This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

www.rsc.org/greenchem
**Potassium modified layered Ln$_2$O$_2$CO$_3$ (Ln: La, Nd, Sm, Eu) materials: Efficient and stable heterogeneous catalysts for biofuel production**

Yashan Zhang$^a$, Lei Jin$^b$, Kevin Sterling$^a$, Zhu Luo$^b$, Ting Jiang$^c$, Ran Miao$^a$, Curtis Guild$^a$, and Steven L Suib$^{a,b}$

Potassium modified layered Ln$_2$O$_2$CO$_3$ (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$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ within 10 min, while the same yield can be reached by 3.0 wt. % Nd$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ 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. Because of its similar physiochemical properties to petroleum-based diesel, biodiesel can be directly used in existing diesel engines. Moreover, biodiesel is biodegradable, non-toxic, more efficient than gasoline because of its oxygen content, and is considered to generate less greenhouse gases due its closed CO$_2$ cycle (carbon in vegetable oil is mainly from the CO$_2$ in air). 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 reactants to achieve this transesterification process. Since such processes are not spontaneous, different catalysts have been evaluated for biodiesel production, such as basic catalysts, acid catalysts, and enzymes; among them, the most common and industrialized way of producing biodiesel involves using a homogeneous basic catalyst such as KOH. 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. Another type of commonly used catalysts for biodiesel production is acid catalysts. Strong liquid acids (H$_2$SO$_4$) are the most common active homogeneous acid catalysts. Apart from their longer reaction time compared to basic catalysts, 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. 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, optical fibers, and catalysts. In the fields of catalysis, in particular, rare earth based materials are widely used in water gas shift (WGS) reactions, zeolite catalysis, and oxidative dehydrogenation of ethane. Among various rare earth metal based materials, rare earth oxycarbonates Ln$_2$O$_2$CO$_3$ (Ln: rare earth) have...
received considerable attention. 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. Type-II compounds are the most promising compounds as catalysts due to their stability and higher durability against both water and carbon dioxide.

In a simplified description, type II Ln$_2$O$_2$CO$_3$ are believed to have the layer-like structures with two-dimensional (Ln$_2$O$_3$)$_2^+$ layers and CO$_2^-$ 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.

In our previous work, La$_2$O$_2$CO$_3$/ZnO heterogeneous basic catalysts were synthesized for transesterifications. A microwave heating method was used for the biodiesel synthesis. In this work, a group of rare earth oxycarbonate type-II Ln$_2$O$_2$CO$_3$ (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$_2$O$_2$CO$_3$ were then compared with industrial homogeneous catalysts. We report that a new group of layered rare earth catalysts. We report that a new group of layered rare earth compounds are the most promising compounds as catalysts due to their stability and (NH$_4$)$_2$CO$_3$ (0.10 mol) were dissolved in 400 mL 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 Ka (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 ($pK_{BH}^+ = -3.0$), $p$-dimethylidiazobenzene (dimethyl yellow, $pK_{BH}^+ = +3.3$), dibromothymol sulfophthalein (thymol blue, $pK_{BH}^+ = +7.2$), 4,4'-dioxynaphthophenone ($pK_{BH}^+ = +9.3$), and 2, 4-dinitroaniline ($pK_{BH}^+ = 15.4$). The samples were calcinated at $+7.2^\circ C$, $4,4'$-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$_2$O$_2$CO$_3$ 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$_2$O(CO$_3$)$_2$ materials took place at around 450 °C to 480 °C, which is due to the transformation of Ln$_2$O(CO$_3$)$_2$ to a layered Ln$_2$O$_2$CO$_3$ 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$_2$O$_3$ materials are formed from the layered Ln$_2$O$_2$CO$_3$ materials. Both mass losses were assigned to the loss of CO$_2$ based on TGA-mass spectrometry analysis. 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$_2$O(CO$_3$)$_2$ materials range from 24 wt.% to 28 wt.% and is in the sequence of: La$_2$O$_2$CO$_3$ > Nd$_2$O$_2$CO$_3$ > Sm$_2$O$_2$CO$_3$ > Eu$_2$O$_2$CO$_3$ 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$_2$O(CO$_3$)$_2$ materials. The thermal stability among these layered Ln$_2$O$_2$CO$_3$ materials is in the sequence of: La$_2$O$_2$CO$_3$ > Nd$_2$O$_2$CO$_3$ > Sm$_2$O$_2$CO$_3$ ≈ Eu$_2$O$_2$CO$_3$.

X-ray diffraction (XRD) patterns have confirmed the transformation from Ln$_2$O(CO$_3$)$_2$ (Fig. 2 a) to layered Ln$_2$O$_2$CO$_3$ (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$_2$O$_2$CO$_3$ (Ln = La, Nd, Sm, Eu) materials (Fig. 2 b) show similar patterns with a slight successive shift (to higher 20 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$_2$O$_2$CO$_3$ (Ln = La, Nd, Sm, Eu) materials are La$_2$O$_2$CO$_3$: 7.91 Å; Nd$_2$O$_2$CO$_3$: 7.81 Å; Sm$_2$O$_2$CO$_3$: 7.68 Å; Eu$_2$O$_2$CO$_3$: 7.62 Å respectively, which are all close to the d spacings reported in the JCPDS database (La$_2$O$_2$CO$_3$: 7.97 Å; Nd$_2$O$_2$CO$_3$: 7.85 Å; Sm$_2$O$_2$CO$_3$: 7.67 Å; Eu$_2$O$_2$CO$_3$: 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.
The basicity test results by indicators and TPDxCO (Ln calcination) contained bulk aggregates. After calcination, synthesized materials (before calcination) contained bulk aggregates. The synthesized layered rare earth oxycarbonates materials (Ln = La, Nd, Sm, Eu) after calcination (JCPDS 37-0804). The BET surface area 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$_2$O$_2$CO$_3$ is the most active catalyst among Ln$_2$O$_2$CO$_3$ materials in the reaction system. Complete yields (~100 %) can be achieved using 0.15 g (3.0 wt.%) synthesized 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$_2$O$_2$CO$_3$ > La$_2$O$_2$CO$_3$ > Sm$_2$O$_2$CO$_3$ ≈ Eu$_2$O$_2$CO$_3$.

**Catalytic Performance**

**Catalytic Results of Ln$_2$O$_2$CO$_3$ Layered Materials at Different Temperatures.** The FAME yields over Ln$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ > La$_2$O$_2$CO$_3$ > Sm$_2$O$_2$CO$_3$ ≈ Eu$_2$O$_2$CO$_3$.

![Fig. 2 XRD patterns of a, synthesized Ln$_2$O(CO)$_3$ (Ln = La, Nd, Sm, Eu) solid materials before calcination (JCPDS 28-0512) and b, synthesized layered rare earth oxycarbonates materials Ln$_2$O$_2$CO$_3$ (Ln = La, Nd, Sm, Eu) after calcination (JCPDS 37-0804).](image)

The ESEM images of Ln$_2$O$_2$(CO)$_3$ are shown in Fig S1 (see Supporting Information (SI)). The synthesized materials (before calcination) contained bulk aggregates. After calcination, Ln$_2$O$_2$CO$_3$ nanorod aggregates were formed. The detailed microstructures (HRTEM) of Ln$_2$O$_2$CO$_3$ are shown in Fig. S2 (a) - (h) (see Supporting Information (SI)); La$_2$O$_2$CO$_3$ shows larger crystallite size than other Ln$_2$O$_2$CO$_3$ materials, which is in accordance with peak broadening results in X-ray diffraction. The synthesized La$_2$O$_2$CO$_3$ and Nd$_2$O$_2$CO$_3$ (Fig. S2 (b)&(d)) showed obvious layered structures, while Sm$_2$O$_2$CO$_3$ and Eu$_2$O$_2$CO$_3$ (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$_2$O$_2$CO$_3$ material as reported in the literature. The BET surface area results are shown in Table S1 (see Supporting Information (SI)), the layered Ln$_2$O$_2$CO$_3$ materials have a surface area ranging from 11 to 19 g/m$^2$ and the Nd$_2$O$_2$CO$_3$ sample has the largest surface area among these four Ln$_2$O$_2$CO$_3$ layered materials. The basicity test results by indicators and TPD-CO$_2$ are also shown in Table S1(see Supporting Information (SI)). The Ln$_2$O$_2$CO$_3$ layered materials all have the same basic strength by indicators tests and the Nd$_2$O$_2$CO$_3$ sample desorbs the largest amounts of CO$_2$ (0.33 mmol/g) among all four layered Ln$_2$O$_2$CO$_3$ materials.

**Comparison of the Catalytic Activity of the Prepared Layered Nd$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ catalyst and 5 wt.% KOH were separately introduced into two
biodiesel production systems: under the same reaction 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$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ 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$_2$O$_2$CO$_3$ materials were used as control samples, to investigate the effects of potassium doping in the layered materials. The XRD patterns of synthesized layered Ln$_2$O$_2$CO$_3$ (Ln: La and Nd) materials by separately using NH$_3$, (NH$_4$)$_2$CO$_3$ mixtures, and KOH/K$_2$CO$_3$ 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-LnO₂CO₃) 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 NH₃-LnO₂CO₃). The d spacings are 7.91 Å for K-La₂O₂CO₃; 7.85 Å for NH₃-La₂O₂CO₃; 7.81 Å for K-Nd₂O₂CO₃; 7.70 Å for NH₃-Nd₂O₂CO₃ respectively. The larger d spacings are simply due to potassium doping in the layered Ln₂O₂CO₃. Studies by Iqbal et al.⁵⁹ and Attfield et al.⁶⁶ 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.⁵⁹ The diffraction patterns of K-Ln₂O₂CO₃ compared to NH₃-Ln₂O₂CO₃ 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 Ln₂O₂CO₃.

Interestingly, K-La₂O₂CO₃ also showed less peak broadening compared to NH₃-La₂O₂CO₃, suggesting possible larger crystallite sizes of potassium doped Ln₂O₂CO₃ and less carbonate group distortion. The comparison of TEM pictures between potassium containing base synthesized Nd₂O₂CO₃ material (Fig. S4 a&b) (see Supporting Information (SI)) and ammonium containing base synthesized Nd₂O₂CO₃ 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 La₂O₂CO₃ and Nd₂O₂CO₃ materials synthesized by NH₃ and (NH₃)₂CO₃ are much less active in transesterification compared to the La₂O₂CO₃ and Nd₂O₂CO₃ materials synthesized by KOH and K₂CO₃ basic mixtures. Doping potassium in the layered Ln₂O₂CO₃ 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 Ln₂O₂CO₃ 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 Nd₂O₂CO₃ 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 Nd₂O₂CO₃ catalyst.

The XRD patterns of Ln₂O₂CO₃ materials after 4th cycle are shown in Fig. 5 (see Supporting Information (SI)). After 4 cycles of successive transesterification, the same layered structure was maintained by La₂O₂CO₃ because of its better thermal and structural stabilities; however, minor new peaks (Nd₂O₂) appeared in the XRD pattern of the Nd₂O₂CO₃ material, similar minor new peaks (Ln₂O₃) can be found for Sm and Eu based layered materials with some of the peaks (related to the Ln₂O₂CO₃ structure) diminishing or disappearing. The small drop in yield (La₂O₂CO₃, Nd₂O₂CO₃) is probably due to the weight loss in the process of recollection and reactivation after several cycles and partial decomposition to Ln₂O₃⁴⁰,⁴¹ La₂O₂CO₃ and Nd₂O₂CO₃ materials were still catalytically active after the 4th cycle because of their better thermal and structural stabilities.

Meanwhile, the Sm₂O₃CO₃ and Eu₂O₃CO₃ materials were totally deactivated during the process because of their decomposition or their poor thermal stabilities. The morphology changes of layered Ln₂O₂CO₃ 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 La₂O₂CO₃ materials before and after the reactions are almost the same, and for layered Nd₂O₂CO₃, Sm₂O₂CO₃, and Eu₂O₂CO₃ materials, the pictures have shown that new structural phases appeared. The appearance of new phases in recycled Nd₂O₂CO₃, Sm₂O₂CO₃, and Eu₂O₂CO₃ 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\(_2\)O\(_2\)CO\(_3\) materials tested by FAAS is shown in Table S3 (see Supporting Information (SI)). Layered Nd\(_2\)O\(_2\)CO\(_3\) material has the largest amount (1.45 wt. %) of potassium among these Ln\(_2\)O\(_2\)CO\(_3\) 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\(_2\)O\(_2\)CO\(_3\) materials nor the lost potassium amount (amount difference between fresh and recycled solid Ln\(_2\)O\(_2\)CO\(_3\) materials) is sufficient to achieve more than 90 % of FAME yield as to the reported potassium contained catalysts.\(^{42, 45}\) The approximate molar percentage of potassium in the solid Ln\(_2\)O\(_2\)CO\(_3\) materials was also calculated. Take K-La\(_2\)O\(_2\)CO\(_3\) material for example; 1.35 wt.% K was detected by AAS, which means, in 100 g of K-La\(_2\)O\(_2\)CO\(_3\) material, there are 1.35 g of K and approximate 98.65 g of La\(_2\)O\(_2\)CO\(_3\) 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\(_2\)O\(_2\)CO\(_3\). The data showed that the molar ratios between K\(^+\) and Ln\(_2\)O\(_2\)CO\(_3\) 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\(_2\)O\(_2\)CO\(_3\) 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\(_2\)O\(_2\)CO\(_3\) layered materials are oxygen vacancies, which are mostly created by potassium doping as shown in Scheme 1a. By introducing potassium in Ln\(_2\)O\(_2\)CO\(_3\), 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\(_2\)K\(_2\)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 recovered 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\(_2\)K\(_2\)O\(_2\)\(_{2x}\)(CO\(_3\))\(_{1-x}\) to Ln\(_2\)O\(_3\), 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\(_2\)K\(_2\)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\(^{5+}\)). Nevertheless, due to the poor thermal and structural stability, Sm\(_2\)K\(_2\)O\(_2\)\(_{2x}\)(CO\(_3\))\(_{1-x}\) and Eu\(_2\)K\(_2\)O\(_2\)\(_{2x}\)(CO\(_3\))\(_{1-x}\), though possessing similar multiple valences, 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\(_2\)O\(_2\)CO\(_3\) material as a heterogeneous catalyst in biodiesel production and a ~80 % FAME yield under mild reaction conditions and a short reaction time by using potassium modified layered La\(_2\)O\(_2\)CO\(_3\) material as a heterogeneous catalyst in biodiesel production and a ~80 % FAME yield under mild reaction conditions and a short reaction time by using potassium modified layered Ln\(_2\)O\(_2\)CO\(_3\) materials 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\(_2\)O\(_2\)CO\(_3\) materials and the industrial homogeneous KOH catalysts have suggested that Ln\(_2\)O\(_2\)CO\(_3\) materials are promising candidates for industrial use. The recyclability and stability tests showed the Ln\(_2\)O\(_2\)CO\(_3\) materials especially Nd\(_2\)O\(_2\)CO\(_3\) are catalysts for fast industrial biodiesel production. This is the first group of heterogeneous catalysts
reported as being highly active with low energy consumption in transesterification reactions with no lanthanide leaching and very low potassium leaching.

Acknowledgements

This work was supported by the National Science Foundation CBET division, under GOALI program 0827800. We would like to thank Drs. Anthony Provatas and Christopher Perkins from Center for Environmental Sciences and Engineering for the XRF analysis, Dr Lichun Zhang from Institute of Materials Science for the TEM analysis. We would also like to thank Dr. Francis Galasso for many helpful discussions.

Notes and references

a Department of Chemistry. University of Connecticut, Storrs, Connecticut 06269. USA. Fax: +1 860 486 2981; Tel: +1 860 486 2797; E-mail: steven.suib@uconn.edu

† Electronic Supplementary Information (ESI) available: [Characterizations details of materials, including SEM and TEM images, XRD patterns, BET surface area data, basicity tests data and leaching tests data.]. See DOI: 10.1039/b000000x/
32. V. V. Brei, Theoretical and Experimental Chemistry, 2008, 44, 320-324.
Potassium modified layered \( \text{Ln}_2\text{O}_2\text{CO}_3 \) (\( \text{Ln}: \text{La, Nd, Sm, Eu} \)) materials: Efficient and stable heterogeneous catalysts for biofuel production

Yashan Zhang\textsuperscript{a}, Lei Jin\textsuperscript{a}, Kevin Sterling\textsuperscript{a}, Zhu Luo\textsuperscript{b}, Ting Jiang\textsuperscript{c}, Ran Miao\textsuperscript{a}, Curtis Guild\textsuperscript{a}, and Steven L Suib\textsuperscript{*a,b}

\textsuperscript{a} Department of Chemistry. University of Connecticut, Storrs, Connecticut 06269. USA. Fax: +1 860 486 2981; Tel: +1 860 486 2797; E-mail: steven.suib@uconn.edu

\textsuperscript{b} Institute of Materials Science. University of Connecticut, Storrs, Connecticut 06269. USA.

\textsuperscript{c} Chemical & Biomolecular Engineering Department, University of Connecticut, Storrs, Connecticut 06269. USA.

Potassium modified layered \( \text{Ln}_2\text{O}_2\text{CO}_3 \) catalysts were prepared for transesterification with high FAME yield under mild reaction conditions.