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Potassium modified layered $Ln_2O_2CO_3$ (Ln: La, Nd, Sm, Eu) materials: Efficient and stable heterogeneous catalysts for biofuel production

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Potassium modified layered $Ln_2O_2CO_3$ (Ln: La, Nd, Sm, Eu) biodiesel catalysts were prepared by a coprecipitation method followed by an overnight reflux. High fatty acid methyl ester (FAME) yield (>95%) was achieved under mild reaction conditions (<100 °C). The FAME yields were investigated as a function of temperature and catalyst weight percentage. $Nd_2O_2CO_3$ shows a better catalytic performance with a higher reaction rate than the industrial homogeneous KOH catalyst using both microwave irradiation and conventional heating methods. Approximately 100% FAME yield can be reached at 95 °C (microwave radiation) by 1.0 wt. % $Nd_2O_2CO_3$ within 10 min, while the same yield can be reached by 3.0 wt. % $Nd_2O_2CO_3$ at 95 °C (conventional heating method). In addition, leaching tests of the catalysts were performed; no leached rare earth metal ions were detected and the amounts of leached potassium were all under 5 ppm (ASTM standard). The synthesized layered $Ln_2O_2CO_3$ materials offer a group of ideal alternative catalysts for industrial biodiesel production.

Introduction

The increasing demand for energy, concerns about environmental consequences of fossil fuels, and depletion of world's fossil fuel reserves, have led to the need for developing alternative transportation biofuels. To be a viable substitute for a fossil fuel, an alternative fuel should not only offer superior environmental benefits, but also be economically feasible. Biodiesel, a compromising renewable diesel fuel made from biological sources such as vegetable oils and animal fats, was originally proposed by Rudolf Diesel[1] a century ago, has been attracting wide attention in recent years.[2-4] Because of its similar physiochemical properties to petroleum-based diesel, biodiesel can be directly used in existing diesel engines.[5, 6] Moreover, biodiesel is biodegradable, non-toxic, more efficient than gasoline because of its oxygen content, and is considered to generate less greenhouse gases[5, 7] due its closed CO_2 cycle (carbon in vegetable oil is mainly from the CO_2 in air).[6, 7] In order to convert fatty acid triglycerides, major composition of Vegetable oil and animal fats, to fatty acid esters (biodiesel), short chain alcohols are most commonly used as coreactants to achieve this transesterification process. Since such processes are not spontaneous, different catalysts have been evaluated for biodiesel production,[8] such as basic catalysts,[9] acid catalysts,[10] and enzymes;[11, 12] among them, the most common and industrialized way of producing biodiesel involves using a homogeneous basic catalyst such as KOH.[13, 14] However, there are major disadvantages of these homogeneous basic catalysts. Neutralization treatment of the product (with a great deal of byproducts) will cause saponification, which makes the ester separation more difficult; moreover, the overall process will generate a great deal of waste water which creates negative environmental effects. The multistep separation process ultimately decreases the yield and increases the cost of biodiesel.[14, 15] Another type of commonly used catalysts for biodiesel production is acid catalysts. Strong liquid acids (H_2SO_4) are the most common active homogeneous acid catalysts. Apart from their longer reaction time compared to basic catalysts, [16] they could cause corrosion problems of the metallic parts of the reaction system. Heterogeneous acid catalysts for biodiesel synthesis have also been limited due to unfavorable side reactions, more critical reaction conditions and even slower reaction rates.[10,17,18.] Therefore, there is a need for alternative catalysts for industrial biodiesel production. Rare earth based materials, with unique properties, are found in many applications such as CO_2 sensors,[19] optical fibers,[20] and catalysts.[21-23] In the fields of catalysis, in particular, rare earth based materials are widely used in water gas shift (WGS) reactions,[24] zeolite catalysis,[23] and oxidative dehydrogenation of ethane.[25] Among various rare earth metal based materials, rare earth oxycarbonates $Ln_2O_2CO_3$ (Ln: rare earth) have received considerable attention.[19, 26, 27] The earth oxycarbonates have three different types of crystal structures: type-I contains square layers (tetragonal), type-II has a hexagonal structure, and type-IA a monoclinic form.[28] Type-II compounds are the most promising compounds as catalysts due to their stability and higher durability against both water and carbon dioxide.[29, 30]

In a simplified description, type II $Ln_2O_2CO_3$ are believed to have the layer-like structures with two-dimensional $(Ln_2O_2)^{2+}$ layers and CO_3^{2-} ions in between. However, some other studies indicate that the crystal structure is more complex; more than one distinct metal site is present in the structure due to the disorientation of the carbonate groups.[31, 32]

In our previous work, $La_2O_2CO_3/ZnO$ heterogeneous basic catalysts were synthesized for transesterifications, A microwave heating method was used for the biodiesel systhesis.[31] In this work, a group of rare earth oxycarbonate type- II $Ln_2O_2CO_3$ (Ln = La, Nd, Sm, Eu) layered materials were successfully synthesized by the same wet chemistry approach and their basic catalytic activities were studied in biodiesel production by both conventional heating and microwave reaction methods. The catalytic performances (reaction rate, stability and recyclability) of $Ln_2O_2CO_3$ were then compared with industrial homogeneous catalysts. We report that a new group of layered rare earth based solid materials achieved a high biodiesel yield (> 95%) in a short reaction time under mild reaction conditions (< 100 °C) by both conventional heating and microwave reaction methods. A group of $Ln_2O_2CO_3$ layered materials are reported, for the first time, as highly active and low energy consuming heterogeneous catalysts for transesterifications.

Experimental

Catalyst Synthesis

In a typical experiment, 0.09 mol of Ln $(NO_3)_3$•$6H_2O$ (Ln= La, Nd, Sm, Eu) was dissolved in 200 mL deionized distilled (D.D.I.) water. The solution was heated up to 85 °C. 0.30 mol of KOH and 0.30 mol of K_2CO_3 were dissolved in 400 mL D.D.I. water to make a basic mixed solution. The basic mixture was then added drop-wise into the hot solution of Ln $(NO_3)_3$•$6H_2O$ until the pH reached 10.00 (white slurries formed in this process). The slurries were transferred into a round-bottom flask and put under reflux in an oil bath at 100 °C overnight. The products from the reflux were washed by D.D.I. water until the pH was the same as that of the D.D.I. water, then dried at 120 °C overnight. The raw products were calcined at 550 °C for 6 h before being used as catalysts for transesterifications reaction.

A control group of materials were also synthesized using a mixture of NH_3 and $(NH_4)_2CO_3$ solution to substitute for the KOH and K_2CO_3 mixed basic solution. In a typical synthesis, 0.03 mol of $Ln(NO_3)_3$•$6H_2O$ (Ln= La, Nd) were dissolved in 70 mL D.D.I. water separately. The two dissolved rare earth solutions were heated on a hot plate separately up to 85 °C. NH_3 (0.10 mol) and 0.10 mol of $(NH_4)_2CO_3$ were mixed and D.D.I. water was added to make a 130 mL basic mixed solution. The basic mixed solution was added drop-wise into the hot solutions of $Ln(NO_3)_3$•$6H_2O$ separately until the pH reached 10.0. The precipitation slurries were transferred into two round-bottom flasks, and separately put under reflux in an oil bath at 100 °C overnight. The products from reflux were washed by D.D.I. water until the pH was the same as that of the D.D.I. water, and then dried at 120 °C overnight. The 7 raw products were calcined at 550 °C for 6 hours before being used as catalysts for transesterifications.

Catalyst Characterization

Thermogravimetric Analyses (TGA). Thermogravimetric analyses (TGA) in air were performed in a Hi-Res TA 2950 thermogravimetric analyzer with the air flow at a rate of 60 mL/min from 25 °C to 900 °C at a heating rate of 10 °C/min.

The Powder X-ray Diffraction (XRD). The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer using Cu Kα (λ = 0.15406 nm) X-ray radiation with a beam voltage of 40 KV and 44 mA beam current. XRD patterns were collected from 5 ° to 75 ° in a continuous mode using a scan rate of 2 °/min.

Scanning Electron Microscope (SEM). The crystal morphologies of the samples were investigated using an environmental scanning electron microscope (ESEM) FEI Quanta FEG 250 with an accelerating voltage of 2 KV. The powder samples were ultrasonically dispersed in ethanol for analysis. The suspensions were deposited on a gold-coated silicon wafer, and allowed to dry in a vacuum system overnight. The wafer was then mounted onto a stainless steel sample holder using carbon tape.

Transmission Electron Microscopy (HRTEM). HRTEM images were obtained using a JEOL 2010 instrument with an energy dispersive spectroscopy (EDS) system at an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in ethanol by sonication; the dispersion was then dropped on a carbon coated copper grid and allowed to dry.

N_2-adsorption. BET surface area measurements were done on a Quantachrome Autosorb iQ2 instrument. Prior to the experiments all samples was degassed at 120 °C for 12 hours.

Temperature Programmed Desorption (TPD-CO_2). TPD-CO_2 was carried out in a furnace with a GC Thermal Conductivity Detector. Catalyst powder (0.3 g) was placed in a quartz reactor and then pretreated at 550 °C in pure He for 6 h. After the pretreatment, a pure CO_2 gas (20 mL/min) was fed 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 were 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).

Basic Strengths Test by Indicators. The H_ acidity function is the accepted parameter for the strength of basic catalyst sites. The basic strength of the samples were determined using various 0.1 wt. % Hammett indicators from Aldrich in methanol; these indicators are dicinnamalacetone (pKBH+ = -3.0), p-dimethyldiazobenzene (dimethyl yellow, pKBH+ = +3.3), dibromothymol sulfophthalein (thymol blue, pKBH = +7.2), 4,4'-dioxyhthalophenone (pKBH+ = +9.3), and 2, 4-dinitroaniline (pKBH+ = 15.4). The samples were calcinated at 550 °C for 6 hours, then cooled to 120 °C in the oven, and rapidly transferred to a weighting bottle after being taken out of the oven. Then, one or two drops of 0.1 wt.% indicator solutions in methanol were added to the samples. Finally the color changes were visually observed and recorded. If, for example, $La_2O_2CO_3$ sample turns red in the presence of 4,4'-dioxyhthalophenone but does not change color in the 2, 4-dinitroaniline solution, the value of H_ was taken as + 9.3.

Atomic Absorption Spectrometer (AAS). The elemental analysis was performed using a PerkinElmer Model 3100 flame atomic absorption spectrometer (FAAS) by the standard calibration method. The solid $Ln_2O_2CO_3$ layered materials (before and after reactions) were firstly dissolved in concentrated HNO_3 and D.D.I. water was then added to reach a designated volume in volumetric flasks. The standard solutions were prepared from the Alfa Aesar Specpure Spectrochemical Analytical standard solutions.

Catalytic Reactions and Products Analysis

Transesterification Process. Transesterification reactions with a conventional heating method were carried out in a temperature controlled oil bath. Canola oil (2.5 g) and methanol (2.5 g) were mixed with 0.25 g (5 wt.%) catalyst into a vial, and the reactants were isolated from the vial cap by a blue PTFE face silicone. Reactions took place at different temperatures and with a vigorous stirring rate of 900 rpm. Transesterification using a microwave heating method were carried out in the Biotage TM Initiator 2.5. The reaction temperature and reaction time were controlled automatically.

Biodiesel Yield Test by Gas Chromatograph. After the transesterification process, the GC samples were prepared by dissolving the oil layer of the products in THF and Heptane, and then analyzed by a 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 x 0.53 mm x 0.16 µm.

The yields of FAME for transesterification process were calculated using the equation in scheme 1S (see Supporting Information (SI)); in which, FAME stands for fatty acid methyl ester, MG stands for monoglycerides, DG stands for diglycerides, and TG stands for triglycerides.

Results

Materials Structures, morphologies and Properties

Thermogravimetric analysis (TGA) is shown in Fig. 1. The first major weight loss of $Ln_2O(CO_3)_2$ materials took place at around 450 °C to 480 °C, which is due to the transformation of $Ln_2O(CO_3)_2$ to a layered $Ln_2O_2CO_3$ material by losing CO_2. The second weight loss between 600 °C and 750 °C is due to the second loss of CO_2, during which Ln_2O_3 materials are formed from the layered $Ln_2O_2CO_3$ materials. Both mass losses were assigned to the loss of CO_2 based on TGA-mass spectrometry analysis.[33-36] The minor loss of weight before these two major weight losses is due to the water component in the structure either by physical absorption or between the layered structures. The total weight losses from $Ln_2O(CO_3)_2$ materials range from 24 wt.% to 28 wt.% and is in the sequence of: $La_2O_2CO_3 > Nd_2O_2CO_3 > Sm_2O_2CO_3 > Eu_2O_2CO_3$ due to the different molar mass of rare earth metals. By subtracting the minor loss (~5 wt.%) caused by water loss from the total weight loss, the percentage of weight loss matches the weight percentage of the two CO_2 molecules lost from the $Ln_2O(CO_3)_2$ materials. The thermal stability among these layered $Ln_2O_2CO_3$ materials is in the sequence of: $La_2O_2CO_3 > Nd_2O_2CO_3 > Sm_2O_2CO_3 \approx Eu_2O_2CO_3$.

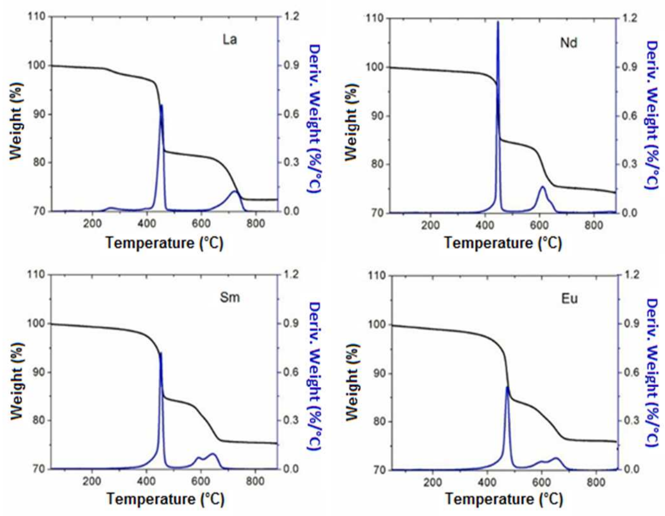


Fig. 1 TGA of prepared $Ln_2O(CO_3)_2$ samples (before calcination).

X-ray diffraction (XRD) patterns have confirmed the transformation from $Ln_2O(CO_3)_2$ (Fig. 2 a) to layered $Ln_2O_2CO_3$ (Fig. 2 b) after calcination at 550 °C for 6 h, which also matched the TGA data we have collected. The X-ray diffraction patterns of a group of layered $Ln_2O_2CO_3$ (Ln = La, Nd, Sm, Eu) materials (Fig. 2 b) show similar patterns with a slight successive shift (to higher 2θ values) in the major peak position due to the size difference of the rare earth metal ions ($La^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+}$). The calculated d spacings of the (002) planes for the $Ln_2O_2CO_3$ (Ln = La, Nd, Sm, Eu) materials are $La_2O_2CO_3$: 7.91 Å; $Nd_2O_2CO_3$: 7.81 Å; $Sm_2O_2CO_3$: 7.68 Å; $Eu_2O_2CO_3$: 7.62 Å respectively, which are all close to the d spacings reported in the JCPDS database ($La_2O_2CO_3$: 7.97 Å; $Nd_2O_2CO_3$: 7.85 Å; $Sm_2O_2CO_3$: 7.67 Å; $Eu_2O_2CO_3$: 7.63 Å). For Nd, Sm and Eu based layered materials, peak broadenings were observed, which may be due to smaller crystallite sizes of synthesized materials.

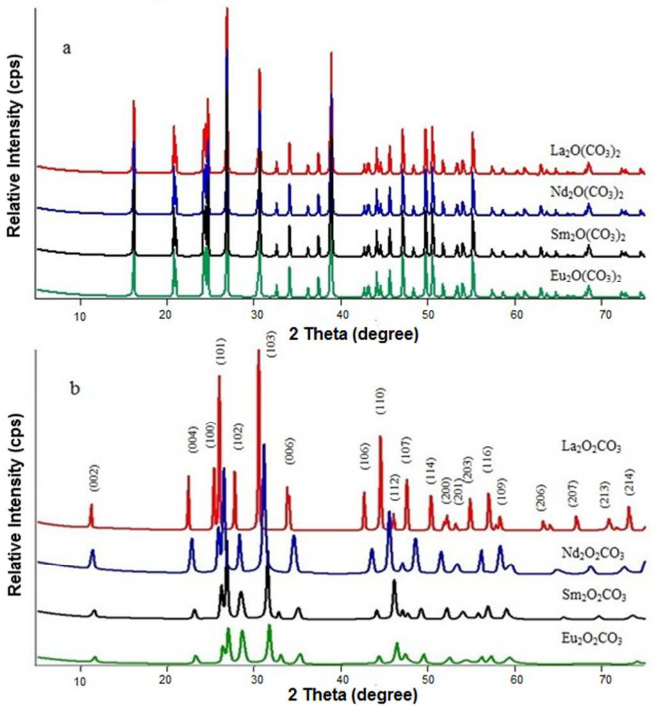


Fig. 2 XRD patterns of a, synthesized $Ln_2O(CO_3)_2$ (Ln = La, Nd, Sm, Eu) solid materials before calcination (JCPDS 28-0512) and b, synthesized layered rare earth oxycarbonates materials $Ln_2O_2CO_3$ (Ln = La, Nd, Sm, Eu) after calcination (JCPDS 37-0804).

The ESEM images of $Ln_2O(CO_3)_2$ are shown in Fig S1 (see Supporting Information (SI)). The synthesized materials (before calcination) contained bulk aggregates. After calcination, $Ln_2O_2CO_3$ nanorod aggregates were formed. The detailed microstructures (HRTEM) of $Ln_2O_2CO_3$ are shown in Fig. S2 (a) - (h) (see Supporting Information (SI)); $La_2O_2CO_3$ shows larger crystallite size than other $Ln_2O_2CO_3$ materials, which is in accordance with peak broadening results in X-ray diffraction. The synthesized $La_2O_2CO_3$ and $Nd_2O_2CO_3$ (Fig. S2 (b)&(d)) showed obvious layered structures, while $Sm_2O_2CO_3$ and $Eu_2O_2CO_3$ (Fig. S2 (f)&(h)) showed less obvious layered structures. The high magnification TEM micrograph in Fig. S2 (b) shows lattice fringes with a lattice spacing of roughly 0.797 nm, which can be identified as the (002) planes of $La_2O_2CO_3$ material as reported in the literature.[37] The BET surface area results are shown in Table S1 (see Supporting Information (SI)), the layered $Ln_2O_2CO_3$ materials have a surface area ranging from 11 to 19 g/m^2 and the $Nd_2O_2CO_3$ sample has the largest surface area among these four $Ln_2O_2CO_3$ layered materials. The basicity test results by indicators and TPD-CO_2 are also shown in Table S1(see Supporting Information (SI)). The $Ln_2O_2CO_3$ layered materials all have the same basic strength by indicators tests and the $Nd_2O_2CO_3$ sample desorbs the largest amounts of CO_2 (0.33 mmol/g) among all four layered $Ln_2O_2CO_3$ materials.

Catalytic Performance

Catalytic Results of $Ln_2O_2CO_3$ Layered Materials at Different Temperatures. The FAME yields over $Ln_2O_2CO_3$ layered materials catalysts are plotted as a function of temperature in Fig. 3. The FAME yield increased with increasing temperatures and a high FAME yield (~100 %) can be reached. $Nd_2O_2CO_3$ was shown to be the most active material, by which ~90 % FAME yield was obtained at temperatures as low as 75 °C and ~100 % FAME yield was obtained at a temperature of 95 °C. The order of catalytic activities is $Nd_2O_2CO_3 > La_2O_2CO_3 > Sm_2O_2CO_3 \approx Eu_2O_2CO_3$.

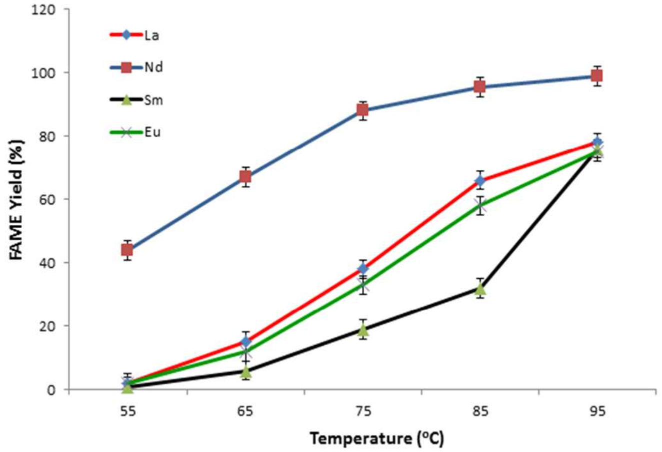


Fig. 3 Results of biodiesel (FAME) yield as a function of reaction temperature by layered $Ln_2O_2CO_3$ materials (Ln: La, Nd, Sm, Eu) (Conventional heating method, 5 wt. % catalysts loaded, reaction time: 1 hour, MeOH: Oil =1 by weight).

Catalytic Results of Different Amount of Catalysts Used in Transesterification. The effect of the amount of catalysts used in transesterification was investigated by varying the weight percentage of catalysts introduced in the reaction system while other reaction conditions remained unchanged as previously mentioned. The results listed in Figs. 4&5 showed that the as synthesized $Nd_2O_2CO_3$ is the most active catalyst among $Ln_2O_2CO_3$ materials in the reaction system. Complete yields (~100 %) can be achieved using 0.15 g (3.0 wt.%) synthesized $Nd_2O_2CO_3$. When $Nd_2O_2CO_3$ was used as the catalyst of transesterification using the microwave heating method, complete yields (~100 %) can be achieved using as little as 0.05 g $Nd_2O_2CO_3$ (1.0 wt. %).

Comparison of the Catalytic Activity of the Prepared Layered $Nd_2O_2CO_3$ Material with Industrial Catalyst KOH. One of the biggest concerns of heterogeneous catalysts is the longer reaction time and higher energy consumption as compared to homogeneous catalysts. In order to compare the catalytic behavior of our layered heterogeneous catalysts and the industrial homogeneous catalyst KOH, 5 wt.% $Nd_2O_2CO_3$ catalyst and 5 wt.% KOH were separately introduced into two

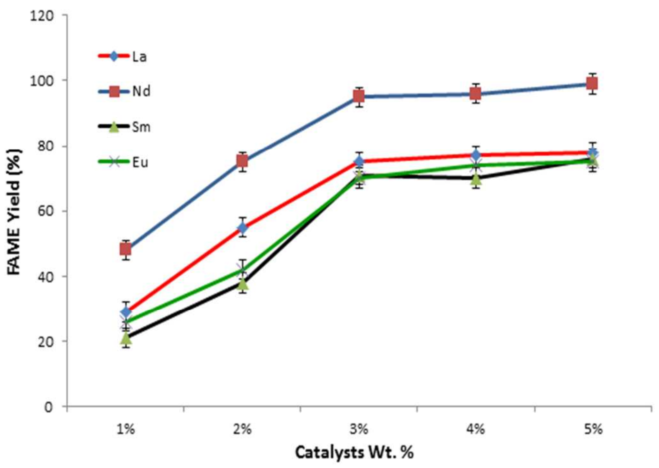


Fig. 4 Results of biodiesel (FAME) yield as a function of different catalyst amounts (weight %) of layered $Ln_2O_2CO_3$ materials (Ln: La, Nd, Sm, Eu) (conventional heating method, reactions temperature: 95 °C, reactions time: 1 hour, MeOH: Oil =1 by weight).

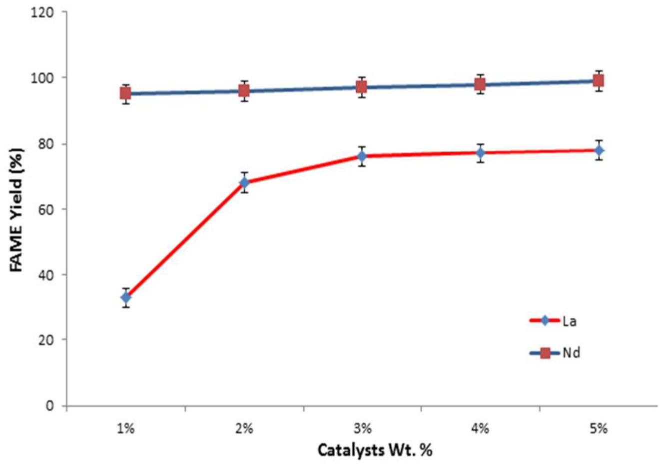


Fig. 5 Results of biodiesel (FAME) yield as a function of different catalyst amounts (weight %) of layered $Ln_2O_2CO_3$ materials (Ln: La, Nd) (microwave heating method, reactions temperature: 95 °C, reactions time: 30 min, MeOH: Oil =1 by weight).

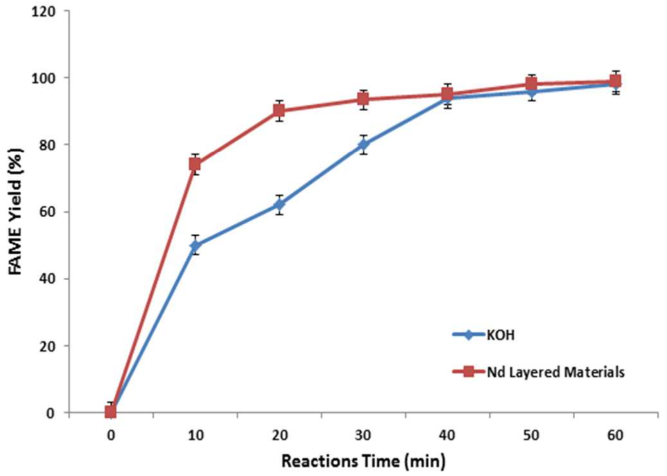


Fig. 6 Results of biodiesel (FAME) yield as a function of reactions time (conventional heating method, reactions temperature: 95 °C, 5 wt.% catalysts, MeOH: Oil =1 by weight)

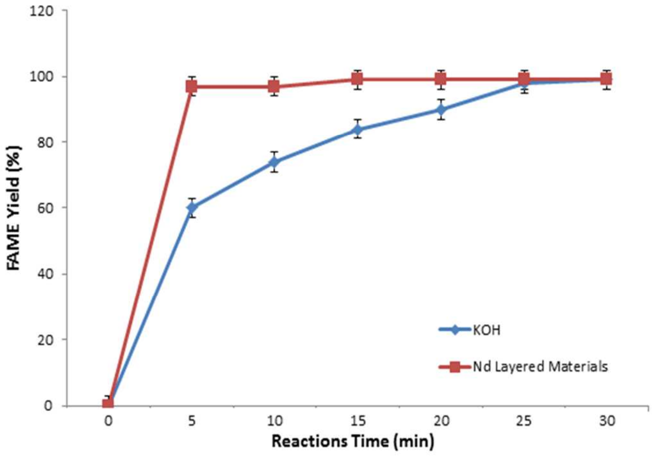


Fig. 7 Results of biodiesel (FAME) yield as a function of reactions time (microwave heating method, reactions temperature: 95 °C, 5 wt.% catalysts, MeOH: Oil =1 by weight).

biodiesel production systems: under the same reactions conditions (95 °C, MeOH: Oil = 1:1 by weight). The results are shown in Figs. 6&7. For the conventional heating method (Fig. 6), it took only 20 min for the reaction to reach ~90 % FAME yield using $Nd_2O_2CO_3$ as the catalyst while it took almost 40 min for the industrial catalyst KOH to achieve the same FAME yield. For the microwave heating method (Fig. 7), the transesterification process was completed within 5 min when $Nd_2O_2CO_3$ was used, while the reaction process was completed in 25 min when KOH was used. In summary, for both conventional heating and microwave heating reaction systems, the layered $Nd_2O_2CO_3$ material showed a much faster reaction rate than commercially used KOH with the same high FAME yield (~100 %). In addition, the microwave heating method is found to be more efficient than the conventional heating method. This might be because the microwave heating method generated "microwave hot spots" on the catalyst surface, which greatly accelerated the reaction rates.[38]

The Comparison of the Catalytic Activity of the Potassium Contained Base and Ammonium Contained Base Synthesized Materials. Ammonium containing base synthesized layered $Ln_2O_2CO_3$ materials were used as control samples, to investigate the effects of potassium doping in the layered materials. The XRD patterns of synthesized layered $Ln_2O_2CO_3$ (Ln: La and Nd) materials by separately using NH_3, $(NH_4)_2CO_3$ mixtures, and KOH/K_2CO_3 mixtures as basic starting materials are shown in Fig. S3 (see Supporting Information (SI)). All synthesized rare earth based layered materials with different starting bases have similar diffraction patterns; however, the materials synthesized using potassium contained bases (labeled as $K^{-}Ln_2O_2CO_3$) have relatively larger d spacings (the d spacings were calculated for the (002) plane based on the raw XRD data) as compared to the materials synthesized using ammonium containing basic solutions (labeled as NH_3-$Ln_2O_2CO_3$). The d spacings are 7.91 Å for $K^{-}La_2O_2CO_3$; 7.85 Å for NH_3-$La_2O_2CO_3$; 7.81 Å for K-$Nd_2O_2CO_3$; 7.70 Å for NH_3-$Nd_2O_2CO_3$ respectively. The larger d spacings are simply due to potassium doping in the layered $Ln_2O_2CO_3$. Studies by Iqbal et al.[39] and Attfield et al.[26] suggested that the lithium ion can be doped into the rare earth layered materials by partly replacing the carbonate groups in the structure. Our study suggested that the introduced potassium, similar to lithium, could partly replace carbonate groups, the resultant structures are derived from hexagonal geometry (space group P63/mmc) as proposed by Iqbal et al. [39] The diffraction patterns of K-$Ln_2O_2CO_3$ compared to NH_3-$Ln_2O_2CO_3$ contain minor additional new peaks, which do not correspond to any known impurity; the additional peaks may reflect carbonate ordering due to potassium doping in layered $Ln_2O_2CO_3$.

Interestingly, K-$Ln_2O_2CO_3$ also showed less peak broadening compared to NH_3-$Ln_2O_2CO_3$, suggesting possible larger crystallite sizes of potassium doped $Ln_2O_2CO_3$ and less carbonate group distortion. The comparison of TEM pictures between potassium containing base synthesized $Nd_2O_2CO_3$ material (Fig. S4 a&b) (see Supporting Information (SI)) and ammonium containing base synthesized $Nd_2O_2CO_3$ material (Fig. S4 c&d) (see Supporting Information (SI)) showed similar features of layered structure.

In the catalytic reaction, 2.5 g Canola oil, 2.5 g methanol and 0.25 g (5 wt. %) were reacted at 95 °C with vigorous stirring for 60 min. The results of biodiesel yield are shown in Table S2 (see Supporting Information (SI)). The $La_2O_2CO_3$ and $Nd_2O_2CO_3$ materials synthesized by NH_3 and $(NH_4)_2CO_3$ are much less active in transesterification compared to the $La_2O_2CO_3$ and $Nd_2O_2CO_3$ materials synthesized by KOH and K_2CO_3 basic mixtures. Doping potassium in the layered $Ln_2O_2CO_3$ materials plays a key role in enhancing catalytic performance in biodiesel catalytic reactions. Further discussion is shown in the section on mechanistic studies.

Recyclability and Stability Tests of Layered $Ln_2O_2CO_3$ Materials

Recyclability and stability are important factors for evaluating feasibility of biodiesel catalysts. The tests were carried out by a direct run process using a conventional heating method. The second and third cycles were carried out by reusing the recycled catalyst from a previous run (no washing and reactivation process) while the fourth cycle involved using the materials collected in the third run and re-calcined in air at 550 °C for 2 hours. After the 3rd cycle of reaction (Fig. 8), the FAME yield for biodiesel production using Nd_2O_2CO3 catalyst dramatically dropped to ~50 %. The loss of active sites was probably the main reason for the drop in the catalytic performance. The active sites in layered materials could be blocked by the organic acid which was produced by the hydrolysis of oil after 3 hours reaction time. On the 4th cycle, we collected the catalysts after the third run and activated them by calcination at 550 °C for 2 hours in air before running and we have obtained ~90 % of FAME yield for the $Nd_2O_2CO_3$ catalyst.

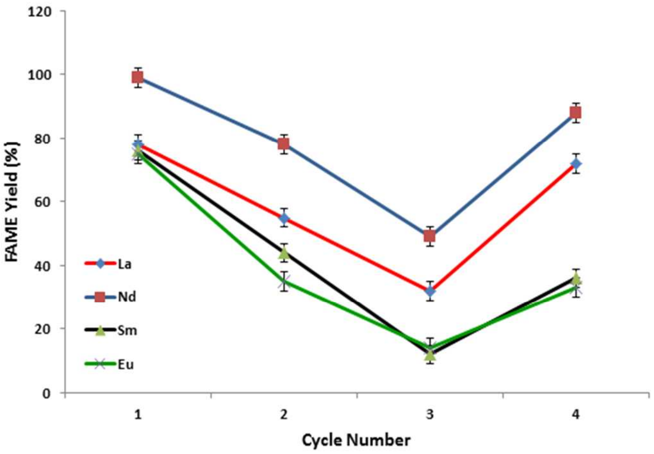


Fig. 8 The recyclability tests of layered $Ln_2O_2CO_3$ materials (Ln: La, Nd, Sm, Eu) (Conventional heating method, reactions temperature: 95 °C, 5 wt.% catalysts loaded, reactions time: 1 hour, MeOH: Oil = 1 by weight).

The XRD patterns of $Ln_2O_2CO_3$ materials after 4th cycle are shown in Fig. S5 (see Supporting Information (SI)). After 4 cycles of successive transesterification, the same layered structure was maintained by $La_2O_2CO_3$ because of its better thermal and structural stabilities; however, minor new peaks (Nd_2O_3) appeared in the XRD pattern of the $Nd_2O_2CO_3$ material, similar minor new peaks (Ln_2O_3) can be found for Sm and Eu based layered materials with some of the peaks (related to the $Ln_2O_2CO_3$ structure) diminishing or disappearing. The small drop in yield ($La_2O_2CO_3$, $Nd_2O_2CO_3$) is probably due to the weight loss in the process of recollection and reactivation after several cycles and partial decomposition to Ln_2O_3.[40, 41] $La_2O_2CO_3$ and $Nd_2O_2CO_3$ materials were still catalytically active after the 4th cycle because of their better thermal and structural stabilities.

Meanwhile, the $Sm_2O_2CO_3$ and $Eu_2O_2CO_3$ materials were totally deactivated during the process because of their decomposition or their poor thermal stabilities. The morphology changes of layered $Ln_2O_2CO_3$ materials before reaction and after recycle are shown in the SEM pictures in Figs. S6 (a) - (h) (see Supporting Information (SI)); in the pictures, the morphologies of $La_2O_2CO_3$ materials before and after the reactions are almost the same, and for layered $Nd_2O_2CO_3$, $Sm_2O_2CO_3$, and $Eu_2O_2CO_3$ materials, the pictures have shown that new structural phases appeared. The appearance of new phases in recycled $Nd_2O_2CO_3$, $Sm_2O_2CO_3$, and $Eu_2O_2CO_3$ materials also agreed with their XRD results. The recycling tests suggested that the catalysts are recyclable and are stable after the 4th cycle. Therefore, the solid layered materials could be used in a scaled-up industrial process as efficient and stable biodiesel catalysts.

Leaching Tests

The potassium amount in solid $Ln_2O_2CO_3$ materials tested by FAAS is shown in Table S3 (see Supporting Information (SI)). Layered $Nd_2O_2CO_3$ material has the largest amount (1.45 wt. %) of potassium among these $Ln_2O_2CO_3$ materials. The comparisons between the potassium amount before and after 4 cycles of transesterification have shown that the potassium is lost during the reaction process. According to the calculation of the actual weights of potassium in the solid catalysts, neither the total potassium amount in fresh solid $Ln_2O_2CO_3$ materials nor the lost potassium amount (amount difference between fresh and recycled solid $Ln_2O_2CO_3$ materials) is sufficient to achieve more than 90 % of FAME yield as to the reported potassium contained catalysts.[42, 43] The approximate molar percentage of potassium in the solid $Ln_2O_2CO_3$ materials was also calculated. Take K-$La_2O_2CO_3$ material for example; 1.35 wt.% K was detected by AAS, which means, in 100 g of K-$La_2O_2CO_3$ material, there are 1.35 g of K and approximate 98.65 g of $La_2O_2CO_3$ in the material. Then these masses were converted to moles by dividing by their molar mass separately. The molar percentage of potassium is the molar amount of potassium divided by the total molar amount of potassium and $La_2O_2CO_3$. The data showed that the molar ratios between K^+ and $Ln_2O_2CO_3$ materials are all around 1:9. Thus the molar ratios between K^+ and Ln^{3+} are all around 1:18. The potassium and rare earth metal amount in biodiesel products tested by X-Ray Fluorescence (XRF) is also shown in Table S4 (see Supporting Information (SI)). There is no detectable (detect limit: 1 ppm) rare earth leaching in the biodiesel products. Even though potassium is lost during the reaction process, most of the potassium ions were leached into the methanol phase instead of the biodiesel products; the amounts of potassium we could trace by XRF are all under the detection limit of alkali metal amounts (5 ppm) by ASTM methods (American Society for Testing and Materials). The leaching tests also suggested these potassium modified layered $Ln_2O_2CO_3$ materials are stable in the biodiesel production. Even though information of the toxicity for the rare earth elements remains relatively scarce, according to the literature no research suggested that oxycarbonates, carbonates, or oxides of rare earth metal have any effect on health or environment. Rare earth salts are regarded as only slightly toxic if they are soluble and nontoxic if they are insoluble. As for the catalysts in this research, no rare earth leaching was detected (< 1 ppm) in the biodiesel product, therefore, the toxicity would not be a great concern here.

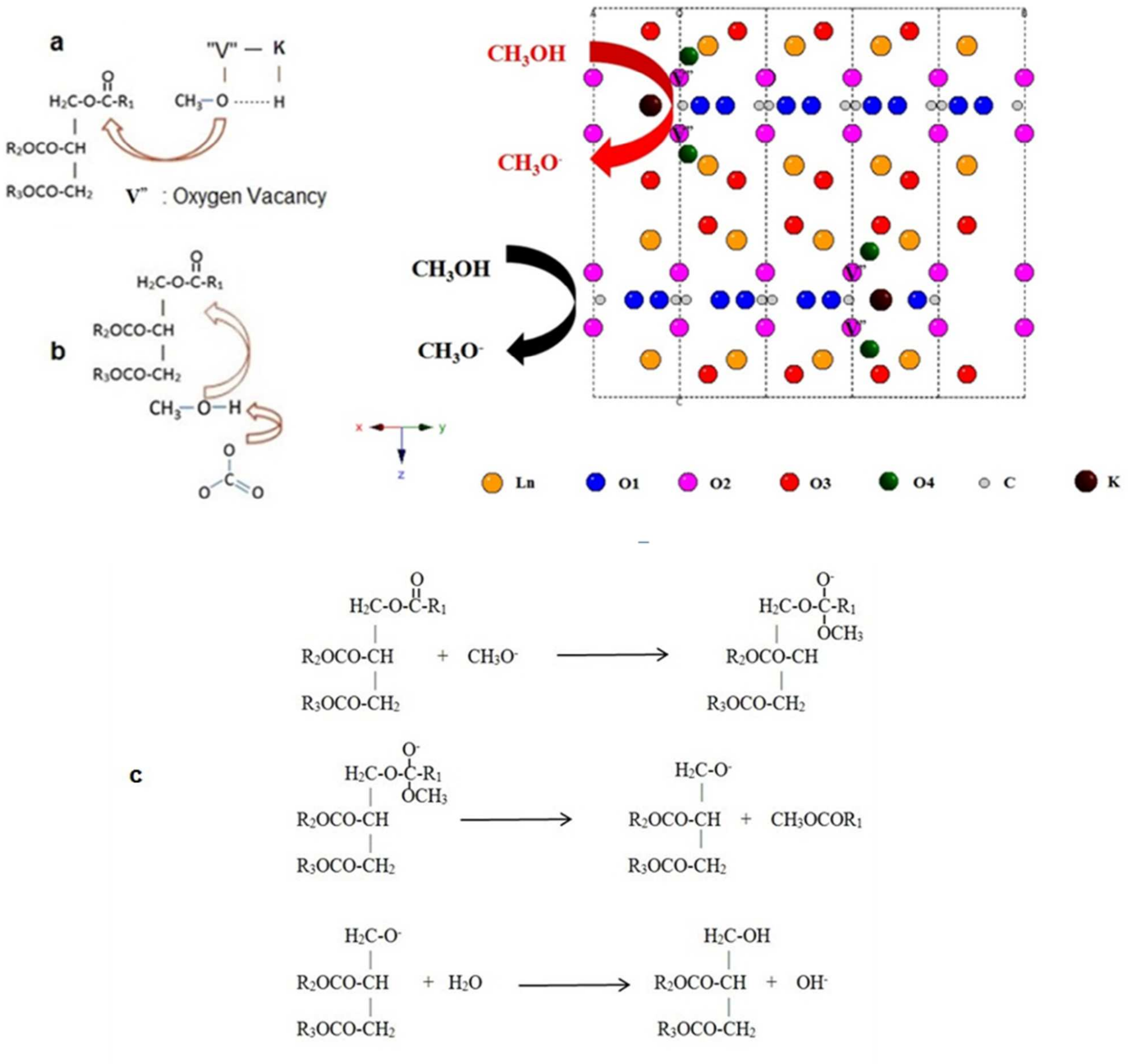
Discussion

Proposed Mechanism

The mechanism of the catalytic transesterification process is proposed as shown in Scheme 1 (structure of the rare earth layered materials was constructed by CrystalMaker Software). The major catalytic active sites in the $Ln_2O_2CO_3$ layered materials are oxygen vacancies, which are mostly created by potassium doping as shown in Scheme 1a. By introducing potassium in $Ln_2O_2CO_3$, dopants displace both C and O1 (of the carbonate group layer) along the ab plane, at the same time partially creating C and O1 (newly displaced) vacancies, and transferring half O2 to interstitial sites to minimize internal repulsion, leading to a formula $Ln_2K_{2x}O_{2+2x}(CO_3)_{1-x}$. The oxygen in hydroxyl group would bond to an oxygen vacancy and the bond between hydrogen and oxygen would break, consequently, a methoxide group would leave the catalysts and react with triglycerides to form FAME. Other active sites could be the oxygen vacancies (intrinsic defects) in carbonate groups between the layers, as shown in Scheme 1. The basic sites of the carbonate group could also attach to the hydrogen in hydroxyl groups and generate the methoxide group for reaction. The reactions between triglycerides and methoxides are also shown in Scheme 1, step by step. The hydroxide ions produced from the last step of the reaction would go back to the materials and bond to the hydrogen that had been left there and form water to be recycled in these transesterification reactions. The active sites in layered materials could be blocked by oil after the reactions, leading to catalytic performance drop. Catalytic activities could be regained after re-calcination; thermal and structure instability, however, would cause partial decomposition of the $Ln_2K_{2x}O_{2+2x}(CO_3)_{1-x}$ to Ln_2O_3, hence decrease of the catalytic performance. Such thermal and structure instability might arise from differences of ionic radii and valences for different rare earth elements. The larger ionic radii gives the layered $Ln_2K_{2x}O_{2+2x}(CO_3)_{1-x}$ better thermal and structure stability, however, multiple oxidation states in Nd as compared to La, offer enhanced catalytic activity (more oxygen vacancies are formed when Nd^{3+} is converted to Nd^{2+}). Nevertheless, due to the poor thermal and structural stability, $Sm_2K_{2x}O_{2+2x}(CO_3)_{1-x}$ and $Eu_2K_{2x}O_{2+2x}(CO_3)_{1-x}$, though possessing similar multiple valances, showed decreased catalytic performance for transesterification.

Conclusions

We report a high FAME yield (> 95 %) under mild reaction conditions and a short reaction time by using potassium modified layered $Nd_2O_2CO_3$ material as a heterogeneous catalyst in biodiesel production and a ~80 % FAME yield under mild reaction conditions and a short reaction time by using alkali element leaching into the biodiesel product. The $Ln_2O_2CO_3$ materials are prepared by an instant co-precipitation method followed by the reflux method and characterized by XRD, TGA, SEM, TEM, and BET. The comparisons between synthesized $Ln_2O_2CO_3$ materials and the industrial homogeneous KOH catalysts have suggested that $Ln_2O_2CO_3$ materials are promising candidates for industrial use. The recyclability and stability tests showed the $Ln_2O_2CO_3$ materials especially $Nd_2O_2CO_3$ are catalysts for fast industrial biodiesel production. This is the first group of heterogeneous catalysts



Scheme 1 Catalytic mechanism of $Ln_2O_2CO_3$ layered materials in transesterification.

reported as being highly active with low energy consumption in transesterification reactions with no lanthanide leaching and very low potassium leaching.

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Notes and references

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Potassium modified layered $Ln_2O_2CO_3$ (Ln: La, Nd, Sm, Eu) materials: Efficient and stable heterogeneous catalysts for biofuel production

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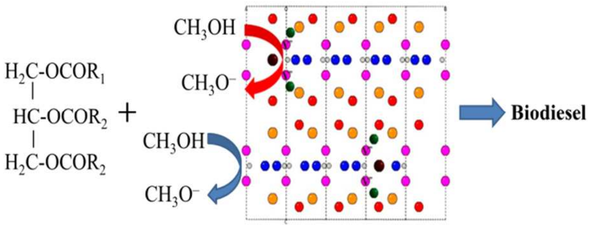

Potassium modified layered $Ln_2O_2CO_3$ catalysts were prepared for transesterification with high FAME yield under mild reaction conditions.