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Article

One-step synthesis of pyruvic acid from glycerol oxidation over Pb promoted Pt/activated carbon catalysts

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ABSTRACT

One-step production of pyruvic acid through selective oxidation of glycerol was investigated using lead promoted platinum/activated carbon (Pb-Pt/AC) catalysts under mild conditions. The results of N₂ physisorption, X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy revealed that the alloy phases of PtPb and Pt₃Pb were favorable for pyruvic acid production from glycerol oxidation, whereas the Pb₃(CO₃)₂(OH)₂ and surface Pb⁰ species inhibited the glycerol conversion. The loading of Pb and the catalyst preparation method (including impregnation and deposition precipitation) affected the formation of different metal species. Pyruvic acid was obtained at a yield of 18.4% on a 5.0 wt% Pb-5.0 wt% Pt/AC catalyst prepared by co-deposition precipitation method and 500 °C argon treatment.

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1. Introduction

The challenges of sustainable development, such as increasing energy consumption, expanding commodity demands, and environmental concerns, are calling for the efficient utilization of renewable resources. As an easily available byproduct of biodiesel production, glycerol has drawn increased attention because of its abundant functional groups [1–3]. Various value-added derivatives from glycerol have been obtained through different reactions, including selective oxidation [4,5], hydrogenolysis [6,7], and dehydration [8,9], increasing the feasibility of using glycerol as a bio-building block. Therefore, to explore new pathways of glycerol conversions and enhance the competitiveness of the biodiesel industry is attractive.

Pyruvic acid (PA) has been widely used as food additives, precursors for drugs and agrochemicals, as well as weight-loss supplements [10,11]. Because of the many promising applications of PA, its commercial market is considerable. PA is produced by fermentation of glucose or dehydrative decarboxylation of tartaric acid [12]. However, the problems of these methods remain challenging because the product separation efficiencies in the biological methods are low, whereas the pyrolysis of tartaric acid consumes a large amount of KHSO₄ and energy [13]. Thus, developing renewable alternative pathways to produce PA under mild conditions is highly appealing.

The one-step transformation of glycerol to PA is a potential option with high atom efficiency, which could be an addition to the reported PA production methods, including oxidations of

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propylene glycol or lactic acid (LA) [14–16]. This one-step pathway is viable in a fermentation method [17], but there are limitations in scaling-up. As for chemical methods, recent progresses on PA production from LA (or lactate) [13,18,19] and LA production from glycerol [20–23] have shed light on this one-step strategy. In liquid-phase LA oxidation to PA, heterogeneous bimetallic catalysts have been frequently adopted [15,18,24]. These catalysts commonly consist of noble metals such as Pt or Pd as active sites, heavy metals such as Pb, Te, and Bi as additives, and carbon as a support [15,18,24]. For glycerol oxidation to LA, we previously reported that a 1.0 wt% Pt/AC catalyst performed well under mild conditions, with almost no PA detected [25]. Hayashi et al. reported that Pb was a key additive for Pd/C catalyst in PA production from LA [15]. Therefore, the introduction of Pb promoter to a Pt/AC catalyst is expected to enhance the product distribution and PA yield during glycerol oxidation.

We report the one-pot production of PA from selective oxidation of glycerol under mild conditions. The Pb loading is optimized for PA selectivity. The Pb-Pt/AC catalysts prepared via different methods are investigated, including impregnation, deposition precipitation, and further calcination under an Ar atmosphere. N₂ physical adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) analyses are adopted to uncover the structure-activity relationships of catalysts.

2. Experimental

2.1. Catalyst preparation

A series of Pb-Pt/AC catalysts were prepared by the following methods. The Pt loading was fixed at 5.0 wt% in all Pb-Pt/AC catalysts.

2.1.1. Impregnation and deposition precipitation method (Im-DP)

An amount of Pb(NO₃)₂ was dissolved in 4 mL of deionized water and impregnated onto 2.0 g of an activated carbon (AC) support. The sample was dried at 120 °C for 12 h and reduced with H₂ at 400 °C for 4 h. Sequentially, Pt was deposited on the as-prepared Pb/AC sample by a deposition-precipitation method [26]. By changing the loading of lead, a series of xPb-5Pt/AC-Im-DP catalysts were obtained (*x* = 1, 3, 5, and 7 wt%, representing the Pb loading). If the 5Pb-5Pt/AC-Im-DP catalyst was further treated with Ar at 500 °C for 4 h, the obtained catalyst was denoted as 5Pb-5Pt/AC-Im-DP-500Ar. The 5Pt/AC-DP catalyst was prepared by a deposition-precipitation method.

2.1.2. Co-deposition precipitation method (Co-DP)

AC support (2.0 g) was firstly dispersed in 200 mL of deionized water. Pb(NO₃)₂ and H₂PtCl₆ were introduced, reduced, and deposited simultaneously on the AC support by a deposition-precipitation method. The catalyst was denoted as 5Pb-5Pt/AC-Co-DP with the loadings of Pt and Pb both at 5.0 wt%. If the catalyst was further treated with Ar at 500 °C for 4

h, it was denoted as 5Pb-5Pt/AC-Co-DP-500Ar.

2.1.3. Co-impregnation method (Co-Im)

An amount of Pb(NO₃)₂ and H₂PtCl₆ were added into 4 mL of deionized water and co-impregnated onto 2.0 g of AC support. The sample was dried at 120 °C for 12 h and treated under H₂ or Ar atmosphere at 500 °C for 4 h. The metal loadings were the same as the catalysts in Section 2.1.2. The obtained catalysts were denoted as 5Pb-5Pt/AC-Co-Im-500H₂ and 5Pb-5Pt/AC-Co-Im-500Ar.

2.2. Catalyst characterization

N₂ physical adsorption of the samples was performed on a Quantachrome Autosorb-1 instrument. The samples were degassed at 250 °C for 12 h before testing. The crystalline phases of the catalysts were tested by XRD with Cu K_{α1} radiation on a PANalytical X'Pert PRO diffractometer at 40 kV and 40 mA. TEM and high-resolution TEM (HR-TEM) were performed on a JEM-2100 electron microscope operating at 200 kV. XPS was performed on a Thermo ESCALAB 250Xi X-ray spectroscopy spectrometer. The monochromatic Al K_α source (1486.6 eV) was operated at 15 kV. The C 1s peak at 284.6 eV was adopted for correction of the charging effects.

2.3. Glycerol oxidation reaction

The glycerol oxidation reaction was performed in a 100-mL three-neck flask in an oil bath, with 25.0 g of glycerol solution (10.0 wt%), 1.90 g of LiOH·H₂O (purity at 90%) and 0.25 g of catalyst [25]. After the reaction, the solution was filtrated, neutralized by H₂SO₄, and diluted with deionized water. An Agilent 1100 high performance liquid chromatography system equipped with a refractive index detector was applied for product analysis. In addition, an Alltech OA-1000 column was used at a separation temperature of 80 °C. The mobile phase was a H₂SO₄ aqueous solution (0.005 mol/L) operated at a flowrate of 0.5 mL/min. All products were identified using the retention time of pure materials and quantified by an external standard method. The glycerol conversion and liquid product selectivity calculations were conducted using the following equations, with Con. representing the conversion of glycerol, *S_a* representing the selectivity of product *a*, *R₀* and *R_t* representing the concentration of glycerol at the reaction time of 0 and *t*, and *P_a* representing the carbon molar concentration of product *a* at the reaction time of *t*. From our experiment observations and literature reports [15,18,24], the possible gas product was CO₂, which was in trace amount and would be converted to carbonate in any basic solutions present.

$$\text{Con.} = (R_0 - R_t) \times 100\% / R_0$$

$$S_a = P_a \times 100\% / \sum P_a$$

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. N₂ physical adsorption results

Table 1

Textural properties of activated carbon (AC), 5Pt/AC-DP and Pb promoted 5Pt/AC catalysts.

Entry	Catalyst	S_{BET}^a (m^2/g)	V_{pore}^b (mL/g)	D_{meso}^c (nm)	D_{micro}^d (nm)
1	AC ^e	1241	1.0	4.8	0.4
2	5Pt/AC-DP	1165	1.0	3.8	0.4
3	1Pb-5Pt/AC-Im-DP	1108	0.9	3.8	0.4
4	3Pb-5Pt/AC-Im-DP	1032	0.8	3.0	0.4
5	5Pb-5Pt/AC-Im-DP	889	0.7	3.2	0.4
6	7Pb-5Pt/AC-Im-DP	843	0.6	3.6	0.4
7	5Pb-5Pt/AC-Im-DP-500Ar	898	0.7	4.8	0.4
8	5Pb-5Pt/AC-Co-DP	849	0.6	3.1	0.4
9	5Pb-5Pt/AC-Co-DP-500Ar	917	0.7	4.8	0.4
10	5Pb-5Pt/AC-Co-Im-500H ₂	905	0.7	4.0	0.4
11	5Pb-5Pt/AC-Co-Im-500Ar	1039	0.8	4.8	0.4

^a Calculated by the Brunauer-Emmett-Teller (BET) method.

^b Determined from the adsorbed nitrogen at a relative pressure (p/p_0) of 0.99.

^c Calculated on the adsorption curve by the Barrett-Joyner-Halenda (BJH) method.

^d Derived from the Horvath-Kawazoe (HK) method [27].

^e Reproduced data from previous work [26].

The N₂ physical adsorption results of the AC support and different catalysts are shown in Table 1 and Fig. 1. The specific surface areas, pore volumes, and average mesopore sizes of 5Pt/AC-DP and xPb-5Pt/AC-Im-DP catalysts were considerably smaller than those of the AC support, whereas the micropore size remained unchanged. This result may be attributed to the partial blockage of mesopores by the deposited metal species [26]. When the Pb loading was increased to more than 3.0 wt%, the catalyst surface areas and pore volumes decreased dramatically, indicating that the blockage was considerable. The blockage was alleviated by treating the samples at 500 °C Ar (or H₂), as shown by the improved surface areas and pore volumes. This result is also shown from the isotherms in Fig. 1, where the introduction of Pb would result in the drop of isotherms, and the 500 °C gas treatment lead to the elevation of isotherms.

3.1.2. XRD analysis

Fig. 1. N₂ physical adsorption-desorption isotherms of xPb-5Pt/AC-Im-DP catalysts (a) and 5Pb-5Pt/AC catalysts prepared by different methods (b).

Table 2

Particle sizes of 5Pb-5Pt/AC catalysts calculated from XRD data and the Scherrer equation.

Entry	Catalyst	Pt (nm)	Pb ₃ (CO ₃) ₂ (OH) ₂ (nm)	PtPb (nm)	Pt ₆ Pb (nm)
1	5Pb-5Pt/AC-Im-DP	8.8	56.4	—	—
2	5Pb-5Pt/AC-Im-DP-500Ar	13.5	—	47.1	26.0
3	5Pb-5Pt/AC-Co-DP	7.5	60.7	—	—
4	5Pb-5Pt/AC-Co-DP-500Ar	14.9	—	52.5	14.2
5	5Pb-5Pt/AC-Co-Im-500H ₂	—	—	—	—
6	5Pb-5Pt/AC-Co-Im-500Ar	13.3	—	—	—

The XRD patterns of the xPb-5Pt/AC-Im-DP catalysts are shown in Fig. 2(a). Characteristic diffraction peaks at 39.8°, 46.2°, 67.5°, and 81.3° are assigned to the Pt(111), (200), (220), and (311) reflections, respectively (JCPDS, 00-004-0802). Metallic Pt particles were present in all the samples. When Pb was supported on the catalysts at a loading of 3.0 wt% or higher, the characteristic reflection peaks of Pb₃(CO₃)₂(OH)₂ (JCPDS, 00-013-131) were observed. The major peaks at 34.2°, 27.1°, 24.6°, and 20.9° are indexed as (110), (015), (104), and (012) planes, respectively.

The XRD patterns of 5Pb-5Pt/AC catalysts prepared by different methods are shown in Fig. 2(b). They were denoted with their preparation method because of their same metal loadings. Characteristic Pt peaks were observed in all the 5Pb-5Pt/AC catalysts except Co-Im-500H₂ (sample (5)). This indicates that Pt particles were highly dispersed on the Co-Im-500H₂ catalyst. In contrast, the Co-Im-500Ar (sample (6)) catalyst shows more intense metallic Pt peaks. This result may be related with the availability of reducers during the reduction process, because H₂ (the reducer of Co-Im-500H₂) is more accessible than AC (the reducer of Co-Im-500Ar). From the XRD patterns, the particle sizes of Pt were calculated using the Scherrer equation (Table 2). The 500 °C Ar treatment of Im-DP and Co-DP catalysts also creates larger Pt particles (untreated at 8 nm vs treated at 14 nm).

Similar to the Im-DP catalyst, characteristic peaks of Pb₃(CO₃)₂(OH)₂ were also observed in Co-DP catalyst. After 500 °C Ar treatment, these signals disappeared because of the decomposition of Pb₃(CO₃)₂(OH)₂ [28]. Platinum lead alloys

Fig. 2. XRD patterns of different samples. (a): (1) 5Pt/AC-DP, (2) 1Pb-5Pt/AC-Im-DP, (3) 3Pb-5Pt/AC-Im-DP, (4) 5Pb-5Pt/AC-Im-DP, (5) 7Pb-5Pt/AC-Im-DP catalysts; (b): (1) 5Pb-5Pt/AC-Im-DP, (2) 5Pb-5Pt/AC-Im-DP-500Ar, (3) 5Pb-5Pt/AC-Co-DP, (4) 5Pb-5Pt/AC-Co-DP-500Ar, (5) 5Pb-5Pt/AC-Co-Im-500H₂, (6) 5Pb-5Pt/AC-Co-Im-500Ar catalysts. Standard stick patterns of Pt, Pb₃(CO₃)₂(OH)₂, PtPb, and Pt₃Pt are shown as references.

emerged, i.e., PtPb and Pt₃Pb (JCPDS, 00-006-0374 and 00-006-0574). For Co-Im-500H₂ and Co-Im-500Ar catalysts, neither Pb₃(CO₃)₂(OH)₂ nor platinum lead alloys were detected.

3.1.3. XPS analysis

The XPS spectra of the xPb-5Pt/AC-Im-DP catalysts were conducted (Fig. 3) to study the oxidation states of the surface metals on the catalysts. The spectra data was processed by a software called XPS Peak 4.1. The backgrounds of curves were subtracted by the Shirley method. A Lorentzian function was

convoluted with an experimental Gaussian curve ($G = 0.2$) for data analysis. The position gap between deconvoluted Pt 4f_{7/2} and Pt 4f_{5/2} peaks was fixed at 3.3 eV, whereas that for Pb 4f peaks was fixed at 5.0 eV. The full width at half maximum of the curve of each group of deconvoluted Pt 4f_{7/2} and Pt 4f_{5/2} peaks was kept the same, with the peak area of Pt 4f_{5/2} being 0.75 times of the area of Pt 4f_{7/2}. A similar method was applied for the Pb 4f spectra.

The Pt 4f spectra of monometallic 5Pt/AC-DP catalyst and bimetallic xPb-5Pt/AC-Im-DP catalysts are shown in Fig. 3(a),

Fig. 3. XPS spectra of Pt 4f (a) and Pb 4f (b). (1) 5Pt/AC-DP, (2) 1Pb-5Pt/AC-Im-DP, (3) 3Pb-5Pt/AC-Im-DP, (4) 5Pb-5Pt/AC-Im-DP, (5) 7Pb-5Pt/AC-Im-DP catalysts.

with two doublet peaks originated from the spin-orbital splitting of the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ states. The deconvoluted peaks of monometallic 5Pt/AC-DP catalyst at 71.5 and 74.8 eV were ascribed to the metallic form of Pt, meaning that its surface Pt species generally remained unoxidized [26]. However, for Pb-promoted catalysts, the deconvoluted peaks at 72.6–72.8 and 75.9–76.1 eV indicate the presence of oxidized Pt species, similar to the results in our previous report [16].

For Pb 4f spectra in Fig. 3(b), the binding energy (BE) peaks were deconvoluted into two or three groups. The BE peaks at 138.5, 137.0–137.4, and 135.5–135.6 eV were ascribed to the Pb^{4+} , Pb^{2+} , and Pb^0 species, respectively [29–31]. Unlike samples (3), (4), and (5), almost no Pb^0 species was detected on the surface of the 1Pb-5Pt/AC-Im-DP catalyst. Therefore, the overall oxidation state of Pb species on 1Pb-5Pt/AC-Im-DP is higher than other xPb-5Pt/AC-Im-DP catalysts, influencing the oxidation state of the surface Pt species, which showed a higher BE peak at 72.8 eV than the other three catalysts at 72.6 eV (Fig. 3(a)).

To observe the influence of the 500 °C Ar treatment on the metal oxidation state, two representative 5Pb-5Pt/AC catalysts (i.e., the Co-DP and the Co-DP-500Ar catalysts) were adopted for XPS analysis (Fig. 4). The Pt 4f peaks (slightly) and the Pb 4f peaks (obviously) shifted to a lower BE position after Ar treatment at 500 °C. Considering that carbon is frequently used as a reducing agent, the treatment of Co-DP catalyst may favor the reduction of metals by the AC support. In addition, the Pt 4f peaks of 5Pb-5Pt/AC-Co-DP (Fig. 4(a), sample (1)) and 5Pb-5Pt/AC-Im-DP catalysts (Fig. 3(a), sample (4)) were of similar shape and position, whereas their Pb 4f peaks were obviously different (Fig. 4(b) vs Fig. 3(b)). In a previous discus-

sion, these two catalysts were of similar XRD patterns (Fig. 2(b)), but the XPS analysis demonstrated that their surface Pb species were different, which would result in different catalytic performance.

3.1.3. TEM analysis

The TEM images of two groups of representative catalysts (Im-DP vs Im-DP-500Ar, Co-DP vs Co-DP-500Ar) are presented in Fig. 5. The Ar treatment at 500 °C resulted in the metal particle aggregation (Fig. 5(b) vs Fig. 5(d)), which agrees with the XRD results. The HR-TEM images demonstrated the respective characteristic lattice fringes of the metallic particles. In images of Im-DP and Co-DP, only characteristic patterns of Pt (111) planes ($d = 2.28$ Å) (JCPDS, 00-004-0802) were observed. However, PtPb alloys (JCPDS, 00-006-0374) were also detected in Im-DP-500Ar and Co-DP-500Ar images. In Im-DP-500Ar, PtPb(101) planes ($d = 3.04$ Å) were observed, whereas in Co-DP-500Ar, PtPb (100) and (102) planes with $d = 3.68$ and $d = 2.20$ Å, respectively, were observed. This also agrees with the XRD analysis that Ar thermal treatment favored the Pt-Pb alloys formation.

3.2. Selective oxidation of glycerol

3.2.1. Optimization of Pb loading for xPb-5Pt/AC-Im-DP catalysts

Table 3 shows the results of glycerol oxidation reactions over 5Pt/AC-DP and xPb-5Pt/AC-Im-DP catalysts with Pb loading ranging from 1.0 to 7.0 wt%. From our previous optimization studies of alkaline salts and their ratios, we adopted LiOH in this work [25]. Although the monometallic Pb/AC cat-

Fig. 4. XPS spectra of Pt 4f (a) and Pb 4f (b). Samples: (1) 5Pb-5Pt/AC-Co-DP, (2) 5Pb-5Pt/AC-Co-DP-500Ar.

Fig. 5. TEM images of Im-DP (a); Im-DP-500Ar (b); Co-DP (c); and Co-DP-500Ar (d) catalysts. The insets are high resolution images showing their characteristic lattice fringes.

alyst showed no activity in converting glycerol (data not shown), the addition of 1.0 wt% Pb to 5Pt/AC catalyst improved catalyst turnover frequency (TOF) compared with the monometallic 5Pt/AC-DP catalyst. For other xPb-5Pt/AC-Im-DP catalysts, the increase of Pb loading resulted in a decrease in catalyst TOF (as well as glycerol conversion), and the changing trend is consistent with that of their N_2 physical adsorption data. This result indicates that the decrease in surface area and pore size can cause the decrease in catalyst activity (Table 1).

As shown in the XRD analysis (Fig. 2(a)), the increase in Pb loading (> 1.0 wt%) leads to $Pb_3(CO_3)_2(OH)_2$ formation. This might be one of the reasons for the decreased surface area and pore volume. For the 1Pb-5Pt/AC-Im-DP catalyst, although its

surface area was smaller, its catalytic performance is higher than that of 5Pt/AC-DP, and no characteristic peaks for $Pb_3(CO_3)_2(OH)_2$ were detected. Therefore, $Pb_3(CO_3)_2(OH)_2$ might be the main reason for the catalyst activity decrease at high Pb loading (> 1.0 wt%).

In addition, the analysis of Pb 4f spectra (Fig. 3(b)) of xPb-5Pt/AC-Im-DP catalysts suggested that surface Pb^0 species are unfavorable for the glycerol conversion. Because the Pb^0 species were observed in all xPb-5Pt/AC-Im-DP catalysts except the 1Pb-5Pt/AC-Im-DP catalyst. The role of Pt species in the enhanced glycerol conversion of the 1Pb-5Pt/AC-Im-DP catalyst could not be determined, because Pt^0 and Pt^{2+} species were detected in all the bimetallic catalysts (Fig. 3(a)).

Table 3

Effects of Pb loading on glycerol conversion and product selectivity for xPb-5Pt/AC-Im-DP catalysts^a.

Catalyst	TOF (h ⁻¹) ^b	Time (h)	Conversion (%)	Selectivity (%)							
				PA ^c	LA	GLYA	TA	GA	OA	AA	FA
5Pt/AC-DP	76.7	2	36.2	0.9	68.3	15.5	2.6	7.8	1.6	1.9	1.4
		6	96.3	0.6	67.7	11.9	5.5	5.7	1.6	2.8	4.2
		10	100	2.8	44.9	1.5	21.9	2.2	22.0	4.6	0.1
1Pb-5Pt/AC-Im-DP	100.8	2	47.6	1.7	61.8	15.3	3.4	9.8	3.6	2.2	2.1
		6	92.3	1.6	56.5	14.9	7.9	6.5	4.5	7.5	0.7
		10	100	8.7	36.7	7.7	17.9	2.7	12.5	13.0	0.7
3Pb-5Pt/AC-Im-DP	74.5	2	35.2	1.2	55.1	21.1	5.1	7.8	5.1	2.4	2.1
		6	80.7	1.5	53.6	20.1	9.3	5.4	5.5	4.0	0.6
		10	98.9	8.6	34.3	12.9	22.3	3.2	12.6	9.3	0.4
5Pb-5Pt/AC-Im-DP	70.3	2	33.2	0.8	61.8	19.0	3.9	6.6	4.0	2.0	1.8
		6	80.4	1.4	63.3	17.7	5.9	3.8	3.0	4.3	0.6
		10	100	14.2	34.9	9.8	19.5	2.0	9.1	10.2	0.3
7Pb-5Pt/AC-Im-DP	72.6	2	34.3	0.8	61.5	21.3	5.1	4.2	3.7	2.2	1.3
		6	88.3	1.3	61.2	19.1	7.0	3.4	3.9	3.7	0.4
		10	100	9.7	35.4	12.6	19.8	2.8	9.4	9.9	0.5

^a Reaction conditions: $t = 90$ °C, $p = 1$ atm, $F_{O_2} = 100$ mL/min, $n_{LiOH}/n_{glycerol} = 1.5$, stirring rate = 800 r/min. ^b TOF was calculated based on the loading of Pt since Pb mainly served as a promoter, and the 2 h reaction data was used for the calculation. ^c PA = pyruvic acid, LA = lactic acid, GLYA = glyceric acid, TA = tartronic acid, GA = glycolic acid, OA = oxalic acid, AA = acetic acid, FA = formic acid.

In terms of the target product PA, the introduction of Pb showed enhanced PA selectivity, which may be because of the presence of Pb and the generation of oxidized Pt species in all the four xPb-1Pt/AC-Im-DP catalysts, which was caused by the Pb promoter as shown in the XPS analysis (Fig. 3(a)). From the product distributions, the introduction of Pb favored PA production and contributed to glyceric acid selectivity. However, the productions of LA and oxalic acid were decreased. This result may be because the presence of Pb favored LA consecutive oxidation towards PA, but not glyceric acid consecutive oxidation and C–C cleavage reaction to oxalic acid [32]. The 5Pb-5Pt/AC-Im-DP catalyst showed the highest performance with a PA selectivity over 14%.

3.2.2. Further investigation on the roles of Pt and Pb species

To further explore the previous speculation on the roles of surface Pb^0 species and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, we prepared a series of 5Pb-5Pt/AC catalysts by different methods. Fig. 6(a) shows the catalyst TOF, and Fig. 6(b) shows the glycerol conversion over these 5Pb-5Pt/AC catalysts with time on stream. As discussed in Section 3.2.1, the decreases in glycerol conversion were related with the Pb^0 species. The comparison of catalyst TOF in Fig. 6(a) and glycerol conversion in Fig. 6(b) between Im-DP and Co-DP could further investigate the role of Pb^0 species. The XRD patterns of Im-DP and Co-DP were similar (Fig.

2), with $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ observed in both of them. Their Pt 4f spectra were also of similar shape and position. However, their Pb 4f spectra (Fig. 3(b) sample (4) vs Fig. 4(b) sample (1)) were different, with the Pb^0 species present only in the Im-DP catalyst. Thus, the lower TOF and glycerol conversion of the Im-DP catalyst might be related with the Pb^0 species.

The role of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ could be illustrated by the following comparison. For the Im-DP and Co-DP catalysts, their TOF and glycerol conversions were generally enhanced after treatment under Ar at 500 °C. On the one hand, this suggests that the removal of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ might be beneficial to glycerol conversion. On the other hand, such an improvement might be related with the formation of PtPb and Pt_xPb alloys. The BE peak shift of Pb to a lower state might be associated with the catalyst performance. The decomposition of

Fig. 6. Effects of preparation method of 5Pb-5Pt/AC catalysts on: catalyst TOF (a); Glycerol conversion (b); and PA selectivity (c). Reaction conditions: $t = 90$ °C, $p = 1$ atm, $F_{\text{O}_2} = 100$ mL/min, $n_{\text{LiOH}}/n_{\text{glycerol}} = 1.5$, stirring rate = 800 r/min.

Fig. 7. TEM images of spent Co-DP (a); Co-DP-500Ar (b) and Co-Im-500Ar (c) catalysts. The insets are high resolution images showing their characteristic lattice fringes. A $d = 2.33$ Å from the patterns is characteristic of Pt_xPb (111) planes (JCPDS, 00-006-0574).

Fig. 8. XRD patterns of spent Co-DP, Co-DP-500Ar and Co-Im-500Ar catalysts. Stick patterns of Pt, PtPb, and Pt_xPb are shown as references.

Pb₃(CO₃)₂(OH)₂ and the formation of Pt_xPb alloys can cause a BE peak shift. Thus, further analysis is still necessary to clarify the mechanism. For simplicity, the following discussion focuses on the Pb₃(CO₃)₂(OH)₂ and Pt_xPb alloy species. For Co-Im-500H₂ and Co-Im-500Ar catalysts, Ar or H₂ treatment at 500 °C prevented Pb₃(CO₃)₂(OH)₂ formation; moreover, neither PtPb nor Pt_xPb alloys were observed. They still showed higher TOF and glycerol conversion than the Im-DP and Co-DP catalysts. Therefore, the removal of Pb₃(CO₃)₂(OH)₂ is essential for enhancing catalyst activity.

Similar to the enhancement effect on catalyst activity, the PA

selectivities of Im-DP and Co-DP catalysts were improved after their treatment at 500 °C in Ar (Fig. 6(c)). The PA selectivity of Co-DP-500Ar was almost 4.6 times higher than that of the untreated Co-DP catalyst, the PA yield reached 18.4% under the present reaction conditions. Thus, the PA selectivity might also be related with the removal of Pb₃(CO₃)₂(OH)₂ and the formation of platinum lead alloys.

The role of PtPb and Pt_xPb alloys could be partly demonstrated by the comparison between the Co-DP-500Ar and the Co-Im-500Ar catalysts. In both cases, the Pt and Pb metals were reduced simultaneously on AC, and their calculated Pt particle sizes were similar (Table 2). The Co-DP-500Ar catalyst contains two more species than the Co-Im-500Ar catalyst, which were the PtPb and Pt_xPb alloys. The former catalyst showed slightly better glycerol conversion and much improved PA selectivity than those of the latter one (Fig. 6). Therefore, the platinum lead alloys might favor the glycerol activation slightly and its transformation towards PA greatly. For fresh catalysts with PtPb and Pt_xPb alloys present (i.e., Im-DP-500Ar and Co-DP-500Ar catalysts), their PA selectivity maintained the highest among all the catalysts tested.

We characterized three representative spent catalysts (i.e., Co-DP, Co-DP-500Ar and Co-Im-500Ar catalysts, with three different phases), to find more information about the role of platinum lead alloys. The alloys were observed only on fresh Co-DP-500Ar catalyst, yet they were observed on all the three spent catalysts, as confirmed by both HR-TEM and XRD analyses (Figs. 7 and 8). In addition, the XPS analysis of spent Co-DP and Co-DP-500Ar showed that the Pb 4f peak of Co-DP shifted

Fig. 9. Pt 4f(a) and (b) Pb 4f XPS spectra of spent 5Pb-5Pt/AC-Co-DP (1) and spent 5Pb-5Pt/AC-Co-DP-500Ar (2).

Table 4 Glycerol conversion and product selectivity over spent 5Pb-5Pt/AC catalysts^a.

Catalyst	Conversion (%)	Selectivity (%)							
		PA ^b	LA	GLYA	TA	GA	OA	AA	FA
5Pb-5Pt/AC-Co-DP-Spent	100	6.1	47.4	15.2	13.8	2.2	6.5	7.3	1.5
5Pb-5Pt/AC-Co-Im-500Ar-Spent	97.0	12.2	37.5	15.7	17.1	15.7	5.6	9.4	0.0

^a Reaction conditions: $t = 90\text{ }^{\circ}\text{C}$, $p = 1\text{ atm}$, 10 h , $F_{\text{O}_2} = 100\text{ mL/min}$, $n_{\text{LiOH}}/n_{\text{glycerol}} = 1.5$, stirring rate = 800 r/min .^b See Table 3.

from 139.4 to 138.6 eV (Fig. 4(b) vs Fig. 9(b)) after the reaction. The surface Pb species on Co-DP-500Ar catalyst remain the same before and after the reaction, whereas the Pb species on spent Co-DP catalysts resemble that of the spent Co-DP-500Ar catalyst, which agrees with the HR-TEM and XRD results. The spent Co-DP and Co-DP-500Ar catalysts were evaluated under the same reaction conditions, and they exhibited slightly better PA selectivity than the fresh ones (Table 4). This suggested that the PtPb and Pt_xPb alloys might be the active sites for PA production. However, their formation and catalytic mechanisms still require further investigation.

We propose a possible reaction pathway for glycerol oxidation to PA and other products (Scheme 1). Glycerol is first dehydrogenated to form intermediates, followed by their dehydration and intramolecular Cannizzaro rearrangement to LA [33,21]. The introduction of Pb was beneficial for glycerol conversion when $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and surface Pb^0 species were absent, and the presence of platinum lead alloys favored the transformation of LA to PA.

4. Conclusions

A one-step production of PA by selective oxidation of glycerol was investigated. Both the Pb loading and the preparation

Scheme 1. Proposed mechanism for selective oxidation of glycerol over xPb-5Pt/AC catalysts.

methods greatly affect the catalyst performance, because of the alteration of Pt and Pb species. The Pt-Pb alloys are favorable for glycerol transformation to PA, whereas the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and the surface Pb^0 species adversely affect glycerol conversion. By treating the 5Pb-5Pt/AC-Im-DP (or 5Pb-5Pt/AC-Co-DP) catalyst under a $500\text{ }^{\circ}\text{C}$ Ar atmosphere, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ can be prevented, and platinum lead alloys can form. The highest PA yield was 18.4% under the present reaction conditions. Further optimization and better understanding of the reaction are required.

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Graphical Abstract

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One-step synthesis of pyruvic acid from glycerol oxidation over Pb promoted Pt/activated carbon catalysts

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Over 18% yield of pyruvic acid was obtained over Pb-Pt/AC catalyst through one-step glycerol oxidation reaction under mild conditions. Both Pb loading and preparation method influenced catalyst activity.

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Pb-Pt/AC催化甘油一步法制备丙酮酸张晨^{a,c}, 王涛^{a,#}, 丁云杰^{a,b,*}^a中国科学院大连化学物理研究所洁净能源国家实验室(筹), 辽宁大连116023^b中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023^c中国科学院大学, 北京100049

摘要: 生物质能具有绿色环保、可再生、来源广泛和安全性高等优点, 成为当前的研究热点. 作为生物柴油的主要副产物, 甘油是一种重要的生物质平台化合物. 甘油的高效利用, 不仅能够获得重要的精细化学品及聚合物, 也可以延长生物柴油的产业链, 降低其生产成本, 增加其市场竞争力.

丙酮酸是一种弱有机酸, 为生物体内葡萄糖分解代谢的中间产物, 在生物能量代谢和物质代谢过程中起着重要的枢纽作用. 同时, 由于它同时含有羧基和酮羰基, 具有很强的反应性, 可参与多种化学反应, 在化学工业中有广泛应用. 目前, 工业上主要采用酒石酸脱水脱羧法生产丙酮酸, 丙酮酸收率可达50–55%, 但生产过程需要消耗大量的KHSO₄粉末, 生产成本低, 且高耗能高污染, 不符合可持续发展的要求. 因此, 利用可再生资源甘油在温和条件下生产丙酮酸显现出良好的应用前景.

目前, 由甘油一步法获得丙酮酸仅可通过发酵法实现, 但是其规模化生产存在效率低、废弃物污染等问题. 因此, 研究化学方法由甘油一步制备丙酮酸可行也十分必要. 本课题组以Pt/AC或Cu-Pt/AC为催化剂进行甘油氧化制备乳酸的研究, 所得产物中几乎未检出丙酮酸; 当以Pb-Pt/C为催化剂进行乳酸脱氢氧化制备丙酮酸, 可获得较高选择性的丙酮酸. 因此, 本文通过向Pt/AC催化剂中引入Pb助剂, 以期调变甘油氧化的产物分布, 从而获得相对高的丙酮酸选择性.

通过浸渍-沉积沉淀法(Im-DP)制备了一系列不同Pb载量(1–7.0 wt%)的xPb-5Pt/AC-Im-DP催化剂, 并采用不同方法制备了一系列5Pb-5Pt/AC催化剂, 用于在温和条件下甘油选择性氧化制备丙酮酸反应中. 结果表明, Pb载量和催化剂制备方法都对其催化活性有显著影响. 当xPb-5Pt/AC-Im-DP催化剂中Pb载量为1%时, 甘油转化率和丙酮酸选择性均较单金属5Pt/AC催化剂高, 但当Pb载量继续升高至3%及以上时, 甘油转化率明显下降. 我们推测这与Pb₃(CO₃)₂(OH)₂物种的形成有

关. 采用该方法制备催化剂时, Pb载量宜为5.0 wt%.

保持Pt和Pb载量均为5.0 wt%, 采用共沉积沉淀(Co-DP)、共浸渍(Co-Im)、以及对催化剂进行500 °C氩气焙烧等, 制备了具有 $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ 物种、铂铅合金物种(PtPb和 Pt_xPb)和两物种均没有的5Pb-5Pt/AC催化剂. 通过评价它们的催化性能, 进一步探究了 $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ 物种、铂铅合金物种、表面金属价态与催化剂活性的关系. 实验表明, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ 和表面 Pb^0 物种不利于甘油的转化, 铂铅合金对甘油转化有一定的促进作用, 对丙酮酸生成显现出明显促进作用. 通过对Co-DP、Im-DP催化剂进行500 °C氩气焙烧, 能够除去 $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ 物种, 同时形成铂铅合金.

综上, 本文在温和条件下, 采用Pb-Pt/AC催化剂进行甘油选择性氧化制备丙酮酸反应. 采用优化的方法制备的5Pb-5Pt/AC催化剂在90 °C条件下反应10 h, 丙酮酸收率可达18.4%, 这是目前甘油一步法氧化制备丙酮酸的最高值. 进一步优化反应条件、催化剂组成与结构, 探索反应机理仍十分必要.

关键词: 甘油氧化; 丙酮酸; 铅助剂; 铂; 活性炭

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