SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF MICRO-MESOPOROUS INORGANIC SOLIDS FOR BIOLUBRICANT PREPARATION

A THESIS
SUBMITTED TO THE
UNIVERSITY OF PUNE
FOR THE DEGREE OF
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IN
CHEMISTRY

BY

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UNDER THE GUIDANCE OF
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CERTIFICATE

This is to certify that the thesis entitled ***"Synthesis, Characterization and Catalytic Activity of Micro-mesoporous Inorganic Solids for Biolubricant Preparation"*** submitted by ***Mrs. Mehejabeen Shaikh,*** for the degree of ***Doctor of Philosophy*** in ***Chemistry,*** was carried out under my supervision at Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune – 411 008, India under the Faculty of Science of University of Pune. Such material obtained from other sources has been duly acknowledged in the thesis.

Date: **Dr. D. Srinivas**

Place: Pune Research Guide

DECLARATION

I hereby declare that the work described in the thesis entitled "***Synthesis, Characterization and Catalytic Activity of Micro-mesoporous Inorganic Solids for Biolubricant Preparation***" submitted for the degree of ***Doctor of Philosophy*** in ***Chemistry*** to the University of Pune, has been carried out by me at the Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune – 411 008, India, under the supervision of ***Dr. D. Srinivas***. I further declare that the material obtained from other sources has been duly acknowledged in this thesis. The work is original and has not been submitted in part or full by me for any other degree or diploma to this or any other university.

Date: **Mrs. Mehejabeen Shaikh**

Place: Pune Research Scholar

dedicated to my parents……

the best parents a daughter could have…

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General Introduction

1.1. Renewable Energy: Rationale and Significance

Renewable energy has been highlighted in the last ten years due to its potential to replace fossil fuel (especially for transportation). Renewable energy sources such as solar energy, wind energy, hydro energy and energy from biomass and waste have been successfully developed and used by different nations to limit the use of fossil fuels. The overly consumed fossil energy in the past has caused energy crisis and environmental pollution. Fossil fuels account over 80.3% of the primary energy consumed in the world, and 57.7% of that amount is used in transportation sector [1]. Non-renewable fossil fuels have limited sources and are depleting fast under the pressure of high energy and fuel demand. Carbon dioxide emission from fossil fuels is another issue contributing to the global warming. These consequences have motivated worldwide research in developing economic and energy-efficient processes for the sustainable production of transport fuels and chemicals. Fig. 1.1 shows the statistics of energy derived from various renewable and fossil fuel resources [2].

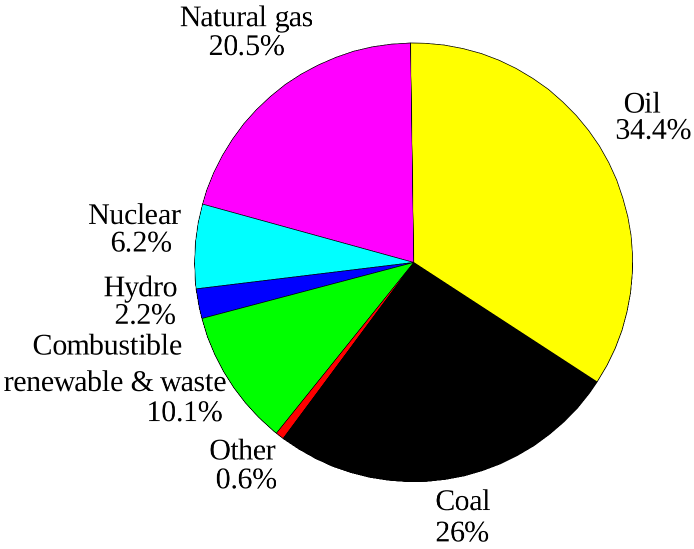


Fig. 1.1. Energy from renewables [2]

Bio-energy is one of the renewable energies, which generally comes from bio-materials of hydrocarbon, e.g. plants. The most early studies on bio-energy were focused on developing bio-materials as fuel, e.g. biodiesel, biolubricant, alcohol–gasoline blends and so on, which are technically skillful today [3, 4]. Biolubricant, a renewable form of energy, consisting of long-chain alkyl esters of fatty acids derived from sources such as vegetable oils and animal fats, has an important potential as alternative fuel [5, 6]. Synthetic lubricants, solid lubricants and vegetable oil-based lubricants are the alternatives to the petroleum-based lubricants, and they are currently being explored world-wide by the scientists and tribologists [7]. Generally, lubricants are solutions or colloids having functional additives, which improve the lubrication properties. Animal oils, vegetable oils, synthetic esters and mineral oils are the examples of modern lubricant base fluids. An excellent lubricant base fluid should have low volatility, excellent heat and oxidative stability, good cold fluidity and high viscosity index.

1.2. Historical Development of Lubricants

Mankind has used lubricants from the early days of civilization to reduce the friction between two moving objects [8]. Grease and oil have been utilized as lubricant in early 2400 B.C. and liquid lubricant was used for transporting sledges in the Sumerian and Egyptian civilizations [9]. From the first century A.D., animal fats and vegetable oils were the principal lubricants used in machinery such as lathes, pulleys and gears [10]. During the period of industrial revolution around 1760, heavy industrial iron and steel machinery were widely introduced. Animal oils such as whale oil and vegetable oil from sources such as palm and groundnut oil saw increased use as lubricants. During this period, mineral oil obtained from the distillation of coal was developed for use as a lubricant. Graphite and talc were also used as a solid lubricant for sliding surfaces. In the 1850s, small quantities of petroleum oil were produced in United States, Canada, Russia and Romania. Petroleum production from oil wells in the United States increased substantially by the 1880s [11].

1.3. Lubricants and their Consumption

By definition, lubricant is a substance introduced to reduce friction between moving surfaces. They are used to decrease friction and wear, protect from corrosion, act as sealants and affect heat transfer. Most of the lubricants are made from mineral oil and some are synthetic chemicals. About 8 million tons of lubricants are consumed every year worldwide (Fig. 1.2). Out of that, 53% is collected as waste, thus, endangering our planet. The use of rapidly degradable lubricants instead of the conventional petroleum-derived lubricants could significantly reduce this environmental pollution.

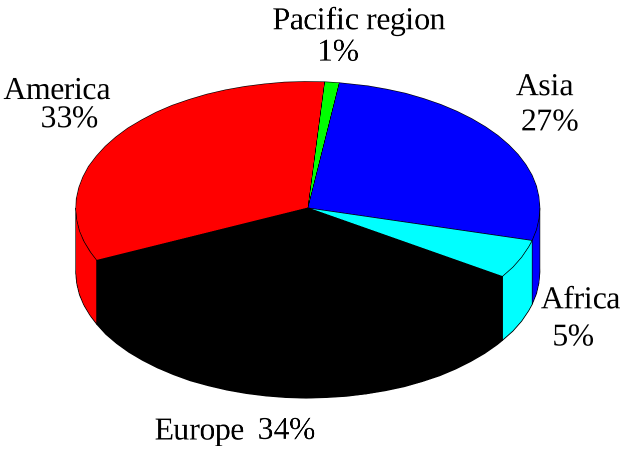


Fig. 1.2. Worldwide consumption of lubricants [12]

Modern lubricants are generally composed of more than 80% base oil and a smaller amount of functional additives [10]. Lubricant properties such as oxidative stability, low-temperature flow properties and lubricity depend on base oil. There are three categories in base oils: mineral oils, synthetic oils and vegetable oils. Traditionally, over 85% of base oils are refined from crude petroleum [13, 14]; however, with decreasing petroleum reserves, growing environmental pollution and high costs of synthetic lubricant, vegetable oils are considered to be potential candidates to supply high quality lubricant base oil for lubricant production. Vegetable oils are the most important renewable raw material for the chemical industry (e.g., in Germany 30% of the 2.7 million tons of renewable raw materials in 2005 were plant oils and heavily used as raw materials for surfactants, cosmetic products, and lubricants [15]. They are also used in paint formulations, as flooring materials and for coating and resin applications [16, 17]. Vegetable oils have several advantages over other raw materials, as they are readily available, relatively low cost, renewable and environmentally friendly. A good lubricant should have the following characteristics.

- High boiling point
- Low freezing point
- High viscosity index - viscosity, which doesn’t vary with temperature as much as mineral oil
- Thermal stability
- Corrosion prevention
- High resistance to oxidation

1.4. Types of Lubricants

Lubricants are generally composed of a majority of base oil plus a variety of additives to impart desirable characteristics. Lubricants are classified into various types.

1.4.1. Solid Lubricants

Grease or Polytetrafluoroethylene (PTFE) is typically used as a coating layer on, for example, cooking utensils to provide a non-stick surface. Teflon tape is used in plumbing, air cushioning and others. Graphite, hexagonal boron nitride, molybdenum disulfide and tungsten disulfide are examples of materials used as solid lubricants, often to operate at very high temperatures. Cadmium and gold are used for plating surfaces which give them good corrosion resistance and sliding properties. Lead, tin, zinc alloys and various bronze alloys are used in sliding bearings. Their powders, alone or as additives, can be used to lubricate sliding surfaces.

1.4.2. Aqueous Lubrication

Aqueous lubrication is of interest in a number of technological applications. Strongly hydrated brush polymers such as PEG can act as lubricants at liquid-solid interfaces.

1.4.3. Base Oil

Lubricants are generally composed of a majority of base oil.

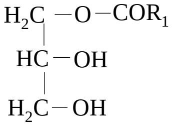
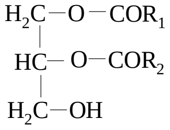
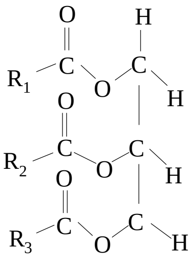
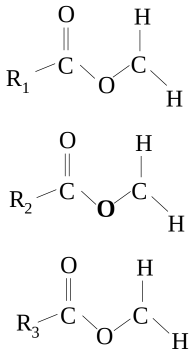
1.4.3.1. Refined Mineral Base Oils. A mineral oil is colorless, odorless, light mixtures of alkanes in the C20 to C50 range from a non-vegetable (mineral) source, particularly a distillate of petroleum. Petroleum is a natural product of decaying living organisms including plants, bacteria and animals [18]. Crude petroleum is a mixture that contains a large array of hydrocarbon molecules (such as paraffin, aromatics, cycloalkanes and alkenes) and small amounts of nitrogen, sulphur, oxygen, metal, and salt. Petroleum hydrocarbon molecules include covalently linked carbon atoms in an array of molecules with different carbon skeletons. Crude petroleum oil is refined by a number of processes that reduce the average molecular weight and remove atoms such as sulphur and nitrogen. Molecular weight reduction (cracking) and hydrogenation optimize the properties of petroleum. After cracking, groups of molecules are separated by fractional distillation; the separation of molecules is based on boiling point. The lowest boiling fraction derived from petroleum comprises small alkanes with one to four carbon atoms. These compounds are readily separated from crude oil. They can be used for heating, cooking and for synthetic precursors for plastic. Lubricating oils are typically derived from fractions that boil at temperatures between 300 and 370 ºC and typically include between 20 and 40 carbon atoms in each molecule [10]. Molecules present in these fractions include long chain alkanes, cycloalkanes and aromatic compounds.

1.4.3.2. Synthetic Base Oils. Synthetic oil is used as a substitute for lubricant refined from petroleum when operating in extremes of temperature, because it provides superior mechanical and chemical properties than those found in traditional mineral oils. In addition, synthetic oils are available with superior viscosity index and biodegradability when compared with mineral oils. Synthetic oils are categorized by their composition or their chemical structure. Typical synthetic fluids include synthetic hydrocarbons (such as polymers of olefins, chlorinated hydrocarbons, condensation products and chemically modified mineral oils), polyether oils, esters, phosphoric acid esters and oils containing silicon. Synthetic oils have many advantages when compared with crude oils; however, the production cost for synthetic oil is generally four to eight times higher than mineral oil. The higher cost limits the market for synthetic oils [19]. Nevertheless, synthesizing polyol esters of vegetable oil fatty acids might lead to a lower cost of synthetic fluid [20, 21].

1.4.3.3. Vegetable Oils. Vegetable oil can be categorized as edible and non-edible. Edible oil, such as canola, soybean and sunflower oil, are used both for human consumption but also for production of biofuels. Non-edible oil, including waste cooking oil and seed oil from *Jatropha* *curcas* is also suitable for biofuel production [22]. Historically, lubricants have been produced from both edible and non-edible vegetable oils.

Oil, ester and diesel have different number of carbon and hydrogen in the compound. Diesel has no oxygen in its composition. Petroleum-based diesel fuels have different chemical structures compared to vegetable oils and esters. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including linear, iso, and cycloparaffins) and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) [23]. The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$. On the other hand, in the case of vegetable oils, triglyceride molecules have molecular weights between 800 and 900 and are thus nearly four times larger than typical diesel fuel molecules [24]. The various vegetable oils and esters are distinguished by their fatty acid compositions. Chemical structures of oil, biodiesel and petroleum diesel are given Table 1.1.

Table 1.1. Chemical structures of oil, ester and diesel

Chemical structure of monoglyceride	Chemical structure of diglyceride	Chemical structure of fat and oil	Chemical structure of ester	Chemical structure of diesel
 $H_2C-O-COR_1$ $HC-OH$ H_2C-OH	 $H_2C-O-COR_1$ $HC-O-COR_2$ H_2C-OH			$C_{12}H_{23}$

Most vegetable oils are triglycerides (TG). Triglyceride is a triesters of glycerol where three fatty acids are linked to the three hydroxyl groups of glycerol *via* ester bonds. The physical and chemical properties of vegetable oil are largely contributed by fatty acid composition and distribution. (Table 1.2) [25]. The composition of oils is reported in terms of the fatty acid profile of the oil or fat [26]. The most important fatty acids contained in plant oils are unsaturated molecules such as oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3), as well as (saturated) palmitic acid (C16:0) and stearic acid (C18:0). At present, the most important sources for oils are rapeseed (canola), sunflower (various qualities) and soybean.

The structures of fatty acids (both chain length and degree of unsaturation) are directly related to their operational stabilities and lubricant properties such as viscosity, viscosity index and low-temperature behavior. The oxidative stability of oils increases with decreasing amounts of polyunsaturated acids. The transesterification reaction of an oil or fat with higher alcohol leads to a biolubricant which is a mixture of fatty esters with each ester component contributing to the properties of the lubricant. Therefore, it is very important and crucial to have the knowledge of fatty acid profile of oil and fat and their properties (Table 1.3) [27].

Fatty acids are classified into the following three categories on the basis of number of double bonds they contain.

1. Saturated fatty acids : Stearic acid [$C_{18:0}$], palmitic acid [$C_{16:0}$], myristic acid [$C_{14:0}$], lauric acid [$C_{12:0}$]
2. Mono-unsaturated fatty acids : Oleic acid [$C_{18:1}$], palmitoleic acid [$C_{16:1}$]
3. Poly-unsaturated fatty acids : Linoleic acid [$C_{18:2}$], linolenic acid [$C_{18:3}$]

Vegetable oils possess many desirable characteristics but are not widely used as lubricant base oils. This is due to the undesirable physical properties of most vegetable oils, which include both a high melting point and insufficient thermal oxidative stability. Compared to mineral oils, vegetable oils have different structures and properties. Vegetable oil oxidizes at a faster rate due to the presence of unsaturated fatty acids. While mineral oils consist mostly of saturated linear, branched, and cyclic hydrocarbons, vegetable oils consist of triacylglycerols with carboxylic groups on hydrocarbon chains with saturated bonds. These structural differences manifest themselves in positive and negative ways. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. However, the applicability of vegetable oils in lubrication is partly limited, as these oils tend to show low oxidative stability and higher melting points [32]. As shown in Fig. 1.3, the hydrogen atoms on the β carbon of the glycerol backbone are susceptible to elimination reactions that would lead to degradation of the molecule.

But these limitations can be minimized by means of chemical modification of oils or application of synthetic esters that may be partially derived from renewable resources. [32-35].

Table 1.2. Fatty acid profile of some common vegetable oils and animal fats [28 - 30]

Vegetable oil	Iodine value	Fatty acid composition (wt %)							
		Lauric C12:0	Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Other
Edible oils									
Soybean oil	128-143	-	-	12	3	27	52	6	-
Sunflower oil	125-140	-	-	7	5	19	68	1	-
Rapeseed oil (Mustard oil)	98-110	-	-	4	1	65	22	8	-
Palm oil	48-58	-	1	45	4	40	10	-	-
Cotton seed oil	103-115	-	1	22	3	19	54	1	-
Coconut oil	7-11	51	18	9	3	6	2	-	Capric acid (6) caprylic acid (5)
Rice bran oil	90-108	-	-	15	2	43	39	1	-
Corn (Maize) oil	103-128	-	-	2	11	28	58	1	-
Peanut / Ground nut/ Arachis oil	84-100	-	-	11	2	48	30	2	-
Non-Edible oils									
Karanja Oil	81-90	-	-	6	7	62	17	-	Eicosanoic acid (3), Dosocasnoic acid (4)
Jatropha oil	82-98	-	1	15	6	55	23	-	
Rubber seed oil	132-148	-	-	10	9	25	40	16	-
Mahua Oil	58-70	-	-	28	23	50	9	-	-
Tung oil	160-175	-	-	4	1	8	4	3	Eleostearic acid (80)
Neem oil	65-80	-	-	16	10	50	16	8	-
Animal Fats									
Chicken Fat (poultry fat)	75	-	1	23	6	42	17	1	C16:1 (8), C20:1 (2)
Fish oil (Menhaden)	167	-	11	20	3	15	2	1	C16:1 (15), C20:1 (1),C18:4 (4), C20:5(5), C20:6 (12)
Beef tallow	35-48	1	3	27	17	42	3	1	C16:1 (4), C17:0 (2)

Table 1.3. Physical properties of common fatty acids [31]

Trivial name	IUPAC name	Formula	Molecular weight (g)	Acid value (mg KOH/g)	Iodine value	M.P. (°C)	B.P (°C) (P, kPa)	Density kg/m^3 (T, °C)
			Saturated Fatty Acids					
Caprylic	Octanoic	$C_8H_{16}O_2$	144.22	389	0	16.5	239.7 (10.13)	861.2 (80)
Capric	Decanoic	$C_{10}H_{20}O_2$	172.27	325	0	31.6	195.9 (10.13)	851.8 (80)
Lauric	Dodecanoic	$C_{12}H_{24}O_2$	200.32	280	0	43.8	218.9 (10.13)	845.4 (80)
Myristic	Tetradecanoic	$C_{14}H_{28}O_2$	228.38	245	0	54.2	241.5 (10.13)	844.0 (80)
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	256.43	218	0	62.8	261.7 (10.13)	839.7 (80)
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	284.49	197	0	69.6	282.4 (10.13)	837.4 (80)
			Monosaturated Fatty Acids					
Palmitoleic	*cis*-9-Hexadecenoic	$C_{16}H_{30}O_2$	254.42	221	100	28-30	218–220 (2.0)	900.3 (15)
Oleic	*cis*-9-Octadecenoic	$C_{18}H_{34}O_2$	282.47	199	90	13.4 (α) 16.3 (β)	223 (1.33)	890.5 (20)
			Polysaturated Fatty Acids					
Linoleic	*9Z,12Z*-Octadecadienoic	$C_{18}H_{32}O_2$	280.45	200	181	- 6.8	224 (1.33)	902.5 (20)
Linolenic	*9Z,12Z,15Z*-Octadecatrienoic	$C_{18}H_{30}O_2$	278.44	202	274	-11	224.5 (1.33)	915.7 (20)

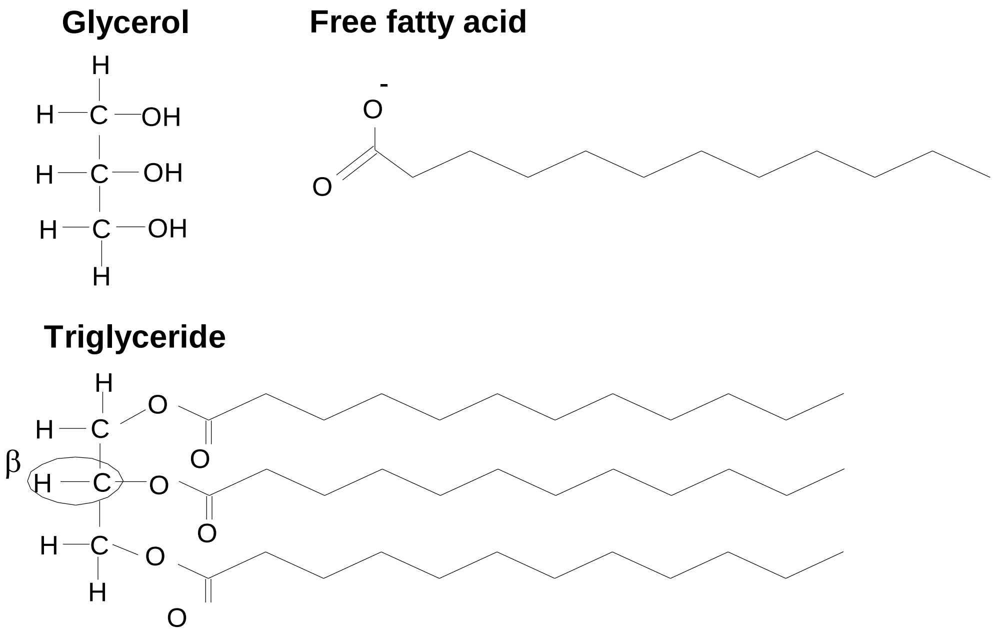


Fig. 1.3. Chemical structures of glycerol, fatty acid and triglyceride

Biolubricants formulated from plant oils should have the following advantages.

i. Higher lubricity leading to lower friction losses, yielding more power, and better fuel economy

ii. Lower volatility resulting in decreased exhaust emissions

iii. Higher viscosity indices

iv. Higher shear stability

v. Higher detergency eliminating the need for detergent additives

vi. Higher dispersancy

vii. Rapid biodegradation and hence, decreased environmental/toxicological hazards.

Esters of fatty acids are known as natural lubricating oils. These esters are valuable chemical compounds which have application in pharmaceuticals, food and cosmetics production [36]. They are also used as raw material for emulsifiers, surfactants and lubricants [37, 38]. The properties of esters depend on the structure of the constituent fatty acids and alcohols, i.e., on the length of their aliphatic chain and the number and relative position of unsaturated bonds. Glycerol, a component of the triglyceride molecule is readily destructible at high temperatures because of presence of β hydrogen atoms in the hydroxyl group of glycerol molecule. These structural features of molecule undergo partial defragmentation and form unsaturated compounds [39]. The compounds formed undergo polymerization, increasing the liquids viscosity and resulting in the formation of precipitate particles. This problem can be solved by replacing glycerol with another polyhydric alcohol which does not contain β hydrogen atoms, i.e., neopentyl glycol (NPG), trimethylol propane (TMP) or pentaerythritol (PE). Polyesters prepared from polyols, such as NPG, TMP, and PE, provide suitable lubricating properties, i.e. high viscosity indices, low pour point temperatures, high flash point, low volatility, and high thermal stability [40, 41]. NPG esters are used as lubricants in jet engines. PE derivatives of carboxylic acids C5–C9 are employed in modern gas turbine engines. TMP esters of oleic acid are among the most widely applied materials for hydraulic fluids at present. These bio-based esters show very good biodegradability, moderate oxidative stability and have a moderate price level. They are generally of high viscosity and display good shear stability. Table 1.4 shows further information regarding synthetic esters available on the market [12]. Synthetic esters of varying lubricity properties could be prepared by chemical modification of fatty acids or oils.

1.5. Chemical Modification of Vegetable Oil

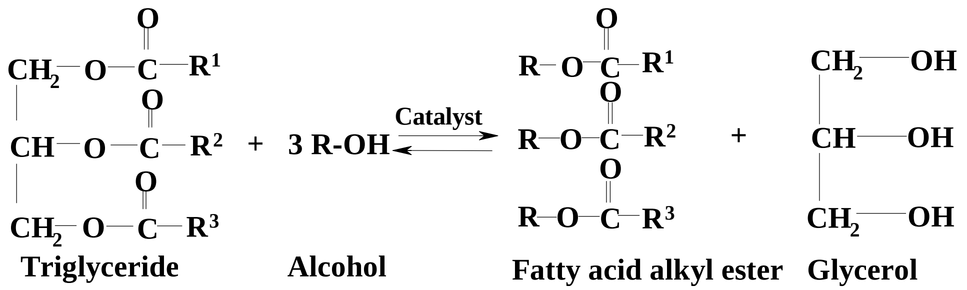
Unmodified vegetable oils as well as modified vegetable oil esters can be used as a base stock for preparation of environmentally friendly, rapidly biodegradable lubricants. Chemically, these are esters of glycerine and long-chain fatty acids (triglycerides). The alcohol component (glycerol) is the same in all vegetable oils. The fatty acids found in natural vegetable oils differ in chain length and number of double bonds. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. However, their thermal, oxidation and hydrolytic stability are limited. Therefore, pure vegetable oils are only used in applications with low thermal stress. The reason for the thermal and oxidative instability of vegetable oils is the structural "double bond" in the fatty acid part and the "β-CH group" of the alcoholic components (Fig. 1.3). Double bonds in alkenyl chains react with the oxygen in the air. The β-hydrogen atom is easily eliminated from the molecular structure. This leads to the cleavage of the esters into acid and olefin. A further weakness of natural esters is their tendency to hydrolyze in the presence of water [42-44]. An improvement of the thermal, oxidative and hydrolytic stability of vegetable oils can be primarily achieved by a chemical modification [45, 46].

Table 1.4. Type and application of synthetic lubricants **[**12]

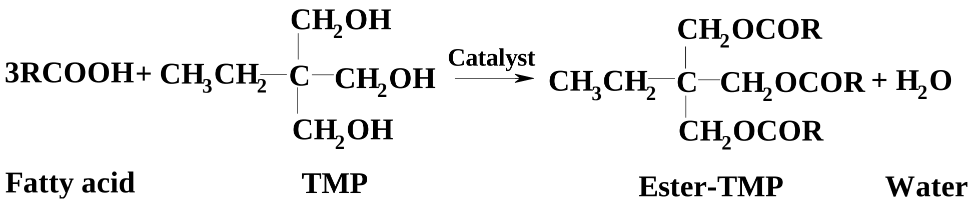
Class	Type	Operating temp (ºC)	Applications	Advantages vs mineral oil	Limiting properties
Synthesized fluids hydrocarbons (SFHs)	Polyalphaolefins, alkylated aromatics, polybutenes, cycloaliphatic	155 to -45	Machine tool spindles, freezer plants-motors, conveyors, bearings	High temperature stability, long life, low temperature fluidity, high viscosity index, improved wear protection,	Solvency/detergency, seal compatibility, low volatility
Organic ester	Dibasic acid ester, polyol ester	204 to -35	Commercial manual transmission	No wax, high temperature stability, long life, low temperature fluidity, solvency /detergency	Seal compatibility, mineral oil compatibility, antiwear and extreme pressure,hydrolytic stability, paint compatibility
Phosphate esters (phosphoric acid esters)	Triaryl phosphate ester, trialkyl phosphate ester, mixed alkylaryl phosphate esters	180 to -18	Hydraulic systems	Fiber resistance, lubricating ability	Seal compatibility, low viscosity index, paint compatibility, metal corrosion, hydrolytic stability
Polyglycols	Polyalkylene, polyoxyalklylene, polyethers, glycols	245 to -20	Gas turbines	Water versatility, high viscosity index, low temperature fluidity, antirust, no wax	Mineral oil compatibility, paint compatibility, oxidation stability

1.5.1. Modifications of the Carboxyl Group

1.5.1.1. Transesterification/ Esterification. Synthesis of biolubricant can be achieved by direct transesterification of vegetable oil or esterification with fatty acids (FA) derived from vegetable oils according to Schemes 1.1 and 1.2. Esterification of FA with alcohol having a long (typically > C8) alkyl groups or with more than one hydroxyl groups can form biolubricant. Direct transesterification of vegetable oils with these alcohols can also produce biolubricants. Homogeneous or heterogeneous acid catalysts can be used for these types of reactions. Although the reaction is faster when a homogeneous acid catalyst such as H_2SO_4, p-toluenesulfonic acid, or phosphoric acid is used, it is difficult to separate the catalyst from the products, and the liquid catalysts often cause reactor corrosion [47, 48]. Heterogeneous acid catalysts are non-corrosive, environmentally benign and present fewer disposal problems. They are more easily separated from the products and can be designed to yield higher activity, selectivity and longer catalyst lifetimes [49].



Scheme 1.1. Transestrification of vegetable oil with alcohol



Scheme 1.2. Esterification of fatty acid with Polyol

1.5.2. Modifications of the Fatty Acid Chain

1.5.2.1. Hydrogenation. Oils and natural fats contain multiple unsaturated fatty acids (linoleic- and linolenic acids, for example) which seriously impair the ageing stability of the oil. Selective hydrogenation can transform the multiple unsaturated fatty acids into single unsaturated fatty acids without increasing the saturated part of the substance. Such selective hydrogenation is necessary to avoid deterioration. One example is, the selective hydrogenation of linoleic acid methylester (C18:2) to oleic acid methylester (C18:1) using Ziegler–Sloan–Lapporte catalysts [palladium-*bis*-(acetylacetonate) and triethylaluminium; Fig. 1.4]. Selective hydrogenation improves the melting point as well as the ageing behavior [50, 51].

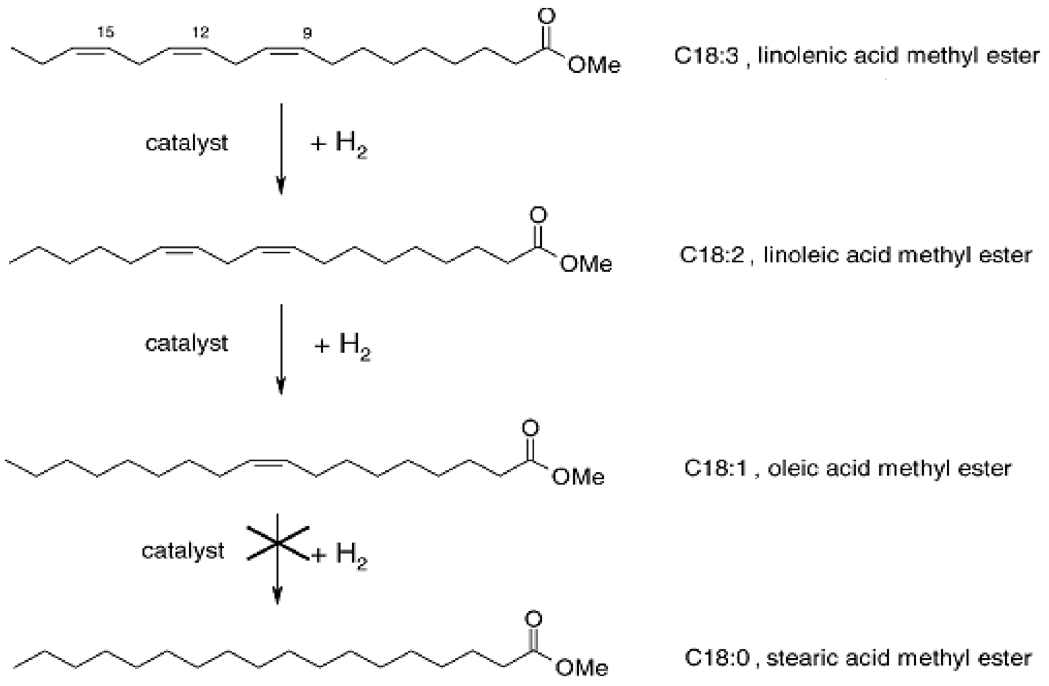


Fig. 1.4. Selective hydrogenation of linolenic acid methyl ester [46]

1.5.2.2. Dimerization/Oligomerisation/Estolide. Oligomeric fatty acids are formed from the condensation of two fatty acids through an acid catalyzed process. C18 fatty acids with one or more double bonds react with each other at temperatures of about 210–250 ºC in the presence of layered aluminosilicate catalysts forming a complex mixture of C36 dicarboxylic acids (dimeric fatty acids), C54 trimer fatty acids and C18 monomer fatty acids [52-54]. These compounds have a variety of potential applications as greases, plastics, inks, cosmetics, viscosity controller for chocolate, emulsifier in margarine, and lubricants [55-57]. These types of lubricants have been developed in order to overcome the deficiencies associated with some vegetable oils, which are known to have poor thermal oxidative stability, low hydrolytic stability and poor low temperature properties [58].

1.5.2.3. Oxidation/Epoxidation. Epoxidizing the C–C double bonds of unsaturated oil results in the formation of oxirane rings that can be easily opened. The ring opening reaction is done in the presence of water or other hydrogen donors (Fig. 1.5). Ring opening of such epoxidised oils with organic acids or alcohols produce epoxy polyol esters and epoxy polyethers. These are widely used in polymer chemistry, e.g. in the areas of paints and dyes. It is possible to vary lubricant property by introducing hetro atoms and functional groups and thus obtain new derivatives and polyfunctional compounds that are acceptable as environmentally friendly lubricants [59-61]. Low hydrolytic stability is related to the ester bases of these lubricants.

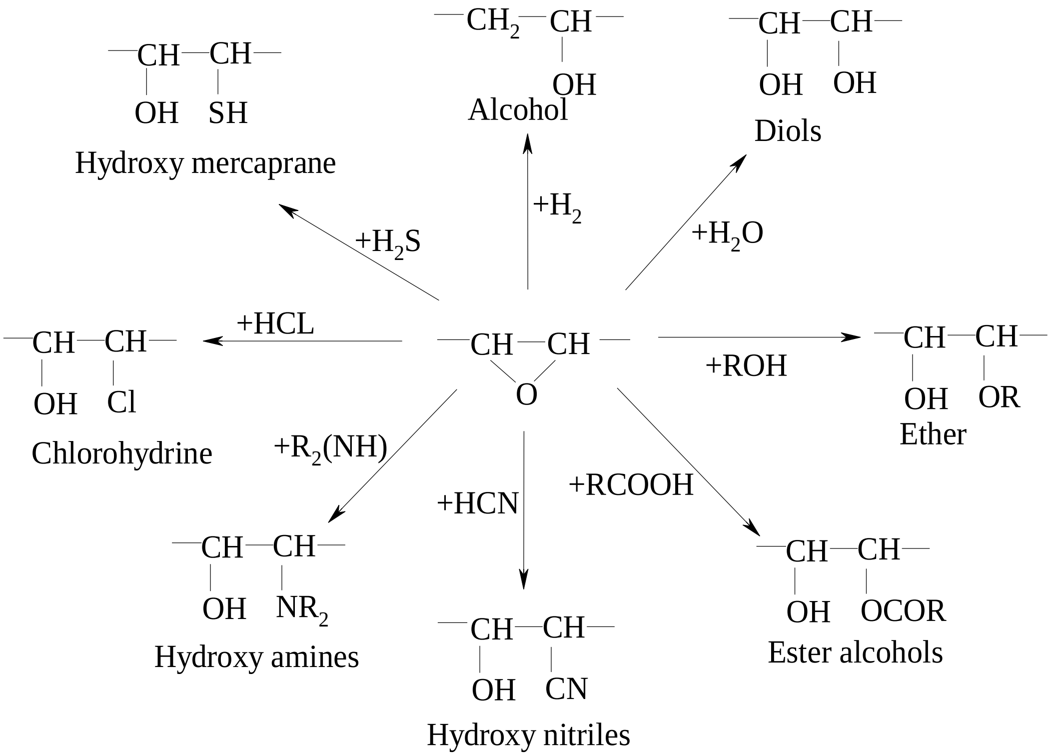


Fig. 1.5. Splitting of epoxy rings

Table 1.5. Properties of mineral oil and biolubricant [55]

Properties	Unit	Mineral oil	Biolubricant	Reference biolubricant
Density	g/cm^2	0.88	0.86	0.925
Flash point	ºC	224	211	204
Pour point	ºC		-27	n.d.
Viscosity 100ºC ($KV_{100\ °C}$)	mm^2/s	19.1	2.28	2.70
Viscosity 40ºC ($KV_{40^o\ C}$)	mm^2/s	62.90	6.39	9.03
Viscosity	-	324	207	148
Acid value	mg/KOH	-	0.01	0.1
Iodine-bromine value	g.I/100g	-	68.4	n.d.

n.d.: no data

1.6. Biolubricant

Environmental concerns and petroleum shortages have encouraged extensive research on biolubricants in recent years. Biolubricants have been the most anticipating as they have useful physicochemical properties. It can be derived from vegetable oils and animal fats, and therefore, their production may be sustainable. They are generally more biodegradable than petroleum-based products, and their use causes less net accumulation of carbon dioxide in the atmosphere. Compared to petroleum based lubricants, vegetable oils, in general, possess high flash point, high viscosity index, higher lubricity and low evaporative losses. Table 1.5 compares the properties of biolubricant with petrodiesel which make biolubricant a good renewable alternative to petrodiesel.

1.6.1. Properties of Lubricants and their Significance

1.6.1.1. Viscosity. It is the resistance to flow. Viscosity varies inversely with temperature.

1.6.1.2. Viscosity Index. It is designated as VI. The rate of change of viscosity with change in temperature is called viscosity index. A good lubricant is one whose viscosity doesn't change much with change in temperature. Therefore, a fluid that has a high viscosity index can be expected to undergo very little change in viscosity as the temperature fluctuates and it is considered to have a stable viscosity.

1.6.1.3. Pour Point. It is the lowest temperature at which oil starts flowing. If oil is used at a temperature below the pour point, the lubrication action will stop.

1.6.1.4. Cloud Point. It is the temperature at which dissolved solids in the oil, such as paraffin wax, begin to form and separate from the oil. As the temperature drops, wax crystallizes and becomes visible. Certain oils must be maintained at temperatures above the cloud point to prevent clogging of filters.

1.6.1.5. Flash Point. It is the lowest temperature at which a lubricant must be heated when the flame is applied to it, when mixed with air, will ignite but not continue to burn.

1.6.1.6. Fire Point. It is the temperature at which lubricant combustion will be sustained and lubricant catches fire and burns continuously when the flame is applied to it. The flash and fire points are usful in determining lubricant's volatility and fire resistance. Fire point of oil is always greater than its flash point.

1.6.1.7. Acid Number** or **Neutralization Number. It is a measure of the amount of potassium hydroxide (KOH) required to neutralize the acid contained in a lubricant. Acids are formed as oils oxidize with age and service.

1.6.1.8. Saponification Number. It is defined as the number of milligram of KOH required to saponify one gram of oil or fat.

1.6.2. Advantages of Biolubricant

- Less emissions because of higher boiling temperature ranges of esters (triglycerides lead to partly gummy structures at high temperatures and can build eye irritant acroleins)
- Total free of aromatics; over 90% biodegradable oils are non-water polluting
- Oil mist and oil vapor reduction, leading to less inhalation of oil mist into the lung
- Better skin compatibility, less dermatological problems
- High cleanliness at the working place
- At least equal and often higher tool life, because higher wetting tendency of polar esters lead to friction reduction.

- Higher viscosity index; this can be an advantage when designing lubricants for use over a wide temperature range. This can also result in lower viscosity classes for the same applications combined with easier heat transfer.
- Higher safety on a shop floor, because of higher flash points at the same viscosities
- Cost savings on account of less maintenance, man power, storage and disposal costs.

1.6.3. Disadvantages of Biolubricant

- Low temperature limitations. Addition of co-solvents such as synthetic fluids or mineral oils can improve the low-temperature properties of vegetable oils.
- Partly worse smell and compatibility with paintings and sealings
- More flushing tendency because of lower viscosity
- Less oxidation and hydrolytic stabilities of vegetable oils
- Filter clogging tendency depending on ester type and formulation
- Depending on the ester type worse air release or foaming and corrosion protection behavior.

1.7. Solid Catalysts for Biolubricants Production

Chemical or enzymatic catalysts are used for the biolubricants synthesis. Generally, industrial processes involved the use of homogeneous acid or basic catalysts, which lead to a mixture of mono-, di-, and triglycerides (biolubricant). Typical homogeneous acid catalysts are p-toluenesulfonic, phosphoric acid and sulfuric acid, while the alkaline are caustic soda, sodium ethoxide, sodium methoxide and tin oxide (SnO) [62-64]. A drawback associated with using homogeneous catalysts is the need for a neutralization step with the formation of soaps and a high salt content. The substitution of homogeneous catalysts by heterogeneous catalysts not only offers advantages in process integrity in terms of easy separation of the products from the catalyst, avoiding neutralization and extraction steps, reducing the waste formation, and recycle of the catalyst but also may improve yield and selectivity to the desired product by designing a specific solid catalyst for the particular process. Application of enzymes as catalysts for the production of biolubricant has also been investigated [65-68]. However, these processes are difficult to set up and expensive and not very efficient because of enzyme reusability issues

Due to economic and environmental aspects, a variety of solid acid catalyst studies have been carried out. The most used solid acids for the production of esters have been ion-exchange organic resins, such as Amberlyst-15, sulfonic acid groups, [69-71], zeolites [72], and silica-supported heteropoly acids [73, 74] and silica–sulphuric acid [67]. However, such type of catalyst show some limitations for catalyzing esterification reactions due to low thermal stability (resins), mass transfer resistance (zeolites) or loss of active acid sites due to high solubility in a polar medium (heteropoly acids).

There is increasing interest in the use of eco-friendly heterogeneous catalysts in terms of green chemistry. Such catalysts provide simpler, cheaper separation processes and reduced waste generation, and moreover can be recycled for several reaction cycles [75]. The need of developing heterogeneous catalysts is gaining attention due to non-toxic nature, ease of separation and reusability [76].

1.7.1. Double-Metal Cyanides

Double-metal cyanides (DMC) are complexes of the general formula $[M^a]_m[M^b(CN)_6]_n$, where M^a is an oxophilic metal and M^b is a transition metal [76]. DMC are known for their efficient catalytic activity in esterification and transesterification reactions. Fe–Zn DMC complexes have the general molecular formula: $K_4Zn_4[Fe(CN)_6]_3.xH_2O$, where x = 6–12.

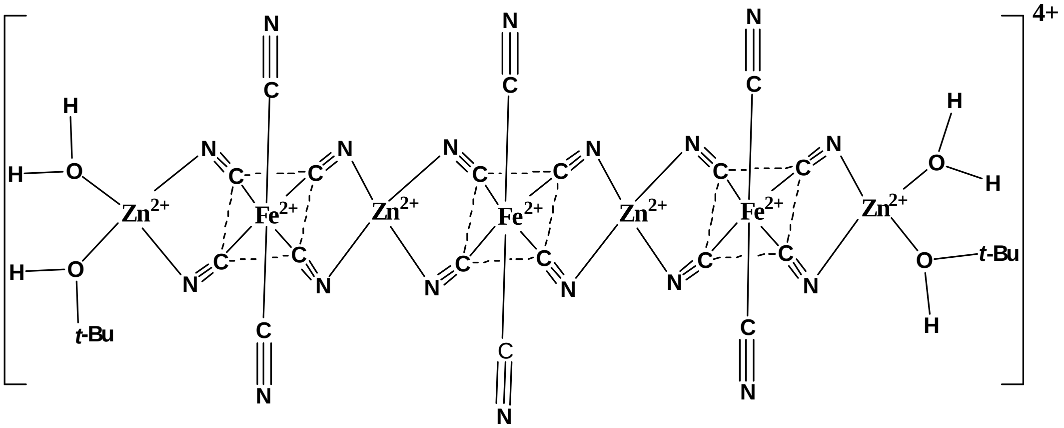


Fig. 1.6. Tentative structure of a DMC complex [76].

The Fe–Zn complexes prepared in the presence of tert-butanol and the polymer surfactant contain, additionally, two butanol molecules in their molecular formula: $K_4Zn_4[Fe(CN)_6]_3.6H_2O.2(tert\text{-}BuOH)$ [76]. These catalysts are Lewis acidic, hydrophobic and insoluble in most of the solvents including aqua regia. Tentative structure of the catalyst is as depicted in Fig. 1.6. Thermogravimetric studies showed that water present in the. structure gets desorbed at 170 °C and a catalyst activated at 170 °C doesn't absorb moisture and hence, is hydrophobic

This catalyst is superior to other solid acid catalysts due to the fact that there is no decrease in activity of the catalyst after use and it can be used even without purification/pre-treatment.

1.7.2. Mesoporous Silica

Meso structured materials such as silica have an exceptional potential to be utilized as heterogeneous acid catalyst in biofuel production. These mesoporous materials (silica) consist of large mesopores which can significantly minimize the diffusion problem for reactants to access into the active sites of the catalyst [77]. Apart from that, the physical and chemical properties of these mesoporous materials can be manipulated by incorporating suitable organic or inorganic functional groups into the mesoporous silica matrix [78]. The use of solid acid catalysts has been proposed for high yields of the desired esters. And these type of reaction employ catalyst such as ion-exchange organic resins (Amberlyst-15) [69], zeolites [79] and silica-supported heteropoly acids [73]. As already discussed above in Section 1.7, they show some limitations in applicability for catalyzing esterification reaction. Moreover, the presence of water can seriously affect the catalytic behavior of these solid acid catalysts due to their highly hydrophilic nature. In connection with this, the incorporation of Ti over mesostructured materials (SBA-12 and SBA-16 materials) have generated effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts in several acid-catalyzed reactions. Ti incorporation in the framework of silica generates Lewis acid sites which are active for esterification reaction. It is known that higher dimensionality in the pore structure facilitates better diffusion and mass transfer behavior.

1.7.3. Zirconium Phenyl Phosphonates

These are layered compounds, essentially two dimensional in character, in the sense that the bonding forces within the layer are much stronger than those between layers. This property allows neutral molecules and charged species to be intercalated into the interlamellar space. As a result, it is possible to manipulate layered compounds to form new and unusual structures. The formation of pillared clays is an example of such manipulation [80] The discovery of zirconium phenyl phosphonate has led to a range of applications of this layered compound as an ion exchanger, proton conductor and as a sensor component [81, 82] and also increased the possibilities for further modification and control in the structure and properties of these layered compounds. Fig. 1.7 shows tentative structures of zirconium phenyl phosphonate phosphite (ZrPP) wherein several orientations of phenylphosphonate phosphate and phosphite groups are possible [83, 84]. This interlayer spacing indicates an interstratified structure in which one layer primarily contains phosphate groups with some phenyl groups randomly dispersed on the layers and the other layer is mainly composed of phenyl groups with some replacement by phosphate groups [85]. The organic phosphate moiety imparts hydrophobic nature to the structure.

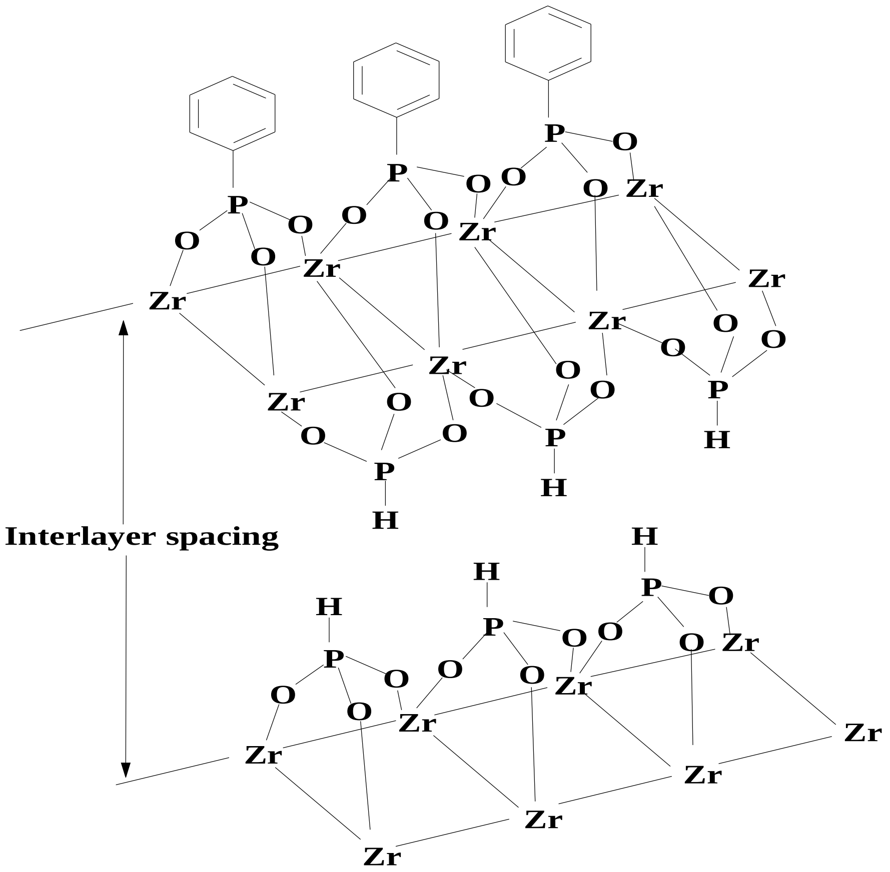


Fig. 1.7. Tentative structure of ZrPP

1.8. Scope and Objectives of the Present Work

Plant-derived lubricants are renewable and biodegradable. Biolubricants manufactured by environmentally-safe processes are gaining more and more attention in recent years, since they do not contain toxic compounds and have advantages like: (1) biodegradability and renewable nature, (2) excellent lubricity, lower friction coefficient than mineral oils, (3) lower evaporation: up to 20% less than mineral oils, (4) higher flash point, reducing the risk of fires in applications, (5) higher viscosity indices and (6) enhanced performance in some applications. Several studies show that biolubricants have a longer lifespan than mineral oil lubricants.

Biolubricants can be synthesized by transesterification of vegetable oils with long chain alcohols or esterification of fatty acid with polyols. This reaction is catalyzed by homogenous alkali or mineral acid catalysts. Use of solid catalysts instead of homogeneous catalysts makes the process more sustainable. Solid catalyst-based processes overcome most of the disadvantages encountered in the conventional processes. Development of more efficient and reusable solid catalysts is highly desirable. The present work deals with the study of esterification of fatty acid with polyhydric alcohol/long chain alcohol using solid acid catalysts for the production of biolubricant base stocks. Catalytic activities of three groups of catalysts viz., Fe-Zn DMC, three-dimensional, mesoporous titanosilicates (Ti-SBA-12 and Ti-SBA-16) and zirconium phenyl phosphonate phosphite (ZrPP) in the production of biolubricants are explored for the first time. The influence of reaction parameters on the catalytic activity is investigated.

1.9. Organization of Thesis

The thesis is divided into six chapters. A brief description of the contents of each chapter is given below.

Chapter 1 presents a general introduction to biolubricants. It describes the various methods and catalyst used in the synthesis of biolubricants. Finally, the objectives and scope of the work are presented.

Chapter 2 describes the synthetic methodologies of various catalyst systems used in this work. A brief description of general reaction procedures and physicochemical characterization techniques employed is also provided. The following are the various solid acid catalysts investigated:

(1) Fe-Zn double-metal cyanide (DMC)

(2) Three-dimensional, mesoporous Ti-SBA-12 and Ti-SBA-16

(3) Zirconium phenyl phosphonate phosphite (ZrPP).

Chapter 3 is sub-divided into two parts. Part I deals with esterification of fatty acids (FA - myristic acid, stearic acid and oleic acid) with glycerol over Fe–Zn DMC catalyst and part II describes transesterification of methyl oleate (MO; a component of biodiesel) with C8 to C12 alcohols (2-ethyl-1-hexanol, 1-decanol and 1-dodecanol). Hydrophobicity of the surface is one the important features that differentiated DMC from other solid acid catalysts in esterification reaction. DMC catalysts with varying acidities were prepared by synthesizing the material at four different temperatures (10, 25, 50 and 80 °C). The catalyst prepared at 50 °C exhibits highest catalytic activity. Influence of reaction parameters (reaction temperature, reaction time, molar ratio of reactants, amount of catalyst, etc.) on the catalytic activity of DMC is examined. Chain-length of FA shows a notable effect on the FA/MO conversion.

Chapter 4 reports the application of three-dimensional, mesoporous titanosilicates, Ti-SBA-12 and Ti-SBA-16 as catalysts for producing biolubricants. Esterification of oleic acid with polyhydric alcohols viz., glycerol (G), trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritaol (PE) is investigated for producing synthetic esters. Type of alcohol influences OA conversion with TMP > G > NPG > PE. The composition of the glyceride esters in the product is controlled or varied by changing OA to polyol molar ratio, temperature, reaction time and type of catalyst used. The titanosilicate catalysts are found reusable and highly active for these reactions. Dispersed tetrahedral Ti ions are the acid sites catalyzing the esterification reaction.

Chapter 5 presents the properties of zirconium phenyl phosphonate phosphite (ZrPP) as a highly active, reusable, solid acid catalyst for producing fatty acid polyols by reacting glycerol or TMP with oleic acid. Zirconium phenyl phosphonate phosphites are prepared with varying phosphorous acid to phenyl phosphonic acid input molar ratio and evaluated as catalysts in the esterification reactions producing oleic acid-glycerol and TMP esters. The catalyst with phosphorous acid/phenyl phosphonic acid molar ratio of 3:1 shows higher catalytic activity and most importantly the DE + TE selectivity than the other preparations. The influence of process parameters on the activity and selectivity of the catalyst is investigated. ZrPP is reusable in at least three recycling experiments.

Chapter 6 provides an overall summary and conclusions of the work presented in the thesis.

By and large, this thesis contributes to a more sustainable catalytic process for biolubricant production via esterification of fatty acids with polyhydric alcohols. Synthetic esters of varying lubricity properties could be prepared using 1) Fe-Zn double-metal cyanide (DMC), 2) three-dimensional, mesoporous Ti-SBA-12 and Ti-SBA-16, and 3) zirconium phenyl phosphonate phosphite catalysts and by varying process parameters, textural and acidic properties of the catalysts and most importantly, the surface hydrophobicity of the catalysts.

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Chapter - 2

Experimental Methodology: Catalyst Preparation and Characterization Techniques

2.1. Introduction

This chapter describes the synthesis of three different solid acid catalysts investigated in this thesis. A brief description of physicochemical characterization techniques and general reaction procedures employed is also provided. The following are the solid acid catalysts investigated:

(1) Fe-Zn double-metal cyanide (DMC) complex

(2) Three-dimensional, mesoporous titanosilicates: Ti-SBA-12 and Ti-SBA-16

(3) Zirconium phenyl phosphonate phosphite (ZrPP) complex

The catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, thermogravimetry and differential thermal analyses (TG-DTA), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), diffuse reflectance ultraviolet-visible (DRUV-vis) spectroscopy, Fourier-transform infrared spectroscopy (FTIR) and solid state nuclear magnetic resonance (NMR) spectroscopy. The acidic properties of the catalysts were investigated by temperature-programmed desorption (TPD) and diffused reflectance Fourier transform infrared (DRIFT) spectroscopy using NH_3 and pyridine as probe molecules, respectively. The fatty acid (FA) content/conversion was determined by acid-base titration method. The composition of polyol esters was determined using a high performance liquid chromatography. The objective of the thesis is to develop efficient solid catalysts for esterification of FA with polyhydric alcohol to produce synthetic, biodegradable, fatty acid polyol esters (biolubricants).

2.2. Catalyst preparation

2.2.1. Double-Metal Cyanide Complex: Fe-Zn DMC

DMC complexes are well-known catalysts for copolymerization of epoxides and CO_2 [1-4]. They are also used in the synthesis of propene oxide-based polyether polyols, such as polypropylene glycols (PPG), which are used in a wide range of polyurethane applications [5-10]. DMC catalysts are hydrophobic and possess zeolite-like cage structures [11]. They are insoluble in most of the organic solvents and even in aqua regia. Hence, it could be used as a solid catalyst. This material was prepared and reported by Sreeprasanth et al. [12] for transesterification of vegetable oils with monohydric alcohols into biodiesel and biolubricants. Hydrophobicity of the surface is one of the important features that differentiate

DMC from other solid acid catalysts. In this thesis, the catalytic activity of DMC is reported, for the first time, for the esterification of fatty acids with polyhydric alcohols. A detailed synthesis of this catalyst is presented below.

Fe-Zn DMC complex was prepared using $K_4Fe(CN)_6{\cdot}3H_2O$ as a source of Fe, $ZnCl_2$ as a source of Zn, *tert.*-butanol as complexing agent and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight = 5800; Aldrich) or poly(ethylene glycol) (PEG; average molecular weight = 4000; s.d. Fine Chem Ltd.) as co-complexing agent. In a typical preparation of a Fe-Zn DMC complex, 0.01 mol of potassium ferrocyanide, $K_4Fe(CN)_6{\cdot}3H_2O$, was dissolved in 40 ml of double-distilled water to prepare solution A. In a separate a beaker, solution B was prepared by dissolving 0.1 mol of $ZnCl_2$ in 100 ml of distilled water and 20 ml of *tert.*-butanol. Solution C was prepared by dissolving 15 g of a tri-block copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) in 2 ml of distilled water and 40 ml of *tert.*-butanol. Solution B was added to solution A slowly over 1 h at 50 °C under vigorous stirring. Precipitation of a solid occurred during the addition. To that mixture, solution C was added over 5–10 min and stirring was continued for another 1 h. The solid was filtered, washed thoroughly with double-distilled water to remove all the uncomplexed ions, and dried at 25 °C for several hours. This material was activated at 100 ºC for 4 h prior to using in the reactions.

In total, four Fe–Zn DMC samples were prepared at 10, 25, 50 and 80 °C as per the general procedure described above. These samples are, hereafter, referred as DMC-X °C where, X corresponds to the temperature of synthesis.

2.2.2. Mesoporous Titanosilicate Molecular Sieves

Ion-exchange organic resins (such as Amberlyst-15) [13], zeolites [14] and silica-supported hetropoly acids [15] are the most used solid acid catalysts for ester production. These catalysts have their own limitation. Due to low thermal stability (resins), mass transfer resistance (zeolites) [16] and loss of active acid sites due to high solubility in a polar medium (heteropoly acids) [15], they are not suitable continuous reactions. Moreover, the presence of water deactivates the catalyst. Incorporation of metal groups over mesoporous structured materials has generated effective solid acid catalyst with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts in several acid-catalyzed reactions [17, 18]. Three-dimensional, mesoporous titanosilicates, Ti-SBA-12 and Ti-SBA-16 belong to this category. They were prepared as reported earlier [19-21].

2.2.2.1. SBA-12. SBA-12 was prepared by a modified procedure of Zhao et al. [22]. In a typical preparation, 160 g of 2 M HCl and 40 g of distilled water were taken a polypropylene beaker. Then, 8 g of Brij76 [$C_{18}H_{37}(OCH_2CH_2)_{10}OH$] was dissolved in it while stirring the mixture at 40 °C for 2 h. Later, 17.6 g of tetraethyl orthosilicate (TEOS) was added over 30 min. Stirring was continued for 20 h. The gel formed was transferred into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 24 h. The solid (as-synthesized SBA-12) formed was filtered, washed thoroughly with distilled water (2 - 3 l) and dried at 100 °C for 12 h. Then, it was calcined at 550 °C for 8 h to remove all the organic matter in it. The calcined SBA-12 was white in colour.

2.2.2.2. Ti-SBA-12. In the preparation of Ti-SBA-12, 8 g of Brij76 was dissolved in 40 g of distilled water and 160 g of 2 M HCl taken in a polypropylene beaker. The mixture was stirred at 40 °C for 2 h. Then, 17.6 g of TEOS was added over 30 min. Later, 0.8 g of titanium iso-propoxide dissolved in 10 ml of iso-propanol was added. Stirring was continued for 20 h. The gel formed was transferred into a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. The solid formed was recovered by filtration, washed thoroughly with distilled water (2 - 3 l), dried at 100 °C for 12 h and calcined at 550 °C for 8 h. The calcined Ti-SBA-12 was white in colour.

2.2.2.3. SBA-16. In a typical synthesis of SBA-16, 7.4 g of Pluronic F127 block-copolymer ($EO_{106}PO_{70}EO_{106}$) was dissolved in 384.3 g of 2 M HCl solution at 40 °C while stirring for 2 h. To it, 28.34 g of TEOS was added over 30 min. The stirring was continued for 24 h. The gel formed was transferred into a Teflon-lined stainless steel autoclave. It was crystallized at 80 °C for 48 h. The solid formed was filtered, washed with distilled water (2 - 3 l), dried overnight at 100 °C and calcined at 550 °C for 8 h. The calcined SBA-16 [22, 23] was white in colour.

2.2.2.4. Ti-SBA-16. In a typical synthesis of Ti-SBA-16, 7.4 g of Pluronic F127 was dissolved in 384.3 g of 2 M HCl solution at 40 °C. After 2 h of stirring, 28.34 g of TEOS was added drop-wise over 30 min and stirred for 4 h. Then, 1.28 g of titanium iso-propoxide dissolved in 10 ml of iso-propanol was added slowly. Stirring was continued for another 20 h. The gel formed was transferred into a Teflon-lined stainless-steel autoclave. It was heated at

80 °C for 48 h. The solid formed was separated by filtration, washed with distilled water (2 - 3 l), dried overnight at 100 °C and calcined in air at 550 °C for 8 h. The calcined Ti-SBA-16 was white in colour.

2.2.3. Zirconium Phenyl Phosphonate Phosphite - ZrPP

Zirconium phenyl phosphonate compounds have application in the fields of electrochemistry [22, 23], microelectronics [24], biological membranes [25, 26], photochemistry [27] and catalysis [28]. These layered inorganic materials have attracted much attention as novel proton conductors, luminescent, magnetic materials, corrosive resistive agents and for encapsulating photoactive molecules [29]. However, there are only a few studies of their application as catalysts [30-32]. General procedure for preparation of zirconium phenyl phosponate phosphite (ZrPP) is given below.

Zirconium phenyl phosphonate phosphite was prepared by precipitation method. In a typical preparation, phenyl phosphonic acid (1 g) and phosphorous acid (0.52 g) were dissolved in 20 ml of double-distilled water [32-35]. To it, 2.04 g of zirconium oxychloride ($ZrOCl_2.8H_2O$) dissolved in 5 ml water was added. While stirring, the solution was heated to dryness at 90 °C. The solid formed was recovered, washed with water (500 ml) and dried at 90 °C overnight. ZrPP, thus formed, was labeled as ZrPP-1, where 1 denotes the molar ratio of phosphorous acid/phenyl phosphonic acid.

ZrPP-2 and ZrPP-3 with phosphorous acid/phenyl phosphonic acid molar ratio of 2 and 3 were prepared in a similar manner taking 1.04 and 1.56 g of phosphorous acid, respectively. Colour: white.

2.3. Catalyst Characterization Techniques

2.3.1. X-ray Powder Diffraction

X-ray diffraction is a non-destructive method for structure analysis. It helps to identify the phases, orientation, structural properties and average crystallite size of crystalline catalyst materials [36]. The XRD method involves interaction between the incident monochromatized X-rays (like Cu K_α or Mo K_α) with the atoms of a periodic lattice. X-rays scattered by the atoms in an ordered lattice interfere constructively as described by the Bragg's law:

$$n\lambda = 2d \sin \theta$$

Here *d* is the spacing between diffracting planes, θ is the incident angle, *n* is any integer, and λ is the wavelength of the beam [36, 37]. X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical (X'pert Pro) diffractometer equipped with a Ni-filtered Cu-K_α radiation (λ = 0.15418 nm, 40 kV and 30 mA) and a proportional counter detector. The diffraction patterns in the small-angle region were recorded in the 2θ range of 0.5–5° with a scan rate of 0.2°/min. Those in the high 2θ region (10–80◦) were recorded at a rate of 4°/min on an X'PERT Pro PANalytical instrument with monochromated CuKα radiation (λ = 0.15406 nm) and a proportional counter detector. Average crystallite size of the materials was determined using the Scherrer equation:

$$L = K\lambda/\beta\cos\theta$$

where θ and λ are the Brag angle and wavelength of incident X-ray radiation, respectively, K is a constant approximately taken as 0.9 and β is the linewidth on the 2θ scale in radians.

2.3.2. Nitrogen Physisorption – Textural Characterization

Surface area and the pore size distribution are fundamental parameters for the characterization of solids and it was developed by Brunauer, Emmett and Teller (BET) [38]. BET theory provides a mathematical model for the process of gas sorption. This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption and is used to measure total surface area and pore size distribution of micropores and mesopores. The BET equation can be represented as:

$$P/V(P_o-P) = 1/cV_m + [(c-1)/cV_m]\,(P/P_o)$$

where P is adsorption equilibrium pressure, P_o is saturation vapour pressure of the adsorbate at the experimental temperature, V is the volume of N_2 adsorbed at a pressure P, V_m is the volume of adsorbate required for monolayer coverage, and c, a constant that is related to the heat of adsorption and liquefaction [38]. A linear relationship between $P/V(P_o-P)$ and P/P_o is required to obtain the quantity of nitrogen adsorbed. The monolayer volume, V_m is given by

1/(S+I), where S is the slope and is equal to (c-1)/cV_m and I is the intercept equal to 1/cV_m. The surface area of the catalyst (S_{BET}) is related to V_m, by the equation:

$$S_{BET} = (V_m/22414)N_a\sigma,$$

where N_a is Avagadro number and σ is mean cross sectional area covered by one adsorbate molecule. The value of σ generally accepted for N_2 is 0.162 nm^2. The most widely used computational procedure for the evaluation of pore size distribution from nitrogen adsorption data is based on the principles first developed by Barrett, Joyner and Halenda (BJH) model in 1951 [39], which is based on speculative emptying of the pores by a stepwise reduction of P/P_o, and allowance being made for the contraction of the multilayer in those pores already emptied by the condensate [39]. The pore size distribution is usually expressed as a plot of $\Delta V_p/\Delta r_p$ versus r_p, where V_p is the mesopore volume, and r_p is the pore radius. Adsorption of nitrogen measured by Brunauer-Emmett-Teller (BET) equation at low pressure (10^{-4} Torr) and liquification temperature of N_2 (77 K) is the standard method for determination of surface area, pore volume and pore size distribution of molecular sieves. All these measurements were conducted on a NOVA 1200 Quanta Chrome instrument. Specific surface area was determined by total surface area of the sample divided by sample weight. About 100 mg of samples were taken in a quartz cell and evacuated at 200 °C for 1 h. After that, the quartz cell was dipped in a liquid nitrogen container up to the sample level and then, started passing nitrogen through it. Adsorption and desorption of nitrogen were measured in the P/P_o range of 0.1 to 0.

2.3.3. Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is an important technique in physicochemical analysis. It is an easy way to identify the presence of certain functional groups in a molecule. The spectra were recorded on a Shimadzu FTIR-8201 PC spectrophotometer in the wave number range of 400 – 4000 cm^{-1}. The samples were made into KBr pellets (1 wt %) or as such in DRIFT mode. In general, neat KBr was used as a reference material.

2.3.4. Diffuse Reflectance UV-Visible Spectroscopy

This technique uses UV-visible light to excite valence electrons to empty orbitals. While UV-visible spectroscopy measures the relative change of absorbance of light as it passes through a solution, diffuse reflectance UV-visible measures the relative change in the amount of reflected light off of a surface. DRUV-Vis spectroscopy is a highly sensitive and powerful technique for identification and characterization of the metal ion's coordination and location (framework or extra framework) in metal-containing solid catalysts [40]. The measurements were conducted on a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere attachment (ISR 2200). In general, spectral grade $BaSO_4$ was used as the reference material.

2.3.5. Temperature-Programmed Desorption

Temperature-programmed desorption (TPD) is a powerful surface science technique that provides information about species present on a surface and their reactions on the surface [41]. Molecules that are attached to a surface are thermally excited by raising the temperature of the surface at a programmed rate, while monitoring the desorbing gas molecules with a mass spectrometer. The increase in temperature causes the rate of desorption. During the experiment, the partial gas pressures are measured, in such a way to monitor the desorption rate of each atomic/molecular species as a function of the temperature. This forms a peak on the pressure versus temperature plot. The shape of the peak gives information about the desorption kinetics. In addition, the area under the pressure verses time curve is proportional to the molecular coverage [42].

Acidity or basicity of solid catalysts can be investigated by adsorption/desorption techniques of basic or acidic probe molecule respectively. For NH_3-TPD, Micromeritics Auto Chem 2910 instrument was used for measuring the acidity of catalysts. From the amount of desorption of the corresponding probe molecule, total acidity of the catalyst was estimated.

2.3.6. Thermal Analysis

This is a technique in which the change in weight of a substance with temperature over a period of time is followed. The temperature is increased at a constant rate for a known initial weight of the substance and changes in weight are accurately recorded at different times [43-45]. When the weights are plotted against temperature a curve characteristic of the substance studied is obtained. Such a curve is called a thermogravimetric curve or a thermogram. This technique is useful for determination of thermal stability, decomposition, chemisorption and purity check. Thermogravimetric analyses of the samples were done under nitrogen (50 ml/min) using a PerkinElmer Diamond TG-DTA instrument at a ramp rate of 10 °C/min in the temperature range of 25 – 1000 °C.

2.3.7. Scanning Electron Microscopy

SEM probes the morphological characteristics of materials. SEM scans over a sample surface with a probe of electrons (5-50 eV) and detects the yield of either secondary or back-scattered electrons as a function of the position of the primary beam. Contrast is generally caused by the orientation that part of the surface facing the detector appears brighter than parts of the surface with their surface normal pointing away from the detector. The interaction between the electron beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample [46]. When an electron from the beam encounters a nucleus in the sample, the resultant Coulombic attraction leads to a deflection in the electron's path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, re-emerging from the incident surface of the sample. Since the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information [47]. A major advantage of SEM is that bulk samples can also be directly studied by this technique. SEM of the catalyst samples in this work were recorded using a SEM Leica 440 instrument operating at 100 kV.

2.3.8. Transmission Electron Microscopy

TEM is typically used for high resolution imaging of thin films of a solid sample for micro structural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high-energy electron beam, which is diffracted by the lattices of a crystalline or semi crystalline material and propagated along different directions, (ii) imaging and angular distribution analysis of the forward scattered electrons (unlike SEM where backscattered electrons are detected), and (iii) energy analysis of the emitted X rays [48]. In detail, a primary electron beam of high energy and high intensity passes through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and thickness, the transmitted electrons form a two-dimensional projection of the sample mass, which is subsequently magnified by the electron optics to produce the so-called bright field image. The dark field image is obtained from the diffracted electron beams, which are slightly off angle from the transmitted beam. Typical operating conditions of TEM instruments are 100-200 keV, 10^{-6} mbar vacuum, 0.5 nm resolution and a magnification of about 10^{5}. The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of mesoporous materials, *viz.*, hexagonal, cubic or lamellar [49]. TEM also provides real space image on the atomic distribution in the bulk and surface of a nano-crystal [38]. TEM of the samples were recorded using a JEOL-model 1200 EX instrument operating at 100 KV.

Details of characterization results of different catalysts are reported in the respective chapters.

2.4. Reaction Procedure

2.4.1. Esterification reactions

Known quantities of oleic acid (OA; C18.1; cis-9-octadecenoic acid) and polyol [glycerol, trimethylolpropane (TMP), neopentylglycol (NPG), and pentaerythritol (PE)] were taken in a glass, round bottom flask placed in a temperature controlled oil bath, fitted with a water-cooled reflux condenser. To it, 5 wt% of catalyst (in powdered form) with respect to OA was added. Temperature of the reaction mixture was raised to a desired value and the reaction was conducted for a specific period. At the end of the reaction, the catalyst was separated by centrifugation. The liquid product was treated with petroleum ether (20 – 30 ml). Two layers formed with the bottom being polyol and the top being OA-glycerides and unconverted OA. Polyol was separated out by decantation. Petroleum ether in the top layer portion was removed by distillation.

Esterification reactions were also conducted keeping polyol constant and changing the chain length of fatty acid [valeric acid (C5), caprylic acid (C8), capric acid (C10), lauric acid (C12.0), myristic (C14.0), stearic (C18.0) and oleic acid (C18.1)].

2.4.2. Transestrification reactions

Methyl oleate (MO) was transesterified with a monohydric C_8 – C_{12} alcohol (2-ethyl-1-hexanol, 1-decanol and 1-dodecanol). In a typical reaction, 6.76 mmol of MO and three equivalents excess of alcohol and 0.06 g of DMC catalyst (3 wt% of MO) were taken in a glass round-bottom flask placed in a temperature-controlled oil bath and connected with a water-cooled condenser. Temperature was raised to a 170 °C and the reaction was conducted for 8 h at atmospheric pressure under a flow of nitrogen. Then, the temperature of the reaction mixture was brought down to 25 °C and the catalyst was separated by centrifugation. Excess, unreacted 2-ethyl-1-hexanol in the reaction product was removed by steam distillation using a rotary evaporator

At the end of the reaction, the solid catalyst was separated from the product mixture by filtration, washed with methanol, dried at 100 °C for 3 h and then reused in a subsequent recycle experiment without any further treatment. The catalyst was reused in five consecutive recycles.

2.5. Product Analysis

2.5.1. High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) is a common technique used to analyze biolubricant. It is used to separate and identify various components in a mixture including fatty acid methyl esters, triglycerides, diglycerides, monoglycerides and fatty acids. The time taken for HPLC analysis is generally shorter than that for gas chromatography (GC), and no derivitization step is needed. In HPLC analysis, the sample is injected into a column with a non-polar stationary phase. A polar mobile phase is then pumped through the column to elute the sample. As the sample moves through the column, different components begin to separate based on polarity. The most polar compounds do not have a tendency to stick to the non-polar stationary phase, but instead move with the polar mobile phase and elute quickly. Non-polar components stick to the stationary phase and are retained longer. A detector at the end of the column detects each compound as it is eluted. Retention times for each compound can be recorded and compared to retention times of known standards to identify the different components of the sample. A variety of detectors can be used with this technique including UV detectors, refractive index detectors, evaporative light scattering detectors and atmospheric pressure chemical ionization mass spectrometry (APCI–MS) in positive–ion mode.

The composition of fatty acid products of the reaction was determined using a Perkin-Elmer (Series 200) high performance liquid chromatography (HPLC) equipped with a quaternary pump, auto sampler, degasser, thermostated column compartment and TotalChrom navigator-PE-HPLC software and fitted with an ELSD detector from Gilson and a reverse-phase Perkin- Elmer Brownlee column (C-18 Spheri-5, 250×4.6 mm with a 5 µm particle size; (Fig. 2.1).

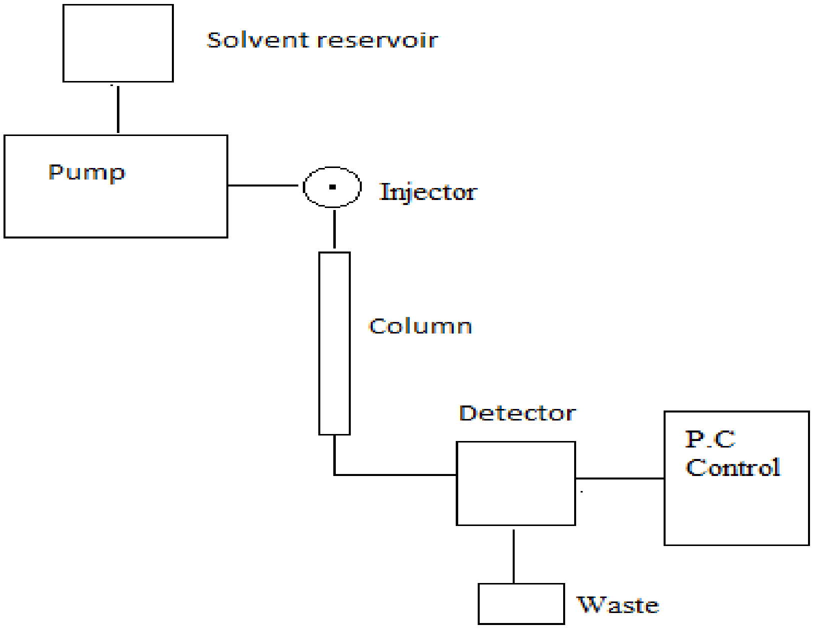

Fig. 2.1. Schematic flow sheet diagram of HPLC

2.5.2. Determination of Acid Value

The acid values of the reaction mixture at the beginning and at the end of the reaction were determined by titration with 0.1 N NaOH solution and using phenolphthalein as indicator. In a typical titration, 0.5 g of fatty acid (oleic acid, OA, for example) or the final product was weighed with an accuracy of 0.001 g and dissolved in 25 ml of a neutral solvent mixture (isopropyl alcohol and toluene in equal volume) taken in a 250 ml conical flask. Three to five drops of phenolphthalein indicator (1%, Merck, India) were added to it. Then the solution was titrated against 0.1 N standardized NaOH solutions till a colourless to pink end-point was achieved. These titrations were done three times and the average value was considered to evaluate the acid value of the material. NaOH (0.1 N) was standardized using 0.1 N oxalic acid solution. The equations employed for determining the acid value and fatty acid conversion are given below.

$$\boxed{\text{Acid Value} = \frac{56.1 \times N_{NaOH} \times V_{NaOH}}{W_{Sample}}}$$

where 56.1 is the molecular weight of KOH as acid value is always reported as mg of KOH per gram of the sample, N_{NaOH} = normality of NaOH, V_{NaOH} = volume of NaOH used and W_{Sample} = weight of the sample taken for titration. Percentage of fatty acid in the reaction product can also be determined using the following equation and the molecular weight of the fatty acid (282 for oleic acid, for example).

$$\boxed{\text{\% of Fatty Acid} = \frac{N_{NaOH} \times V_{NaOH} \times 282}{W_{Sample}} \times 100}$$

2.6. Conclusions

This chapter described the synthesis of catalysts (double metal cyanide – Fe-Zn DMC, three-dimensional, mesoporous titanosilicates – Ti-SBA-12 and Ti-SBA-16, and zirconium phenyl phosphonate phosphate – ZrPP) used in this thesis. It also presented a brief detail of the principles of physicochemical techniques used for characterization of the catalysts. Generalized reaction procedures (for esterification and transesterification) and product analyses by HPLC and acid-value techniques were also presented.

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Chapter - 3

Fe–Zn Double-Metal Cyanide Catalyst for Esterification of Fatty Compounds with Glycerol and Long-chain Alcohol

3.1. Introduction

The increasing use and production of biodiesel has resulted in substantial amount of glycerol accumulation. This has allowed researchers to look for new usages of glycerol [1, 2]. In future, glycerol will be a cost effective raw material for the preparation of valuable chemicals and fuel additives. One such valuable chemical compound is glycerol mono- and diesters of fatty acids that have application in pharmaceuticals, food and cosmetics production. They are used as raw material for emulsifiers and lubricants [3, 4]. In general, these esters can be prepared by three methods: (i) the glycerolysis of vegetable oil, (ii) the hydrolysis of triglycerides, and (iii) the direct esterification of fatty acids (FA) with glycerol [5]. The third option is most widely used as the cost of raw materials is cheaper. Conventionally, the esterification reaction is carried out using homogeneous mineral or Lewis acid catalysts [6, 7]. These catalysts suffer from the inherent disadvantage of corrosiveness, sensitivity to water, difficulty in catalyst recovery, environmental hazard, waste control, etc. Further, large amount of catalyst is needed in these processes.

Several solid acid catalysts including zeolites, ion-exchange resins and metal-incorporated or sulfonic acid-functionalized ordered mesoporous silica materials have been reported [8-11]. Pore-size limitation, loss of activity in presence of by-product water and formation of undesired products of glycerol are some of the issues with these catalysts. There are a few reports on the application of solid base catalysts like MgO [12, 13]. However, based on conversion and selectivity, the acid catalysts are superior to base catalysts for esterification reaction. Base catalysts lead to soap formation and catalyst deactivation in the presence of FA. While the reaction has to be carried out at high temperatures using solid catalysts, the supported or unsupported lipase catalysts [14] are active even at ambient conditions. However, they require longer reaction time (48 h and above). Reusability and cost of enzyme are other problems with the lipases. In view of this, development of an efficient, solid, acid catalyst for production of glycerol esters is highly desirable.

DMC are known for their efficient catalytic activity in esterification and transesterification reactions [15, 16]. Hydrophobicity of their surface is one the important characteristics that differentiate DMC from other solid acid catalysts and make them more efficient. The tetrahedral zinc sites are the active Lewis acid centers that catalyze the reaction. Earlier, Satyarthi et al. [17] reported the efficient catalytic activity of DMC in the esterification of fatty acids (of varying chain length) with methanol. In the first part of this chapter, its application, for esterification of FA with highly polar, polyhydric alcohols like glycerol producing fatty acid glycerides, at moderate temperatures, is reported, for the first time. The concentration of active, tetrahedral zinc sites is varied by preparing the catalysts at different temperatures. A correlation between acidity/surface area and catalytic activity is reported. The influence of chain length of FA on the progress of esterification reaction is studied.

In the second part of this chapter, the synthesis of fatty acid monoesters through the reaction of a fatty acid methyl ester with a long-chain alcohol [2-ethyl-1-hexanol (C_8OH), 1-decanol ($C_{10}OH$) and 1-dodecanol ($C_{12}OH$)] using a Fe-Zn DMC catalyst is reported. Monoesters are categorized as “non-water pollutant” biolubes which reduce the expenses of oil spillage or disposal. By now, it is accepted that more than 90% of all present day lubricants could be formulated to be rapidly biodegradable [18]. The ester oils are normally for high-end usage because of their higher price. Biolubricants are priced twice as high as conventional petroleum lubricants. As a consequence, only a few percentage of the market for slippery fluids is commanded by bio-based lubricants [19, 20]. Currently, they are produced by esterification of a fatty acid or transesterification of vegetable oil with a long-chain alcohol in presence of a homogeneous acid/base catalyst [21-23] or by using an ion-exchange resin [24, 25]. Their synthesis from the reaction of fatty acid methyl esters (FAME-biodiesel) and long-chain alcohol is attractive as a part of biodiesel pool can be converted to more valuable lube product. This diversion makes biodiesel production economical even in the absence of incentives from the government.

Unlike other synthetic oils *ca.* poly alpha-olefins (PAO) and poly alkylene glycols (PAG), the ester oils are miscible with a large number of additives to formulate effective biodegradable lubricants. Currently, more than 10,000 lubricant formulations are needed to meet the world demand of 12 billion gallons per year [26-28]. Through a proper choice of fatty acid and long-chain alcohol, a wide variety of lubricants with custom design properties can be synthesized. Biodegradable lubricants reduce environmental pollution which the conventional mineral oil-based lubricants cause after their usage (*Note!* about 53% of mineral oil lubricants are collected as waste endangering the planet) [18].

In spite of these advantages, cost effective production of synthetic esters is of utmost importance for their wider use. The homogeneous mineral acid or base catalysts currently used are non-reusable. Ion exchange resins have limited thermal stability confining their application to reactions with short chain alcohols only. Use of solid catalysts in place of homogeneous catalysts makes the process attractive and cost-effective. Solid catalysts can be recyclable and processes involving them can be green and zero-waste generating. Silica-sulphuric acid, Amberlyst-15, immobilized lipase (Novozym$^{®}$435), sulfated zirconia and calcium methoxide, are a few solid catalysts reported for monoesters preparation [29-32]. It is shown in this chapter that DMC is highly efficient for transesterfication of methyl oleate (a component of biodiesel) with C8 – C10 alcohols producing the corresponding long-chain alcohol monoester. The lubricant properties of the produced monoesters are also reported.

3.2. Experimental

3.2.1. Material Preparation

The Fe-Zn double-metal cyanide (DMC) complex catalysts were prepared as reported in Chapter - 2 (Section 2.2.1). Glycerol (1,2,3-propanetriol, ≥99.5%) and FA [myristic acid (tetradecanoic acid; C14:0; 99–100%), stearic acid (octadecanoic acid; C18:0; 95%) and oleic acid (cis-9-octadecenoic acid, C18:1; ~99%)] used in the reactions were procured from Aldrich Co. Lauric acid (dodecanoic acid; C12:0) and petroleum ether were purchased from s.d. fine Chem. Ltd., India. Methyl oleate (MO, technical grade 70%) was procured from Sigma-Aldrich Co. 2-Ethyl-1-hexanol (99%) was obtained from Loba Chemie and 1-decanol and 1-dodecanol were from s.d. fine Chem. Ltd. All these chemicals were used as received without any further purification.

3.2.2. Characterization Techniques

X-ray diffraction patterns of the catalysts were recorded on an X'PERT Pro PAnalytical instrument with a monochromated CuKα (λ=0.154 nm) radiation. The diffraction patterns were recorded in the 2θ range of 10-80^{0} with a scan rate of 4^{o}/min and with a step size of 0.02^{o}. The specific surface area (S_{BET}) of the samples was determined using a NOVA 1200 Quanta Chrome instrument. The morphological characteristics of the samples were determined using a FEI Quanta 200 3D dual-beam scanning electron microscope with a tungsten filament as electron source (applied voltage = 500 V – 30 kV; resolution = 3 nm). Fourier transform infrared (FTIR) spectra of the samples as KBr pellets (1 wt %) were measured in the wavenumber range of 400-4000 cm^{-1} with a spectral resolution of 4 cm^{-1} on a Shimadzu 8300 spectrophotometer.

Temperature-programmed desorption of ammonia (NH_3-TPD) measurements were performed on a Micromeritics Auto-Chem 2910 instrument [15].

3.2.3. Reaction Procedure

3.2.3.1. Esterification of FA with Glycerol. A known amount of FA and glycerol was taken in a glass, round-bottom flask placed in a temperature-controlled oil bath and fitted with a water-cooled reflux condenser. A known quantity of Fe-Zn DMC catalyst (7 wt% of FA) was added to it. Temperature of the reaction mixture was raised to a desired value and the reaction was conducted for 8 h. In kinetics studies, samples were withdrawn at regular time intervals. At the end of the reaction, the catalyst was separated by centrifugation. The liquid product was treated with petroleum ether (20 – 30 ml). Two layers formed with the bottom being glycerol and top being fatty acid glycerides and unconverted FA. Glycerol was separated out. Petroleum ether in the top layer was removed using a rotary evaporator. FA conversion was estimated by titration with 0.1 N NaOH solution and using 1,10-phenolphthalein as indicator. The composition of fatty acid glycerides was determined using a Perkin-Elmer (Series 200) high performance liquid chromatograph fitted with an ELSD detector from Gilson and a reverse-phase Perkin-Elmer Brownlee column (C-18 Spheri-5, 250 x 4.6 mm with a 5 µm particle size). The fatty acid glycerides (mono-, di- and tri-) and FA have different boiling points and can be separated from the product mixture by the conventional method of vacuum (short-path) distillation technique.

3.2.3.2. Esterification of Methyl Oleate with Long-chain Monohydric Alcohol. Methyl oleate (MO) was transesterified with C_8 – C_{12} alcohols (2-ethyl-1-hexanol, 1-decanol and 1-dodecanol). In a typical reaction, 6.76 mmol of MO and three equivalent excess of alcohol and 0.06 g of DMC catalyst (3 wt% of MO) were taken in a glass, round-bottom flask placed in a temperature-controlled oil bath and connected with a water-cooled condenser. Temperature was raised to a 180 °C and the reaction was conducted for 8 h at atmospheric pressure under a flow of nitrogen. Nitrogen drives out the by-product methanol formed in the reaction and pushes the equilibrium towards product. Then, the temperature of the reaction mixture was brought down to room temperature (25 °C) and the catalyst was separated by centrifugation/filtraton. Excess, unreacted alcohol in the product mixture was removed by steam-distillation. The product monoester was analyzed by a Perkin-Elmer (Series 200) high performance liquid chromatograph. For kinetics studies, reactions were conducted at five different temperatures (160, 170, 180, 190 and 200 °C) for a period of 4 h. Rate constants were determined from the concentration verses time plots using a pseudo-first order rate equation. Arrhenius equation enabled determination of thermodynamic parameters (activation energy and Gibbs free energy).

3.3. Results and Discussion

3.3.1. Structural Characterization

3.3.1.1. X-ray Powder Diffraction (XRD). Fig. 3.1 shows the XRD pattern of Fe-Zn DMC complexes prepared at different temperatures. The XRD patterns were indexed based on a cubic structure with the unit cell parameter being 0.904 nm. Temperature of synthesis has a marked effect on crystallinity and crystallite size of DMC. As revealed from the peak intensity, crystallinity of DMC increased with increasing temperature from 10 to 25 °C and above that this increase was only marginal. Average crystallite size determined using Scherrer equation and considering the peak corresponding to (111) also showed a similar increase in variation with the synthesis temperature (Table 3.1). Crystallite size of DMC prepared at 10, 25, 50 and 80 °C was found to be 25.9, 35, 36.7 and 39.2 nm, respectively.

Table 3.1. Physicochemical characteristics of Fe-Zn DMC

Catalyst	Crystallite size (nm, from XRD)	Morphology	Particle size (µm, from SEM	S_{BET} (m^2/g)	Acidity (mmol/g, NH_3-TPD)
DMC-10 °C	25.9	Spherical	2.1	69	1.190
DMC-25 °C	35.0	Rectangular	1.0 x 1.2	60	0.992
DMC-50 °C	36.7	Rectangular + Hexagonal	0.82 x 0.97 & 3.2	165	1.056
DMC-80 °C	39.2	No definite shape	-	160	1.101

3.3.1.2. Fourier Transform Infrared Spectroscopy. FTIR spectroscopy is an ideal technique for differentiating the various coordination modes of cyanide groups in metal complexes [33]. $K_4Fe(CN)_6.3H_2O$ shows an intense band due to ν(C≡N) at 2039 cm^{-1}, it shifts to higher wavenumber (2098 cm^{-1}) in Fe-Zn DMC complexes indicating the presence of cyanide group bridging Fe and Zn ions [15] (Fig. 3.2). FTIR spectroscopy also provided clear evidence for the presence of tert.-butanol in the DMC structure, showing distinct IR bands at 2925, 1252 – 1449 and 1092 cm^{-1} due to C-H and C-O stretching vibrations (Fig. 3.2).

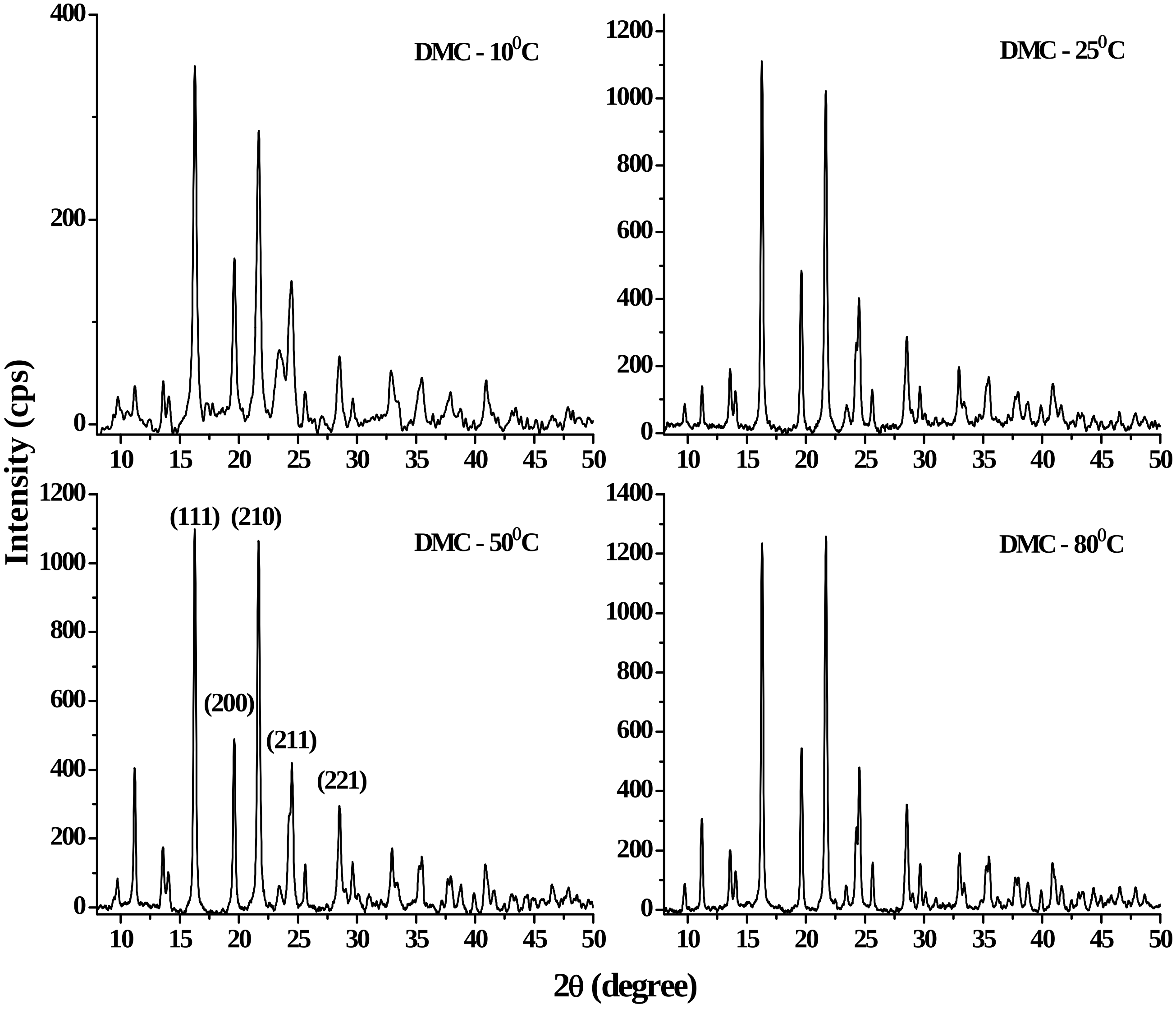


Fig. 3.1. X-ray diffractograms of Fe-Zn DMC catalysts prepared at different temperatures.

With an increase in temperature of synthesis, the number of IR bands especially those due to tert.-butanol have decreased. This decrease is due to increased crystallinity of the materials at higher synthesis temperatures. It is known that higher the symmetry lower is the number of vibrational stretching bands.

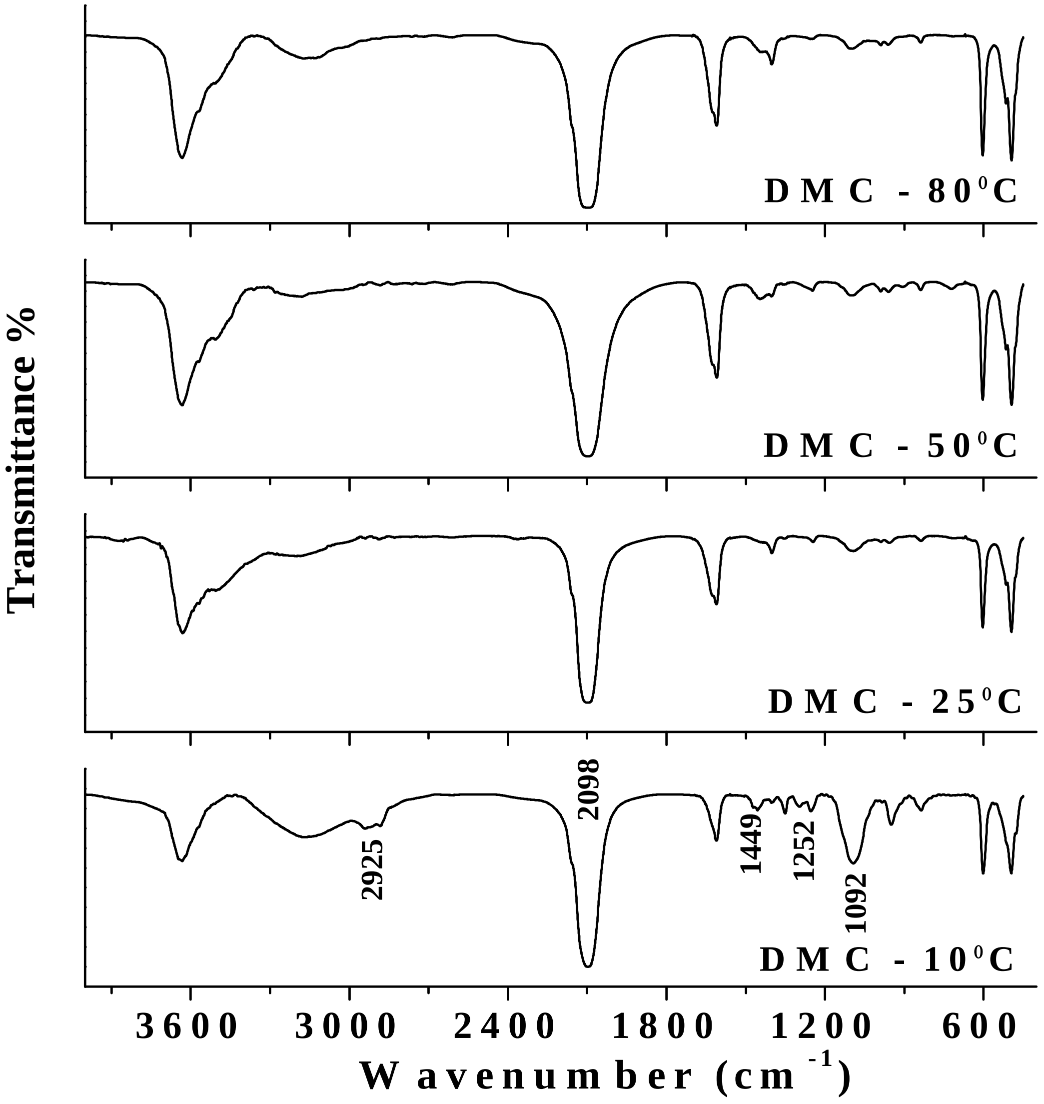


Fig. 3.2. FTIR spectra of Fe-Zn DMC catalysts synthesized at different temperatures.

3.3.1.3. **N_2-*Physisorption***. Temperature of synthesis has a major effect on the specific surface area (S_{BET}) of DMC (Table 3.1). The materials prepared at 50 and 80 °C have higher surface area (165 and 160 m^2/g, respectively) than those prepared at 10 and 25 °C (69 and 60 m^2/g, respectively). The N_2-adsorption/desorption isotherms revealed that DMC is mostly microporous as concluded based on the total micropores area which is 74% of the total specific surface area. The average pore diameter of 2.5 nm reveals the presence of some mesoporosity in DMC [16].

3.3.1.4. Scanning Electron Microscopy and High-resolution Transmission Electron Microscopy. The morphological characteristics of DMC were investigated using SEM (Fig. 3.3). The material prepared at 10 °C has mainly a spherical morphology with an average diameter of 2.1 μm. DMC prepared at 25 °C has a rectangular shape with dimensions of 1.0 x 1.2 μm. The material prepared at 50 °C has particles with rectangular (0.82 x 0.97 μm) or hexagonal (length of the side = 3.2 μm) morphology. Formation of irregular shaped particles was detected in the material prepared at 80 °C. In other words, temperature of synthesis influenced the particle size and morphological characteristics of DMC (Fig. 3.3). HRTEM confirmed the presence of mesoporosity in DMC [16].

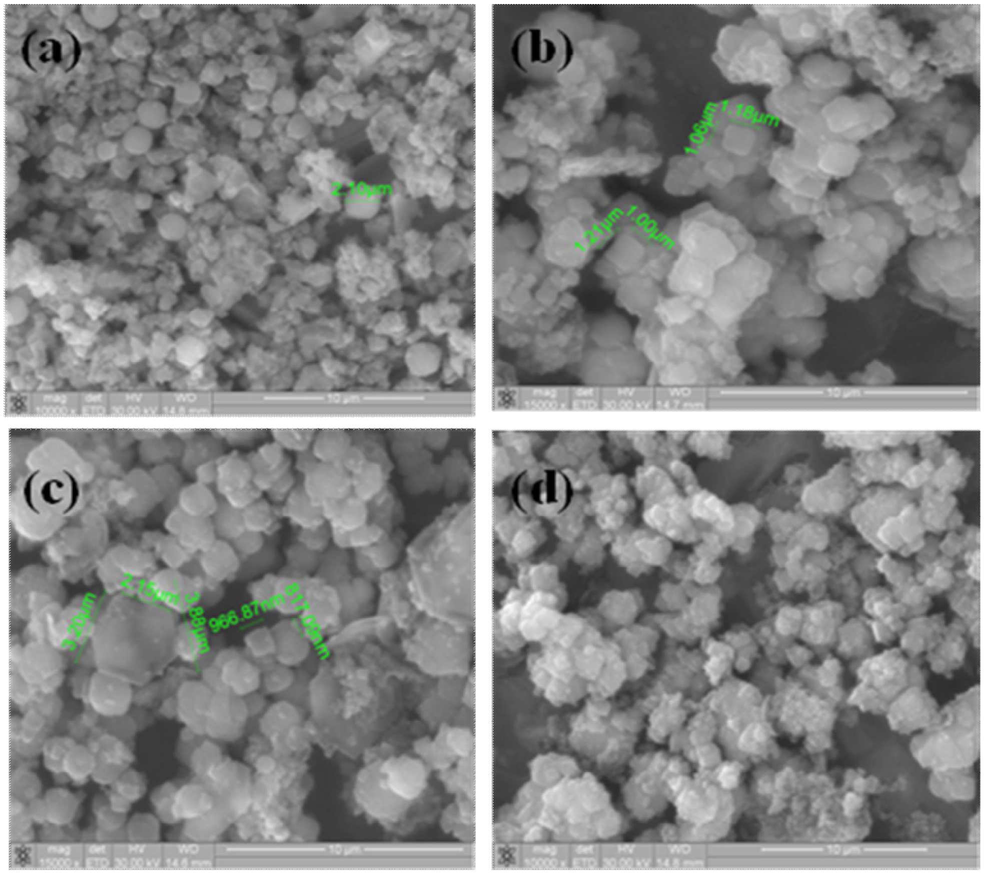


Fig. 3.3. SEM images of Fe-Zn DMC catalysts synthesized at different temperatures.

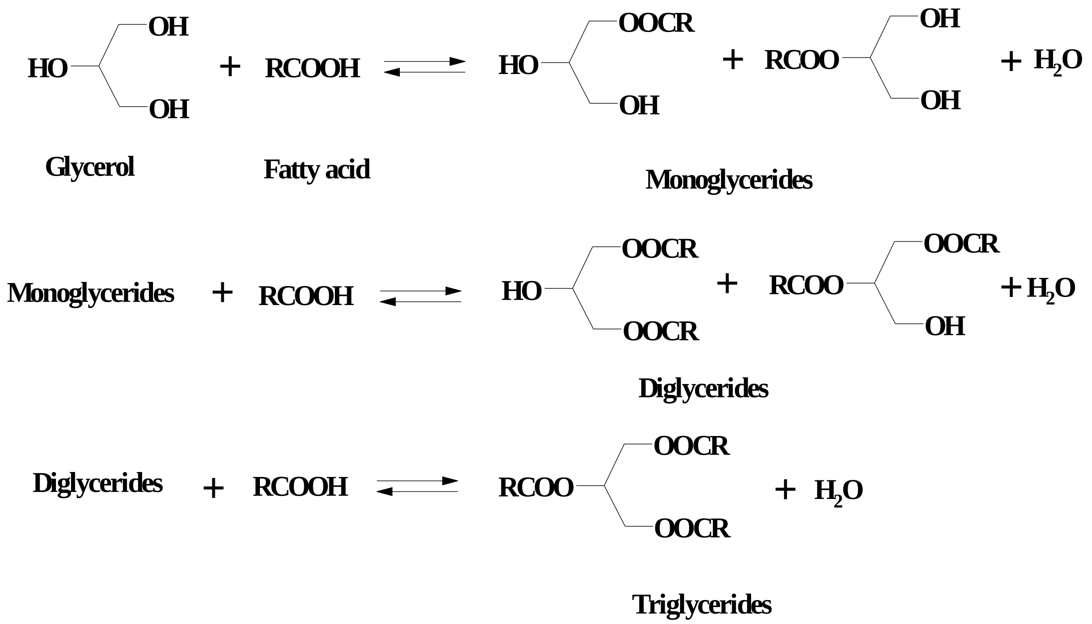
3.3.1.6. Temperature-Programmed Desorption of Ammonia. Fe-Zn complexes showed a broad, asymmetric desorption peak in NH_3-TPD which could be deconvoluted into two peaks with maximum at 160 and 190 °C, respectively [15]. While the former is assigned to weak Lewis acid sites, the latter is attributed to strong Lewis acid sites. The total amount of NH_3 desorbed from different DMC catalysts synthesized at 10, 25, 50 and 80 °C is 1.190, 0.992, 1.056 and 1.101 mmol/g, respectively (Table 3.1).

Diffuse reflectance Fourier transform infrared (DRIFT) spectra of adsorbed pyridine confirmed that DMC is Lewis acidic [15, 16]. Tetrahedrally coordinated Zn^{2+} are the sites of Lewis acidity which are active in transesterification reactions [15]. Water adsorption studies revealed that this catalyst is hydrophobic like silicalite-1 [16]. Based on elemental analysis, the molecular formula of DMC was determined to be $K_4Zn_4[Fe(CN)_6]_3.6H_2O.2(tert.\text{-}BuOH)$ [15].

3.3.2. Catalytic Activity

3.3.2.1. Esterification of FA with Glycerol

Esterification of FA is a three-step, consecutive, reversible reaction. In the first step, monoglyceride (MG) is formed. MG is converted in the second step into diglyceride (DG), which in the third step is converted into triglyceride (TG). One mole of water is produced at each step (Scheme 3.1). In general, esterification of FA with glycerol yields a mixture of mono-, di- and triglycerides. Oleic acid (OA; $C_{18.1}$) is chosen as a representative FA.



Scheme 3.1. Esterification of fatty acid with glycerol

3.3.2.1.1. Effect of Molar Ratio of Reactants. The composition of glycerides in the product mixture was changed by varying the molar ratio of reactant molecules. As the molar ratio of olecic acid (OA) increased more and more amounts of di + triglycerides have formed and as the ratio of glycerol increased monoglycerides have formed in higher amount (Fig. 3.4). At a glycerol/OA molar ratio of 0.5, mono and diglycerides have formed in nearly equal amounts. With increasing glycerol amounts (glycerol/FA molar ratio=1–12) a marginal decrease in conversion of fatty acid was observed. This is due to lower concentrations of FA. Such a behavior was not very obvious when the molar ratio of glycerol was lower (glycerol/FA molar ratio < 1) indicating that rate of esterification is dependent on FA but not on glycerol concentration. Activation of FA is, therefore, the rate determining step.

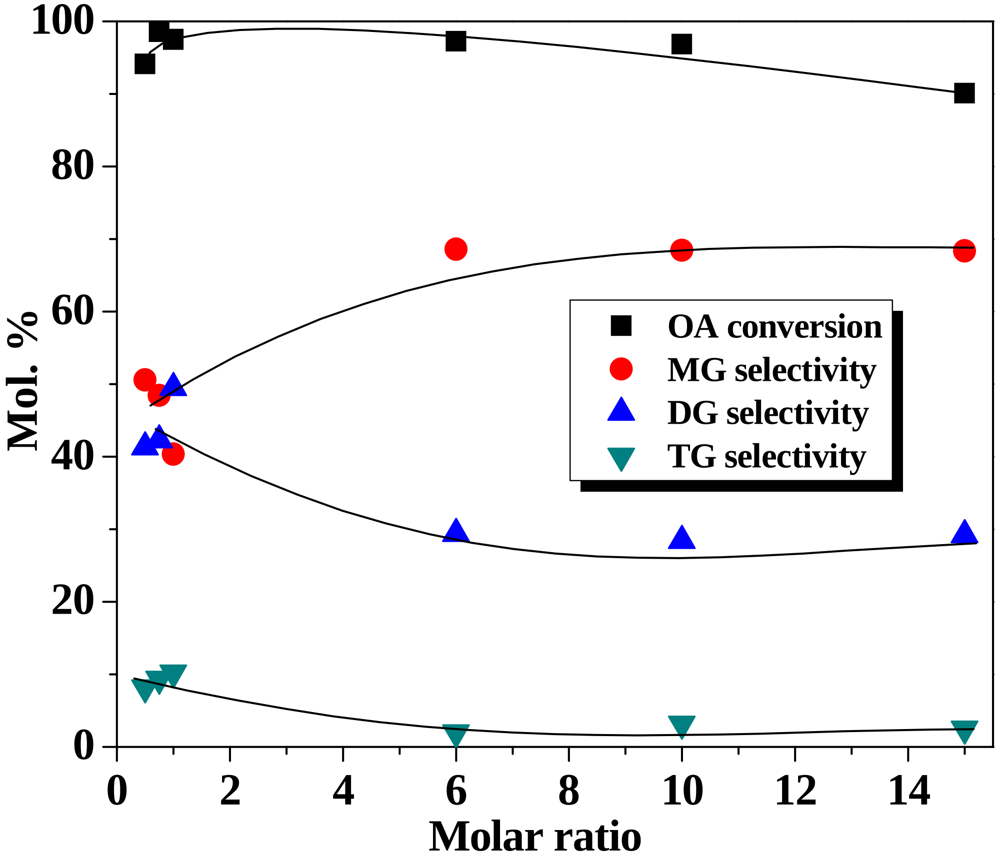


Fig. 3.4. Effect of molar ratio of oleic acid/glycerol on the esterification reaction over DMC-50°C. Reaction conditions: Oleic acid (OA) = 4 g, catalyst = 7 wt% oleic acid, reaction temperature = 180 °C, reaction time = 8 h.

3.3.2.1.2. Influence of reaction temperature. Temperature had a major effect on conversion and product selectivity. Conversion of OA was not significant below 130 °C (Table 3.2). However, it increased with increasing temperature and complete conversion of oleic acid was obtained in just 1 h at 200 °C. Esterification is an endothermic reaction. Hence, the extent of esterification increases with an increase in reaction temperature. Monoglyceride is the predominant product formed with a selectivity of 83.8% at lower temperatures. As the temperature increased, the selectivity for monoglycerides decreases with a concomitant increase in the selectivity for di + triglycerides.

Table 3.2. Effect of temperature on esterification of oleic acid with glycerol over DMC-50°C

Reaction temperature (^{0}C)	Oleic acid conversion (mol%)	Product selectivity (mol%, by HPLC)		
		MG	DG	TG
140	20.9	83.8	15.5	0.6
160	37.3	68.4	29.9	1.6
180	62.7	65.1	33.8	1.1
200	95.0	53.6	39.1	7.3

Reaction conditions: Oleic acid = 4 g, acid : glycerol (molar ratio) = 1 : 1, Catalyst = 7 wt% oleic acid, reaction time = 1 h.

3.3.2.1.3. Influence of reaction time. Fig.3.5 depicts the kinetics of glyceride formation at 180 °C from oleic acid (OA) and glycerol over DMC-50 °C. Nearly 50% conversion of OA was observed in just 30 min and near complete conversion of it was achieved after 6 h. In the initial hours, monoglycerides formed with high selectivity (~79%) and with time, these got converted into di- and triglycerides. At the end of 8 h, the combined selectivity for di and triglycerides was about 59%. The kinetic plot (Fig. 3.5) clearly reveals the consecutive nature of this reaction. Monoglycerides are better emulsifiers than di- and triglycerides and hence, the reaction needs to be conducted at lower temperatures and shorter period of time.

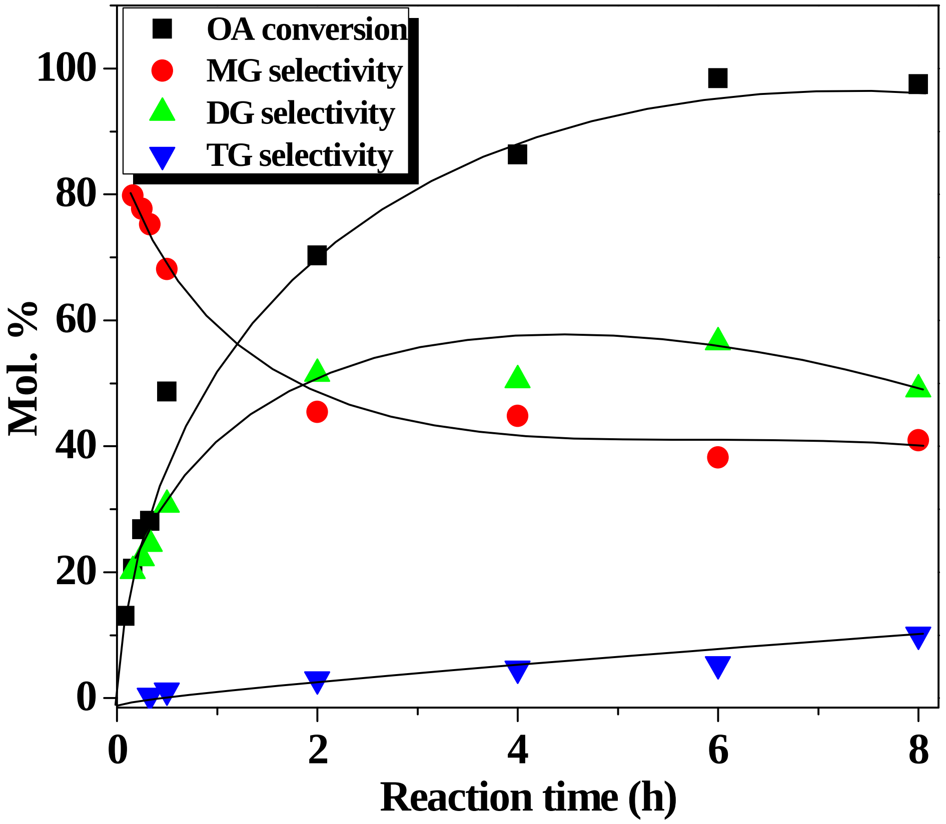


Fig. 3.5. Kinetics of esterification of oleic acid with glycerol over DMC-50°C. Reaction conditions: Oleic acid (OA) = 4 g, acid : glycerol molar ratio = 1 : 1, catalyst = 7 wt% OA, reaction temperature = 180 °C.

3.3.2.1.4. Influence of FA chain length. The catalytic performance of hydrophobic DMC for the esterification of fatty acids of varying chain length (lauric acid, myristic acid, steric acid, oleic acid) with glycerol was studied. Chain-length of FA has a notable effect on conversion while the selectivity of glycerides is nearly the same (Table 3.3). Conversion decreased with increase in the FA chain length. Similar observation was found also by others with mineral acid catalysts. In those cases miscibility of different fatty acids with glycerol was attributed to be the cause for the difference in activity. However, in the present case, the reactions were conducted at elevated temperatures (unlike in the case of mineral acids) and hence, miscibility would not be an issue. In other words, the acids with lower chain length are inherently more easily converted than those with longer chain-length.

Table 3.3. Effect of chain length of fatty acid on esterification reaction with glycerol

Fatty acid	Acid conversion (mol %)	Product selectivity (mol %)		
		MG	DG	TG
Lauric ($C_{12.0}$)	75.0	66.0	28.8	5.2
Myristic ($C_{14.0}$)	75.9	69.4	24.0	6.6
Stearic ($C_{18.0}$)	62.2	77.7	19.0	3.3
Oleic ($C_{18.1}$)	62.7	65.1	33.9	1.0

Reaction conditions: Fatty acid = 3 g, fatty acid: glycerol (molar ratio) = 1:1, reaction temperature = 180 ^{0}C, catalyst = 0.21 g, reaction time = 1 h.

3.3.2.1.5. Influence of addition of water to reaction mixture. Fe-Zn DMC was found to be very active in esterification reactions. Table 3.4 shows the influence of the addition of water on esterification activity and selectivity. As seen from Table 3.4, on adding water to the reaction medium conversion of oleic acid decreased only slightly. Interestingly a marginal increase in triglyceride selectivity was detected. Water must have acted as an emulsifier enhancing the miscibility of reactants. Also DMC is a hydrophobic catalyst and quite stable even if water is formed, it is not competing for adsorption with FA at our reaction conditions. This is a major advantage of DMC catalyst.

Table 3.4. Influence of water addition on esterification of oleic acid with glycerol over DMC-50 °C catalyst

Amount of water added (wt %)	Oleic acid conversion (mol %)	Product selectivity (mol%, by HPLC)		
		MG	DG	TG
0	63.4	67.3	31.7	1.0
0.13	63.7	65.1	33.7	1.2
0.25	58.4	62.7	35.1	2.2
0.5	58.8	62.5	35.2	2.3

Reaction conditions: Oleic acid (OA) = 4 g, OA : glycerol (molar ratio) = 1:1, catalyst = 7 wt. % OA, reaction temperature = 180 °C, reaction time = 1 h.

3.3.2.1.6. Influence of catalyst amount. The amount of DMC-50 °C catalyst was varied from 1 to 10 wt % of OA and the reaction was conducted at 180 °C for 1 h. A linear increase in conversion with the amount of catalyst was detected (Table 3.5). This variation and the correspondence of catalytic activity with the acidity and surface area indicate that there are no transport limitations at the experimental conditions.

Table 3.5. Influence of catalyst amount on esterification of oleic acid with glycerol over DMC-50 °C catalyst

Catalyst amount (wt%)	Oleic acid conversion (mol %)	Product selectivity (mol%, by HPLC)		
		MG	DG	TG
0	47.3	67.7	31.0	1.2
3	53.8	68.1	30.9	1.0
5	58.4	67.3	31.5	1.2
7	62.7	65.1	33.9	1.0
10	68.1	66.6	31.9	1.4

Reaction conditions: Oleic acid (OA) = 4 g, OA : glycerol (molar ratio) = 1:1, reaction temperature = 180 °C, reaction time = 1 h.

3.3.2.1.7. Influence of synthesis temperature. DMC catalysts prepared at different temperatures exhibited different catalytic activities (Table 3.6). DMC-25 °C showed the lowest conversion of OA. DMC-50 °C and DMC-80 °C exhibited the highest activity. This variation can be explained in terms of differences in their acidity and specific surface area. DMC-25 °C has the lowest surface area and total acidity. Hence, it showed lowest conversion of oleic acid. DMC- 50 °C and DMC-80 °C have the highest surface area, thereby enabled highest conversions. DMC-10 °C has high acidity but low surface area and thus showed lower conversion. In other words, these studies reveal that both surface area and acidity influence the catalytic activity of DMC catalysts. The catalyst prepared at 50 °C has optimum values of these parameters and hence proved to be an efficient catalyst. By varying the active site density within a given catalyst particle, Madon and Boudart [34], proposed that if the rate per active site density is constant, then the rate is free from transport artifacts.

Table 3.6. Effect synthesis temperature on the catalytic activity of DMC catalysts in esterification of oleic acid with glycerol

Catalyst synthesis temperature (° C)	Acid conversion (mol %)	Product selectivity (mol %)		
		MG	DG	TG
10	90.8	46.6	42.8	10.6
25	88.5	60.3	30.8	8.8
50	94.5	52.6	38.6	8.7
80	94.6	60.3	30.8	8.8

Reaction conditions: Oleic acid (OA) = 4 g, OA : glycerol (molar ratio) = 1 : 1, catalyst = 7 wt% OA, reaction temperature = 180 °C, reaction time = 4 h.

3.3.2.1.8. Catalyst reusability. Table 3.7 lists the reusability data of DMC catalyst in two recycling experiments. At the end of each run, the catalyst was separated and reused in the next cycle without any washing or activation. The catalyst retained its activity even after its use. The reused catalyst showed similar XRD profile to that of fresh catalyst indicating that the composition and structural integrity of DMC catalyst are not disturbed during esterification runs. In contrast to other acid catalysts, hydrophobic DMC facilitates adsorption and activation of hydrophobic FA molecules and thereby enables higher conversion. DMC catalysts are insoluble in almost all the solvents including aqua-regia. Hence, the question of leaching of metal ions into liquid medium of the reaction mixture doesn't occur.

Table 3.7. Catalyst reusability study

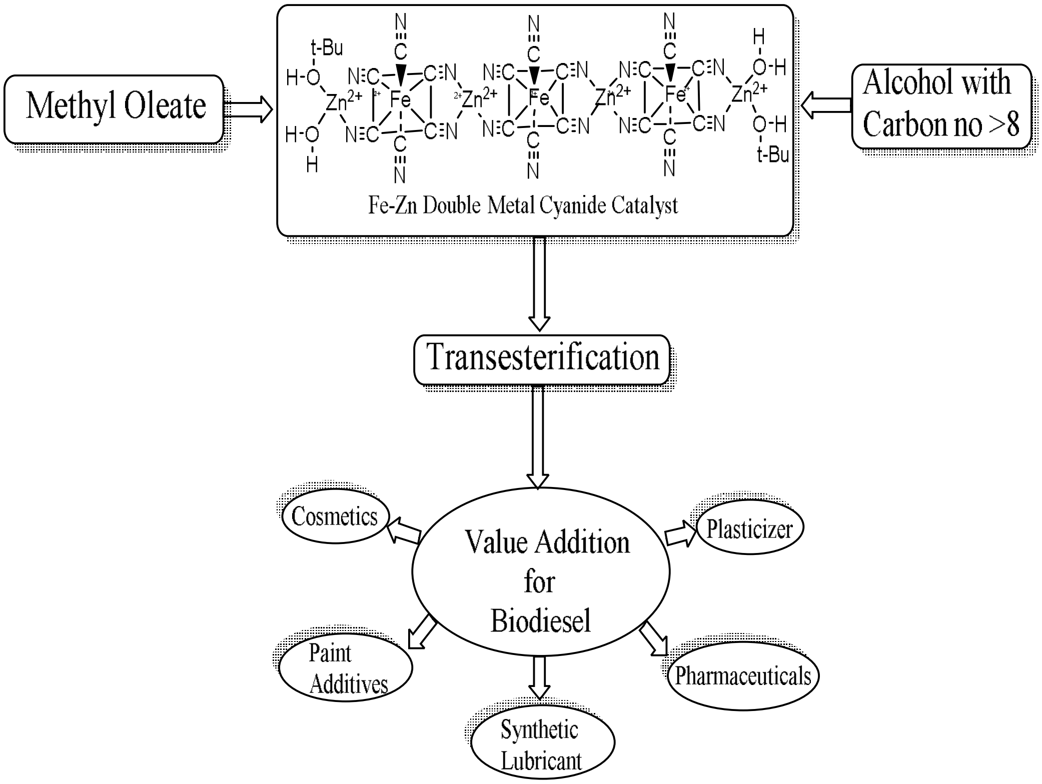
Number of recycles	Oleic acid conversion (mol %)	Product selectivity (mol%, by HPLC)		
		MG	DG	TG
0	63.4	67.3	31.7	1
1	62.0	71.3	27.3	1.4
2	62.7	70.7	28.2	1.1

Reaction conditions: Oleic acid = 4 g, acid: glycerol (molar ratio) = 1:1, catalyst (DMC-50 °C) = 7 wt.% of oleic acid, reaction temperature = 180 °C, reaction time = 1 h.

3.3.2.2. Transestrification of Methyl Oleate with 2-Ethyl-1-hexanol

Ester oils have been widely applied in industry as a major supplement to hydrocarbon oils produced from petroleum [35, 36]. About 10% of global lubricating oil production (including esters) is fully synthetic products. In comparison to hydrocarbon oils, esters have good lubricity. A great majority of ester oils are harmless and easily biodegradable in the natural environment [37, 38]. Ester oils are miscible with a large number of additives to formulate effective biodegradable lubricants.

Transesterification of methyl oleate (MO) with long-chain monohydric alcohols (2-ethyl-1-hexanol, 1-decanol and 1-dodecanol) yields fatty acid monoesters that find application not only in synthetic lubricants but in paint additives, plasticizers, pharmaceuticals and cosmetics (Scheme 3.2). Methanol is a by-product. Formation of ethers via condensation of long-chain alcohols or methanol was not detected at the experimental conditions over DMC catalyst (HPLC, GC and ^{1}H NMR).



Scheme 3.2. Possible structure of DMC and the uses of fatty monoesters.

3.3.2.2.1. Effect of Catalyst Amount. Control experiments at 180 °C for 8 h with 2-ethyl-1-hexanol/MO molar ratio = 3, revealed that this reaction occurs even in the absence of a catalyst. But the yield of 2-ethylhexyl oleate was 37 mol% only (Fig. 3.6). In presence of DMC catalyst, the yield was higher and it increased with increasing amount of the catalyst, reached a maximum of 70 mol% at a catalyst loading of 3 wt% of MO and became stable thereafter. External mass transfer is the possible cause for this behavior at catalyst loadings above 3 wt%. Further optimization studies were conducted taking 3 wt% of the catalyst.

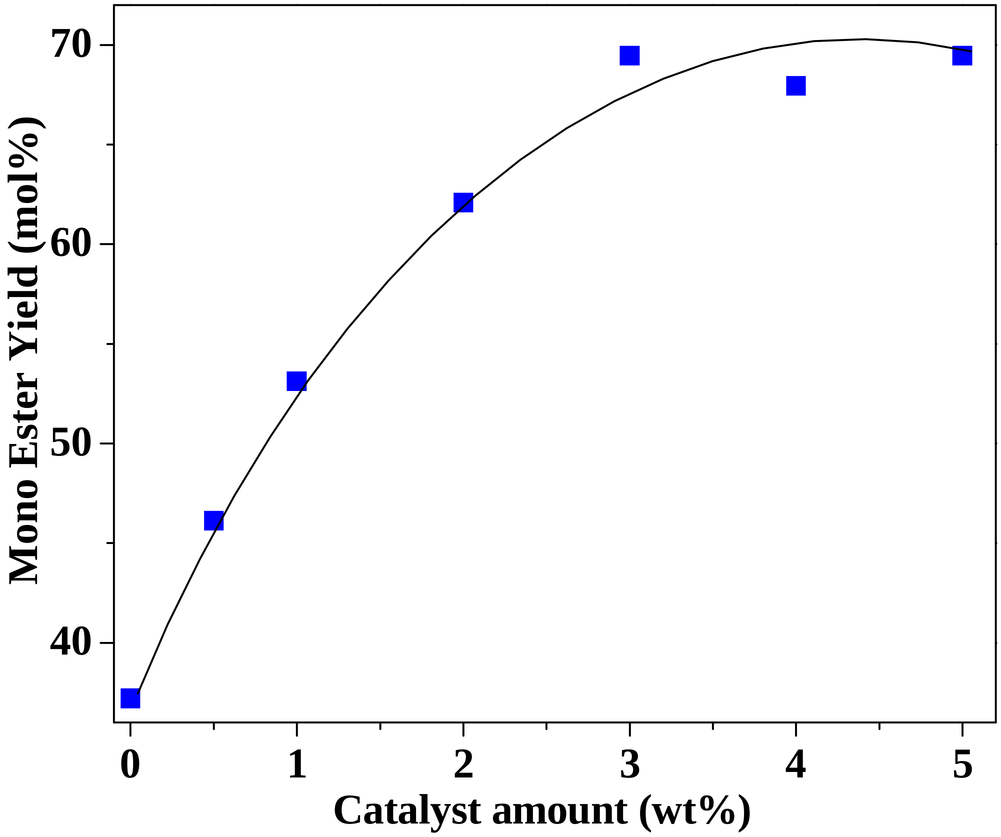


Fig. 3.6. Effect of amount of catalyst (DMC-50 °C). Reaction conditions: methyl oleate (MO) = 2 g, 2-ethyl-1-hexanol = 2.64 g, MO: 2-ethyl-1-hexanol (molar ratio) = 1 : 3, reaction temperature = 180 °C, reaction time = 8 h, pressure = 1 atm, under a positive flow of nitrogen.

3.3.2.2.2. Effect of Molar Ratio of Reactants. Transestrification is a reversible reaction. Excess amount of alcohol shifts the equilibrium towards ester formation [39-41]. In this study the molar ratio of MO/2-ethyl-1-hexanol was varied between 1:1 and 1:15 (Fig.3.7). The yield of 2-ethylhexyl oleate increased with increasing molar ratio of reactant and reached a maximum of 70 mol% at 2-ethyl-1-hexanol/MO molar ratio of 3 and decreased thereafter (reaction conditions: 180 °C, 8 h and catalyst = 3 wt% of MO). At much higher concentrations of 2-ethyl-1-hexanol (molar ratio of 2-ethyl-1-hexanol/MO ≥ 5), accessibility of MO to the active sites would be low and hence, lower yields of 2-ethylhexyl oleate were obtained.

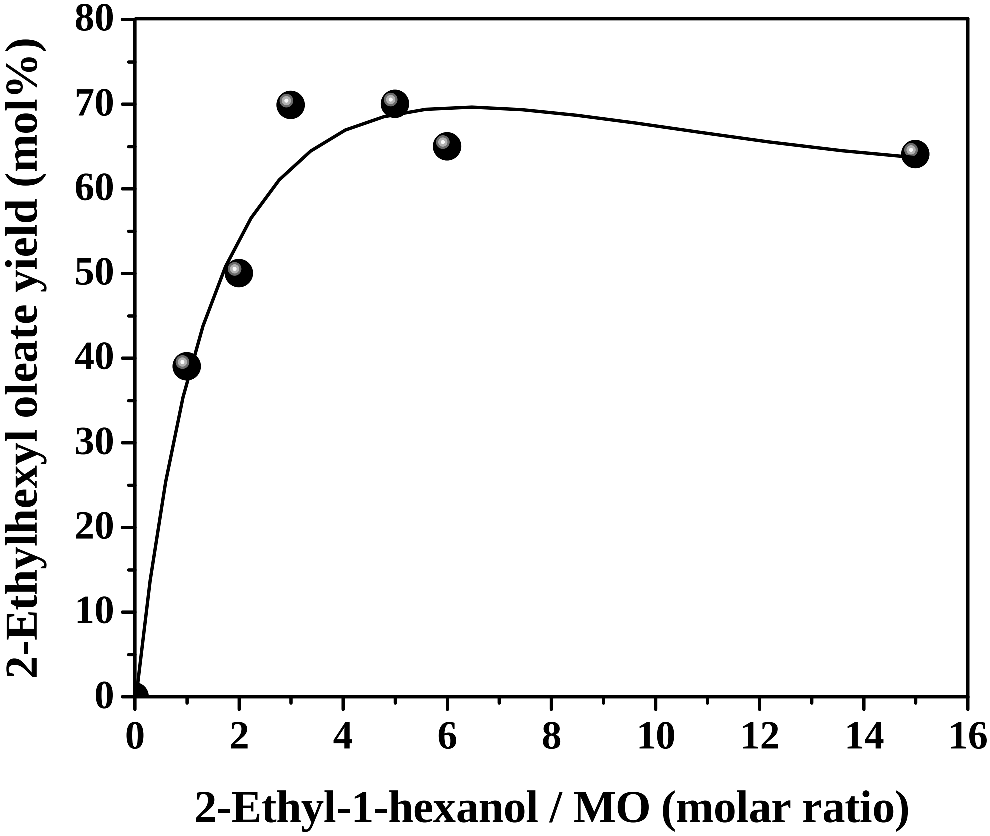


Fig. 3.7. Effect of 2-ethyl-1-hexanol/MO molar ratio on the yield of 2-ethylhexyl oleate. Reaction conditions: MO = 2 g, catalyst (DMC-50 °C) = 3 wt% of MO, reaction temperature = 180 °C, reaction time = 8 h, pressure = 1 atm, under a positive flow of nitrogen**.**

3.3.2.2.3. Effect of Reaction Temperature and Time. Catalyst tests were carried out at various reaction temperatures (160, 170, 180, 190 and 200 °C) using MO : 2-ethyl-1-hexanol (molar ratio) = 1: 3 and catalyst loading of 3 wt% of MO. MO conversion increased with the increase in the reaction temperature. At 200 °C and in 4 h, monoester yield as high as 96.7 mol% was obtained (Fig. 3.8). Most of the known acid catalysts at high temperatures form ethers. The unique feature of DMC is that even at 200 °C, formation of such undesired ether products was not detected. The selectivity for the monoester and methanol were 100%. Under similar reaction conditions, product yield increased with increasing reaction time and attained equilibrium at 8 h. From the conversion verses time plots at five different temperatures, rate constant and energy of activation (E_a from the Arrhenius plot) were determined. The E_a value for DMC-50 °C was determined to be 75.9 kJ/mol. Using Eyring equation enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were determined to be 72.3 kJ/mol and -283.3 J/mol, respectively.

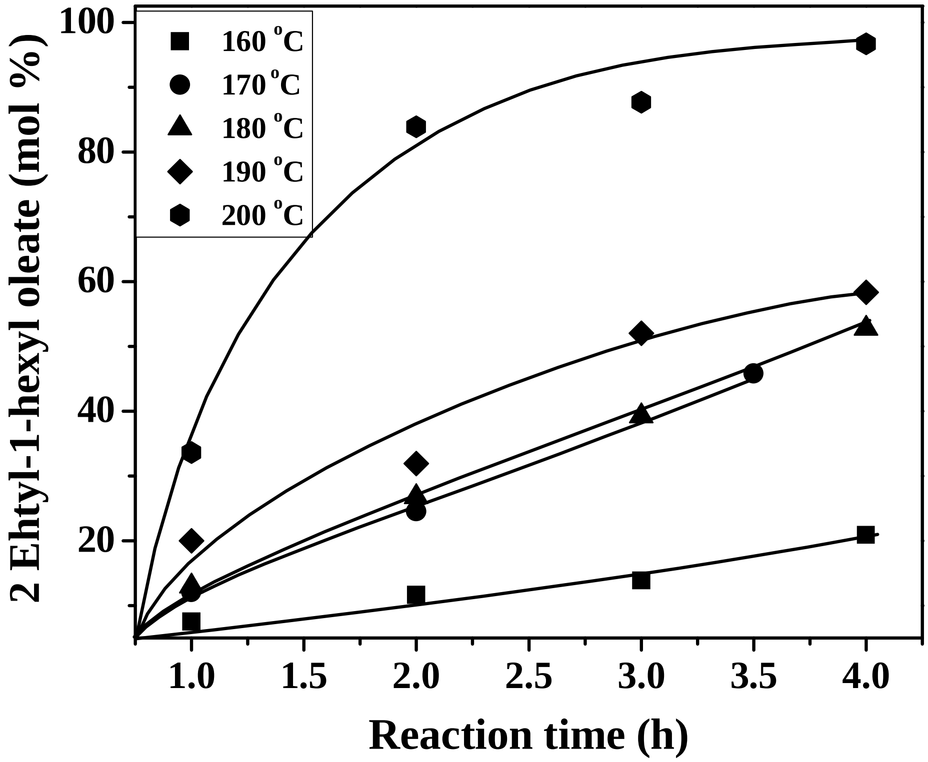


Fig. 3.8. Effect of reaction temperature and time. Reaction conditions: methyl oleate (MO) = 2 g, 2-ethyl-1-hexanol = 2.64 g, MO: 2-ethyl-1-hexanol (molar ratio) = 1 : 3, catalyst (DMC-50 °C) = 3 wt% of MO, pressure = 1 atm, under positive flow of nitrogen.

3.3.2.2.4. Transesterification of MO with Different Alcohols. DMC is effective for transesterification of MO with different long-chain alcohols (Fig. 3.9). A marginal decrease in equilibrium conversion of MO from 70 to 62 mol% was observed when 1-dodecanol instead of 2-ethyl-1-hexanol was used. The monoester product after removal of methanol and unreacted 2-ethyl-1-hexanol was pale yellow in color.

3.3.2.2.5. Catalyst reusability. DMC was reused in four recycling experiments. At the end of each run, the catalyst was separated from the reaction mixture. It was washed with methanol, dried at 100 °C for 12 h and used in another recycle. The yield of 2-ethylhexyl oleate was nearly the same in each recycle. XRD and FTIR spectra of the fresh and spent catalyst (at the end of 4th recycle) were almost the same (Fig. 3.10) confirming the structural integrity of DMC-50 °C in several transesterification runs. No leaching of metal ions was detected as revealed by atomic absorption spectroscopy (AAS) studies.

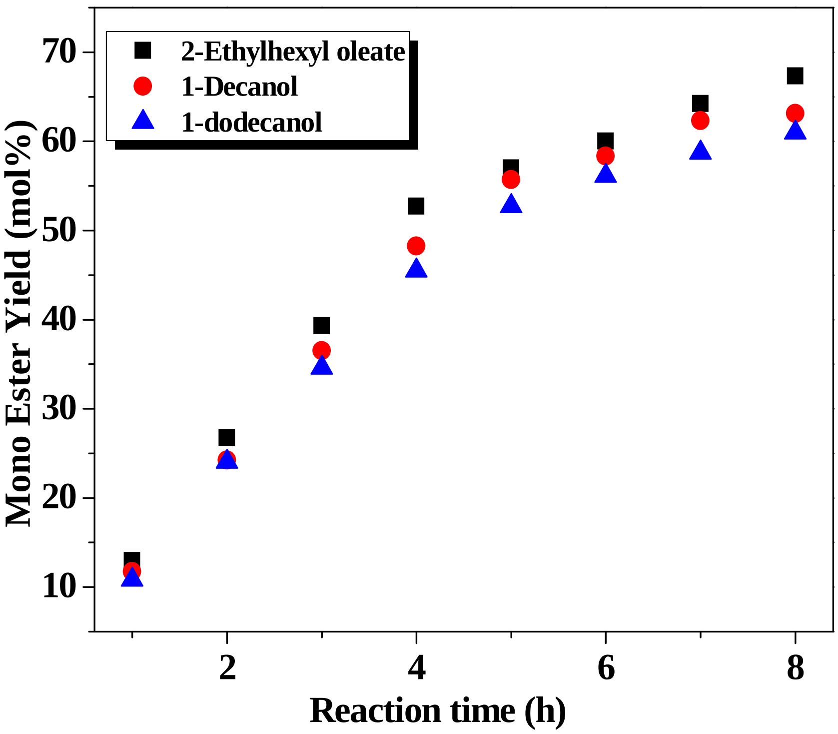


Fig. 3.9. Effect of chain length of alcohol on the yield of fatty monoester. Reaction conditions: MO = 2 g, MO: long-chain alcohol (molar ratio) = 1:3, DMC-50 °C = 3 wt% of MO, reaction temperature = 180 °C, reaction time = 8 h, pressure = 1 atm, under a positive flow of nitrogen.

Physical properties of the monoester biolubricants prepared using DMC-50 °C are reported in Table 3.8. They match well with those of hydrolic oil lubricants confirming that these long-chain alcohol fatty esters are suitable lubricant base oil. Kinematic viscosity long-chain alcohol oleates were higher than that of the starting ester (MO). As expected, 2-ethylhexyl oleate has pour point lower than the other esters and MO.

Table 3.8. Properties of methyl oleate and long-chain alcohol oleate prepared using DMC-50 °C

Test description	Units	Methyl oleate	2-Ethylhexyl oleate	Decyl oleate	Dodecyl oleate	Test method
Kinematic viscosity @ 40 °C	cST	4.628	7.417	9.091	11.93	IS 1448 (P25) 2007
Kinematic viscosity @ 100 °C	cST	1.764	2.423	2.573	3.377	IS 1448 (P25) 2007
Viscosity index	-	-	167	116	169	IS:1448[p.56]
Density @ 15 °C	g/cc	0.8804	0.8717	0.8581	0.8619	IS 1448 (P32) 2008
Acid value	mgKOH/g	Nil	Nil	Nil	Nil	IS:1448[p.1
Flash point (Cleveland open cup)	°C	177	145	123	157	IS 1448 (P69) 2008
Pour point	°C	-15	< -27	-6	+9	IS 1448 (P10, sec 2) 2013, ISO 3016: 1994
Copper strip corrosion for 3 h @100 °C	-	1b (slight tarnish)	1a (slight tarnish)	1b (slight tarnish)	1b (slight tarnish)	IS 1448 (P15) 2011, ISO 2160: 1998
Water content	vol%	<0.05	<0.05	<0.05	<0.05	IS 1448 (P40) 2011

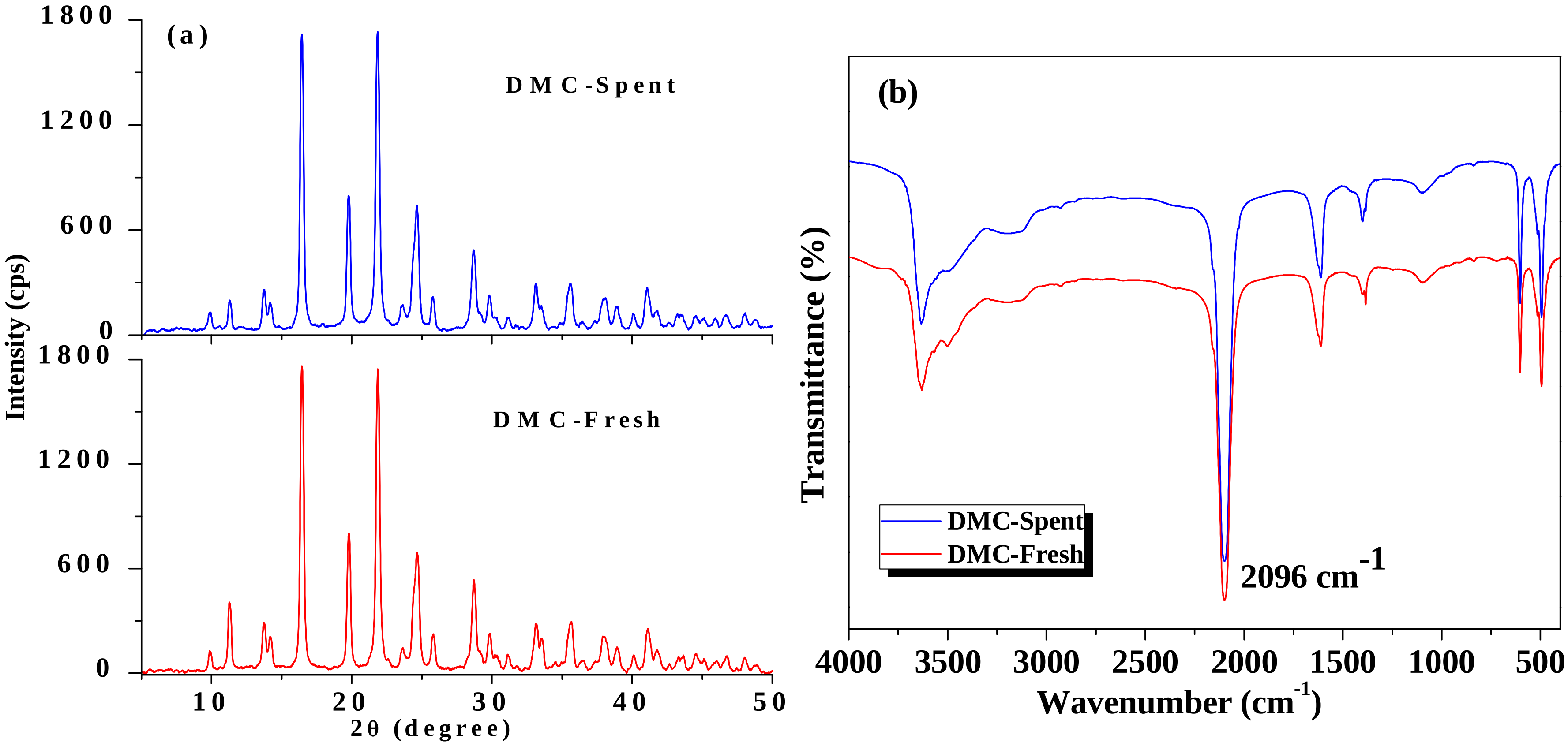


Fig.3.10. (a) XRD and (b) FTIR spectra of fresh and spent DMC-50 °C catalysts

3.3.2.2.6. Tentative Reaction Mechanism. A tentative mechanism for this reaction over Lewis acidic Zn^{2+} active sites in DMC catalyst is shown in Fig. 3.11. Activation of MO at Zn^{2+} site, formation of carbo cation, nucleophilic attack by 2-ethyl-1-hexanol on the carbo cation followed by removal of methanol and 2-ethylhexyl oleate ester formation are the steps involved in the reaction.

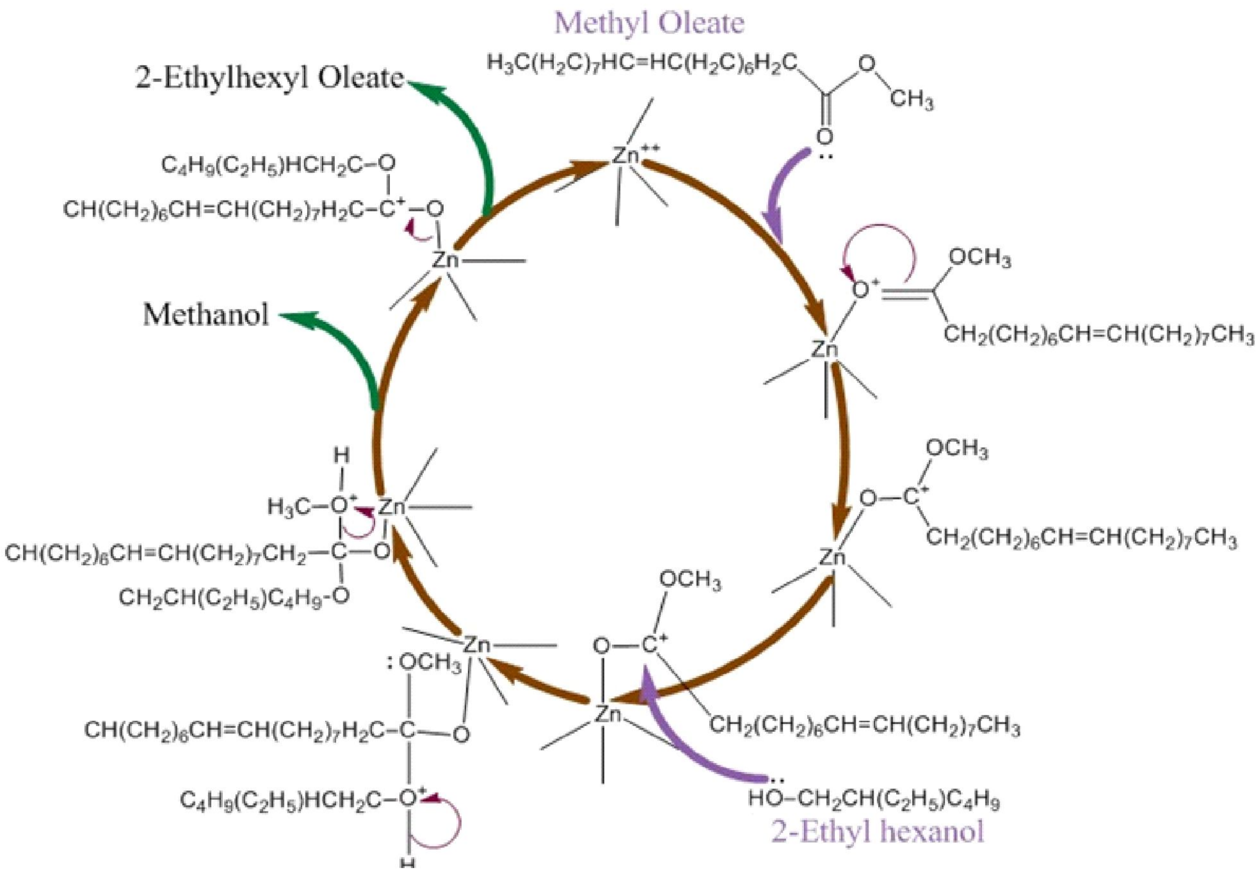


Fig. 3.11. Tentative mechanism for the reaction of methyl oleate with 2-ethyl-1-hexanol.

3.4. Conclusions

Esterification for FA with glycerol was investigated over Lewis acidic Fe–Zn DMC catalysts. Surface area, acidity and hydrophobicity of the catalyst surface are the parameters that influenced the catalytic activity. Monoglycerides can be formed with high selectivity by conducting the reaction at lower temperatures and for shorter period of time. Water formed during the reaction did not deactivate the catalyst as the surface of DMC is hydrophobic. DMC prepared at 50 °C showed better performance.

Catalytic activity of DMC for forming fatty monoester lubricants through transesterification of methyl oleate (FAME-biodiesel) with long-chain alcohols (2-ethyl-1-hexanol, 1-decanol and 1-dodecanol) was also investigated. DMC was reusable in at least four recycling experiments with little loss in catalytic activity. The product long-chain alcohol esters have the desired physical properties required for lubricant applications. Fatty monoester of long-chain alcohols was the selective product over DMC.

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Chapter - 4

Three-Dimensional Mesoporous Titanosilicates as Catalysts for Synthesis of Fatty Acid Polyol Esters

4.1. Introduction

Esters of fatty acids are known as natural lubricating oils. These esters are valuable chemical compounds that find application in pharmaceuticals, food and cosmetics production [1]. They are also used as raw material for emulsifiers, surfactants and lubricants [2, 3]. Worldwide, the lubricant demand in 2010 was about 36.7 million metric tons [4-6].Out of that, about 53% is collected as waste, thus endangering our planet. Use of rapidly degradable lubricants instead of the conventional petroleum-derived lubricants could significantly reduce the environmental pollution. The bio-based lubricants have several advantages [1, 7]. They are biodegradable and renewable. They possess excellent lubricity. Their friction coefficient is lower than that of mineral oils. They have lower evaporation (up to 20% lesser than mineral oils). Their higher flash point reduces the risk of fires in applications such as metal cutting. Finally, they possess higher viscosity indices. However, there are some issues related to their thermal and oxidation stability, poor low-temperature fluidity and hydrolytic instability that restrict their widespread use. But then, these shortcomings can be overcome by using chemically modified vegetable oils in combination with available additives (antioxidants and pour point depressants) and diluents or functional fluids [8-10]. Cost-effective production is one the challenging tasks for their extensive use.

Their manufacture using solid catalysts is expected to lower the production cost [11–17]. Base catalysts cannot be used for fatty acid esterification due to the deactivation and soap formation. Several solid acid catalysts including $WO_3/AlPO_4$,WO_3/ZrO_2, silica-bonded N-propyl sulfamic acid, silica-supported tin oxide, sulfated-zirconia/titania/tin oxide, sulfonic acid/SBA-15, $H_3PW_{12}O_{40}$ supported on ZrO_2 and Ta_2O_5, sulfonated-carbon and Nb_2O_5-MCM-41 have been reported for reactions of fatty compounds with short chain alcohols [18–22]. Their application for biolubricants production using polyhydric alcohols is scarce. Zeolites have attracted great attention in the field of catalysis due to their unique pore structure, high surface area and high stability [23]. However, these materials present severe limitations when bulky reactant molecules like fatty compounds are employed. Of late, greater attention is being paid to use mesoporous solids instead of zeolites to overcome the above limitation [24–26]. Development of catalysts which are stable and do not leach out during reactions with fatty acids is highly challenging.

Among Santa Barbara Amorphous (SBA)-type mesoporous silicas, SBA-12 and SBA-16 attract much attention due to their outstanding stability and three-dimensional mesopore architecture [27, 28]. Anuj Kumar et al [29-31] reported a method for direct synthesis of framework-substituted Ti in Ti-SBA-12 and Ti-SBA-16. These Ti materials exhibited high catalytic activities for epoxidation of cyclic olefins, for the synthesis of β-amino alcohols through ring-opening of epoxides with amines and for hydroxylation of phenol with peroxides. For the first time, the application of Ti-SBA-12 and Ti-SBA-16 as catalysts for producing biolubricants is reported in this chapter. Ti incorporation in the framework of silica generates Lewis acid sites which are active for esterification reaction. Esterification of oleic acid (OA, a representative fatty acid) with polyhydric alcohols viz., glycerol (G), trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritol (PE) is investigated for producing the synthetic esters. The composition of the glyceride esters in the product is controlled/varied by changing OA to polyol molar ratio, reaction temperature, reaction time and type of catalyst used.

4.2. Experimental

Ti-SBA-12 and Ti-SBA-16 materials were prepared as reported in Chapter-2 (Section 2.2.2). Glycerol (1,2,3-propanetriol, ≥99.5%) and FA oleic acid (cis-9-octadecenoic acid, C18:1; ~99%)] used in the reactions were procured from Aldrich Co. Caprylic acid (C8), capric acid (C10) and lauric acid (C12) were procured from s.d. fine Chem Ltd., India. Details on reaction procedure and product analysis are reported in Chapter-2 (Sections 2.4.1 and 2.5).

4.3. Results and Discussion

4.3.1. Structural Characterization

4.3.1.1. X-ray Powder Diffraction. SBA-12 showed an intense main peak at 1.68° corresponding to (002) reflection and two well-resolved, weak peaks at 2.90° and 3.28° attributable to (112) and (300) reflections, respectively. A weak shoulder (to the main peak) at 1.47° due to (100) reflection was also observed. These characteristic features of SBA-12 were consistent with the ordered, three-dimensional, hexagonal mesoporous structure with a space group of $p6_3/mmc$ [31]. SBA-16 showed a strong peak at 0.92° attributable to (110) reflection and two poorly-resolved, weak peaks at 1.2° and 1.9° due to (200) and (211) reflections, respectively. The diffraction patterns of SBA-16 were indexed to an ordered, three-dimensional, mesoporous, cubic structure with a space group of $Im\bar{3}m$ [31]. In the case of Ti containing samples (Ti-SBA-12 and Ti-SBA-16), these peaks shifted to lower 2θ values evidencing an increase in the unit cell and substitution of Ti^{4+} for Si^{4+} in the framework location of mesoporous silica. In the case of Ti-containing materials these peaks shifted to lower 2θ values. Ti incorporation did not alter the integrity of the framework structure [31].

4.3.1.2. Diffuse Reflectance UV-Visible Spectroscopy. Ti-SBA-12 and Ti-SBA- 16 showed absorption bands with maximum at 206 nm (due to Ti with tetrapodal $Ti(Osi)_4$ structure) and 217–220 nm (due to Ti with tripodal $Ti(Osi)_3(OH)$ structure). The spectra indicated the presence of mono-atomically dispersed Ti^{4+} ions in tetracoordination geometry. A weak absorption band at 315 nm for octahedral anatase type Ti species was found in the case of Ti-SBA-12 [31].

4.3.1.3. N_2-Physisorption. The long range mesoporous ordering of Ti-SBA-12 and Ti-SBA-16 catalysts was confirmed by high resolution transmission electron microscopy and N_2 physisorption studies. The SBA-12 materials have a three-dimensional, hexagonal, closed-packed (hcp) mesopore structure whereas the SBA-16 materials have a three-dimensional, body-centered cubic (bcc), cage-like interconnected mesopore structure. Textural properties of Ti-SBA-12 and Ti-SBA-16 along with their all silica samples are reported in Table 4.1 [31].

4.3.1.4. ^{29}Si Magic-Angle Spinning Nuclear Magnetic Resonance. Ordered SBA-12 and Ti-SBA-12 showed signals at −91.8, −100.9 and −110.6 ppm, corresponding to presence of three different types of silica species, Q^2, Q^3 and Q^4. SBA-16 and Ti-SBA-16 showed two signals at −98.1 and −108.5 ppm attributable to Q^3 and Q^4 type silica species, respectively [31]. The downfield shift in Q^3 and Q^4 signals of Ti-SBA-16 was due to differences in the structures of Ti-SBA-16 compared to Ti-SBA-12. Spectral deconvolutions revealed that the signal intensity ratio of $Q^4/(Q^3+ Q^2)$, a representative of surface hydrophobicity, is one order of magnitude higher for SBA-16 than for SBA-12 material. In other words, SBA-16 materials were found to be relatively more hydrophobic than SBA-12 [31]. This conclusion was confirmed further from the thermogravimetric studies of the calcined samples [31].

Acidic properties of these catalysts were determined using pyridine and ammonia as probe molecules [31]. Diffuse reflectance infrared spectra of adsorbed pyridine revealed the presence of Lewis-type acid sites. The density of acid sites was determined (from temperature-programmed desorption of ammonia studies; NH_3-TPD) and listed in Table 4.1.

The characterization studies revealed that the titanosilicates of the present study have (1) Ti ions isolated and substituted for silicon in the framework possessing tetra coordinated geometry, (2) ordered mesoporosity, (3) Lewis acidity and (4) varying hydrophobic surface structure.

Table 4.1. Physicochemical characteristics of Ti-SBA-12 and Ti-SBA-16.

Catalyst	Textural properties (N_2 physisorption)						NH_3-TPD (mmol/g)
	S_{BET} (m^2/g)	Pore volume (cc/g)			Average pore diameter (nm)	Wall thickness (nm)	
		Micro	Meso	Total			
SBA-12	672	0.01	0.63	0.64	3.8	6.72	0.03
Ti-SBA-12(40)	460	0.02	0.62	0.64	5.5	5.20	0.12
SBA-16	800	0.16	0.51	0.67	3.4	8.35	0.04
Ti-SBA-16(50)	910	0.11	0.75	0.86	3.8	8.08	0.09

4.3.2. Catalytic Activity

4.3.2.1. Esterification of OA with Glycerol. The reaction of OA with glycerol (G) yields mono-, di- and triglyceride esters (ME, DE and TE, respectively; Chapter 3 Scheme 3.1.). Variation in their composition generates lubricant chemicals with varied properties. The properties of esters can be varied by changing OA to polyol molar ratio, reaction temperature, reaction time and type of catalyst used. Glyceride esters were synthesized using Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) as catalysts.

4.3.2.1.1. Influence of Molar Ratio of Reactants. Esterification of OA with glycerol was carried out at 180 °C for 3 h taking OA and G in the molar ratio of 3:1, 1:1, 1:2, 1:3 and 1:4. Catalyst with 3 wt% of OA was used. OA conversion and turnover frequency for consuming OA in the formation of mono-, di- and triglyceride esters increased with increasing amounts of glycerol (Table 4.2). Catalytic activity (TOF values) was calculated based on the acidity of the catalysts and Ti content. These values calculated based on acidity were found higher than those calculated using Ti content. Further, the values estimated based on framework Ti were found to be still higher than those based on total amount of Ti. TOF values based on acidity are more accurate than on the Ti content. Ti-SBA-16 (Si/Ti = 50) in reactions with polyhydric glycerol showed higher catalytic activity (OA conversion and TOF) than Ti-SBA-12 (Si/Ti = 40). The esters selectivity is nearly the same over both these titanosilicate catalysts. Glycerol is more hydrophilic. Its conversion over hydrophobic Ti-SBA-16 (Si/Ti = 50) is expected to be more than that on relatively more hydrophilic Ti-SBA-

Table 4.2. Effect of molar ratio of reactants on esterification of oleic acid with glycerol[a]

OA:G (molar ratio)	Ti-SBA-12 (Si/Ti = 40)							Ti- SBA-16 (Si/Ti = 50)						
	OA conversion (mol%)	Ester selectivity (mol%)			TOF (h^{-1})			OA conversion (mol%)	Ester selectivity (mol%)			TOF (h^{-1})		
		Mono	Di	Tri	Based on total output Ti	Based on framework Ti	Based on acidity		Mono	Di	Tri	Based on total output Ti	Based on frame-work Ti	Based on acidity
3:1[b]	38.1	66.8	31.8	1.3	62	76	124	40.1	64.6	33.4	1.9	77	77	174
	(73.3)	(28.6)	(52.9)	(18.4)	(36)	(44)	(72)	(81.3)	(4.4)	(51.3)	(44.3)	(47)	(47)	(106)
1:1	68.0	52.9	43.2	3.9	111	137	221	72.8	32.8	57.9	9.2	139	139	316
1:2	69.3	49.4	44.0	6.5	113	139	226	76.5	48.2	44.7	7.2	146	146	332
1:3	70.6	50.6	44.8	4.5	116	143	230	78.8	54.5	41.8	3.7	151	151	342
1:4	74.0	50.7	44.9	4.3	121	149	241	80.3	51.1	43.9	4.9	154	154	349

[a] Reaction conditions: catalyst = 0.12 g (3 wt% of oleic acid), oleic acid (OA) = 4 g, reaction temperature = 453 K, reaction time = 3 h.

[b] Reaction conditions: catalyst = 0.276 g (3 wt% of OA), OA = 9.19 g; glycerol (G) = 1 g, reaction temperature = 453 K, reaction time = 3 h. Values in parentheses are those results with reaction time = 10 h. Turnover frequency (TOF) = moles of OA converted per mole of total or framework substitute Ti or acidity of the catalyst per hour.

12 (Si/Ti = 40). This importance of surface structure in esterification reaction is more obvious only when the alcohol is changed from monohydric alcohol (methanol, for example) to polyhydric alcohol. In other words, the study with glycerol demonstrates that not only the Lewis acid Ti sites but also the surface structure is equally important in esterification reaction with polyhydric alcohols. Hydrophillic glycerol sticks strongly on hydrophilic surfaces and thereby, leads to lower conversions on such catalyst surfaces

4.3.2.1.2. Influence of Reaction Temperature. Reaction temperature has a significant effect on the esterification reaction (Fig. 4.1). OA conversion increased with increase in temperature from 120 to 200 °C. Formation of triglyceride ester (TE) was observed only above 160 °C. The concentration of di- and triglycerides (DE + TE) increased and monoglyceride (ME) decreased with an increase in temperature. These observations were similar for both Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50). OA conversion as high as 80 mol% with ME selectivity of 60% and DE + TE selectivity of 40% was observed at 200 °C.

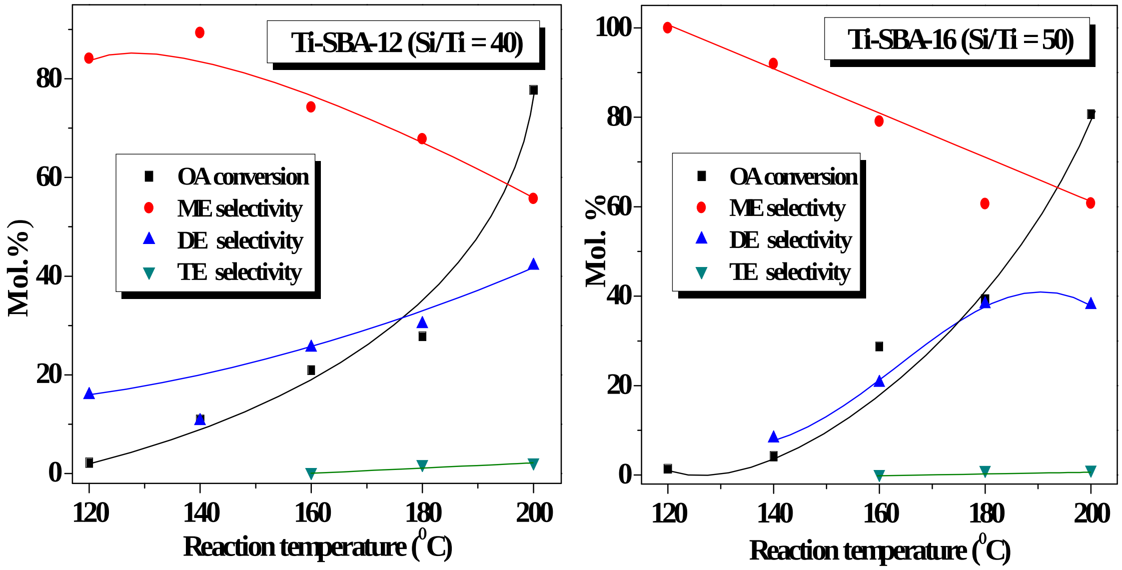


Fig. 4.1. Effect of temperature on the reaction of oleic acid (OA) with glycerol over Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) catalysts. *Reaction conditions:* catalyst = 0.12 g, OA = 4 g, OA : methanol (molar ratio) = 1:1, reaction time = 1 h.

4.3.2.1.3. Influence of Reaction Time. The conversion of OA with reaction time on both Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) is shown in Fig. 4.2. The OA conversion increased with extended reaction time. Significant changes in product selectivity were observed. Selectivity for DE + TE was higher at longer reaction time.

4.3.2.1.4. Influence of Catalyst Amount. The amount of catalyst has also influenced the reaction. OA conversion increased linearly (from 23 to 60 mol% for Ti-SBA-12 (Si/Ti = 40) and from 30 to 65 mol% forTi-SBA-16 (Si/Ti = 50)) with an increase in catalyst amount from 1 to 7 wt% (Fig. 4.3). This increase in conversion was due to the proportional increase in the active site of the catalyst

4.3.2.1.5. Catalyst Reusability. The reusability of Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) catalysts was investigated in four recycling experiments (Fig. 4.4). After each run, catalyst was filtered and washed with methanol and dried at 100 °C for 3 h and then reused. As seen from Fig. 4.4, the esterification activities (OA conversion) of both Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) were almost the same in all the four recycling experiments. Hence, it can be concluded that the catalyst has good reusability. Catalyst reusability is an important criterion for green and sustainable technology.

4.3.2.2. Esterification of Oleic Acid with Different Polyols. Polyols such as TMP, NPG and PE (structures shown in Table 4.2) are all branched molecules and have no labile hydrogen atoms in their structure which are equivalent to the β carbon of glycerol [4]. B-Hydrogen in glycerol backbone is an active site for elimination and oxidation reactions. Therefore, esters of these polyols have greater thermally stability than glycerol esters of the same fatty acids.

TMP is a colourless triol (three hydroxyl groups) with the formula $CH_3CH_2C(CH_2OH)_3$. This compound is often used to produce triesters (TE) compounds which are generally utilized as base oil for various types of lubricating oils. [15, 13, 32-36]. Catalyst holds a prominent role in obtaining a better yield of TMP triesters in less time. Alkaline homogeneous base catalyst tends to react with free fatty acids to produce unwanted soap [37]. Homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and they give rise to serious environmental and corrosion problems [38]. Bondioli [11] reported, powdered metallic zinc and tin (II) oxide, two catalysts that are currently available at an industrially reasonable price for the preparation of polyesters of fatty acids.

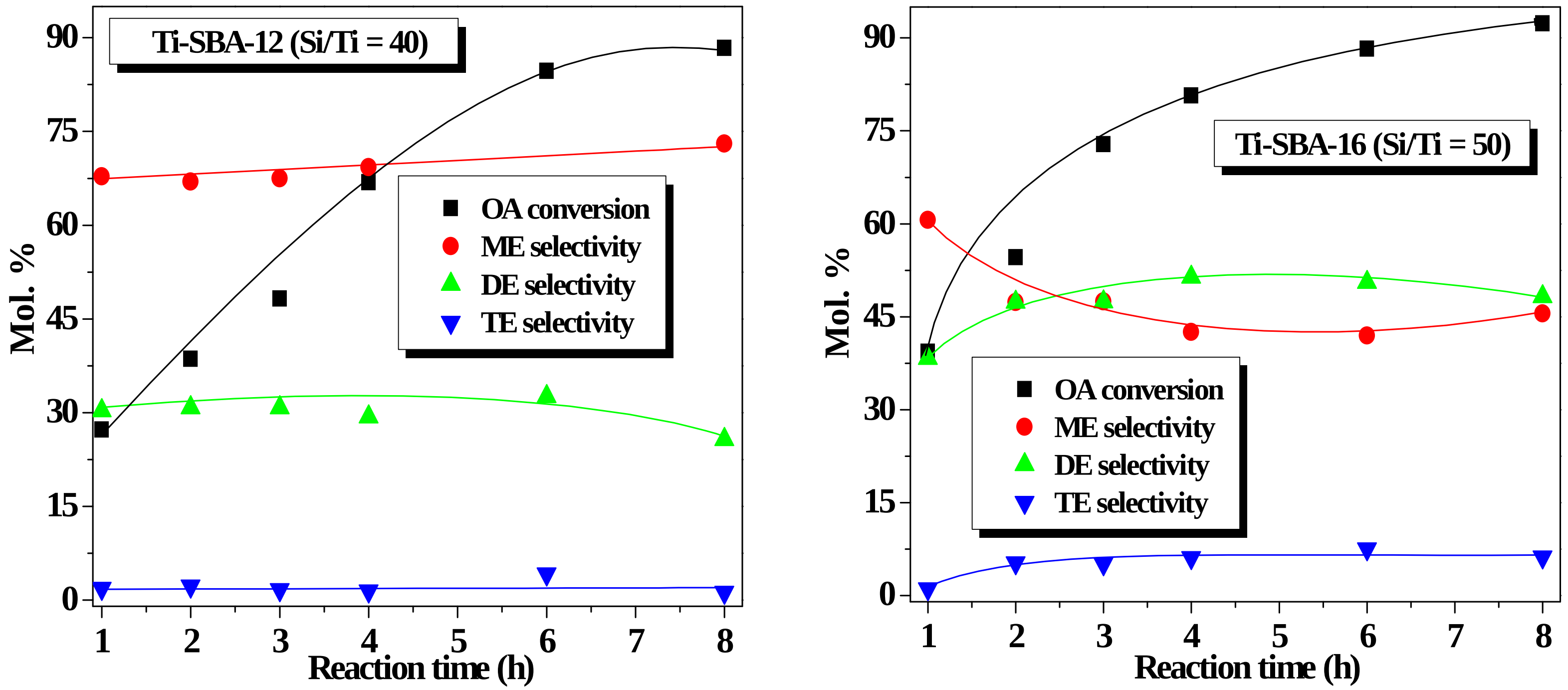


Fig.4.2. Effect of time on the reaction of oleic acid (OA) with glycerol over Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) catalysts. *Reaction conditions:* catalyst = 3 wt% of OA, OA = 4 g, OA: glycerol (molar ratio) = 1:1, reaction temperature = 180 °C.

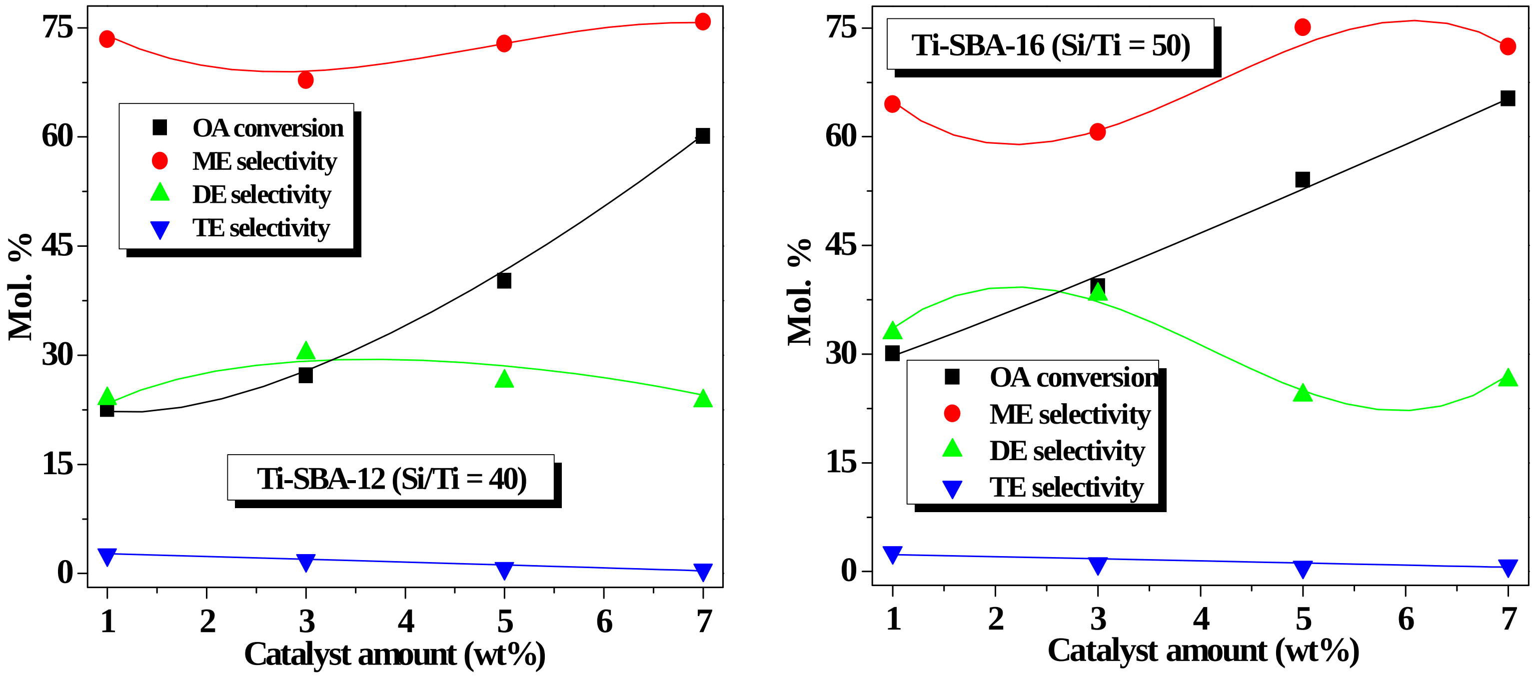


Fig.4.3. Effect of catalyst amount on the esterification of oleic acid (OA) with glycerol over Ti-SBA-12 (Si/Ti = 40) and Ti- SBA-16 (Si/Ti = 50) catalysts. *Reaction conditions:* OA = 4 g, OA: glycerol (molar ratio) = 1:1, reaction temperature = 453 K, reaction time, =1 h.

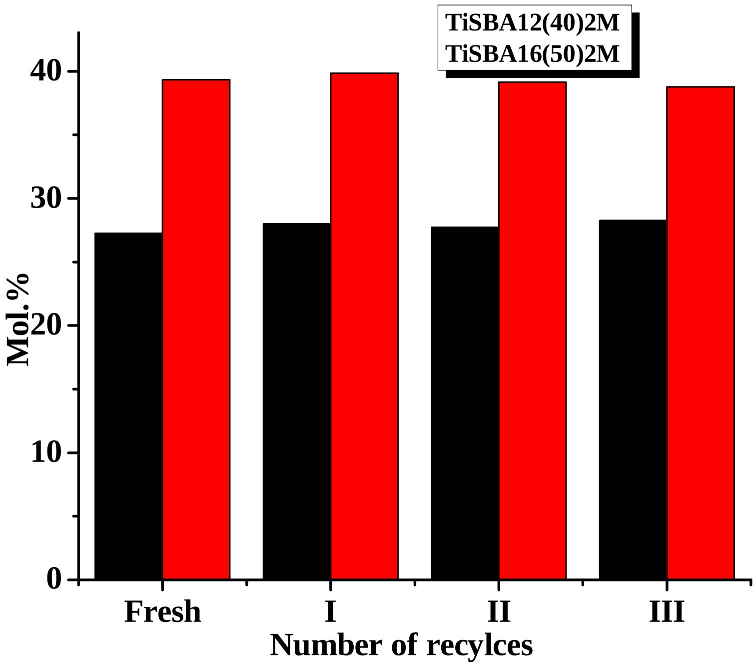
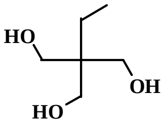
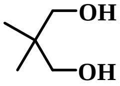
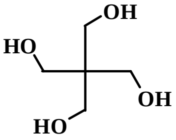


Fig. 4.4. Catalyst reusability in the esterification of oleic acid (OA) with glycerol. Reaction conditions: catalyst = 3 wt% of OA; OA:Glycerol (molar ratio) = 1:1; , reaction temperature = 180°C reaction time = 1 h

However, only 90–95%of the catalyst could be recovered by simple filtration. Highly efficient purification procedures are needed because of the tendency of the catalyst to form metallic soaps of fatty acids. The latter are soluble in esters and may negatively affect the performance of the final product, in terms of its oxidative, thermal and hydrolytic stability. Recently, Masood et al. [12] reported the application of calcium methoxide as heterogeneous catalyst for these reactions. Moisture sensitivity is one of the issues with this catalyst. The mesoporous titanosilicate catalysts of this work are moisture and air insensitive and could be recovered easily without any issue unlike the prior art catalysts for lubricant base oil production.

Having noted the efficiency of Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) catalysts for the reactions of OA with glycerol, the studies were extended to esterifications with trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritol (PE) (Table 4.3).

Table 4.3. Esterification of oleic acid with polyhydric alcohols over Ti-SBA-12 (Si/Ti = 40) and Ti-SBA-16 (Si/Ti = 50) catalysts[a]

Polyol	Catalyst	OA conversion (mol%)	Ester selectivity (mol%)		
			Mono	Di	Tri
Trimethylolpropane	Ti-SBA-12(40)	75.4 (79.5)[b]	62.8 (2.1)[b]	36.2 (56.2)[b]	1.1 (41.7)[b]
	Ti-SBA-16(50)	71.1 (85.6)[b]	70.2 (1.4)[b]	28.1 (54.1)[b]	1.5 (44.5)[b]
Neopentylglycol	Ti-SBA-12(40)	52.4	87.9	12.1	-
	Ti-SBA-16(50)	62.7	86.6	13.4	-
Pentaerythritol[c]	Ti-SBA-12(40)	36.6	72.6	18.4	9.0
	Ti-SBA-16(50)	31.1	77.6	18.8	3.6

[a] Reaction conditions: catalyst = 0.12 g, oleic acid (OA) = 4 g, OA : polyol molar ratio = 1:1, temperature = 180 °C, reaction time = 1 h. [b] Reaction conditions: catalyst = 0.189 g, oleic acid (OA) = 6.3 g, OA : polyol molar ratio = 3:1, temperature = 180 °C, reaction time = 10 h. Error in conversion and selectivity is ± 0.5 mol%. [c] No quadrester product was detected in this case.

The reactions were carried out at 180 °C for 1 h with OA : polyol molar ratio of 1:1. These titanosilicates have been found to be highly active even in these reactions. At our reaction conditions, OA conversion with different polyols decreased in the order: TMP > NPG > G > PE. While TMP and G have three hydroxyl groups resulting in mono-, di- and trimesters (ME, DE and TE), NPG has only two hydroxyl groups and yields ME and DE. PE has four hydroxyl groups and is less active compared to the other polyols perhaps due to its high melting point (260 °C). Formation of a significant amount of di- and triesters (DE and TE; selectivity ~ 98%) was noted when the reaction was conducted with OA: TMP molar ratio of 3:1 and for a reaction time of 10 h. A similar observation was found also for glycerol (DE + TE; selectivity ~ 65%). Ti-SBA-16 exhibited superior activity to Ti-SBA-12 in the esterification of OA with glycerol and others. Glycerol being more hydrophilic molecule adheres more strongly on hydrophilic catalyst surfaces and hinders the activation of hydrophobic OA molecules and their further reaction. Hence, a hydrophobic catalyst would perform better in such esterification reactions with polyols.

4.3.2.2.1. Effect of Reaction Parameters. Table 4.4 shows the effect of OA : TMP molar ratio on OA conversion and product selectivity. As seen from table, increasing the molar ratio of OA/TMP from 1 to 4, a decrease in OA conversion from 90.1 to 54.9 mol% was observed. However, the selectivity for TE had increased. At OA/TMP molar ratio of 4, the selectivity for TE was 19.1 mol%.

Table 4.4. Effect of molar ratio on esterification of oleic acid with TMP

OA:TMP	Ti-SBA-16 (Si/Ti = 50)			
	OA conver. (mol%)	Ester selectivity (mol %)		
		ME	DE	TE
1:3	90.1	71.5	26.5	1.9
1:1	77.8	74.2	24.8	0.9
2:1	66.0	71.1	24.5	4.4
3:1	60.5	52.8	28.5	18.6
4:1	54.9	57.8	23.1	19.1

Reaction conditions: catalyst = 3 wt % oleic acid, temperature = 180 °C, time = 3h.

Fig. 4.5 (a) shows the influences of the reaction period on the esterification of TMP with oleic acid. OA conversion increased (from 49.5 to 89.3 mol%) with increasing reaction time. Also an increase in conversion and selectivity for TE was observed with increasing reaction temperature (Fig.4.5 (b)).

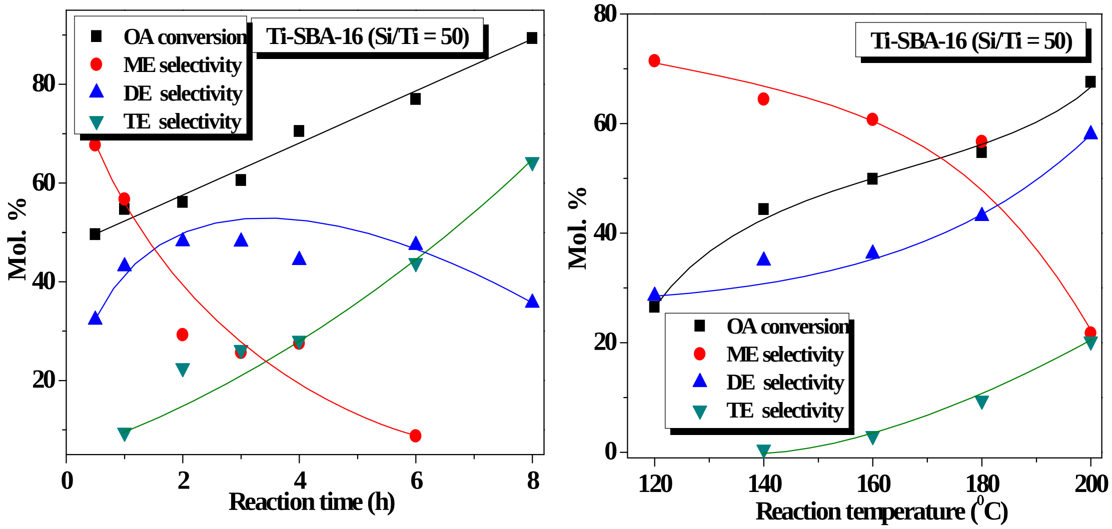


Fig. 4.5. Effect of reaction time (a) and temperature (b) on the esterification of OA with TMP over Ti-SBA-16 (Si/Ti = 50). *Reaction conditions:* catalyst = 3 wt % OA, OA : TMP molar ratio = 3 : 1, reaction temperature = 180 °C, reaction time = 1h.

Table 4.5 presents the catalytic activity data for the esterification of fatty acids of varying chain length with TMP over Ti-SBA-16 (Si/Ti = 50). Conversion decreased with an increase in the chain length of fatty acid. However, an increase in DE + TE selectivity was observed for fatty acids with higher chain length.

Table 4.5. Esterification of fatty acids of varying chain length with TMP over TiSBA-16

Fatty acid (FA)	Fatty acid conversion (mol%)	Product selectivity (mol%) by HPLC		
		ME	DE	TE
Caprylic acid (C8)	73.5	40.5	25.8	33.6
Capric acid (C10)	65.1	38.9	32.5	28.6
Lauric acid (C12)	60.2	26.1	39.6	34.3
Oleic acid (C18.1)	56.1	29.2	48.2	22.6

Reaction conditions: catalyst = 3 wt % fatty acid, fatty acid : TMP molar ratio = 3 : 1, reaction temperature = 180 °C, reaction time = 2h.

Table 4.6 presents the physical properties of OA-glycerol and OA-TMP biolubricants produced over Ti-SBA-16 (Si/Ti = 50) catalyst at reaction conditions of catalyst = 3 wt% of oleic acid, OA : polyol molar ratio = 4:1, temperature = 180 °C and reaction time = 10 h. Properties of these lubricants match with those of commercial lubricants (VP lubricant base oils 700 and 150BS and Servo – gear HP85 and HP90, boat engine oil SAE grade 20W-40, Ultra 40 and 50 and Servo 4T).

Table 4.6. Properties of the biolubricants produced over Ti-SBA-16 (Si/Ti = 50)

Properties	Test Results		Test Method
	OA-glycerol	OA-TMP	
Density@15 ° C	0.9501	0.9629	IS 1448 (P32) 2008
Kinematic viscosity @ 40 ° C	508.9	156.6	IS 1448 (P25) 2007
Kinematic viscosity @ 100 ° C	-	14.95	IS 1448 (P25) 2007
Viscosity index	-	95	IS 1448 (P56) 2008
Pour point ° C	-9	-21	IS 1448 (P10) 2008
Copper strip corrosion for 3 h @ 100 °C	1a (slight tarnish)	1a (slight tarnish)	IS 1448 (P15) 2004; ISO 2160 1998
Lubricity corrected wear scar dia. (wsd 1.4) at 60 °C	284	290	ASTM D 6070

By and large, mesoporous titanosilicate catalysts of the present study are highly active for esterification of OA with polyhydric alcohols producing base oil feedstocks for biolubricant applications. Other than acidity (due to dispersed tetrahedral Ti ions), pore diameter, pore volume and surface hydrophobicity control the OA conversion toward formation of synthetic esters.

4.4. Conclusions

Three-dimensional, mesoporous titanosili-cates (Ti-SBA-12 and Ti-SBA-16) were found to be highly active, selective, stable and reusable catalysts for the esterification reaction of OA with polyhydric alcohol viz., glycerol, trimethylolpropane, neopentylglycol and pentaerythritol. Dispersed tetrahedral Ti ions are the acid sites catalyzing the esterification reaction. Finally, the experimental results showed good catalytic ability of Ti-SBA-16 (Si/Ti = 50) for the esterification of OA with polyhydric alcohols producing biolubricants. Ti-SBA-16 is relatively more hydrophobic than Ti-SBA-12. At OA: TMP molar ratio of 3:1 and at 180 °C and 10 h of reaction, OA conversion as high as 85.6 mol% and DE + TE selectivity of 98.6 mol% was obtained over Ti-SBA-16 (Si/Ti = 50) catalyst. To the best of knowledge, this is the highest per pass polyester yield obtained so far over solid catalyst. The present study with polyhydric alcohols clearly demonstrated the importance of surface hydrophobicity of catalyst in esterification reactions. Higher surface area, pore volume, Lewis acidity and hydrophobicity are the factors responsible for the superior catalytic activity of these catalysts in esterification reactions.

4.5. References

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Chapter - 5

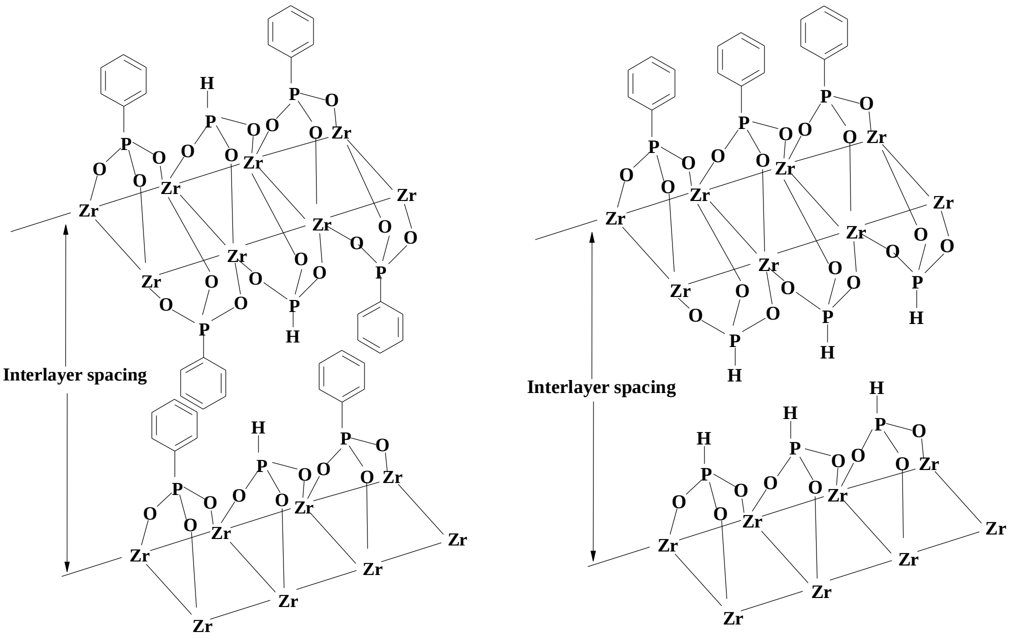
Zirconium Phenyl Phosphonate Phosphite as a Highly Active Solid Acid Catalyst for Producing Fatty Acid Polyol Esters

5.1. Introduction

Polyol esters are a family of synthetic lubricants used in high temperature operations such as industrial oven chains, tenter frames, stationary turbine engines, jet engine lubricants, high temperature greases, fire resistant transformer coolants, fire resistant hydraulic fluids and textile lubricants [1] and [2]. They are also used with the new generation of chlorine-free hydrofluorocarbon refrigerants, such as R-420A [3]. Unlike mineral oils, these esters are wax-free and biodegradable. They can be designed to meet the lubricity requirement equivalent to those of mineral oils. They are prepared by reacting monobasic acids with polyhydric alcohols. Glycerol (3-OH; G), trimethylolpropane (3-OH; TMP), pentaerythritol (4-OH; PE) and dipentaerythritol (6-OH; DiPE) are a few examples of polyhydric alcohols. Elimination of β-hydrogen (in glycerol) with an alkyl group elevates the thermal stability of polyol esters and allows them to be used at higher temperatures. The reaction of a trihydroxy alcohol (glycerol or TMP) with fatty acid results in mono- (ME), di- (DE) and tri- (TE) esters (Scheme 5.1). Among these, DE and TE are compatible for biolubricant applications. Conventionally, these esters are prepared using mineral acid catalysts [2]. Separation of these homogeneous catalysts from the product mixture needs additional process steps making the process economically non-attractive. The mineral acid-based process generates salt by-product and huge amount of waste-water. Replacement of mineral acids with solid acid catalysts makes the process economical and eco-friendly.

Several solid acid catalysts for fatty acid esterification reaction including sulfated zirconia/titania/tungsten oxide, ion-exchange resins, zeolites, sulfonic acid functionalized mesoporous silica, $H_3PW_{12}O_{40}$ supported on ZrO_2 and Ta_2O_3, sulfonated-C, $WO_3/AlPO_4$, WO_3/ZrO_2, silica-bonded N-propyl sulfamic acid, silica-supported tin oxide and DMC, have been reported [4-14]. Water is the by-product in esterification reactions. It competes with reactant molecules for adsorption and suppresses esterification activity. It also reacts and deactivates the active acid sites on the solid catalyst and thereby reducing the life of the catalyst. With all the reported solid catalysts, selectivity for DE and TE (components used in synthetic lubricant applications) is low; monoester is the major product. Hence, development of a hydrophobic and more efficient/selective solid acid catalyst that yields high amount of DE + TE is a desirable objective.

Metal organophosphonates are an interesting class of layered inorganic materials that have attracted much attention as novel proton conductors, luminescent and magnetic materials and corrosive resistive agents [15]. They have also been used to encapsulate photoactive molecules [15]. However, there are only a few studies of their application as catalysts [16-18]. For the first time, the use of zirconium phenyl phosphonate phosphite (ZrPP) as a solid acid catalyst for the synthesis of polyol esters is reported in this chapter. Fig. 5.1 shows tentative structures of ZrPP wherein several orientations of phenyl phosphonate and phosphite groups are possible [19-21]. The organic phosphonate moiety imparts hydrophobic nature to the structure. Interestingly, ZrPP catalysts of the present study are found highly selective for (di + tri) esters than the reported solid catalysts for this reaction.



(a) (b)

Fig. 5.1. Tentative structures of zirconium phenyl phosphonate phosphite.

5.2. Experimental

Zirconium phenyl phosphonate phosphite (ZrPP) catalysts were prepared as reported in Chapter-2 (Section 2.2.3). Phenyl phosphonic acid was procured from Spectrochem Pvt. Ltd., phosphorous acid from Loba Chem and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) from Loba Chem. Oleic acid (OA; cis-9-octadecenoic acid, C18:1; ~99%)] and glycerol (1,2,3-propanetriol, ≥99.5%) used in the reactions were obtained from Aldrich Co. Valeric acid (C5) caprylic acid (C8), capric acid (C10), lauric acid (C12) were purchased from s.d. fine Chem Ltd., India. Details of reaction procedure and product analysis are reported in Chapter-2 (Sections 2.4.1 and 2.5).

5.3. Results and Discussion

5.3.1. Structural Characterization

5.3.1.1. X-ray Powder Diffraction. Zirconium phenyl phosphonate phosphite catalysts ZrPP-1, ZrPP-2 and ZrPP-3 were prepared with phosphorous acid to phenyl phosphonic acid molar ratio of 1:1, 2:1 and 3:1, respectively. These compounds showed XRD patterns (Fig. 5.2) typical of a layered structure [18, 19]. The XRD peaks were broad and indicate amorphous nature in the structure. ZrPP-3 showed peaks at d-values of 11.6, 5.3, 4.4, 3.5, 2.7, 1.74, and 1.33 Å. With decreasing molar ratio of phosphorous acid/phenyl phosphonic acid from 3 to 2 and 1, the interlayer spacing of ZrPP [(001) reflection] had increased from 11.6 to 11.8 and 15 Á, respectively.

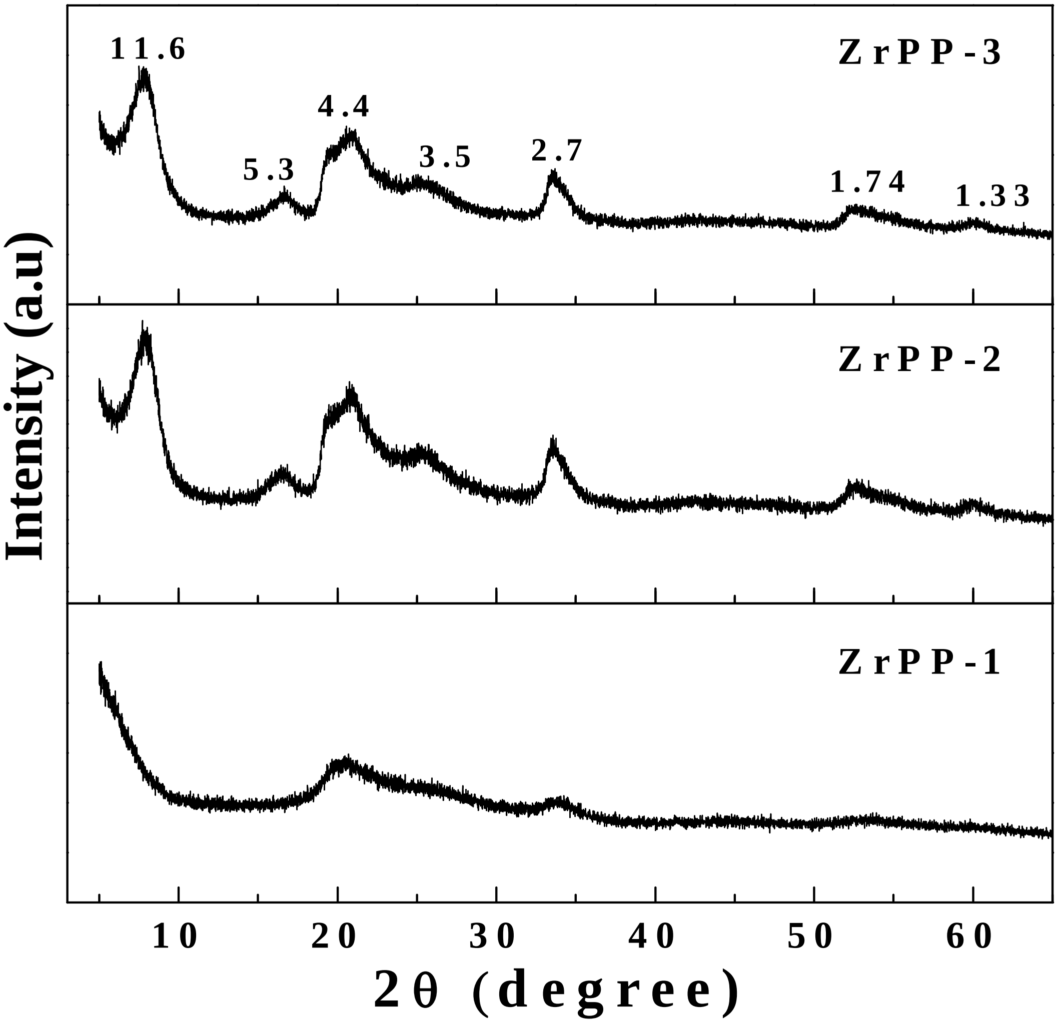


Fig. 5.2. X-ray powder diffractograms of zirconium phenyl phosphonate phosphites

This difference in basal spacing of these materials is due to differences in the amount of hydrated water present in their composition (Table 5.1) [22]. XRD peaks of ZrPP-3 are more intense than those of ZrPP-1 and ZrPP-2. According to elemental and thermogravimetric analyses, one mole of ZrPP-1 is associated with 0.4 moles of hydrated water molecules while ZrPP-2 and ZrPP-3 contained 0.15 and 0.1 moles of water per molecular formula (Table 5.1).

5.3.1.2. Fourier Transform Infrared Spectroscopy. ZrPP samples showed intense FTIR bands at 1015 – 1073 cm^{-1} and weak bands at 692 – 730 cm^{-1} and 2310 – 2447 cm^{-1} (Fig. 5.3). While the intense bands at 1015 – 1073 cm^{-1} are corresponded to P-O stretching vibrations of PO_3 groups, those at 692 – 730 cm^{-1} are attributed to out-of-plane bending vibrations of mono substituted phenyl groups. The band in the region 2310 – 2447 cm^{-1} is assigned to P-H stretching vibrations. Several small bands were also observed in the range 1400-1700 cm^{-1} which could be assigned to aromatic C-H bending vibrational modes [18-22].

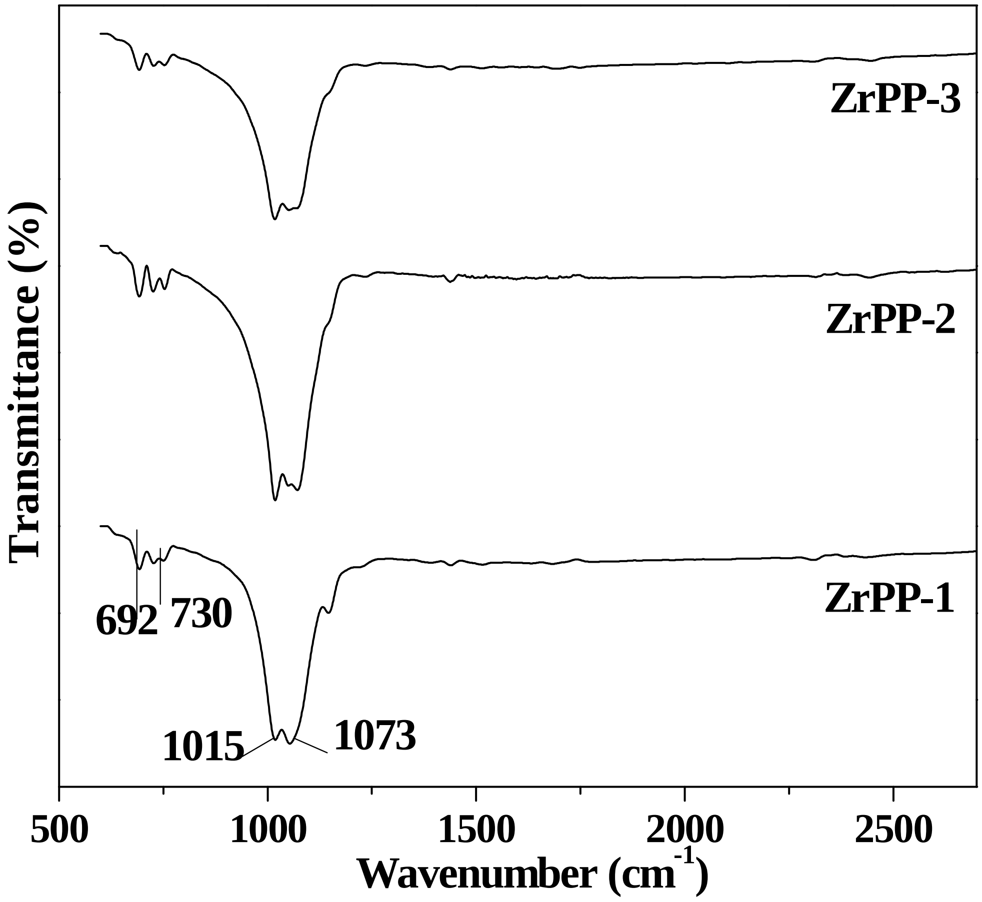


Fig.5.3. FTIR spectra of zirconium phenyl phosphonate phosphite compounds.

5.3.1.3. ^{31}P Magic-Angle Spinning Nuclear Magnetic Resonance. ^{31}P MAS NMR reveals the presence of phosphite and phosphate groups in the catalysts (Fig. 5.4). Two sets of ^{31}P NMR signals at chemical shift (δ) values of -17.2 and -7.6 were observed. While the former is attributed to phosphate groups, the latter is corresponded to phosphorous in phenyl phosphonate moieties. The signals corresponding to ZrPP-3 are more intense than those of ZrPP-1 and ZrPP-2 (Fig. 5.4). This could be due to difference in crystallinity of these compounds.

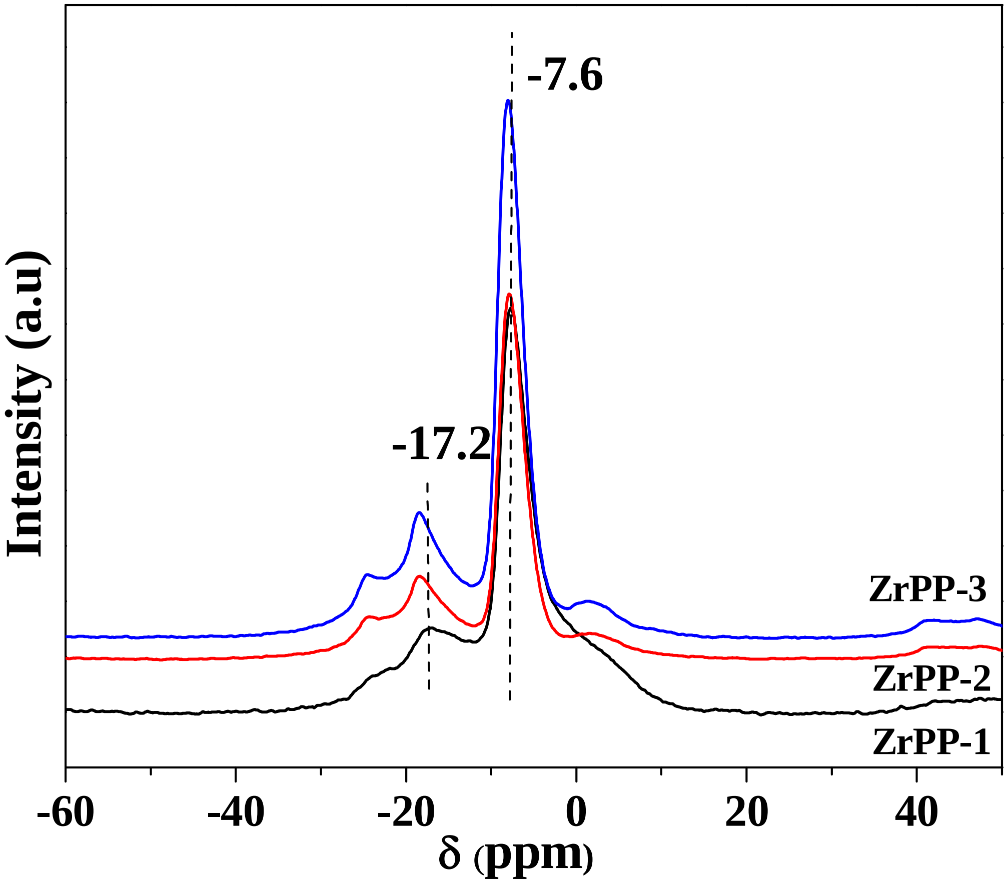


Fig. 5.4. ^{31}P MAS NMR spectra of zirconium phenyl phosphonate phosphite compounds

5.3.1.4. Thermogravimetric Analysis. Fig. 5.5 shows the thermogravimetric analysis of zirconium samples. It showed two stages of weight loss: a minor loss in the temperature range 60 – 100 °C due to weakly bound water (ZrPP-1, 2.1 wt%, ZrPP-2, – 0.8 wt% and ZrPP-3, 0.5 wt%) and a major loss at 400 – 500 °C (ZrPP-1, 18.8 wt%; ZrPP-2, 18.4 wt% and ZrPP-3, 17.9 wt%) due to decomposition of phenyl phosphonate and conversion of ZrPP into zirconium pyrophosphate (ZrP_2O_7) [20].

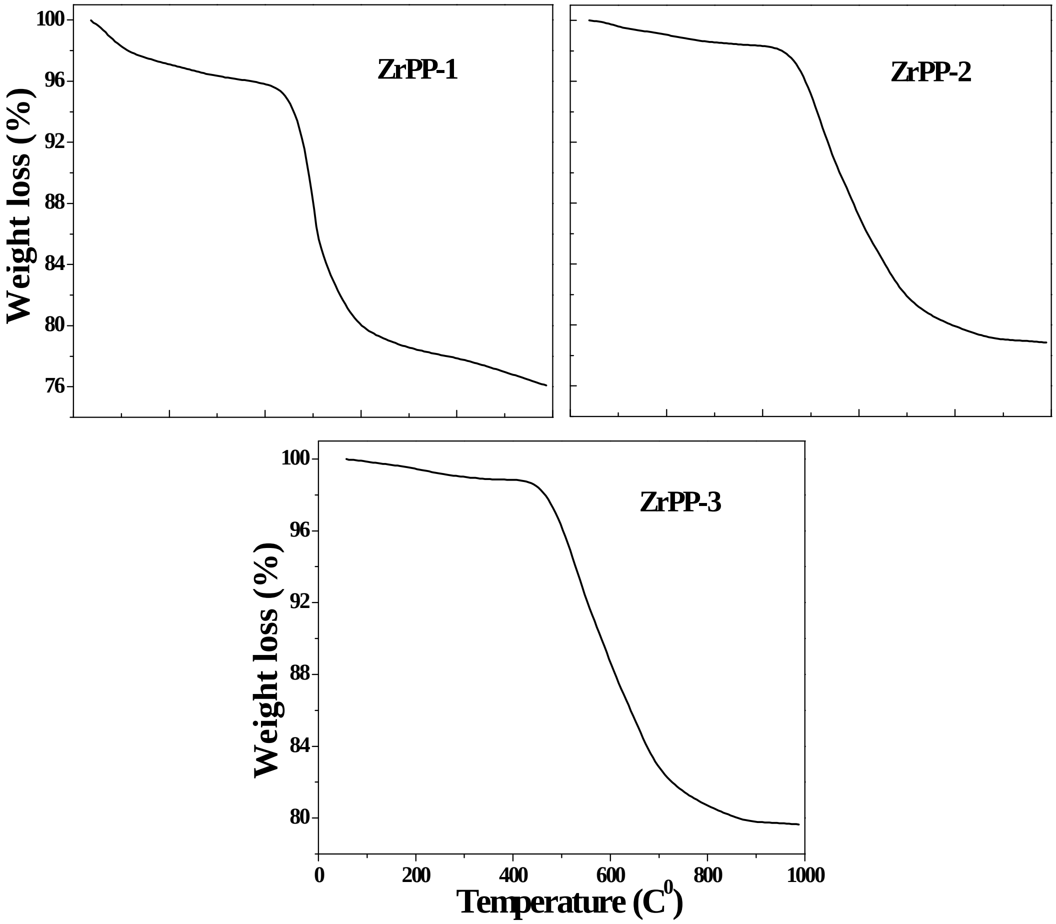


Fig.5.5. Thermogravimetric analysis of ZrPP compounds

Based on the weight loss, molecular formula of ZrPP was determined and listed in (Table 5.1). The %C and %H values determined using the proposed molecular formula and those determined from microanalysis (Table 5.1) are in good agreement with each other (Table 5.1). The experimentally observed %C and %H values for ZrPP samples are as follows: 21.3 and 1.9 (for ZrPP-1), 21.3 and 1.8 (for ZrPP-2) and 20.1 and 1.6 (for ZrPP-3). As the weight loss due to water is very low [0.5 wt% (for ZrPP-3), 0.8 wt% (for ZrPP-2) and

2.1 wt% (for ZrPP-1)] and as it occurs at a temperature < 100 °C unlike in the case of aluminosilicate zeolites (~ 200 °C), the catalysts of the present study are hydrophobic at reaction conditions. It can be stated that the hydrophobicity of ZrPP is much higher than most of the known solid acid catalysts (water adsorption capacity of solid acid catalysts = 5 – 15 wt% while that for ZrPP = 0.5 – 2.1 wt% only).

Table 5.1. Chemical composition, molecular formula and textural properties of ZrPP

Catalyst	Molecular formula	Elemental analysis (wt%)		S_{BET} (m^2/g)	Acidity (mmol/g)		
		C	H		<150 ºC	150–350ºC	Total
ZrPP-1	$Zr(C_6H_5PO_3)_{0.99}(HPO_3)_{1.01}.0.4\ H_2O$	21.3	1.9	439	1.59	-	1.59
ZrPP-2	$Zr(C_6H_5PO_3)_{0.97}(HPO_3)_{1.03}.0.15H_2O$	21.3	1.8	260	0.23	0.09	0.27
ZrPP-3	$Zr(C_6H_5PO_3)_{0.95}(HPO_3)_{1.05}.0.1H_2O$	20.1	1.6	268	0.30	0.07	0.36

5.3.1.5. N_2-Physisorption. The input molar ratio of phosphorous acid/phenyl phosphonic acid has a marked effect on the specific surface area (S_{BET}) and acidity of these complexes. Surface area and overall/total acidity of ZrPP decreased with increasing input molar ratios of phosphous acid/phenyl phosphonic acid (Table 5.1).

5.3.1.6. NH_3-TPD. The acidic property of ZrPP was determined by NH_3-TPD. Two NH_3 desorption peaks [below 150 °C (peak 1) and 150 – 350 °C (peak 2)] were observed for the ZrPP compounds (Fig. 5.6). While the former is corresponded to weak acid sites, the latter is attributed to strong acid sites (Table 5.1). Peak 2 was more apparent in ZrPP-2 and ZrPP-3 than in ZrPP-1 (Fig. 5.6). The input molar ratio of phosphorous acid/phenyl phosphonic acid had a little effect on phenyl phosphonate/Zr and HPO_3^{2-}/Zr molar ratios in the catalyst samples. These ratios for different samples are as follows: 0.99 and 1.01 (for ZrPP-1), 0.97 and 1.03 (for ZrPP-2) and 0.95 and 1.05 (for ZrPP-3), respectively. However, it may be noted that the phosphorous acid/phenyl phosphonic acid molar ratio has a marked effect on adsorbed H_2O/Zr molar ratio which is 0.4, 0.15 and 0.1 for ZrPP-1, ZrPP-2 and ZrPP-3 respectively. The amount of adsorbed water per unit specific surface area of the catalyst also varied in the same order: 2.658 x 10^{-6}, 1.709 x 10^{-6} and 1.036 x 10^{-6} moles/m^2 for ZrPP-1, ZrPP-2 and ZrPP-3, respectively.

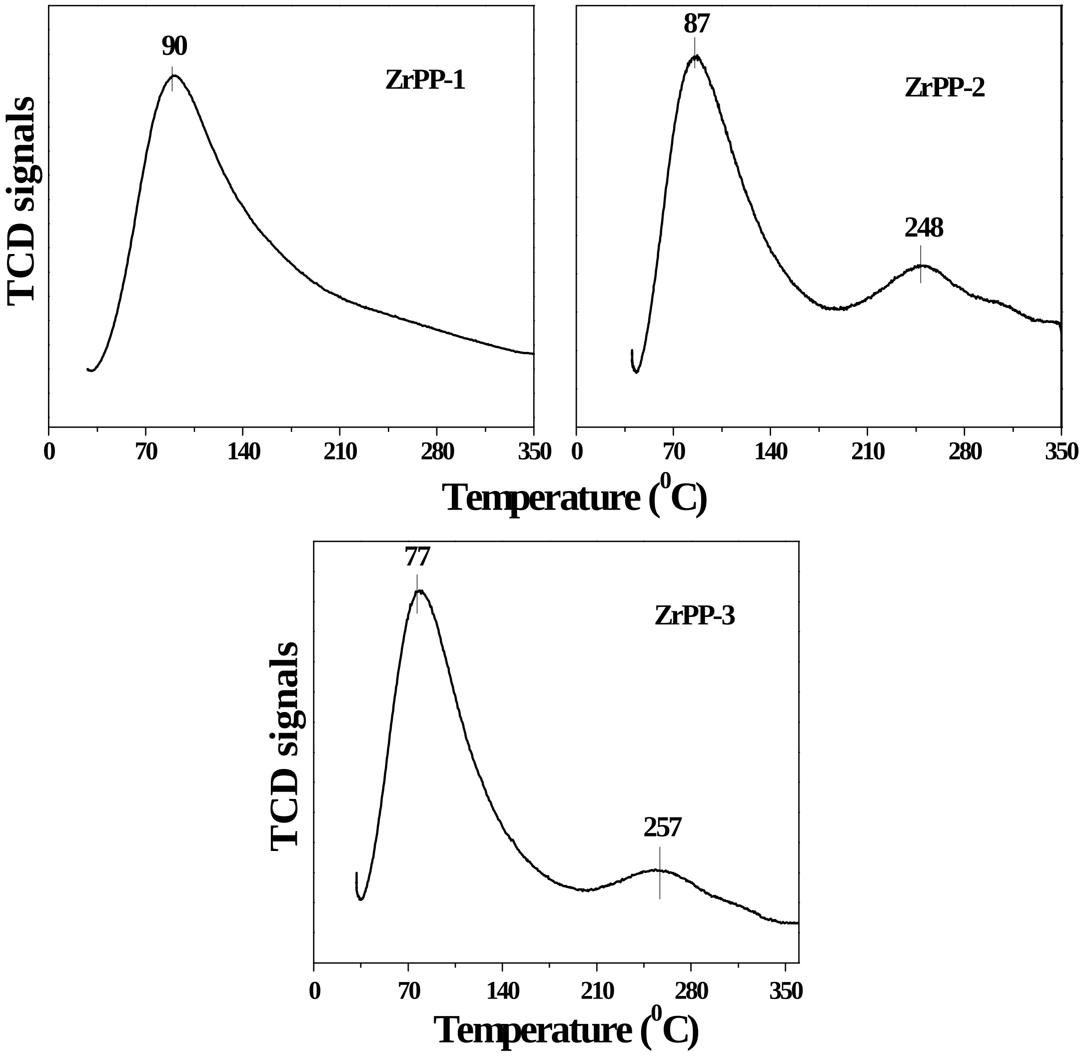
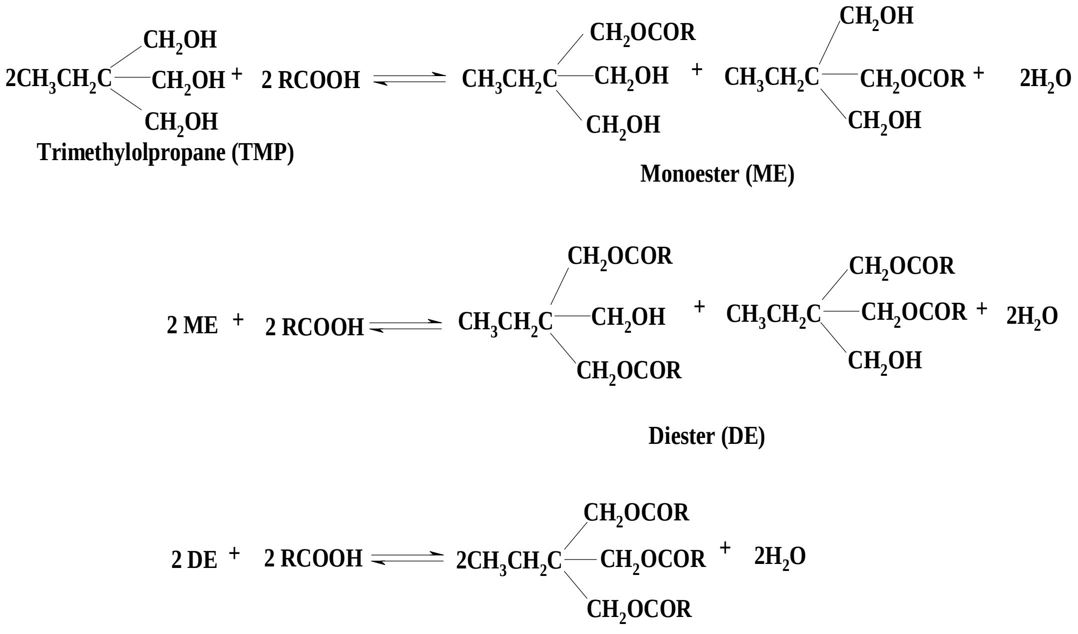


Fig. 5.6. NH_3-TPD plots of ZrPP

These studies reveal that phosphorous acid/phenol phoshonic acid ratio used in the preparation did not alter phenyl/Zr and P/Zr molar ratio, but affected the surface hydrophobicity of the catalysts significantly with ZrPP-3 being the highest hydrophobic one.

5.3.2. Catalytic Activity

Trihydroxy alcohols (glycerol and trimethylolpropane, TMP) were chosen as representative polyols. Oleic acid (OA) was considered as a representative fatty acid. A few reactions were conducted also with fatty acids of varying chain length viz., valeric acid (C_5), caprylic acid (C_8), capric acid (C_{10}) and lauric acid (C_{12}). Esterification of trihydroxy alcohols is a three-step consecutive equilibrium reaction (Scheme 5.1). In the first-step, one mole of polyol reacts with one mole of fatty acid resulting in one mole of monoester (ME) which in the second-step reacts with another mole of fatty acid and yields a diester (DE). In the third-step, DE gets converted into triester (TE). In each step, one mole of water is formed as by-product. Excess of polyol or fatty acid shifts the equilibrium toward right side. The by-product water can compete for adsorption with polyols over hydrophilic catalysts. This issue is less significant with the present set of hydrophobic ZrPP catalysts. This is one of the superior features of the catalysts of the present study.



Scheme 5.1. Esterification of FA with TMP

5.3.2.1. Influence of Phosphorous Acid/Phenyl Phosphonic Acid Molar Ratio. As seen from Table 5.2, catalytic activity (OA conversion) of ZrPP-1 is lower than that of ZrPP-2 and ZrPP-3. Most importantly, the selectivity for DE + TE is higher over ZrPP-3 than on ZrPP-2 and ZrPP-1. Higher hydrophobicity of ZrPP-3 is possibly responsible for its higher selectivity for the desired esters (DE + TE). Remember that water adsorption capacity of ZrPP-3 is only 0.5 wt% while those of ZrPP-2 and ZrPP-3 were 0.8 and 2.1 wt%, respectively. In view of its higher activity and selectivity, all the subsequent catalytic studies were conducted only with ZrPP-3.

Table 5.2. Esterification of OA with glycerol over ZrPP catalysts

Catalyst	Molecular formula	Catalytic activity				
		OA conv. (mol %)	Product selectivity (mol %)			
			ME	DE	TE	DE+TE
ZrPP-1	$Zr(C_6H_5PO_3)_{0.99}(HPO_3)_{1.01}.0.4\ H_2O$	39.6	58.1	39.8	2.1	41.9
ZrPP-2	$Zr(C_6H_5PO_3)_{0.97}(HPO_3)_{1.03}.0.15\ H_2O$	47.6	11.8	71.7	17.0	88.7
ZrPP-3	$Zr(C_6H_5PO_3)_{0.95}(HPO_3)_{1.05}.0.1\ H_2O$	48.9	7.7	66.1	26.3	92.4

Reaction conditions: Oleic acid (OA) = 4 g, glycerol = 0.32 g, catalyst = 5 wt% with of OA, OA : glycerol (molar ratio) = 4: 1; reaction temperature = 180 °C; reaction time = 1 h.

5.3.2.2. Influence of Molar Ratio. The molar ratio of reactants (OA: polyol) has a major influence on OA conversion and product ester selectivity (Table 5.3). With increasing ratio of OA/polyol from 0.5 to 4, a decrease in the apparent conversion of OA from 83.0 to 49.0 mol% was observed. But then, more and more of ME and DE got converted to TE. The total selectivity of DE + TE increased with increasing OA/polyol molar ratio. At OA: polyol molar ratio of 4:1, reaction temperature of 180 °C and reaction time of 1 h, the selectivity for DE + TE was 92.3 mol% in the case of glycerol and 86.0 mol% in the case of TMP. Polyol conversion was 100% at these conditions. This is the highest selectivity achieved so far over a solid catalyst. Hydrophobicity of ZrPP-3 is the cause driving the equilibrium toward DE + TE esters.

5.3.2.3. Influence of Reaction Time and Temperature. As the reaction was prolonged from 1 to 4 h, significant changes in product selectivity were observed. Selectivity for TE increased at longer reaction times (Fig. 5.7). The influence of reaction temperature on the esterification of OA was evaluated by varying the reaction temperature from 140 to 200 °C (Fig. 5.8).

Table. 5.3. Esterification of oleic acid with polyols over ZrPP-3: effect OA: polyol molar ratio

Molar ratio	Polyol = glycerol					Polyol = trimethylolpropane (TMP)				
	OA conv. (mol%)	Product selectivity (mol%)				OA conv. (mol%)	Product selectivity (mol%)			
		MG	DG	TG	DG+TG		ME	DE	TE	DE+TE
0.5:1	83	68	31.2	0.8	32	64.3	94.9	3.5	1.6	5.1
1:1	69	68.9	30.7	0.3	31	60	65.1	32.9	2.0	34.9
2:1	61	28.3	57.2	14.5	71.2	54.2	15.8	74.8	9.4	84.2
3:1	54	20.3	67.6	12.1	79.7	51.6	9.0	74.6	16.4	96.0
4:1	49	7.7	66.1	26.2	92.3	45.2	14.0	68.4	17.6	86.0

Reaction conditions: Polyol = 0.32 g (glycerol) or 0.48 g (TMP), catalyst = 5 wt% of OA; reaction temperature = 180 °C; reaction time = 1 h. ME = monoester, DE = diester and TE =triesters

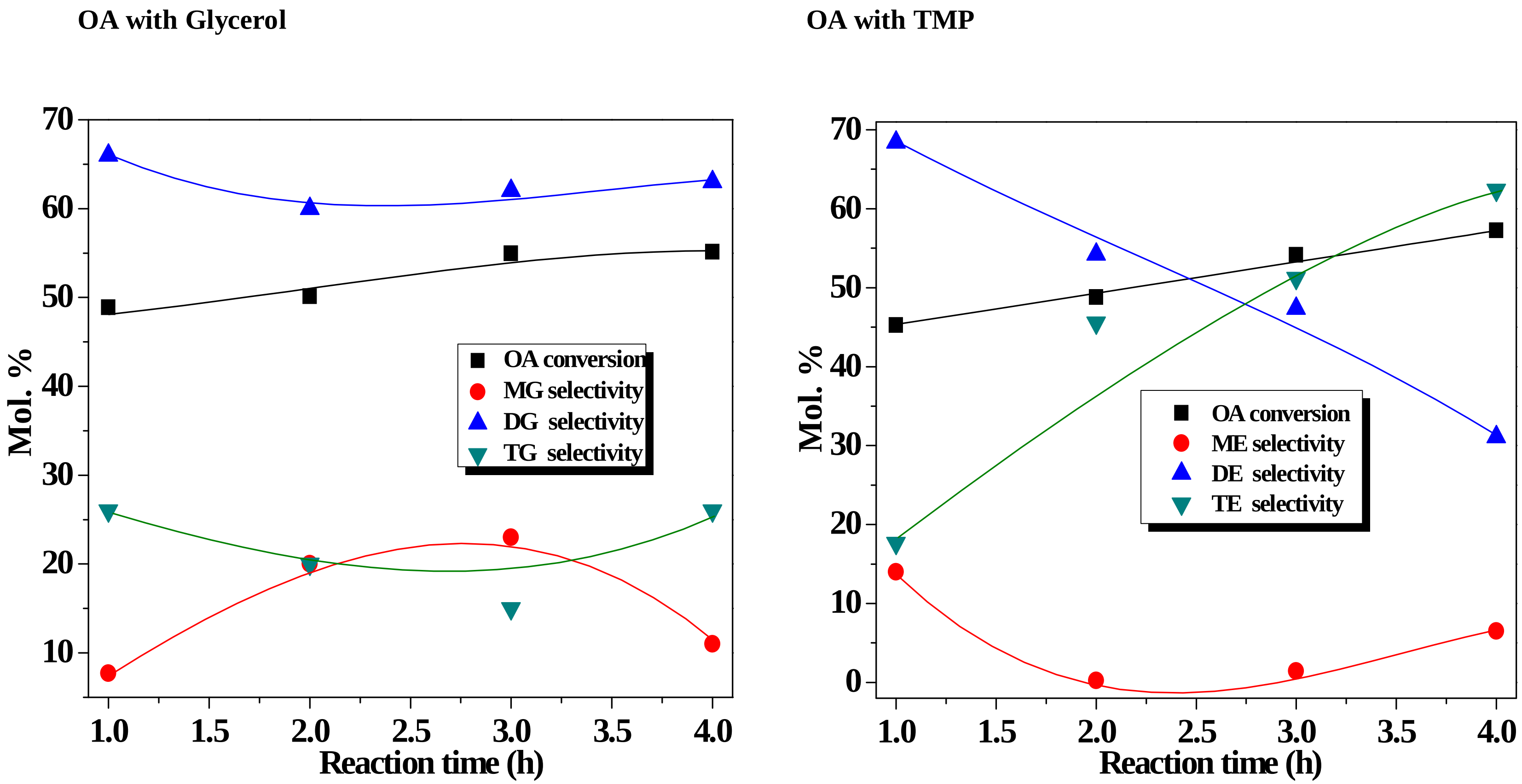


Fig. 5.7. Effect of reaction time on the esterification oleic acid with glycerol (left) and trimethylolpropane (TMP; right) over ZrPP-3 catalyst. Reaction conditions: oleic acid (OA) = 4 g, polyol = 0.32 g (glycerol) or 0.48 g (TMP), OA : polyol molar ratio = 4 : 1 catalyst = 5 wt% of OA, reaction time = 180 °C.

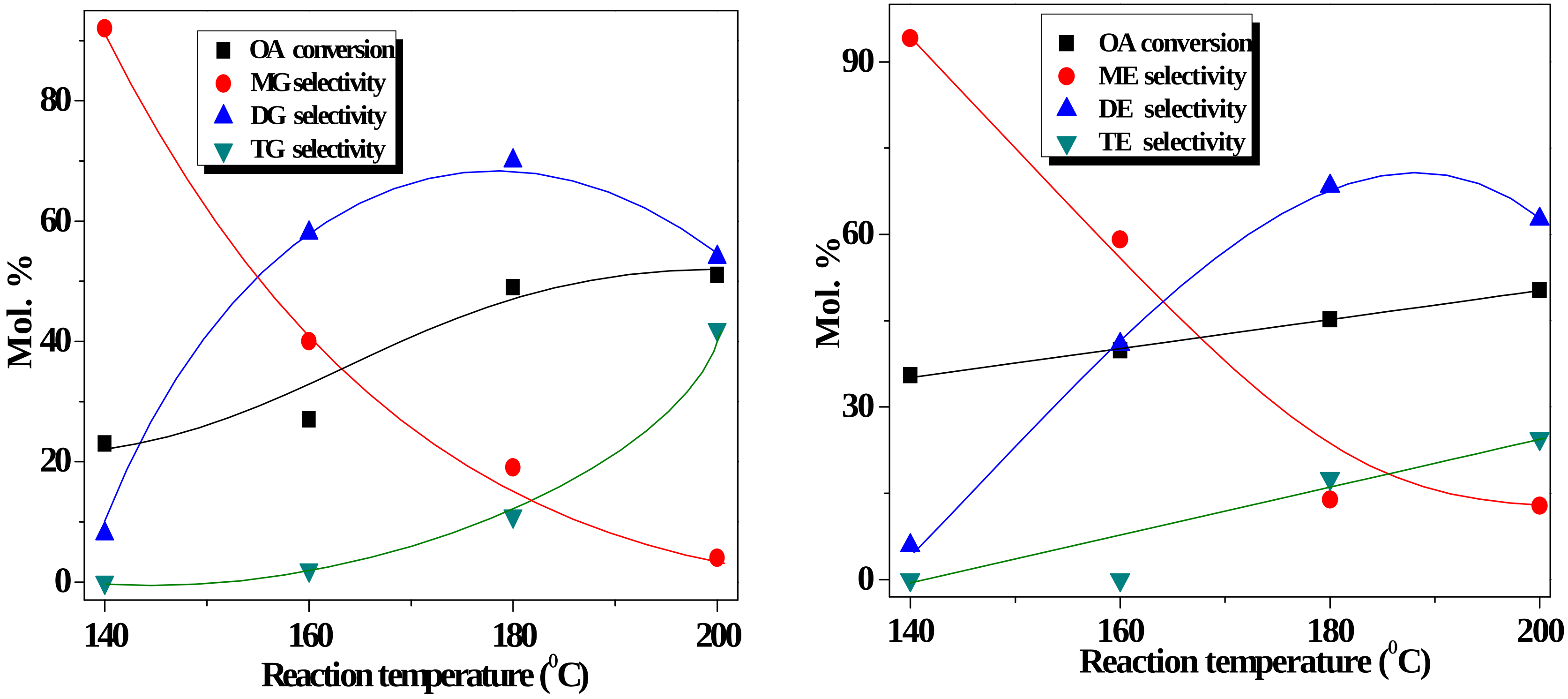


Fig. 5.8. Effect of reaction temperature on esterification oleic acid with glycerol (left) and trimethylolpropane (TMP; right) over ZrPP-3 catalyst. *Reaction conditions:* oleic acid (OA) = 4 g, polyol = 0.32 g (glycerol) or 0.48 g (TMP), OA : polyol molar ratio = 4 : 1 catalyst = 5 wt% of OA, reaction time = 1 h. ME = mono ester, DE = diester and TE = triester.

As expected, the conversion of OA increased with temperature. At the same time, the selectivity also varied. The selectivity to DE + TE increased with increase in temperature. The present catalyst showed considerable activity even at as low reaction temperature as 140 °C.

5.3.2.4. Influence of Catalyst Amount. When the catalyst amount was increased from 3 to 9 wt%, only a moderate increase in OA conversion was observed. Thus, it is clear that the increase in catalyst loading above 3 wt% did not help to improve the initial rate of the reaction. These results suggest that a small amount catalyst is sufficient to attain maximum conversion (Fig.5.9).

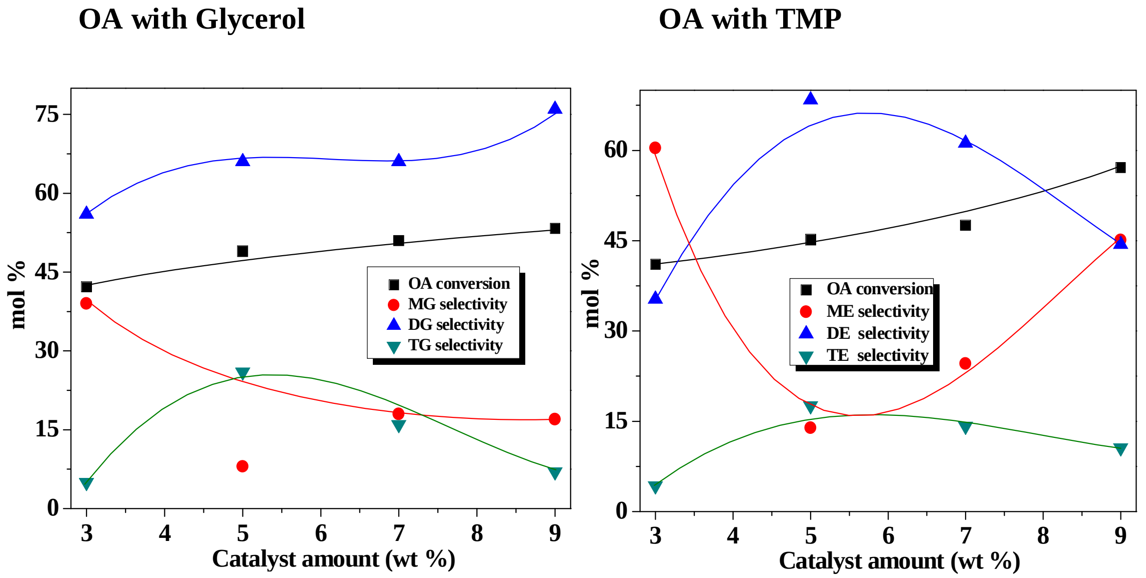


Fig. 5.9. Effect of catalyst amount on esterification oleic acid with glycerol (left) and trimethylolpropane (TMP; right) over ZrPP-3 catalyst. *Reaction conditions:* oleic acid (OA) = 4 g, polyol = 0.32 g (glycerol) or 0.48 g (TMP), OA : polyol molar ratio = 4 : 1 catalyst = 5 wt% of OA, reaction time = 1 h and reaction temperature = 180 °C.

5.3.2.5. Influence of Chain Length of FA. Chain length of fatty acid has a notable effect on conversion and product selectivity (Table 5.4). While the conversion of fatty acid and individual selectivity of TE had decreased, selectivity of DE + TE increased with increasing chain length of the acid i.e., by using oleic acid ($C_{18.1}$) instead of valeric acid (C_5). Addition of water (up to 0.5 wt %) did not alter the esters yield.

Table.5.4. Catalytic data of ZrPP-3 in the esterification of fatty acids with TMP

Fatty acid (FA)	Fatty acid conversion (mol%)	Product selectivity (mol %)			
		ME	DE	TE	DE+TE
Valeric acid (C_5)	82.3	36.9	30.4	32.7	63.1
Caprylic acid (C_8)	75.1	35.5	41.9	22.6	64.5
Capric acid (C_{10})	65.1	32.3	46.6	21.1	67.7
Lauric acid (C_{12})	55.4	29.8	51.1	19.1	70.2
Oleic acid($C_{18.1}$)	45.3	14.0	68.4	17.6	86.0

Reaction conditions: Fatty acid = 4 g, fatty acid : trimethylolpropane (TMP) molar ratio = 4 : 1, catalyst = 5 wt% of fatty acid, reaction temperature = 180°C , reaction time = 1 h. TMP conversion = 100%. ME = mono ester, DE = diester and TE = triester.

5.3.2.6. Catalyst Reusability. ZrPP-3 being hydrophobic is quite stable and reusable in esterification reactions (Fig. 5.10). OA conversion was almost the same in four recycling experiments. At the end of each cycle, the catalyst was separated from the reaction mixture by filtration, washed with methanol, dried at 373 K for 3 h and then reused in subsequent recycle. The catalyst retained its activity even after its use. To establish the structural integrity, the spent catalyst was characterized by XRD and FTIR spectroscopy. As shown in Fig. 5.11, the fresh and spent catalysts have the same finger print features in both XRD and FTIR indicating that the structure of the used catalyst is intact. Compositional integrity was established by microanalysis and energy-dispersive X-ray spectroscopy (EDAS). The %C and %H of the fresh and spent catalysts were nearly the same (20.1 and 1.6 for the fresh catalyst and 21.5 and 1.7 for the spent ZrPP-3 catalyst). EDAX revealed that Zr:P:O:C composition (wt%) of the fresh (51.23:18.77:17.39:12.61) and spent ZrPP-3 (47.34:20.36:18.67:13.63) was also the same. Analysis of the product samples did not show any traces of Zr and P elements in their composition. All these characterization studies of spent catalyst and product mixture, thereby, reveal that ZrPP-3 is a stable and usable solid catalyst.

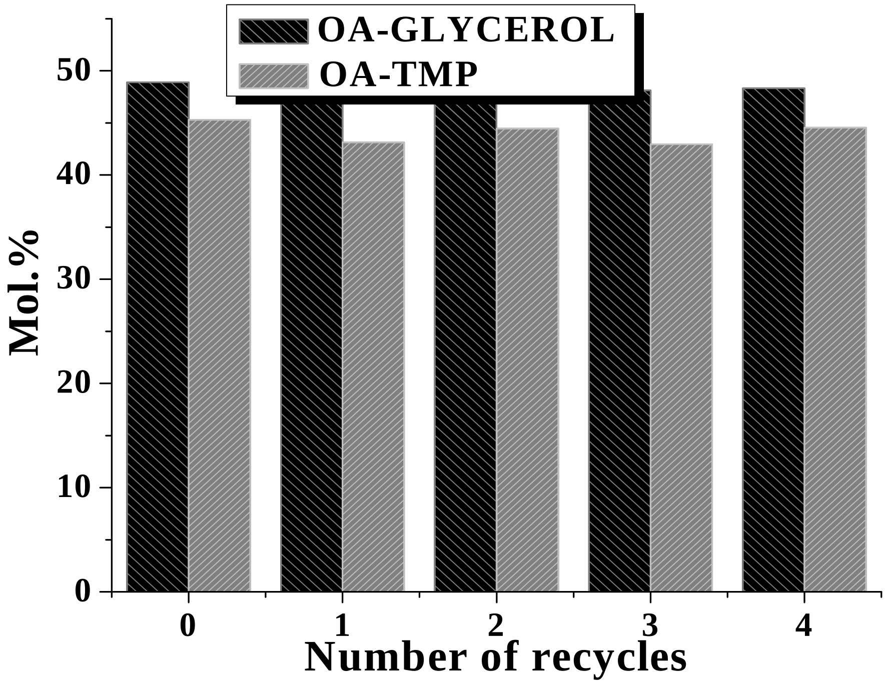


Fig. 5.10. Catalyst reusability study in esterification of OA with glycerol and TMP. *Reaction conditions:* oleic acid (OA) = 4 g, polyol = 0.32 g (glycerol) or 0.48 g (TMP), OA : polyol molar ratio = 4 : 1, catalyst (ZrPP-3) = 5 wt% of OA, reaction temperature = 180 °C, reaction time = 1 h. ME = mono ester, DE = diester and TE = triester.

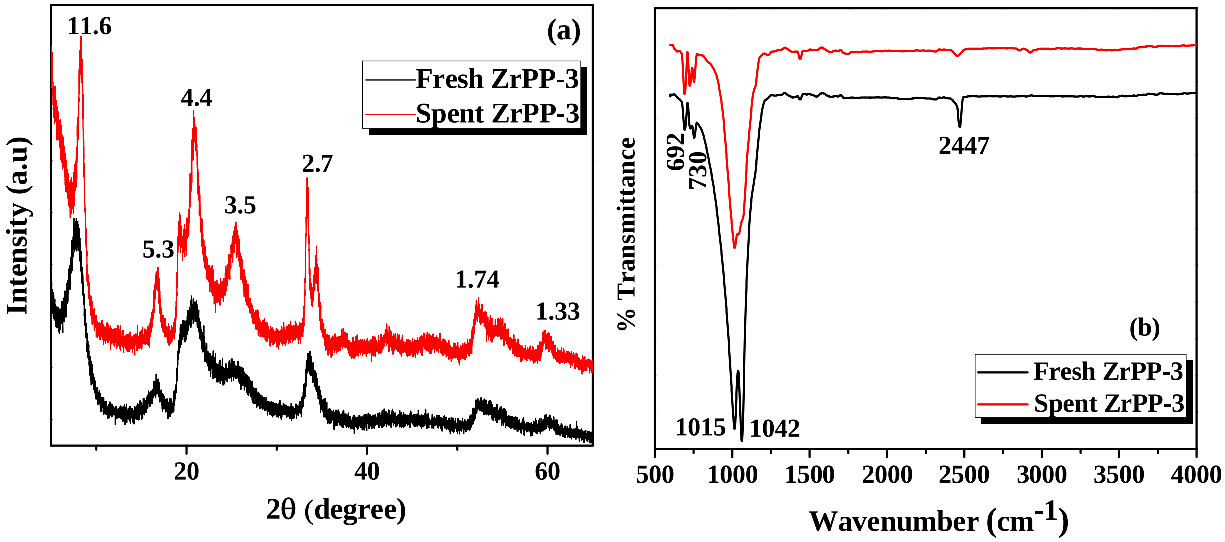


Fig. 5.11. (a) XRD and (b) FTIR of fresh and spent ZrPP-3 catalyst.

With a view to establish that surface hydrophobicity of ZrPP-3 is the cause for its high selectivity for DE + TE esters, experiments were conducted also with a commercial hydrophilic sulfated zirconia (SZ; Saint-Gobain, Norpro) catalyst which has both Brönsted and Lewis acidic active sites. The reactions were conducted at 180 °C taking OA: TMP molar ratio of 4: 1 and catalyst of 5 wt% of OA. Reactions were followed as a function of time for 5 h. As expected, conversion of OA was higher over Brönsted and Lewis acidic SZ than on ZrPP-3 (Fig. 5.12). But then, DE + TE esters selectivity was significantly higher over ZrPP-3 than on SZ catalyst (Fig. 5.12). These studies thus confirm that hydrophobicity plays a major role on product selectivity in reactions with polyhydric alcohols. The by-product water can compete for adsorption with polyols and OA. On hydrophobic surfaces as that of ZrPP-3, only the reactant molecules, OA and polyol adsorb and undergo reaction to form polyol esters. But, on hydrophilic surfaces, competitive adsorption and reverse reactions (hydrolysis) would also be favored reducing the selectivity for DE + TE esters.

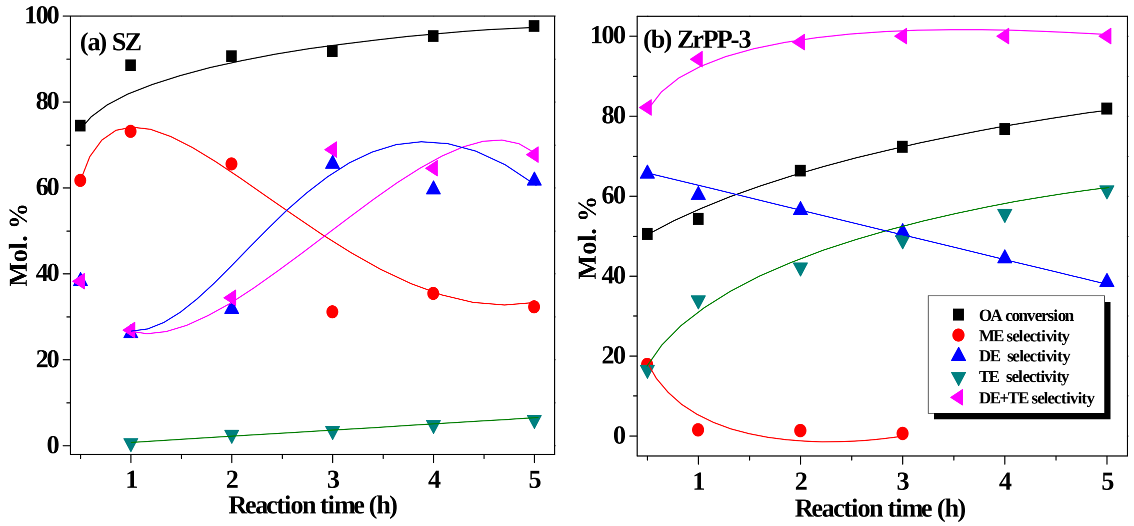


Fig. 5.12. Kinetics of esterification of OA with TMP over (a) SZ and (b) ZrPP-3 catalysts. *Reaction conditions:* oleic acid (OA) = 4 g, trimethylolpropane (TMP) = 0.48 g, OA: polyol molar ratio = 4: 1, catalyst = 5 wt% of OA, reaction temperature = 180 ◦C.

5.4. Conclusions

Zirconium phenyl phosphonate phosphites were prepared with varying phosphorous acid to phenyl phosphonic acid input molar ratio and evaluated as catalysts in esterification reactions of oleic acid with glycerol and TMP. The catalyst with phosphorous acid/phenyl phosphonic acid molar ratio of 3 showed high catalytic activity and most importantly the

DE + TE selectivity. Hydrophobicity of ZrPP and strong acidity are possibly the key features for their high activity and selectivity in polyesterification reactions. ZrPP is a reusable catalyst. It is highly active irrespective of the type of fatty acid and polyol. Synthetic esters of varying lubricity properties could be prepared with this catalyst by changing process parameters or by varying fatty acid and polyol.

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Chapter - 6

Overall Summary and Conclusions

Vegetable oil-derived biolubricants are sustainable alternative to the conventional mineral oil lubricants. They are renewable and have several advantageous features. Their use leads to environmental protection. However, the high cost of their production using homogenous mineral acid and Lewis acid catalysts limit their wide spread utility. Application of solid catalysts in place of homogeneous acid catalysts make the manufacturing process economical and eco-friendly as the solid catalysts are reusable and avoid the tedious steps involved in catalyst separation from the product. Among several methods, transesterification of vegetable oils with long-chain alcohols and esterification of fatty acids (products of vegetable oil refining process) with polyols or long-chain alcohols are the most common methods for producing biolubricants. Development of more efficient, stable and robust solid catalysts is a challenging task to make these processes more attractive.

In this thesis, the catalytic application of three new families of solid catalysts (vis., double-metal cyanide (DMC) complexes, titanosilicates and zirconium phenyl phosphonate phosphites) for production of biolubricants has been investigated. Lewis acidity, mesoporosity and hydrophobicity are some common features of these three sets of catalysts. While Lewis acids are the actives sites for esterification/transesterification reactions to occur, mesoporosity enables facile diffusion of bulky reactant and product lipid molecules and enables access to the active sites. Water is the by-product in esterification reaction of fatty acids. Hydrophobicity of catalyst surface makes sure the adsorption of lipid molecules and not water. It is noted that all these catalysts are highly active in producing lubricant base stocks with varying properties suitable of a wide range of applications. In polyol esters synthesis, while DMC catalysts are selective for polyol monoesters formation, titanosilicates and zirconium phenyl phosphonate phosphite catalysts are selective for di- + triesters formation. These catalysts were found reusable in several recycling studies. Main conclusions from different chapters are provided below.

Chapter – 1 provided general introduction to biolubricants. It provided a brief history of various catalysts used in producing biolubricants. Scope and objective of the work were also provided in this chapter.

Chapter - 2 presented the experimental methodologies adopted in this work. It described the procedures for catalysts preparation, characterization, catalytic activity studies and product identification/quantification.

Chapter – 3 discussed the application of solid Fe-Zn double-metal cyanide catalysts for (i) esterification of fatty acids with glycerol and (ii) transesterification of methyl oleate (a component of biodiesel) with long-chain alcohols in batch reactions. DMC catalysts with varying acidities were prepared by synthesizing the material at four different temperatures (10, 25, 50 and 80 °C). The catalyst prepared at 50 °C exhibited highest catalytic activity. At lower reaction temperature (140 °C) and shorter period of time (< 1 h), high selectivity for monoglycerides (83%) was observed over DMC-50 °C catalyst. Water formed as by-product did not deactivate the catalyst as the surface of DMC is hydrophobic.

Synthesis of fatty acid monoesters through the reaction of a fatty acid methyl ester with a long-chain alcohol [2-ethyl-1-hexanol (C_8OH), 1-decanol ($C_{10}OH$) and 1-dodecanol ($C_{12}OH$)] using a DMC-50 °C catalyst was investigated. Fatty acid monoesters find applications in synthetic lubricants, paint additives, plasticizers, pharmaceuticals and cosmetics. Most of the known acid catalysts at high temperatures form ethers. Formation of such undesired ether product was not observed even at 200 °C over the DMC catalyst of this work. Fatty monoester of long-chain alcohols was the selective product over DMC. Catalyst reusability study revealed that DMC is a stable and reusable catalyst. Surface area, acidity and hydrophobicity of the catalyst surface are the parameters that influenced the catalytic activity. The product long-chain alcohol esters have the desired physical properties required for lubricant applications.

Chapter – 4 offered the catalytic activity studies of three-dimensional, ordered, mesoporous titanosilicate Ti-SBA-12 and Ti-SBA-16 catalysts in the esterification of oleic acid (OA) with polyhydric alcohols viz., glycerol (G), trimethylolpropane (TMP), neopentylglycol (NG) and pentaerythritaol (PE) producing synthetic polyol esters. Ti-SBA-16 (Si/Ti molar ratio = 50) was found superior to Ti-SBA-12 (Si/Ti molar ratio = 40) in the esterification reactions as the former is relatively more hydrophobic than the latter. OA conversion with different polyols decreased in the order: TMP > G > NPG > PE. The influence of reaction parameters in catalytic activity and selectivity was investigated. At an optimum molar ratio of OA : TMP = 3: 1, 180 ^{0}C and reaction time of 10 h, di- + trimesters selectivity as high as 98.6 mol% was obtained using Ti-SBA-16 (Si/Ti = 50) catalyst. Fatty acid chain length was found to have an effect on the product selectivity. Longer chain-length acids lead to selective di + trimester products. The titanosilicate catalysts were reusable. The composition of the polyol esters in the product can be controlled or varied by changing OA to polyol molar ratio, temperature, reaction time and type of catalyst used. Dispersed tetrahedral Ti ions are the acid sites catalyzed the esterification reaction. The physical properties lubricants prepared using Ti-SBA-16 (Si/Ti = 50) catalyst at OA : TMP molar ratio = 4:1, temperature = 180 °C and reaction time = 10 h match with those of commercial lubricants of brand names VP lubricant base oils 700 and 150BS, Servo - gear HP85 and HP90, boat engine oil SAE grade 20W-40, Ultra 40 and 50 and Servo 4T.

Chapter 5 presented the catalytic application of zirconium phenyl phosphonate phosphite (ZrPP) in producing fatty acid polyol esters. ZrPP were prepared with varying phosphorous acid to phenyl phosphonic acid input molar ratio and evaluated as catalysts in esterification reactions of oleic acid with glycerol and TMP. The catalyst with phosphorous acid/phenyl phosphonic acid molar ratio of 3:1 showed high catalytic activity and most importantly the DE + TE selectivity. The influence of process parameters on activity and selectivity of the catalyst was also investigated. With increasing molar ratio of OA/polyol from 0.5 to 4, a decrease in the conversion of OA from 83.0 to 49.0 mol% was observed, while more and more of mono- and diesters got converted into polyol triesters. At OA: polyol molar ratio of 4:1, reaction temperature of 180 ^{o}C with reaction time of 1 h, the selectivity for DE + TE was 92.3 mol% for glycerol and 86.0 mol% for TMP. Hydrophobicity of ZrPP and strong acidity are possibly the key features for their high activity and selectivity in polyesterification reactions. ZrPP was reusable in at least three recycling experiments.

By and large, this thesis reported the catalytic application of three different solid acid catalysts viz., 1) Fe-Zn double-metal cyanide (DMC) complexes, 2) Three-dimensional, mesoporous titanosilicates Ti-SBA-12 and Ti-SBA-16, and 3) Zirconium phenyl phosphonate phosphate (ZrPP) complex, for producing vegetable oil-based biolubricant base stock. These catalysts were found stable and superior to the hither to know solid acid catalysts used for these applications. While DMC catalysts were selective for polyol monoesters formation, Ti-SBA-16 and ZrPP were found selective for polyol di- and trimesters formation, respectively. In general, this work contributes to the area of green and sustainable catalytic processes.

List of Publications

1. Esterification of fatty acids with glycerol over Fe-Zn double metal cyanide catalyst
   Mehejabeen Kotwal, S.S. Deshpande and D. Srinivas
   Catal. Commun. 12 (2011) 1302 - 1306.
2. Three-dimensional, mesoporous titanosilicates as catalysts for producing biodiesel and biolubricant.
   Mehejabeen Kotwal, Anuj Kumar and Srinivas Darbha
   J. Mol. Catal. A: Chem. 377 (2013) 65 – 73.
3. Zirconium phenyl phosphonate phosphite as a highly active, reusable, solid acid catalyst for producing fatty acid polyol esters.
   Poonam Varhadi, **Mehejabeen Kotwal** and D. Srinivas
   Appl. Catal. A: Gen. 462-463 (2013) 129 - 136.
4. Synthesis of fatty monoester lubricant base oil catalyzed by Fe-Zn double-metal cyanide complex
   Ravindra K. Raut, **Mehejabeen Kotwal** and Darbha Srinivas
   Communicated (2014).

Patent

1 Process for the preparation of biodegradable lubricant base oils
Darbha Srinivas and **Mehjabeen Kotwal**
India and PCT (Appln No. 1558DEL2012, date of filing 22 May 2012, CSIR No. 103NF2012.