

Review

# Zeolite-Based Catalysts: A Valuable Approach toward Ester Bond Formation

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**Abstract:** Zeolite-based catalysts are versatile catalytic systems for a wide range of laboratory studies and industrial scale processes. The chemical composition, ion exchange, and pore size structure attributes of zeolites are responsible for their extensive catalytic applications. Esterification is one of the most important and routinely processes in diverse fields of organic synthesis. It has a long history in both industrial processes and laboratory work due to its versatility. This review intends to give a detailed insight into the significance of zeolite-based catalysts for ester bond formation

**Keywords:** zeolites; heterogeneous catalysis; biodiesel; ester functional moiety

## 1. Introduction

Esters are one of the most prevalent and important class of functional groups that are widely found in a broad variety of valuable chemicals such as plasticizers, fibers, solvents, inks, fragrances, lubricants, surfactants, food additives, pharmaceuticals, and other fine chemicals [1,2]. Given their significance, esterification procedures should occupy an outstanding site in the desire to advance safe and sustainable chemical technologies into various industrial practices. Traditionally, esterifications are performed in presence of homogeneous acid catalysts, such as HCl, H<sub>2</sub>SO<sub>4</sub>, phosphoric acid, *p*-toluenesulfonic acid, HF, AlCl<sub>3</sub>, BF<sub>3</sub>, and ZnCl<sub>2</sub> as well as base catalysts, such as KOH and NaOH or methoxide [3–6]. However, the utilization of these homogeneous catalytic processes is not favorable for practical applications, due to their toxicity, corrosivity, non-reusability, and non-recyclability. Other drawbacks of these systems include environmental pollution and difficulty in product isolation and purification. Thus, the development of novel heterogeneous catalytic systems with suitable catalytic performance, while demonstrating good recoverability, is an important challenge in this area [7–16]. In this context, zeolite-based catalysts are one of the most important members of the heterogeneous catalyst family.

Zeolites are microporous crystalline aluminosilicates generally composed of aluminum (Al), silicon (Si), and oxygen. The history of zeolite started with the discovery of the first mineral of this class, stilbite, by the Swedish mineralogist Axel Cronsted in 1756 [17]. The Si/Al ratio is a significant factor of zeolites. The stability of zeolite increases with increasing the ratio of Si/Al in the structure, and their structure remains stable at high temperatures [18]. Presently, a variety of procedures are available

to synthesis hierarchical porous zeolites in the form of composites [19], nanosized crystals [20], and mesoporous crystals [21].

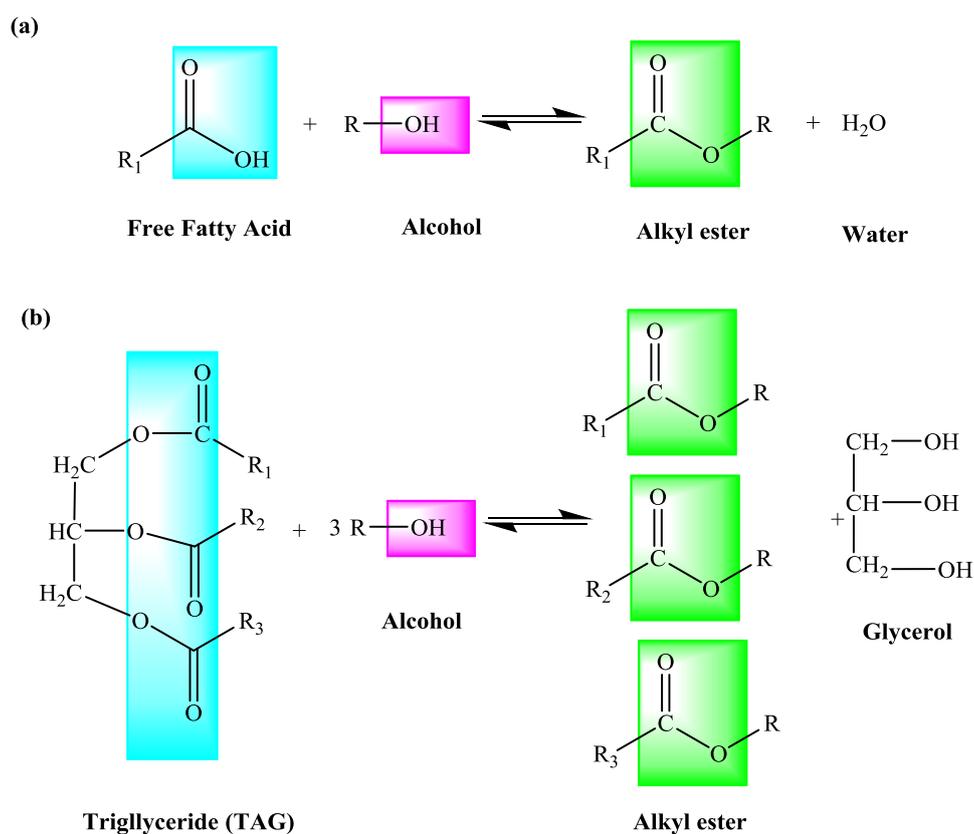
Zeolites are generally classified into two classes: natural and synthetic. Natural zeolites are made when ash layers and volcanic rocks crystallized under reaction with ground water or alkaline/saline lake. The most popular natural zeolites are offretite, chabazite, mordenite (MOR), and faujasite (FAU). On the other hand, synthetic zeolites are formed from diverse materials, such as clays and industrial residues [22–24]. Synthetic zeolites are utilized commercially more than natural zeolites, owing to the uniformity of particle sizes and the purity of crystalline products. The synthetic zeolites, such as X, A, ZSM-5, Y, and beta, have the largest commercial application [25]. They are produced under well-controlled chemical and physical conditions. By varying the synthesis parameters, one may obtain zeolites with different chemical compositions and structural properties. One of the valuable methods to carry out zeolite synthesis is the sol–gel technique. The product properties depend on the pH of the system, reaction mixture composition, reaction time, and operating temperature, as well as the templates used. In sol–gel procedures, other elements (metal oxides, metals) can be easily incorporated. [26,27].

Acidity is an important parameter of zeolites. The zeolitic acidity originates from the charge unbalance between alumina and silica units which alternate within the constant crystalline aluminosilicate framework: these attributes make zeolites suitable and effective catalysts for various organic transformations, such as isomerization, tert-butylation of aromatic compounds, etherification of 5-Hydroxymethylfurfural, and dehydration of methanol to dimethyl ether [28–34].

Zeolites are potentially attractive due to the easy recovery of product/substrate, catalyst recycling, and possible regioselectivity, owing to their constraining pore structures and related acidic properties. They have potential applications in various advanced technologies, such as humidity control; water treatment and purification; drug carriers and heterogeneous catalysis, especially in oil and petroleum refining; and petrochemical industries as solid catalysts due to their appreciable acid activity and shape selective properties [35–47]. Various zeolites can be utilized in esterification and/or transesterification reactions, and their functionality depends on their acidity (strength and number of the acid sites) and pore size features (molecular shape selectivity and concentration effects). The present review draws attention to the application of zeolite-based catalysts in the production of some important organic ester compounds that are widely used in various industries.

## 2. Biodiesel Production

Biodiesel is a mixture of monoalkyl esters of long-chain fatty acids, which is produced from various origins, such as animal fats, vegetable oils, or waste oil, through esterification and/or transesterification with alcohols, especially methanol and ethanol (Figure 1). In comparison with conventional fossil fuels, biodiesel has received remarkable attention as sustainable and alternative fuel owing to its low viscosity, higher cetane value, high flash point, high lubricity, environmental friendliness, and biodegradability [48–52]. Zeolites play a significant and valuable role in the petroleum industry, and in recent years the utilization of these catalysts in biodiesel production has been extensively investigated via their capability to perform both transesterification and esterification reactions. A list of important research reports on biodiesel production in presence of zeolite-based catalysts is summarized in Table 1.



**Figure 1.** Schematic of biodiesel (alkyl ester) production via (a) esterification and (b) transesterification reaction.

**Table 1.** Research reports on biodiesel production in presence of zeolite-based catalysts.

Source	Zeolite Catalyst (Si/Al Molar Ratio)	Type of Alcohol (Alcohol-to-Oil Molar Ratio)	Time (h)/Temperature (°C)	Amount of Catalyst	Reactant -to-Catalyst Weight Ratio	Yield (%)	Reference
Waste frying oil	H-MOR (10)	Methanol (30:1)	3/60	1 g	-	80.9	[53]
Waste frying oil	H-ZSM-5 (25)	Methanol (30:1)	3/60	1 g	-	80.6	[53]
Waste frying oil	H-beta (13)	Methanol (30:1)	3/60	1 g	-	<70	[53]
Waste frying oil	H-FAU (3)	Methanol (30:1)	3/60	1 g	-	<75	[53]
Oleic acid	H-ZSM-5 (25)	Methanol (15:1)	1/60	0.5 g	17.8	~80	[54]
Oleic acid	H-MOR (10)	Methanol (15:1)	1/60	0.5 g	17.8	~80	[54]
Oleic acid	H-FAU (3)	Methanol (15:1)	1/60	0.5 g	17.8	75	[54]
Oleic acid	H-beta (13)	Methanol (15:1)	1/60	0.5 g	17.8	70	[54]
Oleic acid	TPA <sub>3</sub> /H-beta (10)	Methanol (20:1)	6/60	0.1 g	28.2	84	[55]
Waste cooking oil	TPA <sub>3</sub> /H-beta (10)	Methanol (8:1 w/w)	20/60	6 wt %	-	83.9	[55]
Jatropha oil	TPA <sub>3</sub> /H-beta (10)	Methanol (8:1 w/w)	20/60	6 wt %	-	92.6	[55]
Oleic acid	30%SiW <sub>12</sub> /H-beta (10)	Methanol (20:1)	10/60	0.1 g	28.2	86	[56]
Soybean oil	30%SiW <sub>12</sub> /H-beta (10)	Methanol (4:1 w/w)	8/65	0.2 g	25	95	[56]
Soybean oil	30%SiW <sub>11</sub> /H-beta (10)	Methanol (4:1 w/w)	8/65	0.2 g	25	96	[57]
Oleic acid	30%SiW <sub>11</sub> /Hbeta (10)	Methanol (20:1)	10/60	0.1 g	28.2	82	[57]

Table 1. Cont.

Source	Zeolite Catalyst (Si/Al Molar Ratio)	Type of Alcohol (Alcohol-to-Oil Molar Ratio)	Time (h)/Temperature (°C)	Amount of Catalyst	Reactant-to-Catalyst Weight Ratio	Yield (%)	Reference
Oleic acid	11.4%WO <sub>3</sub> /USY (6.1)	Ethanol (6:1)	2/200	10 wt %	-	75.8	[58]
Oleic acid	HUSY (4.8)	Ethanol (6:1)	2/200	10 wt %	-	73.9	[58]
Oleic acid	Zeolite Y (3.1)	Ethanol (6:1)	1/70	5 wt %	20	85	[59]
Oleic acid	FAU (1.98)	Ethanol (6:1)	1.5/70	5 wt %	20	78	[60]
Oleic acid	FAU (1.98)	Ethanol (6:1)	1.5–2/70	5 wt %	20	93	[61]
Palmitic acid	H-Y-60 (30)	Methanol (2:1)	3/70	-	-	100	[62]
Palmitic acid	Pillared HMCM-36	Methanol (30:1)	6/70	0.05 g	25.64	100	[63]
Oleic acid	Beta (50)	Ethanol (20:1)	10/78	0.167 meq/g	-	73.6	[64]
Oleic acid	SO <sub>4</sub> <sup>2-</sup> /La <sub>2</sub> O <sub>3</sub> /H-ZSM-5	Methanol (45:1)	7/100	10 wt %	-	100	[65]
Oleic acid	H-ZSM-5	Methanol (45:1)	7/100	10 wt %	-	80	[65]
Oleic acid	10%SO <sub>4</sub> <sup>2-</sup> /La <sub>2</sub> O <sub>3</sub> /H-ZSM-5 (14)	Methanol (10:1)	4/100	5 wt %	-	100	[66]
Oleic acid	H-ZSM-5 (14)	Methanol (45:1)	4/100	10 wt %	-	55	[67]
Oleic acid	Citric acid/H-ZSM-5 (14)	Methanol (45:1)	4/100	10 wt %	-	83	[67]
Oleic acid	NaA zeolite	Ethanol (15:1)	24/80	-	-	87.18	[68]
Soybean oil	La/β-zeolite (3.9)	Methanol (14.5:1)	4/60	1 g	92.5	48.9	[69]
Soybean oil	KOH/NaX (1.23)	Methanol (10:1)	8/65	3 wt %	-	85.6	[70]
Palm oil	KOH/NaY (4)	Methanol (15:1)	3/60	6 g	16.7	91.07	[71]
Soybean oil	KNa/ZIF-8	Methanol (10:1)	3.5/100	8 wt %	12.5	>98	[72]
Soybean oil	Na/ZIF-8	Methanol (10:1)	3.5/100	8 wt %	12.5	86	[72]
Soybean oil	ZIF-8	Methanol (10:1)	10/100	8 wt %	12.5	11	[72]
Soybean oil	CaO/NaY (3.24)	Methanol (9:1)	3/65	3 wt %	-	95	[73]
Soybean oil	Ce/HUSY (4)	Ethanol (30:1)	24/200	0.001 mol	-	99.8	[74]
Triolein	Na-Beta (> 5000)	Methanol	1/110	-	-	96.6	[75]
Triolein	Zeolite LTA-kaolin (1.16)	Methanol	2.43/62.9	72 wt %	-	92.8	[76]
Sunflower oil	FA/Na-X zeolite (2-3)	Methanol (6:1)	8/65	3 wt %	-	83.53	[77]
Sunflower oil	Sr/ZSM-5	Methanol (9:1)	4/60	-	-	87.7	[78]
Soybean oil	K-La/ZSM-5	Methanol (12:1)	3/60	3 wt %	33.3	90	[79]
Castor oil	La <sub>2</sub> O <sub>3</sub> /NaY	Ethanol (15:1)	0.83/70	10 wt %	10	84.6	[80]
Waste cooking oil	Y756 zeolite	Methanol (6:1)	0.37/476	-	-	26.6	[81]
Waste cooking oil	Y530 zeolite	Methanol (6:1)	0.21/466	-	-	21.9	[81]
Mustard oil	AZ-KX (2)	Methanol (12:1)	7/65	5 wt %	-	84.6	[82]
Canola oil	KOH/ZSM-5-Fe <sub>3</sub> O <sub>4</sub>	Methanol (12.3:1)	3.26/65	9.03 wt %	11.07	93.65	[83]

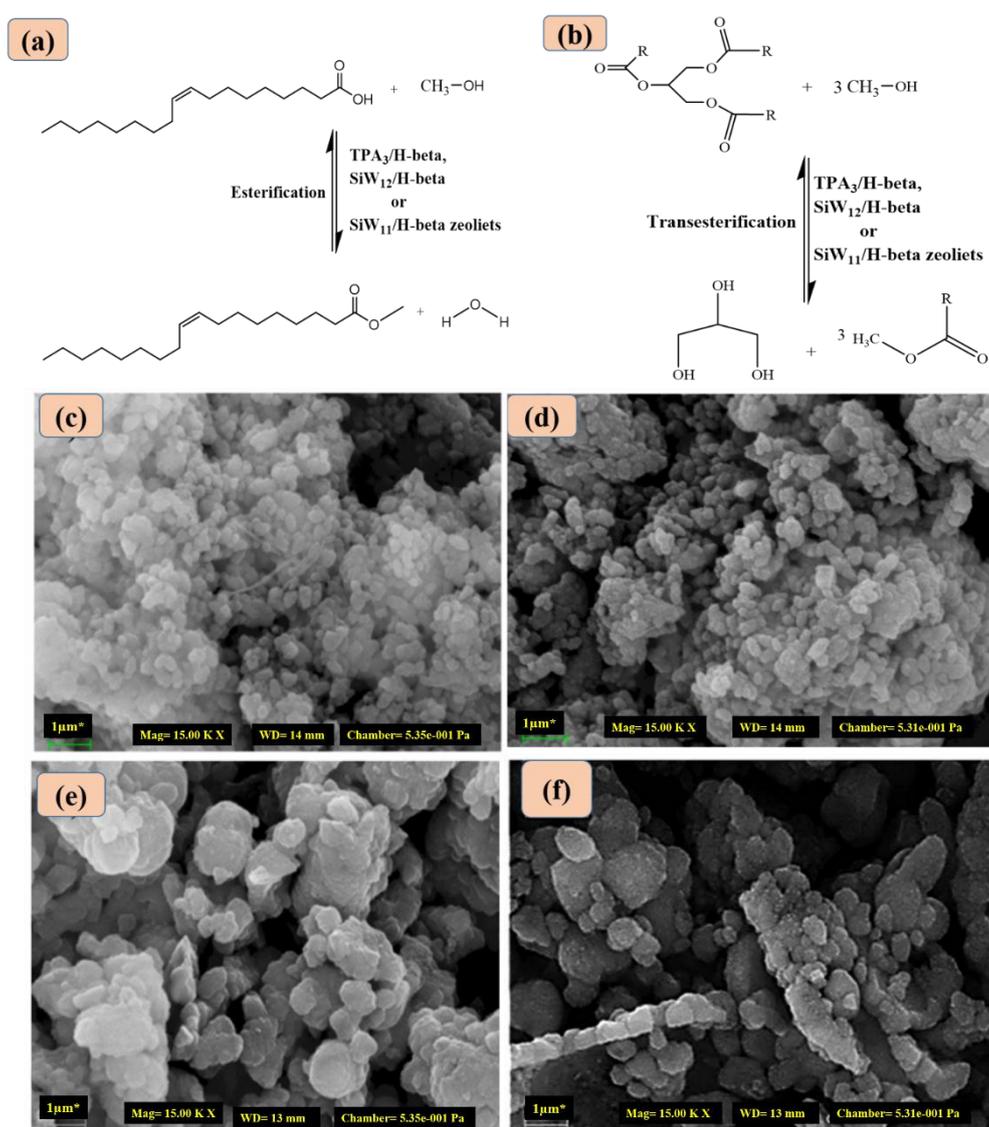
MOR, mordenite; FAU, faujasite; TPA, 12-tungstophosphoric acid; SiW<sub>12</sub>, 12-tungstosilicic acid; SiW<sub>11</sub>, monolacunary silicotungstate; WO<sub>3</sub>, tungsten trioxide; USY, ultrastable Y; La<sub>2</sub>O<sub>3</sub>, lanthanum oxide; FA, fly ash; AZ-KX, acid treated zeolite K-X.

### 2.1. Zeolite-Catalyzed Biodiesel Production by Esterification Reactions

Chung et al. [53] presented the free fatty acid (FFA) esterification with methanol in presence of many zeolite catalysts such as ZSM-5, FAU, MOR, silicalite, and β zeolites. The obtained results showed that a high removal of FFA could be achieved using H-ZSM-5 and H-MOR zeolite catalysts, owing to their acidity and pore structure. In another study by the same research group [54], the performance of zeolite catalysts was evaluated for the esterification of oleic acid in soybean oil. MOR and H<sup>+</sup> ion-exchanged ZSM-5 zeolites with a distinct Si/Al ratio were used to investigate the effect of acidity in the reaction. The oleic acid conversion to biodiesel was around 80% when the amount of

acid in the zeolites was above 0.06 mmol/g. In addition, a linear connection between the conversion of feedstock and acidity was observed, and high catalytic performance was found with enhanced acidity.

$\beta$ -Zeolite is a large-pore high silica material that has received considerable theoretical and experimental investigation. It is a promising candidate for catalysis, owing to its high chemical and thermal stability, hydrophobic character (at higher Si/Al ratios), and surface silanol groups which are the main features of favorable support [84]. Patel et al. [55–57] synthesized heterogeneous acid catalysts comprised of H- $\beta$ -zeolite and some heteropoly acids, such as 12-tungstophosphoric acid (TPA), 12-tungstosilicic acid (SiW<sub>12</sub>), and monolacunary silicotungstate (SiW<sub>11</sub>). The synthesized catalysts showed great efficiency under mild conditions in the esterification of oleic acid (Figure 2a). The scanning electron microscopy (SEM) images showed that the surface morphology of modified catalysts is almost identical to that of H-beta zeolite (Figure 2c–f). It was also reported that after incorporation of TPA, SiW<sub>12</sub>, and SiW<sub>11</sub>, the framework structure of the zeolite support is maintained.



**Figure 2.** (a) Esterification of oleic acid and (b) transesterification of triglyceride with methanol over heterogeneous acid catalysts comprised of H- $\beta$ -zeolite. Scanning electron microscopy (SEM) images for (c) H-beta, (d) TPA<sub>3</sub>/H-beta, (e) SiW<sub>12</sub>/H-beta, and (f) SiW<sub>11</sub>/H-beta [55–57].

Costa et al. [58] investigated the influence of functionalized tungsten oxide ( $\text{WO}_3$ ) onto ultrastable Y (USY) zeolite surface, acidity, and its catalytic efficiency in the oleic acid esterification with ethanol. The prepared catalyst ( $\text{WO}_3/\text{USY}$ ) showed good catalytic activity after 2 h.

In a study by Doyle et al. [59], zeolite Y was synthesized using Iraqi kaolin and examined in the liquid-phase oleic acid esterification with ethanol over a range of experimental conditions, such as catalyst mass loading, alcohol-to-acid molar ratio, and reaction temperature. The optimum reaction conditions were achieved at 5 wt % catalyst loading, 70 °C reaction temperature, and an alcohol/acid molar ratio of 6:1. After 60 min, the oleic acid conversion in the presence of synthesized zeolite from kaolin was about 85%, while the corresponding amount for H-Y-zeolite as a commercial sample was about 76%. Later, the same authors showed that FAU-type zeolites exhibited similar conversion of oleic acid to that reported for H-Y-zeolite [60], while adding of Co-Ni-Pt to the FAU-type zeolites increased its activity for biodiesel synthesis in the same procedure to achieve 89% and 93% for continuous and batch reactors, respectively [61].

Palmitic acid is a constituent of many animal fats and vegetable oils, and it is the most representative saturated fatty acid. Prinsen et al. [62] investigated the palmitic acid conversion to methyl palmitate by using ZSM-5 and H-Y zeolites as solid acid catalysts under mild conditions. After 3 h, H-Y-60 at a ratio of palmitic acid to methanol of 1:2 was the best catalyst (100% conversion). This research demonstrated, there is no clear correlation between the esterification reaction and acid sites number. In addition, it was found that the balance of hydrophobicity/hydrophilicity and small/large pore size were critical properties for biodiesel production using palmitic acid. In another interesting study, Purova et al. [63] reported that pillared MCM-36 zeolite catalyst with large pores, is an efficient catalyst for methyl palmitate production from the palmitic acid esterification with methanol, owing to its mesoporous nature and superiority in the amount of strong Brønsted acid sites. The recycling experiments showed that the acid sites on zeolite catalyst were stable and offered constant activity for four cycles.

## 2.2. Zeolite-Catalyzed Biodiesel Production by Transesterification Reactions

Another significant and common method for biodiesel production is transesterification reaction, which has numerous laboratory and industrial applications. Soybean oil is a biodegradable oil obtained from seeds of the soybean plant. Processed soybean oil is utilized for oil paints and printing inks as a base. The major FFA components of soybean oil are oleic acid (23%), stearic acid (4%), linolenic acid (8%), palmitic acid (11%), and linoleic acid (54%) [85]. This suggests that soybean oil has triglyceride esters of both unsaturated and saturated FFA and is suitable feedstock to study the catalytic behavior. In a study, the La/ $\beta$ -zeolite was synthesized via the ion exchange procedure using the suspension of  $\beta$ -zeolite in aqueous solution of lanthanum nitrate under intensive stirring for 3 h at room temperature, dried for 24 h at 100 °C, and finally calcined at 250 °C for 4 h. The prepared catalyst was utilized as a solid acid catalyst for the soybean oil transesterification. In comparison with  $\beta$ -zeolite, the modified zeolite exhibited better stability and higher conversions for biodiesel synthesis, which was attributed to the higher amount of external Brønsted acid sites [69].

Narkhede et al. [55–57] reported biodiesel synthesis from soybean oil transesterification with methanol over heterogeneous acid catalysts composing  $\text{SiW}_{11}$ -,  $\text{SiW}_{12}$ -, and TPA-supported H- $\beta$ -zeolite (Figure 2b). The influence of diverse reaction factors was investigated to optimize the conditions for maximum conversion. All of the synthesized catalysts showed excellent activity as well as potential of being used as recoverable catalytic systems after simple regeneration without considerable loss in conversion.

NaY- and NaX-types of zeolites are the most frequently utilized ones, as alkali metal cation-exchanged zeolites, for the production of biodiesel. Soybean oil transesterification with methanol by KOH loaded on NaX (KOH/NaX) as a solid heterogeneous catalyst was reported by Xie et al. [70]. Under optimal reaction parameters of an alcohol/oil molar ratio of 10:1, 65 °C reaction temperature, and catalyst loading of 3 wt %, the yield of biodiesel was 85.6% after 8 h, but the yield was reduced to 48.7% in the second use of the catalyst, owing to great leaching of potassium from the

zeolite catalyst. In another research [71], using KOH loaded on NaY in palm oil transesterification with methanol, leaching of potassium after the initial cycle of use was also observed. These researches exhibited that interaction of KOH with NaX and NaY is low, which caused a high loss of effective sites. Diffusion limitation because of the tiny pore diameter is also presented as a problem in these catalysts. Wu et al. [73] presented that NaY zeolite incorporated with CaO exhibited high catalytic performance for the soybean transesterification with methanol. The modified zeolite catalyst was synthesized using microwave irradiation followed by calcination in the air at a high temperature to improve the catalytic performance of pure CaO for biodiesel production. After 3 h of reaction, a biodiesel yield of 95.0% was obtained under the optimal conditions of 65 °C reaction temperature, alcohol/oil molar ratio of 9:1, and catalyst amount of 3.0% (w/w).

Saeedi et al. [72] prepared KNa/ZIF-8 from Na-zeolite imidazolate framework doped with potassium under hydrothermal conditions and used it for soybean oil transesterification. The experimental findings showed very good catalytic activity and stability of KNa/ZIF-8, owing to the high amount of strong and medium basic sites, the uniformity of the elemental composition, and the high surface area (about 1195 m<sup>2</sup>/g). Over a period of 3.5 h and with a methanol/oil molar ratio of 10:1, the soybean oil conversion to biodiesel was above 98%.

The incorporation of cerium (Ce) on HUSY zeolite has been reported to decrease the acid site on both micropore and outside surface area of the zeolite catalyst, increasing the reusability. Borges et al. [74] synthesized Ce/HUSY by calcination of NH<sub>4</sub>USY and impregnation with Ce(NO<sub>3</sub>)<sub>3</sub> solution. Before using, the catalyst was activated via calcination for 4 h at 573 K. The catalytic activities of HUSY and Ce/HUSY zeolite catalysts were examined in biodiesel synthesis from soybean oil transesterification with ethanol at 473 K after 24 h. The obtained results showed that the Ce doping on the HUSY zeolite surface improved the activity and stability of the catalyst in transesterification of soybean oil. After the third cycle, Ce/HUSY showed 99.5% of conversion, compared to 96.4% conversion of HUSY.

Triolein is a major triglyceride composed of oleic acid carboxylic groups, which is mainly found in vegetable oils and animal fats. The structure of triolein with a glycerol backbone comprising three ester linked oleic acid molecules is shown in Figure 3.

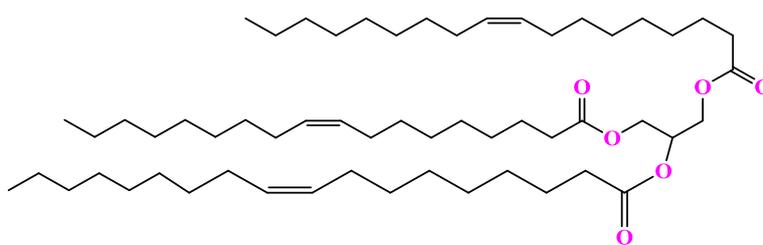


Figure 3. The structure of triolein.

In a study, Wang et al. [75] reported biodiesel synthesis by transesterification of triolein in the presence of  $\beta$ -zeolite as a recyclable and efficient catalyst. The obtained results showed that zeolite materials with a high Si/Al ratio treated with a dilute solution of sodium hydroxide were effective catalysts. Under microwave irradiation, triolein was efficiently converted to biodiesel and glycerol in methanol at 110 °C during 1 h. The catalytic performance was related to the Na cations absorbed at the surface of the zeolite along with its basic sites favoring the preparation of the active sodium methoxide intermediate. The catalyst could be recycled and then reused without significant loss of catalytic activity [75]. In another study, biodiesel was prepared from transesterification of triolein with methanol in presence of zeolite LTA-kaolin catalysts as an effective and reusable catalysts [76]. Under optimal reaction conditions of 146 min reaction time, a methanol/triolein mass ratio of 36.6, 62.9 °C reaction temperature, and a catalyst loading of 2 wt %, the conversion of triolein to biodiesel was 92.8% [76].

Impregnation of lanthanum (La) as an active metal phase to ZSM-5 catalyst, presents bifunctional attributes to ZSM-5, showing both acid and basic sites. In a study by Feyzi et al. [79], the promoted K-La nanocatalysts supported on ZSM-5 zeolite were synthesized via incipient wetness impregnation procedure. It was found that K-La/ZSM-5 nanocatalyst has high basic sites and catalytic activity for biodiesel preparation from soybean oil transesterification. Results showed that the supported catalyst containing 7 wt % of La and 1 wt % of K is an optimal catalyst. Under the optimal operational conditions of a methanol/oil molar ratio of 12:1, 60 °C reaction temperature, and mechanical stirring at 500 rpm for 3 h, the biodiesel yield was 90%. In another study by Feyzi et al. [78], the activities of strontium (Sr) nanocatalysts supported on the ZSM-5 zeolite, Sr/ZSM-5, were investigated in biodiesel synthesis from transesterification of sunflower oil with methanol.

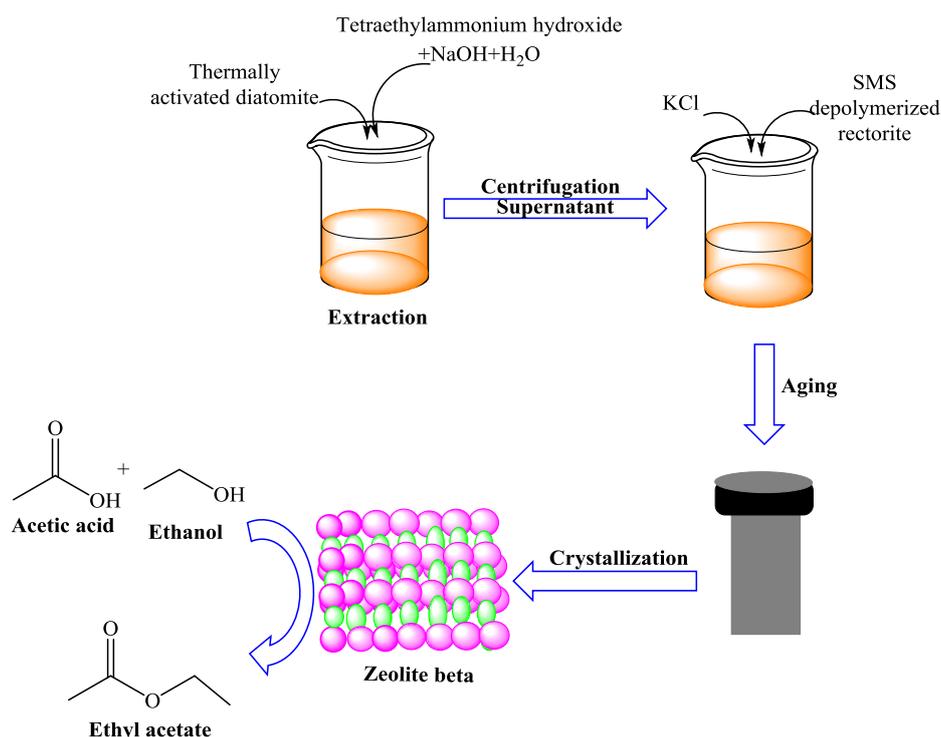
In a study by Du et al. [80], NaY zeolite-supported La<sub>2</sub>O<sub>3</sub> catalysts were synthesized by a physical mixing procedure for the synthesis of castor oil biodiesel. The synthesized catalyst exhibited excellent crushing strength and reusability, which are necessary for industrial applications. Under the optimized conditions of a reaction temperature of 70 °C, an ethanol/oil molar ratio of 15:1, and a catalyst concentration of 10 wt %, the yield of biodiesel was 84% after 50 min.

Brito et al. [81] reported the production of biodiesel from transesterification of waste cooking oil with methanol by several Y-type zeolites with various Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O contents; however, the zeolites were found to give poor efficiency. Optimal reaction conditions were found with zeolite Y530 at 466 °C, a methanol/oil molar ratio of 6:1, and at ~12 min residence time, and with zeolite Y756 within a reaction time of ~22 min at 476 °C and the same feed mixture ratio.

Volli et al. [82] synthesized crystalline zeolites X and A, by alkali fusion followed by hydrothermal crystallization of coal fly ash. The reaction parameters were adjusted to achieve highly crystalline zeolite catalyst based on cation exchange capacity (CEC) and degree of crystallinity. The effect of acid treatment, CEC, temperature of calcination, and Si/Al ratio on zeolites were also investigated. Single-phase pure and highly crystalline zeolite were achieved at a reaction time of 1 h, 550 °C, fly ash/NaOH ratio of 1:1.2, hydrothermal time of 12 h, and hydrothermal temperature of 110 °C. The zeolite developed (AZ-KX) when ion-exchanged with potassium was utilized for biodiesel production from mustard oil transesterification with methanol. It was observed that after 7 h, 5 wt % catalyst concentration, alcohol/oil molar ratio of 12:1, and 65 °C reaction temperature, the conversion of mustard oil to biodiesel was about 84.6%. Rezayan et al. [83] synthesized magnetic mesoporous nanocrystalline KOH/ZSM-5-Fe<sub>3</sub>O<sub>4</sub> and investigated its catalytic activity in biodiesel synthesis via transesterification of canola oil. The effects of reaction time, alcohol-to-oil molar ratio, and catalyst amount parameters were evaluated by Box–Behnken procedure. Under optimal reaction conditions of 65 °C reaction temperature, alcohol/oil molar ratio of 12.3, 3.26 h reaction time, and 9.03% catalyst loading, the yield of biodiesel was 93.65%. After completion of the transesterification reaction, the magnetic catalyst was separated by applying a magnetic field and recycled five times without obvious reduction in catalytic efficiency. Moreover, a kinetics study was performed, which showed that the process obeys the behavior of pseudo-first-order reactions with a frequency factor of  $2.15 \times 10^{17} \text{ min}^{-1}$  and an activation energy of 122.7 kJ mol<sup>-1</sup> [83].

### 3. Zeolite-Catalyzed Production of Acetate, Benzoate, and Phthalate Esters

Zeolites also have a significant role in the production of other important compounds containing ester functional moiety. Ethyl acetate is one of the most significant chemical products and widely used as a solvent for ink, adhesive agent, synthetic resin, and so on [86]. Yue et al. [87] synthesized β-zeolite by employing a thermally activated silicon-rich diatomite, and submolten salt (SMS) depolymerized aluminum-rich rectorite as the starting materials. The synthesized pure-phase β-zeolite containing Brønsted acid sites showed great catalytic activity in the ethyl acetate formation from acetic acid esterification with ethanol (Figure 4).



**Figure 4.** Schematic diagram of preparation of  $\beta$ -zeolite and its application in the synthesis of ethyl acetate via acetic acid esterification with ethanol [87].

Adoor et al. [88] synthesized aluminum (Al)-rich  $\beta$ -zeolite incorporated in sodium alginate pervaporation (PV) membranes and used it in the PV dehydration of acetic acid with ethanol at 30–60 °C. The hydrophilic nature of the Al-rich  $\beta$ -zeolite, along with suitable interaction with the polymer matrix and a molecular sieving effect was observed to be responsible for the relative increase in PV dehydration.

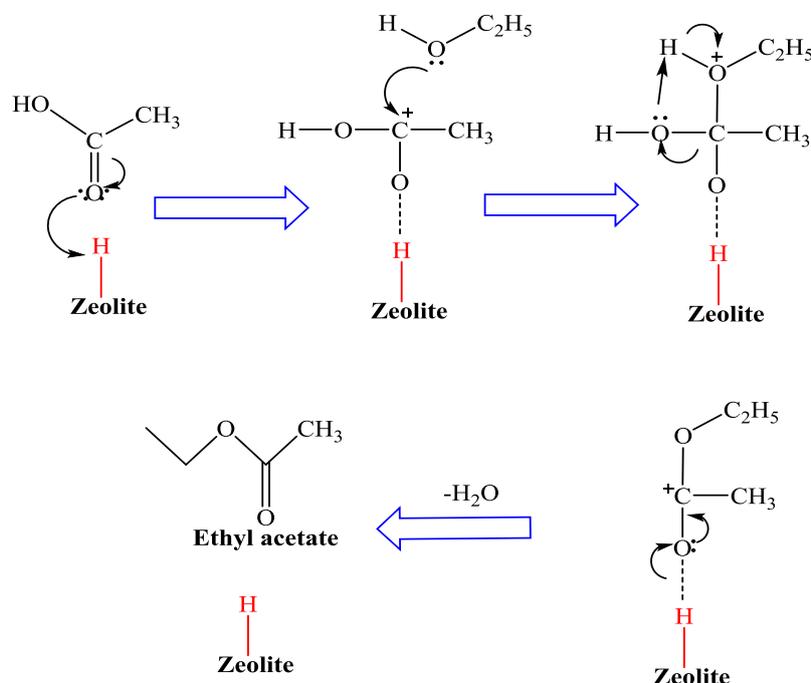
Iglesia et al. [89] synthesized ethyl acetate from acetic acid esterification with ethanol by using zeolite membrane reactors (zeolite A and MOR) with Amberlyst<sup>TM</sup> 15 as the catalyst. Both membranes used were capable to shift the equilibrium reaction owing to product removal within the reaction. MOR membranes exhibited a high resistance to acidic reaction conditions, with high conversions maintained at 90%, with very high separation factors of  $H_2O/HAc$  and  $H_2O/EtOH$  during 5 days of the experiment. In the case of zeolite A, conversion decreased considerably, owing to the instability of the zeolite A membrane in the acidic reaction medium.

In another study, ethyl acetate was prepared by continuous vapor permeation (VP) membrane reactor from acetic acid esterification with ethanol (Figure 5) [90]. The reaction was performed at atmospheric temperature by various types of zeolite membrane. It was found that H-MOR zeolite was the most efficient catalyst, and both H-MOR and chabazite zeolites had good stability over the long-term esterification reaction [90].

In interesting studies by Tanaka et al. [91,92], zeolite T membranes were applied for lactic or acetic acid esterification with ethanol in a batch reactor. The membranes showed high resistance, even being submerged in the acidic environment, and were capable of selectively removing the generated water, thus exceeding the equilibrium limit. In such a way, during an 8 h reaction period, about 100% conversion was reached.

Acetic acid esterification with butyl alcohol is commercially significant, as the product butyl acetate is broadly utilized as a solvent in the preparation of various synthetic products (artificial leather, nitrocellulose, print inks, synthetic resins, adhesives, agricultural chemicals, paint, butyl glycol, butyl acrylate, etc.) and is a flavoring agent for pharmaceuticals and foods [93,94]. In a study by Han et al. [95], the microwave-assisted hydrothermal procedure was applied for the synthesis

of high-performance a- and b-oriented zeolite T membrane. The membranes were applied in the pervaporation-assisted acetic acid esterification with n-butyl alcohol. Zeolite T membranes could efficiently eliminate water from the reaction mixtures and increase the acetic acid conversion without the loss of products or reactants [95].

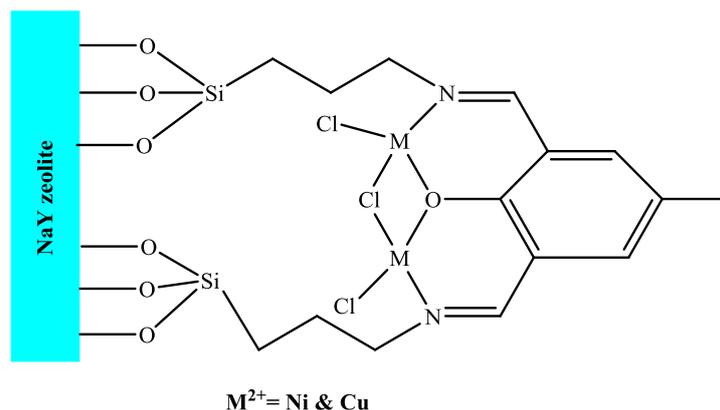


**Figure 5.** Vapor phase acetic acid esterification with ethanol. The adsorbed acetic acid on the zeolite catalyst forms a chemical linkage with the ethanol, followed by intramolecular dehydration to generate the water and ethylacetate [90].

Chen et al. [96] synthesized butyl acetate from the acetic acid esterification with n-butanol using NaY zeolite molecular sieve-supported organophosphonic acid. In order to optimize the reaction conditions, the effects of some parameters, including alcohol-to-acid molar ratio and the amount of utilized catalyst, were investigated. The final conversion was about 96.55%. In addition, the quantum chemistry and kinetics of the reaction were also investigated, and the relevant amounts of the activation energy, protonation energy, Mulliken charge distribution, and pre-exponential factor were obtained. Li et al. [97] synthesized a series of modified beta zeolite by calcining mechanically-mixed oxalic acid-leached  $\beta$  zeolite with various amounts of aluminum fluoride ( $\text{AlF}_3$ ). The texture, structure features, and acidity of the zeolitic catalysts was adjusted by varying the amount of  $\text{AlF}_3$  used. The prepared modified  $\beta$  zeolites were then used as catalysts for acetic acid esterification with sec-butanol. The modified catalyst with a favorable amount of  $\text{AlF}_3$  showed much higher selectivity compared to oxalic acid-leached H-beta zeolite.

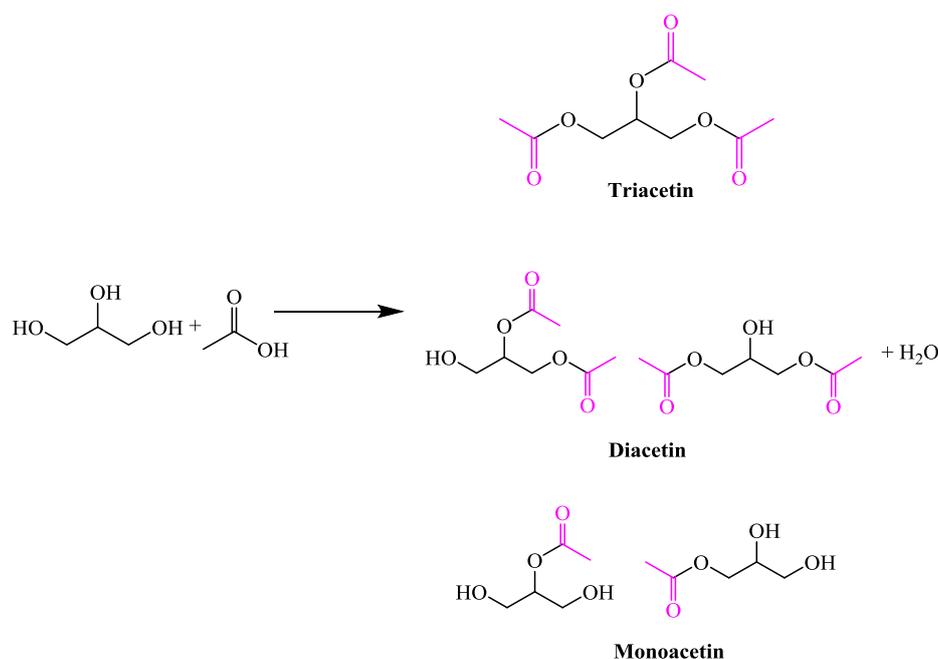
Propyl and isoamyl acetate esters are two of the most significant esters, which have been widely used in various industries and many commercial purposes [98,99]. Li et al. [100] investigated the acetic acid esterification with n-propanol in the presence of the catalyst of ion-exchange resin coupled with NaY zeolite membranes under VP conditions. It was found that the catalyst loading, the initial molar ratio of acid to alcohol, and the temperature of reaction had a considerable influence on the product yield and the permeate flux. The final conversion of the reaction improved from 78.2% to 98.6% for the esterification coupled with VP at a 2:1 molar ratio of alcohol to acid and at 373 k in 420 min [100]. Xue et al. [101] investigated the application of ZSM-5 zeolite membrane in acetic acid esterification with isopentanol by pervaporation. The results showed that under optimal reaction conditions, the isoamyl acetate yield was 98.39% [101].

Zendehdel et al. [102] investigated the utilization of NaY zeolite functionalized by 2,6-diformyl-4-methylphenol (DFP) complexes (Figure 6), for the esterification of different alcohols with acetic acid as a heterogeneous organic catalyst. The obtained results showed that the fixation of Schiff base complexes on the surface of NaY-zeolite, could increase the catalytic performance of the zeolite catalyst. The NaY zeolite supports the Schiff base complexes with available Na ions on the zeolite Y matrix, which gives NaY-NH<sub>2</sub> a strong basic character even without organic bases. Therefore, the fixation of Schiff base complexes over the surface of NaY-zeolite could increase the catalyst performance towards the esterification reactions. The esterification was performed in 2 h at 70 °C with 50 mg, and the maximum conversion of acetic acid was found to be 90% [102].



**Figure 6.** Schematic pattern of immobilization of 2,6-diformyl-4-methylphenol (DFP) complexes [102].

The esterification of glycerol with acetic acid is one of the promising approaches for glycerol utilization and the principal products obtained by this reaction are triacetin, diacetin, and monoacetin, which have many industrial usages (Figure 7). The products like triacetin have various usages, going from cosmetics to fuel additives. Monoacetin and diacetin also have important applications, especially in cryogenics and the production of biodegradable polyesters [103].



**Figure 7.** Glycerol esterification with acetic acid.

In a study, Ferreira et al. [104] presented the glycerol esterification with acetic acid using dodecamolybdophosphoric acid encaged in the USY zeolite catalyst. The ester products were triacetin, diacetin, and monoacetin. A higher loading of the heteropolyacid amount would suppress the catalytic efficiency owing to a decrease in the microporous volume surface area that lead to internal diffusion limitation [104]. Liu et al. [105] synthesized an H-ZSM-5/MCM-41 molecular sieve zeolite catalysts with well-defined micro/mesoporous features. The prepared catalysts showed high activity for selective formation of triacetin, via glycerol esterification with acetic acid. The triacetin selectivity was over 91%, and the glycerol conversion was demonstrated to be 100%, which can be related to the synergistic effect regarding appropriate acidic properties, good stability and excellent diffusion efficiency derived from the combined benefits of mesoporous molecular sieve MCM-41 and microporous molecular sieve H-ZSM-5 [105].

In further studies, the application of zeolites in the production of various acetate derivatives was investigated. In a study by Milina et al. [106], the applicability of zeolites for bio-oil upgrading in the liquid-phase esterification between the characteristic bio-oil constituent *o*-cresol and acetic acid was investigated (Figure 8). The proposed method has considerable significance because phenolics are one of the most plentiful components in bio-oil. The utilization of the phenolic materials to esterify the carboxylic acids in bio-oil does not need external alcohols, which has a unique benefit. It was observed that the yield of final product is dependent on the size of the zeolite micropores and reaction temperature. At 453 K, large pore FAU and beta zeolite catalyzed effective ester production with yields up to 25%, while appreciable esterification was only observed at 473 K over medium-pore zeolites such as ferrierite, ZSM-5, and MOR zeolites. Hierarchical ZSM-5 and FAU zeolite catalysts showed considerably increased acid conversion and ester yield over their conventional microporous counterparts, due to better mass transport associated with intra crystalline mesoporous and lower coking, particularly for access-limited ZSM-5. It was found that while this easy post-synthetic modification of commercially accessible zeolites improved the esterification of acetic acid, it also results in lower Brønsted acid site densities and poor recovering activity [106].

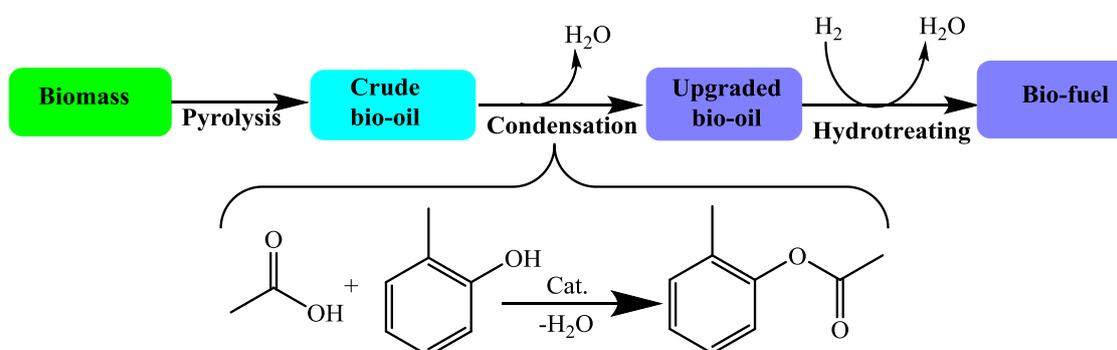
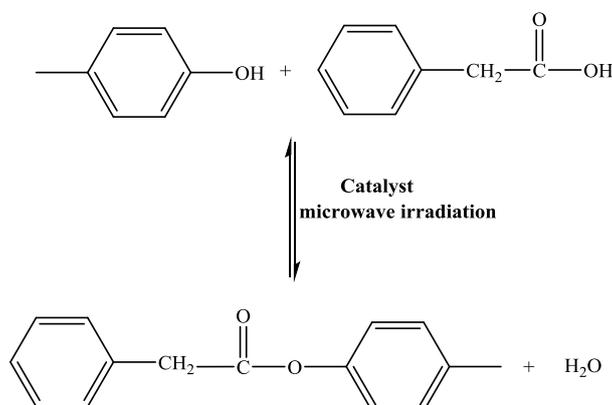


Figure 8. Esterification of acetic acid with *o*-cresol in bio-oil upgrading [106].

*p*-Cresyl phenylacetate is a valuable perfumery ester having narcissus odor with a honey note. It is broadly utilized in beauty care products, blossoms compositions, and jasmine and floral soaps [107]. Shekara et al. [108] reported a green and clean method for the preparation of *p*-cresyl phenylacetate from phenyl acetic acid esterification with *p*-cresol under solvent-free conditions using H- $\beta$  zeolite (Figure 9). It was observed that in comparison with conventional heating, the microwave irradiation can remarkably increase the yield of product in short reaction times. Experimental analysis showed that 100 mg of catalyst, a 2:1 mol ratio of alcohol to acid, a reaction period of 60 min, and a reaction temperature of 463 K, the microwave process with the elimination of water are optimum parameters for high product yield. A nonlinear least-squares method was also utilized to estimate the model parameters. The reaction conditions thus obtained were utilized to evolve simulated values of

conversion. Experimental results had good agreement with the simulated results from the regression coefficient value of 0.987 [108].



**Figure 9.** Schematic representation of synthesis of p-cresyl phenylacetate [108].

Ma et al. [109] reported that zeolites (ZSM-5 and H-Y) are efficient catalysts for the production of phthalates, benzoates, and acetates. It was found that hydrophobicity of zeolites and separation of water from the reaction mixtures are significant parameters for achieving high yields of products. A high yield of acetates was achieved with essentially 100% selectivity. In the case of phthalates, HY was an excellent catalyst and the production of benzoates was slow on the zeolite catalysts [109].

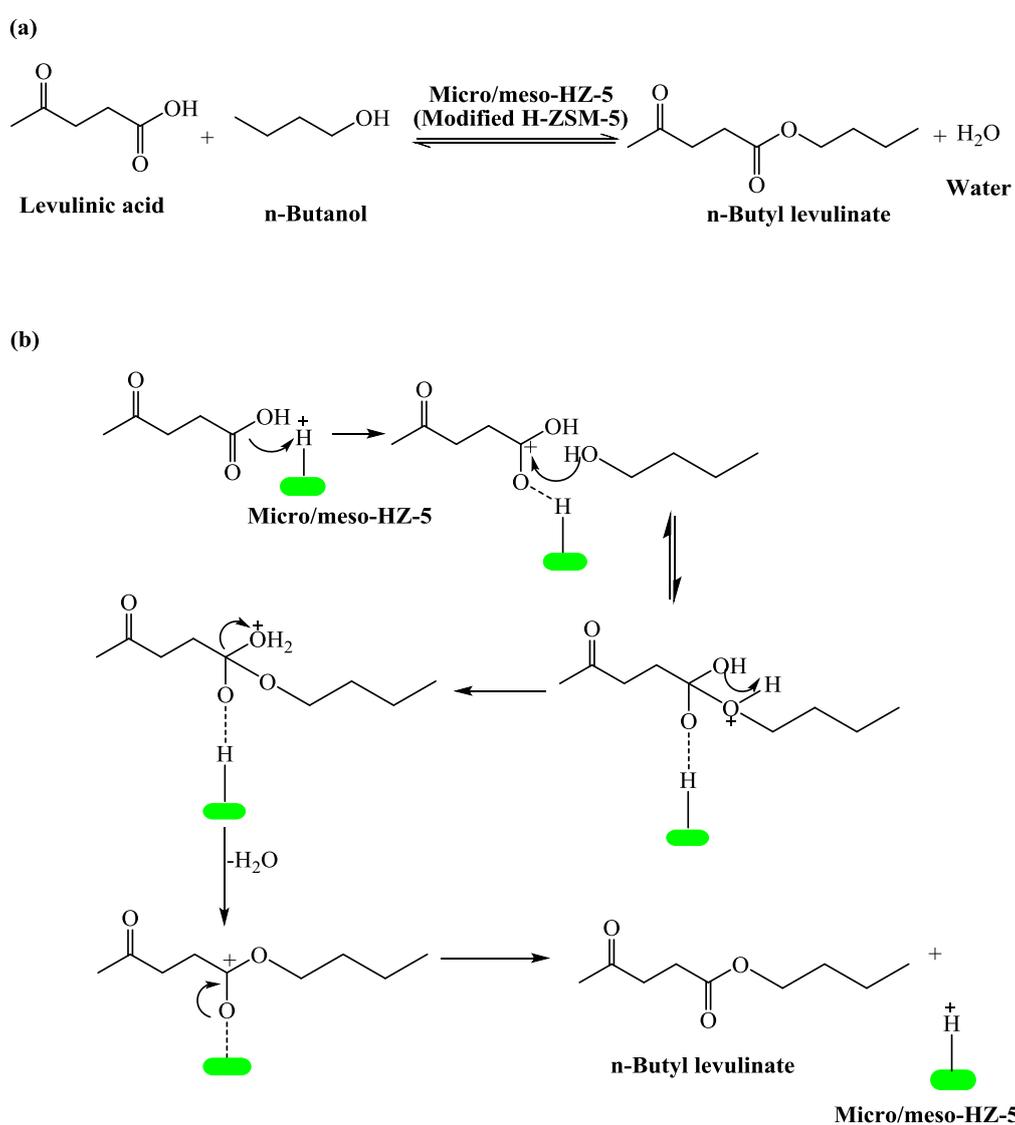
Corma et al. [110] investigated the influence of cation exchange over NaHY zeolite catalysts for the esterification of benzoic and phenylacetic acids with ethanol at a temperature range of 298–383 K. The degree of cation exchange was related to the threshold temperature of the reaction. Acid pre-adsorption showed that protonation of the carbonyl functional moiety of phenylacetic acid was rate-limiting. This was correspondent with the lack of weak Brønsted acid sites needed for ethanol adsorption over the HY-90 and HY-50 zeolites. Dealumination enhanced the surface hydrophobicity, displacing reactively formed H<sub>2</sub>O from the active sites within the esterification reaction and shifting the equilibrium towards the ester. The esterification of p-cresol with phenylacetic acid was also studied, with the strong Brønsted acidic HY-90 and HY-50 zeolites being most active [110].

Kirumakki et al. [111] reported the synthesis of methyl salicylate from esterification of salicylic acid in the presence of dimethyl carbonate (DMC) as a versatile and safe methylating agent over zeolites H-ZSM-5, HY, and H-beta. It was found that zeolites H-ZSM-5 and H-beta were effective catalysts for this reaction, whereas HY was not. The difference in the catalytic performance was related to the acid site strengths and their distribution [111]. In another study, the same research group [112] reported the esterification of benzoic acid and a broad range of substituted benzoic acids in autoclave over H-ZSM-5 and H-β-zeolite using DMC. The reaction was carried out both inside and outside the pores of the zeolites. They observed that the pore structure of the zeolite catalysts comes into play when the molecular diameter of the reactants is higher than the pore size of the zeolites [112]. One year later, the benzyl alcohol esterification with acetic acid over the zeolites HY, HZSM-5, and H-beta was studied by the same research group [113]. The conversion of benzyl alcohol was in the order of H-beta > H-ZSM-5 > HY. The benzyl alcohol conversion was high over H-beta, but due to the formation of dibenzyl ether, the selectivity to benzyl acetate was low. On the other hand, the selectivity to the ester over H-ZSM-5 was 100%, dibenzyl ether not being formed. This was related to shape selectivity owing to the smaller pore size of H-ZSM-5 [113].

#### 4. Production of Other Organic Esters

Levulinic acid esters are valuable chemical compounds that are widely used as solvents, plasticizers and fuel additives [114,115]. In a study, Nandiwale et al. [116] reported the production of n-butyl levulinate, one of the most significant diesel additives, by esterification of levulinic acid with n-butanol in

a closed-batch system over modified H-ZSM-5 (micro/meso-HZ-5) as a suitable heterogeneous catalyst (Figure 10). The obtained results showed that the modified catalyst was very effective, with 98% yield of product and a reusability for six runs. A second-order pseudo-homogeneous model demonstrated that the esterification reaction is carried out in the kinetic regime owing to the high activation energy of  $23.84 \text{ kJ mol}^{-1}$  [116]. Four years later, Morawala et al. [117] synthesized a micro-meso zeolite composite (meso-zeolite) material from alkali-treated microporous ZSM-5 precursor by sol-gel method. In comparison with individual microporous and mesoporous materials, meso-zeolites possess improved physicochemical properties (bimodal porosity, thermal stability, and acidity). The prepared catalyst was utilized as an effective solid acid catalyst in the preparation of *n*-butyl levulinate from esterification of levulinic acid with *n*-butanol. Under the optimized reaction conditions, a higher percent yield of product was achieved in the case of meso-ZSM-5 in comparison with its parent counterparts, which is related to the increased acidity and surface area of the composite material [117].

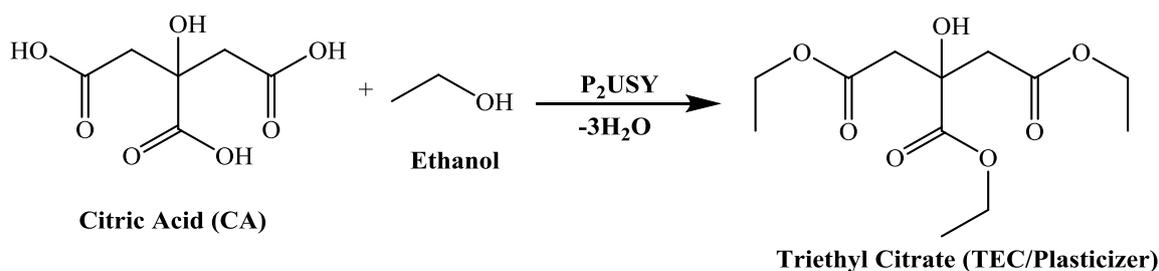


**Figure 10.** (a) Synthesis of *n*-butyl levulinate over micro/meso-HZ-5 and (b) proposed reaction mechanism for the esterification of levulinic acid with *n*-butanol over the micro/meso-HZ-5 catalyst [116].

In another interesting study, *n*-butyl levulinate was synthesized from the esterification reaction of levulinic acid with *n*-butanol using various large and small pore zeolites. This investigation demonstrated that the pore size, porous structure, strength, and acid density are all parameters

affecting the activity of zeolite catalysts in the studied transformation. The preferential order for increasing the yield of the desired product was reported to be: H-beta > H-Y > H-ZSM-5 > H-MOR. The authors concluded that moderate acidity and three-dimensional structures with medium pore sizes, such as that present in  $\beta$ -zeolites, confer these materials a unique combination of attributes, leading to 82% acid conversion with 100% selectivity towards the desired yield [118].

Citrate esters are widely used as nontoxic plasticizers in toys, coatings, medical products, printing ink, cosmetics, and biodegradable polymers food additive [119,120]. Nandiwale et al. [121] reported the synthesis of triethyl citrate (TEC) by citric acid (CA) esterification with ethanol over modified H-ZSM-5 zeolite. Various micro-meso composite samples were synthesized by alkaline treatment of H-ZSM-5 zeolite. Among them, M-HZ-5<sub>0.6</sub> catalyst with 87% crystallinity was found to be an effective catalyst with 96% citric acid conversion, reusability of six cycles, and 64% TEC selectivity [121]. In another study, TEC was synthesized in the presence of parent USY and different percentage phosphonated USY (P-USY) zeolite catalysts in a closed batch reactor (Figure 11). The effects of reaction conditions, such as the reaction temperature (363–403 K), the ratio of catalyst to CA (0.05–0.25), and the ethanol-to-CA molar ratio (5:1–20:1), were investigated in view of maximizing TEC yield and CA conversion. In comparison with USY, P-USY catalysts were observed to be a superior catalyst, which is related to the enhancement of total acidity with phosphonation. Moreover, it was found that P<sub>2</sub>USY (2% phosphorous loaded on USY) was the optimum catalyst with 82% TEC yield and 99% CA conversion [122].



**Figure 11.** Esterification reaction of citric acid with ethanol over P<sub>2</sub>USY zeolite [122].

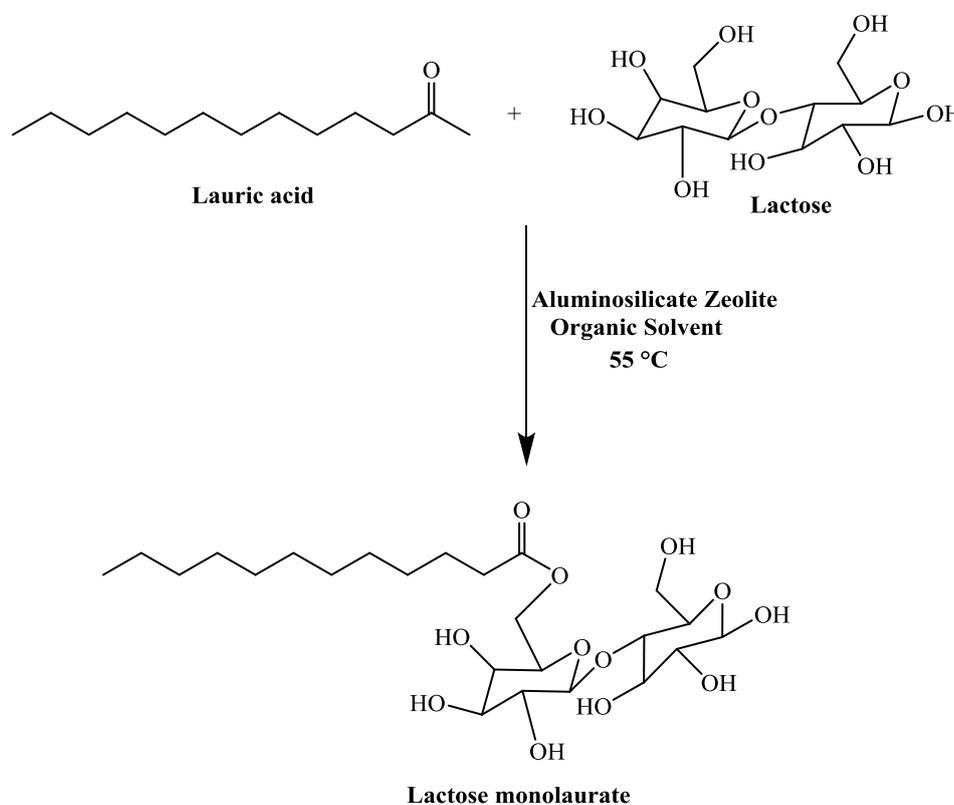
Sorbitol fatty acid esters (SFAEs) are non-ionic surfactants broadly utilized as stabilizers and emulsifiers in the cosmetic and food industries. In a study by Corma et al. [123], SFAEs were synthesized by oleic acid esterification with protected sorbitol in the presence of zeolites as acid catalysts. The goal of this procedure was to control the number of free hydroxyl groups within the reaction to avoid the anhydridization of the sorbitol with formation of dianhydride ethers as well as to decrease the rate of preparation of higher esters (di-, tri-, tetraesters). When the process was performed with a  $\beta$ -zeolite and, especially, with a MOR zeolite catalyst, positive shape selectivity was found such that the ratio of mono- to diesters and the hydroxy value of the final product were higher than when the process was performed under homogeneous catalysts [123].

Jobba oil is a liquid ester composed of long chain monounsaturated fatty acid alcohol. It is widely used in lubricants and cosmetics [124,125]. In an interesting study by Corma and coworkers [126], an analog of jobba oil was prepared via oleic acid esterification with oleic alcohol, in the presence of ultrastable Y zeolites. A maximum in performance was found at 30–40 and ~10 Al/u.c. for USY and HYD dealuminated samples, respectively.

In a study by Zhang et al. [127], kinetic modeling of PV-aided propionic acid esterification with ethanol using T-type zeolite membranes was carried out and then compared with the experimental results obtained, in order to provide further insights on the influence of the operating factors, molar ratio of alcohol to acid, temperature, and the ratio of membrane area to amount of initial reaction liquid. It was found that the propionic acid conversion was about 82.6% without PV but improved in 5 h to 90.8% with PV aid. Moreover, the conversion can be increased to 99.8% at 363 K in 10 h when the molar ratio of acid to ethanol was 1:2 and the ratio of membrane area to the extent of initial reaction liquid was 0.1059 m<sup>2</sup>.kg<sup>-1</sup> [127].

Hasegawa et al. [128] investigated the activity of CHA-type zeolite membrane in the adipic acid esterification with isopropyl alcohol in the presence of  $H_2SO_4$  as catalyst. The yield of product was around 98% with dehydration by the membrane, and 56% without the membrane [128]. The catalytic efficiency of  $\beta$ -zeolite can be increased by dealumination via steam and acid treatments. Srivastava et al. [129] investigated the optimization of catalytic efficiency of  $\beta$ -zeolite by controlled dealumination by either utilizing tartaric or oxalic acid solution of various pH values or steaming up to 500 °C. Acid and structural properties of dealuminated  $\beta$ -zeolite samples were investigated by different methods and their catalytic performance was evaluated in the acylation reaction of naphthalene and 2-methoxynaphthalene with acetic anhydride and in the hexanoic acid esterification with benzyl alcohol.

Sugar-based biosurfactants are healthier and safer alternatives to synthetic surfactants particularly for utilization in the food industry. In a study by Enayati et al. [130], biosurfactants were prepared in various organic solvents from lauric acid esterification with lactose in presence of aluminosilicate zeolite as a commercial industrial catalyst without using lipase or other enzymes (Figure 12). Conversions of 92% were achieved for pure lactose at a 1:2 molar ratio with fatty acid, 46% for the 1:1 ratio, and 37.7% for raw lactose for a 1:2 ratio at 55 °C during 10 days [130].



**Figure 12.** Esterification of lauric acid with lactose over aluminosilicate zeolite [130].

## 5. Conclusions and Perspectives

Zeolites and related silica-based materials (including a broad spectrum of mesoporous and microporous solids with ordered pore structure) show the largest influence on industrial processes, technology, and science in the field of catalysis and materials. Zeolites can provide significant and efficient advantages for many important organic transformations owing to their particular characteristics, including porosity, mechanical resistance, selectivity, appropriate shape, and high adsorption power. In this review, the application of zeolites in the production of some important compounds containing ester functional moiety have been discussed and reviewed. Various zeolites have been applied as highly effective catalysts for practical replacement of the current traditional homogenous catalysts. In most cases, the modified (i.e., by metals and/or introducing meso/macroporosity) zeolite

catalysts could be synthesized with short reaction times by applying commercially available starting materials. The zeolites have adaptability with different reaction parameters such as microwave condition, aqueous media, various organic solvents, and high temperature. Thus, regarding to these various advantages, they can be considered as a good candidate for various industrial applications, including important esterification or transesterification processes utilizing biomass- and lipid-based waste streams. However, there are several challenges that require attention and debate. For instance, this technology requires some improvement in the field of cost optimization and membrane (methods, reproducibility, and materials). Therefore, further studies should be undertaken in order to develop zeolite catalysts with a good performance in industrial processes.

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