

Influence of Pt Particle Size on the Activity of Pt/AC Catalyst in Selective Oxidation of Glycerol to Lactic Acid

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Received: 13 December 2016 / Accepted: 2 March 2017 © Springer Science+Business Media New York 2017

Abstract The size effect of Pt particles on selective oxidation of glycerol to lactic acid was investigated over 1.0 wt% Pt/activated carbon catalysts in base solutions. A series of Pt/activated carbon catalysts with Pt particle size ranging from 10.2 to 3.8 nm were prepared by simply verifying the deposition–precipitation temperature from 0 to 80 °C, which were characterized by XRD, CO pulse chemisorption, H_2 – O_2 titration, TEM and zeta potential analyses. The Pt particle size showed evident impact on the pseudo turnover frequency of the catalyst, with the optimal activity achieved over medium-sized Pt particles. The lactic acid selectivity was less obviously affected by the Pt particle size. Meanwhile, the Pt particle size effect would be altered when factors including base type changed.

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Keywords Glycerol · Aerobic oxidation · Platinum · Particle size · Lactic acid

1 Introduction

Graphical Abstract

As a major by-product of biodiesel manufacture, glycerol is recognized as a valuable platform molecular due to its triple hydroxyl groups. Under different strategies, high-valued derivatives such as lactic acid (LA), propanediol, glyceric acid (GLYA) could be obtained [1–3]. Because of the extensive applications of LA in fields like food industry, cosmetics and pharmaceuticals, a surge of research efforts have been focused on LA production from glycerol [4–6]. Considering that noble metals like Au, Pt and Pd are frequently adopted as active components in LA production, the investigation of particle size effect on LA production from glycerol is worth exploring to improve their utilization efficiency.

Among the many strategies for the preparation of adjustable particle size of metals on catalyst supports, the manipulation of metal particle size is often associated with the introduction of new chemicals (e.g., various precursors, supports and modifiers) or is studied at different metal loadings [7–10], which may bring interference to the investigation of particle size effect. One alternative strategy is the adjustment of thermal treatment conditions, such as reduction temperature and duration time [11, 12]. For example, the Ru cluster size can be tuned from 4 to 12 nm as H₂ reduction temperature increased from 250 to 700 °C [11]. In this work, deposition–precipitation method was adopted for catalyst preparation, and the Pt precursor was reduced and deposited by NaBH₄ in aqueous solution. Like the above H₂-reduction process, the variation in aqueous reduction temperature might also generate Pt particles with tunable size.

Herein, a series of 1.0 wt% Pt/AC catalysts with different Pt particle sizes were prepared by changing the preparation temperature from 0 to 80 °C, and the particle size influence on glycerol oxidation to LA was explored under mild conditions. During a 4-run recycling experiment, the Pt/AC catalyst maintained stable Pt particle size and catalytic performance. Characterizations including XRD, CO pulse chemisorption, H₂–O₂ titration, TEM and zeta potential analyses were performed to gain insight of the catalyst structure–activity relationship.

2 Experimental

2.1 Catalyst Preparation

Deposition-precipitation method was adopted during the Pt/AC catalyst preparation [13]. Typically, 3 g of AC (Tangshan United Carbon) was suspended in 300 mL of deionized water under continuous stirring, and then 0.03 g Pt in form of H₂PtCl₆ solution was added slowly. The process was carried out in a water bath in order to control the preparation temperature from 0 (in an ice-water mixture) to 80 °C. After 0.5 h, excess amount of NaBH₄ solution was introduced dropwise. Then the mixed solution was kept stirring for 6 h. Afterwards, the black precipitates were washed thoroughly with deionized water until Cl⁻ was undetected by AgNO₃, and were separated by filtration before drying in an oven at 120 °C overnight. Each of the Pt/AC catalysts was denoted with a number representing the preparation temperature in Celsius degree, e.g. Pt/AC-20 indicates that the catalyst was prepared at 20 °C.

2.2 Catalyst Characterization

X-ray diffraction (XRD) analysis of catalysts was performed on a PANalytical X'Pert PRO diffractometer with Cu $K_{\alpha 1}$ radiation at 40 kV and 40 mA. TEM analysis was conducted with a JEM-2100 electron microscope operating at 200 kV. The samples were pretreated by ultrasonic dispersion in ethanol. CO pulse chemisorption and H_2-O_2 titration (HOT) were performed on an Altamira Instruments AMI-300 with a thermal conductivity detection device. CO pulse chemisorption was generally operated on a 150 mg sample in a quartz U-tube. Samples were reduced by 10% H₂/Ar at 200 °C for 1 h. Then samples were cooled to 30 °C in He atmosphere. Afterwards, samples were exposed to pulses of 10% CO/He at 30 °C. A CO/Pt stoichiometry of 1 was used for calculations [14]. The HOT experiments were similar. After 10% H₂/Ar reduction of samples at 200 °C for 1 h and He post flush, turn on the 10% O₂/He pulse chemisorption at 30 °C. Afterwards, switch to Ar flush for 1 h before another round of 10% H₂/Ar pulses. A H₂/Pt stoichiometry of 1.5 was used for Pt diameter calculations [15]. Zeta potentials of AC at different temperatures (20-60 °C) were measured on a Malvern Zetasizer ZS90. The AC support was ball-milled to less than 1 µm and suspended in water before test, and the test was performed on the same AC suspension to avoid influence of AC concentration variation.

2.3 Glycerol Oxidation Reaction

The glycerol oxidation reaction was typically performed in a 100 mL three-neck flask under ambient pressure in an oil bath, with 25 g (10 wt%) of glycerol solution, 1.90 g of LiOH·H₂O (purity 90%) and 0.25 g of catalyst being added. When temperature was stable, turn on the oxygen flow (100 mL/min) and the magnetic stirrer (800 r/min). After the reaction, the aqueous solution was filtrated, neutralized and diluted. Then the products were analyzed by an Agilent 1100 high-performance liquid chromatography with a refractive index detector and an Alltech OA-1000 column at 80 °C. The products were identified by the retention time of pure chemicals. The reaction conversion and product selectivity were calculated by the same method reported previously [13].

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 XRD Analyses of Pt/AC Catalysts

The XRD patterns of a series of Pt/AC catalysts prepared at temperatures ranging from 0 to $80 \,^{\circ}$ C are shown in Fig. 1. The wide diffraction peaks at 24.0° and 43.5° are ascribed to activated carbon support [16]. Other diffraction peaks at 39.8° , 46.2° , 67.5° and 81.3° are attributed to the (111), (200), (220), and (311) lattice planes of metallic platinum (JCPDS, 00-004-0802), respectively. As Fig. 1 shows,



Fig. 1 XRD patterns of Pt/AC catalysts prepared at different temperatures. Characteristic diffraction peaks of Pt were marked by *black triangles*

elevated preparation temperature leads to the gradual weakening of Pt diffraction peak at 39.8°, suggesting the

gradually higher metal dispersion and smaller Pt particle size on AC support.

3.1.2 TEM of Pt/AC-20 and Pt/AC-70 Catalysts

The TEM images of Pt/AC-20 and Pt/AC-70 catalysts are presented in Fig. 2 as typical examples. The Pt particle sizes of the two samples exhibit obvious difference. In addition, their Pt particle distributions were statistically measured from the TEM images by counting over 150 particles, with the average diameter of Pt/AC-20 at 4.8 ± 1.0 nm and Pt/AC-70 at 2.5 ± 1.0 nm (Fig. $2a_2$, b_2), respectively. Therefore, elevating preparation temperature of Pt/AC catalysts would favor the dispersion of Pt, which is in good agreement with XRD observations (Fig. 1).

3.1.3 Chemisorption Analyses of Pt/AC Catalysts

In order to get a more thorough picture of the Pt particle sizes of the series of Pt/AC catalysts, CO pulse chemisorption was applied to calculate their respective average Pt nanoparticle size, and HOT analyses were performed as corroboration (Table 1). In line with XRD and TEM



Fig. 2 TEM images and Pt particle size distributions of a Pt/AC-20 and b Pt/AC-70 catalysts

Table 1 The influence of preparation temperature on Pt particle size

Catalyst	D (nm) ^a	ζ ^b		
	CO-pulse	НОТ	(mV)	
Pt/AC-0	10.2	12.6	_c	
Pt/AC-20	8.8	8.2	-17.0 ± 5.2	
Pt/AC-30	7.9	6.4	-11.6 ± 2.5	
Pt/AC-40	4.8	4.3	-8.8 ± 1.5	
Pt/AC-60	4.1	3.6	-2.8 ± 0.1	
Pt/AC-70	4.0	3.8		
Pt/AC-80	3.8	3.6	c	

^aD represents the average Pt particle size calculated from the CO pulse chemisorption data based on hemisphere model

 ${}^{b}\boldsymbol{\zeta}$ represents the zeta potential of AC suspension corresponding to each preparation temperature

^cOut of the detection limitation

analyses, a steady decrease of Pt particle size from 10.2 to 3.8 nm was observed as the preparation temperature increased from 0 to 80 °C (Table 1, CO-pulse data). We assumed that this size-temperature correlation might be caused by the interfacial charge variation of the AC suspension. As shown in Table 1, the zeta potential of AC suspension shifted from around -17 ± 5.2 mV to -2.8 ± 0.1 mV as temperature increased from 20 to 60 °C, i.e., the amount of negative charge on the suspended AC support decreased as temperature increased. As a result, the electrostatic adsorption of Pt⁴⁺ cations might be weaker or less per adsorption site, which would favor the dispersion of Pt⁴⁺ [17, 18]. Therefore, when the NaBH₄ was added to reduce the Pt⁴⁺ cations, the particle size would be bigger at low temperature and smaller at high temperature.

3.2 Results of Glycerol Oxidation Reaction Over Pt/AC Catalysts

Figure 3 and Table 2 shows the evaluation data of a series of Pt/AC catalysts in glycerol oxidation reaction in the presence of LiOH, which is previously examined as a desirable base for LA production [13]. As Fig. 3 shows, with the increase of preparation temperature from 0 to $30 \,^{\circ}$ C (i.e., the decrease of Pt particle size from 10.2 to 7.9 nm), there was a gradual elevation of catalysts' pseudo TOF from 0.50 to 0.70 s⁻¹. However, further increase in preparation temperature (i.e., decrease in Pt particle size) resulted in a dramatic decline in TOF to less than 0.21 s⁻¹.

In Table 2, the 6 h glycerol conversion variation tendency is quite similar to that of TOF. These observations indicated that there is an optimal Pt particle size for catalysts under the current reaction conditions, in line with Lei's report over Pt/CNT and Lakshmanan's work over Au/ CeO₂ [19, 20]. Also, the similar activity of Pt/AC-60, Pt/



Fig. 3 TOF and LA selectivity of Pt/AC catalysts in LiOH solution at glycerol conversion of 20–30%. Reaction conditions: t=90 °C, p=0.1 MPa, n_{LiOH} : $n_{\text{Glycerol}}=1.5$:1, $F_{\text{O2}}=100$ mL/min, stirring speed=800 r/min. TOF was calculated based on the dispersion of Pt obtained from the CO pulse chemisorption data

AC-70 and Pt/AC-80 catalysts might be due to their similar Pt particle sizes (Table 1). In both experimental and theoretical literatures, the Pt (111) planes were indicated as the most active sites in glycerol oxidation reaction [1, 21]. Meanwhile, the Pt (111) planes were also related with the activation of O_2 , side reactions, and the adsorption of products [21, 22]. Therefore, proper exposure of Pt (111) planes would maximize the catalyst performance.

In terms of product distribution, the Pt/AC catalysts generally showed a LA selectivity of less than 60% when glycerol conversion was low (at 20–30%), and catalysts with bigger Pt particle size showed slightly higher LA selectivity (as shown in Fig. 3). When reaction time was prolonged to 6 h, the catalysts all displayed a LA selectivity at over 60%, a GLYA selectivity at over 10%, and the selectivity of other products at lowerthan 10%. The difference in LA selectivity among these catalysts indicates that the Pt particle size would slightly affect the LA selectivity in the initial stage, but the influence would be minor with extended reaction time.

In order to further explore the Pt particle size effect under different basic conditions, six of the Pt/AC catalysts were evaluated in the presence of KOH (as shown in Fig. 4; Table 3). Similar to the variation trend in LiOH solution, the highest TOF (0.63 s^{-1}) was also obtained over the Pt/ AC-30 catalyst (average Pt particle size at 7.9 nm); the catalysts prepared at 60–80 °C were of similar particle size and similar catalytic performance (as shown in Fig. 4).

Unlike the LiOH case, the glycerol conversion at 6 h displayed a different order from their initial TOF order (as shown in Table 3). Glycerol conversion is considered to be related with both the transformation rate at each site (i.e. the TOF of each site) and the number of active site.

Table 2Catalytic performanceof Pt/AC catalysts in glyceroloxidation in LiOH solution

Catalyst	Conversion (%)	Selectivity (%)						
		LA ^a	GLYA	TA	GA	OA	AA	FA
Pt/AC-0	85.2	64.9	15.4	5.4	5.3	1.8	0.8	5.4
Pt/AC-20	96.5	63.9	11.8	8.3	6.6	2.5	1.1	5.7
Pt/AC-30	100	65.1	10.1	11.5	6.4	3.9	1.5	1.5
Pt/AC-40	90.9	62.2	14.0	6.5	7.8	2.3	1.4	5.8
Pt/AC-60	72.6	62.9	18.4	3.9	6.1	2.0	1.2	5.5
Pt/AC-70	72.3	62.2	17.7	4.4	7.3	2.1	1.8	4.5
Pt/AC-80	72.7	60.5	15.9	4.1	8.7	2.4	2.0	6.3

Reaction conditions: t=90 °C, p=0.1 MPa, n_{LiOH} : $n_{Glycerol}=1.5$:1, 6 h, $F_{O2}=100$ mL/min, stirring speed=800 r/min

^aLA lactic acid, GLYA glyceric acid, TA tartronic acid, GA glycolic acid, OA oxalic acid, AA acetic acid, FA formic acid



Fig. 4 TOF and LA selectivity of Pt/AC catalysts in KOH solution at glycerol conversion of 20–30%. Reaction conditions: t=90 °C, p=0.1 MPa, $n_{KOH}:n_{Glycerol}=1.5:1$, $F_{O2}=100$ mL/min, stirring speed=800 r/min. TOF was calculated based on the dispersion of Pt obtained from the CO pulse chemisorption data

With same Pt loading, Pt/AC catalyst (of same weight) with bigger Pt particle size would have fewer active sites. Then, we assumed that in LiOH solution, the major

factor for glycerol conversion is the transformation rate per site; whereas in KOH solution, the dominant factor is the number of active site. The gap in TOF between Pt/ AC-30 and Pt/AC-80 catalysts was narrower in KOH than in LiOH solution, which confirms that the size effect on transformation rate is more obvious in LiOH solution.

The LA selectivity of Pt/AC catalysts in KOH solution was stable (at ca. 40%) when glycerol conversion was maintained at 20–30% or the reaction time was 6 h (with glycerol conversions generally over 60%). In other words, the Pt particle size effect on LA selectivity was even less obvious in KOH than in LiOH solution.

The difference in the Pt particle size effect under different basic conditions is speculated to be associated with the reaction mechanism. LA production from glycerol oxidation involves the dehydrogenation of glycerol to intermediates (glyceraldehyde and dihydroxyacetone) and intermediates' dehydration and Cannizzaro rearrangement to LA [1, 4, 20], which are catalyzed by the synergy effect between base and Pt [13, 21]. In the presence of LiOH or KOH solution, the intermediate distributions and the reaction rate at each step would be different, and the influence of Pt particle size on each step may not be the same.

Table 3 Catalytic performance	
of Pt/AC catalysts in glycerol	
oxidation in KOH solution	

Catalyst	Conversion (%)	Selectivity (%)						
		LA	GLYA	TA	GA	OA	AA	FA
Pt/AC-20	60.6	38.0	21.3	5.9	11.9	2.7	3.6	16.5
Pt/AC-30	64.1	42.9	22.7	6.9	14.7	1.9	3.6	7.3
Pt/AC-40	63.2	42.8	19.0	4.4	10.8	2.6	4.9	15.5
Pt/AC-60	69.9	44.7	16.2	4.2	11.4	2.6	4.8	16.2
Pt/AC-70	73.6	46.2	19.2	4.4	11.8	2.0	5.1	11.4
Pt/AC-80	72.7	44.6	15.6	4.3	13.4	2.8	5.2	14.1

Reaction conditions: t=90 °C, p=0.1 MPa, $n_{KOH}:n_{Glycerol}=1.5:1$, 6 h, $F_{O2}=100$ mL/min, stirring speed=800 r/min

The stability of the Pt nanoparticles was tested over the Pt/AC-70 catalyst (Fig. 5). It exhibited quite stable catalytic performance during the 4-run recycling experiments in KOH solution, with glycerol conversion and LA selectivity being kept at over 77% and 42%, respectively. The TEM image (Fig. 6) of the spent-4th catalyst implies that the Pt nanoparticles maintained good dispersion during the recycling evaluations, which is essential for its practical applications.

4 Conclusions

A series of Pt/AC catalysts with tunable Pt particle size were prepared by changing the preparation temperature during the deposition–precipitation process. Higher



Fig. 5 Recycling experiments of Pt/AC-70 catalyst in glycerol oxidation reaction in KOH solution. Reaction conditions: t=90 °C, p=0.1 MPa, 8 h, n_{KOH} : $n_{Glycerol}=1.5$:1, $F_{O2}=100$ mL/min, stirring speed=800 r/min

preparation temperature favors smaller Pt nanoparticle. The Pt particle size effect on glycerol oxidation to LA has been investigated over Pt/AC catalysts in both LiOH and KOH solutions. In both cases, the Pt particle size shows evident impact on the catalyst activity (represented by pseudo TOF), with the size effect more remarkable in LiOH solution and the optimized Pt particle size at 7.9 nm; however, the Pt particle size effect on LA selectivity was less obvious.

Acknowledgements This work was supported by the National Natural Science Foundation of China (21176236).

References

- 1. Shen YH, Zhang SH, Li HJ, Ren Y, Liu HC (2010) Chemistry 16:7368
- Gong L, Lu Y, Ding Y, Lin R, Li J, Dong W, Wang T, Chen W (2010) Appl Catal A 390:119
- Brett GL, He Q, Hammond C, Miedziak PJ, Dimitratos N, Sankar M, Herzing AA, Conte M, Lopez-Sanchez JA, Kiely CJ, Knight DW, Taylor SH, Hutchings GJ (2011) Angew Chem Int Ed 50:10136
- Purushothaman RKP, van Haveren J, van Es DS, Melián Cabrera I, Meeldijk JD, Heeres HJ (2014) Appl Catal B 147:92
- 5. Xu J, Zhang H, Zhao Y, Yu B, Chen S, Li Y, Hao L, Liu Z (2013) Green Chem 15:1520
- Komanoya T, Suzuki A, Nakajima K, Kitano M, Kamata K, Hara M (2016) ChemCatChem 8:1094
- 7. Feng Y, Yin H, Wang A, Xue W (2015) J Catal 326:26
- Baudouin D, Rodemerck U, Krumeich F, Mallmann AD, Szeto KC, Ménard H, Veyre L, Candy J-P, Webb P B, Thieuleux C, Copéret C (2013) J Catal 297:27
- 9. Ligthart DAJM, van Santen RA, Hensen EJM (2011) J Catal 280:206
- Wei H, Gomez C, Liu J, Guo N, Wu T, Lobo-Lapidus R, Marshall CL, Miller JT, Meyer RJ (2013) J Catal 298:18
- Carballo JMG, Yang J, Holmen A, García-Rodríguez S, Rojas S, Ojeda M, Fierro JLG (2011) J Catal 284:102



Fig. 6 TEM images (a1) and particle distribution (a2) of spent-4th Pt/AC-70 catalyst in KOH solution

- Miller JT, Schreier M, Kropf AJ, Regalbuto JR (2004) J Catal 225:203
- 13. Zhang C, Wang T, Liu X, Ding Y (2016) Chin J Catal 37:502
- 14. Liang D, Gao J, Wang JH, Chen P, Hou ZY, Zheng XM (2009) Catal Commun 10:1586
- 15. Mears DE, Hansford RC (1967) J Catal 9:125
- 16. Dandekar A, Baker RTK, Vannice MA (1998) Carbon 36:1821
- 17. Regalbuto J (2016) Catalyst preparation: science and engineering. CRC Press, Boca Raton
- 18. Hao X, Barnes S, Regalbuto J (2011) J. Catal 279:48
- Lei J, Duan X, Qian G, Zhou X, Chen D (2014) Ind Eng Chem Res 53:16309
- 20. Lakshmanan P, Upare PP, Le NT, Hwang YK, Hwang DW, Lee UH, Kim HR, Chang JS (2013) Appl Catal A 468:260
- 21. Zope BN, Hibbitts DD, Neurock M, Davis RJ (2010) Science 330:74
- 22. Worz N, Brandner A, Claus P (2009) J Phys Chem C 114:1164–1172