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ARTICLE

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

ZHANG Mengyuan[1], LIANG Dan[1], NIE Renfeng[1], LU Xiuyang[2], CHEN Ping[1], HOU Zhaoyin[1,*]

[1]Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China
[2]Department 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, N_2 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

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

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

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byproducts such as CO_2, HCHO and HCOOH over Pd and Pt ctalysts, 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, 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.