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ORIGINAL PAPER

Zirconium–Cerium Oxides Supported on SBA-15 as Catalyst for Shape-Selective Synthesis of Lactic Acid from Glycerol

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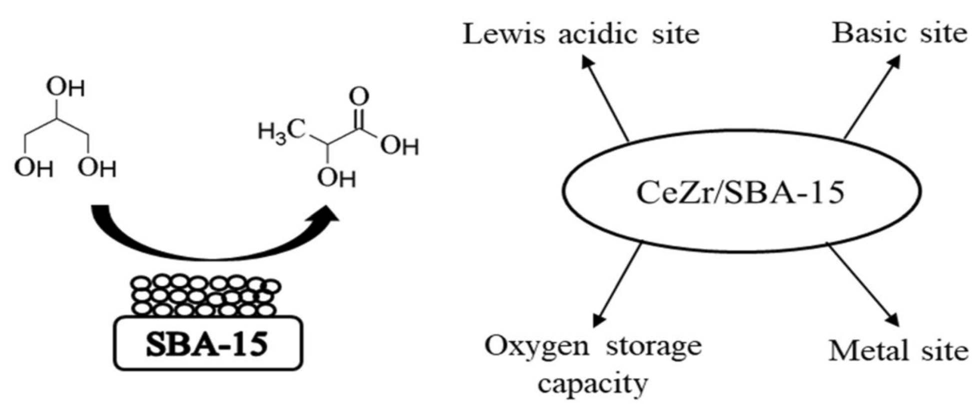
Abstract
The conversion of an oleochemical waste i.e. glycerol into lactic acid (LA) using bifunctional catalyst is receiving intensive research attention. The major concern is to achieve a suitable combination of the non-precious active metals with specific roles to achieve a fast and selective reaction. Catalyst with a Ce-to-Zr ratio of 1:2 and supported on SBA-15 at total active metal loadings between 10 and 40 wt% were prepared via a two-sequential-step post-impregnation method. The catalysts were then characterized using nitrogen adsorption–desorption and SEM analyses to elucidate their properties. They were then employed in selective glycerol oxidation reaction carried out at between 240 and 280 °C for up to 3 h to yield LA. The catalytic performance in terms of glycerol conversion and lactic acid yield was successfully correlated with the physicochemical properties of the catalysts. The highest glycerol conversion of 91.2% of glycerol was obtained using 10 wt% of CeZr/SBA-15 at a catalyst loading of 25 wt% with almost 51.4% of corresponding LA yield. It was attributed to the desired shape selectivity effect in the benzylic rearrangement (Cannizzaro reaction) of pyruvaldehyde to suppress by-product formations.

Graphic Abstract



Keywords Glycerol oxidation · Ce–Zr oxides · SBA-15 support · Base-free medium · Lactic acid yield · Shape selectivity effect

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Statement of Novelty

Glycerol is currently considered an oleochemical waste that justifies its valorization to value-added products. The synthesis of mixed Ce–Zr catalyst supported on SBA-15 via a post-impregnation method is potential to catalyze the selective glycerol oxidation reaction to lactic acid amidst many competitive reactions. The combination of Ce and Zr with oxygen storage capability and basicity properties, respectively in this one-pot synthesis is hardly reported in the literature. This study also elucidates the combined roles of the active metals coupled with the shape-selectivity effect of SBA-15 support to favor the formation of lactic acid under different reaction conditions.

Introduction

Glycerol is currently produced at surplus amounts in various industries such as biodiesel, oleochemical, and soap making industries. For example, around 10 wt% of glycerol out of the total weight of biodiesel produced is generated by the biodiesel industry. To date, there is a need for urgent utilization of the oversupplied glycerol as it is now even considered a waste. Conversions of glycerol to value-added chemicals are among the options available to create higher future demand for glycerol. Various pathways such as selective oxidation, etherification, esterification, trans-esterification, dehydration and carboxylation have been explored to convert glycerol into value-added chemicals [1, 2].

Lactic acid (LA) is one of the value-added glycerol derivatives that at present has proven to be scientifically and industrially significant. This is due to its high demand for applications as a preservative, flavoring agent, humectant, curing agent etc., especially in food, pharmaceutical, and cosmetic industries [3, 4]. The yearly production of LA from conventional markets was at 260,000 tons in 2008. By 2020, it is forecasted that the annual production could reach over 1 million tons to cater to conventional markets as well as the emerging poly-lactic acid (PLA) industry [2]. This organic acid can be conventionally produced either by chemical synthesis or through a certain biochemical route. The current industrial production of LA, which is dominated by a fermentation process, has several drawbacks such as the requirement for a large amount of water, low reaction rate, and high operating costs due to the complicated separation and purification steps in the downstream processes [3]. The high production cost causes the high price of LA leading to restricted industrial applications. There have been aggressive research efforts focusing on designing a greener and sustainable system to obtain LA from glycerol [2, 4]. More specifically, the production of LA by hydrothermal conversion of glycerol using chemical catalysts has received research attention due to foreseeable cost-effectiveness and feasibility of the conversion process.

One of the earliest successes was a base-aided hydrothermal conversion of 0.33 M of glycerol to LA which achieved almost 90% of LA yield at 300 °C [4]. Another research group studied the use of about 10-folds higher glycerol concentration with 1.1 NaOH-to-glycerol molar ratio as the catalyst and they recorded 84.5% of LA yield at 280 °C [5]. Therefore, it could be expected that a higher amount of base was required to catalyze a higher concentration of glycerol. High alkalinity at elevated temperature demands the use of a specific type of reactor to address the concerns with regards to high corrosiveness, especially in industrial-scale operations. In addition, the separation of the homogeneous catalyst after the reaction was rather complicated and polluting. Lakshmanan et al. [6] proved that CeO_2-supported gold nanoparticles could achieve up to 83% of LA selectivity by suppressing other by-products (formic acid, glycolic acid, glyceric acid, and acetic acid). Another research group synthesized carbon-supported monometallic and bimetallic PtRu and AuRu catalysts for glycerol hydrogenolysis at 200 °C and 40 atm of H_2 [5, 6]. Their study revealed that with the addition of NaOH, bimetallic catalysts promoted the production of lactate and propylene glycol. However, the product distribution or selectivity of the bimetallic catalysts were quantitatively comparable to those of the monometallic Ru catalysts at high and neutral pH conditions. Further enhancement could be theoretically achieved using mesoporous support that could effectively introduce the critical shape-selectivity effect to favor the formation of specific products in many oleochemical conversions [5, 7, 8].

In another attempt, Shen et al. [9] tested Au/TiO_2, Pt/TiO_2, Pd/TiO_2 and $AuPt/TiO_2$ catalysts for the oxidation of glycerol to LA. Their results apparently showed that high LA selectivity (85.6%) was achieved with $AuPt/TiO_2$ catalyst at 90 °C, 1.0 atm of O_2, 0.22 mol/L of glycerol, and a NaOH-to-glycerol molar ratio of 4:1. Cu-based catalysts (Cu/SiO_2 and CuO/Al_2O_3) were also tested for glycerol conversion into LA [10]. It was claimed that Cu-based catalysts demonstrated good stability for prolonged use besides achieving high LA yields of around 80% at 200 °C.

Usually, gold, palladium, and ruthenium can show outstanding performances in the oxidation of glycerol, especially when dispersed on suitable porous supports. Hence, commercially available catalysts were screened for hydrogenolysis of glycerol and $Pt/CaCO_3$ emerged as both an active and selective catalyst [11]. Auneau and co-workers observed the formation of LA as an oxidation product of glycerol using Rh/C and Ir/C [12] catalysts. Their studies concluded that higher yield (> 77%) of LA could be achieved in alkaline conditions with the use of an Ir/C catalyst. Later, the conversion of glycerol to LA using CeO_2-supported monometallic (Au and Pt) and bimetallic (Au–Pt) catalysts were also explored [13]. In short, the bimetallic catalysts showed better performance with almost 80% of LA selectivity when 99% of glycerol conversion was achieved at 100 °C with 4 mol/mol of NaOH-to-glycerol ratio. Besides, the Au-Pt/n-CeO_2 catalyst also showed good recyclability for up to 5 cycles without experiencing a significant loss of activity. The catalytic performance of Pd/C catalysts for glycerol conversion into LA was also investigated [14]. Almost 99%

glycerol conversion and 46% LA selectivity were exhibited by the catalyst at a reaction temperature of 230 °C and a NaOH-to-glycerol molar ratio of 1.1. Unfortunately, the main concern of these types of catalyst is the high cost of the active metal components.

To enhance the catalytic performance, Arcanjo et al. [15] investigated the catalytic activity of Pd/C and Pt/C for selective LA synthesis. At a reaction temperature of 230 °C, they achieved almost 99% of glycerol conversion with LA selectivities of 74% and 68%, using 5% Pt/C and 10% Pd/C catalysts, respectively. Furthermore, both catalysts showed excellent stability in five cycles of reaction without experiencing severe loss of activity. However, despite the high conversion and selectivity, the overall productivity was still way too low due to the low initial glycerol concentration used in these studies. Hence, the major issue to be addressed in this study was the possible use of pure glycerol as the reactant to selectively synthesize LA. In general, catalytic behaviors are highly dependent on the structure of the catalysts, specifically the type of support, type of active metals, the porosity of the catalyst, pH of the catalyst and the catalyst's particle size [5, 7]. Herein, 1:2 mol/mol of CeZr oxides as the active components were supported on an ordered mesoporous support (SBA-15) and used as the catalyst to achieve selective glycerol conversion to LA in the absence of a base in the reaction medium. In addition, the roles of reaction parameters such as temperature, active metal loading, the catalyst to reactant ratio, and reaction time on the course of the reaction were also studied. Besides, the catalysts were also characterized for surface and morphological properties for correlation with catalytic behaviors. A better understanding of the intrinsic factors affecting the shape-selectivity in the reaction was expected from this research work.

Materials and Methods

Catalyst Preparation

The CeZr/SBA-15 catalysts were synthesized via a two-step post-impregnation and incipient wetness technique. This method was quantitative in nature so that the chemical composition of the final catalysts would have direct correlation with the synthesis composition. The preparation of SBA-15 support was carried out following a reported method with minor modifications [16]. 7.5 g of Pluronic P-123 (poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)) was first dissolved in a solution containing 70 g of 2 M HCl and 150 g of distilled water and stirred for 16 h. Then, 20 g of tetraethyl orthosilicate (TEOS) was added dropwise into the clear solution and the mixture was left under vigorous stirring at 60 °C for 8 h. The solution was then transferred to an autoclave reactor and left for another 16 h at 80 °C under static conditions. Next, the solid product was filtered, washed with deionized water, and dried at 60 °C for 24 h. The organic template was finally removed by calcination in air at 550 °C for 8 h.

The method described in the literature [17] was employed with some modification for the preparation of the CeZr/SBA-15 catalysts. Four different levels of active metal loadings in the SBA-15 support were prepared i.e. 10 wt%, 20 wt%, 30 wt%, and 40 wt%. Meanwhile, the metal ratio between Ce and Zr was fixed at 1:2 throughout the work. For the preparation of 10 wt% 1:2 CeZr/SBA-15 catalyst, 0.0687 mol/dm^3 of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.1374 mol/dm^3 of zirconium oxonitrate hydrate ($ZrO(NO_3)_2 \cdot xH_2O$ were first dissolved in ethanol. The prepared SBA-15 support was first dried for 1 h at 80 °C prior to use in the impregnation method. The mixture was then stirred until a free-flowing solution was formed. Sodium hydroxide was then added into the resulting mixture until the catalyst reached a pH of 9 and it was then left under stirring for 6 to 7 h at 70 °C. Then, the mixture was subsequently washed with deionized water and dried at 80 °C for 1.5 h. Next, the temperature was increased to 110 °C for 18 h before calcination at 500 °C for 4 h. For other CeZr active metal loadings (5, 10, 20, 30, 40 wt%) in the SBA-15 support, the same method was used with appropriate amounts of the metal precursors.

In this study, the catalyst loading which refers to the weight ratio of the most active catalyst to that of glycerol (catalyst/glycerol wt%) was also varied between 10 and 40% to demonstrate the effect on glycerol conversion and lactic acid yield. In this study, the ranges of the reaction parameter values for the active metal loading (wt%) and catalyst loading (catalyst/glycerol wt%) were decided based on a trial-and-error method to achieve sufficiently high glycerol conversion of above 60% with the corresponding lactic acid yields of above 20% to be at par with the ranges of glycerol conversion and lactic acid yield commonly reported in literature.

The main scope of this work was for characterizing the roles of active metal loading and catalyst loading on the conversion of glycerol and corresponding lactic acid yield. The procedure to prepare all the catalysts was the same except for the amount of active metals loaded into the support. A calcination temperature of 500 °C was also reported to be able to form these metal oxides [6, 16, 17]. As such, the catalysts' active species should be in their oxides form and should not have different chemical phases from one another. Then, differences in the catalytic behaviors could be mainly attributed to their surface characteristics.

Catalyst Characterization

The CeZr/SBA-15 catalysts with different loadings of active metals were characterized using various techniques to elucidate their physical and morphological properties for correlation with their catalytic behaviors. By using a Quantachrome Autosorb 1C surface analyzer operated at liquid nitrogen temperature, surface analysis of all the catalysts was performed. In addition, scanning electron microscopy (SEM) images were obtained using a Quanta FEG 450 SEM for the morphological analysis of the catalysts.

Catalytic Activity Study

A modified stirred stainless-steel Parr reactor was used as the fed-batch reactor to demonstrate the roles of the catalysts in the selective conversion of glycerol to LA. A pressure gauge installed on the Parr reactor was used to monitor the reaction pressure. 30 ml of glycerol and the desired amounts of catalyst (5–40 wt%) were initially charged into the reactor and the reactor vessel was then heated using a heating mantle until the desired temperatures (240–280 °C) were reached. The reaction was then conducted for up to 3 h at the designated temperature at a constant stirring speed of 350 rpm. At the end of the reaction, the reactor was taken out from the heating mantle and quenched with iced-water. The product mixture was then centrifuged at 4,000 rpm for 40 min and the upper layer of the mixture was collected and filtrated using a syringe filter to remove the catalyst. The filtered sample was then diluted with sulfuric acid to adjust the pH to around 3–4 before being further diluted with deionized water. The pre-treated samples were then analyzed by means of an HPLC (Waters-410, Waters Corporation) equipped with a Shodex SH1011 (300 × 8 mm) column and a refractive index detector (RID). All the reaction runs were carried out in triplicate to get the average results to be reported with respective standard errors. In this study, the activity of the catalyst could be reflected by the conversion of glycerol as the sole reactant while the shape selectivity effect of the catalysts could be sufficiently reflected by the yield of lactic acid.

Results and Discussion

Catalyst Characterization

Surface Analysis

In general, all the synthesized catalysts had total surface areas in the range of 343 to 594 m^2/g while that of SBA-15 support was 842 m^2/g (Table 1). The surface area of SBA-15 support was rather similar to the one reported earlier [18]. This indicated a successful synthesis of the SBA-15 support. The total surface area decreased with increasing metal loading and in general, all the catalysts could be classified as highly porous materials. The surface characteristics of the metal loaded catalysts were significantly reduced upon the introduction of the active metal phases, especially at metal loadings above 30 wt%. Theoretically, the higher the loading, the higher the amount of active metals that was introduced into the SBA-15 support. Especially at higher loadings, some of the active metals were expected to have been deposited on the external surface of the support or on the internal walls of the internal pores and this resulted in a certain degree of reduction in the total surface area. In addition, pore narrowing could also be concluded based on the shrinking of the average pore diameter.

It was noted that the micropore area and volume of the 20 wt% 1:2-CeZr/SBA-15 catalyst seemingly did not share the specific reduction trend. The micropore area and volume of this catalyst were surprisingly lower than those of the 30 and 40 wt% catalysts. As such, it could be concluded that some abnormalities must have occurred in the pores during the synthesis method, which caused this non-systematic trend to happen. It could be associated with the partial blockage of pore mouths of the micropores located at the walls of the SBA-15 mesoporous channels [18]. However, the total pore volumes of the SBA-15 support and all the synthesized catalysts were in the range of 0.2444–0.6658 cm^3/g, with SBA-15 support having the highest volume. Also, a decreasing trend in the total pore

Table 1 Surface characteristics of the SBA-15 support and CeZr/SBA-15 mesoporous catalysts at different active metal loadings

Catalyst	Total surface area (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore size (Å)
SBA-15	842	318	524	0.1566	0.6658	56.24
10 w.%-CeZr/SBA-15	594	192	403	0.0949	0.5779	51.72
20 wt%-CeZr/SBA-15	490	125	365	0.0636	0.5337	47.66
30 wt%-CeZr/SBA-15	478	160	317	0.0800	0.4474	46.56
40 wt%-CeZr/SBA-15	343	141	202	0.0719	0.2444	46.07

volume was observed with increasing active metal loading for the catalysts. The range of the total pore volume coincided with the common values reported in previous works to indicate successful formation of mesoporous catalysts [19–21]. This trend also pointed to the satisfactory retention of mesoporosity, especially at metal loadings below 30 wt%.

Apart from the 20 wt% catalyst, all other catalysts followed the general trend; the micropore and mesopore area decreased with increasing metal loading. As stated previously, metal deposition on the external surface of the pores, caused significant reductions in the pore size. In addition, the decrease in the mesoporosity actually suggested that the mesopore channels of the SBA-15 support were successfully deposited with Ce and Zr active metals. This phenomenon indirectly caused the reduction in the specific surface area and average pore size of all the synthesized catalysts with increasing active metal loadings. Besides, the high dispersion of Ce and Zr metals in the mesoporous channels or a probable strong interaction of these metal with the SBA-15 surface might as well explain this observation.

The average pore sizes of SBA-15 and catalysts with 10, 20, 30 and 40 wt% of CeZr catalysts were 56.24 Å, 51.27 Å, 47.66 Å, 46.56 Å, and 46.07 Å, respectively. All the catalysts were in mesoporous size range and this indicated a successful synthesis of the catalysts. This success was indeed critical in this study in order to synthesize mesoporous bimetallic catalysts that were highly active and selective towards glycerol oxidation to LA. Micropores might not be useful to the accelerated diffusion of reacting species while large mesopores could allow the formation of undesired large polymerization products [20].

It should be noted that the average pore size was slightly reduced by the increase in the active metal loading. Whereas reduction of the catalytic activity of this reaction on the basis of glycerol conversion and LA yield was expected, the effect could have been offset by the increase in the higher loading of the active components. The creation of secondary pores on the external surfaces could also result in a significant change in the pore size distribution of the catalysts. The catalyst pore sizes within meso size range generally play a positive role to facilitate the interaction between the reactant molecules with the active sites distributed within the pores, especially for reactions involving bulky molecules [2]. Small pores may cause geometrical constraints, where the reactant molecules could not fit into the internal pores to react. Meanwhile, relatively large pore sized catalysts as synthesized in this study were likely to experience lower diffusion limitations for reacting species in the liquid phase as in the case of this reaction. The catalyst should be able to interact with the glycerol molecules to facilitate the conversion to LA. However, the microporosity was deemed to play minor roles in this catalyst to deny a direct correlation between total surface area and catalytic activity [1]. It was ascribed to the mass transfer limitation within those micropores. In the case of this reaction, accelerated formation and diffusion of the desired product i.e. LA could be allowed while the capture of large by-products was inhibited due to the geometrical effect of the pores [18].

Adsorption Isotherm

Figure 1 shows the nitrogen adsorption–desorption isotherms of the SBA-15 support and all the 1:2-CeZr/SBA-15 catalysts. All samples including the mesoporous SBA-15 support exhibited the typical type IV isotherm (according to the IUPAC classification) [20]. The isotherms are characterized by typical hysteresis loops of H1 isotherms with narrow pore size distribution and closures around relative pressure drops (P/P_o) in the range of 0.45 to 0.90. This indicated that all the synthesized catalysts were significantly porous and had uniform pores arrangement of meso size range. Besides, all the hysteresis curves formed are almost similar to that of SBA-15 support, indicating the success in the synthesis of the mesoporous catalysts with the formation of uniform and regular pore shapes and pore distributions. Also, the physisorption in multilayer fashion as displayed by the hysteresis curves in Fig. 1 is attributed to capillary condensation that mainly occurred within the mesopores of the catalysts. This type of hysteresis is usually demonstrated by catalysts with pores in the size range of 15 to 1000 Å [21].

Meanwhile, the pore size distributions of the SBA-15 and all the synthesized catalysts were also analyzed using the Barrett-Joyner-Halenda (BJH) method as shown in Fig. 2. The catalysts generally had narrow ranges of pore size distribution, proving the pores of the synthesized catalysts were formed in a regular and ordered manner. As can be seen in the figure, the intensity of the peaks gradually decreases with increasing loading of the 1:2-CeZr active components in the SBA-15 support. This was influenced by the tensile strength effect, where the pores filled with N_2 were emptied through a narrower section of the pores of the catalysts during the nitrogen adsorption–desorption process [22]. It is generally hypothesized that due to the physical phenomenon during the adsorption process, at a certain partial pressure, the hysteresis loop will form a closure. Likewise, in this case, it could be concluded that the ink-bottle-shape of the pores and the narrower part of the pore throat could have caused this observation. The pores narrowing might be caused by the irregular active metals and non-framework silica distribution, forming 'plugs' at relatively narrow sections of the pores or pore throats [23]. Thus, the desorption process of the pre-adsorbed N_2 would likely to experience a certain degree of resistance at the throats.

As a matter of fact, the catalytic performance of the synthesized catalysts was expected to be highly dependent on

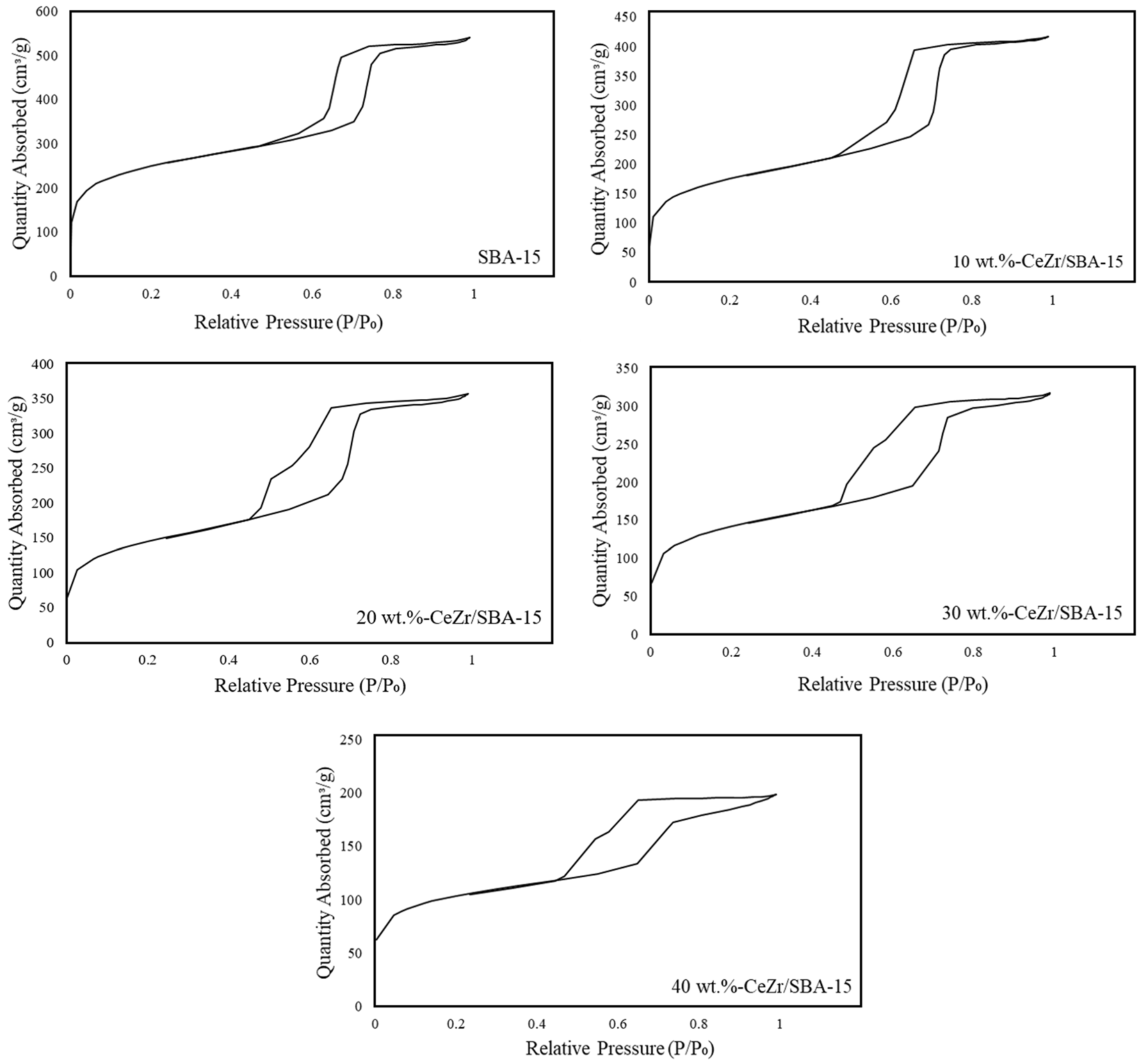

Fig. 1 Isotherm profiles of SBA-15, 10 wt% 1:2-CeZr/SBA-15, 20 wt% 1:2-CeZr/SBA-15, 30 wt% 1:2-CeZr/SBA-15 and 40 wt% 1:2-CeZr/SBA-15 catalysts

the distribution of the active metals in the SBA-15 support. The interdependency of both metals and their interaction with the support could directly influence the product distribution. Ce component in the catalyst was meant for oxygen storage while Zr component provided Lewis acid centers and metallic sites which helped initiate dehydrogenation of glycerol to occur [2]. The Ce sites were also deemed critical to help stabilize the Zr sites in its ionic state. Meanwhile, Zr could also contribute in terms of providing better oxygen storage capacity of Ce at a lower temperature when incorporated into the catalysts together.

SEM Analysis

The SEM micrographs of all the synthesized catalysts are shown in Fig. 3. Generally, they reveal typical morphology of SBA-15 with a porous and fibrous structure as typically seen in the circled region in Fig. 3a [1, 18]. Therefore, this result indicated successful synthesis of all the catalysts because all catalysts samples exhibited extended rod-like morphology with mesoporous structure of SBA-15 as reported earlier [16, 17]. The morphological structure of the catalysts is consistent with high surface area retention as exhibited by the catalysts at active metal loading of 40 wt% as shown in Table 1.

Figure 3 does not reveal visible deposits on the surface of 10 wt.% 1:2-CeZr/SBA-15. Active metals were preferably impregnated inside the internal pores of the support at such low metal loading. However, some metal deposits (small circles) could be detected on the external surface of the 20 wt.% 1:2-CeZr/SBA-15 catalyst (Fig. 3b) that was attributed to the partial deposition of Ce and Zr on the external surface when

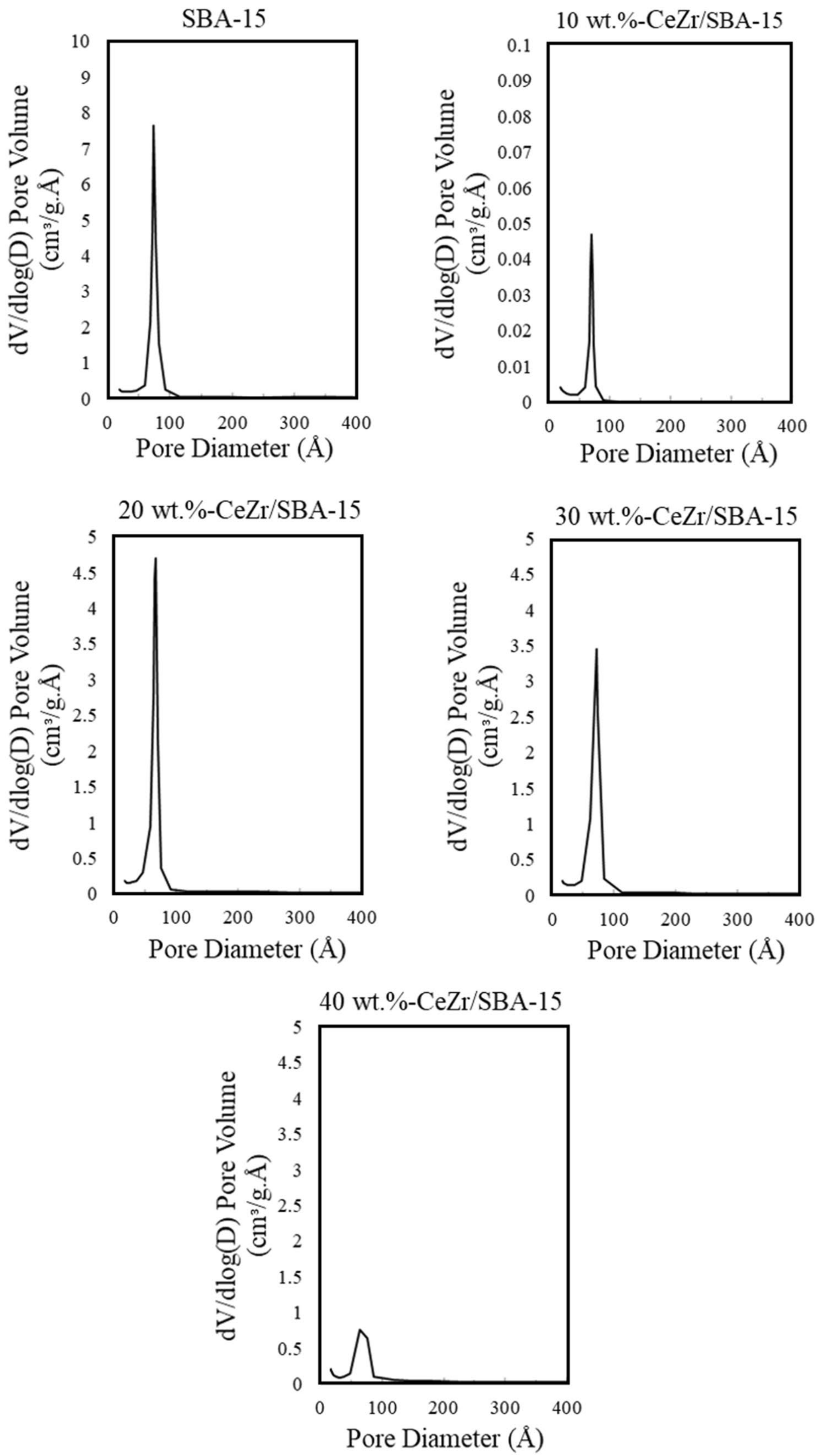

Fig. 2 BJH pore size distributions of SBA-15, 10 wt% 1:2-CeZr/SBA-15, 20 wt% 1:2-CeZr/SBA-15, 30 wt% 1:2-CeZr/SBA-15 and 40 wt% 1:2-CeZr/SBA-15 catalysts

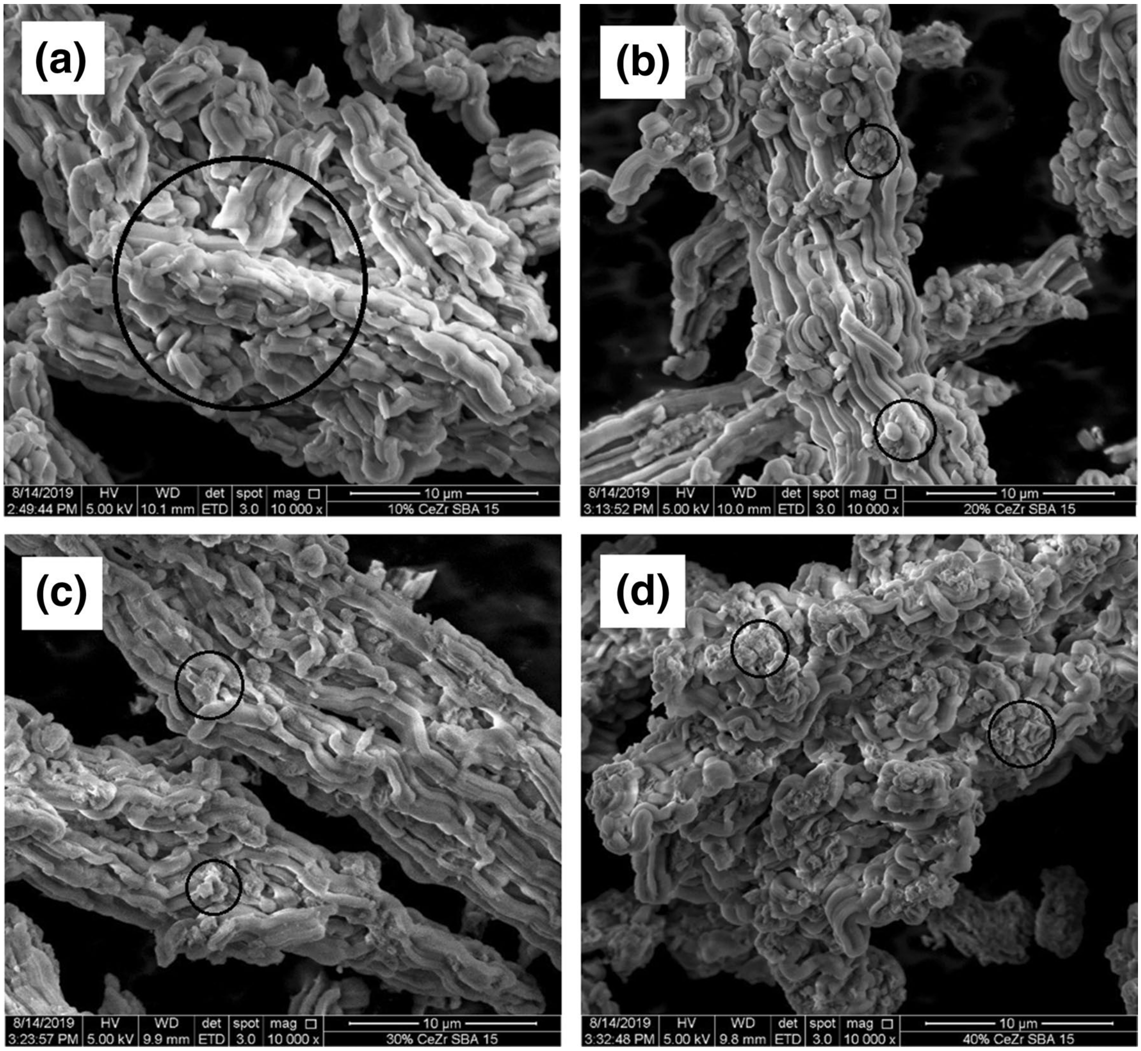

Fig. 3 SEM micrographs of **a** 10 wt% 1:2-CeZr/SBA-15, **b** 20 wt% 1:2-CeZr/SBA-15, **c** 30 wt%1:2-CeZr/SBA-15, **d** 40 wt% 1:2-CeZr/SBA-15 catalysts at a magnification of 10 kX

the metal loading was doubled. Relatively more metal crystallites were found on the external surfaces of the catalysts with higher loadings as seen in Fig. 3c, d. This was generally due to a higher tendency for the formation of metal clusters/crystals on the external surface of support at higher loadings due to partial narrowing of the internal mesopore channels. These observations were consistent with the surface analysis results as shown in Table 1.

Catalytic Activity Study

Effects of Active Metal and Catalyst Loadings

Effects of different active metal loadings (between 5 and 40 wt.%) on the glycerol conversion and LA yield were then investigated and correlations with the characteristics of the catalysts were established. Other reaction parameters such as catalyst loading, reaction temperature and reaction time were kept constant at 20 wt.%, 250 °C, and 2 h, respectively. From Fig. 4a, all the catalysts (except the 5 wt.% 1:2-CeZr/SBA-15) showed high activity with generally above 80% glycerol conversions. The results were impressive considering that pure glycerol was used in this work as compared to a conversion of about 90% by Ni^0/graphite achieved with a glycerol concentration of 1 M as reported by Yin et al. [4]. This suggested the high activity of the catalysts that was mainly attributed to the presence of the active metals on the surface inert mesoporous support.

Evidently, increasing the amount of active metal incorporated into the catalyst from 5 to 10 wt% improved the catalytic activity as suggested by the higher conversion of glycerol from 59.2 to 80.5%. It is known that these metal sites are the main requirement to produce LA [24–26]. The lower activity of the 5 wt% active metal could be attributed

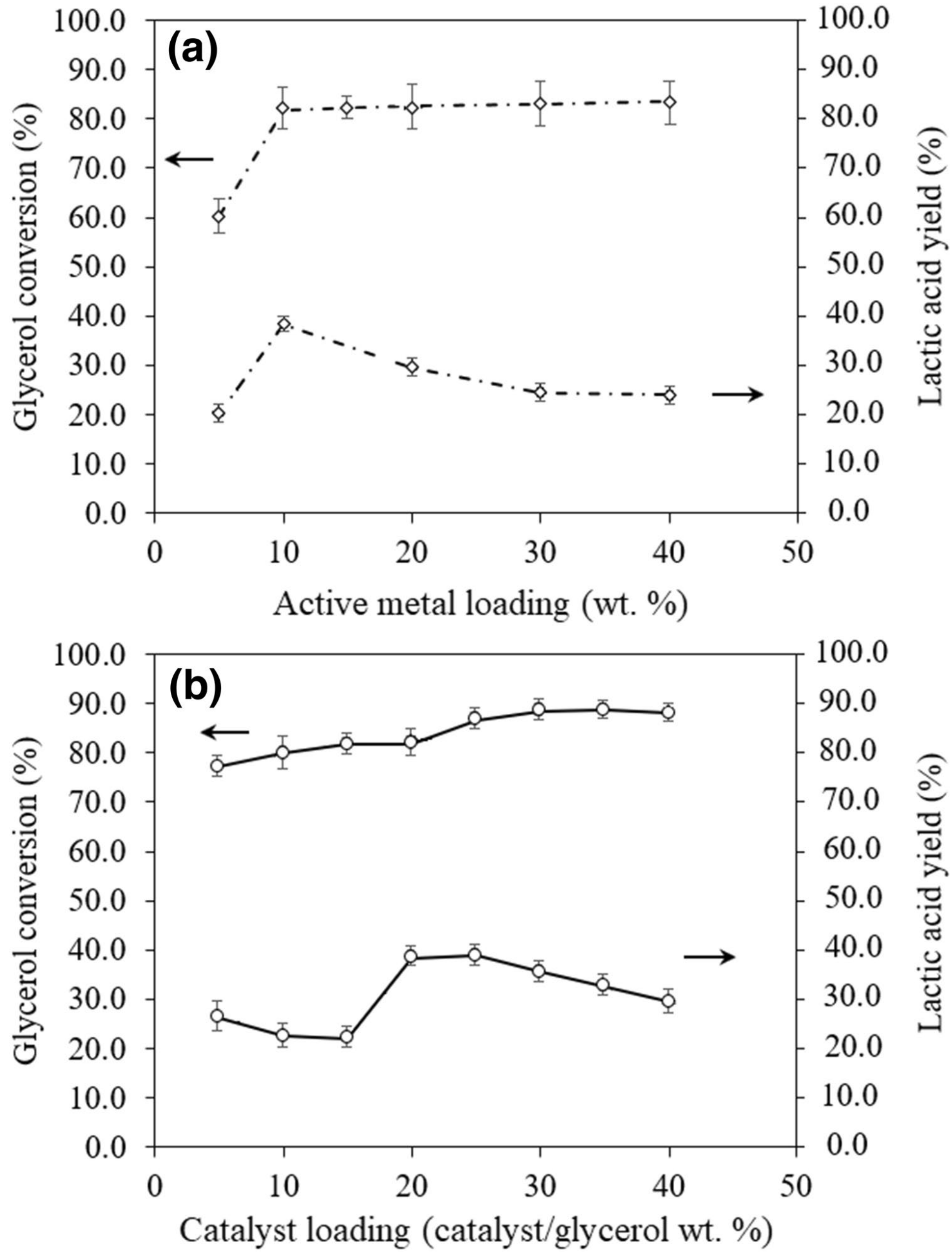

Fig. 4 Effect of different **a** active metal and, **b** overall catalyst loadings on glycerol conversion and LA yield. (Temperature 250 °C, reaction time 2 h)

to the lower number of active sites on the surface of the catalyst. The 5 wt% catalyst metal sites were not sufficient for the reaction to effectively occur. As such, the system was deemed to be a reaction-controlling one. At the same time, such results also suggested the rapid internal diffusion of the reactant in the mesoporous channels of SBA-15 [20]. Marked improvement of the catalytic activity was demonstrated when the active metal loading was doubled to 10 wt%. A sufficiently good dispersion of active metals in the 10 wt% catalyst could be deduced from this result and additional amount of metal sites were fairly accessible by the reactant molecules.

However, further increases from 10 to 40 wt% brought about only minimal increases in the conversion. In this case, an increase in active metal loading did not guarantee the accessibility by glycerol molecules. This claim is also supported by the occurrence of larger metal clusters on the external surface as shown in the SEM images. It has been reported earlier that initial metal incorporation was initially favored in the internal pores while excessive metal loading resulted in preferential deposition on the external surface [13, 15]. However, SBA-15 was seen to be capable of accommodating up to 40 wt. of metal loading without severe loss of surface area and porosity. This was clearly an advantage of this ordered mesoporous support over other non-ordered support materials such as $Mg(OH)_2$ [3], C [8, 14], and TiO_2 [9]. The effect of pore narrowing and partial pore-blocking at higher active metal loadings could have offset the benefit of having higher active metal loading [7].

The catalyst with 10 wt% active metal loading was also found to be the most selective towards LA formation. Almost 38.3% LA yield was achieved after 2 h of reaction to indicate a selectivity of 46.6%. This was slightly better than the result reported by Arcanjo et al. [15] for a Pd/C noble metal catalyst. Thus, the active components played a positive role in the formation of lactic acid and coupled with the shape-selectivity effect of the mesoporous support, almost half of the products was indeed the desired substance [4]. Besides, the low LA yields for 20, 30 and 40 wt% catalysts despite the increasing glycerol conversion were associated with further conversion of reaction intermediates to other undesired by-products. It is observed in Fig. 4a that significant reduction in the LA yield occurred despite the stable glycerol conversion. This suggested that the shape selectivity effect was indeed the highest in 10 wt% 1:2-CeZr/SBA-15 catalysts compared to the other catalysts. This was consistent with the surface characteristics of the catalyst (Table 1), where the catalyst with 10 wt% of active metals had a relatively large mesopore area and average pore size. Its large internal mesopore area basically facilitated the access of the glycerol to the active metal sites. This helped facilitate the reaction as the first step of the catalytic transformation of glycerol to LA which usually involves the dehydrogenation of glycerol to glyceraldehyde. This process mainly occurs on the metallic sites of the catalyst. The narrowing of the internal pores with higher active metal loading could have rendered the location of the reaction to gradually shift from the internal mesopores to external surface with larger pore sizes. Thus, the shape selectivity effect diminished, to the detriment of the LA yield.

Additionally, the average pore size of the 10 wt% 1:2-CeZr/SBA-15 catalyst, which was 51.72 Å (Table 1) also played a role to hinder the formation of by-products such as 2-hydroxypropenal [27]. This result was also consistent with that reported by Laskhmanan et al. [6] who revealed that catalysts with average pore sizes of about 50 Å and smaller generally showed relatively lower LA selectivity as compared to the ones with higher pore diameters. This observation proved that this mesoporous catalyst indeed possessed the most suitable pore characteristics to have a good shape selectivity effect to facilitate selective glycerol conversion to LA. Particularly, it could be associated with the shape selectivity effect of the benzylic rearrangement (Cannizzaro reaction) of pyruvaldehyde to LA while the formation of glyceraldehyde that would lead to the formation of dihydroxy aldehyde was suppressed [1].

Next, effects of the overall catalyst to glycerol weight loading were also studied using the 10 wt% 1:2-CeZr/SBA-15 catalyst (as the most potential catalyst based on Fig. 4a) whilst keeping other variables constant i.e. 250 °C and a reaction time of 2 h (Fig. 4b). Generally, glycerol conversion was expected to increase with increasing catalyst loading. With the increasing amount of catalyst available in the reactor from 5 to 40 wt% relative to glycerol, more active sites would be available to catalyze the reaction and hence, higher conversion rate was demonstrated. The glycerol conversion gradually increased from 77.2 to 88.0% with increasing catalyst loading within this range. The increment in the glycerol conversion was however minimal when the catalyst loading exceeded 30 wt%. The equilibrium between the intermediates during the reaction could be the responsible factor at such high glycerol conversions [6, 8].

It was interesting to note that the highest LA yield (38.9%) was achieved at a catalyst loading of about 25% and a further increase of the catalyst loading beyond that level was detrimental as far as the LA yield was concerned. For example, at 40 wt% catalyst loading, the LA yield significantly dropped to below 30%. The effect of equilibrium limitation would likely the be more significant at higher catalyst loadings due to greater extent of reaction to result in the presence of more intermediates in the system. As a result, competing reaction would gain significance to leading to rapid disappearances of those intermediates to eventually form final products other than LA. Those by-products were such as glyceric acid, pyruvic acid, and lactaldehyde [27].

Still, manipulating the catalyst loading did not bring about much desired effect on the selectivity of the catalyst i.e. the effect of catalyst loading on the conversion and LA yield was rather very minimal and excessive amounts were proven detrimental. In fact, the enhanced activity of this SBA-15-supported bimetallic catalyst could be directly ascribed to the interfacial interaction of both Ce and Zr components coming from their close contact between the bimetallic particles and the particle size effect [28]. This explained why the active metal loading caused better effect on the catalytic activity than the catalyst loading. Instead, other parameters such as reaction temperature, reaction time and type of catalyst should be considered for further improvement of the reaction. However, the best catalyst loading (25 wt%) as suggested by data in Fig. 4b was used to possibly achieve the higher LA yield by manipulating the rection temperature.

Effects of Reaction Temperature

The glycerol conversion and LA yield of 10 wt% 1:2-CeZr/SBA-15 catalyst at a catalyst-to-glycerol loading of 25 wt% were then investigated at different reaction temperatures ranging from 240 to 280 °C. Figure 5 shows that the reaction

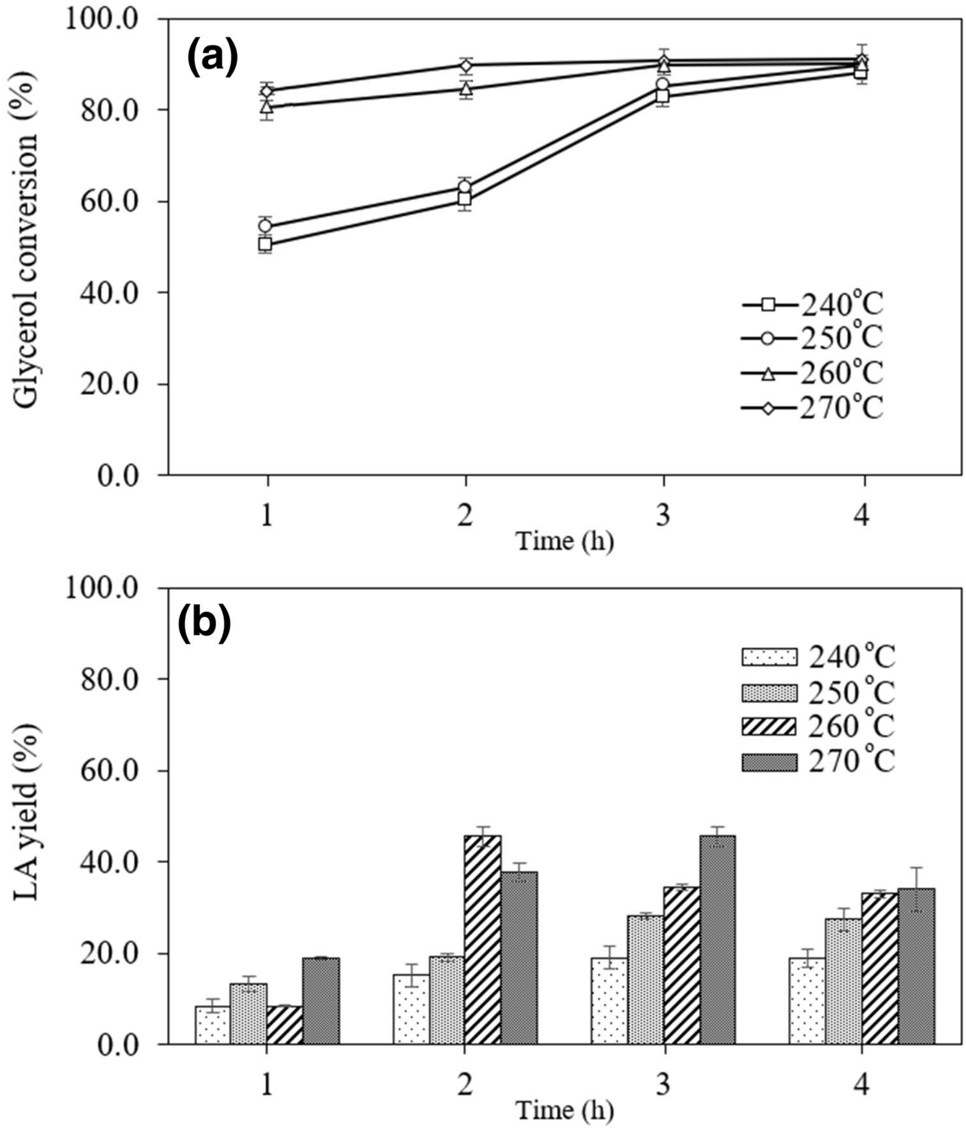

Fig. 5 Effect of reaction temperature on **a** glycerol conversion and, **b** LA yield. (Metal loading 10 wt%, catalyst loading to glycerol 25%, reaction time 2 h)

was significantly influenced by the reaction temperature, especially at low reaction times when the conversions were still low (Fig. 5a). For example, increasing the reaction temperature from 240 to 270 °C for a reaction of 1 h brought about an increase of glycerol conversion from 50.4 to 84.2%. The LA yield was rather low at the beginning of the reaction. This was due to the low conversion of glycerol to LA that could offset the effect of the high selectivity towards LA that was usually observed at low glycerol conversion. Poor conversion at a reaction temperature of 240 °C indicated the stability of glycerol to undergo appreciable reaction initiation step. Meanwhile, the conversion levelled off at about 80% for all the reaction temperatures even though the reaction was extended to 4 h. In this case, the positive effect of increasing the reaction temperature dwindled at longer reaction times. For example, the 30 °C difference in the reaction temperature only managed to improve the glycerol conversion from 88.1 to 91.1% when the reaction runs were extended to 4 h. This observation was due to further oxidative cleavage and dehydrogenation of LA into other undesired products such as glyceric acid and acrylic acid, respectively [13].

In theory, glycerol conversion to LA involves two parallel reactions from glyceraldehyde to glyceric acid and LA [1]. An earlier study suggested that a higher reaction temperature of around 200 °C initially favored LA formation over glyceric acid [28–30]. This was because at higher temperatures, glyceric acid will rapidly be dehydrated to LA. In addition, the dehydrogenation of the primary hydroxyl group of glycerol to glyceraldehyde consumes heat (endothermic) and high temperature is required to achieve appreciable reaction initiation. As such, higher reaction temperature resulted in improved glycerol conversion. With time, the conversion leveled off as the reaction was governed by the equilibrium in the reacting system. However, an attempt to carry out the reaction at 280 °C was discontinued as visible change in the appearance of the reacting mixture was detected and the LA yield significantly dropped to 28.2% to indicate significant decomposition of LA to other products such as formic acid, glyceric acid, glycolic acid, oxalic acid, tatronic acid, and acetic acid at elevated temperatures [31].

The highest yield of LA of about 45.6% was achieved at a reaction temperature of 270 °C in 3 h (Fig. 5b). Longer reaction was detrimental to the yield of the desired product due to the decomposition of LA to other by-products at such a high reaction temperature. This observation was in fact in accordance with the general understanding that the energy possessed by the reacting molecules at lower temperatures was lower and thus, limiting the effective collisions between molecules. However, the result obtained herein was better than those works reported earlier using Au and Pt catalysts [5, 31]. In these previous works, the optimum LA yield only peaked at temperatures around 280 to 300 °C and decreased drastically after that due to LA decomposition. The researchers concluded that at above 265 °C, LA could be easily dehydrated to acrylic acid due to the activation of the α-hydroxy group of LA molecule [5]. Hence, the best temperature to produce the highest LA yield was 270 °C and the reaction should not be extended beyond 3 h.

In this study, the 10 wt% 1:2-CeZr/SBA-15 catalyst showed better performance at shorter reaction times than the one reported earlier [5]. Although their 1% Pt/L-Nb_2O_5 catalyst achieved almost 55.0% of LA yield in only 3 h, the total LA productivity was still relatively lower. This was because the initial glycerol concentration used in their work was just 0.3 M. Meanwhile, Yang et al. [29] used a glycerol solution at a concentration of 1.4 M to achieved 95% LA yield in 8 h using CuO/ZrO_2 catalyst. Clearly, direct comparison could not be accurately made due to different reaction conditions reported by different authors. However, it should be highlighted than the conversion of pure glycerol post extra challenges due to the absence of solvent to facilitate the internal diffusion of glycerol within the internal pores and occurrence of higher concentrations of intermediates that would compete for the interaction with active sites of the catalysts.

Reaction Mechanism

Based on the results obtained in this work, the mechanistic behavior of the 1:2-CeZr/SBA-15 catalyst in the transformation of glycerol to LA could be predicted and it is schematically illustrated in Fig. 6. Oxides of Zr^{3+} and Ce^{4+} were evidently the active components or playing the role as the active sites in this reaction. Since the pH of the catalyst was modified with NaOH during the synthesis procedure, the hydroxyl (^{-}OH) ion would be readily available in the reaction medium. Considering the mechanisms as reported in literature [1, 26] and the experimental results in this study, the first step in glycerol conversion into LA is deemed to be the H atom abstraction from the primary hydroxyl group of glycerol. At first, there will be an electron transfer from Zr^{3+} to Ce^{4+} and this helps to enhance the H abstraction from the hydroxyl group of glycerol. Basically, this is where the synergistic effect between both metals can be seen. In this case, synergistic catalysis is achieved when the electrophile and nucleophile are instantaneously activated by two separate metals to afford a single chemical conversion [32, 33].

In the subsequent step, the oxygen molecule will undergo dissociative chemisorption on the Ce sites [2] and a hydrogen atom from the hydroxyl group of the aldehyde is abstracted and the negatively charged ion subsequently undergo electron transfer forming a double bond with the terminal carbon. This dehydrogenation process eventually forms glyceraldehyde. The hydrogen atom in the reaction medium will then attack the oxygen atom of the hydroxyl group, removing a water molecule to form 2-hydroxypropenal. In the presence of hydroxyl ion, the latter molecule will theoretically undergo keto-enol tautomerization to form pyruvaldehyde. LA will then be formed when the pyruvaldehyde molecule undergoes an internal Cannizzaro reaction in the presence of those hydroxide ions. It is then followed by an electron transfer from the Zr^{3+} to Ce^{4+} sites that help induce the formation of a pseudo-bond between the Zr^{4+} sites and the oxygen molecule of the pyruvic acid. Next, the hydrogen atom which is abstracted in the previous step will attack the negatively charged oxygen molecule, forming primarily LA as the desired product. Thus, it could be claimed that the interaction between both active metals (Ce and Zr) together with the support played positive and complementary roles for the desired formation of LA while allowing the shape selectivity effect to hinder the formation of undesired by-products.

Conclusions

For the first time, the utilization of CeZr supported on ordered mesoporous SBA-15 as a catalyst for selective catalytic glycerol oxidation to LA under base free condition was successfully demonstrated. The hypothesis for the shape-selectivity effect by the ordered mesoporous catalyst was also found to be acceptable. Characterization analyses proved the successful synthesis of the ordered mesoporous catalysts and at suitable composition, the performance of the catalyst towards the desired product could be further enhanced. Some surface defects with regards to partial pore-clogging or narrowing were detected at active metal loadings higher than 20 wt%. The highest glycerol conversion (91.2%) and LA yield (51.4%) were achieved at 10 wt% of CeZr metal loading and a catalyst-to-glycerol

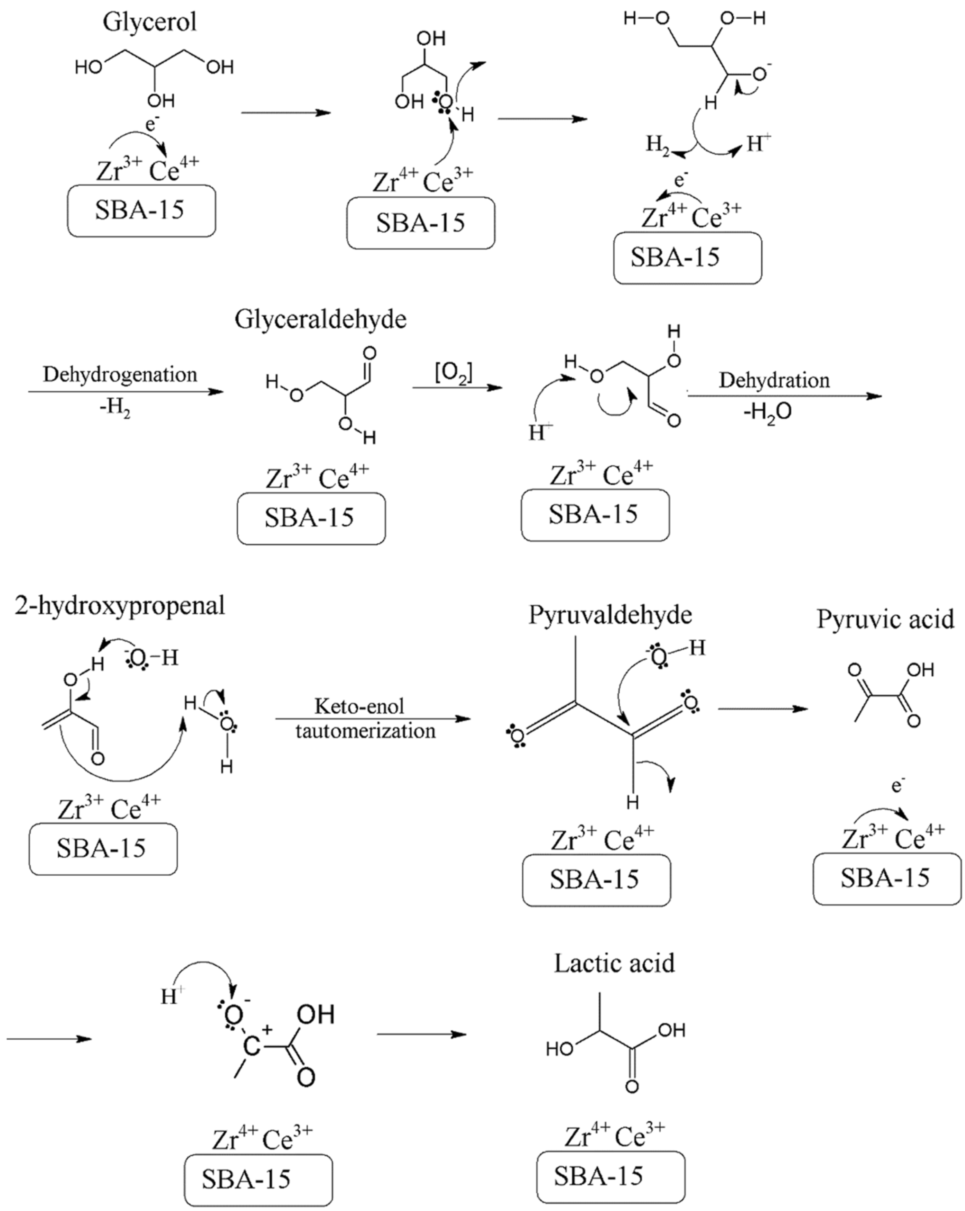

Fig. 6 Proposed scheme for the selective formation of lactic acid on the mesoporous SBA-15-supported CeZr catalyst

weight ratio of 25 wt% at 270 °C after 2.5 h of reaction. This study also revealed the unique shape-selectivity effect of this catalyst towards the activation of the secondary hydroxyl group of glycerol to glyceraldehyde, which is the key step in LA synthesis mechanism. A reaction mechanism was also proposed to provide a better understanding of the synergy between both active metals in the catalyst, as well as the role of the ordered mesoporous support in the favorable transformation of glycerol to LA.

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