

# Heterogeneous Catalysts for Biodiesel Production

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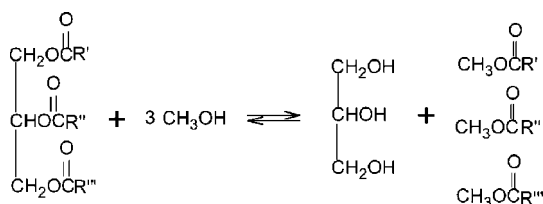
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The production of biodiesel is greatly increasing due to its environmental benefits. However, production costs are still rather high, compared to petroleum-based diesel fuel. The introduction of a solid heterogeneous catalyst in biodiesel production could reduce its price, becoming competitive with diesel also from a financial point of view. Therefore, great research efforts have been underway recently to find the right catalysts. This paper will be concerned with reviewing acid and basic heterogeneous catalyst performances for biodiesel production, examining both scientific and patent literature.

## Introduction

Nowadays, biodiesel (a mixture of fatty acid methyl esters, FAMES) has become very attractive as a biofuel because of its environmental benefits—it has less air pollutants per net energy than diesel and is nontoxic and biodegradable—and because it is produced from renewable sources with high energetic efficiency: biodiesel yields from an estimated 90%<sup>1</sup> to 40%<sup>2</sup> more energy than the energy invested in producing it.

Most biodiesel is produced today by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline catalyst (NaOH, NaOMe):<sup>3–5</sup> The reaction is



normally performed at 60–80 °C. The glycerol and FAME are separated by settling after catalyst neutralization. The crude glycerol and biodiesel obtained are then purified.

However, production costs are still rather high, compared to petroleum-based diesel fuel.<sup>3</sup> There are two main factors that affect the cost of biodiesel: the cost of raw materials and the cost of processing.<sup>3</sup>

Processing costs could be reduced through simplified operations and eliminating waste streams.<sup>6–9</sup> A solution to this

problem could be transesterification in supercritical methanol without using any catalyst.<sup>6,7</sup> As a matter of fact, in this case, the reaction is very fast (less than 5 min) and the absence of catalyst decreases downstream purification costs.<sup>6,7</sup> Even if some production plants use this technology in Europe,<sup>6</sup> the reaction requires very high temperatures (350–400 °C) and pressures (100–250 bar) and thus high capital costs.<sup>6,7</sup>

The use of heterogeneous catalysts could be an attractive solution.<sup>8,9</sup> As a matter of fact, heterogeneous catalysts can be separated more easily from reaction products and the reaction conditions could be less drastic than the methanol supercritical process.

In 2006 a 160 000 t/y commercial plant started up using a heterogeneous catalyst.<sup>8</sup> The plant is based on the Hesterfip-H technology developed by the Institut Français du Pétrole (IFP).<sup>8,9</sup>

The catalyst employed in the Hesterfip-H technology is a mixed oxide of zinc and aluminum.<sup>9</sup> The Hesterfip-H technology operates at 200–250 °C but does not require catalyst recovery and aqueous biodiesel treatment steps: the purification steps of products are therefore much more simplified and very high yields of methyl esters—close to theoretical values—are obtained.<sup>6,9</sup> Glycerol is directly produced with high purity levels (at least 98%) and is free from any salt contaminants.<sup>9</sup> This aspect is very important from the economical point of view because it reduces the cost of obtaining high-grade glycerol, thus increasing the profitability of the process.

Moreover, in order to lower the costs and make biodiesel competitive with petroleum-based diesel, less-expensive feedstocks such as waste fats or nonedible type oils, could be used.<sup>3–7,10</sup> However homogeneous alkaline catalysts in the transesterification of such fats and oils cannot directly be used due to the presence of large amounts of free fatty acids (FFAs);<sup>3–5</sup> for the use of these catalysts, the FFA concentration should be less than 0.5% (w/w) to avoid the formation of high

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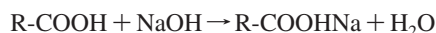
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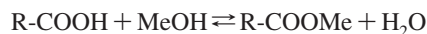
soap concentrations as a consequence of the reaction of FFAs with the basic catalyst:



The soap causes downstream processing problems in product separation because of emulsion formation.<sup>3,6</sup>

Several methods have been proposed to solve these problems,<sup>11</sup> but the most useful seem to be the following:<sup>5,10,12–15</sup>

(a) use of enzymes. A Lypase enzyme catalyzes both transesterification of triglycerides and esterification of FFA



in one step.<sup>9,11–13</sup>

(b) use of acid catalysts. Acid catalyst can also promote esterification and transesterification.<sup>5,10,15</sup>

(c) pre-esterification method. FFAs are first esterified to FAMES using an acid catalyst, and then, transesterification is performed, as usual, by using an alkaline catalyst.<sup>5,10</sup>

Enzyme-based transesterification is carried out at moderate temperatures with high yields, but this method cannot be used in industry today due to high enzyme costs, and the problems related to its deactivation caused by feed impurities.<sup>10,12–14</sup> The enzyme can be immobilized on a support to obtain a heterogeneous catalyst, but again, the use will only be possible if the enzyme costs are reduced—as in the case of enzyme use in detergents, dairy products, textile, and leather processing.<sup>12</sup> However, the use of enzymes is not explored in this review which will be devoted to the use of heterogeneous acid and basic catalysts. More information on the use of enzymes in biodiesel production can be found in recent papers.<sup>10,12–14</sup>

Methods b and c seem to be more attractive.

Concerning method b—use of an acid catalyst for both esterification and transesterification reactions—Zhang et al.<sup>16,17</sup> recently showed, by a technological assessment of different continuous processes, that the homogeneous  $\text{H}_2\text{SO}_4$ -catalyzed process using waste oil is technically feasible and less complex than a two-step process (pre-esterification with homogeneous acid catalyst and alkali-catalyzed steps). However, this process gives rise to problems linked with the corrosive action of the liquid acid catalyst and to the high quantity of byproduct obtained.<sup>5,15</sup> Basu and Norris<sup>18</sup> and more recently Di Serio et al.<sup>15</sup> and Siano et al.<sup>19</sup> showed the possibility to perform triglyceride (TG) transesterification and FFA esterification in a single step, using low concentrations of Lewis acid homogeneous catalysts (carboxylic acid of particular metals). However, this process also gives rise to problems linked with the need to remove catalysts from products by downstream purification.<sup>15</sup> A solid acid catalyst could eliminate these problems.<sup>5,8</sup>

The homogeneous acid-catalyzed pre-esterification of FFA—method c—is a common practice in reducing FFA levels in high FFA feedstock, before performing the base-catalyzed transesterification.<sup>4,5,10</sup> The main drawback of the pre-esterification method c consists again in the necessity to remove the homogeneous acid catalyst from the oil after pre-esterification. So for improving the process, the solution is again the use of a heterogeneous esterification catalyst.<sup>5</sup>

From the above discussion, it is clear that the introduction of a solid catalyst in biodiesel production could reduce its price, so biodiesel could become competitive with diesel also from an economic point of view. Therefore, great research efforts have been underway recently to find the right catalysts.

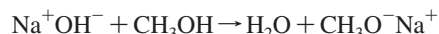
Several general reviews on biofuels and biodiesel production have been published:<sup>3–7,10</sup> one concerns both homogeneous and heterogeneous acid catalysts.<sup>5</sup> In the second part of a general review on biodiesel production, Lotero et al.<sup>20</sup> also included an in-depth review on heterogeneous catalysts used in transesterification reactions.

Together with the scientific and patent literature concerning biodiesel production, in some cases, we have also considered results reported on the transesterification or esterification of model molecules like triacetin or acetic acid to explain the reaction mechanisms and catalytic behavior of heterogeneous catalysts. However, it must be pointed out that in some cases the data obtained with model molecules cannot be used to predict the behavior of oils/fats and fatty acids because the polar and steric effects of the alpha-substituent group can greatly influence the reactivity.<sup>21</sup>

## Heterogeneous Catalysts

**Reaction Mechanisms: A General Overview.** Heterogeneous acid and basic catalysts could be classified as Brønsted or Lewis catalysts, though in many cases both types of sites could be present and it is not easy to evaluate the relative importance of the two types of sites in the reaction. A detailed description of some reaction mechanisms can be found in the paper of Lotero et al.<sup>20</sup> Here for brevity's sake, we will report only a general overview on reaction mechanisms of the different catalyst types.

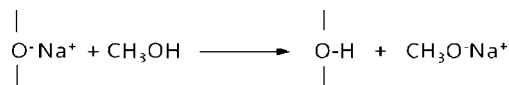
When homogeneous Brønsted basic catalysts, i.e., NaOH, KOH,  $\text{Na}_2\text{CO}_3$ , were mixed with alcohol, the actual catalyst is formed. This is the alkoxide group:



which attacks the carbonyl carbon atom of the triglyceride molecule.<sup>3,20</sup>

Often an alkoxide ( $\text{NaOCH}_3$ ,  $\text{KOCH}_3$ ) is directly used as catalyst.

A similar mechanism is operative in the case of a heterogeneous basic Brønsted catalyst such as basic zeolite:<sup>20</sup> Also in



this case, the formed catalytic specie is a homogeneous alkoxide.

In the case of heterogeneous basic Brønsted catalyst such as resin with quaternary ammonium functionality ( $\text{QN}^+\text{OH}^-$ ), the positive counterions (organic ammonium groups), being bonded

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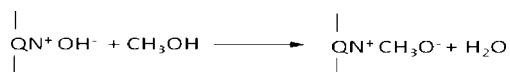
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**Table 1.** Oil = Soybean, 8 g; Methanol/Oil Molar Ratio = 12:1<sup>26</sup>

catalyst	initial FFA conc (% wt)	reaction temp (°C)	reaction time (min)	cat (mol)	FAME yield (%)	final FFA conc (% wt)
uncatalyzed		180	40		2	
uncatalyzed	20.5	180	60		22	10.7
Pb(Ac) <sub>2</sub>		180	40	5.47 10 <sup>-5</sup>	92	
<i>p</i> -toluenesulfonic acid		180	40	5.35 10 <sup>-5</sup>	29	
Pb(Ac) <sub>2</sub>	20.5	180	60	5.38 10 <sup>-5</sup>	57	6.8
<i>p</i> -toluenesulfonic acid	20.5	180	60	6.40 10 <sup>-5</sup>	48	1.1

directly to the support surface, electronically retain the catalytic anions on the solid surface: The reaction occurs between



methanol adsorbed on the cation and ester from the liquid (Eley–Rideal mechanism).

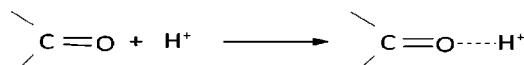
The formation of alkoxide groups is also a fundamental step for heterogeneous basic Lewis catalyst. For example, in the case of ethylacetate transesterification, catalyzed by MgO, the reaction occurs between the methanol molecules adsorbed on a magnesium oxide free basic sites and the ethyl acetate molecules



from the liquid phase (Eley–Rideal mechanism).<sup>22,23</sup> Both homogeneous Brønsted (H<sub>2</sub>SO<sub>4</sub>, *p*-toluenesulfonic acid<sup>5,20</sup>) and Lewis (metal acetate,<sup>10,15,18–20</sup> metal complexes<sup>24</sup>) acid catalysts have been used in biodiesel synthesis, and both catalyze either transesterification and esterification reactions.<sup>25</sup> Brønsted acid catalysts are active mainly in esterification reactions while Lewis acid catalysts are more active in transesterification reactions (see, for example, Table 1<sup>26</sup>).

Table 1 reports data of runs performed by using a series of small stainless steel vial reactors. Both the reagents (oil (FFA = 0.2% w/w) = 2.0 g, methanol = 0.88 g) and a specified amount of the catalyst were introduced into each reactor. All the reactors were then heated in a ventilated oven. The temperature of the oven was initially fixed at 50 °C for 14 min and then increased at a rate of 20 °C/min until the reaction temperature was reached, where the samples were kept for the fixed reaction time. At the end of the reaction, the temperature was quenched by putting the vials in a cold bath. Experimental runs were also performed by adding oleic acid to the reaction mixture. Oleic acid has been chosen as a test molecule for simulating the behavior of FFA. The lead acetate (Lewis acid) has greater transesterification activity than *p*-toluenesulfonic (Brønsted acid) acid, while on the contrary *p*-toluenesulfonic acid is more active than lead acetate in esterification reactions. The lower yield obtained with lead acetate using an acid oil is justified by the strong deactivation of the Lewis catalyst due to the water formed in the esterification reaction.<sup>15</sup>

In both homogeneous and heterogeneous Brønsted acid catalysis, the mechanism pathways proceed through the protonation of the carbonyl group: increasing its electrophi-

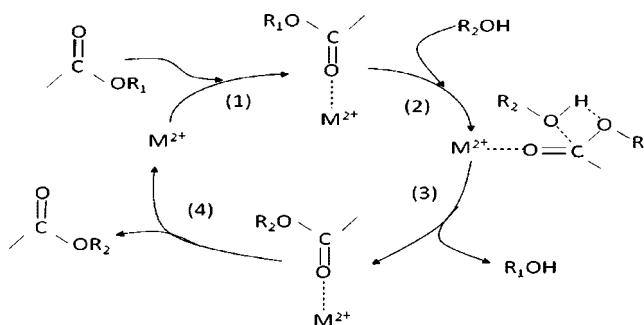


licity and rendering it more susceptible to alcohol nucleophilic attack.<sup>21</sup>

In the case of Nafion supported on silica (Nafion SAC-13), Lopez et al.<sup>27</sup> proposed a mechanistic pathway for triacetin transesterification—a mechanism similar to that accepted for a homogeneous Brønsted acid catalyst. They found activation energy and reaction orders similar to the ones showed by sulfuric acid.<sup>27</sup>

The reaction mechanism in esterification reactions promoted by solid acid Brønsted catalysts is also similar to the homogeneous one.<sup>28</sup> Liu et al.,<sup>28</sup> found that Nafion supported on silica has comparable turnover frequencies (TOF) to H<sub>2</sub>SO<sub>4</sub> and a similar reaction mechanism in esterification of the liquid acetic acid with methanol. The reaction occurs via a single-site Eley–Rideal mechanism involving a nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol as the rate-determining step.<sup>28</sup>

The formation of a more electrophilic species also occurs with homogeneous and heterogeneous Lewis acid catalysts as the first step in the reaction mechanism.<sup>15,29–31</sup> In this case, the



rate-determining step depends on the Lewis catalyst's acid strength. After the Lewis complex formation (stage 1), the alcohol nucleophilic bonding (stage 2), and the new ester formation (stage 3), the new ester desorbs from the Lewis site (stage 4) and the cycle is repeated. If the strength of acidic sites is too high, the desorption of the product is not favored,

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**Table 2. FAME Yield Using CaO as Catalyst at 15 min of Reaction Time**

ref	oil	reaction temp (°C)	methanol/oil molar ratio	cat conc (% w/w)	FAME yield (%)
32	rapeseed	methanol reflux	4.5:1	0.8	10
33	sunflower	192	41.1:1	3.0	50

determining a slow reaction rate.<sup>15,29–31</sup> This mechanism was confirmed for both homogeneous<sup>15,29,30</sup> and heterogeneous catalysts<sup>31</sup> by the observation that an optimal range of strength for Lewis acidic sites exists and that very strong Lewis acidic catalysts are less active in transesterification reactions.<sup>15,29–31</sup>

**Basic Catalysts.** Gryglewicz<sup>32</sup> investigated the possibility of using alkaline-earth metal hydroxides, oxides, and alkoxides to catalyze the transesterification of rapeseed oil at methanol reflux temperature. He found that sodium hydroxide was the most active, barium hydroxide was slightly less active, and that calcium methoxide showed medium activity. The reaction rate was lowest when CaO powder was used as catalyst while magnesium oxide and calcium hydroxide showed no catalytic activity.<sup>32</sup> The high activity of barium hydroxide is due to its higher solubility in methanol with respect to other compounds. The order of reactivity  $\text{Ca}(\text{OH})_2 < \text{CaO} < \text{Ca}(\text{CH}_3\text{O})_2$  agrees with the Lewis basic theory: the methoxides of alkaline-earth metals are more basic than their oxides which are more basic than their hydroxides.<sup>32</sup> Table 2 reports some data about CaO catalytic performance.<sup>32,33</sup> The yield of biodiesel using CaO as a catalyst increases with increase in the temperature and methanol/oil molar ratio, especially in the case of the methanol supercritical state<sup>33,34</sup>—see Table 3 entries 1–3. In the methanol supercritical state, good performances were obtained also with  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ <sup>34</sup>—see Table 3 entries 4–6.

Increases in CaO performances can be obtained using nanocrystalline calcium oxides.<sup>35</sup> The nanocrystalline calcium oxides (crystal size = 20 nm; specific surface area = 90 m<sup>2</sup>/g) give 100% conversion of soybean oil at room temperature after 12 h while the conversion obtained with commercial CaO (crystal size = 43 nm; specific surface area = 1 m<sup>2</sup>/g) is only 2%.<sup>35</sup>

López Granados et al.<sup>36</sup> studied the activity of activated CaO as a catalyst in the production of biodiesel by the transesterification of triglycerides with methanol. The active surface sites of CaO are poisoned by the atmospheric H<sub>2</sub>O and CO<sub>2</sub>. The catalytic activity of CaO can be improved if CaO is subjected to an activation treatment at high temperature ( $\geq 700$  °C) before the reaction—to remove the main poisoning species (the carbonate groups) from the surface—and if the contact with atmospheric air is prevented after this treatment.<sup>36</sup> Even if the catalyst can be reused for several runs without significant deactivation, dissolution of CaO does occur. The catalytic reaction is the result of the contribution of both heterogeneous and homogeneous catalysis for the formation of leached active species and further investigation is necessary to quantify this aspect.<sup>36</sup>

The transesterification rate can be increased using microwave energy,<sup>37,38</sup> because the microwave energy selectively energizes the catalyst's interaction with the reactants.<sup>38</sup>

Table 4 (entries 1 and 2) reports results obtained with  $\text{Ca}(\text{OH})_2$ <sup>38</sup> and  $\text{Ba}(\text{OH})_2$ .<sup>37</sup> The data of Mazzochia et al.<sup>37</sup> confirm that  $\text{Ba}(\text{OH})_2$  is not a completely heterogeneous catalyst. As a matter of fact, when the product obtained after reaction is not washed several times with distilled water, the resulting FAME and glycerine contain ca. 0.06% and 0.25% of barium, respectively.

Good results in transesterification of soybean oil were obtained using ZnO loaded  $\text{Sr}(\text{NO}_3)_2$  followed by calcination at 873 K for 5 h.<sup>39</sup> When the transesterification reaction was carried out at reflux of methanol (65 °C), with a 12:1 molar ratio of methanol to soybean oil and a catalyst amount of 5 wt %, the conversion of soybean oil was 94.7%.<sup>39</sup> The SrO derived from thermal decomposition of  $\text{Sr}(\text{NO}_3)_2$  at high calcination temperatures is probably the main catalytically active specie.<sup>39</sup> However, the used catalyst was significantly deactivated and could not be directly reused for transesterification.<sup>39</sup> Yang and Xie<sup>39</sup> explained the deactivation by the deposition of reactants and products on the active sites and/or by a transformation of the active sites and their interactions during the reaction. However, the leaching of SrO was not examined; notwithstanding, its high solubility in the reaction environment<sup>36</sup> is known.

Sodium silicate catalyzes the transesterification of oils with high rates at moderate temperatures (60–120 °C)—even if no data on catalyst reusability was reported.<sup>38</sup> Also in this case, the use of microwave energy and high methanol/oil ratio greatly increases the performances—see Table 4 entries 3 and 4.

Corma et al.,<sup>40</sup> in a patent mainly devoted to the transesterification of triglycerides with glycerol to prepare monoglycerides, claimed the possibility to use calcined hydrotalcites and magnesium oxides in promoting the transesterification of triglycerides with monoalcohols, even if no examples or experimental data for this reaction are reported in the mentioned patent.

Leclercq et al.<sup>41</sup> tested the use of commercial  $\text{MgO}/\text{Al}_2\text{O}_3$  hydrotalcites and MgO (300 m<sup>2</sup>/g) in the transesterification of rapeseed oil. They found that MgO was more active than hydrotalcite—see Tables 5 and 6 entry 1. On the other hand, Cantrell et al.,<sup>42</sup> successfully used calcined hydrotalcites in promoting the transesterification of glycerol tributyrates with methanol at 60 °C. The rate increases steadily with Mg content, and the most active catalyst  $\text{Al}/(\text{Mg} + \text{Al}) = 0.25$  was 10 times more active than MgO.<sup>42</sup> Xie et al.,<sup>43</sup> for soybean oil transesterification at methanol reflux, found that the most active calcined hydrotalcite has again an atomic ratio  $\text{Al}/(\text{Mg} + \text{Al}) = 0.25$ —see Table 6 entries 2–4—and that a higher active solid is obtained by calcining it at 500 °C; see Table 6 entries 3, 5, and 6. Di Serio et al.<sup>44</sup> and Siano et al.<sup>45</sup> showed the possibility

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**Table 3. FAME Yield Using Basic Catalysts in Methanol Supercritical Conditions**

entry	ref	oil	catalyst	reaction temp (°C)	methanol/oil molar ratio	react time (min)	cat conc (% w/w)	FAME yield (%)
1	33	sunflower	CaO	252	6.0:1	15	3.0	65
2	33	sunflower	CaO	252	41.1:1	15	3.0	99
3	34	soybean	CaO	300	39.3:1	10	0.58	97
4	34	soybean	CaCO <sub>3</sub>	250	39.3:1	10	1.14	87
5	34	soybean	CaCO <sub>3</sub>	300	39.3:1	10	0.67	99
6	34	soybean	Ca(OH) <sub>2</sub>	300	39.4:1	10	0.68	98
7	34	soybean	MgO	300	39.6:1	10	1.29	91

**Table 4. Comparison of the Transesterification Tests of Oil with Methyl Alcohol Carried out under Microwave Irradiation**

entry	ref	oil	catalyst	reaction temp (°C)	methanol/oil molar ratio	reaction time (min)	cat conc (% w/w)	FAME yield (%)
1	37	rapeseed	Ba(OH) <sub>2</sub>	methanol reflux	9:1	15	0.5	97–98
2	38	soybean	Ca(OH) <sub>2</sub>	100	6:1	20	2.0	81
3	38	castor oil	sodium silicate	120	6:1	10	1.5	70
4	38	castor oil	sodium silicate	120	19:1	10	1.5	100

**Table 5. FAME Yield Using MgO as Catalyst**

entry	ref	oil	surface area	reaction temp (°C)	methanol/triglycerides molar ratio	reaction time (h)	cat conc (% w/w)	FAME yield (%)
1	41	rapeseed	300	methanol reflux	75:1	22	10	64
2	44	soybean	36	180	12:1	1	5.0	72
3	44	soybean	229	180	12:1	1	5.0	90

**Table 6. FAME Yield Using Calcined MgO/Al<sub>2</sub>O<sub>3</sub> as Catalyst**

entry	ref	oil	Al/(Mg + Al)	surface area	calcination temp (°C)	reaction temp (°C)	methanol/oilmolar ratio	reaction time (h)	cat conc (% w/w)	FAME yield (%)
1	41	rapeseed	0.30	160	450	methanol reflux	275:1	22	10	34
2	43	soybean	0.28		500	methanol reflux	15:1	9	7.5	28
3	43	soybean	0.25		500	methanol reflux	15:1	9	7.5	66
4	43	soybean	0.22		500	methanol reflux	15:1	9	7.5	50
5	43	soybean	0.25		450	methanol reflux	15:1	9	7.5	45
6	43	soybean	0.25		600	methanol reflux	15:1	9	7.5	57
7	44	soybean	0.25	144	500	180	12:1	1	5.0	92

to use calcined hydrotalcites and MgO for industrial biodiesel production at moderately high temperature. High yields of methyl esters were obtained in 1 h of reaction time at 180–200 °C—see Tables 5 (entries 2–3) and 6 (entry 7).

At least four different types of basic sites have been identified on the surface of MgO and calcined hydrotalcite catalysts.<sup>44</sup> The strongest basic sites (superbasic) promote the transesterification reaction also at very low temperatures (100 °C), while the basic sites of medium strength require higher temperatures to promote the same reaction.<sup>44</sup> The experimental data reported show a correlation not only with the catalyst basicity but also with its structural texture.<sup>44</sup> However, the structural texture of the catalysts examined is dependent on both the precursor and the preparation method.<sup>44,46</sup>

MgO catalyst used to promote transesterification strongly increases the reaction rate in supercritical conditions,<sup>34</sup> as can be seen in Table 3 entry 7.

As vegetable oils, animal fats, and alcohols usually contain water,<sup>44</sup> the influence of the presence of water on MgO and calcined hydrotalcite performances have also been investigated.<sup>44,45</sup> Some runs have been performed at 180 °C in the presence of high water concentration (10 000 ppm).<sup>44</sup> The results show that the activity of both magnesium oxide and calcined hydrotalcite is not affected by the presence of an excess of water.<sup>44</sup> This

last finding is relevant for industrial purposes, because the possibility to operate in the presence moisture reduces the raw material pretreatment costs and opens the possibility to use unrefined bioethanol.

However, Oku et al.<sup>47</sup> showed that in a run performed at 150 °C with 60 g of triolein, 20 g of methanol, and 2.5 g of Mg/Al hydrotalcite after 24 h of reaction, a FAME yield of 77 was produced, but a very high concentration of Mg and Al ions were detected in the products (Mg 17 800 ppm; Al 6900 ppm). So, the problems of catalyst leaching need more in-depth study to confirm the possibility of using MgO and related hydrotalcites as industrial catalysts.

Corma et al.<sup>48</sup> have reported that calcined Li/Al hydrotalcites are more active in glycerolysis of fatty acid methyl esters than the Mg/Al material (or MgO) due to their higher Lewis basicity. Starting from this observation, Shumaker et al.<sup>49</sup> studied the transesterification of soybean oil to fatty acid methyl esters using a calcined Li/Al layered double hydroxide catalyst. It was found that, at the reflux temperature of methanol, near-quantitative conversion of the soybean oil was achieved at low catalyst loadings (2–3 wt %) and short reaction times (~2 h).<sup>49</sup> Catalyst recycling runs showed that the catalyst maintained a high level

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**Table 7. FAME Yield Using Sodium or Potassium Supported Catalyst at Methanol Reflux**

entry	ref	oil	catalyst	CH <sub>3</sub> OH/oil molar ratio	solvent	react time (h)	cat (% w/w)	FAME yield (%)
1	50	soybean	Na/NaOH/ Al <sub>2</sub> O <sub>3</sub>	9:1	THF	1	2.0	75
2	51	triolein	K <sub>2</sub> CO <sub>3</sub> / Al <sub>2</sub> O <sub>3</sub>	25:1		1	6.0	94
3	52	soybean	KNO <sub>3</sub> / Al <sub>2</sub> O <sub>3</sub>	15:1		4	6.5	64
5	53	soybean	KF/ZnO	15:1		4	3.0	80

**Table 8. FAME Yield Using Basic Zeolites and Soybean Oil**

entry	ref	catalyst	methanol/oil molar ratio	temp (°C)	reaction time (h)	cat conc (% w/w)	FAME yield (%)
1	54	NaX	6:1	60	24	10	6.8
2	55	NaX	10:1	65	8	3	~2
3	54	KX	6:1	60	24	10	10.3
4	54	CsX	6:1	60	24	10	7.3
5	54	NaO <sub>x</sub> /NaX	6:1	60	24	10	82
6	55	KOH(4 wt %)/NaX	10:1	65	8	3	28
7	55	KOH(10 wt %)/NaX	10:1	65	8	3	85
8	54	ETS-10	6:1	100	3	10	92

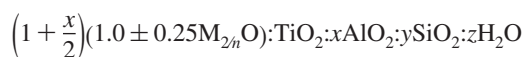
of activity over 3 cycles, although analyses indicate that a small amount of lithium was leached from the catalyst.<sup>49</sup>

The dissolved lithium appears to possess little, if any, catalytic activity; however, fixed-bed experiments over much longer operating times will be required to determine whether lithium leaching is a serious issue for the long-term stability of the catalyst.<sup>49</sup>

Several supported basic catalysts have also been reported in the literature—sodium<sup>50</sup> or potassium<sup>51–53</sup> loaded on a support (normally alumina) using several precursors and treated at high calcination temperatures (500–600 °C). The catalysts showed good activities at low temperatures (see, for example, Table 7), but no data were reported about possible leaching and their stability. K<sub>2</sub>CO<sub>3</sub>, supported on MgO, and Al<sub>2</sub>O<sub>3</sub> both provide good results in rapeseed oil transesterification with methanol at 60–63 °C, but K<sub>2</sub>CO<sub>3</sub> leached into the solution.<sup>20</sup>

Sodium zeolites (NaX<sup>54,55</sup>) gives low performances in transesterification also when exchanged with potassium and cesium (KX, CsX<sup>41,54</sup>)—see Table 8 entries 1–4. The NaO<sub>x</sub>/NaX catalysts—obtained by loading sodium acetate or sodium azide on NaX then calcining at 500 °C—showed higher activity<sup>54</sup> (see Table 8 entry 5). An increase in activity was obtained also by loading KOH<sup>55</sup>—see Table 8 entries 6 and 7. The loaded NaX zeolites, however, suffer from leaching: a reused catalyst, for example, showed a decline in yield from 85.2% to 48.7%.<sup>55</sup>

Basic ETS-10 or ETS-4 (microporous titanium-containing zeolite<sup>56,57</sup>) of general formula



are active catalysts in soybean transesterification with methanol<sup>54,58</sup> also at low temperatures and with low methanol/oil molar

ratios<sup>54</sup>—see Table 8 entry 8. The higher activity of ETS-10 than NaX is due to more basic sites being present on ETS-10 with respect to NaX.<sup>54</sup> The acid form of ETS-10 (1.99% Na, 2.28% K) exhibited very low activity—<1% of triacetin conversion after 8 h reaction time with 2 wt % of catalyst at 60 °C—compared to the basic form (6.14% Na, 5.22% K), ~99% of triacetin conversion in the same reaction conditions.<sup>59</sup> The reused basic ETS-10 showed a significant drop in activity (from 90% to 28% triacetin conversion in the fifth cycle) due to the leaching of sodium and potassium.<sup>59</sup>

Guanidines and biguanides are strong bases as their basicities are in the range of common inorganic bases such as alkaline hydroxides and carbonates.<sup>60–63</sup> Gelbard and Vielfaure-Joly<sup>63</sup> obtained a polystyrene supported biguanide which was strongly active in oil transesterification obtaining more than 94% yield in biodiesel in 60 min at 70 °C with a methanol/oil/catalyst molar ratio of 6.9/1/0.02 and at atmospheric pressure. Moreover, the efficiency of this catalyst remains unaffected for more than ten cycles after which alterations begin to appear. This loss in activity is due to the partial leaching of biguanide units.<sup>63</sup>

Anionic resin (PA308, PA306, PA306s, HPA25 supplied by Mitsubishi Chemical Co.) showed good activity in triolein transesterification with ethanol at 60–100 °C.<sup>64</sup> Resin activity diminishes during the run because of the formation of oleic acid. This is due to a direct ion-exchange reaction of the resin's hydroxyl ion with the oleic acid group of triolein, diolein, or monoolein.<sup>64</sup> However, the resin can easily be regenerated by a three-step regeneration process.<sup>64</sup> A transesterification reaction was carried out using an expanded-bed reactor packed with the most active resin (PA306s).<sup>64</sup> The reactor system allowed the continuous production of ethyl oleate, achieving an ethyl oleate equilibrium concentration with a residence time around 60 min at 50 °C.<sup>64</sup>

Polymeric resin (A26 supplied by Rohm & Hass) with organic quaternary ammonium functional groups (QN<sup>+</sup>OH<sup>−</sup>) is active in triacetin transesterification with methanol at 60 °C. Here, 90%

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triacetin conversion was achieved after 240 min with 1.67 wt % of A26 relative to the total mass of the reaction mixture (6:1 methanol/triacetin molar ratio).<sup>65</sup> Moreover, A26 is also a stable catalyst giving the same results even after four reaction cycles.<sup>65</sup> The stability of the resin is most probably due to the methanol washing of resin before its use. This washing is able to exchange most  $\text{OH}^-$  groups in the resin with  $\text{MeO}^-$  groups that cannot give rise to the formation of carboxylic acid, thereby precluding catalyst deactivation.<sup>65</sup>

**Acid Catalysts.** Since acid catalysts can simultaneously carry out esterification of FFAs and transesterification of TGs, they could help in processing low-cost, low-quality feedstocks (generally high in FFAs), thereby lowering overall production costs.<sup>5,10,20</sup>

Few research studies dealing with transesterification reactions catalyzed by solid acids have been reported in the literature, while many papers are devoted to esterification reactions with solid acid catalysts (mainly acid resins). These papers were reviewed recently by Lotero et al.<sup>5,20</sup>

Lopez et al.<sup>59</sup> tested the activity of several acid catalysts in the transesterification of triacetin with methanol at 60 °C, obtaining the following order of reactivity:  $\text{H}_2\text{SO}_4 > \text{Amberlyst-15}$  (polystyrenesulfonic acid resin)  $> \text{sulfated zirconia (SZ)} > \text{Nafion NR50}$  (perfluorinated alkanes sulfonic acid resin)  $> \text{tungstated zirconia (WZ)} > \text{supported phosphoric acid (SPA)} > \text{zeolite } \beta > \text{ETS-10 (H)}$ . The low activity of zeolite  $\beta$  is due to diffusion limitations in the zeolite pores of the bulky triacetin molecule—the only active sites are those on the external surface. In the case of zeolite ETS-10 (H), the activity is lower because the strength of acid sites is low.

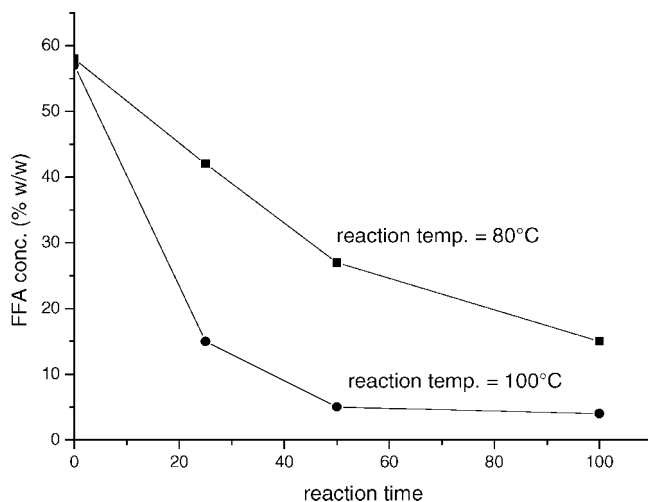
Amberlyst-15, SZ, and WZ exhibited decreases in the rates of triacetin conversion of 40%, 67%, and 44%, respectively, after five reaction cycles of 2 h each. Since in Amberlyst-15, SZ, and WZ 92%, 80%, and 95% of the original sulfur values remain after all the reaction cycles, the catalyst deactivation was mainly due to the blockage of the sites by adsorbed intermediates or product species.<sup>59</sup> Nafion NR50 catalytic activity increased after the first reaction cycle because of swelling, and then, it remained quite stable.<sup>59</sup>

Even though with tungstated zirconia (WZ) the contribution from Lewis acidity could be present, López et al.<sup>25</sup> showed that using a calcination temperature of 750 °C Brønsted acid sites were seen to be solely responsible for catalyzing the triacetin transesterification at 60 °C.

At low temperatures, the activity of acid catalysts in transesterification is normally quite low, and to obtain a sufficient reaction rate, it is necessary to increase the reaction temperature ( $>170$  °C). The sulfonic acid resins cannot be used at these temperatures, and so, they could be used essentially in esterification reactions where they perform well at low temperatures too ( $<120$  °C)<sup>66–69</sup> (see, for example, Figure 1).

The acid resins are stable in these reaction conditions. In fact, Pasiás et al.<sup>69</sup> showed that Purolite CT-275 is not deactivated after the first batch and steady catalyst performances were obtained in the next seven batches. After each batch, the catalyst was not washed after separation but was left to drain overnight.<sup>69</sup>

Esterification is an equilibrium reaction, and the maximum conversion obtainable is regulated by the chemical equilibrium. With few reaction steps an almost-complete conversion of FFAs can be achieved after stripping the methanol and the water



**Figure 1.** Esterification of acid oils over polystyrene sulfonic acid resins (Relite CFS):<sup>68</sup> catalyst conc = 2.6% w/w; methanol/FFA molar ratio = 8.6–8.3.

formed, and feeding fresh methanol.<sup>69</sup> A reactive distillation column has been proposed in order to eliminate the need for batch-stage operations.<sup>67</sup>

Propylsulfonic acid-functionalized mesoporous silica showed good performance in FFA esterification in flotation beef tallow. Starting from an initial concentration of 7% FFA, a final FFA concentration of 0.3 was achieved within 60 min at 120 °C with a methanol/FFA weight ratio of 20:1 and an FFA/catalyst weight ratio of 9:1.<sup>70</sup> The same catalyst reused in a successive run loses its original activity because of the adsorption of organic polar impurities present in beef tallow.<sup>70</sup> This problem can be eliminated by the prepurification of flotation beef tallow with adsorption of the impurities onto activated silica (TriSyl 300).<sup>70</sup>

Stable and very active esterification catalysts can be prepared by the incomplete carbonization of natural products such as sugar, starch, or cellulose and their successive sulfonation.<sup>71,72</sup> The “sugar catalyst” has higher activity in oleic acid esterification than other acid solids most likely because of the higher concentration of acid sites on the surface.<sup>72</sup> It was found that the sugar catalyst still retained a high proportion (93%) of its original catalytic activity in the methyl oleate formation reaction, even after more than 50 cycles of successive reuse.<sup>72</sup> This catalyst gives also higher yields (90% after 15 h at 80 °C) in the biodiesel production from waste oils (FFA conc = 27.8% w/w) than other acid solids.<sup>72</sup>

The sugar catalyst is a promising catalyst because it is thermally stable until 275 °C,<sup>72</sup> so it could be used at higher temperatures than sulfonic acid resins (120 °C) with a probable strong reduction in the reaction time required to obtain high yields of biodiesel. This must be investigated in greater depth, in particular with regard to the stability of the catalyst in the reaction environment at higher temperatures.

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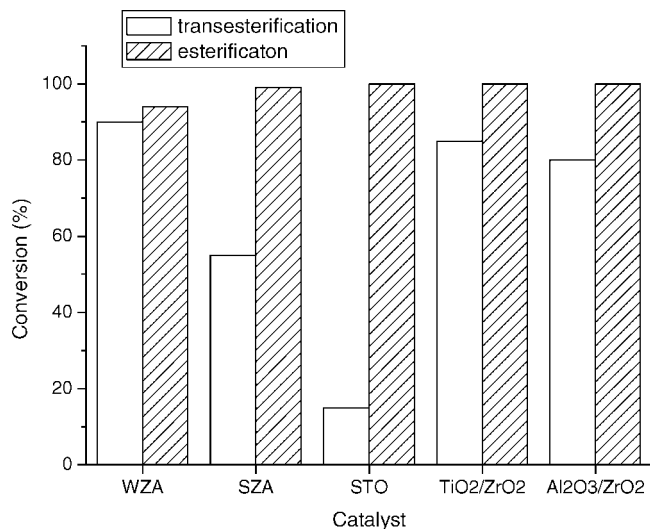
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**Figure 2.** Transesterification of soybean oil and esterification of *n*-octanoic acid with methanol in a flow reactor under atmospheric pressure.<sup>73,74</sup> catalyst = 4 g; (transesterification) flow rate of methanol 4.4 g/h, soybean oil 3 g/h; (esterification) flow rate of methanol 3 g/h; *n*-octanoic acid 3 g/h.

Furuta et al.<sup>73</sup> evaluated tungstated zirconia–alumina (WZA), sulfated zirconia–alumina (SZA), and sulfated tin oxide (STO) in the transesterification of soybean oil with methanol at 200–300 °C and the esterification of *n*-octanoic acid with methanol at 175–200 °C, using a packed-bed reactor. WZA was the most active catalyst in transesterification followed by SZA, while STO is less active (see Figure 2). In esterification, however, the activity order is inverted: STO > SZA > WZA (see Figure 2). In any case, tungstated zirconia–alumina seems to be a promising catalyst because it gives high conversion in transesterification and esterification reactions and is stable under the reaction conditions.<sup>73</sup>

Also TiO<sub>2</sub>/ZrO<sub>2</sub> (11 wt % Ti) and Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> (2.6 wt Al) catalysts showed promising performances in soybean oil transesterification and *n*-octanoic esterification<sup>74</sup> (see Figure 2).

Good results were also obtained by Lacome et al.<sup>75</sup> with catalysts obtained supporting zirconia on alumina (see Table 9). In the transesterification of crude palm kernel oil and crude coconut oil with methanol, Jitputti et al.<sup>76</sup> found the following reaction activity order for the acid catalysts: sulfated zirconia (SZ) ≥ sulfated tin oxide (STO) > ZnO > ZrO<sub>2</sub> (see Figure 3). The higher FFA and water concentration in coconut oil with respect to crude palm kernel oil reduces the activity of all the catalysts (see Figure 3), showing the sensitivity of catalysts to impurities.<sup>76</sup> Moreover investigation of the best catalyst (SZ) indicates that the spent SZ is fully deactivated and cannot be directly reused for reactions. It can, nevertheless, be regenerated by resulfatation and calcination.<sup>76</sup>

Wang et al.<sup>77,78</sup> found that ferric sulfate is a good catalyst in the esterification of FFAs contained in waste cooking oil (acid

value 75.9 mg KOH/g). After methanol evaporation, the ferric sulfate was recovered by filtration. This catalyst after calcinations at 460 °C, to remove the adsorbed organic substance, can be reused giving virtually the same performance as the fresh one.<sup>77,78</sup> However, since ferric sulfate is soluble in methanol (only 90% of the whole catalyst amount is recovered), a small amount of the solid catalyst remains in the oil after methanol distillation. So, it is not clear if ferric sulfate is a homogeneous or heterogeneous catalyst.

The ferric sulfate was also used by Portnoff et al.<sup>38</sup> in the esterification and transesterification of an acid oil (20 wt % oleic acid in soybean oil). The runs were performed using a microwave device, and good performances were obtained in both esterification and transesterification reactions—for example, 100% of oleic acid and 96% of soybean oil were converted after 1 h at 130 °C with 5% w/w of catalyst. No data was reported on the content of iron sulfate in the final product.

Zn acetate is a good catalyst for transesterification reactions,<sup>29,30</sup> and recently, Di Serio et al.<sup>15</sup> found that it can be used to catalyze the esterification and transesterification of oils with high FFA concentrations. One of the first reported attempts to heterogenize the zinc catalyst for oil transesterification is contained in the English patent GB795573<sup>79</sup> which describes the use of a zinc silicate as catalyst in the transesterification of coconut oil at 250–280 °C. However, this catalyst gives rise to a leaching of Zn due to zinc soap formation because of the necessity of using a very high temperature.<sup>80</sup>

ZnO was reported as a catalyst in an oil transesterification performed by Stern et al.<sup>80</sup> in a batch reactor. The ZnO gives good results as can be seen in Table 10.<sup>80</sup> ZnO was also supported on alumina by impregnation of Zn(NO<sub>3</sub>)<sub>2</sub> followed by calcination at 500 °C (cat A = 29% zinc) or mixing alumina gel with ZnO and calcinating the mixture at 600 °C (cat B = 25% zinc).<sup>80</sup> The two zinc alluminates are fairly similar in their performances and are more stable than commercial spherules of ZnO.<sup>80</sup> For example, in runs performed in a packed-bed reactor at 235 °C with 60 min of contact time, 91.4% (cat A) and 94.3% (cat B) of methylester yields were obtained, and for temperatures < 240 °C, a maximum concentration of Zn in the products obtained with the A catalyst was 5 ppm.<sup>80</sup> In the zinc aluminate catalyst, the ghanite phase is present (zinc aluminate spinel defined by formula ZnAl<sub>2</sub>O<sub>4</sub>)—details on the synthesis of the zinc aluminate catalyst are reported in US patent application 2004/0234448 A1.<sup>81</sup> The catalyst is deactivated by water, and to obtain high biodiesel yield (>99%), the water in the reaction environment must be less than 1500 ppm.<sup>82</sup> The catalyst is active in both the esterification and transesterification of acid oil,<sup>83</sup> but no data have been reported on the lifetime of the catalyst. These data are important in identifying whether it is possible to use the zinc aluminate catalyst with acid oil since

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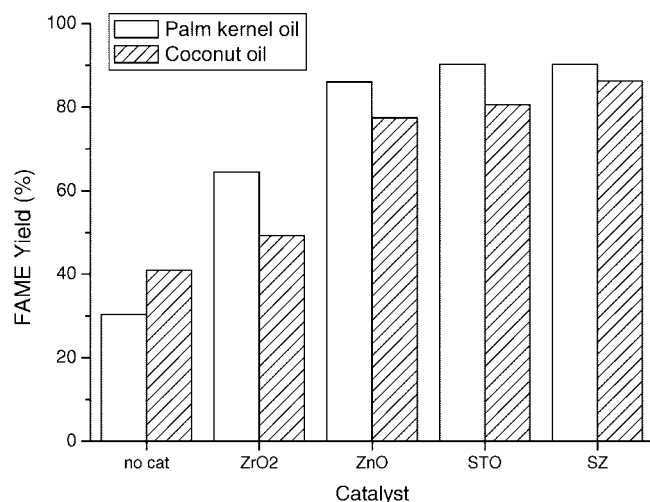
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Table 9. Transesterification of Rapeseed Oil<sup>75a</sup>

run	catalyst	cat comp (% w)	FAME yield (%) 2 h	FAME yield (%) 7 h	elution (ppm)
1	Zr/ Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub> : 14.7	58	90	<1
2	cat used in run 1			90	
3	Ti/ Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub> : 12.5	68	95	<1
4	cat used in run 3			95	
5	Sb/ Al <sub>2</sub> O <sub>3</sub>	Sb: 13.8	86	96	2
6	cat used in run 5			96	

<sup>a</sup> Catalyst = 5 g; methanol = 25 g; oil = 25 g; T = 200 °C.

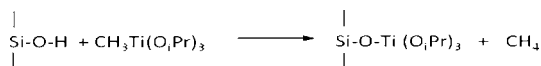


**Figure 3.** Transesterification of crude palm kernel oil (1.05% FFA, moisture content 0.09%) and crude coconut oil (2.25% FFA, moisture content 0.17%);<sup>76</sup> catalyst conc = 3% w/w, methanol/oil molar ratio = 6, T = 200 °C, reaction time = 4 h.

a soap formation was noted in the presence of high FFA concentration.<sup>80</sup>

Li and Xie<sup>84</sup> reported that high yields of biodiesel (96%) can be obtained in the transesterification of soybean oil at methanol reflux temperature after 26 h of reaction using metallic zinc and iodine as the catalytic system. However, no data on the recovery of the catalyst was reported in the paper, and even if the catalytic activity was attributed to Lewis acid sites, no characterization of these sites was carried out.<sup>84</sup>

Titanium alkoxides show good activity as homogeneous catalysts in transesterification reactions,<sup>29,30</sup> and also, the heterogenized titanium alkoxide species are active in the transesterification reaction.<sup>85</sup> This catalyst was obtained by Blandy et al.<sup>85</sup> by grafting CH<sub>3</sub>Ti(O<sub>i</sub>Pr)<sub>3</sub> on silica: However, the catalyst



is strongly deactivated by water and greatly dehydrated reagents are needed.<sup>85</sup>

More stable catalysts with TiO<sub>2</sub>/SiO<sub>2</sub> were proposed for the transesterification of soybean oil.<sup>86,87</sup> These catalysts (G-TiO<sub>2</sub>/SiO<sub>2</sub>) were prepared by grafting different amounts of titanium isopropoxide (Ti(O<sub>i</sub>Pr)<sub>4</sub>) onto the silica surface in a nitrogen atmosphere, followed by steam hydrolysis and calcinations. Depending on titanium loading, different types of titanium

species could be present, ranging from dispersed surface TiO<sub>x</sub> species, both in tetrahedral and octahedral coordination, to small TiO<sub>2</sub> crystallites.<sup>88</sup> The obtained results on G-TiO<sub>2</sub>/SiO<sub>2</sub> catalysts are shown in Figure 4.

The observation that 3–11% w of TiO<sub>2</sub> showed small difference in the activities can be justified considering that we have two different operating effects: (1) decreasing dispersion of TiO<sub>2</sub> with increasing grafted amounts and (2) formation of new sites. The two effects are contrasting, which explains why the activity does not change significantly in the range studied. For an amount of TiO<sub>2</sub> greater than a monolayer, the activity drops with a decrease in dispersion and the consequent disappearance of the Lewis sites of suitable strength. The appearance of new, stronger Lewis sites observed on Fourier transform infrared (FTIR) analysis for the less widely dispersed catalysts has no effect on catalytic activity.<sup>31</sup> The strength of these sites is similar to that found on crystalline (anatase) TiO<sub>2</sub> which showed no catalytic activity in the reaction. These findings are in agreement with the results observed for homogeneous catalysts:<sup>15</sup> an optimal range of strength for Lewis acidic sites exists, and very strong Lewis acidic catalysts are less active in transesterification reactions. The TiO<sub>2</sub>/SiO<sub>2</sub> catalysts are stable in the reaction environment. A catalyst prepared by the impregnation of titanium alkoxide on silica (I-TiO<sub>2</sub>/SiO<sub>2</sub>) and the titanium silicalite TS-1 after runs performed at 200 °C after 24 h of reaction did not leach Ti ions in the products<sup>47</sup> (see Table 11).

The TS-1 catalyst, where the titanium atoms are well dispersed in the crystalline structure, has better performances mainly for the glycerin yield than I-TiO<sub>2</sub>/SiO<sub>2</sub> catalyst (see Table 11). In the case of the I-TiO<sub>2</sub>/SiO<sub>2</sub> catalyst, the preparation method adopted (impregnation) very probably gives rise to not-well-dispersed TiO<sub>x</sub> species which can rise to side reactions of glycerin due to their higher acidity. Acid catalyst such as H-ZMS5 and Mordenite, for example, rise to the double dehydration of the byproduct glycerol to produce acrolein and water at temperatures above 250 °C.<sup>20,89</sup>

Also heterogeneous catalysts prepared by titanium alkoxide impregnation on alumina and successive calcination have been tested.<sup>75</sup> The Ti/Al<sub>2</sub>O<sub>3</sub> catalysts claimed by Lacome et al.<sup>75</sup> have good activity, are stable, and do not give rise to leaching (see Table 9). However, the catalyst prepared supporting Sb on alumina was more active<sup>75</sup> (see Table 9).

The mixed oxides of zinc, titanium, and alumina or mixed oxides of bismuth, titanium, and alumina produce results similar to titanium oxide supported on alumina in runs performed in a fixed bed reactor.<sup>75,90</sup>

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Table 10. Transesterification of Rapeseed Oil over ZnO as Catalyst<sup>80</sup>

oil (g)	methanol (g)	catalyst (g)	temp (°C)	FAME yield (%) 2 h	FAME yield (%) 6 h
120	120		227	57	75.6
120	120	1.2	225–230	88	92.7
120	120	1.2 (reused)	225–230	91.1	94.3
180	60	1.8	170–175	59.4	

Table 11. Transesterification of Triolein<sup>47a</sup>

catalyst	temp (200 °C)	FAME yield (%)	glycerine yield (%)	elution (ppm)
TS1	200	77	53	nd
I-TiO <sub>2</sub> /SiO <sub>2</sub>	200	74	21	nd
HTiNbO <sub>5</sub>	200	80	56	nd
TiVO <sub>4</sub>	150	79	51	nd
FeVO <sub>4</sub>	150	66	20	Fe: nd V: 130
CeVO <sub>4</sub>	150	65	24	Ce: nd V: 250
Co <sub>2</sub> VO <sub>7</sub>	150	43	15	Co: nd V: n.d.
V <sub>2</sub> O <sub>5</sub>	150	88	32	V: 70

<sup>a</sup> Catalyst = 2.5 g; methanol = 20 g; oil = 60 g; reaction time = 24 h.

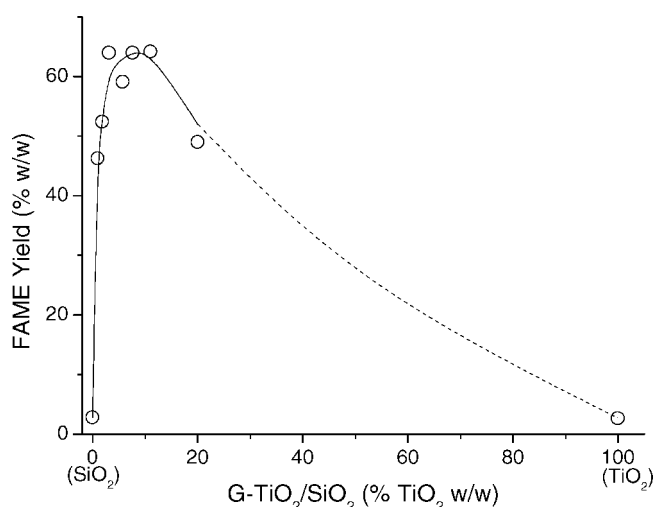


Figure 4. Transesterification of soybean oil over G-TiO<sub>2</sub>/SiO<sub>2</sub> catalysts<sup>87</sup>; catalyst conc. = 5% w/w; methanol/oil molar ratio = 12; *T* = 180 °C; reaction time = 1 h.

The titanium compound of general formula ATi<sub>x</sub>MO<sub>(2x+3)</sub>—wherein A represents a hydrogen atom or an alkaline metal atom, M a niobium atom or a tantalum atom, and *x* is a natural number not greater than 7—have been also filed for oil transesterification.<sup>47</sup> The catalysts obtained are stable, give high glycerol yield (see Table 11) and display good activities: a FAME yield of 91% and glycerol yield of 91% were obtained in a fixed-bed reactor at 200 °C and 35 bar using HTiNbO<sub>3</sub> as catalyst and residence time *W/F* = 1.97 g cat/(g feed h) (methanol/oil molar ratio = 9).<sup>47</sup>

Vanadate metal compounds are stable, active catalysts in oil transesterification with TiVO<sub>4</sub> being the most active (see Table 11).<sup>47</sup> This catalyst is also more active than HTiNbO<sub>3</sub>, giving the same yields with lower residence times: a FAME yield of 90% and glycerol yield of 91% were obtained in a fixed bed reactor at 200 °C and 50 bar using TiVO<sub>4</sub> as the catalyst and residence time *W/F* = 0.89 g cat/(g feed h) (methanol/oil molar ratio = 5.4).<sup>47</sup>

Pure vanadium oxide (V<sub>2</sub>O<sub>5</sub>) is more active in transesterification than TiVO<sub>4</sub> but gives place to very lower glycerol yield<sup>47</sup> (see Table 11).

Catalysts based on vanadyl phosphate (VOPO<sub>4</sub>·2H<sub>2</sub>O), mainly used in hydrocarbon oxidation catalytic reactions but also active in some other reactions involving Brønsted and Lewis

Table 12. Transesterification of Soybean Oil over VOPO<sub>4</sub> Catalyst<sup>a</sup>

ref	run	catalyst	init FFA conc (% w)	FAME yield (%)	final FFA conc (% w)
91	1			8	
92	2		10.0	25	6.5
91	3	fresh		78	
91	4	used in 3		30	
91	5	regenerated		78	
92	6	fresh	10.0	79	2.5

<sup>a</sup> Catalyst conc = 5% w/w; methanol/oil molar ratio = 12; *T* = 180 °C; reaction time = 1 h.

acid sites, such as dehydration, have shown interesting behavior also in vegetable oil transesterification with methanol.<sup>91,92</sup> VOP-based catalysts are very active in the transesterification of vegetable oil with methanol to produce biodiesel despite their low specific surface area (see Table 12 runs 1 and 3).<sup>91</sup> Similar results were obtained with substituted metal vanadyl phosphate ([M(H<sub>2</sub>O)]<sub>x</sub>VO<sub>(1-x)</sub>PO<sub>4</sub>·2H<sub>2</sub>O with M = Al, Ga, Fe, or Cr and *x* = 0.20 or 0.18).<sup>92</sup>

The characterization/reactivity results showed that the activity of the catalysts is strictly correlated to the structural/surface characteristics of the catalysts.<sup>91</sup> In particular, the dehydration of the catalysts, that can be obtained by submitting the VOPO<sub>4</sub>·2H<sub>2</sub>O precursor to calcination treatments at high temperatures (400–500 °C), have a positive effect on the activity. No leaching phenomena were observed. The catalysts have shown a deactivation process strongly affected by the temperature (see Table 12 run 4). It has been shown that deactivation is due to the progressive reduction of the surface vanadium species from V<sup>5+</sup> to V<sup>3+</sup> by methanol. Deactivation is reversible and catalyst activity can easily be restored by calcination in air<sup>91</sup> (see Table 12 run 5). The vanadyl phosphate catalyst can be used also in presence of high FFA concentration being also active in esterification reaction<sup>92</sup> (see Table 12 run 6).

Double-metal cyanide Fe–Zn proved to be promising catalysts resulting active in transesterification of oil<sup>93,94</sup> (see Table 13 runs 1 and 2). These catalysts are Lewis acidic, hydrophobic (at reaction temperatures of about 170 °C), and insoluble. Moreover, they can be used even with oils containing significant amounts of FFA and water, probably due to the hydrophobicity of their surface (see Table 13 runs 3–5). The catalysts are active even in esterification reaction, reducing the concentration of FFA in nonrefined oil or in used oil (see Table 13 runs 3 and 4). However, the activity in esterification reaction gives

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**Table 13. Transesterification over Double-Metal Cyanide Fe–Zn Catalyst<sup>93a</sup>**

run	oil	acid value oil (mg KOH/g)	water (% w/w)	conv (based on glycerine, mol %)	acid value FAME (mg KOH/g)
1	sunflower	0.41		96.5	0.27
2	palm	0.54		98.3	0.27
3	used margarine	5.43		98.0	1.24
4	rubber seed	31.16		97.1	2.11
5	sunflower	0.41	5	93.9	7.31

<sup>a</sup> Catalyst = 3% w/w; methanol/oil molar ratio = 15;  $T = 170\text{ }^{\circ}\text{C}$ ; reaction time = 8 h.

place to the hydrolysis of oil when a high concentration of water is present (see Table 13 run 5).

### Conclusion

Nowadays, biodiesel is produced in great amount and its production continues to grow. The main technology used in the industrial production is based on the transesterification of refined oils with methanol using basic homogeneous catalysts. However, the problems related with this technology (mainly in product purification) have stimulated research in the field of heterogeneous catalysis for biodiesel production. In particular, industry is making great research efforts to find the right catalyst, and today, a plant based on an IFP heterogeneous catalyst is on stream. However, the research has not stopped there because several tasks still need to be done.

One of the most difficult challenges is finding a heterogeneous catalyst which has comparable activity of the IFP catalyst at lower temperatures than the ones used in IFP technology ( $\sim 220\text{--}240\text{ }^{\circ}\text{C}$ <sup>79</sup>). As a matter of fact, at such high temperatures, the process pressure is high (40–60 bar<sup>79</sup>), too and consequently plant construction costs are high. Many

of the catalysts presented above seem to be good candidates for industrial process development, but we must point out that an industrial catalyst must also be resistant to poisoning and to the leaching of active components. Unfortunately, not all of the cited papers included a deep examination of the catalyst stability. Even if the right method to correctly check the resistance to poisoning and/or to leaching is through performing continuous runs in a packed-bed reactor, also runs performed in a well-stirred batch reactor can provide useful preliminary information.<sup>36,49,59</sup>

The above discussion shows that the amount of research in the field of heterogeneous catalysis for biodiesel production has strongly increased in the last years. Even though the best catalysts must have several qualities—i.e., catalyze transesterification and esterification, not be deactivated by water, be stable, not give rise to leaching, be active at low temperature, have high selectivity—positive results will be probably achieved over the next few years if the research efforts will continue at the same rate as today.

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