Chinese Journal of Catalysis 37 (2016) 502–509

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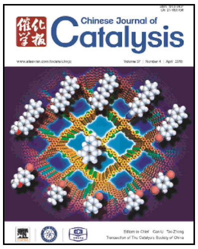

Article

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

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ARTICLE INFO

Article history:
Received 6 January 2016
Accepted 30 January 2016
Published 5 April 2016

Keywords:
Glycerol
Lactic acid
Platinum
Activated carbon
Oxidation
Base type

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 LiOH/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.

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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This work was supported by the National Natural Science Foundation of China (21176236).
DOI: 10.1016/S1872-2067(15)61055-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 4, April 2016

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 H_2 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/TiO_2-catalyzed aerobic oxidation of glycerol at 90 °C in NaOH with a LA yield of around 86%. Similar results have been achieved on Au/CeO_2 and Pt-Au/CeO_2 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 H_2PtCl_6 (Pt ≥ 38%, Shanghai Jiuyue, China) solution was added. After 0.5 h, an excess amount of $NaBH_4$ (> 98%, Tianjin Hainachuan Science and Technology, China) solution was introduced dropwise. The suspended black solution was stirred for 6 h. Afterward, the black precipitate was filtered and washed with deionized water until Cl^- was not detectable with $AgNO_3$ 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% H_2/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, O_2 flow was initiated at 100 mL/min with magnetic stirring at 800 r/min. After the reaction, the aqueous solution was filtered, neutralized with H_2SO_4 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. H_2SO_4 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 oth-