Elucidation of morphology developed of Ca$_x$Ce$_y$/ZrO$_2$ solid catalyst for the production of lactic acid from glycerol conversion

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Abstract. Monometallic and bimetallic noble metal supported catalysts have been tested for the catalytic glycerol oxidation to lactic acid. Modification of zirconia, (ZrO$_2$) using CaO, which is an alkaline earth metal as the base source and Ce as the metal source to give, 30wt%Ca$_x$Ce$_y$/ZrO$_2$ was investigated. The catalysts were prepared using co-precipitation method at different of Ca$_x$ to Ce$_y$ ratios (x:y = 1.0:0.5 – 1.0:3.0) and subsequently calcined at 800 °C. Subsequently, the glycerol reaction to lactic acid was carried out at a 250 °C for 2 h in a base free condition using pure glycerol. The interaction between the metallic sites and CeO$_2$ support showed was characterized to elucidate the developed morphology of catalyst. The textural and structural properties of the catalysts were studied using Field emission scanning electron microscope (FESEM) and Transmission electron microscope (TEM). It was found that the morphology of the catalyset well developed and contribute to the significant reaction activity through the reaction mechanism. The spent catalyst also could produce the lactic acid and the morphology is still in a good condition showing capability of cyclability.

1. Introduction
Glycerol is a very important industrial feedstock for conversion into several high value chemicals. Their applications are found in food, cosmetic, drug and tobacco industries. Chemical products formed from glycerol valorization are such as lactic acid, polyglycerol, 1,2 propanediol, hydrocarbons, glyceric acid, dihydroxyacetone, hydrogen and olefins [1–5]. Recently, lactic acid has emerged as one of the promising products. A number of literatures have reported several effective means to produce significant yield of lactic acid such as through hydrothermal reaction, hydrogenolysis, selective oxidation and fermentation processes [3,6,7]. However, drawbacks of fermentation methods are such as low productivity, low efficiency, high cost of enzymes, limited space–time yield, poor scalability and the need for complicated
purification methods. Thus, a greener and more economical production of lactic acid using catalytic conversion has been extensively explored.

Lactic acid is an important high-value chemical that is typically used as a raw material for the production of medicines, cosmetics, fragrances, and polylactic acid, which is a carbon-neutral bioplastic [8]. Oxidation reaction is a high temperature reaction, requiring the catalyst with a high thermal stability. CeO2 catalyst has attracted much attention due to its good oxygen storage capacity, thermal resistance and redox promotion property [9–11]. The chemical basicity properties of the catalyst was contributed by CaO, as the important modification according to Marinkovic et al. [12]. It was evident that the strong basicity of the catalyst could enhance catalytic dehydration and benzylic acid rearrangement of the dihydroxyacetone intermediates to lactic acid. In addition, Ca leaching could be minimized by coupling with La2O3 or CeO2 as an appropriate support [13]. Atsushi et. al. [14] found that the combination of the two metal oxides which have both Bronsted acid and Lewis acid sites accelerated rates of lactic acid formation. ZrO2 could be a suitable solid support due to its surface catalytic sites properties such as high concentration of hydroxyl groups and coordinative unsaturated Lewis acidic-basic Zr4+ O2− pairs. These features were believed to potentially enhance the catalytic ability of the transition metal active sites [15]. Thus, this potential created the interest to explore the suitability of a CaxCey/ZrO2 mixed oxide catalyst in this oxidative reaction. The catalyst was hypothesized to be effective for this reaction on the basis of its basicity and oxygen storage capacity roles to selectively convert glycerol to lactic acid.

Bimetallic Ni-Co catalysts supported on CeO2 were developed by Zhenchen et. al. [16] and found that the introducing Co into the supported catalysts was important to prevent the aggregation of Ni into large particles. A comprehensive study on the incorporation of CaxCey onto ZrO2 support is still needed for enhancing stronger the metal-support interaction which can affect the catalytic activity. In this study, the structure of CaxCey/ZrO2 catalysts in the oxidation reaction of glycerol is reported. The morphology of metal-support developed were analysed towards lactic acid production, which might give the fundamental insight into the catalytic mechanism of the catalyst. In-depth characterization provided new understanding on the nature of active sites structure of the resulting CaxCey/ZrO2 catalysts, while their activity and selectivity in the oxidation reaction of glycerol to lactic acid were demonstrated. The performance of the catalysts was specifically studied at different Ca to Ce ratios as an attempt to correlate the activity data with the structural properties of these solids. The catalytic properties and performance of the catalyst were to be correlated, to generate significant conclusions on their behaviours in the glycerol selective conversion to lactic acid.

2. Materials and Method

2.1 Materials

Glycerols (98 % purity), calcium nitrate hexahydrate, Ca(NO3)2.6H2O, cerium nitrate hexahydrate, (Ce(NO3)3.6H2O), zirconyl chloride octahydrate (ZrOCl2.8H2O), ammonium hydroxide, NH3OH (99 % solution in water), sodium hydroxide, NaOH (90%) and sodium bicarbonate, Na2CO3 (90%) were purchased from Fluka. Deionized water (DI) was used throughout the study for the preparation of the support and catalyst. All the chemicals were of reagent grade and were used as received without further purification.

2.2 Preparation of support material

Zirconia (ZrO2) was prepared based on a work reported by Yang et al. [17]. An aqueous solution of zirconium chloride octahydrate (ZrOCl2.8H2O) was first prepared using DI water and stirred for 30 min. Then, the pH value of the solution was adjusted to pH 10-11 by dropwise addition of ammonium hydroxide solution (25 %). Stirring of the solution was then continued for 3 h. The resultant solution was then filtered with DI water to remove all the contaminants and then dried overnight at 100 °C. The sample was then calcined at 500 °C for 3 h and used as the catalyst support.
2.3 Preparation of mixed oxide catalysts
The support material was first dispersed in DI water and the required amounts of Ca(NO₃)₂ and Ce(NO₃)₂ solutions were added dropwise under stirring. Then, calculated amounts of 1M NaOH and Na₂CO₃ were also added dropwise to maintain the pH at 11-12. The temperature of the mixture was set at 80 °C for 5 h on a hotplate stirrer. After that, the suspension was filtered and the solid was washed with deionized water to eliminate all traces of base (pH test). Then, the catalysts were dried overnight at 80 °C followed by calcination at 500 °C for 4 h. The catalysts are represented as 30% wt/wtCaₓCeᵧ/ZrO₂ (x and y indicate the serial ratios of the active components in the samples).

2.4 Characterization of catalyst
The catalyst’s surface morphology was studied by means of a field emission scanning electron microscope (FESEM Carl Zeiss SMT, Oberkochen, Germany). Transmission electron microscope (TEM, Eftem Libra 120) was used to observe the internal morphology of the catalysts. Catalyst sample of about 0.05 g was first dispersed in 3 ml of 100 % acetone. Then, the suspension was shaken vigorously and the suspended powder (light powder) was sucked out slowly with a micropipette and dropped on the grid for the analysis.

2.5 Catalyst activity
Batch hydrothermal glycerol reaction was carried out in a 50 mL stainless steel autoclave at a stirring speed of 250 rpm as shown in figure 1. The standard reaction was carried out under the following reaction conditions: 533 K, 2 bars of initial O₂ pressure, 99% aqueous glycerol, 20 wt. % of catalyst for 2 h of reaction. After being purged for 15 minutes, the reactor was heated to the desired reaction temperature of 250 °C and the O₂ pressure was then increased to about 10 bar. The liquid-phase products were analysed by means of a gas chromatograph with a SHODEX capillary column (50 m × 0.32 mm) and a flame ionization detector. The catalytic performance demonstrated by the catalysts was evaluated based on glycerol conversion as well as the yield and selectivity of lactic acid using high performance liquid chromatograph (HPLC). To confirm the presence of intermediate products in identifying the mechanism of the oxidation reaction, some liquid samples were also analysed with Gas chromatography–mass spectrometry (GCMS) equipped with a BPX5 capillary column (30 x 0.25 mm) at a heating rate 30˚ C/min and in the range of 40-225 °C.

Figure 1. Schematic diagram of batch pressurized reactor
3.0 Results and Discussion

3.1 Morphology of mixed oxide catalyst by FESEM analysis

Clear changes in the morphologies of the catalyst after modification of the ZrO$_2$ support with different Ca$_x$Ce$_y$ ratios were observed by FESEM. Pure ZrO$_2$ support (figure 2 (a)) appears to have a nubby structure, the surface of which was dense and compact. The morphology was apparently uniform and it contained quasi-spherical like microparticles with inner-aggregate pores particles as described by Majedi et al. [18]. As the ratio of Ca$_x$Ce$_y$ was further increased from 1.0:0.5 (figure 2 (b) to 1.0:2.0 figure 2(c), clearer but much smaller external pore structure was formed. Ca$_1$Ce$_2$/ZrO$_2$ (figure 2 (c)) exhibited much different morphological structure as compared to that of ZrO$_2$ support, showing high dispersion of metal on the ZrO$_2$ support and was consistent with that of platinum on Ce/ZrO$_2$ catalysts [19]. In addition, calcination process could also contribute to the formation of a hollow, porous, and fluffy products as the reactions that occurred would release a large amount of gas and heat.

![Figure 2](image_url)

**Figure 2.** FESEM of images at a 20kX magnification of (a) ZrO$_2$, (b) Ca$_1$Ce$_1$/ZrO$_2$ and (c) Ca$_1$Ce$_2$/ZrO$_2$ catalysts

3.2 Morphology of mixed oxide catalyst by TEM analysis

The TEM image in figure. 3 (a-d) shows the differences morphology developed by addition of different amount of Ca and Ce on particles of the ZrO$_2$ support. The pure ZrO$_2$ support (figure 3 a) exhibited particles with diameters in the range of 15 to 30 nm. As the combined introduction of Ca and Ce,
particles agglomeration was clearly observed (Fig. 3 (b, c)) onto the ZrO₂ surface suggesting that the metallic phases were fairly well dispersed, and this was consistent with a report by Wang et al. [20]. This agglomeration was probably due to the fact that the presence of CaₓCeᵧ on the modified zirconia particles allowed their interaction and caused the particles to sinter, forming a new catalyst structure. As the CaₓCeᵧ ratio was increased from 1.0:0.5 to 1.0:2.0, figure 3 (d), the formation of more organized and uniform spheres that were attached together was clearly observed with no visible difference in the porosity between the two types of catalyst. Thus, the presence in certain amount of Ca and Ce could play a significant role in transforming nonporous ZrO₂ support to porous catalyst materials and caused an increment in the particle size of the mesostructures support. The enlargement of the pores suggested that the dispersion of CaₓCeᵧ onto the support, i.e. ZrO₂ most probably occurred on the external pores which resulted in a partial blockage of the internal pore structure.

Figure 3. TEM images at a 25kX magnification of (a) pure ZrO₂ support (b) Ca₁Ce₁/ZrO₂ (c) Ca₂Ce₁/ZrO₂, and (d) Ca₁Ce₂/ZrO₂ catalysts.

3.3 Comparison fresh and spent catalyst by FESEM_EDX analysis
The morphology of CaCe/ZrO₂ catalyst fresh and spent in one cycle of oxidation reaction has been compared. The comparison also has been analyzed in term of glycerol conversion, lactic acid yield and selectivity percentage as well as tabulated in table 1. The corresponding EDX (table 1) analysis (figure 4) was shown in order to know quantitatively the differences in amount of active metal leached
and the structure itself. It can be clearly observed in EDX analysis that the amount of Ca, Ce and O decreased throughout the cycle. The amount of Ca dropped from 5.29 to 1.42 wt % and the amount of Ce dropped from 12.86 to 4.64 wt%. The percentage of Zr less after spent in a one cycle about 7.45%, however, the oxide form is higher. The increment of oxide, O form maybe due to the high temperature of pressurized reaction, then some intermediate metal was transformed to the oxide state, thus oxide, O is increased about 13.6%. As for the ZrO₂, no significant reduction was observed for the spent catalysts compared to that of the fresh catalyst. These results indicate the interaction and cooperation of active metal with zirconia which was responsible for the stability of the catalyst.

Table 1. EDX results of the fresh and spent catalysts

| Catalyst | Weight percent (%) | Glycerol conversion (%) | Lactic acid (%) |
|----------|--------------------|------------------------|-----------------|
|          | Ca     | Ce    | O     | Zr | Yield | Selectivity |
| Fresh    | 5.29   | 12.86 | 27.35 | 54.50 | 94.1   | 42.8         | 45.5          |
| Spent    | 1.42   | 4.64  | 31.07 | 50.44 | 96.1   | 37.3         | 38.9          |

Figure 4 (a) and (b) shows no significant differences on the structure before and after catalyst has been spent by observing the small external pore structure was not collapsed. This morphology was synchronized with the value of Zr from EDX analysis that there is no significant reduction on the weight percent of Zr detected. However, more agglomerate particle was not form for spent catalyst that showed that is the Ca and Ce agglomerate has been leached throughout the reaction.

3.4 Mechanism of lactic acid production

To explore the reaction pathways and mechanism for the glycerol conversion to lactic acid catalyzed by Ca₅Ce₅/ZrO₂ in the presence of O₂, several control experiments were performed at different reaction time. The products were analyzed with GCMS and HPLC. It was demonstrated that glycerol oxidation is an environmentally clean method by using oxygen as oxidant and could be operated at mild reaction conditions (low temperature and pressure) [21]. Generally, the selective oxidation of glycerol tends to follow the base catalyse steps in which benzylic acid rearrangement to lactic acid is facilitated by four equivalents of base in the reaction [22,23]. From GCMS analysis results in table 2, all the intermediates were detected at small percentages indicating that the intermediate were converted to the desired final

![Figure 4](image-url)
products i.e. lactic acid. According to Feng et al. [24], 1,2-PDO could also be oxidized to lactic acid. Then, from HPLC analysis, lactic acid was detected as final product with the addition of low concentration of sulphuric acid.

Table 2. Products detected in glycerol oxidation reaction by catalysed by CaₙCeₓ/ZrO₂ catalyst

| Elements/Reaction time | Area (%) |
|------------------------|----------|
|                        | 1 h      | 1.5 h   | 2.0 h   |
| Glycerol               | 36.77    | 35.64   | 3.1     |
| Glyceraldehyde         | 3.71     | -       | 0.51    |
| Pyruvaldehyde          | 1.16     | 5.29    | -       |
| Acetol                 | -        | 0.05    | 0.21    |
| 1,2 PDO                | 1.67     | 5.2     | 37.48   |

From both GCMS and HPLC results by using CaₙCeₓ/ZrO₂ as mixed oxide catalyst in oxidation reaction of glycerol to produce lactic acid, the reaction mechanisms seem to follow route 1 of oxidation mechanism as proposed by Ftuoni et al. [25] (figure 5).

4. Conclusions
Solid mixed metal oxide catalysts, with Ca, as the base component in the form of 30wt%CaₙCeₓ/ZrO₂ were prepared by precipitation route and then evaluated for the catalytic oxidation reaction of glycerol to lactic acid. The nature and the composition of active metal could significantly influence the catalyst structure and lactic acid production. The morphology formation of supported mixed oxide was proven by FESEM_EDX and TEM analysis. The pathway of mechanism has been evaluated by HPLC and
GCMS were successful. The higher ratio of Ce at a Ca:Ce composition of 1:2 and deposited onto ZrO\textsubscript{2} was found success. The activity of the catalysts was explained by the formation of the Ca-Ce-O mixed oxide phase by metal-support interactions showed by FESEM and TEM images. Even though the metal interaction has been leached in spent catalyst but still could produce lactic acid and maintain the structure itself and proven capability to be cycle. For next research, the ability to cycle the catalyst will be further study to further improve the cyclability in regeneration method.

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