catalyst sample. Between two runs, the catalyst was separated from the reaction mixture by centrifugation, washed and dried. The initial activity of the catalysts increased with acid concentration on the catalyst till a maximum value, after which initial activity decreased with a further increase in acid strength. The increase in catalytic activity with acid concentration at lower acid loading may be explained by kinetic effect, while the decrease in activity on further increase in acid loading was explained by limitations on internal diffusion of the support. PW2-AC was observed to have the highest initial activity. It resulted in the highest glycerol conversion (86%) with a selectivity of 63%, 25% and 11% to DAG, MAG and TAG respectively after 3 h of reaction. The high selectivity of PW2-AC to DAG can be explained as DAG and DAG are formed through further conversion of MAG. Stability tests on PW2-AC showed that there was a decrease in catalytic activity from the first run to the second run but after the third run, the catalytic activity stabilised. PW2-AC was found to be quite stable and only 10% of PW was lost from the activated carbon support in the stability reactions. This can be explained by PWs strong adsorption over activated carbon. The much lower conversion of the reaction in the absence of catalyst, with acetic acid which had been in prolonged contact with the catalysts indicates PW leaching from the activated carbon support to be small.

Rodriguez et al. [31] used sulphonated zirconia as solid acid catalysts for the esterification reaction. Catalysts were prepared using sol- gel technique and are denoted as SZ-H, where H is the hydrolysis ratio. Catalysts were characterised using Nitrogen Physisorption, XRD patterns, XPS analysis and NH_3- TPD measurements. No linear correlation was observed between the textural properties and hydrolysis ratio. The maximum desorption temperature was similar for all catalysts ranging between 380 and 406, and thus the authors concluded that the distribution of acid sites was not depenednent on the hydrolysis ratio. SZ-6 exhibited the most number of strong acid sites even though it had relatively fewer weak acid sites. A higher hydrolysis ratio, resulted in a lower proportion of weak sites. The total acidity of the samples was highest for SZ-6, followed by SZ-1, then SZ-3 and lowest for SZ-0. Esterification reactions were carried out in a batch process in a round bottom flask. Stability of the catalyst for reuse was also tested. In the absence of any catalyst the final yield of the esterification reaction was 20%. With SZ-0, no improvement was observed, probably due to low surface area. SZ-1 gave an acetylation yield of 57%, SZ-3 gave 38% and SZ-6 gave 63% after 24 h. Non-sulfated zirconia gave an yield of 20% after 24 h, suggesting that sulfate anion is active for the acetylation reaction. It was observed that catalytic activity was higher when acid site density was lower. This may be because dense arrangement of acid sites presents a greater steric hinderance for the approach of the glycerol molecule. The distribution of the esters in the product was found to be independent of the catalyst and depended only on the reaction equilibrium. For all catalysts, major product was MAG with DAG yield less than 2% and no TAG. In the leaching test, preferential leaching of sulphur was observed. The leaching values are highest for SZ-6. This can be attributed to low mechanical resistance shown by SZ-6. The results of the recyclability test performed on SZ-1 showed that the catalytic activity reduces with every run and the catalyst is deactivated after the fourth run. The liquid medium filtered in the recyclability tests is tested for catalytic activity and gave an yield of 30%, which is better than yield in the absence of catalyst. However liquid medium from further runs didn't show catalytic activity as the solids have already been impoverished.

Troncea et al. [32] studied the use of Magnesium fluoride as an environmental friendly catalyst in the esterification of glycerol with acetic acid and the effect of unconventional methods of activation such as microwaves and ultrasound radiation on the reaction conditions. The catalysts were synthesized from metallic Mg using the fluorolytic sol–gel method [34]. Different concentration of HF was used to prepare a series of MgF_2 catalysts. Commercial zeolite was used for reference. Catalyst characterization was carried out using XRD, MAS-NMR, TEM, thermal analysis, XPS, and elemental analysis [19,21]. It was observed that the BET surface area and pore volume increased with increase in the HF concentration. The pore sizes decreased with an increase in HF concentration. The bronsted acid site concentration decreased while that of lewis acid sites increased. Activation was done in three ways – microwaves, thermal and unltrasound. Esterification reactions were carried out with catalysts activated by the different methods and product analysis was done. The products obtained were MAG, DAG and TAG. In the reaction using conventional thermal energy for activation, the conversion after 22 hours is still below 100%. When a blank run was carried out, esterification occurred but the conversion was found to be much lower and only MAG was obtained. With the conventional catalyst, H-BEA zeolite, a lower conversion is obtained and it has a lower selectivity to DAG as compared to the Magnesium fluoride catalyst samples. Selectivity to TAG was dependent on the ratio of lewis sites to Bronsted sites, and therefore the MgF_2 sample with the highest concentration of HF (87%) and the lowest amount of Bronsted sites showed the highest selectivity to DAG +TAG (94%). The authors concluded that to achieve best activity for the esterification reaction, the hydroxylated MgF_2 sample should have low acid site density and high ratio of lewis sites to bronsted sites. These properties can be generated by manipulating the ratio of HF during preparation. Microwave and ultrasound methods of activation resulted in faster conversion of glycerol and higher selectivity to DAG+ TAG as compared to conventional thermal activation.

Sanchez et al. [35] investigated porous carbon materials functionalized with sulfonic acid for the esterification reaction. The porous carbons were synthesised first by a direct synthesis carbonization (DC) and a template assisted carbonization process (TAC). The carbon samples were functionalised using two sulphating agents. Catalyst characterization was done using IR spectroscopy and N_2 adsorption. The above prepared catalysts and commercial catalyst Amberlyst-36 were used to test catalytic activity with reaction temperature varied from 378 to 423K. Elemental analysis which was used to calculate the percentage of sulphur showed that DC method had lower concentration of than that developed by the TAC method. High values of specific area, greater than500 m^2/g were obtained for TAC method for temperatures above 673K. However, the direct carbonisation method resulted in a non porous material with a low BET surface area of $4m^2/g$. Functionalisation of the activated carbon with the sulphate group was confirmed by elemental analysis and FT-IR spectra. It was reported that samples carbonised at lower temperature have greater density of SO_3H group and result in higher selectivity to TAG. The use of TAC- 673 (catalyst prepared by template assisted carbonisation at 673K) catalyst in the esterification reaction of glycerol with acetic acid resulted in glycerol conversions above 99% with selectivity to TAG selectivity 50%. Esterification at the same conditions using a conventional catalyst such as Amberlyst-15 also gave over 99% glycerol conversions however selectivity to TAG was only about 10%. Therefore catalysts prepared by functionlisation of activated carbon with sulphate groups are active for the esterification of glycerol and can be considered as alternatives to commercial catalysts.

Trejda et al. [36] conducted this study to prepare mesoporous silica and niobiosilicate material of SBA-15 type modified with MPTMS by the post synthesis procedure and to examine their stability and activity to catalyse the esterification of glycerol. Mesoporous silica sieves of SBA-15 type were made by standard procedure [37]. For catalyst characterization, XRD patterns, nitrogen desorption isotherms, BET surface area, elemental analysis IR and UV spectra and acidic titration were used. It was observed from the XRD patterns that the incorporation of the MPTMS did not change either of the hexagonal structure or the material ordering. The nitrogen desorption isotherms also supported the mesoporous structure. The BET surface area is found to be quite high for all samples ranging from 525-835 m^2/g. The functionalisation with MPTMS leads to a decrease in surface area, as well as pore diameter and pore volume. From the titrations it was concluded that the acidic sites were accessible and active for use for catalytic purposes. The reaction was carried out in the liquid phase in a batch reactor with reflux, in an atmosphere of nitrogen at 1 atm, and at a temperature of 423 K for 4 hours. The molar ratio of acetic acid to glycerol was 9:1 and 100 mg of the catalyst was used. The catalyst stability was also studied by conducting a reuse test by centrifuging and drying the catalyst and then using it for a second and later third run. The conversion for the blank reaction was found to be 63% with di and mono-acetyl glycerol was the main product. The use of catalysts leads to an increase in conversion, up to 80% with silicate materials and 90% with niobiosilicate materials. Even with application of catalyst, the selectivity is highest for diacetyl glycerol. Glycerol conversion did not significantly change after the second and third run in the reuse test, though selectivity to triacetyl glycerol went down significantly in the second run. Thus the materials prepared using the one pot synthesis method can be used for the catalysis of the esterification of glycerol, however they were not found to be very stable.

Goncalves et al. [39] attempted to use $H_3PW_{12}O_{40,}$ heteropolyacid, a versatile Bronsted acid catalyst to promote esterification of glycerol into MAG and DAG. The performance of the catalyst was compared to that of conventional bronsted acids like p-toluene sulfonic acid (PTSA) and sulfuric acid, and effects of the molar ratio of acetic acid to glycerol, acid strength and concentration of the catalysts on glycerol conversion and product selectivity was studied. The reaction was carried out at 60 ^oC for 8 hours at acetic acid to glycerol molar ratio varying from 3:1 to 12:1. Reaction samples were taken at intervals of 60 minutes and analysed using gas chromatography. Stability of the HPW catalyst was tested by conducting consecutive runs with the same catalyst sample. In between runs, catalyst was collected by heating the solution to remove esters and remaining reactant. The collected catalyst was washed and dried and then used in the next run. In the absence of catalyst, only MAG was formed as product and with an increase of the acetic acid to glycerol molar ratio, an increase in glycerol conversion was obtained however DAG selectivity was low even after 8 h of reaction. The presence of $H_3PW_{12}O_{40}$ was found to affect both the conversion and selectivity drastically. Glycerol conversion was found to increase with acetic acid to glycerol ratio till 1:9, but decreased on further increasing the ratio to 1:12. In all HPW-catalyzed reactions; glycerol conversion exceeded 90%. Whenever higher ratios were used it was observed that, the maximum MAG concentration was obtained within 2 hours and DAG concentration increased with further reaction. Thus it was suggested that DAG forms via 2 alternative routes: directly from glycerol and through two consecutive reactions from the point at which the MAG concentration reaches a maximum. The catalytic performance was compared with other Bronsted acids with acidity order as HPW>H_2SO_4 >PTSA. In HPW-catalyzed reactions, the glycerol conversion reached 95%, with a selectivity of 66% to MAG and 34% to DAG. In H_2SO_4 catalyzed reactions, selectivity of 54% to MAG and 27% to DAG where obtained. The values of both conversion and selectivity were lower than the above two in the case of p-toluene sulphonic acid (PTSA). Therefore, HPW presented a higher selectivity to DAG as can be seen. For estimating rate constant, the authors initially assumed a dependence of pseudo first-order in relation to the glycerol concentration, and built plots of ln [glycerol] versus time for the HPW-catalyzed reactions at different temperatures. However the plots showed a low regression coefficient, indicating that the relationship was not linear. The authors then followed an approach of second-order and plots of (1/[glycerol] t = ti −1/[glycerol] t = 0) versus time were drawn. These plots had a high linearity coefficient.

Therefore second order dependence was proven. The slope of these plots was used to calculate the rate constant using the pseudo-second order rate law. The change in rate constant with temperature was used to calculate the activation energy for the reaction by employing the Arrhenius equation. The activation energy of the HPW-catalyzed glycerol esterification reaction with acetic acid was reported 22.9 kJ mol-^{1}. In the case of reusibilty reactions, high glycerol conversion and product selectivity were obtained in all catalytic runs. There was good recovery of the HPW catalyst after the consecutive runs and hence the HPW catalyst was considered to remain stable after multiple recycles.

Rodriguez et al. [40] compared the performance of five types of ion exchange resins for glycerol acetylation. In contrast to most works where acetic acid is employed in excess in order to maximise selectivity of triacetin, this work uses an excess of glycerol with the objective if consuming low value glycerol. For the study two Amberlyst resins, Amberlyst-15 (A-15) and Amberlyst-36 (A-36) and three Dowex resins, Dowex 50Wx2 (D-2), Dowex 50Wx4 (D-4) and Dowex 50Wx8 (D-8) were chosen. The catalytic tests were conducted in a round bottom reactor at 378 K and atmospheric pressure. Molar ratio of acetic acid to glycerol was maintained at 1:8, and 0.25g catalyst/ 40 ml glycerol was used. Samples of the reaction mixture were collected at regular intervals and were analysed by gas chromatography. The effect of catalyst loading, catalyst pre treatment and addition of water to the reaction was studied. Recyclabity tests were also carried out to check stability of catalysts. The blank reaction took more than 24h to achieve equilibrium. All catalysts studied were active for the esterification reaction and reached equilibrium in less than 5 h. The conversion with all catalysts was almost the same. The rate of reaction was highest for D2, followed by D8, A36, D4 and A15 in that order. D-2 showed the highest activity, probably due to the lower cross linkages. The higher number of acid sites of A-36 was identified as the reason of the higher activity of A-36 as compared to A-15.All catalysts resulted in MAG as the major product, with a small amount of DAG and almost no TAG formation. Increasing the catalyst loading from 0.1g to 0.25 g had a significant effect on the acetic acid conversion; however increasing the catalyst loading beyond 0.25 g had no effect. It was reported that drying of catalyst before use gave better performance as presence of water promotes hydrolysis of esters. Results of the reusability tests indicated that neither resin shows a drop in catalytic activity in consecutive runs and thus both resins are stable catalysts than can be reused.

Zhou et al. [41] studied the esterification of glycerol over different solid acids and the effect of changing temperature and acetic acid to glycerol molar ratio on the reaction. They used commercial resins (Amberlyst 15) and acid zeolites (HZSM-5 and HUSY) as catalysts. Of all the solid catalysts, Amberlyst-15 showed the highest conversion and the highest selectivity to TAG and DAG. The zeolites, HSZM-5 and HUSY showed the lowest conversion and selectivity. The authors reported that the esterification of glycerol was a consecutive reaction. Without a catalyst, glycerol conversion of 70% was obtained, however the selectivity to DAG and TAG was very low. Therefore the reaction has self- catalysis properties and the function of catalyst is primarily to increase selectivity to DAG and TAG, the desired products. Amberlyst 15 resulted in good selectivity to DAG+TAG and a MAG selectivity of less than 20%. The zeolites gave a much poorer selectivity to DAG and TAG. This was explained based on the larger size and space demanding nature of DAG and TAG , which makes diffusion and formation inside the pores of the zeolite difficult, thus resulting in poor selectivity to DAG+TAG. When the acetylation of glycerol was carried out with acetic anhydride, 99% glycerol conversion and 100% selectivity to TAG was obtained. Therefore, acetylating ability of anhydride is significantly better than that of acetic acid. However, the high cost of acetic anhydride and the very fast rate of reaction, which makes it difficult to control are hindrances to the use of acetic anhydride for acetylation of glycerol. Both the glycerol conversion and selectivity to DAG + TAG increased on increasing the acetic acid to glycerol molar ratio. This could be explained by the fact that higher acetic acid ratio shifts the equilibrium in the forward direction, and that it lowers the viscosity of the reaction mixture thus facilitating mass transfer between the catalyst and the other phases. On varying the temperature from 80 to 110 deg c, it was found that the glycerol conversion and selectivity to DAG and TAG both increase with an increase in temperature. Three dimensional plots of AA: glycerol ration, temperature and selectivity or conversion were plotted to identify the most optimal parameters to optimise the reaction.

2.2 Sulfated alumina catalysts

Yang et al. [33] prepared sulphated alumina by impregnating Al_20_3 with aqueous sulphuric acid. Different sulphated alumina species were formed depending upon the concentration of sulphuric acid used for impregnation. They studied the preparation and activity of sulphated alumina as sulphated metal oxides are supersacidic catalysts that are active for the acylation of aromatics.

They reported three types of sulphate species – surface sulphate, multilayer sulphate and crystallised (Al_2 (SO4)$_3$) being formed identified by the DTG peaks. XRD patterns for sulphated alumina impregnated with [H_2SO_4] < 2.4M showed no peaks other than those corresponding to alumina, whereas for [H_2SO_4] > 2.4M showed a characteristic (Al_2 (SO4)$_3$) peak. Surface sulphate species were mainly induced for [H_2SO_4] < 0.8M. The superacidic sites were also identified in the NH_3- TPD analysis by a peak around 400 ^oC. Multilayers were observed to be formed for [H_2SO_4] > 0.8M. These were represented in the NH_3- TPD analysis by a peak around 250 ^oC. Crystallised (Al_2 (SO4)$_3$) was observed to be formed for [H_2SO_4] > 2.4M. The surface sulphate species showed high thermal stability and induce superacididty that shows good results for isomerisation on n-butane to iso-buutane. Multilayer sulphate shows lower thermal stability and exhibits weaker acidity, while (Al_2 (SO4)$_3$) is neutral and both of these are inactive towards isomerisation.

Mekhemer et al. [46] prepared sulphated alumina catalysts by impregnating AlO and AlH with aqueous solution of Ammonium sulphate ($(NH_4)_2SO_4$) or sulphuric acid (H_2SO_4). They then studied the effect of varying the loading level of sulphate ions (3, 6 and 10 wt%), and whether the sources of the sulphate ions used was $(NH_4)_2SO_4$ or H_2SO_4 on the textural, structural, and acidic properties of the catalysts. They also studied the activity of the catalysts towards propanol conversion reactions. XRD patterns showed that sulfation does not significantly affect Al_2O_3, irrespective of source and content of sulfation. The BET surface area was found to decrease with increase in sulphate content. Pyridinie absorption results indicated that sulfation increases strength of Lewis acid sites. The sulfated alumina catalysts were active for the catalytic decomposition of 2-propanaol and the catalysts loaded with 6 wt% acid were found to be the most active.

Objectives

Different catalysts have been explored for esterification of glycerol with acetic acid including resins zeolites, heteropolyacids on supports, sulfated zirconia and activated carbon based catalysts. High glycerol conversions have been reported with several catalysts; however design a suitable catalysts system for high yield of the most valuable TAG and stability of catalyst is the big challenge. It is known that, esterification reaction is positively influenced by the acidic nature of catalysts. Sulfated alumina has been reported as promising catalysts for many reactions such as requiring acidic sites isomerization of paraffins and acylation of aromatics. Moreover, no information is available regarding the activity and product selectivity for glycerol esterification reaction over alumina based catalysts. In this study, alumina-based catalysts were synthesized and examined for esterification of glycerol to improve TAG yield.

The objectives of the present work were:

1. Synthesis of Cu/ γ-Al_2O_3 or Ni/γ-Al_2O_3 , Cu-Ni/ γ-Al_2O_3 and sulfated alumina catalysts.
2. Characterization of catalysts by various techniques such as specific surface area measurement, X-ray diffraction study (XRD), temperature programmed desorption (TPD), Fourier transform infrared spectroscopy (FTIR), inductive coupled plasma mass spectrometer (ICP-MS) to determine the physicochemical properties of the fresh and used catalysts.
3. To study the effect of composition of Cu or Ni, Cu-Ni and sulfated alumina on the activity and product selectivity of the catalyst in esterification of glycerol.
4. To study the esterification of glycerol over all the catalysts synthesized and investigate the effect of reaction parameters such as temperature, reaction time, metal loading, on catalytic activity product selectivity and yield.
5. To determine the metal leaching, catalyst stability and reusability.
6. To determine the kinetic parameter for sulfated alumina catalyst.

4. Experimental details

4.1 Materials

Cu $(NO_3)_2.3H_2O$ (>99%, Himedia Chemicals, India), Ni $(NO_3)_2.6H_2O$ (>99%, Merck Specialities, India) were used as metal precursors and γ-Al_2O_3 (Merck Specialities, India) was used as the catalyst support. Sulphuric acid (98%, Thomas Baker, India), Glycerol (99.9%, Merck Specialities, India) and acetic Acid (99.5%, Rankem, India) were used as reactants. Monoacetin (50%, Alfa Aesar, India, Diacetin (50%, Alfa Aesar, India) and triactein(99%, Alfa Aesar, India), and Butanol (99%, Rankem, India) were procured and used.

4.2 Catalyst synthesis

4.2.1. Synthesis of Cu-Ni catalysts

Copper – nickel monometallic and bimetallic catalysts supported on γ-Al_2O_3 were prepared by wetness impregnation method with 20 wt% metal loading. Required amount of metal precursors Cu $(NO_3)_2.3H_2O$ and Ni $(NO_3)_2.6H_2O$ were dissolved in millipore water and mixed with γ-Al_2O_3. Bimetallic catalysts were made using three different Cu: Ni weight ratios – 1:3, 1:1 and 3:1. The slurry obtained was allowed to age for 24 h at room temperature, dried in an oven for 12 h at 110 ^oC and then calcined in air at 400 ^oC for 4 h. The catalysts were labelled, Cu/ γ-Al_2O_3, Ni/ γ-Al_2O_3, Cu-Ni (1:3)/ γ-Al_2O_3, Cu-Ni (1:1)/ γ-Al_2O_3, and Cu-Ni (3:1)/ γ-Al_2O_3.

4.2.2. Synthesis of sulphated alumina

Sulphated alumina with three different sulphate loadings was prepared following the method proposed by Yang et al [33]. Three concentrations of Sulphuric acid were prepared – 0.2M, 2M and 4.8M and 1 gm γ-Al_2O_3 was impregnated with them. The impregnated slurries were stirred for 10 minutes, kept at atmospheric conditions for 5 hours and dried at 110° C for 24 hours. Each sample was then calcined at 550° C for 3 hours, and stored in separate vials. The catalysts were labelled 0.2 M SO_4^{2-}/ γ-Al_2O_3, 2 M SO_4^{2-}/ γ-Al_2O_3 and 4.8 M SO_4^{2-}/ γ-Al_2O_3 respectively.

4.3 Catalyst characterization

N_2 adsorption desorption experiments were carried out on Micromeritics Accelerated Surface Area and Porosimetry (ASAP-2020) system at liquid nitrogen temperature (-196^{o}C). Before analysis, samples were degassed under vaccum at 300 ^{o}C for 6h. Multipoint BET method was used to calculate the surface area of all samples at a relative pressure of 0.05-0.3. BJH (Barret, Joyner and Halenda) method was used to calculate the pore size distribution considering the desorption branch.

The phase composition of the catalysts was investigated by powder X-ray diffraction (XRD) (Bruker AXS D8, CuKα). XRD patterns were recorded in the two theta range of 10^{o} to 80^{o} at a rate of 0.02^{o}/s with a time constant of 3 s.

Temperature programmed desorption (TPD) with ammonia was carried out to determine the acidic properties of the catalyst. Micromeritics Pulse Chemsorb 2720 instrument equipped with a thermal conductivity detector (TCD) was used for the experiments. Prior to TPD experiments, the catalyst samples were pre-treated at 150 °C for 2 h in a flow of helium. After pre-treatment, the catalyst samples were allowed to cool at room temperature. Then samples were saturated with 27% NH_3/He gas mixture with a flow rate of 30 cc/min for 1h. To remove the excess ammonia, samples were flushed with helium. The ammonia-TPD was performed using 20 cc/min of helium, heating the samples from 30°C to 700 °C at a heating rate of 10 °C/min while continuously monitoring the thermal conductive detector signals.

FT-IR analysis of the sulphated alumina catalysts was carried out to check the presence of the sulphate group on the support. Fourier Transform Infrared (FT-IR) analysis was carried out with a Thermo Nicolet Model magna 760 by preparing KBr pellets and analysis was done in the range of 500 to 4000 cm^{-1}.

The reaction mixture after five hours of reaction was subjected to ICP- MS analysis to check for leaching of metal from the catalyst support into the reaction medium.

The used Cu-Ni/ γ-Al_2O_3 catalyst after consecutive runs was subjected to X ray diffraction, and its XRD patterns were compared to those of fresh catalyst. Used SO_4^{2-}/ γ-Al_2O_3 catalysts were analyzed using FT-IR and their FT-IR spectra was compared to fresh catalyst.

4.4 Catalytic tests

The esterification reactions were carried out at 110 °C and atmospheric pressure in a round bottom flask equipped with a reflux and a magnetic stirrer. A molar ratio of 1:9 of glycerol to acetic acid and catalyst loading of 0.25 g was maintained for all reactions. Reactions were carried out with γ-Al_2O_3, Cu-Ni series and SO_4^{2-}/ γ-Al_2O_3 catalysts. Blank reaction, without a catalyst and reaction with pure γ-Al_2O_3 were also carried out. Samples were taken at intervals of 1 hour, filtered, cooled to room temperature and analysed using gas chromatography.

4.5 Product analysis

A Newchrom GC (Model: 6800, India) equipped with AB-PONA (stationary phase, 50 m × 0.2 mm) column was used to detect the product component mainly MAG, DAG and TAG. The flame ionization detector was used with injector temperature of 260° C and detector temperature of 280° C in an isothermal program at 200° C. The analysis was carried out using n-Butanol as the internal standard. Calibration curves were used to calculate concentration of feed and products in the product mixture. The glycerol conversion and product selectivity were defined as proposed by Zhou et al. [41]:

$$\text{Conversion of glycerol or acetic acid } (\%) = 1 - \frac{\text{Moles of glycerol or acetic acid remaining}}{\text{initial moles of glycerol or acetic acid}} \times 100$$

$$\text{Selectivity of MAG, DAG or TAG } (\%) = \frac{\text{Moles of monoacetin, diacetin or triacetin formed}}{\text{Total moles of MAG} + \text{DAG} + \text{TAG}} \times 100$$

5. Results and discussion

5.1 Catalyst characterization

5.1.1 Textural properties

Table 5.1 shows the textural properties of the catalyst samples. The specific surface area is determined by the BET method and the pore volume and pore size are determined by the BJH method. It was observed that the impregnation of sulphuric acid on alumina leads to a decrease of the specific surface area and the pore volume. This may be due to the blockage of pores by the active species (SO_4^{2-}). The impregnation of copper and nickel also leads to a decrease in surface area in case of Cu-Ni/ γ-Al_2O_3 monometallic and bimetallic catalysts.

Table 5.1

Textural characteristics of catalysts

Sample	BET surface are (m^2/ g)	Pore Volume (cm^3/ g)	Pore diameter average (A^o)
γ-Al_2O_3	107	0.20	57
0.2M SO_4^{2-}/ γ-Al_2O_3	52.1	0.092	62.9
2M SO_4^{2-}/ γ-Al_2O_3	8.4	0.012	38.3
4.8M SO_4^{2-}/ γ-Al_2O_3	2.4	0.002	117.6

5.1.2 X- Ray Diffraction

The XRD patterns of the sulfated alumina catalysts are shown in Fig. 5.1. Peaks at $2\theta = 44.6^o$ and 67.4^o corresponding to alumina were obtained on all three SO_4^{2-}/γ-Al_2O_3 catalysts which confirmed the presence of monoclinic phase of Al_2O_3 (JCPDS: 86-1410). For the samples prepared, 0.2M SO_4^{2-}/ γ-Al_2O_3 showed no peak apart from the ones corresponding to Al_2O_3, while 2M SO_4^{2-}/ γ-Al_2O_3 and 4.8M SO_4^{2-}/ γ-Al_2O_3 showed the characteristic peak at 25.5° corresponding to $Al_2(SO_4)_3$. Along similar lines, Yang et al. [33] reported that besides the peaks corresponding to Al_2O_3, the SO_4^{2-}/ γ- Al_2O_3 samples impregnated with $[H_2SO_4] \leq 2.4$ M do not exhibit any additional peaks, and samples impregnated with $[H_2SO_4] \geq 2.4$ M show a characteristic diffraction peak at $2\theta = 26^o$, corresponding to $Al_2(SO_4)_3$ (JCPDS: 81-1835).

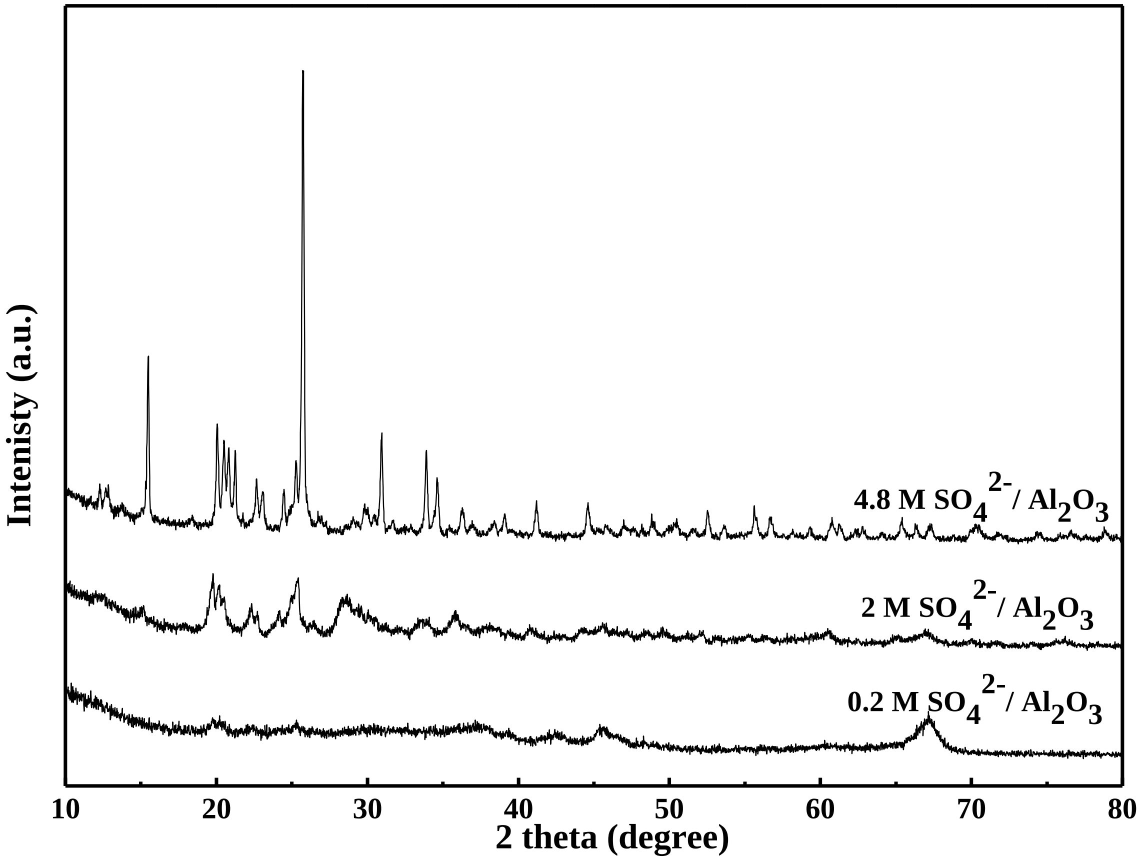

Fig. 5.1 XRD patterns of SO_4^{2-}/ γ-Al_2O_3 catalysts

5.1.3 FT-IR analysis

The FT-IR spectra of the SO_4^{2-}/ γ-Al_2O_3 catalysts are presented in Fig. 5.2. For all three SO_4^{2-}/ γ-Al_2O_3 catalysts, the broad peak obtained in the wave number region of 3000-3400 cm^{-1} and the peak obtained at the wave number of 1632 cm^{-1} is corresponds to the hydroxyl groups present in alumina [42]. The band obtained at 1100 cm^{-1} in the FT-IR spectra is attributed to the symmetric vibrations in a sulfate group [43].

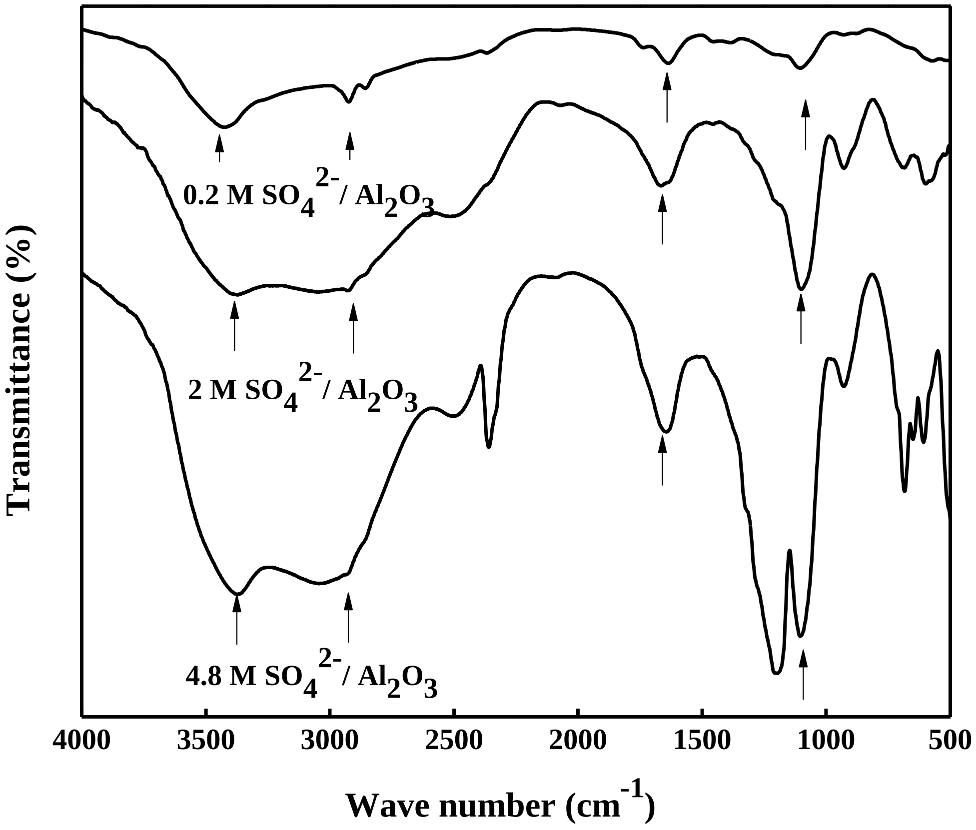

Fig. 5.2 FT-IR spectra of SO_4^{2-}/ γ- Al_2O_3 catalysts

5.1.4 Acidity measurements

Acidity is the most important catalytic function of sulfated metal oxides. The NH_3- TPD results obtained for the SO_4^{2-}/ γ- Al_2O_3 catalysts and γ-Al_2O_3 are shown in Fig. 5.3. All samples showed broad TPD profiles indicating that the surface acidic strength is widely distributed [27]. 2M SO_4^{2-}/ γ-Al_2O_3 and 4.8M SO_4^{2-}/ γ- Al_2O_3 showed a broad peak that stretched from around 250 °C to 500 °C. The intensity of the peak obtained for both samples was unchanged. This is similar to results obtained by Yang et al. [33] who found that the intensity of strong acidic peaks remained unchanged for $[H_2SO_4] \geq 2.4$ M. The acidity of the samples is listed in Table 5.2. It is observed that the impregnation of H_2SO_4 on γ-Al_2O_3 leads to an increase in acidity. The acidity of 0.2M

SO_4^{2-}/ γ-Al_2O_3 is only slightly higher than that of γ-Al_2O_3, and among the samples prepared, the highest acidity was obtained for 2M SO_4^{2-}/ γ- Al_2O_3. In case of Cu -Ni/ γ-Al_2O_3 monometallic and bimetallic catalysts it is observed that the impregnation of metal leads to reduction in total acidity of the catalyst. The acidity of monometallic and bimetallic catalyst is in the range of 0.407 - 0.562 mmol NH_3 gcat.$^{-1}$, which is lower than the acidity of γ-Al_2O_3 (1.203 mmol NH_3 gcat.$^{-1}$).

Table 5.2

Acidity of catalysts

Catalyst	Acidity (mmol NH_3 gcat.$^{-1}$)
γ-Al_2O_3	1.20
0.2M SO_4^{2-}/ γ-Al_2O_3	1.32
2M SO_4^{2-}/ γ-Al_2O_3	2.51
4.8M SO_4^{2-}/ γ-Al_2O_3	1.98
Cu /γ-Al_2O_3	0.56
Cu-Ni(3:1)/γ-Al_2O_3	0.70
Cu-Ni(1:1)/γ-Al_2O_3	0.61
Cu-Ni(1:3)/γ-Al_2O_3	0.89
Ni/γ-Al_2O_3	0.41

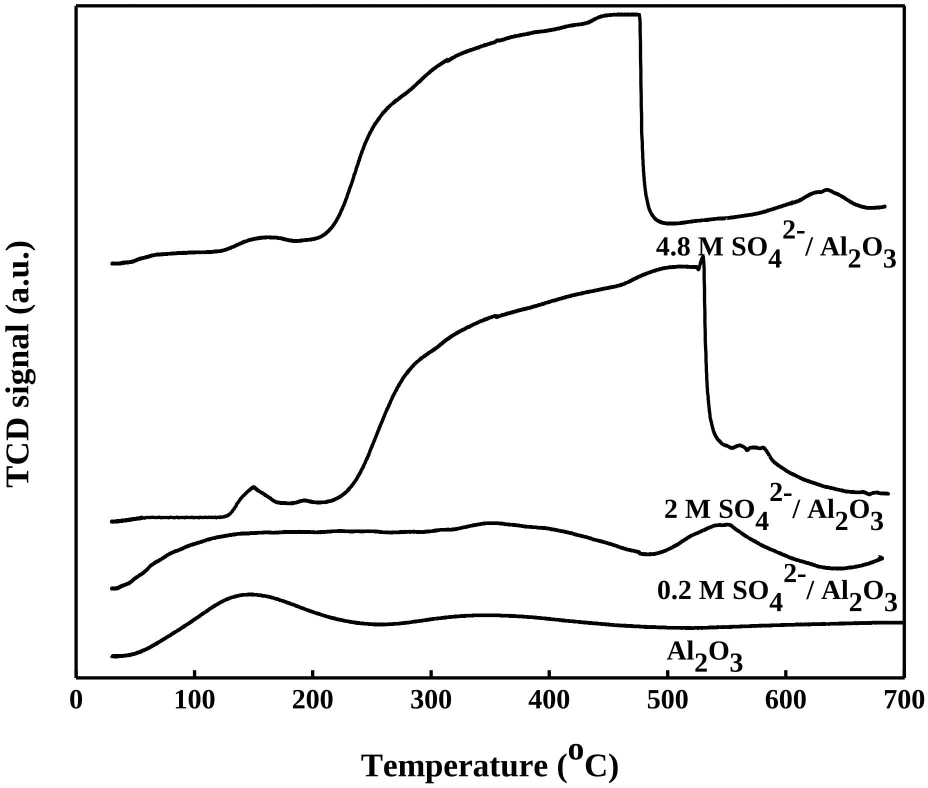

Fig. 5.3 NH_3- TPD profiles of SO_4^{2-}/ γ-Al_2O_3 catalysts

5.2 Catalytic performance

5.2.1 Catalytic activity for Cu -Ni / γ-Al_2O_3 catalysts

When the reaction was carried out in the absence of catalyst, glycerol conversion of 81% was obtained after five hours of reaction. Only γ-Al_2O_3 shows no catalytic effect for the esterification reaction as reaction with γ-Al_2O_3 resulted in glycerol conversion of 81% after 5 hours. With the Cu-Ni/ γ-Al_2O_3 catalysts higher conversion is obtained in the same period. It was observed that the impregnation of metal on Alumina has a positive effect on the esterification reaction. Fig. 5.4 represents the variation in glycerol conversions with time obtained during the catalytic tests.

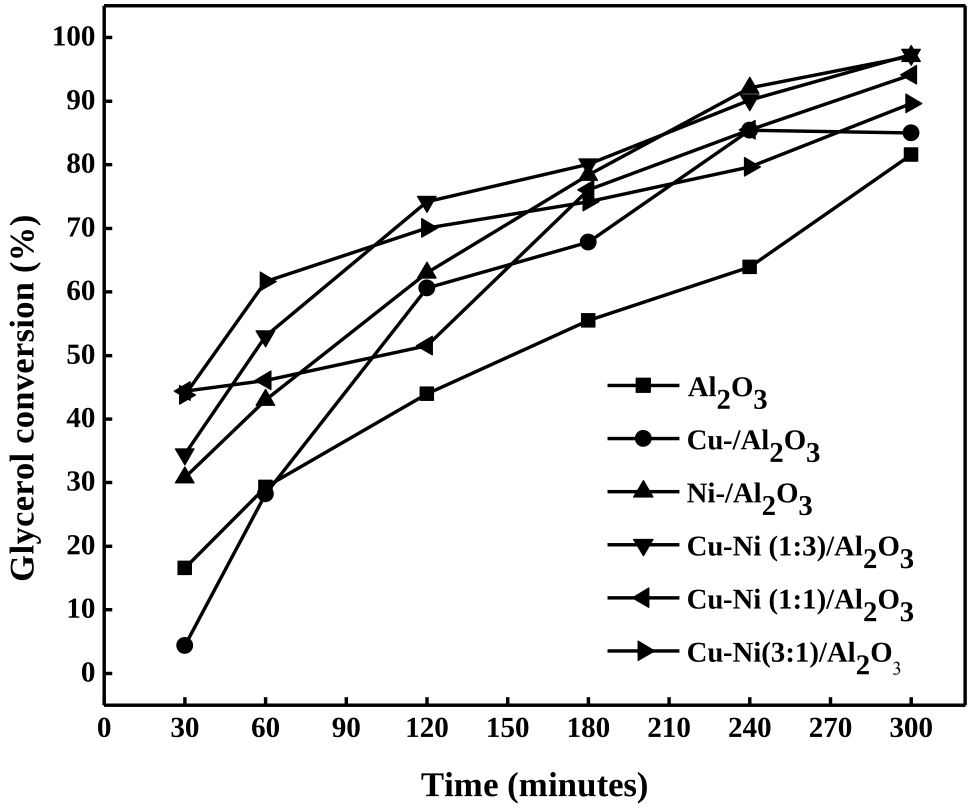

Fig. 5.4 Glycerol conversion with time over Cu-Ni / γ-Al_2O_3 catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

Table 5.3

Catalytic behaviour of Cu-Ni catalysts for glycerol esterification.

Catalyst	Conversion (%)	Selectivity (%)			Yield
		MAG	DAG	TAG	TAG (%)
Cu/ γ-Al_2O_3	84.9	70.7	27.0	2.3	1.9
Cu-Ni(3:1)/ γ-Al_2O_3	89.6	75.4	23.2	1.4	1.2
Cu-Ni(1:1)/ γ-Al_2O_3	94.1	77.6	21.2	1.2	1.1
Cu-Ni(1:3)/ γ-Al_2O_3	97.3	68.9	28.5	2.5	2.5
Ni/ γ-Al_2O_3	97.1	68.9	28.4	2.6	2.6
γ-Al_2O_3	81.6	86.7	12.9	0.5	0.4

Reaction Conditions: Temperature - 110 ^oC, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

Depending on the catalyst, the reaction is accelerated in different ways. Table 5.3 shows the glycerol conversion and selectivity to the products obtained by the esterification reactions after 5 h of the reaction. With Cu/γ-Al_2O_3 only a slightly better glycerol conversion (85%) was obtained. On increasing Ni content from Cu-Ni (3:1) to Cu-Ni (1:3) glycerol conversion increased from 89% to 97%. With monometallic Ni/ γ-Al_2O_3 also 97% glycerol conversion was obtained. It was observed that with increasing Ni content the activity of the catalyst increases. This is similar to the results of catalytic tests using Cu-Ni/ γ-Al_2O_3 catalysts for hydrogenolysis of 1,3 butadiene reported by Kang et al. [44], where activity reduces on addition of second metal. Ni/ γ-Al_2O_3 gives similar results to bimetallic catalysts, as has been reported earlier for hydrogenolysis reaction by Gandarias et al. [45].

Catalyst activity for esterification of glycerol with acetic acid has been related to acidity of catalyst and higher acidity has shown to result in better activity [31]. For the prepared catalysts, Cu-Ni (1:3)/ γ-Al_2O_3 has the highest acidity and also gives the highest glycerol conversion (97%). However, Ni/ γ-Al_2O_3 which gives comparable conversion (97%) has a much lower acidity. The higher activity of Cu-Ni (1:3)/ γ-Al_2O_3 can also be explained on the basis of higher density of strong acidic sites [27].

For all the catalyst, the main products of the reaction are Mono-acetyl glycerol (MAG), Di-acetyl glycerol (DAG) and tri- acetyl glycerol (TAG). The change in product selectivity with time is shown for Ni/ γ-Al_2O_3 in Fig. 5.5. Initially only MAG was formed and the selectivity to MAG varied from 98% after 30 minutes to 68% after 5 hours. As the reaction progressed, DAG and TAG were formed. The selectivity to DAG increased from 1.8% after 30 minutes to 28% after 5 hours. Traces of TAG were observed after 3 hours of reaction and the selectivity to TAG was 2.6% after 5 hours of reaction.

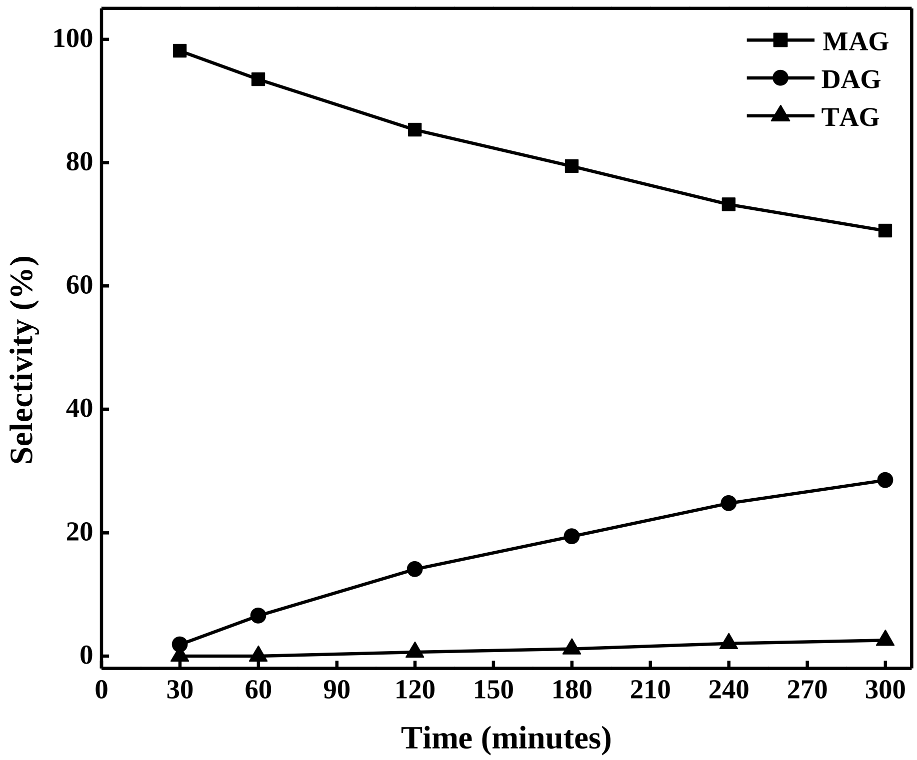

Fig. 5.5 Trend in product selectivity with time for glycerol esterification catalysed by Ni/ γ-Al_2O_3

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

Fig. 5.6, Fig. 5.7 and Fig. 5.8 show the trend of selectivity to MAG, DAG and TAG respectively for the different Cu/ Ni on γ-Al_2O_3 catalysts with time.

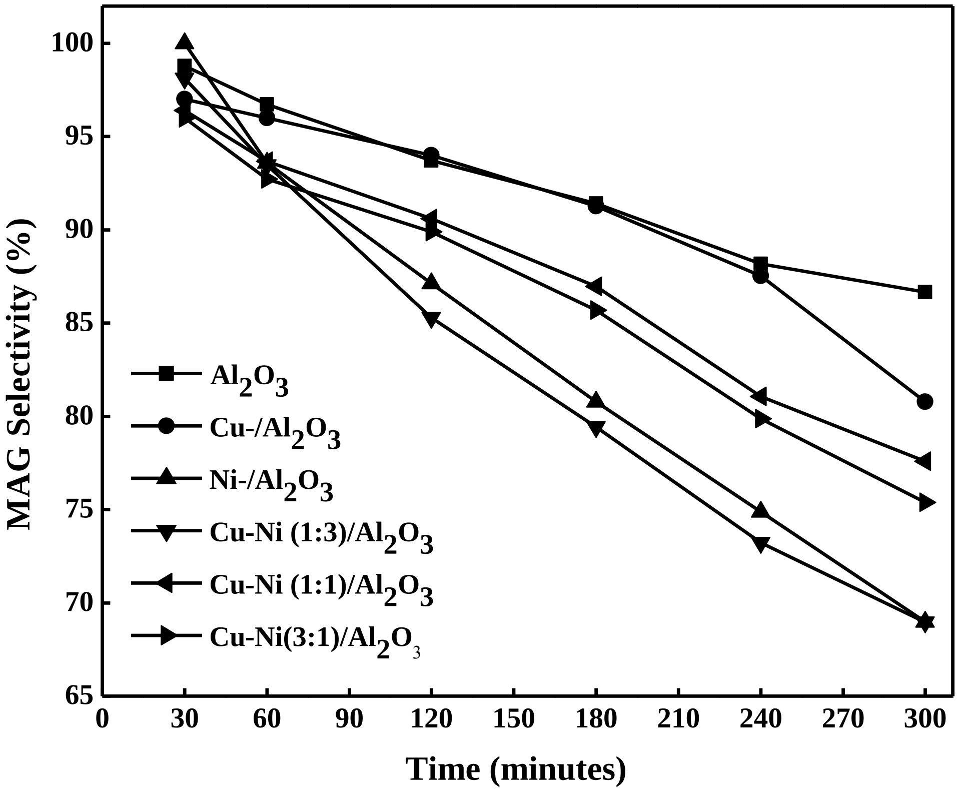

Fig. 5.6 Selectivity to MAG with time for esterification of glycerol for Cu-Ni / γ-Al_2O_3 catalysts Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

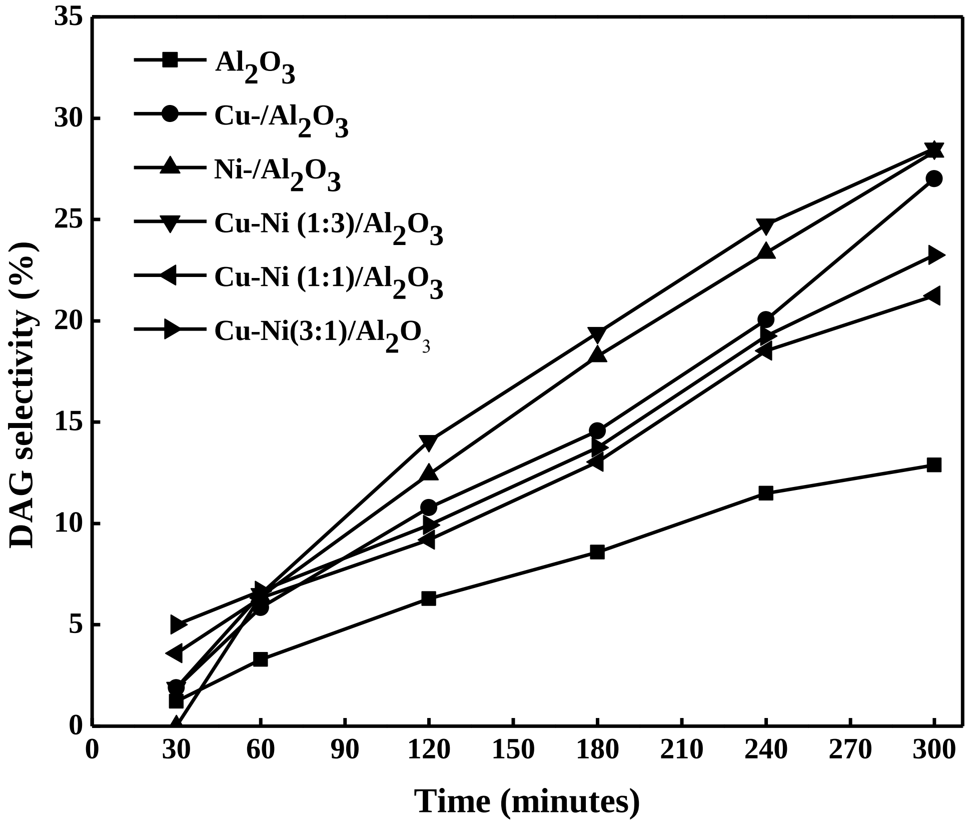

Fig. 5.7 Selectivity to DAG with time for esterification of glycerol for Cu-Ni / γ-Al_2O_3 catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

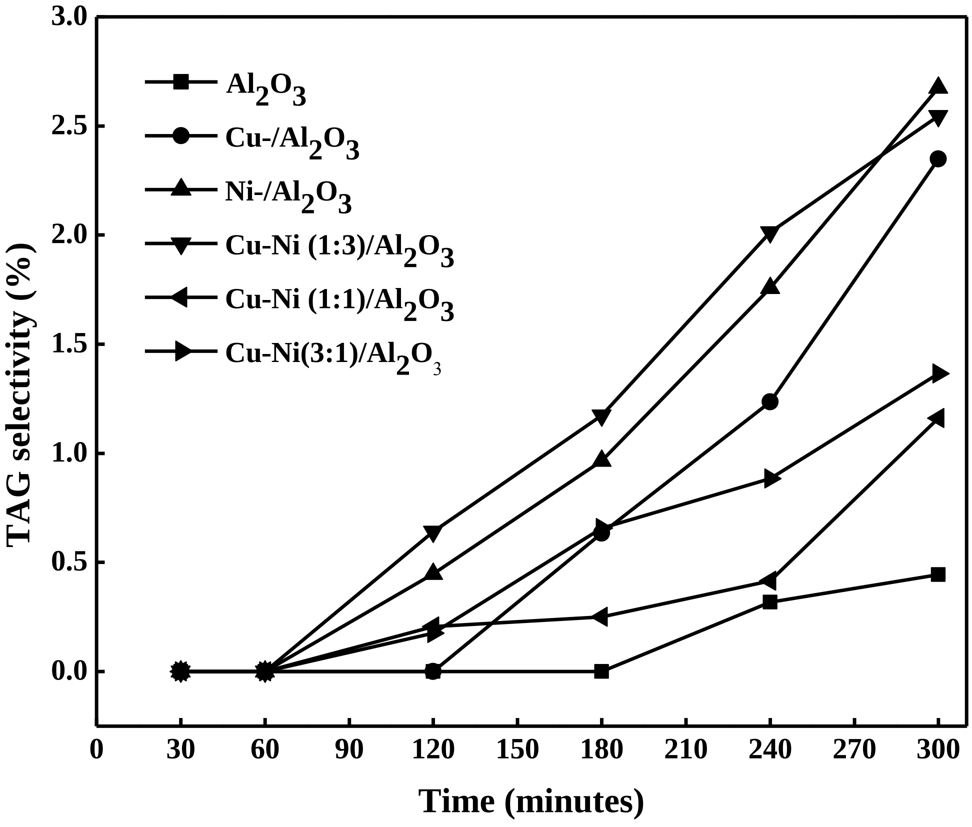

Fig. 5.8 Selectivity to TAG with time for esterification of glycerol for Cu-Ni / γ-Al_2O_3 catalysts
Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,
Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

Ni/ γ-Al_2O_3 and Cu-Ni (1:3)/ γ-Al_2O_3 catalysts showed the highest selectivity to TAG, the most desired product. Ni/ γ-Al_2O_3 and Cu-Ni (1:3)/ γ-Al_2O_3 resulted in TAG selectivity of 2.6% and 2.5%, respectively (Table 5.3), after 5 hours of reaction.

5.2.2 Catalytic activity over sulfated alumina (SO_4^{2-}/ γ- Al_2O_3) catalysts

Three variants of SO_4^{2-}/ γ- Al_2O_3 were prepared with varying concentrations of Sulphuric acid and their catalytic activity for esterification of glycerol was tested. Fig. 5.9 shows glycerol conversion with time for the SO_4^{2-}/ γ- Al_2O_3 samples tested.

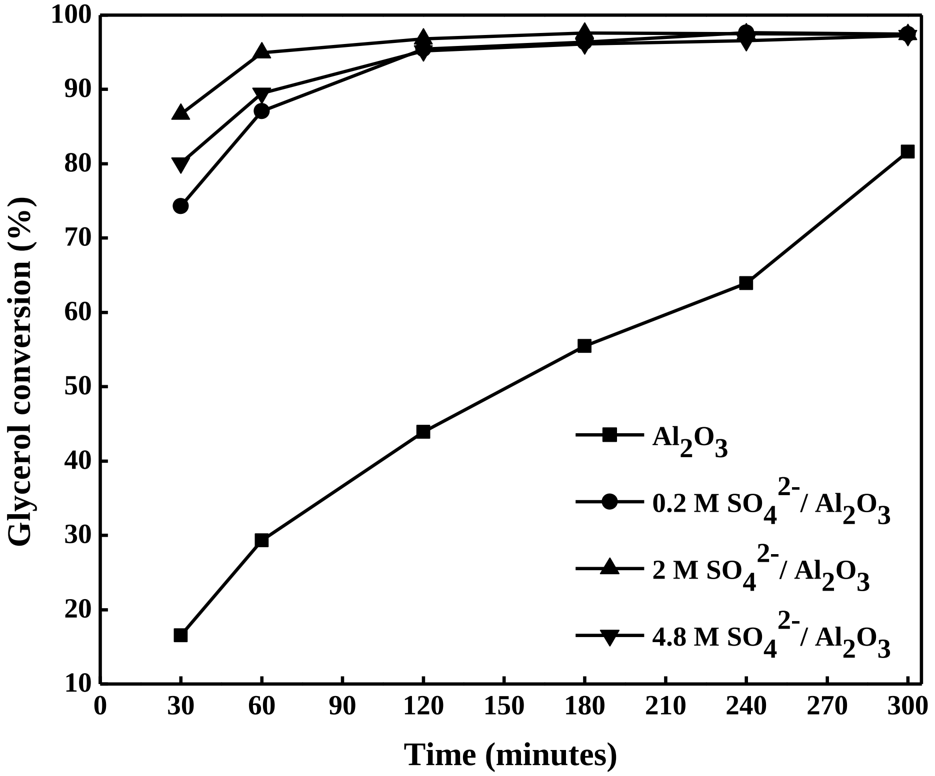

Fig. 5.9 Glycerol conversion with time for SO_4^{2-}/ γ-Al_2O_3 catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

All SO_4^{2-}/ γ-Al_2O_3 catalysts showed better glycerol conversion than pure γ-Al_2O_3. High glycerol conversions were obtained for all three variants – 0.2M SO_4^{2-}/ γ-Al_2O_3, 2M SO_4^{2-}/ γ-Al_2O_3 and 4.8M SO_4^{2-}/ γ-Al_2O_3 and for all three SO_4^{2-}/ γ-Al_2O_3 catalysts, glycerol conversion exceeded 90% within 2 hours of the reaction. Conversion exceeded rapidly in the first hour, after which the rate of increase slowed. For all three catalysts glycerol conversion stabilized at 97% after three hours of reaction. It was observed that the catalytic activity increases with the H_2SO_4 concentration until a maximum value which was obtained with the 2M SO_4^{2-}/ γ-Al_2O_3 catalyst. With higher sulphuric acid concentration impregnated in alumina, a decrease in catalytic activity is observed. It was observed that glycerol conversion was faster in the reaction with 2M SO_4^{2-}/ γ- Al_2O_3 as compared to 0.2M SO_4^{2-}/ γ- Al_2O_3 and 4.8 M SO_4^{2-}/ γ- $Al_2O_{3.}$ The catalytic activity can be explained on the basis of the acidity of the catalysts. It was observed that glycerol conversion increases with an increase in total acidity of the catalyst.

The major products of the esterification reaction were Monoacetyl glycerol (MAG), Di- acetyl glycerol (DAG) and tri- acetyl glycerol (TAG). The selectivity of MAG decreases with time and that of DAG and TAG increases with time. . The change in product selectivity with time is plotted for 2M SO_4^{2-}/ γ-Al_2O_3 in Fig. 5.10. MAG selectivity varied from 75% after 30 minutes to 27% after 5 hours. DAG selectivity varied from 23% at 30 minutes to 49% at 5 hours, reaching a maximum of 51%. TAG selectivity increased as the reaction progressed and reached a maximum of 23% after 5 hours.

Fig. 5.11, Fig. 5.12 and Fig. 5.13 represent the trend in selectivity to MAG, DAG and TAG respectively for the SO_4^{2-}/γ-Al_2O_3 catalysts. For all catalysts the MAG selectivity reduces from more than 70% after 30 minutes to less than 40% after 5 hours. The DAG selectivity increases as the reaction progresses and rises to about 50% after three hours. After three hours, the DAG selectivity was observed to remain around 50%. Traces of TAG are observed at 30 minutes and TAG selectivity rises continuously as the reaction progresses. The increase in DAG and TAG selectivity as the reaction progresses can be attributed to the consecutive esterification of MAG to give higher esters.

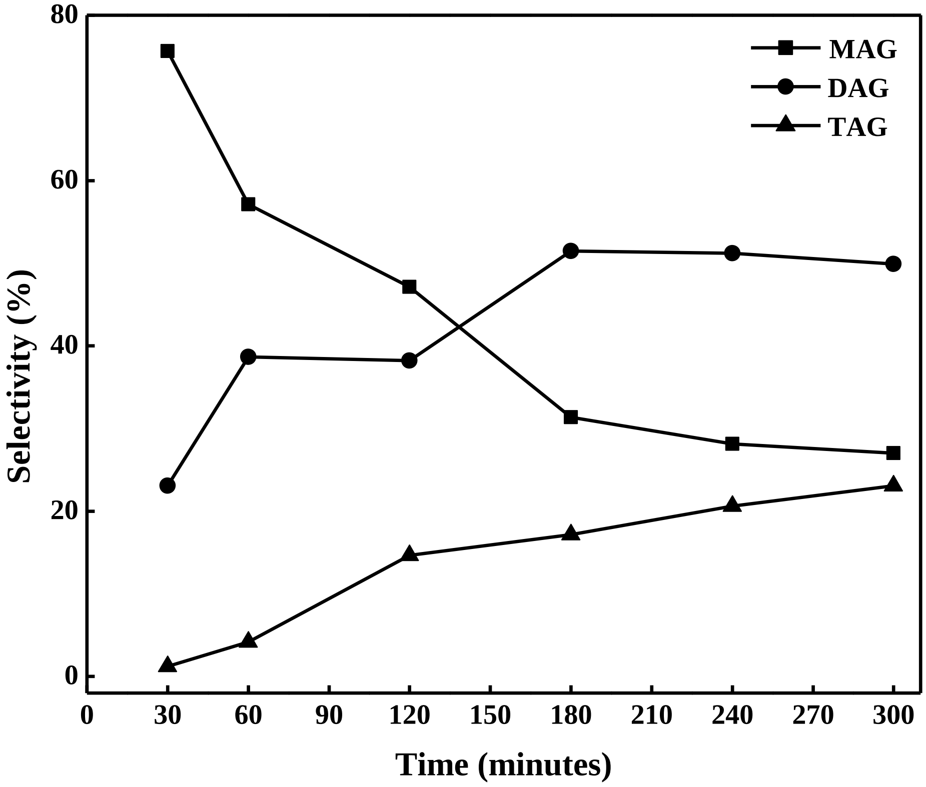

Fig. 5.10 Trends in product selectivity for esterification of glycerol with 2M $SO_4^{2-}/\gamma\text{-}Al_2O_3$ catalysts

Reaction Conditions: Temperature - 110 ^{o}C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. -0.25 g

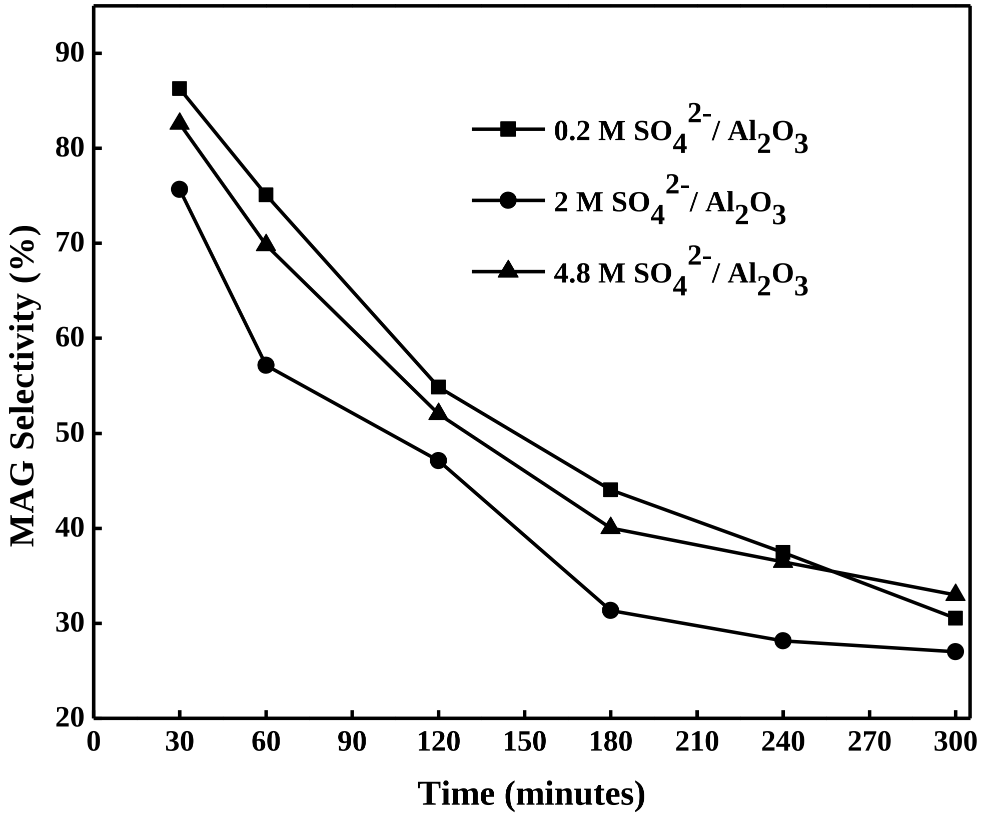

Fig. 5.11 Trends of selectivity to MAG with time for $SO_4^{2-}/\gamma\text{-}Al_2O_3$ catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. - 0.25 g

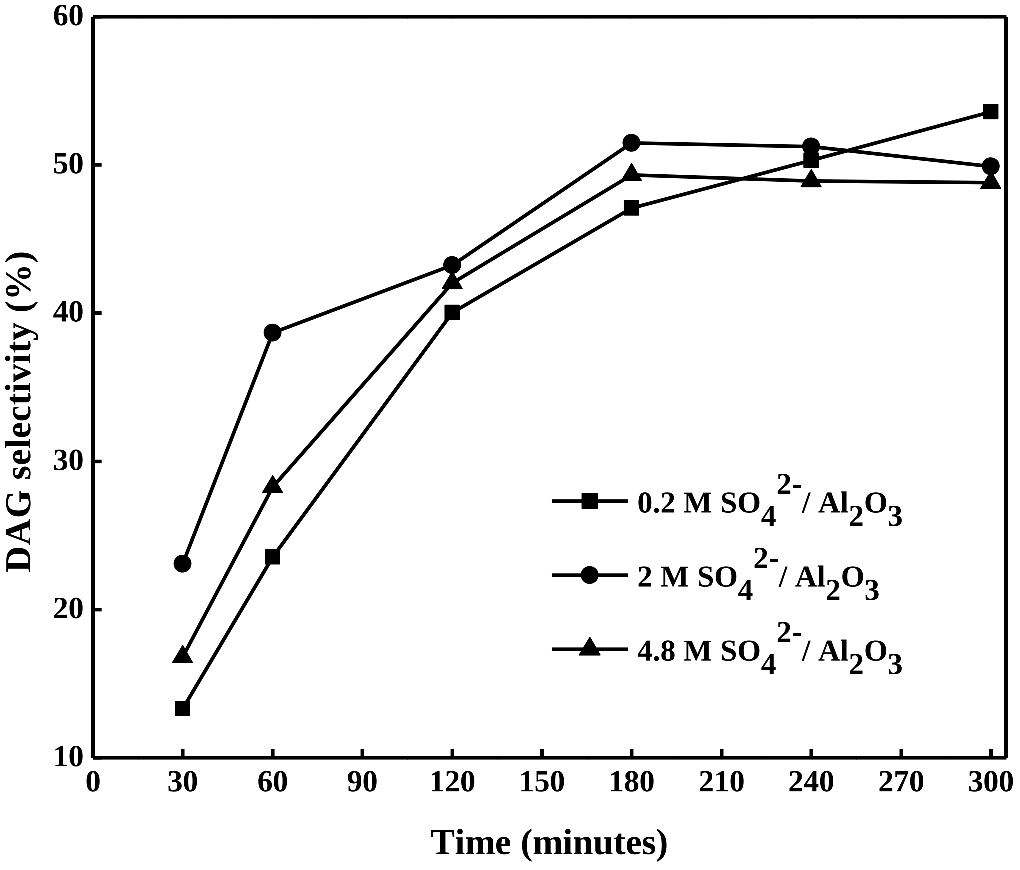

Fig. 5.12 Trends of selectivity to DAG with time for $SO_4^{2-}/\gamma\text{-}Al_2O_3$ catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h, Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. - 0.25 g

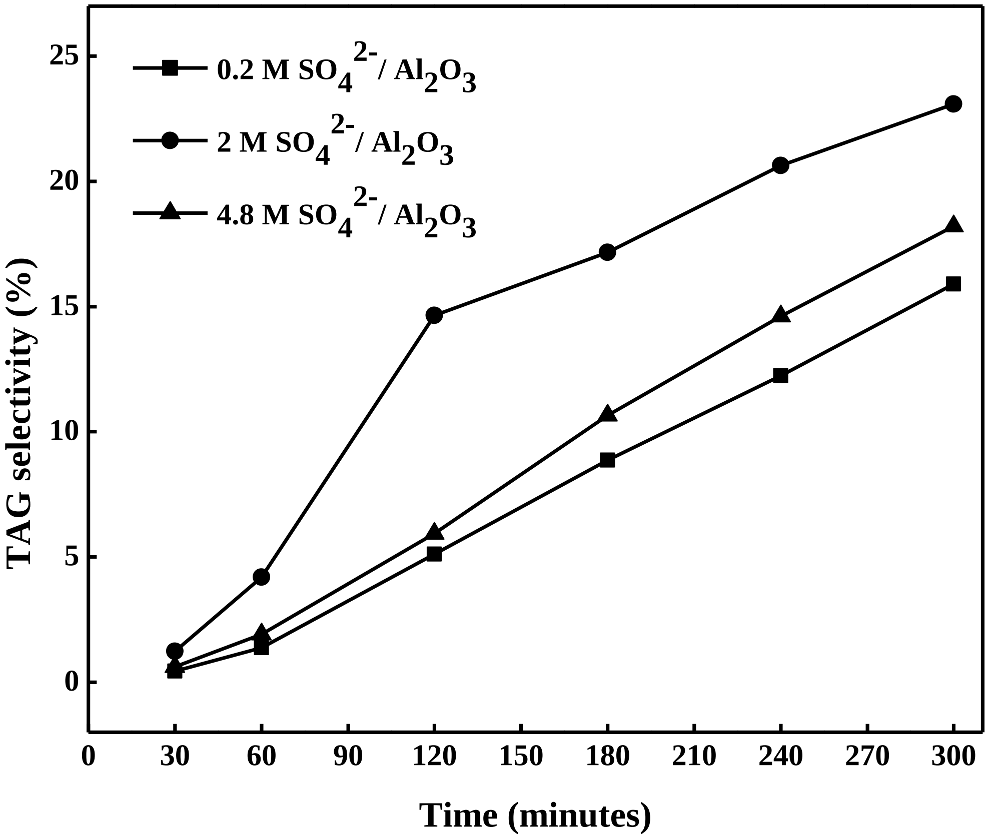

Fig. 5.13 Trends of selectivity to TAG with time for SO_4^{2-}/γ-Al_2O_3 catalysts

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. - 0.25 g

The TAG selectivity for all SO_4^{2-}/ γ-Al_2O_3 catalysts was higher than that obtained with γ- Al_2O_3. (Table 5.4). Therefore sulfation has a positive effect on TAG selectivity. The highest TAG selectivity was obtained with 2M SO_4^{2-}/ γ-Al_2O_3, as 23% after 5 hours of reaction. 0.2 M SO_4^{2-}/ γ-Al_2O_3 gave a TAG selectivity of 15% after five hours and 4.8 M SO_4^{2-}/ γ-Al_2O_3 gave a TAG selectivity of 18% after the same period. All SO_4^{2-}/γ-Al_2O_3 catalysts gave higher selectivity to TAG than the Cu-Ni/ γ-Al_2O_3series of catalysts.

Table 5.4

Catalytic behaviour over different catalysts in glycerol esterification.

Catalyst	Conversion (%)	Selectivity (%)			Yield TAG (%)
		MAG	DAG	TAG	
γ-Al_2O_3 (a)	81	86.66	12.89	0.44	0.35
0.2M SO_4^{2-}/ γ-Al_2O_3 (a)	97	30.53	53.57	15.88	15.5
2M SO_4^{2-}/ γ-Al_2O_3 (a)	97	27.01	49.89	23.09	22.5
4.8M SO_4^{2-}/ γ- Al_2O_3 (a)	97	32.98	48.80	18.21	17.7
H_2SO_4 (b)	98	54	27	Traces	Traces
Sulfated zirconia (c)	-	98	2	Traces	Traces
Sulfated activated carbon (d)	99	-	-	17	17

(a) Reaction Conditions: glycerol: Acetic acid (molar ratio) – 1:9, reaction temperature: 110 ^oC , reaction time: 5h, catalyst wt.: 0.25 g.

(b) Reaction Conditions: glycerol: Acetic acid (molar ratio) – 1:3, reaction temperature: 60 ^oC , reaction time: 8h, catalyst conc.: 0.03 mmol [39]

(c) Reaction Conditions: glycerol: Acetic acid (molar ratio) – 1:82, reaction temperature: 55 ^oC , reaction time: 24h, catalyst conc.: 6.25 gm/ l [31]

(d) Reaction Conditions: glycerol: Acetic acid (molar ratio) – 1:9, reaction temperature: 105 ^oC , reaction time: 4h, catalyst conc.: 5% (w/w) [35]

Table 5.4 compares the performance of SO_4^{2-}/ γ-Al_2O_3 catalysts to that of sulphuric acid and other sulfated supports. It can be seen that, though glycerol conversion is greater than 97% for sulphuric acid as well as other sulfated supports, the TAG selectivity is not high. In case of H_2SO_4 and sulfated zirconia only traces of TAG were obtained. With activated carbon functionalized with sulphuric acid higher TAG selectivity was obtained (17% at 105 °C and up to 50% at 200 °C). The present work tested catalytic effect of sulfated alumina at 110 °C and found TAG selectivity to be 23%.

5.2.3 Catalysts stability

Ni/ γ-Al_2O_3 and 2M SO_4^{2-}/ γ-Al_2O_3, which gave the best results in the Cu-Ni/ γ-Al_2O_3 series and SO_4^{2-}/ γ-Al_2O_3 series respectively were subjected to further tests to check catalytic stability.

Table 5.5

Stability studies of Ni/ γ-Al_2O_3

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. - 0.25 g

Experiment	Glycerol conversion (%)	MAG selectivity (%)	DAG selectivity (%)	TAG selectivity (%)
1st Run	97	68	29	3
2nd Run	92	65	32	3
3rd Run	88	69	29	2

Table 5.5 represents glycerol conversion and product selectivity for consecutive batch runs carried out with Ni/ γ-Al_2O_3. Loss in catalytic activity is observed in every consecutive run, and glycerol conversion reduces from 97% for the first run to 88% for the third run. This behavior may be attributed to leaching of metal from the catalyst into the liquid phase.

The used catalyst samples after each run were characterized and their XRD patterns were compared to that of the fresh Ni/ γ-Al_2O_3 catalyst. From Fig 5.14 it can be seen that the peaks corresponding to NiO at 2 theta = 43^o and 37^o were of significantly lower intensity for used catalysts as compared to fresh catalysts. This may be attributed to leaching of metal from the catalyst surface into the liquid phase.

The reaction mixture collected after 5 hours of reaction was subjected to ICP- MS analysis and was tested for nickel. The results confirmed presence of nickel in the reaction mixture and hence confirmed leaching of the metal from the catalyst surface into the liquid phase.

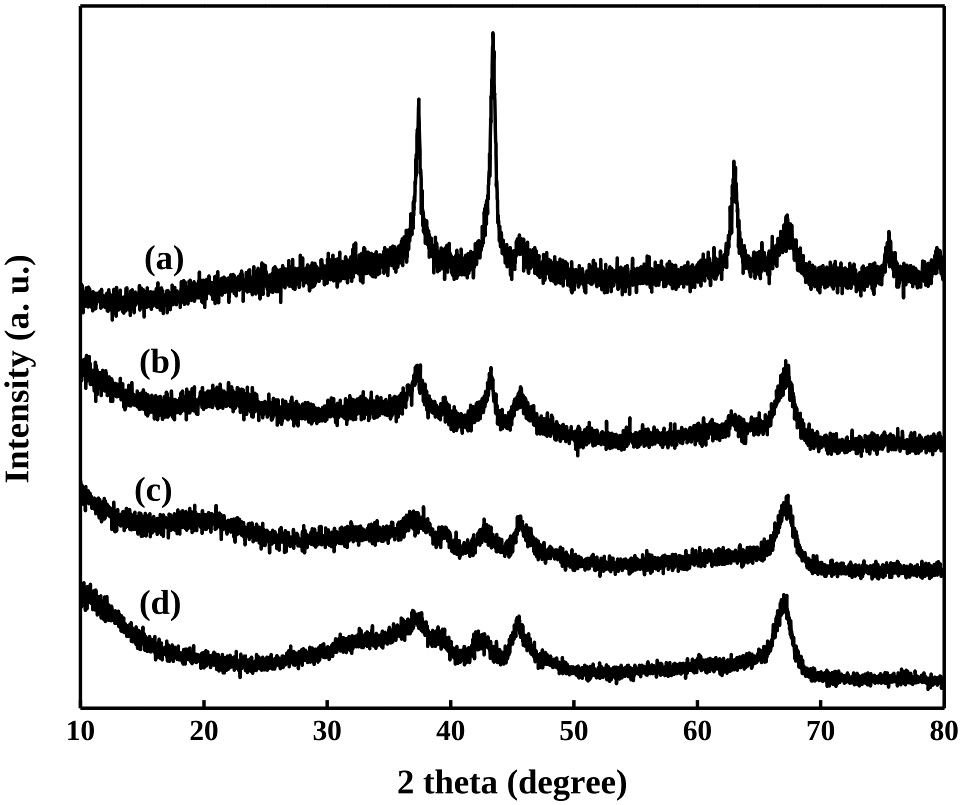

Fig. 5.14 XRD patterns of fresh and used Ni/ γ-Al_2O_3 catalysts

a- Fresh catalyst
b- Catalyst after 1st run
c- Catalyst after 2nd run
d- Catalyst after 3rd run

Table 5.6

Stability studies of 2M SO_4^{2-}/ γ-Al_2O_3

Reaction Conditions: Temperature - 110 °C, Presuure - 1 atm, Reaction time -5h,

Molar ratio of glycerol to acetic acid - 1:9, Catalyst wt. - 0.25 g

Experiment	Glycerol conversion (%)	MAG selectivity (%)	DAG selectivity (%)	TAG selectivity (%)
1st Run	97	32	47	21
2nd Run	97	35	46	19
3rd Run	97	35	47	18

Table 5.6 shows the glycerol conversion and selectivity in consecutive batch runs with the same catalyst. In case of 2M SO_4^{2-}/ γ-Al_2O_3, no loss in activity was observed and glycerol conversion was maintained at 97% after third use of catalyst. There was a slight decrease in TAG selectivity from 21% to 18% from the first to the third run.

Fig. 5.15 shows the FT-IR spectra of fresh and used 2M SO_4^{2-}/ γ-Al_2O_3. It can be seen that the peak corresponding to sulfate group at 1100 cm^{-1} is intact in the used catalysts.

Therefore, 2M SO_4^{2-}/ γ-Al_2O_3 can be considered a stable catalyst for the esterification of glycerol with acetic acid reaction.

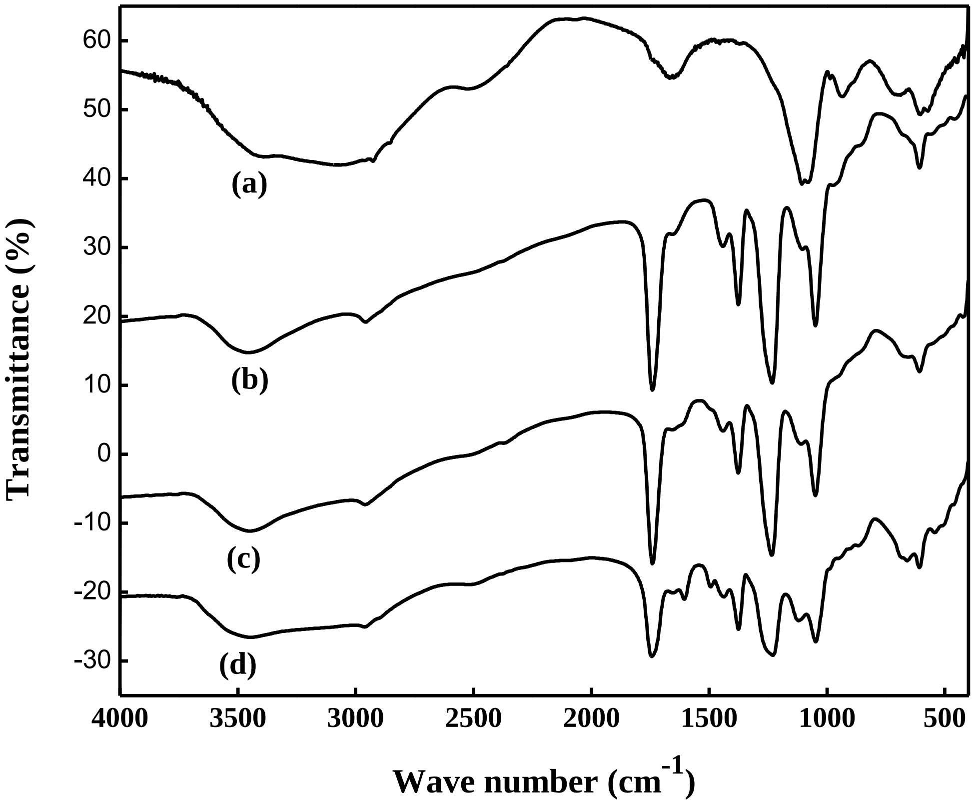

Fig. 5.15 FT-IR patterns of fresh and used 2M SO_4^{2-}/ γ-Al_2O_3 catalysts

a- Fresh catalyst
b- Catalyst after 1st run
c- Catalyst after 2nd run
d- Catalyst after 3rd run

5.3 Kinetics study over 2M SO_4^{2-} / Al_2O_3 catalyst

Studies on reaction kinetics for glycerol acetylation are not commonly found in literature. So here, the Arrheius equation is employed to determine the rate constant at different temperatures, estimate order of the reaction and determine the activation energy for the reaction.

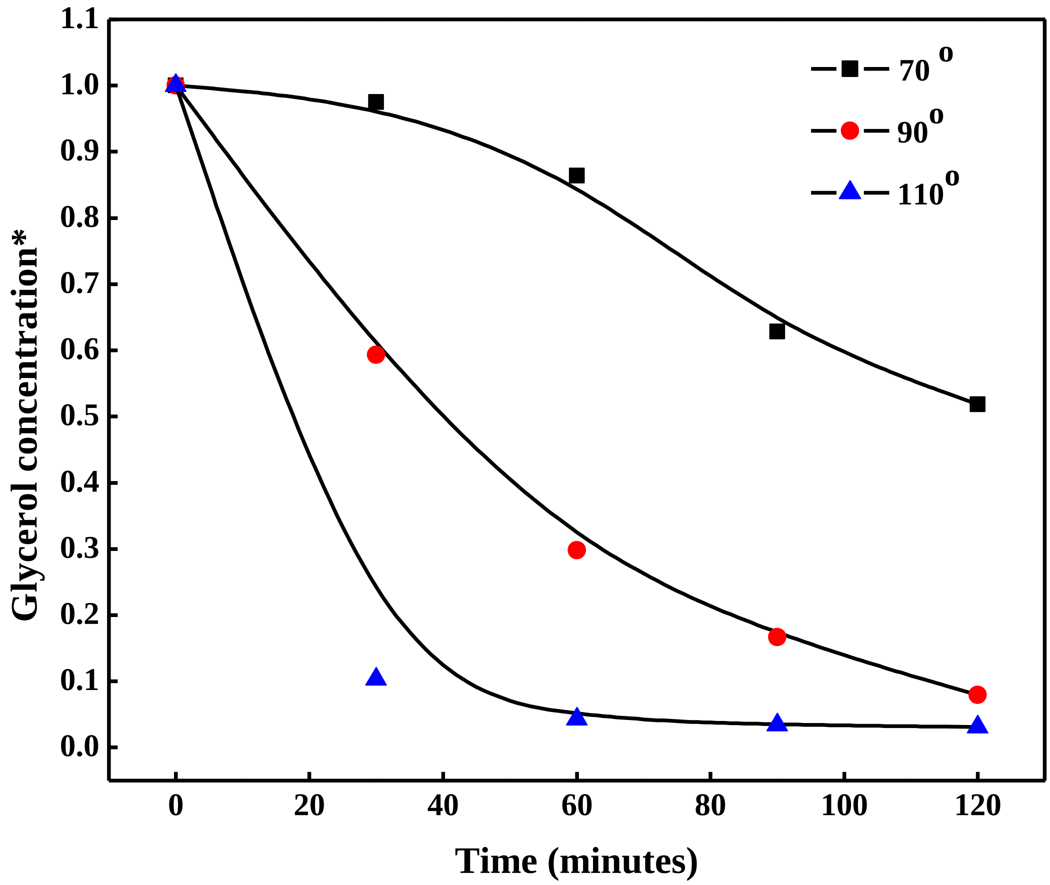

Fig. 5.16 Effect of temperature on trend of glycerol concentration with time

Reaction Conditions: Glycerol: Acetic acid (molar ratio) = 1:9, reaction time: 5h, catalyst wt.: 0.25 g

As the esterification reaction was performed by reacting glycerol (G) with excess amounts of acetic acid (A), the concentration of acetic acid can be assumed to remain constant and reaction rate is defined with respect to glycerol concentration alone. The generalized reaction rate can be expressed as

$$-rG \ = \ -\frac{dC_G}{dt} = k_1 \, C_G{}^{x} \, C_A{}^{y} \tag{1}$$

Initially, a pseudo first order reaction was assumed.

Since acetic acid (A) is present in excess, the concentration of glycerol (G) is the limiting reactant. Therefore, the reaction rate will be dependent on the concentration of glycerol and the proposed pseudo first order reaction rate can be written as follows:

$$-rG \ = \ -\frac{dC_G}{dt} = k_1 \, C_G \tag{2}$$

By integration equation 2 reduces

$$\ln\left(\frac{C_G}{C_{GO}}\right) = \ -k_1 t \tag{3}$$

The plots of ln (C_G/ C_{GO}) are obtained and represented in Fig. 5.17, where C_{GO} is the initial concentration of glycerol and C_G is the concentration of glycerol at any given time. The slope of the straight line fit to the curves is k, the rate constant for the reaction at the particular temperature.

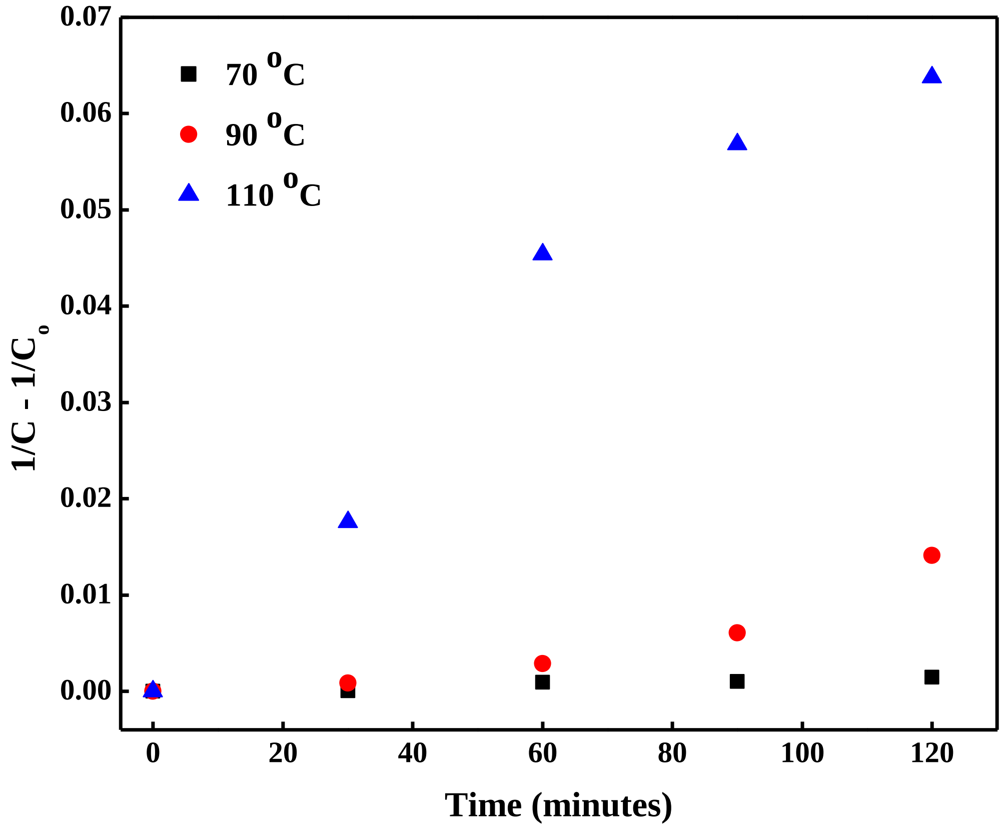

Fig. 5.17 Kinetic curved obtained from 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol at different temperatures: first order dependence to glycerol concentration

C – Concentration of glycerol

C_o –Initial concentration of glycerol

The values of rate constant (k) obtained as the slope of each plot and the linearity coefficients are listed in table 5.7

Table 5.7

Rate constant values for pseudo first order dependence on glycerol conversion

Temp (°C)	k (slope) (min $^{-1}$)	Regression
70	0.00659	0.93419
90	0.0205	0.99811
110	0.03622	0.89884

The effect of changing temperature on the rate constant was used to calculate activation energy by employing the Arrhenius equation.

$$k \ = Ae^{\frac{-E_a}{RT}} \tag{4}$$

Where, k: rate constant; A: Arrhenius constant; E_a: Activation energy, R: Universal gas constant; T: temperature

Employing the equation, it is clear that the slope of a plot of (ln k) versus 1/T will be equal to (E_a/R). The plot of (ln k) versus 1/T is shown in Fig. 5.18

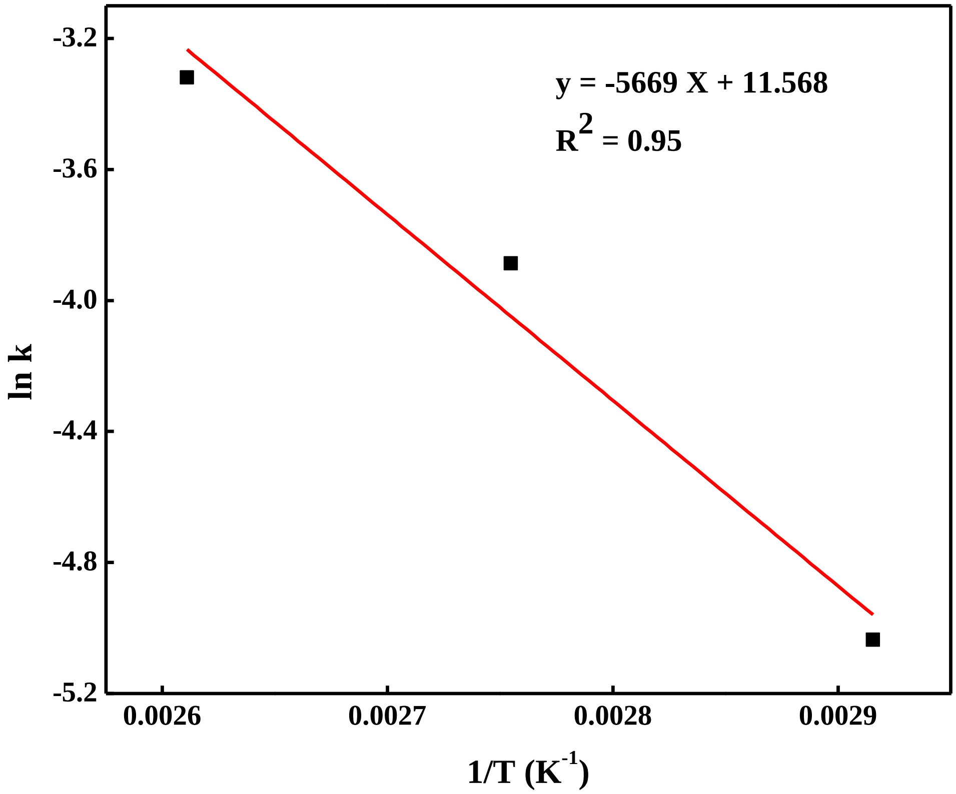

Fig. 5.18 Arrhenius plots of 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol

The activation energy of 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol was found to be 47.13 kJ mol^{-1}.

Then, pseudo second order dependence to glycerol concentration was also studied to check if second order gives better fit.

Since acetic acid (A) is present in excess, the concentration of glycerol (G) is the limiting reactant. Therefore the reaction rate will be dependent on the concentration of glycerol and the proposed pseudo first order reaction rate can be written as follows

$$-rG = -\frac{dC_G}{dt} = k_1 \, {C_G}^2 \qquad (5)$$

On integration equation 5 reduces to

$$\frac{1}{C_G} - \frac{1}{C_{GO}} = k_2 t \qquad (6)$$

The plots of ($1/C_G – 1/C_{GO}$) versus time are obtained and represented in Fig 5.19, where C_{GO} is the initial concentration of glycerol and C_G is the concentration of glycerol at any given time. The slope of the straight line fit to the curves is k, the rate constant for the reaction at the particular temperature.

The effect of changing temperature on the rate constant was used to calculate activation energy by employing the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

Where, k: rate constant; A: Arrhenius constant; E_a: Activation energy, R: Universal gas constant; T: temperature

Employing the equation, it is clear that the slope of a plot of (ln k) versus 1/T will be equal to (E_a/R). The plot of (ln k) versus 1/T is shown in Fig. 5.20

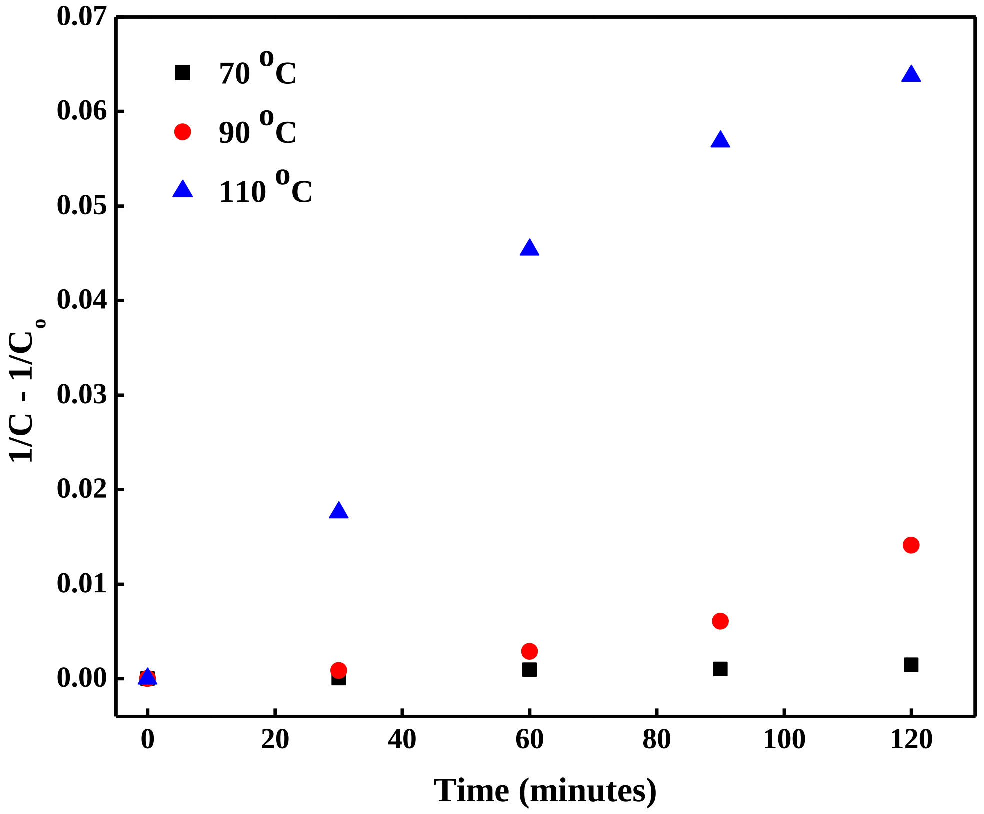

Fig. 5.19 Kinetic curved obtained from 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol at different temperatures: second order dependence to glycerol concentration

C – Concentration of glycerol

C_o –Initial concentration of glycerol

The values of rate constant (k) obtained as the slope of each plot and the linearity coefficients are listed in Table 5.8

Table 5.8

Rate constant values for pseudo second order dependence on glycerol conversion

Temp (°C)	k (slope) (lt mol^{-1} min^{-1})	Regression
70	1.19316E-5	0.95231
90	9.02306E-5	0.8727
110	5.9331E-4	0.97898

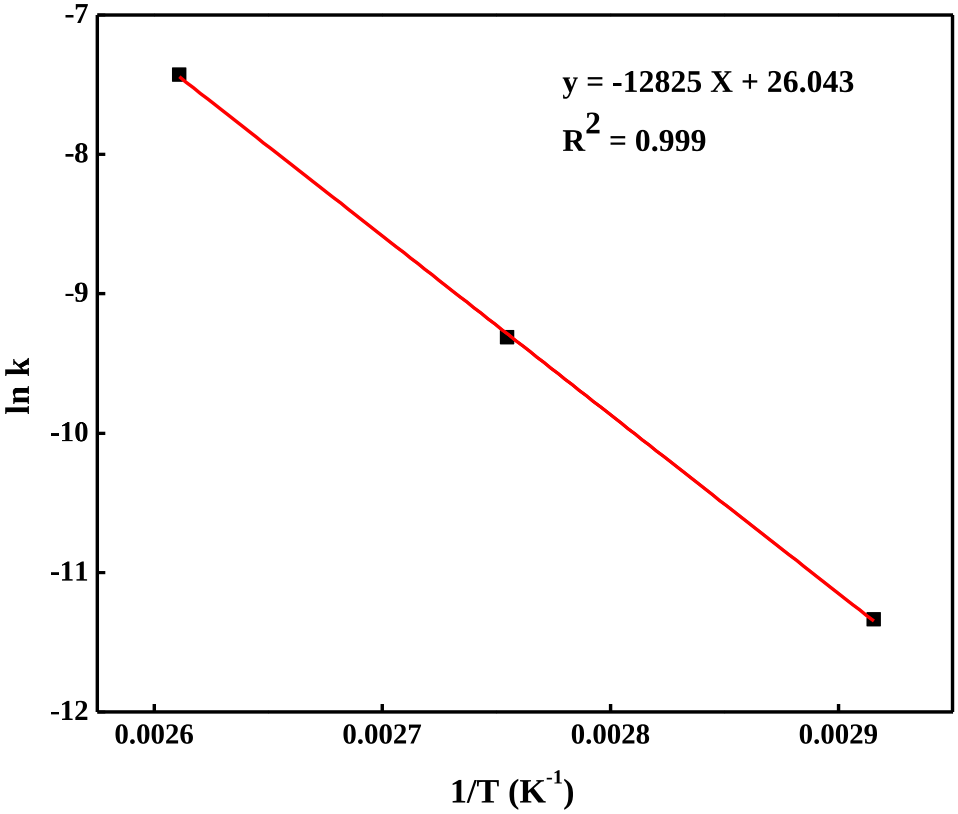

Fig. 5.20 Arrhenius plots of 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol; second order dependence

The activation energy of 2M SO_4^{2-} / Al_2O_3 catalysed esterification of glycerol was found to be 106.62 kJ mol^{-1}. This is close to the value of 101 kJ mol^{-1} reported by Zhou et al. [47].

Conclusions

This work showed that both Cu-Ni bimetallic and monometallic catalysts supported on alumina and sulfated alumina catalysts demonstrate good catalytic behavior towards acetylation of glycerol and yielded MAG, DAG and TAG as products.

The impregnation of sulfate group on alumina was confirmed by the presence of the bands corresponding to sulfate group in the FT-IR spectra and the peaks corresponding to sulfate groups in the XRD patterns. Impregnation of sulphuric acid resulted in decrease of BET surface area of alumina. The NH_3- TPD study showed that 2M SO_4^{2-} / Al_2O_3 catalysts were more acidic than alumina and 2M SO_4^{2-} / Al_2O_3 was the most acidic catalyst.

For the Cu-Ni monometallic and bimetallic catalysts, activity was found to increase with increase in Ni content on the catalyst, and Cu-Ni (1:3)/ Al_2O_3 and Ni/ Al_2O_3 catalysts were found to be the most active, resulting in 97% glycerol conversion and 2.5% and 2.6% selectivity respectively to TAG. All SO_4^{2-} / Al_2O_3 catalysts were very active, giving greater than 85% glycerol conversion within one hour of reaction and 97% after three hours. Overall, 2M SO_4^{2-} / Al_2O_3 catalyst was found to be the most active catalyst resulting in a glycerol conversion of 97% within 2 hours of reaction and TAG selectivity of 23% after five hours of reaction. In case of sulfated alumina catalysts, initially, catalytic activity was increased with increasing sulfuric acid concentration used for impregnation, and then it was decreased with further increase in concentration. The trends in activity of the catalysts can be explained by the acidity of the catalysts, activity increases with acidity. The sulfated alumina catalysts showed better selectivity to TAG compared to other catalysts.

It was found that the rate of reaction increased with increase in reaction temperature. Kinetic measurements showed that the dependence of the reaction rate to glycerol concentration was pseudo second order. The activation energy of the 2M SO_4^{2-} / Al_2O_3 catalysed reaction was found to be 100 kJ mol^{-1}.

Stability of the catalysts was tested by conducting reusability tests with three consecutive runs. For Ni/ Al_2O_3 catalyst, the glycerol conversion dropped from 97% with fresh catalyst to 88% after the third run. The loss in activity could be due to leaching of metal in acidic medium.

However, with 2M SO_4^{2-} / Al_2O_3 catalyst, there was no loss in activity was observed even after three consecutive runs and the catalyst can be considered stable for the esterification of glycerol with acetic acid.

Future recommendations:

- Sulfated alumina catalysts can be further tested to study effect of parameters like temperature (greater than 120 °C), molar ratio of acetic acid to glycerol and catalyst loading.
- This reaction may be further tested for 100% glycerol conversion with different catalysts.
- Derivation of kinetic model to estimate values of kinetic and thermodynamic parameters.

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