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Reaction Mechanism of Glycerol Oxidation to 1,3-Dihydroxyacetone and Glyceraldehyde on Pt Catalyst: A Density Functional Theory Study.

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Highlights
- The adsorption properties of glycerol are investigated.
- The reaction mechanism for selective oxidation of glycerol is elucidated.
- The selectivity towards DHA and GLAD is explained.
- The role of O2 and H2O is clarified.

1. Introduction

Catalytic oxidation of glycerol (GLY), a highly functionalized molecule which could be used to synthesize many essential building block products such as detergents, plastics and anti-freeze agents, has attracted extensive attention in the past decades. Chemo-selective oxidation with air or oxygen is a promising route for the production of various high-value fine chemicals such as glyceric acid (GLYA), glyceraldehyde (GLYAD), dihydroxyacetone (DHA), and hydr-oxypyruvic acid (HA). While major research efforts have been focused on carboxylic acid derivative formation during glycerol oxidation, selective synthesis of GLYAD and DHA still remains a grand challenge. Achieving high selectivity towards DHA and GLAD is very difficulty since most existing catalysts are found to be very active for deep oxidation to carboxylic acids. The plausible mechanism and factors determining catalyst activity and product selectivity including acidity/basicity of solid support, pH and product inhibition effect are not yet fully understood in current studies. It is of great importance to have a deep understanding of the catalytic oxidation mechanism of GLY to DHA and GLYAD.

2. Methods

All calculations were performed using DMol3 module of Materials Studio 8.0 (MS)[1]. The module is able to deal with the molecular in the gas phase, the solution and the solid surface by using the density functional theory. The meta generalized gradient approximation (meta-GGA) in the M06-L parameterization was used in all calculations[2]. With the consideration of electronic polarization effect, the double numerical plus polarization (DNP) basis set was used in the calculation. The transition state was completely determined by LST/QST. The allowable deviations of the total energy, gradient and displacement are $1.0 \times 10-5Ha$ 、 $0.002Ha/Å$ and $0.005Å$, respectively. A periodic four-layer slab with sixteen atoms per layer was modeled representing a 4×4 unit cell and a vacuum of 18 Å in thickness was used to separate the surface from its periodic image in the direction along the surface normal. The reciprocal space was sampled with a 3× 3×1 k-point grid generated automatically using the Monkhorst-Pack (MP) method[3].

3. Results and discussion

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GLYAD is formed through the dehydrogenation of GLY. Actually, both the pure Pt(111) and the Pt(111) with adsorbed oxygen atom can play the role of dehydrogenation. The activation energy barriers in the two cases are 11.56 kJ/mol and 18.92 kJ/mol, respectively. However, we find that the Pt(111) with adsorbed hydroxyl can't facilite the breaking of C-H bond. This is consistent with the experimental result that DHA products can't be generated under alkaline conditions.
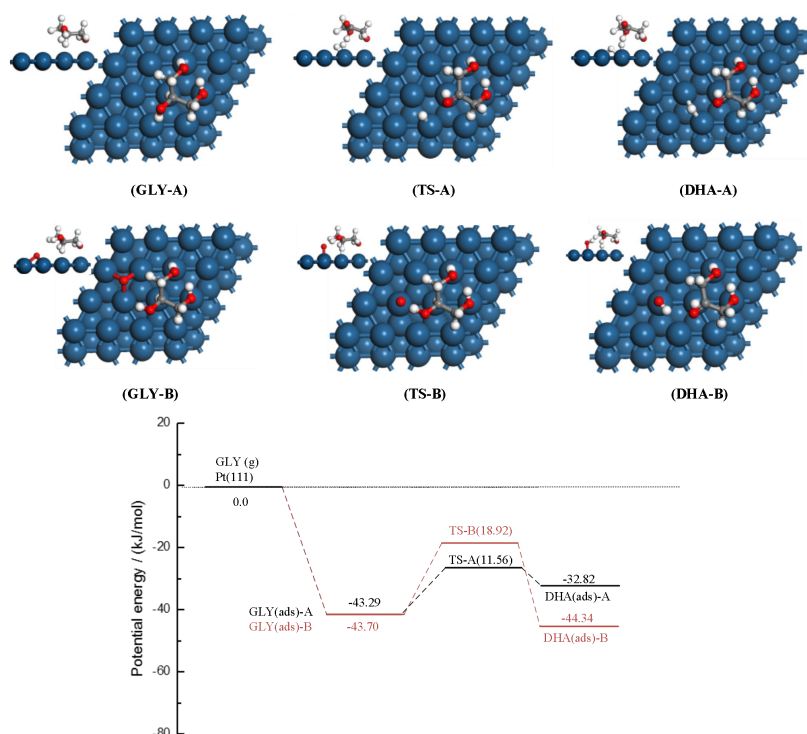

(GLY-A)   **(TS-A)**   **(DHA-A)**

(GLY-B)   **(TS-B)**   **(DHA-B)**

Figure 1. Energetic profile for the dehydrogenation of GLY to DHA.

(A represents the pure Pt(111). B represents the Pt(111) with adsorbed oxygen atom.)

4. Conclusions

We use density functional theory to study the plausible mechanism for selective GLYAD and DHA synthesis from glycerol over Pt based metal catalysts. The adsorption energies of different reactants and products, metal-support interaction, atomic arrangement of Pt nanoclusters and the activation barriers of rate-determining steps for DHA and GLYAD formation are compared. In addition, the role of O_2 and H_2O in the oxidation process is elucidated to reveal the plausible reaction mechanism in aqueous phase. Details of computational model discrimination and parameter estimation will be discussed in the presentation.

References

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