

Article

Selective oxidation of glycerol to lactic acid over activated carbon supported Pt catalyst in alkaline solution



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ABSTRACT

Pt/activated carbon (Pt/AC) catalyst combined with base works efficiently for lactic acid production from glycerol under mild conditions. Base type (LiOH, NaOH, KOH, or Ba(OH)₂) and base/glycerol molar ratio significantly affected the catalytic performance. The corresponding lactic acid selectivity was in the order of LiOH > NaOH > KOH > Ba(OH)₂. An increase in LiOH/glycerol molar ratio elevated the glycerol conversion and lactic acid selectivity to some degree, but excess LiOH inhibited the transformation of glycerol to lactic acid. In the presence of Pt/AC catalyst, the maximum selectivity of lactic acid was 69.3% at a glycerol conversion of 100% after 6 h at 90 °C, with a Li-OH/glycerol molar ratio of 1.5. The Pt/AC catalyst was recycled five times and was found to exhibit slightly decreased glycerol conversion and stable lactic acid selectivity. In addition, the experimental results indicated that reaction intermediate dihydroxyacetone was more favorable as the starting reagent for lactic acid formation than glyceraldehyde. However, the Pt/AC catalyst had adverse effects on the intermediate transformation to lactic acid, because it favored the catalytic oxidation of them to glyceric acid.

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1. Introduction

Biofuel synthesis via transesterification of plant or animal oil has become a promising alternative route for sustainable energy production, and also produces glycerol as a major by-product during the manufacturing process. Therefore, the transformation of glycerol into value-added chemicals is vital to the overall competitiveness of the biofuel industry [1,2]. The structural characteristic of triple hydroxyl groups makes glycerol an excellent chemical feedstock for the synthesis of versatile high-value derivatives, such as lactic acid (LA), glyceric acid (GLYA), and 1,3-propanediol [3–6]. In particular, LA is an important building block chemical that is widely used in the food, cosmetics, and pharmaceutical industries. Notably, polylactic acid has the potential to replace conventional oil-based polyethylene terephthalate (PET) plastics because of its biodegradability and biocompatibility [7]. It is estimated that the worldwide demand for LA will reach 600 kt in 2020 [8]. At present, LA is mainly produced by fermentation from carbohydrates; however, this process is time-consuming and involves complex separation steps [9]. As a result, the chemical transformation of glycerol to LA is attracting extensive efforts from the academic and industrial communities.

The chemical production of LA from glycerol has been in-

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vestigated through different approaches, including hydrothermal reactions [10-12], hydrogenolysis methods [13,14] and catalytic selective aerobic oxidations [3,15,16]. Kishida et al. [10] reported hydrothermal decomposition of glycerol to LA in the presence of NaOH at 300 °C, where the LA molar yield could reach 90%. Meanwhile, the catalytic hydrogenolysis of glycerol to LA has been explored over Ru and Pt catalysts at 200 °C under 4 MPa H2 in basic solutions, achieving yields no higher than 58% [13]. Unfortunately, severe reaction conditions (including high temperature and pressure) have been major concerns in scaling up the reaction. Thus, the selective oxidation of glycerol to lactic acid in basic aqueous solution is still attractive under mild reaction conditions. Shen et al. [3] first reported a one-pot Au-Pt/TiO2-catalyzed aerobic oxidation of glycerol at 90 °C in NaOH with a LA yield of around 86%. Similar results have been achieved on Au/CeO2 and Pt-Au/CeO2 catalysts under basic conditions [15,16].

Generally, the production of LA from glycerol oxidation over supported noble metal catalysts is assisted by concentrated NaOH solution, typically with a NaOH to glycerol molar ratio of 4 [16–18]. However, to date, there have been few reports on glycerol oxidation to lactic acid in different alkaline solutions. In an Au-Pt/C-catalyzed 1,2-propanediol oxidation process, Ryabenkova et al. [19] reported that the presence of LiOH afforded the highest lactate yield amongst the different alkalis (LiOH, NaOH, KOH, CsOH, and RbOH). Given that each hydroxide alkali possesses a specific ionic radius, their respective alkali solubility, solution viscosity, and oxygen solubility may affect the catalytic reaction behavior [20,21].

Carbon materials have been widely used as supports in heterogeneous catalysis because of their unique advantages, including large specific surface area, stability in both acidic and basic solutions, and easy recovery of the noble metal. Until recently, carbon-supported catalysts were investigated to produce LA from glycerol oxidation; however, GLYA was generated as the major product. For example, Chornaja et al. [17] and Ketchie et al. [18] reported less than 5% LA selectivity over Pd/C and Au/C catalysts, respectively. Heeres et al. [16] also investigated the conversion of glycerol to LA over Au/C catalysts and obtained 27% LA selectivity, which was the highest yield on carbon-supported catalysts at the time. Therefore, further investigation of carbon-supported catalyst is attractive from both academic and industrial perspectives.

Herein, we report a study on glycerol oxidation to produce LA over Pt/activated carbon (Pt/AC) catalyst in alkaline aqueous solution under O_2 at atmospheric pressure. The effects of base type (LiOH, NaOH, KOH, and Ba(OH)₂) and base/glycerol molar ratio on catalytic performance were also investigated. We expect that this work will form the basis of a practical method for LA production from glycerol using AC-supported catalysts.

2. Experimental

2.1. Catalyst preparation

Pt/AC catalyst was prepared by a deposition-precipitation

method [3]. In a typical experiment, 3 g of AC (Tangshan United Carbon, China) was suspended in 300 mL of deionized water with vigorous stirring, and 0.03 g of Pt as H₂PtCl₆ (Pt \ge 38%, Shanghai Jiuyue, China) solution was added. After 0.5 h, an excess amount of NaBH₄ (> 98%, Tianjin Hainachuan Science and Technology, China) solution was stirred for 6 h. Afterward, the black precipitate was filtered and washed with deionized water until Cl⁻ was not detectable with AgNO₃ solution. The solid was dried at 120 °C for 12 h. AC was washed with deionized water to remove surface ash and ground to 100–200 mesh before use.

2.2. Catalyst characterization

Metal analysis was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 7300 DV, and showed that the Pt loading of the catalyst was 0.9 wt% (designed loading was 1 wt%). The glycerol/Pt molar ratio was calculated based on the 0.9 wt% loading. Physical adsorption was carried out on a Quantachrome Autosorb-1 instrument. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas. The *t*-plot method was applied to calculate the external and micro surface areas. Total pore volume was calculated based on the amount of nitrogen adsorbed at a relative pressure (p/p_0) of 0.99. Before the test, samples were outgassed at 250 °C for 12 h. Transmission electron microscopy (TEM) was conducted with a JEM-2100 electron microscope operating at 200 kV. The metal particle size distribution was calculated by counting approximately 140 particles in TEM images. CO pulse chemisorption was performed on a 150-mg sample in a quartz U-tube on an Altamira Instruments AMI-300 with a thermal conductivity detection (TCD) device and an OmniStar GSD 320 mass spectrometer. After 10% H₂/Ar reduction at 200 °C for 1 h and Ar post flush, 10% CO/He pulse chemisorption was initiated at 30 °C. A CO/Pt stoichiometry of 1 was used for calculations [22].

2.3. Glycerol oxidation reaction

The glycerol oxidation reaction was carried out in a three-neck flask (100 mL) at atmospheric pressure in an oil bath. A known amount of base and catalyst (0.25 g) were added into glycerol solution (25 g, 10 wt%). When the solution temperature stabilized, O₂ flow was initiated at 100 mL/min with magnetic stirring at 800 r/min. After the reaction, the aqueous solution was filtered, neutralized with H₂SO₄ aqueous solution, and diluted with deionized water. The products were analyzed by high-performance liquid chromatography (HPLC) on an Agilent 1100 instrument equipped with a refractive index detector (RID). The analysis used an Alltech OA-1000 column with a separation temperature of 80 °C. H₂SO₄ aqueous solution (0.005 mol/L) was used as the mobile phase at a flow rate of 0.5 mL/min. All products were identified by comparing retention times with those of pure materials; quantification was by the external standard method. Glycerol conversion and liquid product selectivity were calculated according to the literature with the carbon balance generally more than 90% unless otherwise noted [23]. The spent catalyst was separated, washed thoroughly with deionized water, and dried before use in recycling experiments.

3. Results and discussion

3.1. Effects of Pt/AC and NaOH on glycerol oxidation to lactic acid

The Pt/AC-catalyzed glycerol oxidation was conducted and the results are summarized in Table 1. In all reactions, the products were obtained as salts, but for simplicity and comparison they were marked as the acid forms. The coexistence of Pt/AC and NaOH led to LA production, giving 58.5% glycerol conversion and 44.9% LA selectivity. By-products were also detected, including GLYA, tartronic acid (TA), glycolic acid (GA), oxalic acid (OA), acetic acid (AA), and formic acid (FA). Reaction intermediates such as glyceraldehyde (GIA), dihydroxyacetone (DHA), and pyruvaldehyde (PyA), if at all present, could not be detected under the reaction conditions.

For a better understanding of the roles that the metal catalyst and base played in the oxidation reaction, single variable analyses were performed without Pt/AC or base (Table 1). In the absence of Pt/AC catalyst, NaOH converted a trace amount of glycerol to form GA (33.4%) as the main product, together with 17.5% selectivity for LA and 24.6% selectivity for GLYA. In a base-free environment, glycerol conversion was 18.6% with 86.3% selectivity for GLYA over Pt/AC catalyst, and the target LA was not detected. The results demonstrate that Pt/AC catalyst plays a decisive role in glycerol activation, probably because the primary H-elimination occurs much more easily on a metallic catalyst than in basic solution alone [24]. The role of the base is to increase the rate of glycerol oxidation by aiding the initial deprotonation over the Pt catalyst, and favorably shift the equilibrium by forming salt products [24]. Meanwhile, the base also favors the intramolecular Cannizzaro rearrangement over LA production [3,12]. This suggests that the collaboration of the metal catalyst and base is indispensable for LA production from glycerol oxidation, which is in line with Liu's report [25].

The glycerol oxidation pathways that lead to LA and GLYA are different (Scheme 1). Glycerol is first dehydrogenated to GlA and DHA intermediates by the coordination of Pt/AC and base. They then undergo either base-catalyzed dehydration together with intramolecular Cannizzaro rearrangement to LA, or further metal-catalyzed oxidation to GLYA, TA, and C–C cleavage products such as GA or FA [3,16,26]. However, the mechanism for the transformation of intermediates GlA and

Table 1

Comparison of catalyst and base performances in glycerol oxidation.

Catalyst	$n_{\rm NaOH}/$	Conversion		Selectivity (%)					
	$n_{ m glycerol}$	(%)	LA	GLYA	TA	GA	0A	AA	FA
Pt/AC	4	58.5	44.9	18.4	7.9	14.1	1.6	2.1	11.0
None	4	5.9	17.5	24.6	0	33.4	0	4.0	20.5
Pt/AC	None	18.6	0	86.3	0.1	13.4	0.1	0.1	0
Reaction conditions: $t = 90$ °C, $p = 0.1$ MPa, 6 h, $F_{02} = 100$ mL/min, stir-									

Reaction conditions: t = 90 °C, p = 0.1 MPa, 6 h, $F_{02} = 100$ mL/min, stir ring speed = 800 r/min, $n_{glycerol}/n_{Pt} = 2400$.



Scheme 1. Proposed reaction pathway for glycerol conversion to lactic acid and by-products on Pt/AC.

DHA to LA or GLYA remains unclear. Their respective selectivity toward LA may provide useful information in the design of an improved catalyst system.

To gain insight into the formation pathway for LA and GLYA from GIA or DHA, a series of experiments were performed in NaOH aqueous solution under an O2 atmosphere with either GIA or DHA as the starting reagent. At 5 min of reaction time, GIA or DHA had disappeared completely and the main products were LA and GLYA, with small amounts of other products (TA, GA, OA, and FA; not shown here). Figure 1 (filled symbols) depicts the plot of LA/GLYA molar ratio as a function of reaction time on stream in the presence of the base but without the metal catalyst. DHA reaction showed higher LA/GLYA molar ratios than that of GlA reaction, indicating that DHA as the substrate was relatively more favorable than GIA to form LA. In general, DHA can produce LA at low temperatures of 15-140 °C; however, GIA generates LA at higher temperatures of 200-300 °C [13,27-29]. The latter reaction probably needs to overcome a high energy barrier because the formation of LA is favored from GIA at higher temperature. Another possibility may be related to the transformation rate, which could be in-



Fig. 1. LA/GLYA molar ratio variation with or without Pt/AC in NaOH solution. Reaction conditions: substrate = 0.1 mol/L DHA or GlA, NaOH/substrate molar ratio = 4:1, $m_{Pt/AC}/m_{substrate solution}$ = 1:1000, other conditions same as Table 1.

ferred from Lookhart's observation that DHA was dehydrated much faster than GIA [30]. Furthermore, the LA/GLYA molar ratio was almost constant as reaction time increased, which indicates that the further oxidation of GLYA to TA and C–C spilling of products occurred relatively slowly, and thus maintained a stable LA/GLYA ratio.

Figure 1 (open symbols) shows LA/GLYA molar ratio variations in NaOH aqueous solution with Pt/AC catalyst. For DHA reaction, the LA/GLYA molar ratio dropped slightly from 5.5 to 5.3. In contrast, for GIA as substrate, the LA/GLYA ratio decreased remarkably from 4 to less than 2. Obviously, when Pt/AC was added, LA formation was inhibited and GLYA production was facilitated regardless of GIA or DHA as substrate. Interestingly, Pt/AC catalyst accelerated the transformation of GIA to GLYA over that of DHA. Chornaja et al. [17] also reported that the rate of GIA oxidation to GLYA was higher than GIA transformation to LA using a Pd/Al₂O₃ catalyst in alkaline aqueous solution. Thus, we depict the possible pathway for LA production as shown in Scheme 2. DHA is firstly dehydrated to PyA in basic solution, followed by a base-catalyzed rearrangement of PyA to LA, and accompanied with DHA isomerization to GIA and further oxidation to GLYA over Pt/AC catalyst. In other words, DHA may take one step less than GIA toward LA, which may contribute to its better assistance for LA production. Therefore, by careful control of alkaline conditions, a higher DHA/GlA ratio may be achieved, which would facilitate the selectivity to LA.

3.2. Effect of different hydroxides on glycerol oxidation to lactic acid

The use of a base is a crucial factor in glycerol oxidation to LA, so we further investigated the effect of alkali type on the performance of glycerol oxidation over Pt/AC catalyst (Table 2). Three alkali-metal hydroxides (LiOH, NaOH, and KOH) and one alkaline-earth hydroxide Ba(OH)₂ were used. Other alkaline-earth hydroxides were not adopted because of their poor solubilities [11,31]. When LiOH was used as the base, the glycerol conversion was 60.4% and LA selectivity was 60.1% after 6 h, which was the highest among the four alkalis. When NaOH was introduced, the glycerol conversion and LA selectivity

Table 2	
Glycerol oxidation reaction with different bases over Pt/AC cataly	st

Deee	$n_{\rm base}/$	Conversion	Selectivity (%)						
Base	$n_{\rm glycerol}$	(%)	LA	GLYA	TA	GA	OA	AA	FA
LiOH	2	60.4	60.1	17.9	4.5	7.5	2.8	1.4	5.8
NaOH	2	62.6	51.2	13.6	5.4	11.9	5.7	1.8	10.4
КОН	2	63.4	43.3	17.1	5.8	11.3	2.8	5.0	14.7
Ba(OH)2	1	41.8	24.8	29.3	0.2	20.9	0.9	5.0	18.9
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ring speed = 800 r/min, $n_{glycerol}/n_{Pt}$ = 2400.

were 62.6% and 51.2%, respectively. In KOH aqueous solution, the glycerol conversion was similar to LiOH and NaOH, but LA selectivity decreased to 43.3%. Ba(OH)₂ showed much lower glycerol conversion (41.8%) and LA selectivity (24.8%). The former three hydroxides have lower electric charge, lower molecular weight, and smaller structure than Ba(OH)₂, which might enable them to dissociate and move rapidly in the reaction solution, providing dissociated hydroxyl ions to promote the reaction networks. In contrast, the higher electric charge and larger ionic radius of Ba(OH)₂ might favor the undesirable LA decomposition to C₁ and C₂ products [11]. Therefore, alkali-metal hydroxides were a better choice than alkaline-earth hydroxide Ba(OH)₂ for LA production.

Although the three alkali-metal hydroxides showed similar glycerol conversions, their LA selectivities were obviously different in the order of KOH < NaOH < LiOH (Table 2). This suggests a mechanism whereby the metal ion exerts significant influence on the oxidation behavior. Changes in the metal ion radius causes several physicochemical properties, such as solution alkalinity, solubility of oxygen, and viscosity [21,32].

In Group IA, alkalinity is positively related with radius length (Table 3). The stronger alkalinity might improve the deprotonation process during the glycerol oxidation reaction. Thus, their glycerol conversions exhibited the same order as their alkalinities and radii. The highest LA selectivity was obtained in LiOH aqueous medium, which might be related to the oxygen solubility in solution. We tested the oxygen solubility in basic reaction solution and found that LiOH solution dissolved more oxygen than NaOH and KOH (Table 3), which was consistent with Battino's report [33]. According to Davis et al. [34], the role of O_2 is to assist the regeneration of hydroxide ions via



Scheme 2. Possible DHA and GIA conversion pathway toward LA and GLYA.

Table 3Comparison of ionic radius, viscosity, k_{sca} , and oxygen solubility. a

Base	Ionic radius ^b	Viscosity ^c	$k_{ m sca}$ d	Oxygen solubility ^e
	(pm)	(mPa∙s)	(L/mol)	(mg/L)
LiOH	76	1.66	0.091	30.1
NaOH	102	1.50	0.181	29.1
КОН	138	1.16	0.176	28.8
a D		1	(0.0 .0/)	

^a Because water is in absolute majority (90 wt%) in reaction solution, all the physicochemical parameters are considered valid.

^b Theoretical 6-coordinate ionic radius. Variation trend at other coordinate numbers is similar [32].

 $^{\rm c}$ Calculated by linear interpolation on literature data between 0.7 and 4 mol/L at 25 °C [20].

^d The oxygen solubility could be represented as k_{sca} (i.e., the Setschenow salt effect parameter); these data were acquired for base concentrations of 0.8–1.2 mol/L [35].

 $^{\rm e}$ Data obtained by iodometric method (Chinese GB 7489-87, totally equivalent to ISO 5813:1983) after 20 min oxygen bubbling and 2 min standing at room temperature (20 °C) with base/glycerol ratio of 0.5. Other conditions identical to those described in Table 2 except that no catalyst was added to avoid disturbance.

the catalytic decomposition of a peroxide intermediate over Pt sites. When more oxygen is dissolved, the hydroxide ions regenerate faster and promote LA production in the presence of Pt/AC catalyst. Besides, it is possible that a smaller metal ion radius might favor the glycerol dehydrogenation toward more DHA, thus enhancing LA formation, and this proposal still requires verification.

3.3. Effect of LiOH/glycerol molar ratio on glycerol oxidation to lactic acid

Further optimization reactions were performed in LiOH medium at different LiOH/glycerol molar ratios and the results are shown in Table 4. Before reaching a molar ratio of 1.5, both glycerol conversion and LA selectivity were enhanced with elevated LiOH concentration, and the maximum LA selectivity was 69.3% at 100% glycerol conversion. However, further elevation of the LiOH/glycerol molar ratio caused a decrease in both reaction activity and LA selectivity. Glycerol conversion dropped significantly to 69.3% at a molar ratio of 1.75 and further dropped to 60.4% at a ratio of 2. The LA selectivity gradually decreased from 69.3% to 60.1% when the LiOH/glycerol molar ratio increased from 1.5 to 2.0. This indicates that the optimum LiOH/glycerol molar ratio was 1.5 under our reaction conditions, with relatively high LA selectivity at full glycerol conversion.

Table 4

Glycerol oxidation reaction at different LiOH/glycerol molar ratios.

LiOH/glycerol	Conversion			Sele	ctivity	(%)		
molar ratio	(%)	LA	GLYA	TA	GA	0A	AA	FA
1.0	73.6	52.6	17.1	5.0	13.5	3.2	3.0	5.6
1.25	89.7	56.7	15.2	6.1	11.1	3.4	2.9	4.6
1.5	100	69.3	8.0	9.4	5.9	2.5	1.4	3.5
1.75	69.3	61.8	15.8	4.4	8.0	2.6	1.5	5.9
2.0	60.4	60.1	17.9	4.5	7.5	2.8	1.4	5.8

Reaction conditions: t = 90 °C, p = 0.1 MPa, 6 h, $F_{02} = 100$ mL/min, stirring speed = 800 r/min, $n_{glycerol}/n_{Pt} = 2400$.

At low LiOH/glycerol molar ratios, the reaction products were almost acidic, indicating that the amount of base might be insufficient to aid the dehydrogenation reaction from the hydroxyl groups of glycerol and to further catalyze the Cannizzaro rearrangement to LA formation. Such an insufficiency would suppress both glycerol conversion and LA selectivity. When more LiOH was added, the dehydrogenation reaction proceeded faster toward intermediates GIA and DHA. Simultaneously, the base-catalyzed rearrangement of intermediates was promoted to generate more LA.

When LiOH/glycerol molar ratios were above 1.5, the glycerol conversion dropped drastically. This may be a result of declines in mass transfer rate and oxygen solubility, which were caused by increased base ratio and viscosity [20,35]. The oxygen diffusivity and oxygen solubility decline rapidly owing to the LiOH concentration increase. Thus, the oxidation dehydrogenation on the Pt/AC catalyst may be affected, leading to lower glycerol conversion and corresponding GIA or DHA intermediates. The LA selectivity also dropped because the extra base may facilitate glycerol transformation to GIA, which is likely to form more GLYA in the presence of Pt/AC.

3.4. Effect of reaction time on glycerol oxidation to lactic acid

Figure 2 shows the glycerol conversion and variation in product selectivity as a function of reaction time at the optimized LiOH/glycerol ratio of 1.5. Glycerol was converted completely within 6 h. There was a near-linear increase in glycerol conversion, which implied that Pt/AC maintained activity during the oxidation reaction. Furthermore, LA had the highest selectivity at any glycerol conversion among the reaction products, indicating that LA was the dominant product. The LA selectivity reached a maximum (69.3%) after 6 h and then decreased slightly. The AA selectivity increased slightly, implying that LA was not stable and might decompose to AA. It was noted that the selectivity of GLYA decreased remarkably because of the consecutive oxidation of GLYA to TA and OA.

The stability of the Pt/AC catalyst was tested in a recycling experiment for five runs. As shown in Fig. 3, the glycerol con-



Fig. 2. Variation of the glycerol conversion and product selectivity with time on stream. Reaction conditions: t = 90 °C, p = 0.1 MPa, $F_{02} = 100$ mL/min, stirring speed = 800 r/min, $n_{glycerol}/n_{Pt} = 2400$.



Fig. 3. Recycling tests of Pt/AC catalyst for 4-h glycerol oxidation reaction. Reaction conditions: t = 90 °C, p = 0.1 MPa, $F_{02} = 100$ mL/min, stirring speed = 800 r/min, $n_{glycerol}/n_{Pt} = 2400$.

version decreased from 63.6% to 52.9% after five runs, but the selectivity of LA was still around 60%. Metal analysis by ICP-OES revealed that Pt leaching was below the limit of detection and negligible. However, the specific surface area of the Pt/AC catalyst decreased after five runs (Table 5), which might be ascribed to chelation of product on the catalyst surface, which would prevent the glycerol from accessing the Pt active sites [36]. The pore size distribution based on the NL-DFT method also confirmed the possibility of reactant blockage because the number of pores around 1.9 nm decreased after reaction (Fig. 4). In addition, the average particle size of Pt increased from 4.4 to 5.5 nm after five runs (Fig. 5). CO pulse

Table 5

The specific surface areas and total pore volumes of fresh and spent $\ensuremath{\text{Pt/AC}}$ catalysts.

Catalyst	$S_{\rm BET}a$ (m ² /g)	$S_{\rm macro^b}(m^2/g)$	$S_{\rm micro} (m^2/g)$	$V_{\rm total}$ c (cm ³ /g)
Fresh	970.8	278.7	692.1	0.65
Spent	687.0	221.4	465.6	0.54

^aCalculated by the BET method.

^bCalculated by the *t*-plot method.

^c Calculated based on the amount of nitrogen adsorbed at a relative pressure (p/p_0) of 0.99.



Fig. 4. Pore size distributions of fresh and spent Pt/AC catalysts.



Fig. 5. TEM images of (a) fresh and (b) spent 5-time Pt/AC catalysts; Pt particle size distributions of (c) fresh and (d) spent 5-time Pt/AC catalysts.

chemisorption of the fresh and spent catalyst also confirmed the slight agglomeration of Pt, with the average particle size increasing from 7.1 to 11.7 nm; Pt dispersion declined from 16.8% to 10.2%, which may influence the catalyst activity to some degree [37]. Further detailed investigation is necessary to elucidate the deactivation mechanism.

4. Conclusions

Lactic acid was prepared as the major product by treatment of glycerol in alkaline aqueous solution in the presence of a Pt/AC catalyst. The promotion effect of LiOH was stronger than the other bases (NaOH, KOH and Ba(OH)₂) in terms of glycerol conversion to LA. Reaction intermediate DHA was more favorable as the starting reagent for LA formation than GlA, but the Pt/AC catalyst accelerated further oxidation of DHA and GlA to GLYA. In addition, the Pt/AC catalyst retained high activity and LA selectivity after five runs in a catalyst recycling experiment.

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Graphical Abstract doi: 10.1016/S1872-2067(15)61055-5 Chin. J. Catal., 2016, 37: 502–509 Selective oxidation of glycerol to lactic acid over activated Food carbon supported Pt catalyst in alkaline solution additive Chen Zhang, Tao Wang*, Xiao Liu, Yunjie Ding* Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Cosmetics University of Chinese Academy of Sciences Pt/AC + LiOH additive cerol 0.1 MPa O₂ Pt/activated carbon catalyst works efficiently for lactic acid production from glycerol under mild conditions. Different alkalis actic acid PLA greatly influence both glycerol conversion and lactic acid selectivyield > 65 ity, among which LiOH is optimal.

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