Catalysis Today 147S (2009) S220–S224

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A new heterogeneous ZnL_2 catalyst on a structured support for biodiesel production

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ARTICLE INFO

Article history:
Available online 6 August 2009

Keywords:
Biodiesel production
Batch to continuous
Zinc amino acid complex
Structured catalyst
Cordierite monolith
Transesterification reaction

ABSTRACT

Although the transesterification reaction of triglycerides with alcohols (using acid or alkaline catalysts) is well known and practiced on a commercial scale, there is plenty of scope to improve this process. The turning of a batch into a continuous process, and the use of a catalyst that is more favourable to fatty acids in the feed, are challenges of particular interest. With these objectives in mind, results are presented of experiments in which a zinc amino acid complex [ZnL_2], was used as a catalyst. This was fixed onto a structured monolith support (cordierite), so as to enable the catalysts to be retained in a fixed bed. To advance this work, reaction experiments were performed in a 120 ml batch reactor, using 10 mm × 10 mm × 10 mm sections of catalyst coated monolith (1.1 mm square channels, 62 cells cm^{-2}). With a 12:1 molar ratio of methanol and rapeseed oil (triglyceride), at 195 °C and 20 bar, and using 0.3 g of zinc catalyst (coated on a monolith), it was shown that 54% of the triglyceride was converted into biodiesel. This compares very favourably with a conversion of 69% in batch experiments, when 0.3 g of the catalyst was dispersed in the solution in the form of a very fine powder. Interestingly, it was also shown, that the cordierite monolith support on its own exhibited catalytic activity (27% conversion of the triglyceride).

1. Introduction

The use of vegetable oils to make biodiesel provides a sustainable source of organic carbon, and despite concern over competition with the food supply chain, this will continue to be used in many countries as a source of fuel. This is clearly evident in the EC document on the vision of the year 2030 and beyond [1]. A rapid expansion in production capacity has been observed [2] not only in countries such as Germany, Italy, France and the United States, but also in developing countries such as Brazil, Argentina, Indonesia and Malaysia.

When reviewing the literature, it is clear that there are a variety of different methods that could be used to produce biodiesel, and transesterification is one of the main commercial pathways. As described in the literature [3], early descriptions of the transesterification reaction appeared in [4–6]. The basic reaction may be represented in Fig. 1.

The fatty methyl esters (FAME) represent the biodiesel formed. According to a review of biodiesel production [7], because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side and the reaction can be catalyzed by alkalis or acids. Alkali-catalyzed transesterification is more often used in commercial processes as it is much faster than the acid-catalyzed reactions. However, in an alkali-catalyzed reaction, if water is present with the reactants, then the saponification reaction produces soap. This in turn lowers the yield of esters, and creates problems with: the separation of ester and glycerol, and also with the water washing step. If water and free fatty acid content is high in the feedstock, then acid transesterification can be used. Alternatively, to overcome the problem of water and free fatty acids in the feed, a two-step reaction may be followed, e.g. [8]. In the first step, the acid-catalyzed reaction is performed (using sulphuric acid), and this is followed by an alkali-catalyzed reaction (using NaOH).

Although the transesterification reaction of triglycerides with alcohols (using acid or alkaline catalysts) is well known and practiced on a commercial scale, there is plenty of scope to improve this process [9]. For example, by responding to the following:

Challenges (i) to (vi)

(i) Increasing the rate of the first step in the reaction (limited by mass transfer).
(ii) Identifying a catalyst to deal with the variation in feed composition (fatty acids cause problems).
(iii) Decreasing the time for the separation step at the end of the reaction.
(iv) Turning the semi-batch reactor into a continuous reactor (to reduce residence time, plant ‘foot-print’, and increase the transportability of a mobile plant).

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doi:10.1016/j.cattod.2009.07.060

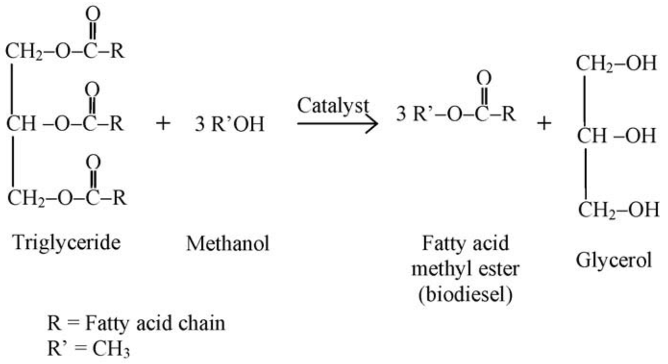

Fig. 1. Transesterification reaction.

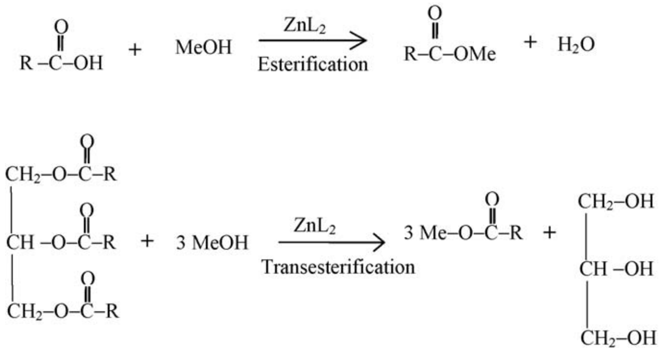

Fig. 2. Proposed reactions scheme for zinc amino acid complexes [14].

(v) Increasing the purity of the glycerol (produced as a by-product), or converting glycerol to a more useful product.
(vi) Reducing the amount of water in the reactor effluent stream (e.g. use of a fixed bed catalyst).

1.1. Examples of continuous processes

In the literature there are a number of studies on continuous flow systems, endeavouring to respond to some of the Challenges (e.g. ii, iii, iv), for example:

(a) Reactants were fed into a long tube (50.8 cm long, 5.08 cm in diameter) that acted as the reactor [10]. To achieve good mixing of the reactants, the fluid passed through a static in-line mixer, and also a high shear mixer before the reactants entered the tubular reactor. In this continuous flow system they managed to achieve high conversions of the triglyceride, e.g. >97%.
(b) The performances of various designs of batch reactor with a continuous oscillatory flow reactor have been compared [11]. The reactants flowed through a mixing unit, and then the flow reactor, which consisted of 8 meso tubes (tube length 730 cm) with U-bends, providing a total volume of 103 ml. What is particularly interesting about these oscillatory reactors is that they achieve good mixing, and by careful choice of operating conditions, the equivalent of plug flow can be obtained. In the early phase of the reaction ($t < 2.5$ min), there appeared to be two phases present, then after $t > 2.5$ min, the fluid was described as optically homogeneous. This indicates the importance of having an intense mixing region at the start of the reaction.
(c) A description is provided [12] of how to improve the separation of glycerine from the products by adding a third gaseous component (e.g. carbon dioxide, pentane) with the reactants. Experiments were described at reaction conditions of 573 K and 13 MPa (in tubular reactor: 4 mm i.d. and 4 m length) and 473 K and 5 MPa (in a fixed bed: i.d. 13 mm and 0.83 m length).
(d) A metal oxide was used as a catalyst, at elevated pressures (172 bar) and temperatures (300–450 °C), and supercritical flow conditions were claimed to have been achieved [13]. The reactants flowed through a tubular reactor (1 cm i.d. and 15 cm long), packed with sulphated metal oxide microspheres. The residence time was of the order of 60 s to achieve high conversions of the triglyceride (e.g. 87%).

1.2. Zinc amino acid complexes [ZnL_2] as catalysts

In order to respond to Challenge (ii), it was recently shown [14], that zinc amino acid complexes [ZnL_2] can be effective homogeneous catalysts for a situation where fatty acids (e.g. stearic acid) are present in the vegetable oil (see Fig. 2). This was shown by performing experiments in a batch reactor, using a 1:6 molar ratio of rapeseed oil:methanol, and a 1:12 molar ratio of soyabean oil and stearic acid: methanol. The catalyst was shown to be effective at a temperature of 180 °C, which is significantly higher than temperatures (50–80 °C) at which the alkali/acid-catalyzed reactions normally take place, but less severe than conditions described in [12,13]. However, a pressure of 20 bar also had to be imposed, in order to suppress the vaporization of the alcohol, and conversions of the triglyceride up to 95% were achieved.

In the experiments described [14], ZnL_2 was dispersed in the reactants in the form of a fine powder (16–144 μm). This meant that at the end of the reaction, the catalyst would remain mainly dispersed in the products. So, if the catalyst could be supported on a structured support, that would then enable it to be retained in a fixed bed. Thus another two of the Challenges (iii, iv) could be addressed, and this aspect is considered in this paper.

2. Experimental

2.1. Catalyst preparation

First, in order to become familiar with the ZnL_2 catalyst system, some preliminary experiments were conducted with the powdered system, in order to feel satisfied that the way in which the catalyst was prepared would match the results observed in earlier work [14]. Following confirmation of this aspect, it was decided to try to use a standard form of monolith cordierite support for the catalyst. This standard form is used for catalytic converters, and the monolith had 1.1 mm square channels and a cell density of 62 cells cm^{-2}.

After trying a number of different coating techniques, the following method of coating was considered satisfactory for preliminary trials.

First, 0.5 g of ZnL_2 powder was dissolved in 200 ml of water, by heating and mixing the solution at 100 °C for 20–30 min, until the solution appeared homogeneous. While the solution was still hot, small section of monolith (10 mm × 10 mm × 10 mm, 10 pieces) were then dipped in the solution, 2–3 times. The excess liquid was then blown out using a jet of air. The coated monoliths were then dried using a hot air blower at a temperature of about 100 °C. The dried samples were then placed in a furnace, in the presence of a continuous flow of nitrogen, and heated to 200 °C. This process was repeated three times, in order to increase the catalyst loading on the support (e.g. 5 wt% of ZnL_2).

2.2. Experimental conditions

These were as follows:

(a) The molar ratio was 12:1 of methanol and rapeseed oil (triglyceride).

(b) The liquid volume consisted of 20 ml of methanol mixed with 37 ml of rapeseed oil, and this was placed in a 120 ml autoclave.
(c) Small pieces of catalyst coated monolith (containing 0.3 g of ZnL_2) were inserted into the reactor. The autoclave was then sealed and placed in a graphite bath that was electrically heated.
(d) The reaction lasted 2 h, at 195 °C and 20 bar, with the stirrer set at a speed of 1500 rpm.

At the end of the designated reaction period, the autoclave was rapidly cooled in a stream of water, and the product mixture was then poured into a flask filled with water to quench the reaction. This mixture was then allowed to settle (20–30 min), until a clear biodiesel layer was visible.

2.3. Experimental results

A sample from the biodiesel layer was then taken, and analysed using NMR. The percentage conversion of triglycerides to FAME was determined using information in the NMR on methyl ester protons and the protons of the glyceryl moiety in the triglycerides, e.g. [15].

To help visualize the nature of the catalyst surface, SEMs were taken of the powdered catalyst (see Fig. 3), the blank monolith (see Fig. 4), and the coated monolith (see Fig. 5). These will help to support the discussion of the experimental results.

Various experiments were performed and these are summarised in Table 1.

For the freshly coated monolith with ZnL_2, a conversion of 54% of the triglyceride to biodiesel (FAME) was determined. Considering that these are very early results, this is encouraging, as this compares favourably with a figure of 69% conversion obtained in repeat experiments with 0.3 g of powdered ZnL_2 catalyst. This is very important, as it shows that the method of coating the monolith had not had any significant adverse effect on the catalytic properties of this catalyst. Also, comparing the surface morphology in the SEMs in Figs. 3 and 5, similar forms of the rod-like ZnL_2 structures (≈1 µm in diameter and 1–10 µm long) appear in the magnified pictures of the surface of the particle and of the coated monolith support. Estimates of the geometric external surface area of the monolith and the powdered catalyst indicate that the

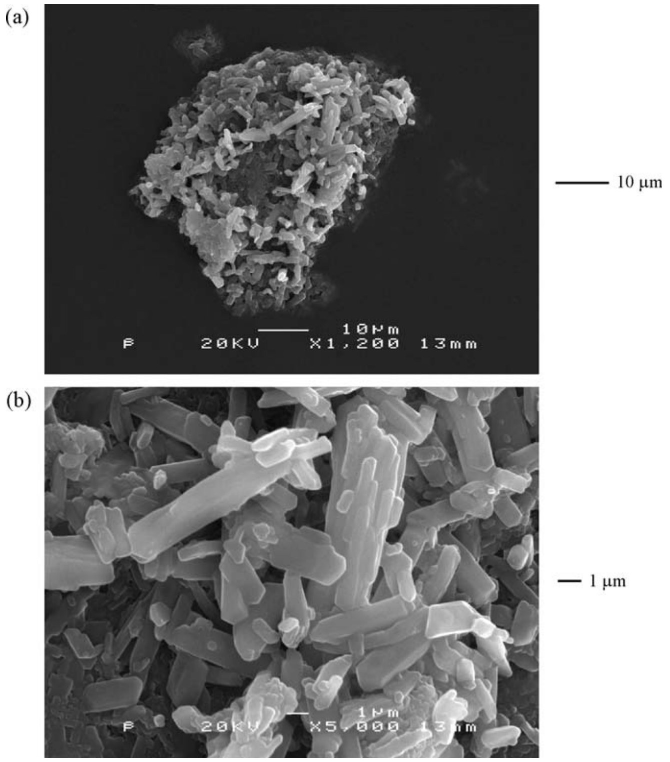

Fig. 3. Example SEM of the powdered ZnL_2 catalyst: (a) example of a particle, (b) magnified view of surface (with permission, Kolaczkowski, University of Bath).

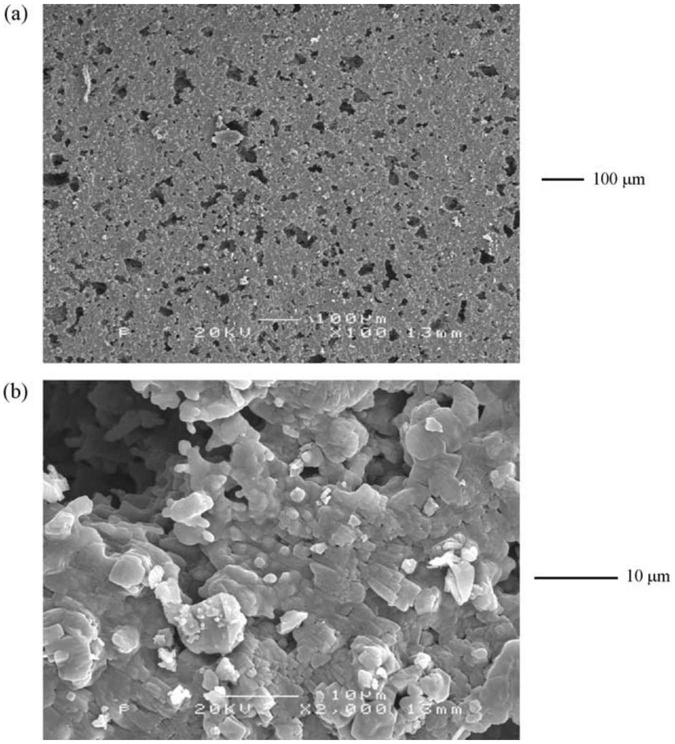

Fig. 4. Example SEM of the cordierite monolith: (a) view of surface, (b) magnified view of surface (with permission, Kolaczkowski, University of Bath).

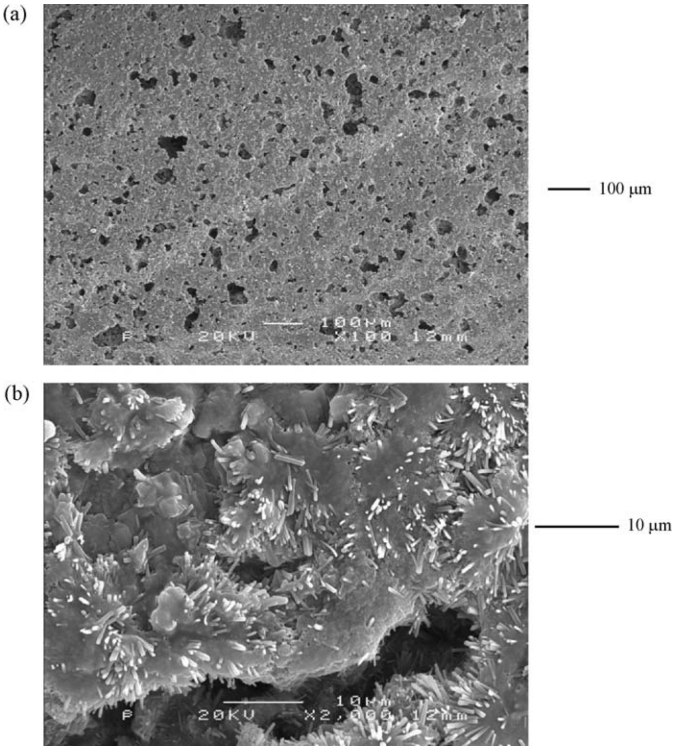

Fig. 5. Example SEM of the ZnL_2 coated cordierite monolith: (a) view of surface, (b) magnified view of surface with ZnL_2 rod-like structures (with permission, Kolaczkowski, University of Bath).

Table 1
Summary of experiments.

Catalyst system	Conversion of triglyceride to FAME	Comments
No catalyst	0.3%	Blank experiment
ZnL_2 powder	69%	Repeat of conditions reported in [14]
Cordierite monolith coated with ZnL_2		
(a) Freshly prepared	54%	Preliminary tests to assess activity with time
(b) After 24 h of use	57%	
No catalyst on cordierite monolith	27%	Blank experiment to assess the catalytic activity of the cordierite support.

external surface area of the monolith will be about 30 times lower than the powdered catalyst. So if the rate had been calculated on the basis of geometric surface area, then the rate for the monolith would have been very much higher. So it may even be that the method of coating the monolith had actually increased the activity of the catalyst, or the cordierite itself exhibited catalytic activity. It is important to state, that in this study it would be premature to try to make an absolute comparison of the reaction rates, as these are not intrinsic kinetics (i.e. in the absence of external or internal mass transfer effects).

This experiment was then repeated using the retrieved samples of coated monolith, and even after 24 h of use, similar results were obtained (57% *versus* 54% conversion of the triglyceride to FAME). This showed that in the period tested, significant catalyst loss/deactivation had not occurred. However, the extent of catalyst adhesion has not yet been investigated, but this will feature in subsequent work.

At similar conditions, further experiments were then performed with uncoated samples of cordierite monolith, to see if the cordierite exhibited any form of catalytic activity. From these, it was found that 27% conversion of the triglyceride to FAME was achieved (*versus* 54%) which is in itself interesting. This would suggest that the cordierite is catalytically active, and further evidence may be obtained from the literature. For example [16], the use of a number of alkaline-earth metal oxides (MgO, CaO, SrO) as catalysts for the transesterification reaction (edible soybean oil with methanol) have been studied. It was found [16] that both SrO and CaO were very active catalytically, whereas the MgO had a low level of activity. As the structure of cordierite corresponds [17] to $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, then the MgO could have exhibited some activity in our experiments (especially as temperatures were a lot higher than in [16]). Also, in the literature [18], the catalytic activity of MgO functionalized mesoporous materials for the transesterification of blended vegetable oil with ethanol was studied. These experiments were also performed at higher temperatures (220 °C), and silica loaded with MgO was found to be the most effective of all of the catalysts tested in that paper [18]. So this provides further evidence that the MgO in the cordierite could show catalytic activity especially at elevated temperatures.

Experiments were also performed, where the reaction was briefly stopped, and a sample was withdrawn from the reactor for analysis. In this way it was possible to monitor the progress of the reaction as a function of time. An example of such a plot is shown in Fig. 6, and these profiles will help in further work when attempts are made to match mathematical models of rate expressions with the experimental data.

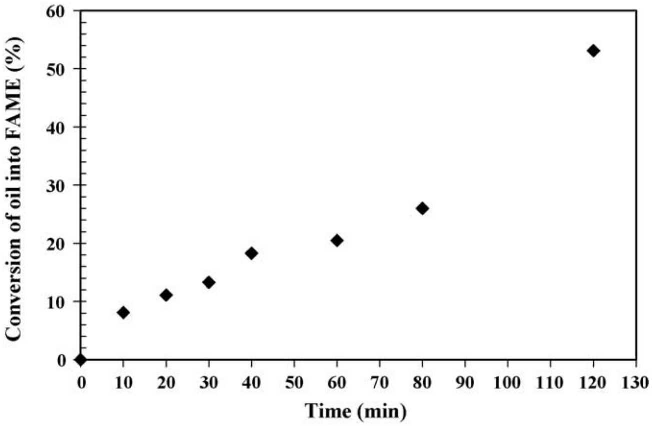

Fig. 6. Example of a batch experiment with a ZnL_2 coated monolith (T = 195 °C; P = 20 bar (g); molar ratio of methanol to oil = 12:1; initial concentration of oil = 0.71 mol l^{-1}; initial concentration of methanol = 8.53 mol l^{-1}; mass of ZnL_2 = 0.3 g coated on cordierite monolith).

This shape of plot is not unusual for a transesterification reaction, and it arises from the combination of series and parallel reactions that take place in this system—especially as the concentration of the intermediate species such as diglyceride and monoglyceride increase and then decrease. It is too early to propose a detailed explanation of the intermediates formed with the ZnL_2 catalyst studied, but examples of reaction schemes for alkali-catalyzed reactions are available in the literature, e.g. [19].

3. Concluding remarks

A coating procedure was developed to immobilize the zinc amino acid complex [ZnL_2] on a cordierite monolith support, such that the catalyst still remained active for the transesterification reaction studied. This was the major achievement in this study.

In repeat experiments using the coated monolith, after 24 h of use, the catalyst was shown to remain active. Longer term trials will now need to be performed.

From the SEM studies on the coated monolith, the distribution of the ZnL_2 catalyst in the form of rod-like structures is most interesting, as is the way in which they are anchored to the cordierite support. In future work, it is planned to improve the coating method, and to investigate if the coating process and method of interaction with the support actually increases the activity of the catalyst.

Having established the viability of immobilizing the ZnL_2 on a structured cordierite support, work is now in progress to construct a continuous tubular flow reactor, which will contain catalyst coated monoliths. Reaction experiments will then be performed to assess optimal operating conditions, determine reaction kinetics, and to evaluate catalyst durability.

Acknowledgements

The award of an overseas study bursary to Ms. Umi Aisah Asli, by the Ministry of Education in Malaysia is gratefully acknowledged. Special thanks to Dr. Chris Chuck (University of Bath) for helpful discussions.

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