ESTERIFICATION OF ACRYLIC ACID WITH 2-ETHYL HEXANOL OVER SULFATED FERUM PROMOTED ZIRCONIA

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ABSTRACT

Acrylate polymer belongs to a group of polymers which could be generally referred as plastics. 2-ethyl hexyl acrylate, in which when it is polymerized, it becomes an ingredient in paints, coatings, textiles, adhesives, plastics and many other applications. Homogeneous acid commonly used as reaction catalysts are toxic, corrosive and difficult to be removed from the reaction medium while solid catalysts are easier to be removed and recycled from the reaction products. This will make the reaction process longer and reduce the waste production which gives environment and economic value to nature and industry respectively. The research objective is to determine the effectiveness of heterogeneous catalyst, sulfated ferum promoted zirconia (ZFS) in catalyzing esterification of acrylic acid with 2-ethyl hexanol to produce 2- ethyl hexyl acrylate (2EHA). The research needs to determine the maximum reaction condition for 2EHA esterification reaction and catalyst characterization using XRD, TGA and FTIR. Sulfated Ferum Promoted Zirconia shows the presence of tetragonal phase shape from XRD analysis which is a crystal shape and proved that the catalyst produces is ZFS. Thermal stability studies using TPD shows that the catalyst is stable to catalyze the reaction up until 570°C with total decomposition of 11.89 % (1.081mg). FTIR analysis show the presence of component of S=O region which is known as pyrosulfates group and OH group where the reaction conversion depends on the presence of these group. From the reaction analysis, the best reaction condition for esterification of 2-Ethyl Hexyl Acrylate using Sulfated Ferum Promoted Zirconia catalyst is 90ºC for 8 hours with 1:3 acrylic acids to 2 ethyl hexanol molar ratio using 1.5wt% catalyst loading. The reaction conversion from this reaction condition is 77.22%.

ABSTRAK

Polimer acrylate adalah sebahagian dari kumpulam polimer yang kebiasaaanya dirujuk sebagai plastik. 2 ethyl hexyl acrylate (2EHA) apabila dibentuk kepada bentuk polimer, menjadi bahan utama dalam pembuatan cat, lapisan pelindung, bahan tekstil, bahan kimia pelekat dan plastik. Asid homogenus yang biasa digunakan dalam pemangkin industri sangat toksik dan mengakis malah sukar dipisahkan dari bahan reaksi tindak balas semasa proses, juga sukar untuk digunakan semula. Ini menyebabkan kesan terhadap alam sekitar dan memanjangkan masa proses penghasilan sesuatu produk dalam industri, malah menyebabkan kerugian dari segi ekonomi dan penghasilan hasil buangan yang berbahaya. Objektif penyelidikan ini adalah bertujuan untuk mencari titik optimum keadaan tindakbalas untuk menghasilkan ester 2EHA seperti suhu,masa tindak balas, peratus berat pemangkin dan nisbah molar serta menganalisa karekter pemangkin menggunakan analisa analitikal seperti *X-Ray Diffraction* (XRD), *Thermogravimetry Analysis* (TGA) dan *Fourier Transform Infrared* (FTIR). Keputusan analisa mendapati, pemangkin yang dihasilkan adalah dalam keadaan kristal dan mempunyai fasa tetragonal yang mana membuktikan pemnagkin yang dihasilkan ialah Sulfated Ferum Promoted Zirconia (ZFS) seperti yang dirujuk di kenyataan literatur. Kestabilan therma dapat dilihat dan keputusan menunjukkan pemangkin dapat bertindak denagn stabil sehingga suhu mencecah 570°C dengan kehilangan peratusan sebanyak 11.89% (1.081mg). Ujian FTIR menunjukkan kehadiran kumpulan *polysulfates* S=O dan OH yang mana kumpulan ini berperanan dalam memangkinkan tindak balas kimia. Hasil dari ujian pengesteran, kondisi terbaik untuk menjalankan esterifikasi dari kajian ini ialah pada suhu 90°C selama 8 jam, 1:3 nisbah asid kepada alcohol dan 1.5% berat pemangkin digunakan. Kadar peratusan penghasilan ester dari kondisi terbaik itu ialah 77.22 %.

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%	percentage
T_m	melting temperature
rpm	rotation per minute
µL	Micro litre
g	gram
mL	millilitre
˚C	degree celcius
Ppm	part per million

LIST OF ABBREVIATIONS

2EHA	2-Ethyl Hexyl Acrylate
ZFS	Sulfated Ferum Promoted Zirconia
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatoghraphy
TGA	Thermogravimetry Analysis
TFA	Trifluoroacetic Acid
WZ	Tungsted Zirconia
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the decade, polymer remains in production industry due to extraordinary range of properties of polymeric materials. This role ranges from natural biopolymers to familiar synthetic plastics and elastomers. Polymer plays an essential and ubiquitous role in everyday life. Wide applications of the polymer make the polymer still relevant with the world demand, which initiates the development and improvement of polymer. Acrylate polymer belongs to a group of polymers which could be generally referred as plastics. Acrylate ester monomer is commonly used in the production of copolymer and homopolymer.

Ester are widely used in industry such as polymer production and derived from reaction of an oxoacid with a hydroxyl compound such as an alcohol or phenol. Low molecular weight of ester is commonly used as fragrances. Ester chemical formulas typically written in the format of RCO_2R' where R and R' are the organic parts of the carboxylic acid and alcohol respectively.

Acrylic acid has served for more than 30 years as an essential component in the production of some of most commonly used industrial and consumer products, where two-thirds of the acrylic acid manufactured in the United State is used to produce acrylic ester such as methyl acrylate, butyl acrylate, ethyl acrylate and 2-ethyl hexyl acrylate, in which when it is polymerized, it becomes an ingredient in paints, coatings, textiles, adhesives, plastics and many other applications (Gerlinde*et al*., 2007). 2-Ethyl Hexyl Acrylate is one of the acrylate produced through the reaction of acrylic acid with 2- Ethylhexanol and is a highly demand acrylate by industry due to multiple uses in polymer production.

In several applications, for example pressure-sensitive adhesives, Poly (2-Ethyl Hexyl Acrylate) (P2EHA) is used, because of its low T_g value of 50ºC, good oil resistance and adhesion to various substrates. Moreover, it is polar compared to elastomers based on hydrocarbons (Kris *et al.*, 2006). T_g is glass transition temperature that is a transition of liquid to solid like state may occur with either cooling or compression and always lower than the melting temperature, T_m. Other example of 2-Ethyl Hexyl Acrylate are pharmacological product, industrial coatings, agricultural coatings, graphic paper, acrylic fibers for floor covering and clothing, flocculants, dispersants, anti-scalants and acrylates binder.

1.2 Problem Statement

A conventional production of ester usually uses strong basic or acidic solution such as NaOH, KOH and H_2SO_4 as catalyst. These are homogeneous catalysts. The homogeneous catalysts widely are used in industry for decades, are strong mineral acid or basic and the reaction proceeds in liquid phase at moderate temperature and at moderate pressure.

However, these homogeneous acid catalysts are toxic and corrosive. Moreover, they are difficult to be removed from the reaction medium. The challenge is actually to replace them by other acid catalysts due to these considerations and pollution problems, and solid catalysts are easier to be removed from the reaction products and to recycle (DuPont *et al.,* 1996).

To have an easier separation of the products and a more facile regeneration of used catalysts, replacement of soluble acids by solid catalysts such as acidic resins Amberlysts or acidic salts of $H_3PW_{12}O_{40}$ was a quite attractive alternative (Essayem *et al.,* 2007). Therefore, heterogeneous solid acid catalyst is more frequently used since it is easier to be handled and easy to be separated from products. Solid heterogeneous catalyst does not only reduce the overall production costs but also environmental-friendly. The implementation of environmental-friendly heterogeneous solid catalysts is preferable to eliminate the drawbacks being associated with homogeneous catalysts such as corrosiveness, production of waste and energy intensive separation operations.

The shortcoming in the production of 2-ethyl hexyl acrylate is the use of homogeneous catalyst; sulphuric acid which is commonly used in industry is toxic, corrosive and difficult to be removed from the reaction medium. In this study, heterogeneous solid acid catalyst; sulphated zirconia are used to convert the raw material into 2-ethl hexyl acrylate (2EHA). The raw materials used are Acrylic Acid and 2- Ethylhexanol. The sulfated zirconia with promoted ferum is used in this study based on the previous study which mentioned that this catalyst can be avoided from the fast deactivation of catalyst.

1.3 Statement Of Objective

The objective that needs to be achieved in this research is:

- To determine the effectiveness of heterogeneous catalyst, sulfated ferum promoted zirconia (ZFS) in catalyzing esterification of acrylic acid with 2-ethyl hexanol.

1.4 Research Scopes

A scope is proposed for this study in order to achieve the objective. The scope of research is listed as below:

- To study the effect of catalyst loading, molar ratio, reaction temperature and reaction time for sulfated ferum promoted zirconia (ZFS) in esterification of acrylic acid with 2-ethylhexanol.
- To study the sulfated ferum promoted zirconia thermal stability.
- To determine the catalyst produced is sulfated ferum promoted zirconia (ZFS) by using XRD that use in esterification of acrylic acid with 2-ethylhexanol.
- To determine the active group by using FTIR analysis.

1.5 Rational and Significant of Study

The advantages of 2- Ethylhexyl Acrylate polymer are its flexibility, weather ability, adhesion, internal plasticization, resistance to abrasion and oils or greases and range of hardness.

To fulfil the demand of 2-Ethylhexyl Acrylate, this ester must be able to be produced in high quantity with high quality at a short range of time but at a low cost as possible and apply the awareness of environment pollution. As explained, production of 2-Ethylhexyl Acrylate will commonly use sulphuric acid as catalyst in esterification process, but it is toxic, corrosive and hard to be removed from the reaction medium. Then, sulphated ferum promoted zirconia is introduced for this esterification process as heterogeneous catalyst to improve the production performance. Solid catalyst is easier to be removed from the reaction products and to be recycled. Fe is introduced as promoter to sulfated zirconia and the research has shown that improvement in its resistance to deactivation.

Heterogeneous catalysis affects the environment by increasing the efficiency of industrial processes. Heterogeneous catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. Heterogeneous solid catalysts are preferable to eliminate the drawbacks being associated with homogeneous catalysts such as corrosiveness. Besides, separation of the catalyst from the reaction product will reduce the total production time and this will give huge impact in the economic value to the industry due to the increasing of the 2EHA annually production amount.

According to Laura et al., (2009), Sulfated Zirconia can be recycled several times without significant loss of activity and it is highly stable which could open the possibility for an environmental friendly catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Acrylic acid and esters are perhaps the most versatile series of monomers for providing performance characteristics to thousands of polymer formulations. Their performance characteristics which impart varying degrees of tackiness, durability, hardness and glass transition temperatures promote consumption in many end-use applications. Major markets for acrylate esters include surface coatings, textiles, paper coatings, adhesives and sealants, and plastics and many more variety of products produced from this acrylate ester polymerization make it a highly and worldwide demand. Global demand for crude acrylic acid is forecasted to grow at 4.8% annually during 2010–2015, driven by growth in superabsorbent polymers (SAPs) at 5.6% and acrylate esters at 4.3%.

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2.2 Esterification

Esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. Esters can also be formed by other reactions such as reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-O-COR'). Common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing the water that is formed. In this research, 2- Ethylhexyl Acrylate is produced by reaction of acrylic acid that is simplest unsaturated carboxylic acid with 2- Ethylhexanol or isoethanol, a fatty alcohol. Esterification of acrylic acids is a fundamental step in producing 2-Ethylhexyl Acrylate, an ester that is used in the production of homopolymer and copolymer. Figure 2.1 shows the reaction equation for esterification process of acrylic acid with 2-ethyl hexanol.

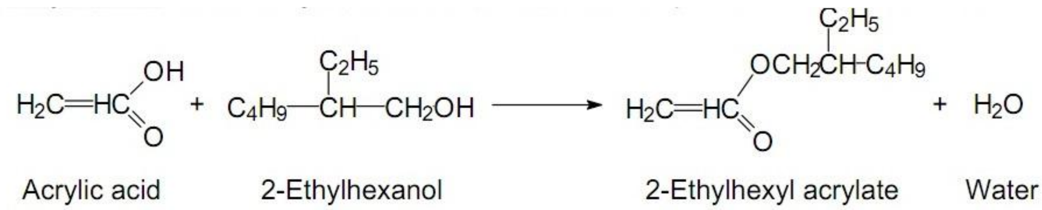

Figure 2.1 Esterification of Acrylic Acid with 2-ethyl hexanol

Early studies into the chemical mechanism of esterification, concluded that the ester product (R-CO-OR') is the union of the acyl group (R-C=O-) from the acid, RCO-OH, with the alkoxide group (R'O-) from the alcohol, R’-OH rather than other possible combinations.

Esterification of secondary alcohol is much more difficult to be achieved compared to primary alcohol. Lower nucleophilicity of oxygen atom and steric effect of these substrates hinder the formation of the corresponding ester. Slow reaction rates and reversible reaction may limit the conversion. (Bhorodwaj*et al.* 2010)

According to Kuriakose et al. (2004), in the presence of aromatic alcohol, selective esterification of bifunctional carboxylic is a useful organic synthesis reaction. The esters obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics.

Esterification is a reversible reaction that therefore, the reactions are equilibrium reactions and needed to be driven to completion according to Le Chatelier’s principle. Esterifications are among the simplest and most often performed organic transformation. According to Kuriakose et al. (2004); esterification of acrylic acid with but-1-ene over sulfated Fe and Mn promoted zirconia, Mn and Fe did not improve the catalytic properties of sulfated zirconia as far as activity and selectivity to sec-butyl acrylate (90–95%) are concerned but strongly improved its resistance to deactivation.

2.3 Catalyst

Catalyst is used in the esterification process to enhance or accelerate chemical reaction process. Catalysts can be divided into two types, homogeneous catalysts such as such as sulphuric acids (H_2SO_4), sodium hydroxide (NaOH) and hydrochloric acids (HCl), heterogeneous catalyst such as solid acid catalysts sulfated zirconia (ZS), zeolites, alumina and resins.

There is other type of catalyst, autocatalysis that only occurs when a single chemical reaction whose reaction product is itself the catalyst for the reaction. Autocatalysis reactions' reaction velocity is much compliance to be influenced by the reaction temperature, in other words, the pressure plays a proportion role to the effect of temperature of equipment.

Reactions involving heterogeneous catalytic reaction commonly occur at the interface between the solid catalyst and the fluid or gas phase. The overall reactions can be broken down into the sequence of individual steps shown in Figure 2.2.

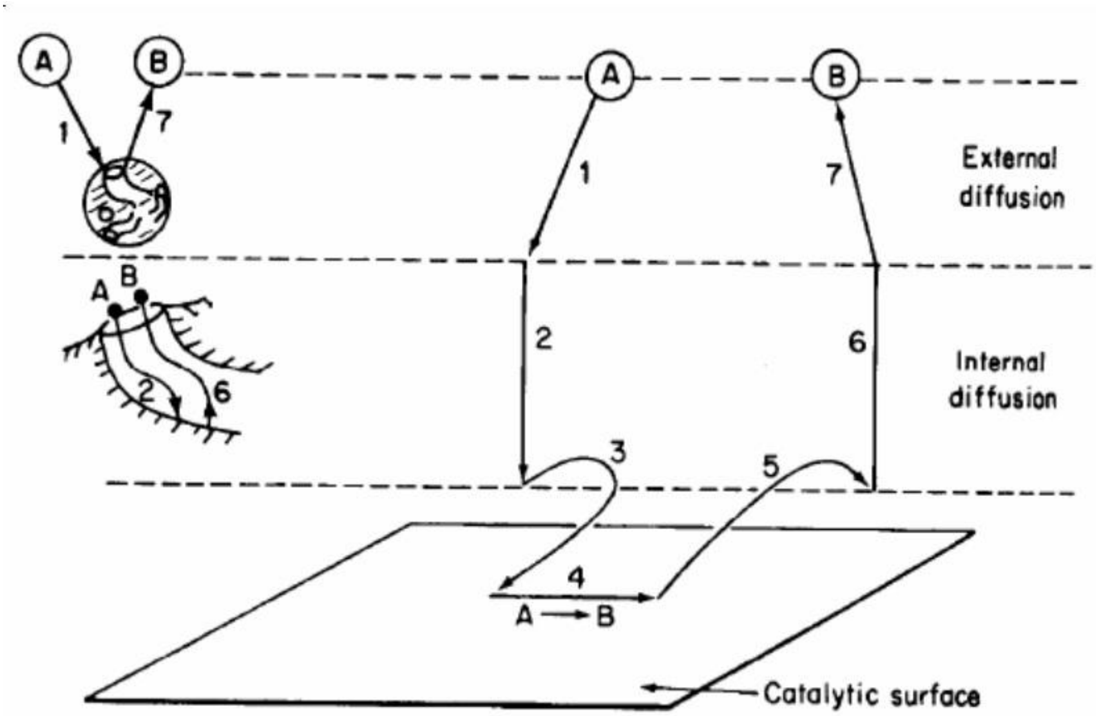

Figure 2.2 Steps in a heterogeneous catalytic reaction

The reactions are catalyzed in the steps involving external diffusion, internal diffusion, desorption and adsorption. The reactant from the bulk fluid will diffuse (mass transfer) to the surface of the catalyst. Then, the reactants will diffuse from the pore mouth, through the catalyst pores, to the immediate vicinity of internal catalytic surface. The adsorption happens to the reactant on the catalyst surface followed by reaction process. After the reaction takes place, the product will be removed from the catalyst surface in desorption process and further diffuse through the interior of the catalyst to the pore mouth at the external surface. The mass transfer of the reactant occurs from the external surface back into the bulk fluid. These processes explain about the steps in Figure 2.2.

2.3.1 Homogeneous Catalyst

Homogeneous catalysis is a chemistry term describing a catalyst which is in the same phase (solid, liquid or gas) as the reactants. According to Lotero et al (2005), currently, homogeneous catalyst is most used because it is cheaper as compared to the solid catalyst. Homogeneous catalysts can be categorized into two types which are acid catalyst and base catalyzed. Most people prefer to use homogeneous acid catalyst since it is faster (4000 times) than homogeneous base catalyst.

These are the example of acid catalyst and base catalyst:

Base catalysts:

Sodium hydroxide (NaOH), potassium hydroxide (KOH

Acid catalysts:

Sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), calcium carbonate ($CaCO_3$)

Performance comparison between various homogeneous acid catalysts such as sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid is done by Donato et al. (2007). Sulfuric acid and methanesulfonic acid have the conversion rate over 80%. Comparing sulfuric acid to the methanesulfonic acid in term of price and availability, sulfuric acid is more preferable. However, some concerns about these catalysts are they might be harmful to the environment if not treated carefully. Besides, homogeneous catalysts are hard to be separated since the product has to undergo separation process because the product and the catalyst are mix together. Although effective, the homogeneous catalysts suffer from several drawbacks, such as the existence of side reaction with reactant, corrosive nature.

Commonly, heterogeneous catalysts are more preferred than homogeneous catalyst. Heterogeneous catalyst is preferred and beneficial as the catalyst can be regenerated thus reduces the catalyst cost, utilization of lower quantity feed stocks for acrylate production, simplification of separation process thus reduces capital cost, as well as the decrease in wastewater which develops environmental friendly process.

2.3.2 Heterogeneous Catalyst

Fundamentally, heterogeneous catalysis is basically a catalyst in a different phase to the reactants. Separation of catalyst and products is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.

From previous studies by KuYu *et al*., (2009), the esterification is done using ethanol and acetic acid over rare earth oxide and alumina promoted sulfated zirconia (SZ). In their findings, both surface area and pore diameter of the SZ catalysts after being promoted with rare earth oxide and alumina were significantly enhanced. Only tetragonal ZrO_2 (zirconia) crystal phase was formed for all samples. While the synthesis process of ethyl acetate by the esterification of ethanol and acetic acid occurs, the catalytic activity of the SZ catalyst could not be promoted by only doping with rare earth oxides, including La_2O_3, Ce_2O_3 and Yb_2O_3. However, double promotion with Yb_2O_3 and Al_2O_3 could greatly enhance the catalytic activity and stability of the SZ catalysts. Their work shows that changes in catalyst activity were in close correlation with variations of the amount of moderately strong and super strong Lewis acidity. The loss of sulphur species by solvation and coking during the reaction led to the catalyst deactivation. Solvation is the process of attraction and association of molecules of a solvent with molecules or ions of a solute.

Previous research about the esterification of free fatty acid, caprylic acid with ethanol is about to determine the effect of three different solid acid catalysts in esterification process. Three different solid acid catalysts that have been used are sulfated zirconia, tungstated zirconia and titania zirconia. The study shows that sulfated zirconia catalyst was found to be the most active for this reaction. However, its activity was not easily regenerated. Meanwhile, titania zirconia and tungstated zirconia have greater activity in esterification and it is easier to regenerate compared to sulfated zirconia by recalcination in air. Thus, tungstated zirconia catalyst is a most suitable catalyst in esterification process of free fatty acid (Lopez *et al*. 2008). But, there is no previous study about esterification of acrylate using sulphated zirconia.

According to Essayem *et al*. (2007), sulfated Zirconia that is used in this esterification research between acrylic acid with 2- ethyl hexanol, presents a potential interest due to its characteristics which are strong acidity, active as resins, besides, it is more selective. However, previous studies observe that sulphated zirconia deactivate rapidly, which preludes its use to replace Amberlyst resin. Study complemented with theoretical calculations allowed us to suggest that sulfated zirconia is as a very strong acid such as 100% sulfuric acid that make it able to compete with sulphuric acid which is a popular catalyst. Sulfation of other oxides such as iron oxide or alumina was also found to deeply increase their acidic strength but to a much lesser extent from the previous study. The found out that Mn particularly and Mn–Fe are active promoters not in the sense ofbetter activity but in the sense of a better resistance to poisoning and deactivation. Addition of promoters to sulphated zirconia did not increase the acid strength of the zirconia.

Previous research about Effect of Mn and Fe on the Reactivity of Sulfated Zirconia explained that, as a consequence of the foreign ions in the lattice, the unit cell size shrinks, and due to the lower valence of Mn or Fe in comparison with Zirconia, oxygen defects are generated in the bulk. The sulfate may become more reactive because of the change in support structure, or near-surface vacancies may act as a catalyst in the reduction process because they can accept negative charges. Electrons may also intermittently be localized at the more easily reducible promoter ions (Klose *et al.,* 2005). Definitely, the promoters enhance the oxidation potential of sulfate.

Table 2.1 shows the summaries from the previous studies that relate to the solid catalyst research.

Table 2.1 Summary from previous studies that relate to solid catalyst research and esterification research.

REACTION/ RESEARCH	CATALYST	FINDING	AUTHOR
Effect of Mn and Fe on the Reactivity of Sulfated Zirconia toward H2 and n-Butane	Sulfated Zirconia (SZ)	Manganese or irons do not enhance the Brønsted acid strength of SZ.Promotersthus do not improve the hydride abstraction or protonationability of the catalyst	Klose *et al* (2005)
Esterification of acrylic acid with but-1-ene	Sulfated Fe and Mn Promoted Zirconia	Mn and Fe did not improve the catalytic properties of sulfated zirconia, but strongly improved its resistance to deactivation	Essayem *et al.*, (2007)
Esterification and transesterification on tungstated zirconia	Tungstated Zirconia (WZ)	Tungstated Zirconia exhibited optimum catalytic activity after being calcined at T= 800ºC.	Lopez *et al*.,(2007)
Esterification of dodecanoic acid with 2-ethylhexanol	Sulfated Zirconia (SZ)	SZ catalyst is not deactivated by leaching of sulphate groups when trace amounts of water is present in the organic phase and easily hydrolysed in free water.	Omota *et al*., (2003)
Esterification of ethanol and acetic acid	Rare earth oxide and alumina promoted sulfated zirconia	Both surface area and pore diameter of the sulphated zirconia catalysts after promoted with rare earth oxide and alumina were significantly enhanced	KuYu*et al*., (2009)

Esterification of acrylic acid with 1-butanol	Solid Oxides: $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (I), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (II), WO_3ZrO_2, TiOSiO, $SiO_2Al_2O_3$; Organic Resin: Amberlyst 15 , Amberlite 200C, Nafion-H, Nafion-SiO2; Liquid Catalyst: $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, H_2SO_4	Amberlyst and mordenite gave lower values of the rate constant. The higher activities per unit proton of $Cs_{2.5}$ and Nafion are probably due to the superacidity. Besides acidity, the specific reaction rate may depend on the acid sites such as hydrophobicity	Chen *et al.*,(1999)
Esterification of Acrylic Acid and Methacrylic Acid with Olefin Oxides Catalyzed	Nitroxyl mono or poly-radical	Nitroxyl radical are effective and selective catalyst and also are inhibitors of polymerization of the starting materials and final product.	Radugina *et al.*, (1988)
Esterification of propanoic acid by butanol and 2-ethylhexanol	Carbon supported heteropolyacids and heteropolyacids pure	The recycling of these catalysts has shown that a deactivation occurs, due to the redissolution of the polyanion in the reaction medium.	DuPont and Lefebvre (1996)
Esterification of phthalic anhydride with 2-ethylhexanol	Sulfated zirconia and supported Heteropolyacids	The superacidicsulphated zirconia and supported HPAs were found to be efficient catalysts for the present esterification reaction	Thorat *et al.*, (1992)
Esterification of butyl hexanol with acrylic acid	Sulfated zirconia & Zirconia Phosphate	Crystallin phase catalyst have good thermal and chemical resistivity. Sulfated Zirconia	Patel et al.,(2008)

		is very good solid catalyst and it is easily deactivated by losing sulphate ions.	