Mixed Oxide Catalyst for the Oxidation of Glycerol to Lactic Acid: Influence of the Preparation Method and Calcination Temperature

Noraini Razali[1,*] and Ahmad Zuhairi Abdullah[2]

[1]*Faculty of Chemical Engineering, Universiti Teknologi MARA, Cawangan Terengganu, Bukit Besi Campus, 23200, Dungun, Terengganu, Malaysia*

[2]*School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia*

** **Corresponding author:***

tel: +604-5996411
email: chzuhairi@usm.my

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Abstract: *The selective oxidation reaction of glycerol to produce lactic acid is a high-temperature reaction, and requiring a catalyst with high thermal stability. The mixed metal oxide is one of the potential catalysts to be explored. In this study, prepared CaCe supported on ZrO_2 catalyst with two preparation methods (co-precipitation and impregnation), and calcination temperatures (800 and 600 °C) were investigated. The oxidation reaction of glycerol to lactic acid was carried out at 250 °C for 2 h in a base-free condition using pure glycerol as a reactant. The catalysts were characterized using XRD, TGA, XPS, SEM and basicity test to evaluate and correlate the physical and chemical properties with their catalytic performance. It was found that the catalyst prepared by co-precipitation and calcined at 800 °C exhibited the highest catalytic performance. The high lactic acid yield of 38.8 and 95% glycerol conversion were achieved. The catalyst was successfully developed with sufficient porosity and high intensity of mixed metal structure that contributed to the desired high performance. Improvement in the basicity and formation of surface oxygen vacancies was attributed to cationic Ce^{4+}/Ce^{3+} elements leading to the promotion of lactic acid yield and high glycerol conversion.*

Keywords: *mixed metal oxide catalyst; oxidation; impregnation; co-precipitation; calcination*

■ INTRODUCTION

The production of lactic acid from glycerol has been receiving a lot of attention due to the efficient role of glycerol as a raw material in producing various useful chemicals [1]. Selective oxidation and hydrothermal reactions using solid catalyst have been found as potential techniques to promote high yield and selectivity of lactic acid. Different types of solid catalysts have been studied, such as monometallic, bimetallic, alkaline metal catalyst, alkaline earth metal catalyst, and supported catalyst [2-4].

One important application is the selective oxidation reaction which involves the roles of oxygen capacity in the reaction mechanism. Ceria catalysts feature in a variety of catalytic reactions. CeO_2 catalyst has attracted much attention due to its good oxygen storage capacity, thermal resistance and redox promotion property [5-7]. The chemical basicity property of the catalysts was contributed by CaO, as an important modification in the development of mixed oxide catalyst. 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 La_2O_3 or CeO_2 as appropriate support [8].

ZrO_2 could be suitable solid support due to its surface catalytic sites properties such as the high concentration of hydroxyl groups and coordinative unsaturated Lewis acidic-basic $Zr4^+O^{2-}$ pairs. These features are believed to potentially enhance the catalytic ability of the transition metal active sites [9]. Thus, this potential has created the interest to explore the suitability of a $CaOCeO_2/ZrO_2$ mixed oxide catalyst in the oxidative reaction of glycerol.

According to He et al. [10], the catalyst preparation method is a critical factor in determining the interaction between the active metal components and the support. Therefore, it is important to compare the characterization and activity of the catalysts prepared by different synthesis methods and calcination temperatures. Hence, modification of the prepared catalyst would be expected to have an important influence in improving the activity. Thus, incorporation of CaO and CeO_2 into zirconia support seemed to result in a properly mixed oxide catalyst for further study, and its activity can be further improved with necessary modifications.

■ EXPERIMENTAL SECTION

Materials

Glycerols (98% purity), calcium nitrate hexahydrate, $Ca(NO_3)_2{\cdot}6H_2O$, cerium nitrate hexahydrate, ($Ce(NO_3)_2{\cdot}6H_2O$), zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), ammonium hydroxide, NH_3OH (99% solution in water), sodium hydroxide, NaOH (90%) and sodium bicarbonate, Na_2CO_3 (90%) were purchased from Fluka. Deionized water (DI) was used throughout the study for the preparation of the support and catalysts. All chemicals were of reagent grade and were used as received without further purification.

Procedure

Preparation of mixed oxide catalysts

Zirconia (ZrO_2) support was prepared based on a work reported by Yang et al. [11] by using zirconium chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), and adjusting the pH of the solution to 10–11 by dropwise addition of ammonium hydroxide solution (25%). The sample was then calcined at 500 °C for 3 h and used as the catalyst support. The support material was first dispersed in DI water and the required amounts of $Ca(NO_3)_2$ and $Ce(NO_3)_2$ solutions were added dropwise under stirring. Then, calculated amounts of 1 M NaOH and Na_2CO_3 were also added dropwise to maintain the pH at 10–11. The temperature of the mixture was set at 80 °C for 5 h on a hotplate stirrer. The suspension was then filtered, and the solid was thoroughly washed with deionized water to eliminate all traces of base (pH test). The catalysts were dried overnight at 80 °C followed by calcination at either 600 or 800 °C for 4 h.

Mixed oxide catalysts were also prepared using an impregnation method by mixing the calcined zirconia with an aqueous solution of metal precursors ($Ca(NO_3)_2$ and $Ce(NO_3)_2$. The number of precursors used was calculated to obtain (30 wt.%) of active metal loading with a certain ratio of Ca and Ce. The solution was mixed for 24 h to ensure that metal dissolved and dispersed thoroughly on the surface of zirconia. The impregnated catalysts were then calcined in a muffle furnace at 600 and 800 °C for 4 h. The solids obtained were dried in an oven at 120 °C for 2 h before use in the oxidation reaction.

Characterization of the catalysts

The crystalline phases in the prepared catalyst samples and the average crystallite sizes were examined by X-ray diffraction (XRD) method using a Bruker diffractometer operated at 40 kV and 30 mA. The XRD patterns of the samples were obtained using with CuKα irradiation in the 2θ range of 5–90° with a step size of 0.03 °L. Thermal gravimetric analysis (TGA) was performed to observe any significant change in the weight loss of the catalysts. About 5 mg of the catalyst sample was heated from 31 to 800 °C at a heating rate of 10 °C/min in and an airflow of 25 mL/min by using simultaneous thermal analyzer (STA, 6000 from Perkin-Elmer USA).

X-ray photoelectron spectroscopy (XPS) study was carried using an AXIS Ultra DLD system equipped with AlKα X-ray source (1486.6 eV) by Kratos. Both of wide and narrow XPS scan spectra were obtained by scanning a 300 mm × 700 mm area at 7.5×10^{-9} torr ultravacuum environment inside the sample chamber. The analysis was performed using a hybrid lens mode with the slot aperture. The energy of the hemispherical analyzer was set at 160 eV for the survey scan and 20 eV for the narrow scan. The spectra were analyzed by a vision software with vision manager and processing abilities. For background subtraction and curve fitting, a linear method was used. The catalysts surface morphologies were studied utilizing a field emission scanning electron microscope (FESEM Carl Zeiss SMT, Oberkochen, Germany).

Hammett indicator method

Hammett indicator method was used to measure the basic strength of the catalyst samples (H_) [12]. In this procedure, 25 mg of the sample was first vigorously dispersed in 5.0 mL of Hammett indicator solutions and allowed to reach equilibrium for about 2 h until no significant change in the color intensity was observed. Results were reported as being higher than the weakest Hammett indicator which experienced color change, but lower than the strongest indicator that did not exhibit any color change. The Hammett indicators used in this study were 4-chloroaniline (H_ = 26.5), 4-nitroaniline (H_ = 18.4), 2,4-dinitroaniline (H_ = 15.0), phenolphthalein (H_ = 9.3), bromothymol blue (H_ = 7.2) and neutral red (H_ = 6.8).

Basicity test

The basicity of the catalysts was determined using Hammett indicator-benzoic acid titration method [13]. First, the 10 mg catalyst was shaken in a conical flask with 2.0 mL of Hammett indicator solution that had been diluted with methanol. 0.1 mol/L benzoic acid was then added dropwise into the conical flask, and the basic catalyst was neutralized using the benzoic acid. When the basic color disappeared, the volume of benzoic acid used was recorded. The basicity (mmol/g) of solid bases was evaluated by Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration until its color changed back to the original color.

Catalyst activity

Batch hydrothermal glycerol reaction was carried out in a 50 mL stainless steel autoclave at a stirring speed of 280 rpm. The standard reaction was carried out under the following reaction conditions: 99% aqueous glycerol, 20 wt.% of catalyst for 2 h of reaction. After being purged with O_2 for 15 min, the reactor was heated to the desired reaction temperature of 250 °C, and the O_2 pressure was maintained at about 7 bar. The liquid-phase products were analyzed through a gas chromatograph with a SHODEX capillary column (50 m × 0.32 mm × 0.25 µm) 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.

■ RESULTS AND DISCUSSION

Characterization of the Prepared Catalyst

The XRD analysis confirmed the formation of crystalline CaO and CeO_2 on ZrO_2 in the synthesized samples. When prepared by co-precipitation, a solid with two independent phases of the two oxides was formed as indicated by XRD. The latter phase decorates the surface of ZnO as indicated by a clear role of calcium and cerium in the surface chemistry at (CeO_2ZrO_2, cubic, 2θ = 28.3 and 34.4°) and ($CaOZrO_2$, cubic: 2θ = 60.3 and 47.5°) of the mixed oxide catalyst. The CaCeZCP catalyst exhibited stronger diffraction peaks than the CaCeZIMP catalysts. Meanwhile, the CaCeZ800 catalyst exhibited higher crystallinity with a more intense peak due to the presence of CaO and CeO_2 phase compared to CaCeZ600 catalyst.

The sizes of the crystalline metal oxides of CaO and CeO_2 were calculated from the XRD diffraction peaks using the Scherrer equation. $CaCeZrO_2CP$ and $CaCeZrO_2800$ catalysts exhibited a larger size of crystalline oxides of CaO and CeO_2, with a crystal size of about to 200 nm, while $CaCeZrO_2IMP$ catalyst exhibited the smaller size of 140 nm. It is shown that the method of preparation and different calcination temperatures affected both the structure and crystalline size of the CeO_2 and CaO in the catalysts (Fig. 1). Increasing calcination temperature to 800 °C would increase the intensity of XRD reflexes due to the increase in the crystallinity, and it is in agreement with the findings by Al-Fatesh et al. [14].

In addition to the XRD analysis, thermogravimetric analysis (TGA) was also performed on the $CaCeZrO_2$ systems with the results, as shown in Fig. 2. TGA experiment provided information about water and nitrate ion losses as the catalyst was heated from 0–800 °C. The initial water loss was observed in the temperature range of 0–200 °C, followed by NO_3^{2-} ions decomposition between 600 °C and < 800 °C. Almost 10 wt.% mass decrease was observed in this temperature range due to the loss of nitrate ions from the ZrO_2 surface.

Nitrate ions contributed greatly to the catalyst's basicity and consequently the catalytic activity. It was,

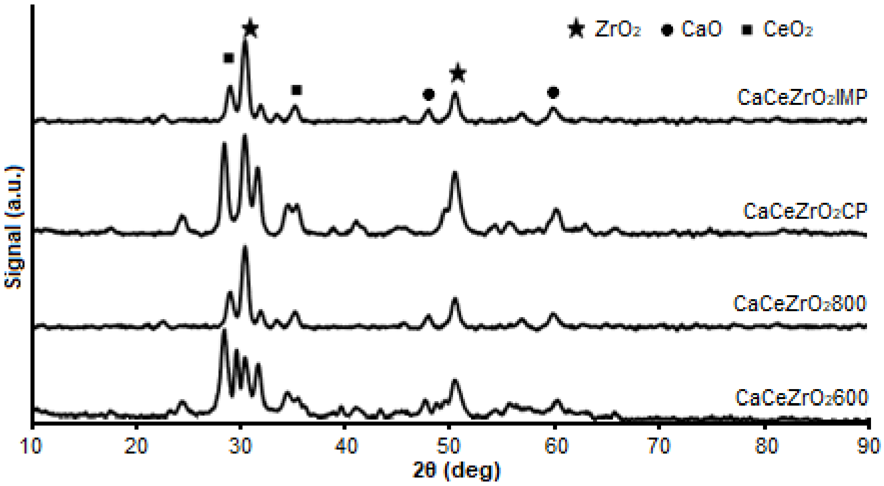

Fig 1. XRD patterns of the prepared catalysts

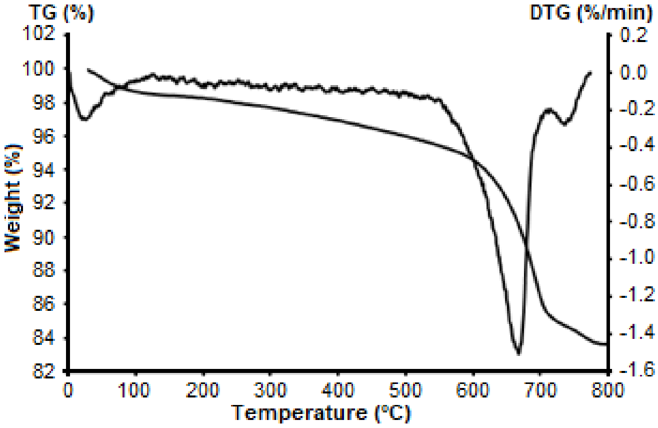

Fig 2. TGA profiles of $CaCeZrO_2800$ catalyst

therefore, important to understand the temperature range of nitrate loss to demonstrate the stability of the catalysts in terms of thermal stability of the synthesized materials. From the results, the catalyst was found to be thermally stable at a temperature of around 800 °C.

A significant change in the morphology was influenced by the preparation method and calcination temperature, as shown in Fig. 3. All of the catalytic materials had different morphologies. $CaCeZrO_2IMP$ catalyst as shown in Fig. 3(a) appears to have a uniform and quasi-spherical particles with inner-aggregate pores particles. However, as for the $CaCeZrO_2CP$ catalyst, the

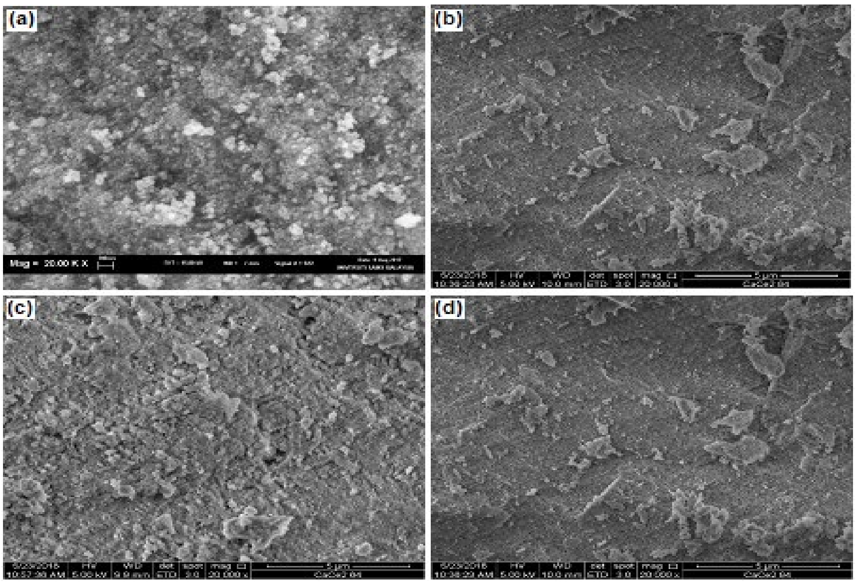

Fig 3. SEM of images at 20.0 k magnification of (a) $CaCeZrO_2IMP$ (b) $CaCeZrO_2CP$ (c) $CaCeZrO_2600$ (d) $CaCeZrO_2800$ catalysts

aggregates of metal oxide forming small porous structures are visible (Fig. 3(b)).

As the calcination temperature was increased, the morphology of $CaCeZrO_2600$ (Fig. 3(c)) and $CaCeZrO_2800$ (Fig. 3 (d)) also showed significant differences. The catalyst calcined at 800 °C exhibited more uniform and more porous surface suggesting high dispersion of Ca and Ce on the ZrO_2 support. In addition, calcination process could also contribute to the formation of a hollow, porous, and fluffy product as the reactions that occurred would release large amounts of gas and heat. Ozawa et al. [15] suggested that uniform dispersion of CeO_2 over the surface after calcination could result in better dispersion of the active phase. Uniform morphology and crystalline metal of $CaCeZrO_2$ mixed oxide catalyst indicated to the successful preparation method of coprecipitation at high calcination temperature.

Table 1 shows the X-ray photoelectron spectroscopy (XPS) results collected in order to study the chemical composition and state of the mixed oxide catalysts. It shows the XPS spectra in the O 1s, Ce 3d, Ca 2p, and Zr 3d BE ranges. For $CaCeZrO_2600$, the O 1s spectrum shows a peak at 528.7, while for $CaCeZrO_2800$, the O 1s spectrum shows a peak at 529.6, and this peak is attributed to chemisorbed oxygen. According to the Piumetti et al. [16], the signal at 528.6–528.9 eV corresponds to O (i.e. O^{2-}), whereas the peak at 529.9–531.4 eV can be ascribed to surface oxygens (i.e. O_2^{2-}, O^-, OH^-, CO_3^{2-}). For $CaCeZrO_2800$, the signal related to the O species appears at a slightly higher BE (529.6 eV); thus, revealing a lower nucleophilicity of the lattice oxygen ions. A richer population of O species was obtained for high-surface area materials rather than because of the richer population of surface hydroxyls, carbonates and adsorbed oxygen [16].

In the Ce 3d region, three peaks within 880–920 eV are recorded at $3d_{5/2}$ and $3d_{3/2}$. The Ce^{3+}/Ce^{4+} content of $CaCeZrO_2800$ (15.81%) is higher than that of $CaCeZrO_2600$ (10.70%) because of the higher thermal treatment used during the preparation method [16]. The mixed oxide catalyst showed the presence of CaO and CeO in both the cationic as well as in the metallic states. The occurrence of cationic Ca species confirms the interaction between CaO and CeO nanoparticles, which was expected to lead to Ce^{3+}/Ce^{4+} and oxygen deficient sites in the ceria [17].

The Zr 3d spectra in the 181.9–182.3 eV range denote the Zr $3d_{5/2}$ state, whereas the signal at 184.4 eV corresponds to the Zr $3d_{3/2}$ levels. Based on the binding energy of Zr $3d_{5/2}$, Ce-Zr mixed oxide can be well distinguished from the ZrO_2 phase (182.9 eV) [18]. In the case of powder catalyst, a strong Ce-Ca interaction could lead to the formation of Ce–Ca–O mixed oxide system characterized by the enhancement of Ce^{3+}/Ce^{4+} ion concentration [18].

The basic properties (basic strength, surface basicity) seemed to influence the catalytic activity. The basicity values obtained by using Hammett indicator and benzoic acid titration were in good agreement with the catalytic activity results. The highest value of basicity (0.020 mmol/g) produced the highest yield (38.8%) and selectivity (40.6%) of lactic acid. The conversion of glycerol theoretically increases when the catalyst basicity increases [19]. The basic sites for $CaZrO_2$ and $CeZrO_2$ showed H_ in the range of 6.8–7.2. Upon the incorporation of Ca and Ce, higher basicity, H_ in the range of 9.8–15.0 was observed; thus, showing a higher yield of lactic acid due to the surface basic sites value.

Table 1. Summary of XPS results for $CaCeZrO_2$ catalysts calcined at 600 and 800 °C

Catalyst	Binding energy/eV (Atomic concentration (%))			
	Ce 3d	O 1s	Ca 2p	Zr 3d
$CaCeZrO_2600$	895.7	528.7	345.7	181.7
	(10.7)	(46.91)	(10.85)	(7.36)
$CaCeZrO_2800$	897.6	529.6	345.6	181.6
	(15.81)	(50.54)	(13.26)	(8.18)

Table 2. Performance of the $CaCeZrO_2$ catalysts at different preparation conditions

Catalyst	Hammett indicator	Basicity (mmol/g)	Glycerol conversion (%)	Yield (%)	Selectivity (%)
$CaZrO_2$	6.8–7.2	0.008	96.5	29.5	30.5
$CeZrO_2$	6.8–7.2	0.005	96.3	28.3	29.3
$CaCeZrO_2$CP	9.8–15.0	0.020	95.4	38.8	40.6
$CaCeZrO_2$IMP	9.8–15.0	0.015	90.2	32.5	36.1
$CaCeZrO_2$600	9.8–15.0	0.010	95.8	29.3	30.6
$CaCeZrO_2$800	9.8–15.0	0.020	95.4	38.8	40.6

Performance of the Prepared Catalyst

The activity of $CaCeZrO_2$ catalysts prepared with two preparation methods and calcination temperatures are shown in Table 2. Catalytic tests showed that $CaCeZrO_2$ catalysts prepared by coprecipitation gave higher glycerol conversion (95.4%) and lactic acid yield (38.8%) in comparison to those prepared by impregnation method (90.2%, 32.5%, respectively). According to Chen et al. [20], the production of lactic acid requires a strong base with a hydrophilic surface to facilitate the mass transfer between glycerol and the catalyst. It could be due to the fact that the pore structure of calcined catalyst was uniform and it was sufficiently porous to provide sufficient reaction to occur as shown in Fig. 3(a-b). Glycerol was expected to be able to diffuse easily inward into the pores of the catalyst. The interaction with CaO and CeO_2 on the internal and external of the basic sites catalyst surface generated with the cooperation of CaO and oxygen storage capability of CeO_2. The porous morphology and crystalline phase of mixed oxide were confirmed from SEM and XRD analysis results, respectively.

Effects of calcination temperature on the performance of the catalyst were investigated at 600 and 800 °C. Results showed that the conversion of glycerol remained at the same value (95%), but lactic acid yield increased from 29.30 to 38.80%, for $CaCeZrO_2$600 and $CaCeZrO_2$800, respectively. Based on the XPS results, the amounts of CeO_2, Ca and O of the catalyst produced with a calcination at 800 °C were relatively higher (15.80, 13.26, and 50.54%, respectively) as compared at those of the catalyst calcined at 600 °C (10.70, 10.85, and 46.91%, respectively). Thus, the conversion of glycerol to lactic acid was believed to be affected by the amount of active CaO and CeO_2 with the presence of ZrO_2 at high calcination temperature as observed in the XPS results. Sietsma et al. [21] reported that low dispersion of active metal on support was due to the redistribution during drying at low temperature. Al-Fatesh and Fakeeha [22] suggested that high temperature should be employed to ensure sufficient decomposition of the salt used, solid state reactions of the support and reactions between deposited oxides. A nanocrystalline IrO_2 structure was studied by Xu et al. [23], and they showed that almost no IrO_2 nanoparticles were generated due to amorphous coating that was not fully decomposed at low calcination temperature. Consequently, it affected the total number of active sites available to catalyze their reaction.

Therefore, the highest activity achieved by $CaCeZrO_2$ catalyst was attributed to the significant formation of the desired surface structure of mixed metal oxide formed at a calcination temperature of 800 °C and prepared with the coprecipitation method.

■ CONCLUSION

Incorporations of calcium and cerium onto the zirconia support led to the formation of an efficient catalyst for lactic acid production from glycerol. High yield of lactic acid (38.80%) with 95.4% glycerol conversion was achieved. Investigation on the preparation method of catalyst and calcination temperature revealed the significant influences on the yield of lactic acid and glycerol conversion. Well-developed porous structure, high crystallinity of CaO, and CeO_2 supported on ZrO_2 and basicity properties made it possible to convert glycerol to lactic acid selectively. Thus, the $CaCeZrO_2$ catalyst was deemed and suitable for application as a solid catalyst for lactic acid production from glycerol.

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