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$ZnO/La_2O_2CO_3$ layered composite: A new heterogeneous catalyst for the efficient ultra-fast microwave biofuel production

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ABSTRACT

The search for solid state materials with high catalytic activities and with no leaching into the reaction medium is one of the key steps toward reducing the cost of producing biodiesel. We report a high biodiesel yield (>95%) in less than 5 min under mild reaction conditions (<100 °C) on a $ZnO/La_2O_2CO_3$ heterogeneous catalyst, showing no catalyst leaching into the reaction medium. The $ZnO/La_2O_2CO_3$ catalyst is prepared by a co-precipitation method and characterized by X-ray diffraction (XRD), thermogravimetric analyses (TGA), transmission electron microscopy (SEM), and transmission electron microscopy (TEM). The fatty acid methyl ester (FAME) yields as function of different amounts of catalyst was also investigated. Less than 1.0 wt.% catalyst can be used in the reaction to get higher than a 95% FAME yield under mild reaction conditions. The catalytic performance is maintained after storing the catalyst in Ar for a month and no catalyst leaching into the products was found based on XRF analysis. The catalyst has a higher reaction rate than the homogeneous KOH catalyst with the assistance of microwave irradiation. All of these results promote the industrial application of the synthesized $ZnO/La_2O_2CO_3$ as an ideal catalyst for fast biodiesel production, avoiding many of the issues found in both commercial and independently published catalysts.

1. Introduction

Currently people are approaching the peak-high rate in consuming petroleum for energy and chemicals. Although new sources may continue to emerge, diminishing petroleum reserves and growing concerns about global climate change necessitate the development of fuel production pathways based on renewable resources. A mixture of fatty acid methyl esters (FAME), also known as biodiesel, formed from the transesterification of the triglycerides present in the vegetable oils with methanol has emerged as a promising green energy for the substitution of fossil fuels [1–5] due to the uptake of CO_2 (photosynthesis) by the plants used to produce the fuel. However, the total energy used for the cultivation of plants that contain vegetable oils and conversion of the vegetable oils into biodiesel should be lower than the energy of biodiesel produced (life cycle assessment (LCA > 1), so that the use of biodiesel corresponds to solar energy conversion and the biodiesel is a renewable clean energy. Therefore, it is essential to minimize energy consumption for the transesterification process to convert the vegetable oils into biodiesel [1].

Both acidic and basic catalysts can catalyze the transesterification of vegetable oils for biodiesel production and basic catalysts are preferred due to the lower energy consumption required than as the case for acid catalysts [6]. Industrially, homogeneous base catalysts are used, including sodium or potassium hydroxides or alkoxides. However, removal of the basic catalysts from the products is problematic. For example, neutralization after reaction with acid results in some degree of saponification (i.e., hydrolysis of the ester and formation of the corresponding sodium carboxylate); formation of emulsions makes ester separation difficult, and energy and labor intensive operation increases the cost of biodiesel production. Further, a large amount of alkaline wastewater is generated, which must be treated before its disposal [7].

A highly active heterogeneous catalyst can eliminate the drawbacks of the homogeneous catalyst used in the industrial process. In principle, this approach can eliminate the need for water to be used to remove the catalyst, the formation of soap, and the formation of emulsions, thereby largely simplifying the purification process.

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Many solid catalysts have been investigated in the past few years [8]. However, some important questions from a fundamental point of view remain unclear. For example, most of the reported catalysts for biodiesel production require high temperatures (>150 °C) high pressures (up to 1000 psi), and long reaction times (from 2 h to 24 h) to get greater than 90% FAME yield [4,7,9–14], all these conditions require a much higher energy consumption than the homogeneous process used in industry.

Although the use of alkali and alkali-earth metal oxide based catalysts, such as KOH/Al_2O_3 [15], KF/Al_2O_3 [11], CaO [7,16], MgO [17], and $MgLaO_x$ [18] has been published as being highly active under mild conditions (<100 °C), catalyst leaching into the reaction medium due to the solubility of alkali and alkali-earth metal oxides make them unsuitable for heterogeneously catalyzed biodiesel production. Lin et al. [19–21] reported mesoporous silicate–alkaline earth oxide based recyclable catalysts for biodiesel production at low temperature (80 °C), but long reaction time (40 min–30 h) is required to get higher than 95% FAME yield and the amounts of calcium leached into the reaction medium remains unclear. To our knowledge, there is no non-alkali or non-alkali-earth metal oxide based catalyst reported which is highly active (>90% FAME yield) under mild reaction conditions (short reaction time, $T < 100$ °C) with no leaching into the reaction medium. Here, we report a new $ZnO/La_2O_2CO_3$ based solid material that has these properties. By using this material as the heterogeneous catalyst, the high biodiesel yield (>95%) in less than 5 min under mild reaction conditions (<100 °C) was observed with the assistance of microwave irradiation, showing no catalyst leaching into the reaction medium. These low temperature activities, short reaction time, and no leaching into the reaction medium promise minimum energy consumption and solid potential in industrial application. To the best of our knowledge, this is the first example of an inexpensive, highly active and low energy consuming heterogeneous catalyst without a leaching problem.

2. Experimental

2.1. Catalysts preparation

The zinc–lanthanum-mixed oxide catalyst was prepared by an *in situ* precipitation method. 17.84 g (0.06 mol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 51.96 g (0.12 mol) of $La(NO_3)_3{\cdot}6H_2O$ were dissolved in 800 mL D.D.I.W. (doubly de-ionized water) in a 1500 mL beaker. The solution was then heated to 85 °C, followed by precipitation until a pH = 10 using a basic solution. The basic solution was prepared by dissolving 16.8 g KOH and 41.4 g K_2CO_3 in 400 mL D.D.I.W.

After refluxing the resulting suspension for 24 h, the precipitate was filtered and washed with D.D.I.W. to remove by-products until the pH of the filtrated water reached 7.0. The resultant catalyst was oven-dried at 120 °C for 12 h and finally calcined at 550 °C for 6 h before use.

2.2. Catalyst characterization

The catalysts were characterized using several techniques: X-ray diffraction (XRD) patterns were obtained using a Scintag 2000 XDS instrument with a Cu Kα X-ray source with a beam voltage of 45 kV and 40 mA beam current.

Thermogravimetric analyses (TGA) were performed on a Hi-Res TA 2950 thermogravimetric analyzer with 60 mL/min of air flow from 25 to 850 °C at a heating rate of 10 °C/min.

High resolution scan electron microscopy (HRSEM) photographs were taken on a Zeiss DSM 982 Gemini emission scanning microscope with a Schottky Emitter at an accelerating voltage of 2 kV with a beam current of 1 μA. The samples were ultrasonically dispersed in ethanol for analysis. The suspensions were deposited on a gold-coated silicon wafer.

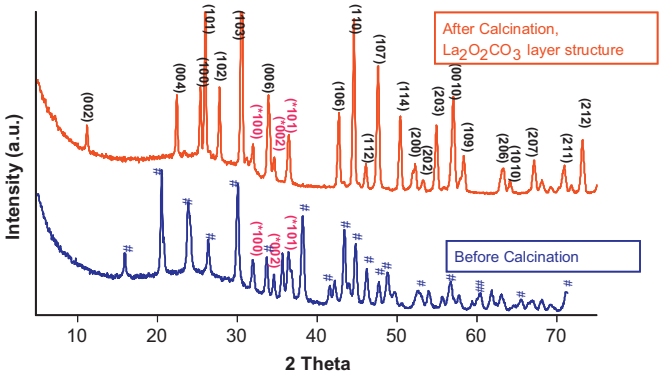

Fig. 1. XRD pattern of the prepared catalysts. Results show a mixture of ZnO (*) zincite and $La_2O(CO_3)_2{\cdot}xH_2O$ (#) before calcination and ZnO (*) and type II $La_2O_2CO_3$ layered structure (JCPDS: 37-804) after calcination.

Transmission electron microscopy (HRTEM) was also used to check the morphology and structure of the catalyst. HRTEM studies were carried using a JEOL 2010 instrument with an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in 2-propanol. Then a drop of the dispersion was placed on a carbon coated copper grid and allowed to dry.

Temperature programmed desorption (TPD-CO_2) was carried out in a furnace with a quadrupole residual MS gas analyzer. Catalyst powder (0.3 g) was placed in a quartz reactor and then pretreated in He flow (20 mL/min) at 550 °C for 2 h to dry the catalyst. After the pretreatment, a pure CO_2 gas (20 mL/min) was feed at room temperature for 2 h, followed by feeding He flow (20 mL/min) for another 2 h to remove the physically absorbed CO_2. The basic sites of the catalyst was analyzed by following the $m/z = 44$ signal with the temperature range from room temperature to 550 °C in pure He flow (20 mL/min).

2.3. Catalytic reactions

All experiments were carried out in a Biotage™ 5 mL microwave vial with a cap. In a typical reaction, 3.2 mL canola oil, 2.7 mL methanol (mass ratio 1:1), and 5 wt.% catalysts were introduced into the vial and sealed with the open-top vial cap with a PTFE liner. The Biotage™ Initiator 2.5 equipment was used as the microwave source. The reaction temperature and reaction time were controlled automatically. After the reaction is finished, the oil products were filtered and dissolved in THF and heptane and analyzed with an HP 5890 Serious II gas chromatograph coupled with a FID detector. The column used was a Restek Biodiesel TG column with dimensions of 14 m × 0.53 mm × 0.16 μm.

3. Results

3.1. Catalyst characterization

3.1.1. XRD

Fig. 1 shows the XRD pattern of the zinc–lanthanum-mixed oxide catalyst before and after activation at 550 °C. The results indicate a mixture of ZnO (zincite) and $La_2O(CO_3)_2{\cdot}xH_2O$ structure (JCPDS: 28-512) before activation and a mixture of ZnO (zincite) and type II $La_2O_2CO_3$ layered structure (JCPDS: 37-804) after activating at 550 °C for 6 h. Conventionally, $La_2O_2CO_3$ layered materials are prepared by calcining La_2O_3 under CO_2 atmosphere at a high temperature, requiring more complicated setup and parameters control [22–27]. Here, we used a simple wet chem-

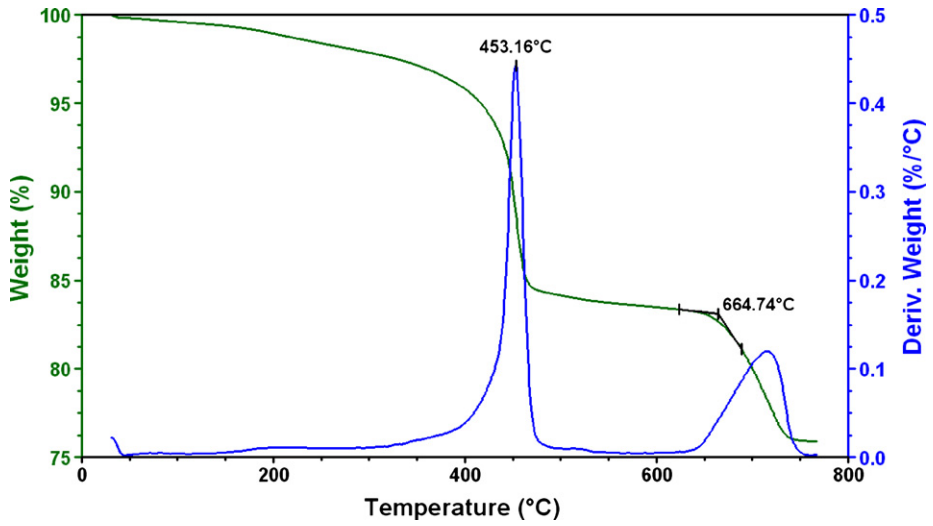

Fig. 2. TGA of the prepared sample before calcination.

istry method and the $La_2O_2CO_3$ layered material was successfully synthesized.

3.1.2. Thermal analysis

Thermogravimetric analysis (TGA) showed (Fig. 2) the first mass loss at around 450 °C and the second at around 700 °C. Both the mass losses were assigned to the loss of CO_2 based on TGA mass spectrometry analysis. At a temperature around 450 °C, the transformation of $La_2O(CO_3)_2$ into a $La_2O_2CO_3$ layered material occurs as confirmed from the XRD analysis. The mass loss at around 700 °C is due to the second loss of CO_2 and formed La_2O_3 from the $La_2O_2CO_3$ layered material, which was also supported by the XRD patterns.

3.1.3. High resolution scan electron microscopy (HRSEM) and transmission electron microscopy (HRTEM)

Fig. 3 shows typical morphologies of the prepared materials before (Fig. 3a) and after (Fig. 3b) calcinations at 550 °C for 6 h. A nano-fiber like morphology of ZnO was shown in both materials with an average diameter of about 50 nm (Fig. 3a and b). The bulk like material before calcination can be assigned to $La_2O(CO_3)_2$, which changed to $La_2O_2CO_3$ layered materials after calcination with nano-rod like morphologies. The nano-rod nature of the $La_2O_2CO_3$ layered material was further confirmed by HRTEM (Fig. 3c) imaging. The length of the nano-rods ranges from 50 to 100 nm. The high magnification image reveals the rod diameter ranges from 30 to 50 nm. Increasing magnification in Fig. 3d clearly shows the lattice fringes of a nano-rod showing the lattice spacing of the (0 0 2) planes of the layered materials ($d \sim 7.8$ Å). Results from HRSEM and HRTEM also suggest that ZnO is physically mixed with the $La_2O_2CO_3$ layered material.

3.1.4. Temperature programmed desorption (TPD)

The TPD-CO_2 measurements are carried out for Zn/La catalysts to know the total basic strength of the catalyst. The corresponding

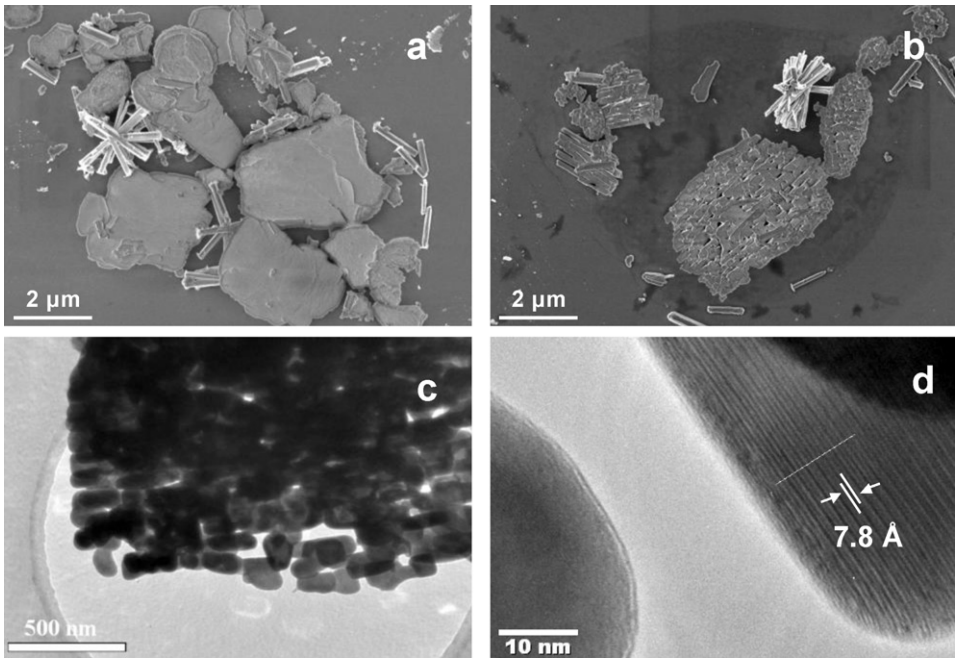

Fig. 3. SEM and TEM images of the prepared sample, (a) before calcination; (b)–(d) after calcination.

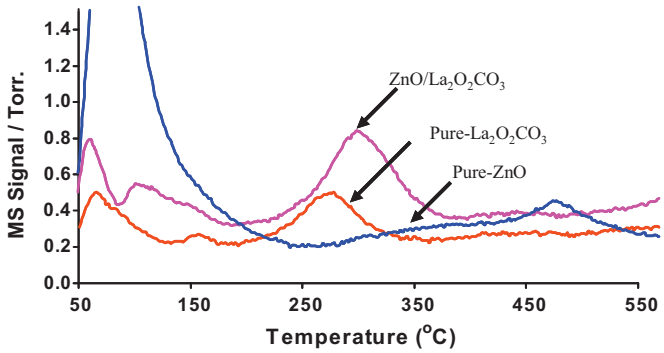

Fig. 4. TPD-CO_2 profile of the prepared catalysts.

TPD profiles are shown in Fig. 4. The catalysts exhibit two desorption ranges. One is centered at around 80 °C and can be assigned to the weak basic sites, and the second one between 200 °C and 400 °C can be assigned to the strong basic sites [18]. Results from comparison with the strong basic sites on pure ZnO and pure $La_2O_2CO_3$ prepared with the same method indicate that the Zn/La catalysts appear to be more basic than the pure ZnO and $La_2O_2CO_3$ ones and the dominant strong basic sites are provided by the $La_2O_2CO_3$ material. Pure ZnO material has a great deal of weak basic sites but little strong basic sites, but mixing ZnO with $La_2O_2CO_3$ by the reported synthetic method can increase the strong basic sites of the $La_2O_2CO_3$ material, as can be seen from Fig. 4.

3.1.5. Catalytic results

The catalytic activity of thermally activated $ZnO/La_2O_2CO_3$ materials has been evaluated in the transesterification of sunflower oil with methanol, under heterogeneous. Fig. 5 shows the FAME yields on the prepared catalysts as a function of temperature. The yields to FAME parallel the reaction temperature and reached 99% when the reaction occurred at 85 °C, promising high catalytic activity of the catalyst under mild reaction conditions. No conversion of the canola oil was detected working with pure ZnO. Less than 70% FAME yield was obtained with pure $La_2O_2CO_3$ layered material under the same reaction condition.

4. Discussion

4.1. Effect of the reaction time during the transesterification of canola oil

Generally, microwave radiation has a selective heating function [28]. Some studies on microwave-assisted synthesis of biodiesel reveal that the reaction takes place on the internal and external surfaces of solid catalysts [29]. The radiation directly act on the catalyst and "microwave hot spots" can be created under microwave radiation [30]. The "microwave hot spots" might accelerate the transesterification reaction in a short reaction time, saving a great deal of time required in the biodiesel production. Here we studied FAME yield as a function of time on the prepared $ZnO/La_2O_2CO_3$ catalyst. As shown in Fig. 6, the reaction reached equilibrium only after 5 min at 85 °C, and the yield of FAME was approximately 99%, promising low time consumption for the transesterification reaction using microwave radiation on the prepared catalyst.

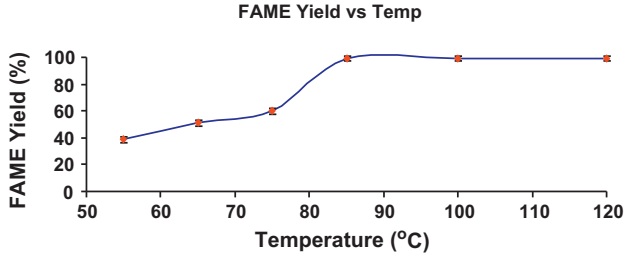

Fig. 5. Results of FAME yield as a function of reaction temperatures. The FAME yield increases continuously as reaction temperature increases and 99% yield was obtained at 85 °C, showing high catalytic activity of the catalyst at mild reaction conditions (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating, 30 min).

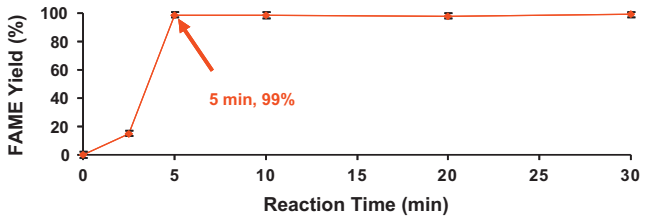

Fig. 6. Results of FAME yield as a function of reaction time (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating).

4.2. Comparison of the microwave radiation with conventional heating

To study the effect of microwave radiation and conventional heating on the yield of FAME, we carried out reactions using an oil bath and controlling temperature in the same way as in the microwave system. As shown in Fig. 7, the reaction reached equilibrium at around 20 min under conventional heating, and the FAME yield was 95%, showing that the prepared $ZnO/La_2O_2CO_3$ is also a very efficient catalyst under conventional heating compared with the reported heterogeneous catalysts. Furthermore, under microwave radiation, the transesterification can be completed in less than 5 min under the same reaction conditions. This indicated that much less time was needed and higher yield of FAME could be obtained under microwave radiation compared to conventional heating. This might due to the effect of possible "microwave hot spots" occurred on the catalyst surface [29], which accelerates the reaction a great deal.

4.3. Comparison of the catalytic activity of the prepared $ZnO/La_2O_2CO_3$ material with industrially used KOH homogeneous catalyst

An important drawback of most solid catalysts used in the biodiesel production is their low reaction rate in comparison with the homogeneous process. In order to determine the reaction rates using the prepared $ZnO/La_2O_2CO_3$ catalyst, after activation at 550 °C, we have compared the catalytic behavior of a 5 wt.% catalyst with a methanolic solution containing 5 wt.% KOH (homogeneous process). The FAME yield of the activated $ZnO/La_2O_2CO_3$ is higher

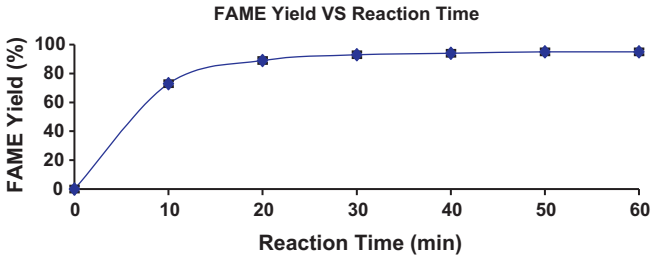

Fig. 7. Results of FAME yield as a function of reaction time using conventional heating (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1).

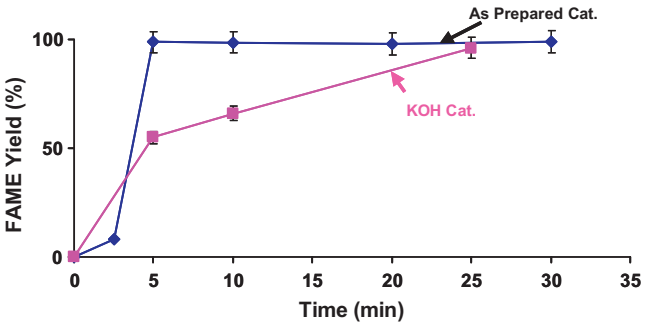

Fig. 8. Evolution of the FAME yields with the time for KOH dissolved in methanol (5 wt.% catalyst) and synthesized $ZnO/La_2O_3CO_3$ (5 wt.% catalyst) (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating).

than the values of the homogenous process, as shown in Fig. 8. After 5 min of reaction time, only 55% FAME yield was detected while 99% was achieved when using the prepared $ZnO/La_2O_2CO_3$ heterogeneous catalyst. The reaction did not reach equilibrium until 20 min of reaction time under the same reaction condition while the reaction was complete in less than 5 min using the prepared heterogeneous catalyst, and the FAME yield was 99%. The comparison of the homogeneous and heterogeneous processes indicates that our solid catalyst could be used as a more efficient and inexpensive alternative to conventional homogeneous catalysts used in the industrial homogeneous process. The acid–base properties of these composite catalysts are likely important in term of selectivity, activity, and stability.

4.4. Effect of amount of catalysts used during the transesterification of canola oil

The effect of amount of catalysts on the transesterification reaction was studied by varying the catalysts between 0 and 0.25 g (5 wt.%); other reactions conditions remained the same. The results listed in Fig. 9 demonstrate clearly that as synthesized $ZnO/La_2O_2CO_3$ is very active in this reaction system, and that even small amounts (0.05 g, 1 wt.%) can lead to complete yield (99%). However, with the use of 0.03 g of the catalyst (~0.6 wt.%), only 12% FAME yield was detected. This observation suggests that the FAME yield might be limited by mass transfer limitations.

4.5. Effect of the catalyst storage condition

In order to study the stability of $ZnO/La_2O_2CO_3$ catalyst under different storage conditions, we have left a certain amount of activated catalyst in air for 3 weeks, and then the catalytic performance was evaluated. Fig. 9 demonstrates that the catalytic activity of the catalyst decreased when in contact with air. The reaction was complete and higher than 95% FAME yield obtained only when 5 wt.% of the catalyst was charged while keeping all the other conditions the same. This is due to the basic catalyst carbonation with CO_2 contained in air, decreasing the catalytic activity. (The catalytic activity can be regenerated by recalcination of the catalysts at 550 °C for another 2 h, a 96% FAME yield was obtained using 0.1 g of catalyst.) However, we stored a certain amount of activated catalyst in argon for 4 weeks, and the catalytic performance was then evaluated. The results (Fig. 10) indicated that the catalytic activity was maintained in argon, and a 99% FAME yield can be achieved when only 1 wt.% catalyst was charged to the reaction, thus confirming the excellent catalytic activity of the $ZnO/La_2O_2CO_3$ in biodiesel production under mild conditions and that proper storage is necessary to maintain catalyst activity.

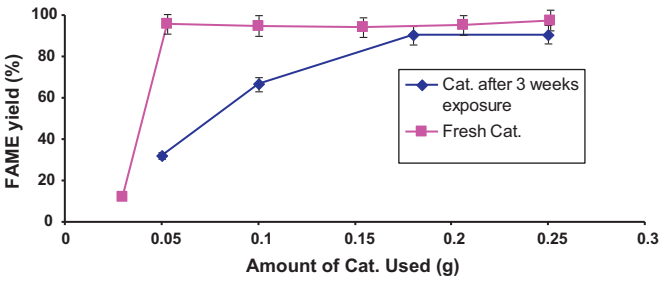

Fig. 9. Results of the catalyst stability test. The catalyst deactivated when exposed to air (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating, 30 min).

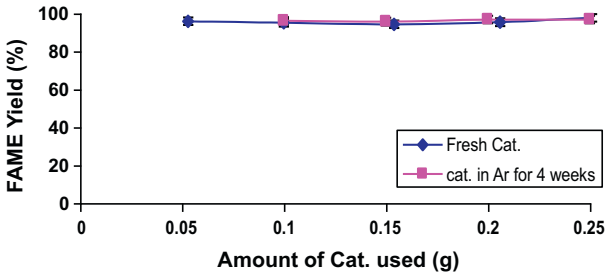

Fig. 10. Results of catalyst stability test. The catalyst was sealed in Ar for 4 weeks (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating, 30 min).

4.6. Effect of methanol to oil molar ratio

The molar ratio of methanol to oil is another important parameter that affects the FAME yields. Stoichiometrically, 3 mol of methanol are required for each mole of oil. However, in practice, the reaction generally requires a large excess of methanol to shift the equilibrium favorably. Here we used conventional heating to discuss the influence of various amounts of methanol to oil molar ratios in order to eliminate the variation caused by microwave heating. As shown in Fig. 11, with the presence of 5 wt.% of the prepared catalyst, a FAME yield of more than 90% can still be obtained when the molar ratio was very close to 12:1. Therefore, a 12:1 molar ratio of methanol to canola oil can be used to obtain high FAME yields using the prepared $ZnO/La_2O_2CO_3$ layered materials as the catalyst.

4.7. Recycled experiments

The stability and recyclability of the prepared catalyst is a very important issue. This has been checked determining the catalytic behavior of the recycled catalysts without any solvent washing process. Fig. 12 shows the recycling experiments carried out under microwave irradiation under the most active conditions. The sec-

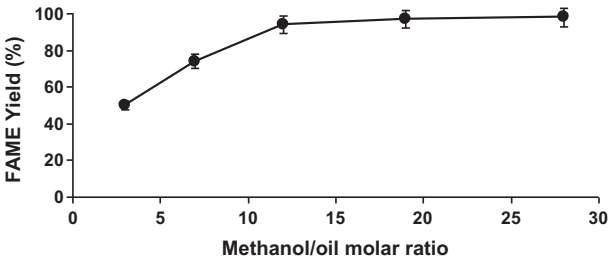

Fig. 11. Results of FAME yield as a function of different methanol/oil molar ratio (molecular weight ~900 g/mol, methanol/canola oil weight ratio of 1 corresponds to around 28:1 in molar ratio, 5 wt.% catalyst, reaction temperature = 85 °C, conventional heating, 1 h).

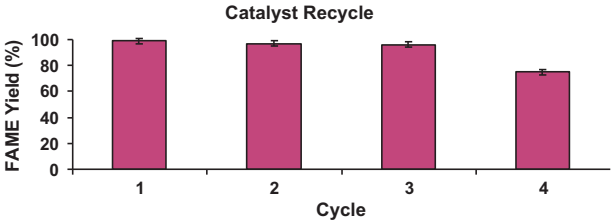

Fig. 12. Effects of reutilization of catalyst on the FAME yield (5 wt.% catalyst, reaction temperature = 85 °C, methanol:canola oil weight ratio = 1, microwave heating, 30 min).

ond cycle was performed using the catalyst recycled from the 1st run directly (no washing and reactivation process) and a 98% FAME yield was achieved. The third cycle was carried out using the materials collected in the second run and activated in molecular oxygen at 550 °C for 2 h, and the 97% FAME yield obtained from the 3rd cycle determined that the prepared $ZnO/La_2O_2CO_3$ catalyst could be recycled and reactivated. However, only 75% FAME yield was obtained in the 4th cycle, this might be due to the loss of catalyst during the re-collection and reactivation process.

4.8. Catalyst leaching test

The determination of the amount of the catalyst leached by dissolution of the solid in the reaction medium is very important. This is relevant for the following reasons. First, leached metal ions can form unwanted soap and water byproducts. Second, the presence of the catalyst in the alcoholic phase and in the ester phase has implications in water consumption for rinsing of the products, creating environmental issues, and increasing the biodiesel cost. Finally, the degree of leaching affects the number of runs when working in a continuous process. Here, we determined the amount of Zn and La of the synthesized Zn–La–oxides leached into the biodiesel by XRF analysis. The results indicated that there is no soluble substance leached away from the synthesized Zn–La–oxides.

5. Conclusion

We report a high biodiesel yield (>95%) in less than 5 min under mild reaction conditions (<100 °C) on a $ZnO/La_2O_2CO_3$ heterogeneous catalyst showing no catalyst leaching into the reaction medium. The $ZnO/La_2O_2CO_3$ catalyst is prepared by a co-precipitation method and characterized by XRD, TGA, SEM, and TEM. The FAME yield as function of different amount of catalyst used was also investigated. Less than 1.0 wt.% catalysts can be charged into the reaction to get higher than 95% FAME yield under mild reaction conditions. The catalytic performance is maintained after storing the catalyst in Ar for a month and no catalyst leaching into the products was found based on XRF analysis. The catalysts even have higher reaction rates than the homogeneous KOH catalysts with the assistance of microwave irradiation. The microwave assistance promises very short reaction time needed for biodiesel production. All these results promote the potential industrial application of the synthesized $ZnO/La_2O_2CO_3$ as an ideal catalyst for fast biodiesel production. This is the first example of a highly active, inexpensive, and low energy consuming heterogeneous catalyst without a leaching problem.

Acknowledgements

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