



First-principles calculation of activity and selectivity of the partial oxidation of ethylene glycol on Fe(0 0 1), Co(0 0 0 1), and Ni(1 1 1)



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ABSTRACT

To recycle ethylene glycol (HOCH₂CH₂OH) fuel in alkaline fuel cells, active and selective catalysts for partially oxidizing HOCH₂CH₂OH to glycolic acid (HOCH₂COOH) and oxalic acid ((COOH)₂) are required at the anode; in other words, complete oxidation of HOCH₂CH₂OH to CO₂ prevents ethylene glycol recycling. We investigate catalyst activity and selectivity for oxidizing HOCH₂CH₂OH to HOCH₂COOH on Fe(0 0 1), Co(0 0 0 1), and Ni(1 1 1) via first-principles calculations. We calculate the oxidation reaction path from HOCH₂CH₂OH to HOCH₂COOH without C–C bond dissociation to avoid CO₂ generation. Partial oxidation of HOCH₂CH₂OH to HOCH₂COOH without C–C bond dissociation proceeds as follows: O–H bond dissociation of HOCH₂CH₂OH to generate HOCH₂CH₂O; C–H bond dissociation of HOCH₂CH₂O to generate HOCH₂CHO; C–H bond dissociation of HOCH₂CHO to generate HOCH₂CO; and OH addition to HOCH₂CO to generate HOCH₂COOH. The activation energies for O–H bond dissociation of HOCH₂CH₂OH and C–H bond dissociation of HOCH₂CH₂O and HOCH₂CHO on Fe(0 0 1) are 20.2, 22.8, and 35.2 kcal/mol, respectively, which are the lowest of the three surfaces. Thus, Fe(0 0 1) is most active. To determine the selectivity, we compare the bond dissociation activation energies. The activation energies for C–C bond dissociation of HOCH₂CH₂OH and HOCH₂CH₂O on Fe(0 0 1) (66.7 and 39.5 kcal/mol, respectively) are higher than those for O–H bond dissociation of HOCH₂CH₂OH (20.2 kcal/mol) and C–H bond dissociation of HOCH₂CH₂O (22.8 kcal/mol), implying that the O–H bond of HOCH₂CH₂OH and C–H bond of HOCH₂CH₂O dissociate before the C–C bond dissociation during oxidation on Fe(0 0 1). In contrast, the activation energies for C–H and C–C bond dissociation of HOCH₂CHO (35.2 and 32.8 kcal/mol, respectively) are similar. The C–H and C–C bonds therefore dissociate during HOCH₂CHO oxidation. On Co(0 0 0 1) and Ni(1 1 1), the activation energies for C–C bond dissociation of HOCH₂CH₂O and HOCH₂CHO are lower than those for their C–H bond dissociation. Therefore, Fe(0 0 1) is more active and selective than Co(0 0 0 1) and Ni(1 1 1) for the partial oxidation of HOCH₂CH₂OH to HOCH₂COOH.

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1. Introduction

An alkaline fuel cell (AFC) does not require a Pt electrode catalyst, which is essential in other fuel cells, such as polymer electrolyte fuel cells and phosphoric acid fuel cells [1,2]. The Pt electrode catalyst is an obstacle to the wide use of fuel cells because of the low abundance of Pt; thus, AFCs have attracted much attention. Although hydrogen gas is used in conventional

AFCs, using liquid alcohol as the fuel has advantages, including easier transportation and storage when using than hydrogen gas. In particular, ethylene glycol (HOCH₂CH₂OH) has a high energy density and boiling point, which are important for the safe operation of fuel cells. Therefore, AFCs with HOCH₂CH₂OH as fuel have been investigated extensively [2–6].

Takeguchi, Yamauchi, and colleagues proposed a unique AFC that permits the recycling of HOCH₂CH₂OH fuel [7–9]. HOCH₂CH₂OH must be partially oxidized to glycolic acid (HOCH₂COOH) or oxalic acid ((COOH)₂), and then these products can be reduced back to HOCH₂CH₂OH. In contrast, previous AFCs using HOCH₂CH₂OH completely oxidized HOCH₂CH₂OH to CO₂ to achieve a high

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electromotive force [1,2,4,5,10–15]. HOCH₂COOH is also generated as an intermediate product during the partial oxidation of HOCH₂CH₂OH to (COOH)₂ [6,12,16]. Recycling the HOCH₂CH₂OH fuel from the oxidized products such as HOCH₂COOH and (COOH)₂ prevents CO₂ emission from the AFCs and allows the realization of a clean energy system. In addition, the recycling is more cost effective than the fuel production from the difficult-to-reduce CO₂ as long as partial oxidation of HOCH₂CH₂OH is achievable. Recently, the electrochemical reduction of (COOH)₂ to HOCH₂COOH using an electrolyzer [9,17,18] and a photocatalytic reaction [19] has been realized. Thus, recycling the HOCH₂CH₂OH fuel is possible if HOCH₂CH₂OH can be partially oxidized without generating CO₂ and the electrochemical reduction of HOCH₂COOH to HOCH₂CH₂OH can be realized. Recycling HOCH₂CH₂OH requires a highly active and selective catalyst for the partial oxidation of HOCH₂CH₂OH to HOCH₂COOH or (COOH)₂ at the anode. To develop such a catalyst, the catalytic reaction mechanism for the partial oxidation of HOCH₂CH₂OH must be clarified. Transition metals such as Fe, Co, and Ni are desirable for the AFC anode catalyst because of their relatively high abundance in the earth. However, the partial oxidation of HOCH₂CH₂OH to HOCH₂COOH or (COOH)₂ over these catalysts without generating CO₂ remains poorly understood.

First-principles calculations can be used to elucidate the chemical reactions of gaseous fuels, such as hydrogen and alcohol, on metal surfaces [20–26] including the oxidation processes of methanol on Pt(1 1 1) [23] and ethanol on Ni(1 1 1), Pt(1 1 1), or Pd(1 1 1) [24–26]. To investigate the activity of the alcohol molecules, the activation energies for the dissociation of the O–H, C–H, C–O, and C–C bonds were evaluated. For HOCH₂CH₂OH oxidation, the activation energies for the O–H, C–H, and C–C bond dissociation of HOCH₂CH₂OH on a Pt surface were calculated and the reaction paths for oxidation were estimated [27–29]. Most studies have focused on the C–C bond dissociation in a multi-electron electrochemical reaction to obtain a high electromotive force in the AFC. However, for recycling HOCH₂CH₂OH, a selective catalyst that suppresses C–C bond dissociation is required, because C–C bond dissociation leads to complete oxidation and CO₂ generation. In addition, the catalyst should be a non-noble metal to avoid problems with low abundance and minimize cost. Therefore, to develop non-noble-metal catalysts for the partial oxidation of HOCH₂CH₂OH to HOCH₂COOH or (COOH)₂, we must clarify the catalytic reaction mechanisms for the partial and complete oxidation reactions of HOCH₂CH₂OH on Fe, Co, and Ni surfaces, which are typical non-noble-metal catalysts.

In this article, we investigate the processes involved in the oxidation of HOCH₂CH₂OH to HOCH₂COOH on Fe(0 0 1), Co(0 0 1), and Ni(1 1 1) via first-principles calculations. To elucidate the oxidation of HOCH₂CH₂OH without C–C bond dissociation, we calculated the activation energies for the dissociation of the O–H, C–H, and C–C bonds of a HOCH₂CH₂OH molecule and the intermediate products, which are fundamental processes in HOCH₂CH₂OH oxidation. Furthermore, we discuss the activity and selectivity of the partial oxidation of HOCH₂CH₂OH based on the calculated activation energies for the O–H, C–H, and C–C bond dissociation. Finally, we suggest a suitable metal for the partial oxidation of HOCH₂CH₂OH to HOCH₂COOH without C–C bond dissociation.

2. Methods

The activation energies for the oxidation of HOCH₂CH₂OH to HOCH₂COOH on the metal surfaces were calculated with the first-principles code DMol³ based on density functional theory [30,31]. This code solves the Kohn–Sham equations self-consistently. We used a double numerical basis set including d-polarization functions and effective core potential. The Per

dew–Burke–Ernzerhof generalized gradient approximation (PBE GGA) [32,33] was used for the exchange–correlation energy. The reason for our choice of the PBE GGA was as follows. GGA is superior to the local density approximation for describing the properties of Fe, Co, and Ni, such as structure and magnetic moment [34]. Here, PW91 [35], PBE [32,33], and RPBE [36] were well chosen as GGA functionals. Mueller et al. showed that the activation energy for H₂ dissociation on Ni(1 1 1) calculated with PBE was in good agreement with the experimental value; however, those calculated with PW91 and RPBE were very different from the experimental value [37]. In addition, by first-principles calculation with the PBE functionals, Jiang et al. calculated the bond dissociation processes of CO on Fe(0 0 1), and the activation energy for CO dissociation on Fe(0 0 1) was in good agreement with the results of temperature-programmed desorption [38]. Wang et al. calculated the activation energies for CO₂ reforming processes of CH₄ on Ni(1 1 1) and revealed that the dissociation of the C–H bond in CH₄ is the rate-determining step, which was in good agreement with isotopic experiments [39]. Moreover, many previous first-principles calculations have used the PBE to investigate chemical reactions on Fe(0 0 1), Co(0 0 1), and Ni(1 1 1). Therefore, following on from these previous studies, we also chose the PBE GGA as the exchange–correlation energy in the present study. Spin polarization was considered for all systems. The multipole expansion and a global cutoff of 4.1 Å were used. Co(0 0 1) and Ni(1 1 1) surfaces were used because these are the most stable surfaces for Co and Ni, respectively. Fe(0 0 1) and Fe(1 1 0) showed a similar surface energy [47], however it is believed that Fe(0 0 1) is more stable during the surface cleavage due to the surface relaxation and reconstruction [48]. Thus, chemical reactions on Fe(0 0 1) were well studied. In fact, many researchers have adopted these three surfaces to compare the adsorption and bond dissociation of molecules on Fe(0 0 1), Co(0 0 1), and Ni(1 1 1) surfaces by first-principles calculations. For example, Wang et al. investigated O–H, C–H, and C–C bond dissociation for C₂H₅OH on transition-metal surfaces such as Co(0 0 1) and Ni(1 1 1), and determined the order of the activities of the transition-metal surfaces [25]. Klinke et al. investigated H₂ dissociation on Co(0 0 1) and Ni(1 1 1) and revealed the adsorption states at various levels of coverage [40]. Gajdo et al. calculated the vibrational frequencies of CO molecules on metal surfaces such as Co(0 0 1) and Ni(1 1 1), which were in good agreement with experimental results, to determine the adsorption states of CO on transition-metal surfaces [41]. Wang et al. calculated the adsorption energies of CH₃O on metal surfaces such as Fe(0 0 1) and Ni(1 1 1) and revealed the order of the adsorption energies depending on the d-band center of those surfaces [42]. Cai et al. studied the spin polarization properties of C₄H₄S adsorbed on Fe(0 0 1), Co(0 0 1), and Ni(1 1 1), and determined that the highest spin polarization of C₄H₄S occurred on Fe(0 0 1) [43]. As shown in the above studies, many researchers have chosen Fe(0 0 1), Co(0 0 1), and Ni(1 1 1) for comparing the catalytic reaction activities of Fe, Co, and Ni surfaces. Therefore, we also employed Fe(0 0 1), Co(0 0 1), and Ni(1 1 1) in our comparison of the oxidation reaction activities and selectivities of Fe, Co, and Ni surfaces. Therefore, we also employed Fe(0 0 1), Co(0 0 1), and Ni(1 1 1) in our comparison of the oxidation reaction activities and selectivities of Fe, Co, and Ni surfaces. Here, 4 × 4, 3 × 6, and 3 × 6 surface unit cells consisting of 48, 54, and 54 atoms were used for Fe(0 0 1), Co(0 0 1), and Ni(1 1 1), respectively. For Fe(0 0 1), Co(0 0 1), and Ni(1 1 1), 2 × 2 × 1, 3 × 2 × 1, and 3 × 2 × 1 k-point meshes were used, respectively, under the three-dimensional periodic condition. All of the metal surfaces consisted of three layers, and a vacuum layer of 30.0 Å was inserted between the repeated slabs to avoid interactions between the adjacent slabs. All layers of the slab model were fixed, because the effect of the relaxed surface on the accuracy of

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