Research Article

Teerapat Hasakul, Sunthon Piticharoenphun*, Dussadee Rattanaphra, Sasikarn Nuchdang, and Wilasinee Kingkam

A study of the precipitation of cerium oxide synthesized from rare earth sources used as the catalyst for biodiesel production

https://doi.org/10.1515/gps-2022-0069
received February 17, 2022; accepted June 14, 2022

Abstract: This work aimed to study the preparation of cerium oxide (CeO₂) used as the catalyst for biodiesel production from palm oil. The precipitation method was used in the catalyst synthesis. The effects of oxalic concentrations and stirring rates in the precipitation process were investigated. Oxalic acid was added into cerium (Ce) in ethylenediaminetetraacetic acid solution to form Ce oxalate before the Ce oxalate was calcined to obtain CeO₂. The results showed that oxalic concentrations and stirring rates slightly affect the morphology of CeO₂. However, these parameters considerably affect the amount of basic sites of CeO₂. The basicity of CeO₂ plays the main role in catalyzing the transesterification reaction for biodiesel production. When CeO₂ was used as the catalyst in biodiesel production from palm oil under operating conditions using a 5% catalyst, methanol-to-oil molar ratio of 30:1, reaction temperature of 150°C, 13.8 bars, and 3-h reaction time, CeO₂ obtained from 3% oxalic concentration and 400 rpm stirring rates in the precipitation process provided the highest %FAME in the range of 93.9–94.2% since it had higher basicity. In addition, the decrease in surface area of CeO₂ after the use was less severe than that of basicity due to catalyst deactivation.

Keywords: precipitation, cerium oxide, rare earth, biodiesel, transesterification

1 Introduction

At the present, there is a potential for the problem of fossil energy shortages to occur in the future due to development in several sectors such as industries, transportation, and logistics. Furthermore, the use of fossil energy such as benzene and diesel can generate environmental problems, such as air pollution, global warming, and PM2.5 dust (particulate matter with the size of 2.5 µm or smaller) [1,2]. Therefore, it is necessary to find other energy sources which are renewable, sustainable, and environmental-friendly for environmental and energy security. There are several types of alternative energy, such as wind energy, solar energy, water energy, hydrogen energy, and biodiesel, which can be used instead of fossil energy. Biodiesel is one such alternative energy that has shown its suitability for use in agricultural countries such as Thailand. Biodiesel can be produced from various oil plants. For example, rice bran oil was proposed as a promising renewable source for biodiesel production as well as those from palm, jatropha, coconut, and soybean plants, which are abundant in nature [3–8]. However, some properties of biodiesel such as density and viscosity, which affect the fuel supply system and spray characteristics, need to be improved in order to be efficiently used in diesel engines [9]. The combustion of biodiesel does not emit sulfur dioxide, and biodiesel is also labeled as “carbon-neutral.” The net amount of CO₂ emission from the combustion of biodiesel does not increase in the atmosphere since the oil plants consume CO₂ for photosynthesis and are used as raw materials for biodiesel production. Thus, biodiesel is green, eco-friendly, and sustainable energy that can be practically used.

Biodiesel can be synthesized using several methods. Biodiesel production on the industrial scale mostly uses NaOH or KOH as the catalyst. However, the use of NaOH and KOH, which are homogeneous catalysts, generates large amounts of wastewater, and the separation of
catalysts for reuse was not easily carried out [10]. Therefore, heterogeneous catalysts are expected to solve these drawbacks from the use of homogeneous catalysts. Several heterogeneous catalysts such as MgO, CaO, and SrO were studied in biodiesel production [11–13]. However, the leaching problem was found when these catalysts mentioned earlier were used [14]. The reuse of these catalysts cannot be carried out to reduce the production cost. It might affect the purification process of biodiesel from catalyst leaching. Thus, it is necessary to study other catalysts which reduced the leaching problem. Therefore, cerium oxide (CeO₂) has gradually gained attention for use as the catalyst in transesterification reactions due to its good thermal stability [15]. This might reduce the leaching problem, and the catalyst can be reused several times.

CeO₂ was one type of heterogeneous catalyst which has been studied. CeO₂ has wide applications in various areas such as microelectronics, optoelectronics, fuel cell technologies, gas sensors, oxygen storage, ceramics, and biomedical applications [16,17]. As CeO₂ in nanoparticle form provides a good thermal property, large oxygen storage, and flexible capacity in valence transformation, it can be used as an additive that is added to biodiesel. The CeO₂-containing biodiesel helps diesel engines to reduce toxic emissions such as soot, smoke opacity, NOₓ, CO, and HC [18]. In addition, CeO₂ can be used as the catalyst in several reactions such as photocatalytic reactions, oxidation reactions, and transesterification reactions [19–21]. For transesterification reaction in biodiesel production, CeO₂ as a heterogeneous catalyst has been more studied since CeO₂ showed strong durability, resulting in several reuses. For transesterification reaction in biodiesel production, CeO₂ has been studied for use as the catalyst. CeO₂ contained basic sites which are active sites to catalyze the transesterification reaction [10]. However, most works have studied mixed oxide between other elements and cerium (Ce) [22–25]. In this work, CeO₂ in the form of oxide was used to catalyze the transesterification reaction.

Ce is an element in the lanthanide group. Ce compounds can be found in natural minerals such as alanite, bastanite, monazite, cerite, and samarskite. The main source of Ce is bastanite and monazite [26]. CeO₂ synthesis can be carried out using several methods such as precipitation, hydrothermal, solvothermal, sonochemical, spray pyrolysis, microemulsification, sol–gel, plant-mediated, and fungus-mediated methods [27–29]. In this work, the precipitation method was used to synthesize CeO₂ since this method is simple, cheap, and easy to scale up [30]. There are several Ce sources used as the precursor in the synthesis such as Ce nitrate hexahydrate, Ce carbonate, Ce hydroxide, and Ce chloride [29–32]. Here, the Ce source was obtained from the Thailand Institute of Nuclear Technology. The Ce source was in the form of Ce in ethylenediaminetetraacetic acid solution (Ce in ethylenediaminetetraacetic acid [EDTA] solution), which was obtained and then purified using the ion exchange method [33]. The Ce source in this work was originally from natural minerals such as monazite ore. After decomposition and purification of monazite ore, a large amount of Ce in EDTA solution was obtained. Therefore, this Ce source can be suitably used to prepare adequate amounts of CeO₂ catalyst for large-scale production of biodiesel. In addition, the precipitation method was used for CeO₂ preparation, which is simple, cheap, and easy to scale up. Therefore, the catalyst cost could be economical when CeO₂ is used as the catalyst for commercial biodiesel production.

 Oxalic acid was used as the precipitant. Oxalic acid is one of the chemicals which is commonly used to separate rare earth elements from solutions since it has an affinity with rare earth elements [34]. After the addition of oxalic acid into Ce in EDTA solution, Ce oxalate was formed and then calcined to obtain CeO₂. In this work, the effect of oxalic concentrations and stirring rates in the precipitation which affected the properties of CeO₂ used as the catalyst in transesterification reaction for biodiesel production were studied.

## 2 Materials and methods

### 2.1 Materials

Ce in ethylenediaminetetraacetic acid solution (Ce in EDTA solution) was obtained from the Thailand Institute of Nuclear Technology. Oxalic acid (C₂H₂O₄·2H₂O, 99.5%, AR/ACS) was from Loba Chemie PVT. Ltd., and methanol (CH₃OH, 99.5%, AR) was from QREC company. Palm oil was purchased from a commercial company (Morakot brand, Thailand).

### 2.2 Catalyst preparation and its characterization

Ce in the form of dissolved Ce in EDTA (called, Ce in EDTA solution) was obtained from the purification process of mixed rare earth ores using ion exchange resin [33]. The concentration of Ce in EDTA solution was measured using ICP-OES. The main rare earth elements in the
The palm oil of 113 mL and 5 g CeO₂ were added in a Parr stirred batch reactor (Model 4568) with the stirring rate of 600 rpm under an N₂ atmosphere at 13.8 bars. The mixture was heated to 150°C. Then, the methanol of 142.6 mL was fed into the reactor. The reaction was carried out for 3 h. After that, the mixture was separated to obtain biodiesel, using a centrifuge at 3,000 rpm for 30 min. Biodiesel was baked at 110°C for 12 h to remove the residue of methanol. The %FAME was measured using GC-FID (Clarus 600, PerkinElmer), following the EN14104-2011 standard method. The catalyst was washed two times using methanol and was then measured using BET, CO₂-TPD, XRD, and SEM techniques.

3 Results and discussion

Oxalic acid is one of the chemicals which is commonly used as the precipitant to separate rare earth elements from the solution. In general, oxalic acid has an affinity with rare earth elements. The precipitation of dissolved rare earth elements using oxalic acid can be performed for all pH ranges [34]. In this work, Ce in EDTA solution was added to an oxalic solution. The white precipitates (Ce oxalate) were formed immediately after the oxalic solution was added. The precipitates were filtered and then calcined. After the calcination, Ce oxalate was transformed into CeO₂, which was pale yellow. For the precipitation process, the addition of oxalic solution was stopped when the final pH of the solution was 4. At pH = 4 of the solution, CeO₂ provided the larger basic sites than those of pH = 3 and 2, respectively (see Supplementary material). The basic sites of CeO₂ play the main role in catalyzing the transesterification reaction for biodiesel production [35–37]. As a result, CeO₂ obtained from pH = 4 offered more %FAME than those of pH = 3 and 2. Therefore, the final pH = 4 of the solution in the precipitation process was suitable and chosen for the precipitation in the next experiment.

Although the use of the final pH = 4 in the precipitation showed a higher %FAME than those of lower pH, a smaller amount of CeO₂ was obtained. In addition, a larger amount of Ce in EDTA solution was consumed during the precipitation using the final pH = 4, in order to obtain the same amount of CeO₂ from those of lower pH. It was expected that the use of higher pH than pH = 4 consumed a greater amount of Ce in EDTA solution and obtained less CeO₂. Therefore, it might not be suitable to use higher pH than pH = 4 in the precipitation for use on a commercial scale. Therefore, the final pH = 4 of the solution in the precipitation was chosen to be used in the next experiment.

3.1 The effect of oxalic concentration

In this section, the concentrations of oxalic concentration used were 0.5% and 3% w/v. The XRD patterns of CeO₂ synthesized using 0.5% and 3% oxalic concentrations are shown in Figure 1. The peaks were observed at 28.5°, 33.0°, 47.5°, 56.5°, 59.1°, 69.5°, 76.9°, 79.2°, and 88.7°, assigned to crystal planes of (111), (200), (220), (311), (222), (400), (331), (420), and (422), respectively [38]. Although the use of 0.5% and 3% oxalic provided different Ce to oxalic ratios, XRD patterns of CeO₂ from
both samples were similar. The precipitates of Ce oxalate were calcined at a high temperature of 900°C. All amounts of Ce oxalate were completely transformed into CeO₂. Therefore, the different XRD patterns from both samples were not clearly observed. From Figure 2a and b, SEM micrographs of CeO₂ synthesized using 0.5% and 3% oxalic concentration are illustrated. The CeO₂ particles were spherical and were attached via a rod. As listed in Table 1, surface area and pore size of CeO₂ synthesized using 0.5% and 3% oxalic concentrations were not much different. It was reported that the solubility of Ce oxalate decreased in the presence of higher oxalic concentrations [40]. Therefore, the use of 3% oxalic concentration decreased the solubility of Ce oxalate more than that of 0.5% oxalic concentration in a shorter time, affecting the precipitate formation. It could be said that the use of 3% oxalic concentration lowers the ratio of Ce to oxalic acid more than that of 0.5% oxalic concentration. Therefore, the use of 3% oxalic concentration offered low supersaturation, and there were few nuclei in the system. The remaining ions can improve the growth of nuclei. However, the use of 0.5% oxalic concentration might lead to the agglomeration of Ceoxalate due to the higher ratio of Ce to oxalic acid. As a result, CeO₂ synthesized using 0.5% oxalic concentration might have a little larger size and less surface area than that of 3% oxalic concentration. The concentration of oxalic acid had little effect on the morphology of CeO₂ [41].

![Figure 1: XRD patterns of CeO₂ synthesized using 0.5% and 3% oxalic concentration at 400 rpm stirring rate.](image)

![Figure 2: SEM micrograph (26,700× magnification) of CeO₂ synthesized using different oxalic concentration: (a) 0.5% oxalic and (b) 3% oxalic concentration at 400 rpm stirring rate.](image)

| Catalysts                  | Surface area \(\text{m}^2\cdot\text{g}_{\text{cat}}^{-1}\) | Pore size \(\text{nm}\) | Basicity \(\mu\text{mol-CO}_2\cdot\text{g}_{\text{cat}}^{-1}\) | %FAME |
|----------------------------|----------------------------------------------------------|------------------------|------------------------------------------------|--------|
| CeO₂ at 0.5% oxalic conc.  | 6.53                                                     | 15.3                   | 517.99                                         | 82.7   |
| CeO₂ at 3% oxalic conc.    | 6.75                                                     | 13.12                  | 613.09                                         | 94.2   |
However, the basicity of CeO$_2$ synthesized using 3% oxalic concentration (613.09 µmol·CO$_2$·g$_{\text{cat}}$−1) was considerably more than that of CeO$_2$ synthesized using 0.5% oxalic concentration (517.99 µmol·CO$_2$·g$_{\text{cat}}$−1), as shown in Table 1. The peaks of desorption of CO$_2$ between 600°C and 800°C as shown in Figure 3 indicate that basic sites of CeO$_2$ synthesized using 0.5% and 3% oxalic concentration provided strong basic sites [42]. As the final pH = 4 of the solution was controlled, the use of 3% oxalic concentration showed less ratio of Ce to oxalic acid than that of 0.5% oxalic concentration in a shorter time. This might affect the structure of Ce oxalate particles during the formation of precipitates, resulting in different amounts of basic sites of CeO$_2$ as the final product [43,44]. The greater amount of basic sites of CeO$_2$ from the use of 3% oxalic concentration in precipitation provided 94.2% FAME, which was more than that of 82.7% FAME obtained from 0.5% oxalic concentration, as shown in Table 1. Therefore, 3% oxalic concentration is the suitable concentration and so was chosen for the next experiment due to the higher basicity of CeO$_2$. The basicity of the catalyst plays the main role in the catalysis of transesterification reaction. The high activity of catalysts in transesterification reaction was attributed to high numbers of basic sites and the basic strength [35–37]. Therefore, the high %FAME can be obtained using high basicity catalysts in the transesterification reaction.

The 94.2% FAME obtained from CeO$_2$ using 3% oxalic concentration in precipitation was slightly lower than the standard value (96.5%) [45]. In comparison with other works, mixed oxide CaO–CeO$_2$ used as the catalyst provided %FAME in the range of 95–98% under mild operating conditions [46–48]. One work by Soodjit et al. [21] used CeO$_2$ obtained from the precipitation method and using the same Ce source of this work. Their results showed that 88.92% FAME was obtained under more crucial operating conditions, compared to this work. However, the precipitation conditions were not similar to this work. This showed that the precipitation conditions should be controlled to improve the catalytic activity of CeO$_2$ for transesterification reaction. Therefore, the other parameters in the precipitation conditions should be further investigated in order to add more potential to CeO$_2$ for use as catalysts in large-scale biodiesel production.

### 3.2 The effect of stirring rates in precipitation

In this section, the effect of stirring rates was studied using 200, 400, 600, and 800 rpm in the precipitation with a 3% oxalic concentration. The XRD patterns of CeO$_2$ from different stirring rates are shown in Figure 4 and are assigned to the crystal planes of CeO$_2$, as mentioned above [38]. The morphology of CeO$_2$ using different stirring rates looked similar for all samples, as shown in Figure 5. Table 2 shows the surface areas and pore sizes of CeO$_2$ obtained using different stirring rates. The surface area slightly increased at higher stirring rates. Stirring improves mass transfer and prevents local supersaturation [39]. In addition, the use of high stirring

![Figure 3: CO$_2$ desorption of CeO$_2$ synthesized using a 3% oxalic concentration at a 400 rpm stirring rate.](image)

![Figure 4: XRD patterns of CeO$_2$ synthesized using 200, 400, 600, and 800 rpm stirring rates at 3% oxalic concentration.](image)
rates can break up the particles into small particles. The surface area of CeO₂ at 200 rpm was 5.11 m²·g_cat⁻¹, and the surface area of CeO₂ increased to 5.54 m²·g_cat⁻¹ at 600 rpm. At higher stirring rates, the shear force could break up the particles, leading to smaller particles and higher surface area [39,49]. However, the surface area of CeO₂ decreased to 5.35 m²·g_cat⁻¹ at 800 rpm, possibly because high stirring rates facilitate particle collision to form particle aggregate [50]. The sizes of CeO₂ particles from all stirring rates were not much different from those observed in Figure 5. However, CeO₂ particles at 800 rpm stirring rate agglomerated more tightly than those at lower stirring rates. This resulted in less surface area at the higher stirring rate of 800 rpm. The pore sizes of CeO₂ decreased as stirring rates increased. As shown in Table 2, the basicity of CeO₂ was the highest at the stirring rate of 400 rpm.

**Table 2: Properties of CeO₂ using different stirring rates at 3% oxalic concentration**

| Catalysts     | Surface area (m²·g_cat⁻¹) | Pore size (nm) | Basicity (µmol·CO₂·g_cat⁻¹) | %FAME |
|---------------|---------------------------|----------------|------------------------------|-------|
| CeO₂ at 200 rpm | 5.11                      | 39.35          | 490.41                       | 92    |
| CeO₂ at 400 rpm | 5.11                      | 17             | 531.1                        | 93.9  |
| CeO₂ at 600 rpm | 5.54                      | 13.51          | 431.53                       | 91.9  |
| CeO₂ at 800 rpm | 5.35                      | 15.25          | 288.59                       | 83.4  |

Figure 5: SEM micrograph (26,700× magnification) of CeO₂ synthesized using different stirring rates: (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm at 3% oxalic concentration.
Figure 6: CO₂ desorption of CeO₂ synthesized using a 400 rpm stirring rate at 3% oxalic concentration.

Figure 7: XRD patterns of CeO₂ before and after the reaction using 3% oxalic concentration (at 400 rpm stirring rate) and using 400 rpm stirring rate (at 3% stirring rate).

Figure 8: SEM micrograph (26,700× magnification) of CeO₂: (a) 3% oxalic before reaction, (b) 3% oxalic after reaction (the sample in (a) and (b) used 400 rpm stirring rate), (c) 400 rpm before reaction, and (d) 400 rpm after reaction (the samples in (c) and (d) used 3% oxalic concentration).
The CO2 desorption of CeO2 at 400 rpm is illustrated in Figure 6, which shows the desorption peaks of strong basicity between 600°C and 800°C. The stirring rates might affect the morphology of CeO2, which was mentioned above, leading to the change in the basicity of CeO2. The high basicity of the catalyst provided a high activity to catalyze transesterification reaction. Therefore, CeO2 at 200, 400, and 600 rpm showed %FAME, which was similar as they provided high basicity. The highest 93.9% FAME was obtained from CeO2 at 400 rpm. As CeO2 at 800 rpm had low basicity, the lowest %FAME was offered at 83.4%, as given in Table 2.

### 3.3 The change in properties of CeO2 before and after reaction

In this section, CeO2, after use as the catalyst for transesterification reaction, was measured and compared to CeO2 before the reaction. The XRD patterns and morphology of CeO2 using 3% oxalic concentration and 400 rpm stirring rate are presented in Figures 7 and 8. It was found that the XRD peaks and the morphology of CeO2 before and after the reaction looked similar. The difference was not clearly observed from XRD and SEM results. The XRD patterns and the morphology of CeO2 from other samples are presented in Supplementary information. However, the surface area and basicity of CeO2 decreased after the reaction, as shown in Table 3. The surface areas of most samples were reduced moderately. In addition, most samples considerably lost basicity after the reaction. These might be the result of the leaching of the catalyst and the effect of surface poisoning such as the adsorption of compounds on the active sites of the catalysts [12,48].

### 4 Conclusions

In conclusion, oxalic concentrations and stirring rates used in the precipitation slightly affect the morphology but considerably influence the basicity of CeO2. As the basicity of catalysts is the main factor in catalyzing transesterification reaction, the greatest amount of basic sites from CeO2 obtained using 3% oxalic concentration and 400 rpm stirring rates provided the highest %FAME in the range of 93.9–94.2%. After the reaction, the change in surface area and basic sites of CeO2 were observed. It was found that the decrease in surface area was less severe than that of the basicity of CeO2. Therefore, the precipitation conditions in CeO2 preparation are one way to improve CeO2 properties to be suitable for use as the catalyst in biodiesel production. Other parameters in the precipitation such as aging times, precipitation temperatures, and calcination temperatures, including the reuse of CeO2 and reaction kinetics, should be further studied, in order to obtain biodiesel qualities within the standard values and be able to enlarge the biodiesel production for commercial use in the future.

**Acknowledgment:** SP would like to thank Silpakorn University Research, Innovation and Creative Fund for financial support and Thailand Institute of Nuclear Technology for supporting Ce in EDTA solution as the Ce source. Colin Liddle was also thanked for the English correction.

**Funding information:** Silpakorn University Research, Innovation and Creative Fund.

**Author contributions:** Teerapat Hasakul: doing the experiments and writing original draft; Sunthon Piticharoenphun:
writing manuscript, formal analysis, and project administration; Dussadee Rattanaphra: formal analysis, review, and measurement; Sasitkarn Nuchdang: measurement; Wilasinee Kingkam: measurement.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: All data generated or analysed during this study are included in this published article and its supplementary files.

References

[1] Ataban AE, Silitonga AS, Badruddin IA, Mahlia TMI, Masjuki HH, Mekhilef S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renew Sust Energ Rev. 2012;16:2070–93.

[2] Liu Y, Zhang W, Yang W, Bai Z, Zhao X. Chemical compositions of PM2.5 emitted from diesel trucks and construction equipment. Aerosol Sci Eng. 2018;2(51):51–60.

[3] Pleanajai S, Gheeewala SH. Full chain energy analysis of biodiesel production from palm oil in Thailand. Appl Energy. 2009;86:2559–66.

[4] Prueksakorn K, Gheeewala SH. Full chain energy analysis of biodiesel from Jatropha curcas L. in Thailand. Environ Sci Technol. 2008;42:3388–93.

[5] Nakpong P, Wootthikanokkhan S. High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. Renew. Energy. 2010;35:1682.

[6] Tippayawong N, Kongiareon E, Jompakdee W. Ethanolysis of soybean oil into biodiesel: Process optimization via central composite design. J Mech Sci Technol. 2005;19(10):1902–9.

[7] Khwanpruk S, Upparanyuy S. Mitigation of air pollutants from oil refineries. J Environ Sci. 2008;20:3490–4.

[8] Hoang AT, Tabatabela M, Mphahlele M, Carlucci AP, Olcer AI, Le AT, et al. Rice bran oil-based biodiesel as a promising renewable fuel alternative to petrodiesel: A review. Renew Sust Energ Rev. 2021;135:110204.

[9] Hoang AT. Prediction of the density and viscosity of biodiesel and the influence of biodiesel properties on a diesel engine fuel supply system. J Mar Eng Technol. 2021;20(5):299–311.

[10] Adashevi IM, Aroua MK, Abdul AAR, Sulaiman NMN. The effects of catalysts in biodiesel production: A review. J Ind Eng Chem. 2013;19:14–26.

[11] Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: A review. Fuel Process Technol. 2009;90:770–7.

[12] Boey PL, Maniam GP, Hamid SA. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. Chem Eng J. 2011;168:15–22.

[13] Queda N, Bonzi-Coulibaly YL, Ouedraogo IWK. Deactivation processes, regeneration conditions and reusability performance of CaO or MgO based catalysts used for biodiesel production-Review. Mater Sci Appl. 2017;8:94.

[14] de Sousa FP, dos Reis GP, Cardoso CC, Mussel WN, Pasa VMD. Performance of CaO from different sources as a catalyst precursor in soybean oil transesterification: kinetics and leaching evaluation. J Environ Chem Eng. 2016;4(2):1970–7.

[15] Laha SC, Ryooh R. Synthesis of thermally stable mesoporous cerium oxide with nanocrystalline frameworks using mesoporous silica templates. Chem Commun. 2003;17:2138–9.

[16] Lijing H, Yumin S, Lanhong J, Shikao S. Recent advances of cerium oxide nanoparticles in synthesis, luminescence and biomedical studies: a review. J Rare Earths. 2015;33(8):791–9.

[17] Ramachandran M, Subadevi R, Sivakumar M. Role of pH on synthesis and characterization of cerium oxide (CeO2) nanoparticles by modified co-precipitation method. Vacuum. 2019;161:220–4.

[18] Hoang AT. Combustion behavior, performance and emission characteristics of diesel engine fuelled with biodiesel containing cerium oxide nanoparticles: A review. Fuel Process Technol. 2021;218:106840.

[19] Chung KH, Park DC. Water photolysis reaction on cerium oxide photocatalysts. Catal Today. 1996;30:157–62.

[20] Naitjina NE, Garcia T, Solsona B, Taylor SH. The influence of cerium to urea preparation ratio of nanocrystalline ceria catalysts for the total oxidation of naphthalene. Catal Today. 2008;137:373–8.

[21] Soodjit P, Sirinokakun P, Rattanaphra D, Yoosuk B, Egashira R. Synthesis of biodiesel catalysed by rare earth solid catalyst. International Conference on Innovations in Engineering and Technology (ICIET 2013). Bangkok, Thailand; 2012 Dec 25th–26th. p. 229–32.

[22] Kunjachan C, Kurian M. Cerium oxide-based nanostructures as efficient catalysts for transesterification of methylate with n-butanol. Cleaner Eng Technol. 2021;4:100232.

[23] Reyero I, Moral A, Bimbela F, Radojevic J, Sanz O, Montes M, et al. Metallic monolithic catalysts based on calcium and cerium for the production of biodiesel. Fuel. 2016;182:668–76.

[24] Kim M, DiMaggio C, Yan S, Salley SO, Ng KYS. The effect of support material on the transesterification activity of CaO-La2O3 and CaO-CeO2 supported catalysts. Green Chem. 2011;13:334–9.

[25] Russbueldt BME, Hoelderich W. New rare earth oxide catalysts for the transesterification of triglycerides with methanol resulting in biodiesel and pure glycerol. J Catal. 2010;271:290–304.

[26] Kokare BN, Mandhare M, Anuse MA. Liquid-liquid extraction of cerium (IV) from salicylate media using n-n-octylaniline in xylene as an extractant. J Chin Chem Soc. 2010;57(4):431–5.

[27] Yin L, Wang Y, Pang G, Koltypin Y, Gedanken A. Sonochemical synthesis of cerium oxide nanoparticles-Effect of additives and quantum size effect. J Colloid Interface Sci. 2002;246:78–84.

[28] Dhali A, Self W. Cerium oxide nanoparticles: A brief review of their synthesis methods and biomedical applications. Antioxidants. 2018;7:97.

[29] Nyoka M, Choonara YE, Kumar P, Kondiah PPD, Pillay V. Synthesis of cerium oxide nanoparticles using various methods: Implications for biomedical application. Nanomaterials. 2020;10:242.

[30] Yu JB, Yang ZG, Wang ZH, Tu TS, Zhang ZQ, Li JY, et al. Synthesis of cerium oxalate hydrate by precipitation technique under external magnetic field. Rare Metals. 2017;1–8.
Kovacevic M, Agarwal S, Mojet BL, Ommen JGV, Lefferts L. The effects of morphology of cerium oxide catalysts for dehydrogenation of ethylbenzene to styrene. Appl Catal A-Gen. 2015;505:354–64.

Yamashita M, Kameyama K, Yabe S, Yoshida S, Fujishiro Y, Kawai T, et al. Synthesis and microstructure of calcia doped ceria as UV filters. J Mater Sci. 2002;37:683–7.

Rattanaphra D, Chuoykaew P. Puriﬁcation process and characterization of cerium oxide from mixed rare earth. TICHE International Conference. Nakornratchasima, Thailand: 2012 Oct 25th–26th.

Han KN. Characteristics of precipitation of rare earth elements with various precipitants. Minerals. 2020;10:178.

Umdu ES, Seker E. Transesteriﬁcation of sunﬂower oil on single step sol-gel made Al2O3 supported CaO Catalysts: Effect of basic strength and basicity on turnover frequency. Bioresour Technol. 2012;106:178–81.

Sun J, Yang J, Xu X. Basicity-FAME yield correlations in metalation modiﬁed MgAl mixed oxides for biodiesel synthesis. Catal Commun. 2014;52:1–4.

AVRK R, Dudhe P, Chelvam V. Role of oxygen defects in basicity of Se doped ZnO nanocatalyst for enhanced triglyceride transesteriﬁcation in biodiesel production. Catal Commun. 2021;149:106258.

Poggio E, Jobbagy M, Moreno M, Laborde M, Marino F, Baronetti G. Inﬂuence of the calcination temperature on the structure and reducibility of nanoceria obtained from crystalline Ce(OH)CO3 precursor. Int J Hydrog Energy. 2011;36:15899–905.

Zhaogang L, Mei L, Yanhong H, Mitang W, Zhenxue S. Preparation of large particle rare earth oxides by precipitation with oxalic acid. J Rare Earths. 2008;26(2):158–62.

Chung CY, Kim EH, Lee EH, Yoo JH. Solubility of rare earth oxalate in oxalic and nitric acid media. J Ind Eng Chem. 1998;4(4):277.

Yan M, Wei W, He S, Zuoren N. Preparation and morphology of nano-size ceria by a stripping precipitation using oxalic acid as a precipitating agent. J Rare Earths. 2012;30(12):1265–9.

Ali B, Yusup S, Quitain AT, Alnarabiji MS, Kamil RNM, Kida T. Synthesis of novel graphene oxide/bentonite bi-functional heterogeneous catalyst for one-pot esterification and transesteriﬁcation reactions. Energy Convers Manag. 2018;171:1801–12.

Hellgardt K, Chadwick D. Effect of pH of precipitation on the preparation of high surface area aluminas from nitrate solutions. Ind Eng Chem Res. 1998;37:405–11.

Yan M, Wei W, Zuoren N. Inﬂuence of pH on morphology and formation mechanism of CeO2 nanocrystalline. J Rare Earths. 2007;28:53–7.

Tsoutsos T, Tournaki S, Gkouskos Z, Paraiba O, Giglio F, Garcia PQ, et al. Quality characteristics of biodiesel produced from used cooking oil in Southern Europe. ChemEngineering. 2019;3:19.

Thisartarn W, Kawi S. An active and stable CaO-CeO2 catalyst for transesteriﬁcation of oil to biodiesel. Green Chem. 2011;13:3423.

Zheng YC, Yu XH, Yang J. Synthesis of CaO-CeO2 catalysts by soft template method for biodiesel production. IOP Conf Ser: Earth Environ Sci. 2017;69:012048.

Zhang N, Xue H, Hu R. The activity and stability of CeO2@CaO catalysts for the production of biodiesel. RSC Adv. 2018;8:32922–9.

Mei L, Mitang W, Zhaogang L, Yanhong H, Jinxiu W. Cerium oxide with large particle size prepared by continuous precipitation. J Rare Earths. 2009;27(6):991–6.

Sung MH, Choi IS, Kim JS, Kim WS. Agglomeration of yttrium oxalate particles produced by reaction precipitation in semi-batch reactor. Chem Eng Sci. 2000;55:2173–84.