

# Research on Catalytic System for Oxidation of Ethylene Glycol in Pt/C Alkali-free Environment

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**Abstract**—In this paper, the oxidation of ethylene glycol is discussed, especially the selective oxidation of ethylene glycol to produce glycolic acid (GA). Ethylene glycol is used as an important chemical intermediate in several industrial applications, especially in the production of chemicals and materials. The oxidation of ethylene glycol involves a complex reaction mechanism and product distribution, and the yield and selectivity of glycolic acid are improved by reaction conditions. Different reaction conditions were used, including different reaction temperatures, glycol concentrations. In addition, the influence of solvent selection on the reaction path and product distribution was also discussed, and the results showed that the selectivity and conversion rate of glycolic acid were ideal when water was used as a solvent. The catalyst was then analyzed by high-performance liquid chromatography (HPLC) and other characterization methods (such as X-ray diffraction, transmission electron microscopy) to confirm the high activity and stability of the catalyst. In summary, this study provides a green and efficient synthesis method for the preparation of glycolic acid by ethylene glycol oxidation, and provides new insights for the design and optimization of catalysts.

**Keywords**—Glycolic acid; Ethylene glycol; Green chemistry; Selective oxidation; Pt/C

## I. INTRODUCTION

In today's world, non-renewable fossil resources such as oil and natural gas are not only the key source of fuel, but also the foundation of the chemical industry, which plays a vital role in the development of human society. In view of this, the active development and utilization of renewable resources has become an urgent and important task at present. Among them, biomass is a green and renewable organic carbon resource that uses solar energy to fix carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) in nature by relying on the photosynthesis of plants [1]. In this context, the selective conversion of biomass [2] and its derivatives into high value-added chemicals through catalytic means has become one of the key strategies for efficient utilization of biomass resources.

Ethylene glycol is the simplest diol with the same type of primary hydroxyl group. Possible products for selective oxidation of ethylene glycol include ethanalaldehyde, glyoxal, oxalic acid, and glycolic acid [3-4]. As a key intermediate in organic synthesis, glycolic acid has a wide range of applications in many fields, including leather, machinery, oil and gas, laundry and textiles, cosmetics, chemical additives, and chemical cleaning [5]. At present, the synthesis of glycolic acid is mostly achieved in a high-pressure and high-temperature environment with the help of acid-catalyzed reactions of formaldehyde and carbon monoxide [6], but there are some problems in the synthesis process, such as serious environmental pollution, technical difficulty, high cost, difficulty in glycolic acid separation and purification, and poor selectivity. Therefore, it is of great significance to develop a more efficient and green glycolic acid synthesis method.

Van Haasterecht team [7] prepared Cu/CNF catalysts with carbon nanofiber-supported active component Cu nanoparticles, which converted ethylene glycol to glycolic acid with high selectivity under anaerobic conditions and alkaline media, with a glycol conversion rate of 82% and a selectivity of glycolic acid of 96%. Zhan Yulu group [8] prepared a homogeneous catalyst [Cp\*Ir(bpyo)]OH, in which ethylene glycol was reacted with cascade dehydrogenation and canizaro to produce glycolic acid under alkaline medium and oxygen-free conditions, and the yield of glycolic acid could reach 81%. Du Feng group [9] developed a self-activating Pt/NaY catalyst with excellent performance by oxidizing ethylene glycol to prepare glycolic acid under alkali-free conditions. At 70 °C and 1 MPa, the conversion rate of ethylene glycol was 97%, and the selectivity of glycolic acid was 77 percent. Hao Yan team [10] prepared an electron-coupled Pt Mn/MCM-41 catalyst with PtMn<sub>2</sub>O<sub>3</sub> interface by a combination of impregnation and in-situ doping, and the ethylene glycol conversion rate was 92.1%, the selectivity of glycolic acid was 93.8%, and the yield of glycolic acid was 81% at 60 °C and 8 h. Honghong Shi group [11] reported a highly active and highly selective Pt-Fe alloy catalyst with CeO<sub>2</sub> as the support. Under alkaline conditions, the complete conversion of EG was completed within 4 h at 70 °C and ambient O<sub>2</sub> pressure, and the selectivity of glycolic acid reached 62%.

This study uses ethylene glycol as the raw material and pure water as the solvent to explore the product distribution and screen suitable reaction catalysts. By controlling the reaction temperature, concentration, and time, the optimal conditions are studied, and the post-reaction solution is analyzed using high-performance liquid chromatography (HPLC). Additionally, various additives are introduced to investigate their effects on the experiment.

## II. EXPERIMENTAL

### A. Materials

Purified water was purchased from Hangzhou Wahaha Group Co., Ltd. Concentrated sulfuric acid was purchased from Shandong Yantai Shuangshuang Chemical Reagent Co., Ltd. (China). Platinum on carbon (Pt/C) catalysts and standard compounds including acetaldehyde, glycolic acid, and ethylene glycol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

### B. Catalytic Alcohol Oxidation Reaction Procedure

All reactions were carried out in a three-neck flask. A solution of ethylene glycol at a specific concentration was prepared, and the required amount of Pt/C catalyst (typically 0.15 g) was added to the solution, which was then transferred to the flask. After sealing the reactor, it was purged with 0.1 MPa oxygen to remove any residual air. The reactor was then heated to the desired temperature (30–70 °C) and stirred at 600 rpm for the required reaction time (0.5–8 h). After the reaction, the resulting solution was collected in 1.5 mL sample vials for analysis.

### C. Characterization

**Powder X-ray Diffraction (PXRD):** PXRD patterns were recorded using a Bruker X-ray diffractometer with Cu K $\alpha$  radiation at a scanning speed of 10°/min in the 2 $\theta$  range of 5° to 90°. This analysis was used to confirm the crystalline phases of Pt and the carbon support. **Transmission Electron Microscope (TEM) Analysis:** The morphology, phase composition, elemental distribution and other microstructures of the precious metal Pt in the samples were characterized by the Talos F200S transmission electron microscope from Thermo Fisher Scientific with an accelerating voltage of 200 kV. The process of sample preparation is as follows: take an appropriate amount of sample and place it in absolute ethanol, make the sample evenly dispersed in ethanol by ultrasonic, drop the dispersed liquid on the carbon support film, stand still, and test the sample after the ethanol is completely volatilized. Electron microscopy images and composition of the catalyst were then obtained. **HPLC Analysis:** Product separation and quantification were carried out on an Aminex HPX-87H column equipped with a UV detector. A 0.005 mol/L aqueous sulfuric acid solution (286  $\mu$  L sulfuric acid in 1 L water) was used as the mobile phase at a flow rate of 0.6 mL/min, with an injection volume of 20  $\mu$  L at 35 °C.

## III. RESULTS AND DISCUSSION

In our previous research, we demonstrated that cellulose can be directly converted to ethylene glycol (EG), with glyoxal (GD) serving as an intermediate, highlighting its importance in EG production[12-13]. Under similar conditions, we further explored the selective oxidation of EG to glycolic acid (GA) using Pt/C catalyst without the addition of alkali. Figure 1a shows the product distribution of EG oxidation at different reaction temperatures. The oxidation of EG produces GD and GA, with GD selectivity reaching a peak of about 50% at 30 °C. In contrast, GA selectivity sharply increases to 70% at 50 °C, and then decreases at higher temperatures. At both temperatures, the combined selectivity of GA and GD is relatively low, indicating that these compounds mainly act as intermediates, forming various other products. Under the optimal conditions of 50 °C, we evaluated the effect of EG concentration on catalytic activity (Figure 1b). The data show that the catalyst activity increases with increasing substrate concentration, reaching 0.78 h<sup>-1</sup> at 2.75 g/L EG. However, the selectivity of the target products decreased rather than increased. GD selectivity remained below 50%, while GA selectivity rapidly decreased from 80% at 1.25 g/L EG to 60% at 2.75 g/L. This suggests that lower EG concentrations promote the selective formation of GA, while higher concentrations enhance the activity but also promote the formation of various intermediates, thereby reducing the selectivity for the desired products, GA and GD. Therefore, catalyst deactivation primarily results from the strong chemical adsorption of reaction intermediates on platinum surface sites[13-15]. Specifically, the Pt catalyst is particularly susceptible to poisoning by the strong adsorption of intermediates derived from alcohol dissociation[16]. This poisoning effect is attributed to the formation of strongly bound carbonaceous species, which occupy active sites and hinder further catalytic turnover.

Figure 2a shows the product distribution of GA and GD at different EG reaction times. Under the conditions of 40 °C, the conversion of ethylene glycol and glycolic acid selectivity rapidly increased within 0.83 h of the reaction. As the reaction time continued, the conversion of ethylene glycol kept increasing, but the selectivity of glycolic acid remained around 50%. When the reaction time reached 2 h, a 30% conversion of ethylene glycol and 50% glycolic acid selectivity was achieved. After 2 h, the selectivity for glycolic acid quickly decreased. This may be due to the further oxidation of glycolic

acid, leading to the formation of by-products and thus reducing the selectivity for the target product. Meanwhile, the conversion of the raw material continued to increase with time. Figure 2b shows the product distribution of GA and GD at different EG conversion rates. At 15% EG conversion, the GA selectivity was 70%, and the GD selectivity was 27%. As the conversion rate increased to 20%, the GA selectivity slightly increased to about 80%, while the GD selectivity decreased to 18%. After the EG conversion rate exceeded 55%, the GA selectivity significantly decreased, reaching 65% at 60% conversion and 58% at 66% conversion. At these high conversion rates, the GD selectivity remained very low. It is noteworthy that GD selectivity initially increased and then steadily decreased, while GA selectivity increased and then slowly decreased, indicating that GD plays an intermediate role in the oxidation process of EG to GA. The reaction rate constant for the formation of GD is lower than that for its conversion to GA, maintaining a higher selectivity for GA.

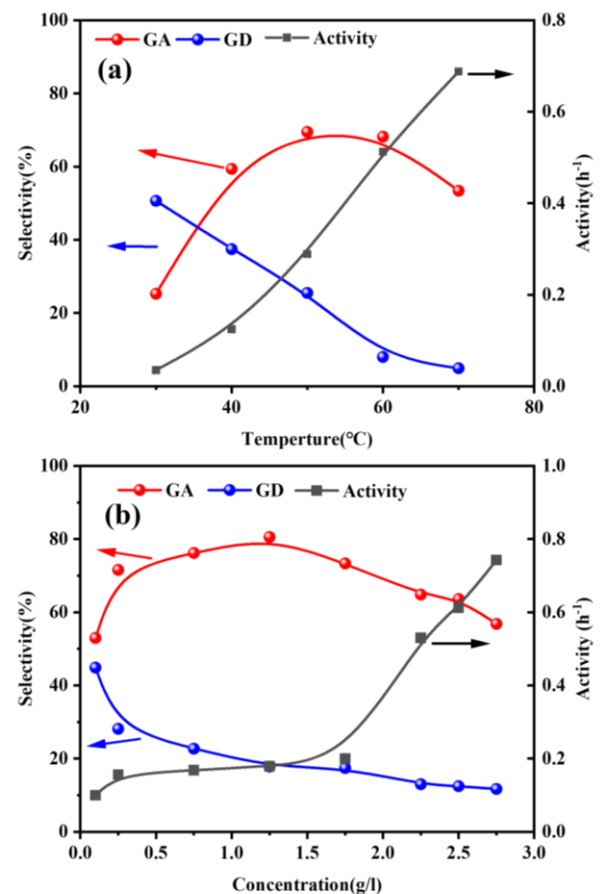
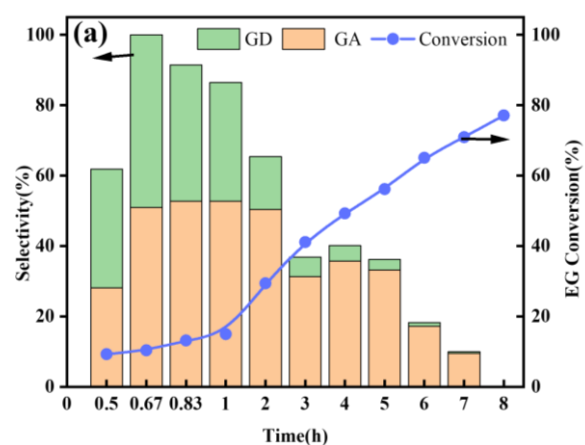


Fig. 1. (a) Effect of reaction temperature on the catalytic performance (reaction conditions: 0.15 g catalyst, 0.75 g/L EG solution, 2 h, 0.1 MPa O<sub>2</sub>), and (b) effect of EG concentration on the catalytic performance (reaction conditions: 0.15 g catalyst, 50 °C, 2 h, 0.1 MPa O<sub>2</sub>).



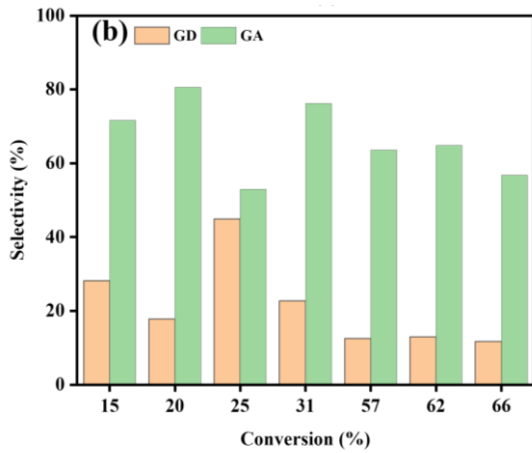


Fig. 2. (a) Effect of reaction time on the catalytic performance (reaction conditions: 0.15 g catalyst, 0.75 g/L EG solution, 0.1 MPa O<sub>2</sub>); (b) The product distribution at different EG conversion (reaction conditions: 0.15 g catalyst, 50 °C, 0.1 MPa O<sub>2</sub>).

In the ethylene glycol oxidation reaction, the choice of solvent has a significant impact on the reaction path and product distribution. The polarity, acidity, alkalinity and other properties of the solvent not only affect the stability of the reaction intermediates, but also affect the activity and selectivity of the catalyst [17]. For example, the team of Academician Shi Jianlin and Associate Professor Chen Li song efficiently oxidized ethylene glycol to glycolic acid in a 0.5 M KOH solution containing 1 M ethylene glycol through electrocatalytic method, achieving high selectivity and high Faraday efficiency of glycolic acid [18]. In addition, the study of the preparation of Pt/C catalysts by solvothermal-assisted glycol reduction shows that the acidity and alkalinity of the solvent have an important impact on the coordination mechanism and final performance of the catalysts.

In recent years, researchers have conducted extensive research on the catalytic mechanism, catalyst design and application of ethylene glycol oxidation reaction. The realization of ethylene glycol oxidation reaction (EGOR) can provide ideas for the upgrading and recycling of polyethylene terephthalate (PET) [19]. However, the key to achieving these applications lies in understanding the EGOR mechanism and developing efficient and stable selective oxidation catalysts. For example, the transition metal alloying strategy for the Pd and d regions has been shown to be an effective strategy to

improve the performance of EGOR in alkaline environments [20]. In addition, by optimizing electrochemical conditions, such as potentiometric cycling strategies, the stability of the catalyst and the Faraday efficiency of the reaction can be significantly improved [21].

Although some progress has been made in the existing research, there are still many challenges in the research on the effects of different solvents on the oxidation reaction of ethylene glycol. For example, how to achieve efficient and selective oxidation of ethylene glycol in different solvents, and how to improve the efficiency and product selectivity of oxidation reaction through solvent design and regulation, still need further in-depth research. Therefore, the effects of different solvents on the oxidation reaction were then investigated.

As can be seen from Table 1, there is no product generation in the blank experiment; In the blank experiment when methanol is used as a solvent, a small amount of ethanolaldehyde will be generated, but there is no glycolic acid, indicating that the reaction still needs oxidants and catalysts. When oxygen and catalyst are introduced, methanol is used as a solvent, the selectivity is 51.65%, and the conversion rate is only 9%. When water was used as a solvent, the selectivity was 93.85% and the conversion rate was 52%. Obviously, the oxidation effect of ethylene glycol is not as good as when water is used as a solvent. These results therefore indicate that the best solvent to obtain high product selectivity is water.

Finally, the characterization of the Pt/C catalyst revealed structural and chemical signatures that favored high catalytic performance and durability. The XRD profile (Figure 3) shows characteristic peaks at  $2\theta = 25^\circ$  and  $40^\circ$ , corresponding to the metallic Pt, indicating the predominance of the active metal site. The transmission electron microscopy (TEM) images in Figures 4a, b show that the average size of Pt is about 2.0 nm. The high-resolution TEM image of the Pt crystal structure in Figure 5c shows a well-defined lattice. The inset in Figure 4c shows that the d-spacing of 0.227 nm between adjacent lattice planes corresponds to the {111} plane [22]. This is a type of crystal plane that is associated with high catalytic activity. Overall, these results highlight the catalyst's high activity, durability, and resistance to structural or chemical degradation under reaction conditions.

TABLE I. Effect of different solvents on the reaction

Solvent	Pre-reaction concentration g/l	Post-reaction concentration g/l	EG conversion rate%	GD concentration g/l	GA concentration g/l	GD selectivity%	GA selectivity%	Total selectivity%
-	0.76	0.77	-	/	/	/	/	
Blank - 10% methanol solvent	0.72	0.7	3.67	0.01	/	29.83	/	29.83
water 10%	0.76	0.33	52.71	0.06	0.39	14.61	79.24	93.85
methanol solvent	0.76	0.69	9.45	0.03	0.009	41.48	10.18	51.65

Reaction conditions: 0.15 g catalyst, 0.75 g/L EG solution, 0.1 MPa O<sub>2</sub>, 50 °C, 2h.

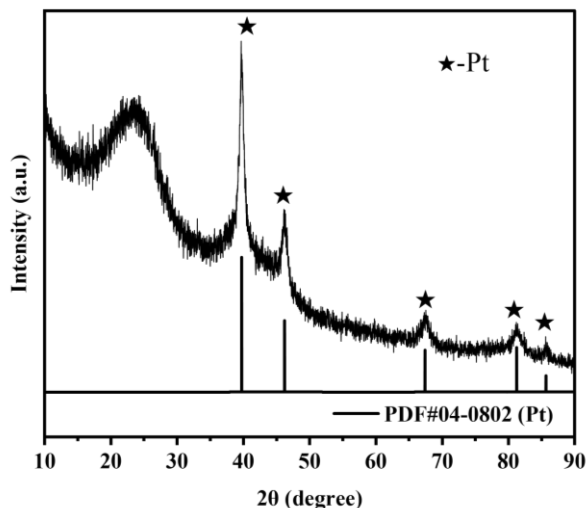


Fig. 3. Powder X-Ray diffraction (XRD) pattern of Pt/C.

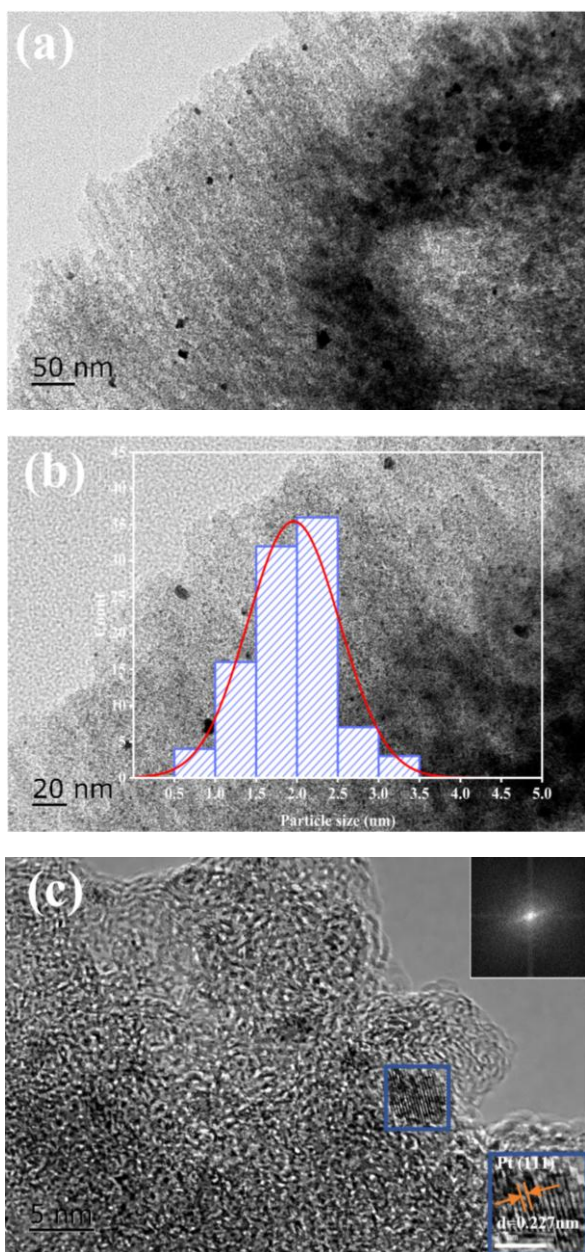


Fig. 4 (a) Typical transmission electron microscopy (TEM) images of Pt nanoparticles at different magnifications and (b, c) corresponding size distributions of samples with high-resolution TEM images.

## CONCLUSION

In summary, the green pathway for the preparation of GA was proved by the selective oxidation of ethylene glycol. First, the oxidation of ethylene glycol was studied in detail, and 78% GA selectivity was obtained in an oxygen atmosphere in an aqueous solution at 50 °C. Then, oxidizing additives are added to promote the oxidation of thermally unstable intermediates and enhance C-C cleavage. Therefore, phenolic acids are found to have good properties, especially ascorbic acid, and the selective properties of glycolic acid reach about 78%.

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