



Propylene glycol oxidation over silver catalysts: A theoretical study



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ABSTRACT

A theoretical interpretation of the mechanism of gas phase propylene glycol oxidation to methylglyoxal over silver catalysts is considered. A model system represented four-atom silver cluster interacting with process adsorbates and/or intermediates has been proposed. Main process routes comprising partial oxidation of the said diol to aldehydes (methylglyoxal, lactaldehyde, acetaldehyde, etc.) as well as diol total oxidation are considered, and the corresponding reaction profiles are represented. The main structural and energetic parameters for the key reaction adsorbates and intermediates and thermochemical data for their main transformations are predicted. The results obtained can be used in further modeling of both vapor- and liquid phase oxidation of propylene glycol over silver catalysts.

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1. Introduction

Various organic compounds are known to be valuable products of propylene glycol (PG) oxidation, including methylglyoxal, lactaldehyde, acetaldehyde, lactic and pyruvic acids, etc. [1–4]. Catalysts based on Pt [5,6], Au [7], Pd [8], their alloys [9–11], iron phosphates doped with molybdenum [12,13], were shown to be used in the process. Recently, an interest arose to Ag-based catalysts for liquid and gas phase PG oxidation [1,2,14].

In situ EELS and TPD studies of mechanism of PG oxidation over Ag single crystal were carried out in Refs. [1,2] under reduced pressures and low temperatures. The main process intermediates and final products were revealed. It is widely known that the use of nanosized particles as a catalyst significantly effects on surface reactivity and routes of transformations of organic compounds [15–17]. Thus, Ag particle sizes were shown to determine the catalyst selectivity and product distribution (C₂ and/or C₃-containing products) in the course of propylene glycol oxidation in liquid phase conditions [11,14]. However, the authors do not discuss the reasons for selectivity changes during formation of main products, when silver nanoparticles are used. Moreover, there were no attempts to analyze the interactions with oxidants. Researchers point out that the use of nanoparticles provides the opportunities for low-temperature activation of oxygen, which allows oxidizing propylene glycol under conditions of liquid phase process to form

more oxygen-containing products, i.e. lactic, pyruvic and other acids. As a rule, the authors insist on direct selective PG oxidation, namely, implementation of atomic oxygen into alcohol molecule. For instance, in Refs. [11,13] no attention is paid to the mechanism of oxygen activation over the catalyst surface. Only two main directions of PG oxidation are discussed: (1) via terminal group into lactic acid, and (2) via secondary O–H group through acetol followed by Cannizzaro reaction to lactic acid and C–C bond cleavage to form acetic and formic acids. Thus, the issue of oxygen activation is also of significant importance.

Thus, one can consider Ag-based catalysts as promising materials for industrial manufacturing. Patents [18,19] demonstrate that PG oxidation can be carried out in external diffusion mode over bulk silver catalyst modified with various compounds of vanadium, phosphorus, tin, lead, etc. The process can be carried out at elevated temperatures (530–600 °C). Nevertheless, high-temperature PG oxidation was not yet thoroughly investigated experimentally and theoretically.

In our previous work [20] we have demonstrated that small cluster models can effectively predict the mechanisms of complex heterogeneous catalytic processes of diol oxidation over Ag catalysts for the case of ethylene glycol (EG) oxidation to glyoxal. Within the framework of the present research we'd like to show that the proposed approach can be applied to PG oxidation. The proposition is based on experimental evidences clearly demonstrating similarity between the processes of PG and EG oxidation, including common reaction intermediates (O [21–28], H and OH [29], formate and carbonate species [30–32]) and components.

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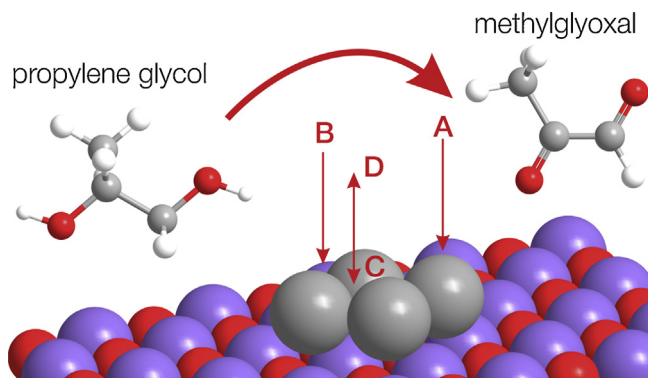


Fig. 1. Schematic representation of the Ag_4 cluster model used in calculations. The role and nature of support was not taken into consideration.

To the best of our knowledge, there were no attempts to look at the process under consideration from theoretical point of view, while DFT-based approaches were shown to successfully describe both interactions and peculiarities [33–36] as well as main products and key intermediates of catalytic processes [37–39]. In Ref. [40] a comprehensive investigation of 1,2-PG properties was carried out. Formaldehyde [41,42], molecular oxygen [43,44,21,22], carbon dioxide [52], hydrogen [58,59] were studied using different theoretical approaches. However, geometry and parameters of the main reaction products and most important reaction intermediates were not determined using common approaches. Thus, the aim of the present paper is to undertake systematic theoretical study of PG oxidation and predict geometrical parameters of the main products and intermediates of the process as well as forecast the interaction energies within the system.

2. Computational details

In the present paper the methodology described in Ref. [20] was used. Systems containing neutral Ag_4 cluster and/or adsorbates/intermediates were calculated at B3LYP/DGDZVP level of theory. The calculations were carried out using the Gaussian'09 program package installed at SKIF "Cyberia" supercomputer of Tomsk State University [45,46]. Initial silver state was represented by four-atom cluster with planar geometry. The distance between two adjacent silver atoms in the initial structure was 4.086 Å as in the bulk silver [47]. Calculations of the tetrahedron-like initial state of silver cluster were carried out for comparison with planar Ag_4 cluster, and the tetrahedron-like state was found to be less stable. Gas-phase molecule and/or process intermediates were placed no less than 1.4 Å above the cluster surface in atop (A), bridge (B), "hollow, above" (C), and "hollow, in-plane" (D) adsorption sites (Fig. 1). The energy of gas-phase molecule/intermediate interaction with the cluster was determined as a difference between total energy of the adsorbate(intermediate)/cluster system and a sum of isolated adsorbate(intermediate) and silver cluster energies. In cases of oxygen-containing systems, the interaction energies were determined as a difference between total energy of the adsorbate(intermediate)/O-precovered clusters and a sum of energies of isolated adsorbate(intermediate) and oxygen-containing silver clusters. Positive and negative energy values correspond to exothermic and endothermic processes, respectively.

Geometry of all the obtained structures was fully optimized. Predicted change in energy of less than $-1.0\text{D}-08$ was taken as convergence criterion. In all cases the nature of stationary point was checked by vibrational frequency calculations. The majority of the optimized structures was in global energy minima and had real frequencies only. Vibrational frequency scaling factor of 0.965

was used for DGDZVP basis set. The absence of imaginary vibrational frequencies confirmed the stationary character of structures. When the structure had imaginary frequencies, IRC calculations were carried out to determine the transition state. The thermodynamic parameters of the molecules calculated were corrected for zero-point vibrational energy (ZPVE) and reduced to normal conditions (298.15 K, 1 atm) using thermal corrections to enthalpy and free energy. The parameters were also calculated for real process conditions (830 K, 1 atm) corresponding to the maximal selectivity towards methylglyoxal observed under real process conditions.

In three-carbon molecules and intermediates we denote carbon-1, carbon-2 and carbon-3 as methyl, secondary and primary carbon atoms, respectively.

3. Results and discussion

3.1. Tentative mechanism of PG partial oxidation over Ag catalysts

Our preliminary lab tests of new PG oxidation catalysts (the catalysts were described in Ref. [20] and references therein) showed that PG oxidation proceeds via similar steps as in case of EG oxidation. Thus, kinetic, transient and external diffusion temperature modes can be distinguished. Among the main products were methylglyoxal, acetol, lactaldehyde, formaldehyde, acetaldehyde, carbon mono- and dioxide, water and molecular hydrogen as well as trace amounts of carbon acids (i.e., lactic, acetic, etc.). Judging on product distribution one can see that both partial and total oxidation of diol take place over silver catalysts, and formation of various products is caused by high reactivity of initial substances and intermediates. It is noteworthy that oxoacids are not stable under high-temperature gas-phase oxidation conditions and readily convert to carbon oxides.

There were quite a few in situ studies of the process under consideration. It was suggested that O–H bond activation and C–H bond scission are general mechanisms for the partial oxidation of diols over $\text{Ag}(110)$. The issues of stability of adsorbed 1,2-propanedioxy, generated via O–H bond activation of 1,2-propanediol by oxygen adatoms on $\text{Ag}(110)$, was discussed in Ref. [1]. Stability was shown to depend on the relative concentration of adsorbed 1,2-propanedioxy and atomic oxygen. Under oxygen-rich conditions O–H bond activation was considered to be the predominant process followed by C–H bond activation and C–C bond scission resulting in formation of formaldehyde, water, formate and acetate by 275 K. Acetol was shown to evolve at 335 K, while gaseous CO_2 , H_2O , acetol, lactaldehyde and 1,2-propanediol evolve at 360 K. Methylglyoxal, acetol, and lactaldehyde are evolved at 415 K and accompanied by the evolution of additional gaseous CO_2 and H_2O due to formate decomposition in the presence of adsorbed O (OH). It was shown that molecular hydrogen is not evolved. Initial C–H bond activation was suggested to occur preferentially at the central carbon of 1,2-propanedioxy species, and then it occurs at carbon-1.

In Ref. [2] the adsorption and reaction of 1,2-propanediol (1,2-PG) on clean and oxygen-activated $\text{Ag}(110)$ has been studied using temperature-programmed reaction spectroscopy (TPRS), isotopic labeling experiments, and electron energy loss spectroscopy (EELS). It was shown that under oxygen lean conditions the diol adsorbs reversibly, desorbing with activation energy of ~ 64 kJ/mol at 265 K from a monolayer state and at 215 K from a multilayer state. 1,2-PG was shown to react with adsorbed oxygen over O-precovered surfaces to form 1,2-propanedioxy and water. C–H bond scission begins at 285 K and results in formation of a mixture of acetol, lactaldehyde, hydrogen, water and other products in the temperature range between 285 and 380 K. Pre-adsorbed $^{18}\text{O}_{(a)}$ atoms are incor-

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