Shiff base complexes of zinc(II) as catalysts for biodiesel production

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ABSTRACT

New zinc(II) compounds containing functionalized Schiff bases have been prepared and characterized. The complexes catalyze the transesterification of soybean oil in mild conditions, and their activity can be modulated by a fine selection of the anions and/or of the substituents on the ancillary bidentate ligand. The compounds are active in the esterification of fatty acids and could therefore also be used to produce biodiesel from waste oils.

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1. Introduction

Biodiesel (a mixture of Fatty Acid Methyl Esters, FAME) is the second most common biofuel produced in the world and the most common in Europe. The UE Directive 2009/28/EC stated that a mandatory 10% minimum target has to be achieved by all Member States for the share of biofuels in transport petrol and diesel consumption by 2020.

Nowadays the majority of biodiesel is produced by transesterification with methanol of refined edible oils such as rapeseed, sunflower, palm, soybean, etc. However, most of these raw materials do not fulfill the sustainability criteria indicated by the UE Directive 2009/28/EC, and so they shall not be taken into account for measuring compliance with the requirements of this Directive concerning national targets. Instead, the waste vegetable or animal oils widely fulfill the sustainability criteria and so are more convenient from an ecological point of view. Moreover the use of waste oil is also economically of great interest. Currently more than 85% of the cost of biodiesel obtained from edible vegetable oils is the cost of raw materials.

Biodiesel is produced today by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline homogeneous catalyst (NaOH, NaOMe): the reaction is normally performed at 60–80 °C. Glycerol and FAME are separated by settling after catalyst neutralization. The crude glycerol and biodiesel obtained are then purified.

However, homogeneous alkaline catalysts cannot be used directly with waste oils due to the presence of large amounts of free fatty acids (FFA) [1]; in fact, for the use of these catalysts the FFA concentration should be less than 0.5% (w/w) [1]. Several methods have been proposed to solve this problem [2]; one of these solutions is to use either a homogeneous or heterogeneous acid catalyst which can catalyze the esterification of FFA and transesterification of glicerides [1–3].

The use of homogeneous Brønsted acids (mainly H_2SO_4) was proposed, but because their transesterification activity is low, high acid concentrations are necessary which lead to an increase in the waste formation deriving from catalyst neutralization [1]. Several heterogeneous acids were also used (ion-exchange resin, metal oxides, heteropolyacids, etc.) [1–3]. In general these catalysts show good performances in esterification of FFA, but the activity in glycerides transesterification is not satisfactory. Moreover a great number of these catalysts showed a rapid deactivation due to leaching [4,5], fouling of catalytic surface by products/reagents [6] and/or changing of oxidation state of the active species [6,7].

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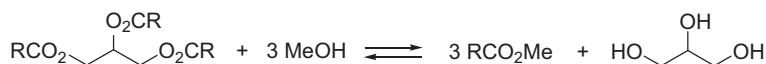
Scheme 1. Transesterification of soybean oil with methanol.

A few years ago it was demonstrated that homogeneous Lewis acid can be used for triglyceride transesterification with methanol [8] and, in particular, that the homogeneous metal carboxylates can be used in biodiesel production from oils with high FFA concentration [9,10].

However, three main drawbacks are linked with the latter class of catalysts: (1) the best transesterification performances was shown by Pb carboxylates salts; (2) the necessity to use high reaction temperature and pressure ($T > 190\,°C$, $P > 20\,bar$); (3) the homogeneity of the catalyst with the consequent problem of purification of the products.

For industrial application, it is obviously necessary to select a safer metal, *e.g.* zinc, which shows significant activity, likely to be improved. For example, it was shown that the activity of metal carboxylates catalysts increases with the carbon numbers of the carboxylate anions [9,11].

In some cases, the use of ligands also increases the catalyst activity. For example, in the same reaction conditions, the FAME yield was 52 or 78 using as catalyst zinc crotonate or zinc crotonate with stoichiometric quantity of quinoline, respectively [11]. Moreover, Schiff base–zinc complexes proved to be good catalysts for ester methanolysis of (*rac*)-1-phenylethanol picolinic acid ester (PEP) [12].

AMP (2-aminomethylpyridine) zinc complexes anchored on a polymer showed a heterogeneous catalytic activity on the transesterification reaction of various substrates by methanol at room temperature [13]. For the latter complexes a strong effect of the anions of the starting zinc salts was observed, too [13].

Clearly, the use of ligands and of different types of anions influences the acidity of the metal center, and, as a consequence, its catalytic activity. However, the acidity should not be the highest possible, as a matter of fact the interactions between the metal atom and the incoming transesterification reagents must not be too strong, because this would slow down the addition-release mechanism of the reagents at the metal atom [2,14–16].

The present work fits into this context, and describes a library of Shiff base complexes of zinc(II) with the general formula reported in Fig. 1.

The ligands differ in the R function, which controls the stereoelectronic properties of the corresponding complexes, while the additional hydroxyl group is potentially useful for anchoring the catalysts on a solid matrix.

Moreover the complexes also differ for the anions X.

The complexes were tested in the transesterification of soybean oil with methanol (Scheme 1), to study the influence on the catalytic activity of the ligands and of the anions.

One of the better catalysts was also tested with oil containing high FFA concentration to check the possibility of using this catalyst in the production of biodiesel from waste oils. In this case also the catalyst was also tested in the esterification of free fatty acids (Scheme 2).

X= Cl, AcO, CF₃CO₂, CF₃SO₃
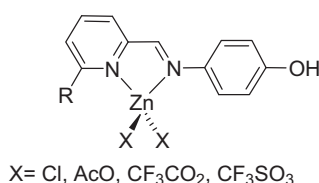
Fig. 1. General formula of synthetised Shiff base complexes of zinc (II).

2. Experimental

2.1. Materials and general methods

All reagents were purchased from Aldrich and used without further purification. THF was distilled from LiAlH₄. The newly synthesised complexes are reported in Table 1. Most of these were synthesised following a general procedure (see Section 2.2.1), while for some of them a specific procedure was adopted. Ligand **1** was described elsewhere [17]. The compounds showed satisfactory zinc elemental analysis, which combined to relative integrations in the NMR spectra unequivocally assign the structure to the complexes. NMR spectra were recorded at 200 MHz (Varian Model Gemini spectrometer) and dmso-d₆ was used as a solvent. The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; br, broad peak.

2.2. Synthetic procedures

2.2.1. General procedure for the synthesis of zinc catalysts

Pyridinecarboxaldehyde (2.00 mmol) and solid ZnX₂ (X = Cl or AcO, 2.00 mmol) were added to a suspension of *p*-aminophenol (0.218 g, 2.00 mmol) in 5 ml of acetone (diethyl ether in the case of **9**). Immediate formation of a yellow–orange precipitate was observed, which was collected by filtration, washed with acetone and dried under vacuum (yield: >90%).

^{1}H NMR [200 MHz, dmso-d₆, (CHD₂)₂SO (δ 2.55) as internal standard]:

Zn(**1**)Cl₂: 9.76 (s, 1H), 8.81 (d, 1H, $^3J_{H-H} = 5.0\,Hz$), 8.65 (s, 1H), 8.06 (m, 2H), 7.66 (dd, 1H, $^3J_{H-H} = 7.0\,Hz$), 7.26 (d, 2H, $^3J_{H-H} = 8.4\,Hz$), 6.75 (d, 2H).
Anal. Calcd Zn: 19.5%. Found: 18.6%.
Zn(**2**)Cl₂: 9.82 (br, 1H), 8.80 (br, 1H), 7.95 (m, 2H), 7.45 (m, 3H), 6.87 (d, 2H, $^3J_{H-H} = 8.6\,Hz$), 3.34 (s, 3H).
Anal. Calcd Zn: 18.8%. Found: 17.6%.
Zn(**3**)Cl₂: 9.74 (s, 1H), 8.50 (s, 1H), 8.05 (d, 1H, $^3J_{H-H} = 8.0\,Hz$), 7.81 (t, 1H, $^3J_{H-H} = 8.0\,Hz$), 7.67 (d, 1H), 7.27 (d, 2H, $^3J_{H-H} = 8.4\,Hz$), 6.78 (d, 2H).
Anal. Calcd Zn: 15.8%. Found: 15.5%.
Zn(**4**)Cl₂: 9.62 (s, 1H), 8.49 (s, 1H), 7.82 (t, 1H, $^3J_{H-H} = 7.6\,Hz$), 7.68 (d, 1H), 7.27 (d, 2H, $^3J_{H-H} = 8.4\,Hz$), 6.91 (d, 1H), 6.80 (d, 2H), 3.91 (s, 3H).
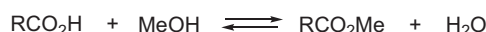Anal. Calcd Zn: 17.9%. Found: 16.9%.
Zn(**5**)Cl₂: 9.61 (s, 1H), 8.65 (s, 1H), 8.11 (d, 2H, $^3J_{H-H} = 8.8\,Hz$), 7.96 (m, 3H), 7.30 (d, 1H, $^3J_{H-H} = 8.8\,Hz$), 7.05 (d, 2H), 6.81 (d, 2H), 3.81 (s, 3H).
Zn(**6**)Cl₂: 9.65 (s, 1H), 8.66 (s, 1H), 8.18 (d, 2H, $^3J_{H-H} = 6.8\,Hz$), 8.10–7.90 (m, 3H), 7.56 (d, 2H), 7.32 (d, 2H, $^3J_{H-H} = 9.0\,Hz$), 6.82 (d, 2H).
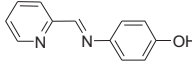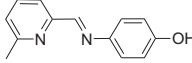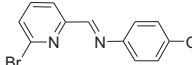Zn(**7**)Cl₂: 9.68 (s, 1H), 8.99 (s, 1H), 8.74 (s, 1H), 8.60 (dd, 1H, $^3J_{H-H} = 8.0\,Hz$, $^4J_{H-H} = 1.8\,Hz$), 8.32 (dd, 1H, $^3J_{H-H} = 8.0\,Hz$), 8.25–8.0 (m, 3H), 7.83 (t, 1H), 7.37 (d, 2H, $^3J_{H-H} = 8.8\,Hz$), 6.84 (d, 1H).
Anal. Calcd Zn: 14.4%. Found: 14.4%.
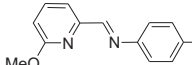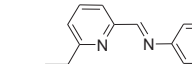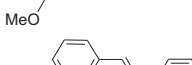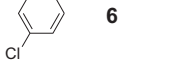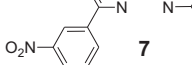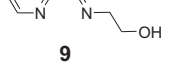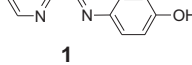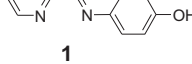
$$RCO_2H + MeOH \rightleftharpoons RCO_2Me + H_2O$$

Scheme 2. Esterification of free fatty acids.
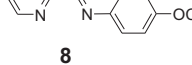
Table 1
Ligands and zinc catalysts.

Ligands	Catalysts
1	Zn(**1**)Cl₂
2	Zn(**2**)Cl₂
3	Zn(**3**)Cl₂
4	Zn(**4**)Cl₂
5	Zn(**5**)Cl₂
6	Zn(**6**)Cl₂
7	Zn(**7**)Cl₂
8	Zn(**8**)Cl₂
9	Zn(**9**)Cl₂
1	Zn(**1**)(AcO)₂
1	Zn(**1**)(CF₃CO₂)₂
1	Zn(**1**)(CF₃SO₃)₂

Zn(**9**)Cl₂: 8.69 (d, 1H, $^3J_{H-H}$ = 3.5 Hz), 8.62 (s, 1H), 8.24 (t, 1H, $^3J_{H-H}$ = 7.6 Hz), 8.06 (d, 1H), 7.79 (dd, 1H), 4.96 (br, 1H), 3.70 (br, 4H).
Anal. Calcd Zn: 22.8%. Found: 20.1%.
Zn(**1**)(AcO)₂: 9.90 (br, 1H), 8.80 (s, 1H), 8.70 (d, 1H, $^3J_{H-H}$ = 3.8 Hz), 8.10 (m, 2H), 7.64 (dd, 1H, $^3J_{H-H}$ = 7.0 Hz), 7.43 (d, 2H, $^3J_{H-H}$ = 8.0 Hz), 6.81 (d, 2H), 1.76 (s, 6H).
Anal. Calcd Zn: 17.1%. Found: 15.4%.

2.2.2. Preparation of Zn(**1**)(CF₃CO₂)₂ and Zn(**1**)(CF₃SO₃)₂

In the case of trifluoroacetate or trifluoromethanesulfonate derivatives it was necessary to isolate the ligand **1** prior to its coordination to the metal center, since the one pot procedure described in Section 2.2.1 was not successful.

A solution of the zinc precursor ZnX₂ (X = CF₃CO₂ or CF₃SO₃, 2.00 mmol) in 5 mL of diethyl ether was added to solid **1** (0.396 g, 2.00 mmol) suspended in 5 mL of diethyl ether. After 72 hours of stirring the yellow precipitate was collected by filtration, washed with diethyl ether and dried under vacuum.

^{1}H NMR [200 MHz, dmso-d₆, (CHD₂)₂SO (δ 2.55) as internal standard]:

Zn(**1**)(CF₃CO₂)₂: 9.93 (s, 1H), 8.83 (d, 1H, $^3J_{H-H}$ = 4.4 Hz), 8.74 (s, 1H), 8.23 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 8.02 (d, 1H, $^3J_{H-H}$ = 7.4 Hz), 7.82 (t, 1H, $^3J_{H-H}$ = 5.4 Hz), 7.19 (d, 2H, $^3J_{H-H}$ = 7.6 Hz), 6.74 (d, 2H, $^3J_{H-H}$ = 8.6 Hz).
Anal. Calcd Zn: 13.4%. Found: 10.6%.
Zn(**1**)(CF₃SO₃)₂: 9.93 (s, 1H), 8.82 (d, 1H, $^3J_{H-H}$ = 4.4 Hz), 8.74 (s, 1H), 8.23 (t, 1H, $^3J_{H-H}$ = 7.2 Hz), 8.02 (d, 1H, $^3J_{H-H}$ = 7.4 Hz), 7.82 (t, 1H, $^3J_{H-H}$ = 5.4 Hz), 7.19 (d, 2H, $^3J_{H-H}$ = 7.6 Hz), 6.74 (d, 2H, $^3J_{H-H}$ = 8.6 Hz).
Anal. Calcd Zn: 11.6%. Found: 10.7%.

2.2.3. Preparation of Zn(**8**)Cl₂

Complex Zn(**8**)Cl₂ was obtained by reacting ZnCl₂ with ligand **8**, which was prepared in situ by reacting **1** with triethoxysilylpropylisocianate.

A mixture of **1** (0.396 g, 2.0 mmol) and triethoxysilylpropylisocianate (0.54 g, 2.2 mmol) was refluxed in dry THF. After 3 h solid ZnCl₂ (0.27 g, 2.0 mmol) was added and hexane was added to precipitate an orange solid, which was collected by filtration, washed with hexane, and dried under vacuum (yield: 70%).

^{1}H NMR [200 MHz, dmso-d₆, (CHD₂)₂SO (δ 2.55) as internal standard]:

Zn(**8**)Cl₂: 8.77 (d, 1H, $^3J_{H-H}$ = 5.0 Hz), 8.66 (s, 1H), 8.05 (m, 2H), 7.77 (t, 1H, $^3J_{H-H}$ = 6.0 Hz), 7.61 (dd, 1H, $^3J_{H-H}$ = 8.0 Hz), 7.38 (d, 2H, $^3J_{H-H}$ = 8.6 Hz), 7.13 (d, 2H), 3.74 (q, 6H, $^3J_{H-H}$ = 6.9 Hz), 3.02 (q, 2H), 1.52 (m, 2H), 1.14 (t, 9H), 0.57 (m, 2H).
Anal. Calcd Zn: 11.2%. Found: 9.6%.

2.2.4. Catalytic runs

The screening of the catalysts was performed using a series of 5–6 small stainless steel vial reactors. Both the reagents (soybean oil, FFA < 0.2%, w/w) and methanol and a defined amount of the catalyst were introduced in 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 it reached the reaction temperature. At the end of the reaction, the samples were quenched by putting the vials in a cold bath. Experimental runs were also performed by adding oleic acid to the reactants. Oleic acid was chosen as the test molecule for simulating the behavior of FFA.

Blank runs (without catalysts) were also done taking into account any contribution of non-catalytic mechanisms to FAME yield and FFA conversion.

The FAME yields were determined using the H NMR technique [18]. FFA conversion was determined by measuring the residual FFA concentration by titration [19].

3. Results and discussion

3.1. Synthesis of complexes

The ligands and the zinc catalysts are reported in Table 1. The synthesis of the complexes did not require the previous isolation of the ligands, but could be carried out in one simple step, by reacting in situ the amine with the appropriate pyridinecarboxaldehyde in
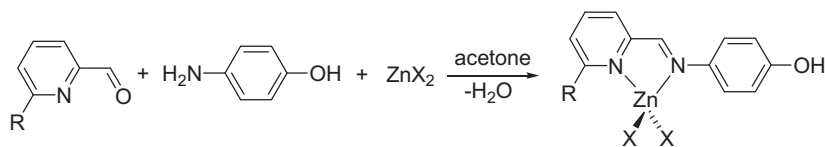
Scheme 3. Synthesis of the catalysts.

the presence of a stoichiometric amount of zinc chloride or zinc acetate (Scheme 3).

Only in some specific cases was it necessary to isolate the bidentate ligands prior to their coordination, as described in detail in Section 2.

Most of the complexes were sparingly soluble in common organic solvents, and their NMR characterization was performed in dmso-d_6. The presence of the CH=N bond was clearly shown by the presence of the expected singlet at high frequency (δ 8.5–9).

As alluded in the Introduction, the architectures of the ligands was dictated by at least three important factors:

(i) convenient synthesis and commercial accessibility;
(ii) availability of a function (in this case –OH) useful for heterogeneization. The feasibility of this strategy was demonstrated by decorating Zn(**1**)Cl$_2$ with a triethoxysilylpropylcarbammate linkage. The triethoxysilyl group in the corresponding product Zn(**8**)Cl$_2$ is known to react readily with the surface of silica affording the heterogeneized form of the catalyst (Scheme 4) [20]
(iii) the opportunity to control the Lewis acidity of zinc, through modulation of the electronic properties of the ligands, which span from electron-withdrawing (*e.g.* **7**) to electron-donating (*e.g.* **4**).

This latter target was also pursued by using four different anions with the following order of coordinating ability: $Cl^- > CH_3CO_2^- > CF_3CO_2^- > CF_3SO_3^-$. As a confirmation of this trend, the spectra of Zn(**1**)(CF$_3$CO$_2$)$_2$ and Zn(**1**)(CF$_3$SO$_3$)$_2$ in dmso-d_6 were identical (see Section 2.2.2), which suggests that both anions are readily displaced by solvent molecules affording cationic solvato-species [Zn(**1**)(dmso)$_n$]$^{2+}$. This possibility was confirmed through conductivity measurements. Solutions of both Zn(**1**)(CF$_3$CO$_2$)$_2$ and Zn(**1**)(CF$_3$SO$_3$)$_2$ in DMSO showed a molar conductivity (80 S cm^2 mol^{-1}) within the range expected for electrolytes [21]. As expected, in the same solvent Zn(**1**)Cl$_2$ and Zn(**1**)(CH$_3$CO$_2$)$_2$ were found to be non-conductive.

3.2. Catalytic runs

The *trans*-esterification of soybean oil was performed by stirring a mixture of oil, methanol and the appropriate catalysts according to the conditions reported in Tables 2–5.

First of all, it is important to point out that in the adopted reaction condition the contribution to FAME yield of the non-catalytic reaction is very low (see, entry B.1 of Table 2).

Table 2
Influence of ligands on Zn(N–N′)Cl$_2$ catalytic activity. Reaction conditions: $T = 150\,°C$; soybean oil = 2 g; methanol = 0.88 g; Cat. = 0.30 mmol; React. time = 60 min.

Run	Catalyst	FAME yield (%)
B.1	–	<2%
B.2	**1**	<2%
B.3	ZnCl$_2$	29
B.4	Zn(**1**)Cl$_2$	57
B.5	Zn(**2**)Cl$_2$	35
B.6	Zn(**3**)Cl$_2$	9
B.7	Zn(**4**)Cl$_2$	48
B.8	Zn(**5**)Cl$_2$	76
B.9	Zn(**6**)Cl$_2$	39
B.10	Zn(**7**)Cl$_2$	84
B.11	Zn(**8**)Cl$_2$	67
B.12	Zn(**9**)Cl$_2$	59

Table 3
Influence of anions on Zn(**1**)X$_2$ catalytic activity. Reaction conditions: soybean oil = 2 g; methanol = 0.88 g; Cat. = 0.30 mmol; React. time = 60 min.

Run	Catalyst	T (°C)	FAME yield (%)
B.4	Zn(**1**)Cl$_2$	150	57
C.1	Zn(**1**)(CH$_3$CO$_2$)$_2$	150	93
C.2	Zn(**1**)(CF$_3$CO$_2$)$_2$	150	95
C.3	Zn(**1**)(CF$_3$SO$_3$)$_2$	150	51
C.4	Zn(**1**)(CH$_3$CO$_2$)$_2$	120	91
C.5	Zn(**1**)(CF$_3$CO$_2$)$_2$	120	44

Table 4
Influence of (**1**) ligand of Zn(CH$_3$CO$_2$)$_2$ on catalytic activity. Reaction conditions: $T = 150\,°C$; soybean oil = 2 g; methanol = 0.88 g; React. time = 60 min.

Run	Catalyst	Cat. amount (mmol)	FAME yield (%)
D.1	Zn(CH$_3$CO$_2$)$_2$	0.30	22
D.2	Zn(CH$_3$CO$_2$)$_2$	0.06	12
C.1	Zn(**1**)(CH$_3$CO$_2$)$_2$	0.30	93
D.3	Zn(**1**)(CH$_3$CO$_2$)$_2$	0.06	52

Table 5
Influence of FFA concentration on activity of Zn(CH$_3$CO$_2$)$_2$ and Zn(**1**) (CH$_3$CO$_2$)$_2$ catalytic systems. Reaction conditions: $T = 150\,°C$; Oil (FFA conc., 7%) = 2 g; Methanol = 0.88 g; Cat. = 0.06 mmol; React. time = 60 min.

Run	Catalyst	FFA conv. (%)	FAME yield (%)
E.1	–	<1	2
E.2	Zn(CH$_3$CO$_2$)$_2$	30	16
E.3	Zn(**1**)(CH$_3$CO$_2$)$_2$	26	48
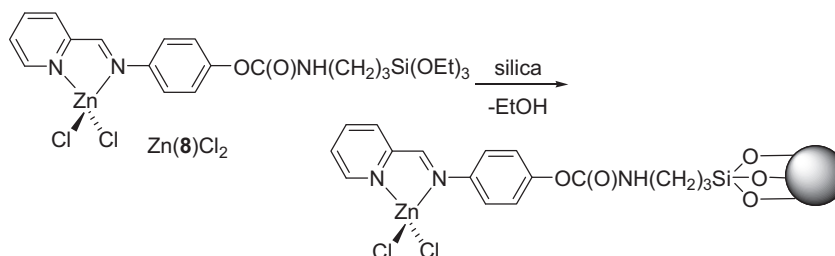
Scheme 4. Strategy for the heterogeneization of the catalyst.

Moreover, the ligands without the presence of metal ions showed a low activity (see, entry B.2 of Table 2).

The early experiments were designed to evaluate the influence of the properties of the N,N′-ligands, and were carried out by studying the activity of the corresponding dichlorozinc complexes (see Table 2).

The acidity of the catalytic site has an important effect on the performance. In fact, the highest activity was offered by the nitro-species Zn(**7**)Cl$_2$, which promoted 84% (entry B.10) of conversion to biodiesel. On the other hand, in the presence of moderate electron-donor ligands (**2** and **4**, entries B.5 and B.7) the yield resulted lower than that observed with free ZnCl$_2$ (Table 2), although in these cases the interference of steric effects cannot be ruled out. Instead, these apparently prevail in the presence of bulky substituents in the ortho position of the pyridine ring, as in Zn(**3**)Cl$_2$, which promote only 9% of conversion to biodiesel (B.6).

The effect of the anions is instead reported in Table 3. It is evident that high conversion can be achieved through fine tuning of the basic property of the anion. In fact, a strong Lewis base (Cl$^-$) plausibly competes with the substrate in the coordination to the metal site, thus inhibiting its activity (57%, B.4). On the other hand, the presence of a weak donor (CF$_3$SO$_3$$^-$) excessively enhances the acidity of the metal center, which is therefore deactivated by a strong coordination of the product (51%, C.3).

The delicate balance between these two effects is satisfied by the intermediate behavior of CH$_3$CO$_2$$^-$ and CF$_3$CO$_2$$^-$, which promote almost quantitative conversion at 150 °C (C.1 and C.2). Lowering the temperature to 120 °C allows to discriminate between the two anions, disclosing the higher ability of the acetate ion (91% *vs* 44%, C.4 *vs* C.5).

Given these premises, further catalytic runs were carried out using acetate ions in combination with ligand **1** by varying the conditions of catalyst loading (Table 4).

Two different concentrations (0.30 and 0.06 mmol) were used, and the results compared with those achieved under identical conditions using the simple Zn(CH$_3$CO$_2$)$_2$. In all cases, the use of the ligand significantly increased the obtained FAME yields.

A further refinement was carried out by introducing a percentage of FFA (Free Fatty Acids, 7%) in the oil phase, to determine the activity of the catalyst Zn(**1**)(CH$_3$COO$_2$)$_2$ towards the esterification reaction in comparison with Zn(CH$_3$COO$_2$)$_2$ and without the catalyst (Table 5).

This demonstrates that the Zn(**1**)(CH$_3$COO$_2$)$_2$ catalyst combines the significant trans-esterification activity with a certain attitude towards FFA esterification and so it can be considered as good candidate for the heterogeneization on a solid support (using the procedure previously described) to obtain an heterogeneous catalyst which could be used for biodiesel production from waste oils.

4. Conclusions

This work demonstrates that it is possible to obtain molecular species of zinc(II) capable of catalyzing the transesterification of soybean oil in mild conditions. Their activity can be modulated by a fine selection of the anions and/or of the substituents on the ancillary bidentate ligand. The compounds are also active in the esterification of fatty acids. Future work will involve the heterogeneization of the catalysts on solid matrices, by employing the OH group present on the ligand scaffold, and the study of the activity of corresponding complexes containing other Lewis acids.

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