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Reaction Characteristics for Base-free Oxidation of Glycerol with Oxygen over Pt-based Catalysts

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Highlights

- Oxidation of the secondary hydroxyl group of glycerol is thermodynamically preferred.
- Pt-Sb/CNTs in comparison with Pt/CNTs displays enhanced activity and selectivity to DHA.
- Glycerol oxidation is a typical structure-sensitive reaction over Pt-based catalysts.

1. Introduction

Heterogeneous catalytic oxidation of glycerol using clean oxidizing agents such as air or oxygen, instead of costly and polluting stoichiometric oxidants, has attracted tremendous attention for economic and environmental concerns.[1] Owing to its three hydroxyl groups, glycerol can be oxidized to a large variety of products. Selective oxidation is, therefore, a big challenge. Investigation on reaction characteristics and thus developing effective catalysts to control the chemoselective orientation of glycerol oxidation reaction is highly desirable.[2]

In this work, thermodynamic analysis of glycerol oxidation was first performed to probe the reaction characteristics. Carbon nanotubes (CNTs) supported Pt and Pt-Sb catalysts were comparatively studied to gain an improved understanding of structure-performance relationship. Size effects of both Pt/CNTs and Pt-Sb/CNTs catalysts were further investigated to explore highly efficient and cost-effective Pt-based catalysts.

2. Methods

CNTs supported Pt and Pt-Sb catalysts were synthesized by incipient wetness impregnation method and characterized by TGA, HRTEM, XRD and XPS. These catalysts were applied to catalyze base-free oxidation of glycerol with O_2 at 60 ^oC in a batch reactor. The quantitative analysis of the reaction mixtures was performed by a high-performance liquid chromatograph using the external standard method.

3. Results and discussion

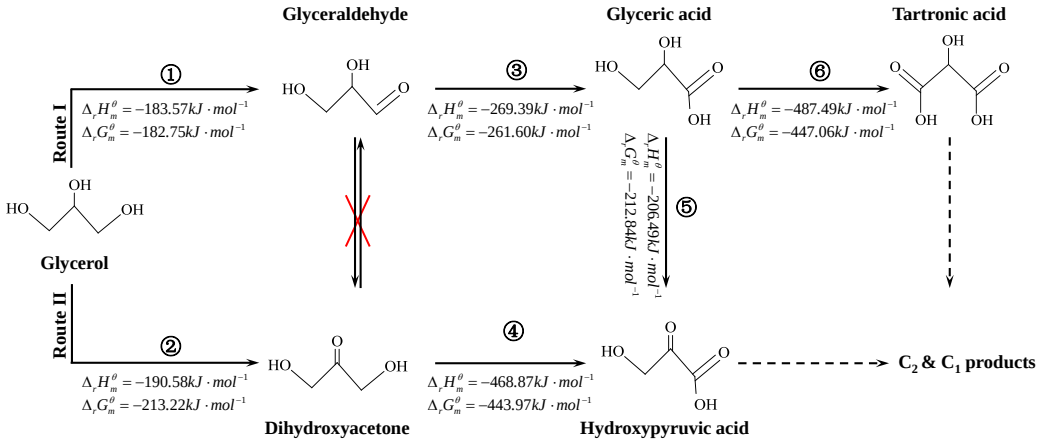

Figure 1. Reaction network for base-free oxidation of glycerol over Pt-based catalysts, which is only based on the evolution of C_3 species for the sake of clarity.

Thermodynamic analysis, a powerful tool for setting and evaluating process was carried out to identify the preferred reaction pathway for base-free oxidation of glycerol. In our previous studies [3], the interconversion between glyceraldehyde (GLYD) and dihydroxyacetone (DHA) is not observed for the base-free oxidation over Pt-based catalysts, and five kinds of dominant C_3 products are detected. The plausible reaction network is schematically shown in Figure 1, and the calculated $\Delta_r H_m^\theta$ and $\Delta_r G_m^\theta$ are also presented. It can be seen that the Route II is thermodynamically favorable in comparison with the Route I. This indicates that from the thermodynamic point of view, DHA is preferred to be produced.

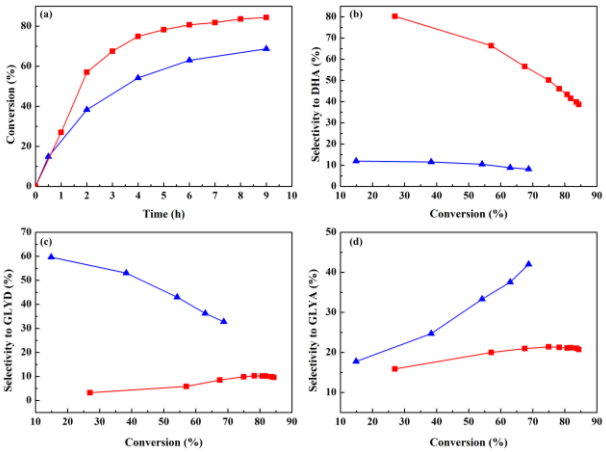

Figure 2. Comparison between catalytic performance for base-free oxidation of glycerol over Pt-based catalysts. Key: ▲ Pt/CNTs; ■ Pt-Sb/CNTs. (a) Glycerol conversion, (b) selectivity to DHA, (c) selectivity to GLYD, and (d) selectivity to GLYA.

To explore the reaction characteristics over the carbon supported Pt-based catalysts, Pt/CNTs and Pt-Sb/CNTs catalysts with similar Pt particle sizes were tested for the reaction, and the results are shown in Figure 2. Clearly, the Pt/CNTs catalyst favors the oxidation of the primary hydroxyl groups of glycerol to GLYD and glyceric acid (GLYA), while the introduction of a second metal Sb is found to facilitate the oxidation of the secondary hydroxyl group of glycerol to DHA. That is to say, the Pt-Sb/CNTs catalyst in comparison with the Pt/CNTs catalyst displays superior activity and selectivity to DHA.

Different sized Pt/CNTs and Pt-Sb/CNTs catalysts were also prepared and tested for base-free oxidation of glycerol. The results show that glycerol oxidation is a typical structure-sensitive reaction over both catalysts. By tuning the catalyst particle size toward more Pt active sites, a highly efficient Pt-based catalyst can be developed.

4. Conclusions

The reaction characteristics for base-free oxidation of glycerol over Pt-based catalysts have been investigated. The oxidation of the secondary hydroxyl group of glycerol to DHA is found to be thermodynamically preferred. In comparison with the Pt/CNTs catalyst, the Pt-Sb/CNTs catalyst displays enhanced activity and selectivity to DHA. Over both catalysts, glycerol oxidation is a typical structure-sensitive reaction. The insights revealed here could shed new light on the rational design and optimization of Pt-C nanocatalysts for selective oxidation of glycerol under base-free conditions.

References

[1] C. H. Zhou, N. J. Beltramini, Y. X. Fan, G. Q. Lu, Chem. Soc. Rev. 37 (2008) 527-549.
[2] B. Katryniok, H. Kimura, E. Skrzyńska, J. S. Giradon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul, F. Dumeignil, Green Chem. 13 (2011) 1960-1979.
[3] J. Q. Lei, X. Z. Duan, G. Qian, X. G. Zhou, D. Chen, Ind. Eng. Chem. Res. 53 (2014) 16309-16315.

Keywords
Base-free oxidation of glycerol; Reaction characteristics; Pt-based catalysts