非碱性条件下不同粒径的碳载体负载 Pt 催化剂上甘油的选择性氧化

张梦媛¹, 梁 丹¹, 聂仁峰¹, 吕秀阳², 陈 平¹, 侯昭胤^{1,*}

¹浙江大学化学系催化所, 浙江杭州 310028

²浙江大学化学工程与生物工程系, 浙江杭州 310027

摘要: 采用浸渍法制备了不同粒径的活性炭负载的 Pt 催化剂, 并运用扫描电镜、N₂ 吸附-脱附、透射电镜和 X 射线衍射对催化剂进行了表征。结果表明, 当活性炭载体的粒径从 253.2 μm 下降至 9.3 μm 时, 其表面积或孔体积变化不大, Pt 颗粒高度分散于载体表面, 平均粒径为 2.8~5.5 nm。这些高度分散的 Pt 催化剂在非碱性条件下的甘油氧化反应中表现出较高的活性, 且随着载体粒径的减小而明显提升。其中粒径为 9.3 μm 的活性炭负载的 Pt 催化剂上, 游离的甘油酸收率达到 47.6%, 且催化剂可以重复使用。

关键词: 甘油氧化; 非碱性条件; 载体尺寸; 活性炭; 铂

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*通讯联系人. 电话/传真: (0571)88273283; 电子信箱: zyhou@zju.edu.cn

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Oxidation of Biodiesel Glycerol over Pt Supported on Different Sized Carbon Supports in Base-Free Solution

ZHANG Mengyuan¹, LIANG Dan¹, NIE Renfeng¹, LU Xiuyang², CHEN Ping¹, HOU Zhaoyin^{1,*}

¹Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China

²Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China

Abstract: Recent progress in the selective oxidation of biodiesel glycerol in aqueous solution by Au, Pt and alloy catalysts was reviewed. A series of Pt catalysts on different sized carbon supports were prepared and characterized by scanning electron microscopy, N₂ adsorption, transmission electron microscopy, and X-ray powder diffraction. The average particle size of the carbon supports was decreased from 253.2 to 9.3 μm by ball milling, but their surface area and pore volume were only slightly changed. Pt was highly dispersed on these different sized carbon supports with an average particle size between 2.8–5.0 nm. Glycerol oxidation was catalyzed by these highly dispersed Pt catalysts in a base-free aqueous solution. The activity of the Pt catalysts increased with decreasing particle size of the carbon support, which was attributed to the higher accessibility of reactants to the Pt nanoparticles. The best yield of glyceric acid reached 46.7% and the catalyst was stable during six recycles.

Key words: glycerol oxidation; base-free solution; support size; carbon support; platinum

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*Corresponding author. Tel/Fax: +86-571-88273283; E-mail: zyhou@zju.edu.cn

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Biodiesel has similar properties to the diesel from crude oil that is used as a fuel in vehicles. It can be produced from

vegetable oil or waste cooking oil that contains fatty acids. The major advantage of biodiesel has over crude oil derived diesel is that biodiesel is derived from a renewable resource, it uses CO_2 in its production, and it gives lower particles, CO , HC emission in the exhaust [1–3]. The total EU27 biodiesel production in 2008 was over 7.7 million metric tons, which was an increase of 35.7% from 2007 (<http://www.ebb-eu.org/>). For every 3 moles of methyl esters produced, 1 mole of glycerol (1,2,3-propanetriol) is obtained as a byproduct, which is approximately 10 wt% of the total product. A major surplus of glycerol has become a problem from the increasing biodiesel production, and the current disposal of surplus glycerol is by incineration [1–3]. The catalytic conversion of glycerol to value-added products by a solid catalyst has attracted much attention in the past few years.

The selective oxidation of glycerol is one of the most important functional group transformations in organic synthesis and fine chemicals production. A large number of valuable chemicals such as glyceric acid with medicinal uses and significant biological value can be synthesized [4,5]. Traditionally, glyceric acid is synthesized by a homogeneous oxidation processes using large amount of oxidants like potassium permanganate, nitric acid or bichromate. However, these methods are restricted to the laboratory scale because of the toxicity or corrosion of the reagents, and chemical wastes produced [6]. Enzyme fermentation for the selective oxidation of glycerol also has several disadvantages including low activity and stability [6].

Chemically selective oxidation of glycerol in the liquid phase over heterogeneous noble metal nanoparticles using air or oxygen was firstly studied by Kimura et al. [7,8] and Gallezot et al. [9–11]. Since then, much attention has been focused on this process for its possible economic and environmental benefits. Hutchings and coworkers have contributed much to the catalytic oxidation of glycerol over gold and Au-Pd alloy. They found that the activity of the catalyst depends strongly on the basicity of the reaction medium. Under base-free conditions, the main products were undesirable C_1 byproducts such as CO_2 , HCHO and HCOOH over Pd and Pt catalysts, and supported Au catalysts were totally inactive [12]. As long as NaOH was present, 100% selectivity for glyceric acid at high conversion was readily achieved on Au/C [13]. It was proposed that the base aids the original dehydrogenation by H abstraction of one of the primary OH groups of glycerol and that this overcomes the rate limiting step in the oxidation. The performance of supported Au catalysts [14], and the influence of Au particle size [15], composition of Au-based alloys [16] and reaction conditions [17] had been investigated in detail. Alloying Pd with Au can significantly enhance the selective oxidation of glycerol, and the most active catalysts were produced using

a sol-immobilisation preparation method [16,18].

Parti and coworkers also performed many researches on the preparation methods, particle size distribution [19] and surfaces of Au, Au-Pd and Au-Pt catalysts for glycerol oxidation [20–22]. The best selectivity for glyceric acid reached 92% at 100% glycerol conversion at 30 °C with a NaOH /glycerol ratio of 4 and 0.3 mol/L glycerol [21]. Single phase bimetallic Au/Pd catalysts with Au:Pd ratios from 9.5:0.5 to 2:8 were used for the selective oxidation of glycerol [23,24]. The advantage of using an alloy lies in its higher activity and prolonged catalyst life [25]. The strong synergetic effect between gold and palladium that enhanced the activity and stability was only present in a basic environment [26,27].

In a strong base solution (0.3 mol/L glycerol, 0.6 mol/L NaOH , 1.01×10^5 Pa O_2 , 333 K), Davis found that monometallic Au was more active than monometallic Pd, but Pd exhibited a higher selectivity for glyceric acid. The activity of the bimetallic Au-Pd catalyst was lower than that of monometallic Au, but it exhibited a higher selectivity for glyceric acid [28]. Peroxide was also formed during glycerol oxidation and its concentration was correlated with increasing base concentration [29]. The peroxide formed caused C–C bond cleavage and increased the formation of C_1 products during glycerol oxidation.

The activities of gold nanoparticles on different supports such as carbon black, activated carbon and graphite, and TiO_2 , MgO and Al_2O_3 for glycerol oxidation were investigated by Claus et al. [30,31]. They found that carbon supported gold catalysts were highly active under the same reaction conditions, and that the selectivity of the Au/C catalyst could be controlled by changing the base concentration and reaction time. The selectivity for glyceric acid was less stable at a higher NaOH /glycerol ratio [30].

In base solution, Zope et al. [32] reported that oxygen atoms from hydroxide ions instead of molecular oxygen are incorporated into glycerol during the oxidation. Density functional theory calculations suggested that the reaction path involves both solution-mediated and metal-catalyzed elementary steps. Molecular oxygen was proposed to participate in the catalytic cycle not by dissociation to atomic oxygen but by forming hydroxide ions by the catalytic decomposition of a peroxide intermediate [32]. Similar results were also reported by Kwon et al. [33] in the electrocatalytic oxidation of glycerol.

In summary, Au-based catalysts were popular in published papers. The activity of Au depended strongly on the basicity of the reaction medium and it was totally inactive without NaOH [32]. In alkaline solution, the sodium glycerate formed and the reaction mixture need neutralization and acidification in order to get the free glycerol acid. These procedures would be inconsistent with green production and

the catalytic reaction mechanism of glycerol oxidation is masked by the excess added NaOH [5]. At the same time, glyceric acid is easily over-oxidized to byproducts like hydroxypyruvic acid, tartronate and oxalate in alkaline solution [5,29–33].

In 2009, we found that the selective oxidation of glycerol to glyceric acid can be performed on small sized Pt catalysts under base-free conditions [34,35]. Prati and coworkers and Hutchings and coworkers also found that H-mordenite supported Au-Pt alloys [36] and MgO supported Au-Pt alloys [37] can catalyze the selective oxidation of glycerol to glyceric acid without a base. The best yield of glyceric acid reached 81% (with a 100% conversion of glycerol) over AuPt/H-mordenite. However, the stability of these catalysts in the reaction mixture (strongly acidic, $\text{pH} < 2.0$, with the conversion of glycerol higher than 50%) was not disclosed. In a base-free solution, it is also interesting to note that the secondary hydroxyl group in glycerol was preferentially oxidized on the surface of Pt-Bi nanoparticles and the formation rate of dihydroxyacetone (DIHA) was high at the beginning of reaction [7–9,38–40]. However, Pt-Bi also catalyzes the further oxidation of DIHA to a series of byproducts such as oxalic acid and CO_2 , and the selectivity of DIHA decreased quickly with the increased conversion of glycerol.

Previous works also found it is difficult to increase the conversion of glycerol by simply decreasing the particle size of Pt (in the range of 1.2–8.0 nm) because the accessibility to small Pt particles deposited in the micropores of the active carbon was hindered [34,35]. Recently, it was reported that micropore-free multiwall carbon nanotube (MWCNT) supported Pt [41,42] and Au [43–46] catalysts were more active and selective for glycerol oxidation than Pt/AC and Au/AC, respectively. However, MWCNTs are expensive, and the pretreatment of commercial MWCNTs and support of Pt particles on these are complicated [34,42].

In this study, a series of different sized active carbon was prepared by simple ball milling in order to increase the accessibility to their micropores. Pt catalysts supported on different sized active carbon supports were prepared by impregnation and *in situ* HCHO reduction, and used for glycerol oxidation in a base-free aqueous solution. These catalysts were characterized and discussed in order to achieve a good understanding of the effect of the physical properties of the support on the activity of Pt.

1 Materials and methods

1.1 Catalysts preparation

A commercial active carbon (Tangshan Jianxin Active Carbon Co., Ltd.) was first ball milled at room temperature

for different times in a planetary ball milling apparatus (XQM series inverter planetary ball mill, Nanjing) in order to decrease the particle size of the active carbon. The active carbon (20 g) and quartz balls (200 g, 3–12 mm) were mixed and put into a ceramic pot. The ceramic pot was rotated at a rotation rate of 250 r/min. The original active carbon and ball milled samples were pretreated with a solution of 30 wt% H_2O_2 at 50 °C for 5 h and then washed with distilled water. The suspension was filtered off and dried overnight at 60 °C in vacuum. The samples were labeled as MCx, where x stands for the ball milling time.

Second, a solution of platinum chloride was added dropwise to a stirred suspension of 5.0 g carbon support at 50 °C and reduced with 4.0 ml formaldehyde (37 wt% of HCHO in H_2O) at 50 °C for 1 h (at a final pH value of 9.0). The slurry was filtered off and washed with distilled water until it was free of chloride. This catalyst (denoted as S0) was kept moist before use. Catalysts Sx were prepared similarly to S0 using different MCx supports. The loading of Pt in these catalysts was 5 wt%.

1.2 Catalyst characterization

The particle size distributions of the original carbon and ball milled carbon supports were determined by a laser particle sizer (Beckman Coulter Inc. USA). The textures of these carbon supports were characterized by nitrogen adsorption at –196 °C using an OMNISORP 100CX system (COULTER Co., USA). All samples were pretreated at 250 °C for 2 h under high vacuum. The surface area and pore volume of the carbon supports were calculated from the adsorption isotherms. The microstructure and morphology of these carbon supports were observed by scanning electron microscopy (SEM, HITACHIS-4700).

The morphologies of the catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD analysis was performed on a Rigaku automated power X-ray diffractometer system ($\text{Cu } K_\alpha$ radiation, 45 kV, 100 mA, RINT 2500, Japan). Diffraction data was recorded using continuous scanning at 0.02°/s and a step of 0.02°. TEM images were obtained using an accelerating voltage of 200 kV (TEM, JEOL-2010F). Samples were first ground to a fine powder and dispersed on Cu grids in tetrachloromethane under ultrasonic treatment.

1.3 Glycerol oxidation reaction

A thermostat equipped with a magnetic stirrer (MAG-NEO, RV-06 M, Japan), thermocouple, glass reactor (100 ml) and gas supply system was employed for the oxidation of glycerol. Glycerol solution (50 ml, 0.1 g/ml) and catalyst (0.5 g) were added into the reactor. A constant flow

of oxygen (150 ml/min) was introduced into the suspension when the temperature reached 60 °C. The reaction mixture was stirred at 1000 r/min. After reaction for 6 h, the catalyst was removed by filtration and the aqueous solution was analyzed using a high performance liquid chromatograph equipped with a refractive index (RI) detector and a Zorbax SAX column (HPLC, Agilent 1100 series). All products were confirmed with the standard mass spectrum in the database and those of standard products purchased from Alfa Aesar, SIGMA or TCI. These analysis procedures were described in detail in the references [42,47].

2 Results and discussion

2.1 Properties of the carbon supports

The SEM images of the carbon supports are shown in Fig. 1. The original active carbon was large particles with most of them in the range of 200–300 μm (Fig. 1(a)). The size of the carbon particles did not show a significant decrease after 5 h ball milling (Fig. 1(b)). These particles were completely crushed and a homogeneous size distribution appeared when the ball milling time was prolonged to 50 h (Fig. 1(d)). The carbon particles in the original active carbon had different shapes with many sharp edges, corners and macropore openings on the surface (Fig. 1(a)). Roughly spherical particles with flat edges were obtained by ball milling (Fig. 1(d)). In the high magnification images (20000 time, inset in each graph), it was observed that many different sized pores in the 1–6 μm range were randomly dis-

tributed on the surface of original carbon particles (Fig. 1(a)). Most of the larger sized pores (above 2 μm) were destroyed after 5 h milling (Fig. 1(b)). These large pores (1–6 μm) originated from the structure of the raw materials of the active carbon and were formed during the dry distillation process. The macropores were not present in MC50 (Fig. 1(d)) and the average particles size was decreased to 9.3 μm (Table 1).

Table 1 Structure of the carbon supports and Pt particle size

Catalyst	Particle size (μm)	Pore volum (cm^3/g)		Surface area (m^2/g)	$d_{\text{Pt}}^*/\text{nm}$	
		$V_{\text{meso and macro}}$	V_{micro}		XRD	TEM
S0	259.2	0.3480	0.5123	1449	5.0	3.2
S5	153.1	0.3507	0.5037	1414	—	2.8
S15	35.5	0.3715	0.4906	1381	4.2	3.0
S50	9.3	0.3723	0.5034	1409	3.4	3.1

*Loading of Pt was 5 wt%.

Figure 2 shows the particle size distribution of the original active carbon and the ball milled samples. The particle sizes of the original active carbon were in the range of 43 to 1000 μm (with an average particle size of 259.2 μm). After this was ball milled for 5 h, some small particles (2–80 μm) were formed, and the average particle size was decreased to 153.1 μm (Table 1). Prolonging the milling time to 15 and 50 h caused the average particle size to further decrease to 35.5 and 9.3 μm , respectively.

The textures of the original active carbon and ball milled samples characterized by N_2 adsorption are summarized in Table 1. The surface area of the original active carbon was

Fig. 1. SEM images of original carbon (a), MC5 (b), MC15 (c), and MC50 (d).

Fig. 2. Particle size distributions of the supports.

1449 m²/g with a mesopore volume (including macropore volume) of 0.3480 cm³/g. After this ball milled, the surface area of MC5 and MC15 were decreased slightly to 1414 and 1381 m²/g, respectively, while the mesopore volume were increased to 0.3507 and 0.3715 cm³/g. However, prolonged milling time to 50 h did not give any more significant changes for surface area nor pore volume as compared with that of MC15. Although the SEM images and particle size of these carbon supports were different, these differences only contributed slightly to the surface area and pore volume of micro- and meso-pores.

2.2 Platinum nanoparticles on the different supports

The TEM images of S0, S5, S15, and S50 catalysts are shown in Fig. 3.

Fig. 4. XRD patterns of catalysts S0 (1), S5 (2), S15 (3), and S50 (4).

The percentage histograms of the Pt particle distribution are shown at the bottom of the TEM images. The average Pt particle size in the TEM image (shown in Table 1) was calculated by $d_{\text{TEM}} = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i was the number of particles with diameter d_i . Highly dispersed Pt particles were detected on catalyst S0 (Fig. 3(a)) and the majority of the Pt particles were in the 2.0–4.0 nm range (mean 3.2 nm). Catalysts S5 (Fig. 3(b)), S15 (Fig. 3(c)) and S50 (Fig. 3(d)) also showed high dispersions of Pt particles, and the Pt particles were in the 2.0–3.0 nm (mean 2.8 nm), 2.0–4.0 (mean 3.0 nm) and 2.0–4.0 nm (mean 3.1 nm) ranges, respectively. These highly dispersed Pt particles were attributed to the high surface area of the carbon supports [34,35].

XRD patterns of the catalysts are compared in Fig. 4. The typical diffraction peaks of cubic Pt crystallite were detected at 39°, 46°, and 67° with all catalysts. Active carbon

Fig. 3. HR-TEM images and particle size distribution of the Pt catalysts. (a, e) S0; (b, f) S5; (c, g) S15; (d, h) S50.

Table 2 Oxidation of glycerol using Pt catalyst on different carbon supports

Catalyst	Conversion (%)	GLYA yield (%)	Product selectivity (%)					
			GLYA	DIHA	GLYCA	GLYHD	HPYA	C ₁ ^a
S0	50.0	23.7	47.4	17.0	13.6	2.1	2.1	17.9
S5	56.3	34.6	61.5	18.3	6.9	1.9	0.0	11.4
S15	60.2	42.3	70.3	14.3	5.8	4.1	0.0	5.5
S50	70.3	46.7	66.4	13.6	4.0	10.4	0.0	5.6

Reaction conditions: catalyst 0.5 g, aqueous solution of glycerol 50 ml (0.1 g/ml), 60 °C, oxygen 150 ml/min, 6 h.

GLYA: glyceric acid; DIHA: 1,3-dihydroxyacetone; GLYCA: glycolic acid; GLYHD: glyceraldehydes; HPYA: hydroxypyruvic acid.

^aMono-carbon products (mainly like CO_x and formaldehyde) were also detected.

has weak wide peaks centered at 27° and 43° [JCPDS 75-0223]. The intensity of the diffraction peaks of Pt was enhanced in the order of S5, S50, S15, and S0. The crystallite sizes of Pt calculated by the Scherrer-Warren equation (Table 1) had the same trend as shown in the TEM analysis.

2.3 Oxidation of glycerol

The activities of the catalysts for glycerol oxidation at 60 °C in a base-free aqueous solution are presented in Table 2. The conversion of glycerol and selectivity for glyceric acid over S0 were 50.0% and 47.4%, respectively. In addition to glyceric acid, considerable amounts of 1,3-dihydroxyacetone (selectivity of 17.0%), glycolic acid (selectivity of 13.6%) and C–C cleavage products (C₁, selectivity of 17.9%) were detected with S0. This result agreed well with published works [12–14,28–33]. The activity of Pt catalysts supported on different sized active carbon supports increased with decreasing particle size of the carbon supports and the selectivity for free glyceric acid was increased to 70.3% over S15. The highest conversion of glycerol reached 70.3% over S50, but the selectivity for glyceric acid was decreased slightly to 66.4%, which was due to the formation of glyceraldehydes. It was quite interesting that the detected amounts of glycolic acid and C–C cleavage products were lower with S15 and S50.

A previous work found that the activity of large sized Pt particles (>10 nm) had poor activity for glycerol oxidation, and they needed the addition of NaOH to improve the conversion of glycerol. But smaller Pt particles (with a Pt particle size < 6 nm) gave quite good glycerol conversion, stable selectivity and good recycled activity under a base-free condition, and the promotion effect of added NaOH was limited. The conversion of glycerol was similar when the particle size of Pt was smaller than 6.0 nm [34,47]. That is, it is difficult to further increase the conversion of glycerol by decreasing the particle size of Pt or by adding NaOH to the reaction mixture. The results in this work showed that decreasing the particles size of the carbon support can increase the activity for glycerol oxidation. The product distribution further indicated that a suitably sized carbon sup-

port is very important in order to increase the yield of glyceric acid.

The above characterization results disclosed that the surface area and pore volume of the different carbon supports were only changed slightly (see Table 1), and similarly sized Pt particles were formed on these supports. Thus, the increased activity of Pt catalysts on small sized carbon supports should be attributed to the higher accessibility of reactants to the active Pt nanoparticles. The lower activity of catalyst S0 with the larger carbon particles was attributed to its specific pore structure that restricted the necessary contact between reactants and active metal site. In other words, the higher accessibility provided by a small sized carbon support with a well dispersed active metal allowed better gas-liquid-solid contact, which resulted in enhanced reactivity. It was concluded that a suitable physical morphology of the carbon support was more effective for improving the chemoselective conversion of glycerol.

The stability of the S50 catalyst for the selective oxidation of glycerol in a base-free solution is shown in Fig. 5. The conversion of glycerol decreased slightly from 70.3% to 68.1% after six cycles, but the selectivity for glyceric acid remained stable. The result showed that this catalyst is stable for the selective oxidation of glycerol.

Fig. 5. Stability of S50 for the selective oxidation of glycerol.

3 Conclusions

A series of different sized carbon supports (from 253.2 to 9.3 μm) were prepared by ball milling. Highly dispersed Pt

particles were formed on these supports. The activity of these Pt catalysts for selective glycerol oxidation to glyceric acid increased with decreasing particle size of the carbon support. In addition, the amount of glycolic acid and C–C cleavage products decreased with decreasing particle size of the carbon support. We concluded that the enhanced activity of Pt catalysts on small sized carbon support was due to the higher accessibility of reactants to the active Pt nanoparticles.

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