Unraveling the Reaction Mechanism of HCHO Catalytic Oxidation on Pristine Co$_3$O$_4$ (110) Surface: A Theoretical Study

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Abstract: Various reaction mechanisms for the catalytic degradation of formaldehyde (HCHO) remain to be debated. Density functional theory (DFT) was applied to investigate whether the catalytic oxidation of HCHO on pristine Co$_3$O$_4$ (110) surface follows the Mars-van Krevelen (MvK) mechanism or the Langmuir–Hinshelwood (L-H) mechanism. Firstly, HCHO and O$_2$ co-adsorb on the surface and two H atoms from HCHO are peculiarly prone to transfer to O$_2$, forming CO and HOOH. For the MvK mechanism, CO$_2$ is generated through CO grabbing a lattice oxygen. Meanwhile, the O–O bond of HOOH is broken into two OH groups. One OH fills the oxygen vacancy and its H atom moves to another OH group for H$_2$O formation. For the L-H mechanism, CO directly obtains one OH group to generate COOH. Subsequently, the H atom of COOH transfers to another OH group along with CO$_2$ and H$_2$O generation. Both two mechanisms exhibit a similar maximum activation barrier. The lattice oxygen in the MvK mechanism and the surface-absorbed OH group in the L-H mechanism are the key reactive oxygen species. The small difference in energetic span further suggests that the catalytic cycle through the two mechanisms is feasible. This theoretical study provides new insight into the catalytic reaction path of HCHO oxidation on pristine Co$_3$O$_4$ surface.

Keywords: pristine Co$_3$O$_4$ (110) surface; MvK mechanism; L-H mechanism; density functional theory

1. Introduction

Formaldehyde (HCHO) is one of the most concerning indoor pollutants leading to hazardous effects on human health [1,2], and significant efforts have been made to settle indoor HCHO emissions. Room-temperature catalytic oxidation represents an attractive technology for complete conversion of HCHO to H$_2$O and CO$_2$ without the formation of harmful by-products or secondary pollutants, thus making it the most promising HCHO removal technique compared with conventional adsorption and photo-catalytic oxidation [3–7]. Supported noble metals (e.g., Pt [8], Pd [9], Au [10], and Ag [11]) are the most effective catalysts for HCHO catalytic oxidation at room temperature. Nevertheless, the high price and scarcity of noble metals may restrain their wide application in the long term. Transition metal oxides, such as MnOx [6], Co$_3$O$_4$ [12], CeO$_2$ [13], TiO$_2$ [14], and their composites [15–17], exhibit comparable catalytic performance and are cost-effective for low temperature HCHO oxidation. Among these catalysts, Co$_3$O$_4$-based catalysts have recently been attractive for low-temperature catalytic applications due to their strong oxidative...
capacity, high oxygen redox capability, and facile generation of reactive oxygen species (ROS) [18].

The catalytic path of HCHO oxidation can follow three mechanisms, including the Langmuir–Hinshelwood (L-H) mechanism, Eley–Rideal (E-R) mechanism, and Mars-van Krevelen (MvK) mechanism. Numerous experimental studies proved that the reaction path of HCHO oxidation on Co$_3$O$_4$-based catalysts mainly follows the L-H mechanism [19–22]. These studies utilized oxygen vacancy (O$_V$) engineering or load noble metals to enhance the catalytic activity of Co$_3$O$_4$-based catalysts at room temperature. Surface-adsorbed ROS obtained by dissociating O$_2$ from oxygen vacancies or noble metal sites are generally considered to be the most important ROS. For the L-H mechanism, the reaction starts from HCHO and O$_2$ co-adsorption on surface to form carbonaceous intermediates and ROS, and then the adsorbed carbonaceous intermediates are oxidized by ROS into CO$_2$ and H$_2$O. Different from the L-H mechanism, the details of the E-R mechanism are that pre-adsorbed O$_2$ first forms ROS, which then makes contact with HCHO and further oxidizes it into CO$_2$ and H$_2$O. However, the MvK mechanism that the catalytic oxidation of HCHO may follow is usually less frequently mentioned [11]. For the MvK mechanism, lattice oxygen (O$_{latt}$) oxidizes HCHO into CO$_2$, accompanied by the formation of an oxygen vacancy. Then, adsorbed O$_2$ dissociates on the oxygen vacancy into two active O atoms, one fills the O vacancy and the other combines with H atoms derived from HCHO for H$_2$O generation. Thus, the biggest difference between the MvK mechanism and the L-H mechanism is whether surface adsorbed ROS or O$_{latt}$ participates in HCHO oxidation, yet the possibility that these two routes are jointly involved in the catalytic oxidation of HCHO cannot be ignored.

In order to investigate the catalytic oxidation mechanism of HCHO on the Co$_3$O$_4$ surface, the selection of crystal facets with high reactivity is crucial. It is generally believed that increasing the exposure of the (110) surface facilitates the catalytic oxidation of various gaseous pollutants on Co$_3$O$_4$ [23–25], since the Co$_3$O$_4$ (110) surface possesses a large amount of Co$^{3+}$ active sites, which can efficiently chemisorb reactants. Ma et al. indicated that mesoporous 2D-Co$_3$O$_4$ exhibited preferable HCHO oxidation activity compared to Co$_3$O$_4$ nanosheets, which can be explained by the dominance of the Co$^{3+}$-rich (110) surface in 2D-Co$_3$O$_4$ [19]. Similarly, Bai et al. compared nano-Co$_3$O$_4$, 2D-Co$_3$O$_4$, and 3D-Co$_3$O$_4$ catalysts and found that the high HCHO oxidation activity of 3D-Co$_3$O$_4$ was attributed to greater (110) surface exposure [12]. The theoretical study by Deng et al. suggested that the catalytic oxidation of HCHO followed the MvK mechanism on the perfect Co$_3$O$_4$ (110) surface, while on the Co$_3$O$_4$ (110) surface with oxygen vacancies it followed the L-H mechanism [26]. However, whether the HCHO oxidation on the pristine Co$_3$O$_4$ (110) surface follows the L-H mechanism remains to be further explored.

Herein, this work focuses on comparing the MvK mechanism and L-H mechanism of HCHO oxidation on the pristine Co$_3$O$_4$ (110) surface through density functional theory (DFT). The activation barriers, reaction energy, and maximum energetic span ($\delta E$) of elementary reactions for possible reaction paths have been examined. The results help to broaden the fundamental understanding of reaction mechanisms of HCHO oxidation over Co$_3$O$_4$-based catalysts.

2. Results and Discussion

2.1. Possible Adsorption Species

According to the experimental studies of the HCHO oxidation over Co$_3$O$_4$-based catalysts, a complete catalytic oxidation process is usually accompanied by the formation of intermediates such as CH$_2$O$_2$, HCOOH, and HCOO [17,19,27]. These intermediates are gradually oxidized by ROS (including O, OH) and finally generate CO$_2$ and H$_2$O [20,28,29]. Therefore, there indeed exists different kinds of possible species in the reaction of HCHO oxidation to CO$_2$ and H$_2$O. In order to explore the reaction mechanism in detail, the (110)-B termination was chosen to model the Co$_3$O$_4$ surface (the reasons for choosing (110)-B
termination are detailed in Section 3.1). The p(2 × √3) supercell slabs were utilized for the Co3O4 (110)-B surface, which are visualized in Figure 1.

**Figure 1.** (a) Bulk Co3O4, (b) top view and (c) side view of Co3O4 (110)-B surface. Co3+, Co2+, and O atoms are shown in light blue, dark blue, and red, respectively. In addition, in the top view of structures, the atoms at the top and sub layers are illustrated in ball-and-stick model, and the rest are in line model. These illustrations are utilized throughout this paper. The unit of bond lengths are Å.

The location of all possible intermediates on the Co3O4 (110) surface should be confirmed. The most stable adsorption configurations of HCHO and O2 have been given in Figure 2. In addition, Figure 3 presents the adsorption configurations of possible intermediates. The corresponding adsorption energies and key structural parameters are listed in Table 1.

**Figure 2.** The most stable adsorption configurations together with electron density difference of HCHO (a,b) and O2 (c,d) on the Co3O4 (110) surface. The unit of bond lengths are Å.

**Figure 3.** The most stable adsorption configurations of possible intermediate species involved in HCHO oxidation to CO2 and H2O on Co3O4 (110) surface.
Table 1. Adsorption energies and key structural parameters of the stable configurations for the possible adsorbed species involved in HCHO oxidation to CO$_2$ and H$_2$O on Co$_3$O$_4$ (110) surface.

| Species | $E_{ads}$ (eV) | Adsorption/Configuration | Distance (Å) | Bonding Details | Bond Length (Å) |
|---------|---------------|--------------------------|--------------|----------------|----------------|
| HCHO    | 1.28          | C-O$_{2c}$, O-Co$_{3+}$  | 1.467, 1.898 | C-O            | 1.372          |
| HCO     | 3.45          | C-O$_{2c}$, O-Co$_{3+}$  | 1.315, 2.222 | C-O            | 1.250          |
| CO      | 3.57          | C-two O$_{2c}$           | 1.281, 1.349 | C-O            | 1.283          |
| HCOOH   | 0.76          | C-O$_{2c}$, O-Co$_{3+}$  | 1.455, 1.969 | C-O            | 1.355          |
| COOH    | 3.71          | C-O$_{2c}$, O-Co$_{3+}$  | 1.303, 2.025 | C-O/C-O        | 1.260/1.355    |
| HCOO    | 2.23          | O-Co$_{2c}$, O-Co$_{2+}$ | 2.006, 2.104 | C-O/C-O        | 1.260/1.279    |
| CO$_2$  | 0.01          | away from the surface    | —            | C-O            | 1.181          |
| HOOH    | 1.13          | O-Co$_{3+}$              | 2.077        | O-O            | 1.483          |
| OOH     | 1.26          | O-Co$_{3+}$              | 1.909        | O-O            | 1.455          |
| O$_2$   | 0.85          | O-Co$_{3+}$              | 1.930, 1.937 | O-O            | 1.310          |
| H$_2$O  | 0.74          | O-Co$_{3+}$              | 2.140        | O-H            | 0.979          |
| OH      | 2.35          | O-Co$_{3+}$              | 1.849        | O-H            | 0.979          |
| O       | 2.87          | O-Co$_{3+}$              | 1.750        | —              | —              |
| H       | 3.74          | H-O$_{2c}$              | 1.002        | —              | —              |

HCHO, HCO, CO HCHO and HCO both adsorb on the surface by C atom bonding to the O$_{2c}$ site and O atom bonding to the Co$_{3+}$ site, and their adsorption energies are 1.28 and 3.45 eV, respectively. CO adsorbs on the surface via the C atom located on the middle of two O$_{2c}$ atoms and the O atom bonded to a Co$_{3+}$ site with the adsorption energy of 3.57 eV.

HCOOH, COOH, HCOO, CO$_2$ HCOOH and COOH adsorb on the surface via C atom connecting to the O$_{2c}$ site and the O atom connecting to Co$_{3+}$ site, and their adsorption energies are 0.76 and 3.71 eV, respectively. HCOO adsorbs on surface with two O atoms connecting to two Co$_{3+}$ sites with the adsorption energy of 2.23 eV. CO$_2$ weakly adsorbs on the surface by O atom bonding to the Co$_{3+}$ site with the adsorption energy of 0.01 eV.

HOOH, OOH, O$_2$ HOOH, OOH, and O$_2$ are all located on the surface via O atom bonding to Co$_{3+}$ site, and their adsorption energies are 1.13, 1.26, and 0.85 eV, respectively.

H$_2$O, OH, O, H H$_2$O, OH, and O adsorb on the surface via O atom connecting to Co$_{3+}$ site, and their adsorption energies are 0.74, 2.35, and 2.87 eV, respectively. H atom connects to O$_{2c}$ with an adsorption energy of 3.74 eV.

To better understand the desorption behavior of the obtained product CO$_2$ and H$_2$O molecules at ambient conditions, the desorption time ($\tau$) is implemented [30], which is expressed in Section 3.1. The calculated desorption time for CO$_2$ and H$_2$O molecules at ambient temperature are $1.14 \times 10^{-3}$ and 1.76 s, respectively, indicating that CO$_2$ and H$_2$O molecules are physical adsorbed. Therefore, they can desorb easily from the Co$_3$O$_4$ surface, which facilitates the complete catalytic reaction.

2.2. Reactions Starting from HCHO and O$_2$ Co-Adsorbing on Co$_3$O$_4$ (110) Surface

From the result of the adsorption calculation, the adsorption energies of HCHO and O$_2$ are 1.28 eV and 0.85 eV, respectively, suggesting that HCHO presents stronger adsorption capability than O$_2$ on Co$_3$O$_4$ (110) surface. While for the co-adsorption configuration (Figure 4), HCHO and O$_2$ locate on two different sites and maintain a distance of 2.35 Å. Therefore, HCHO and O$_2$ can co-adsorb on Co$_3$O$_4$ (110) surface without rejection. The O–O bond length of the adsorbed O$_2$ molecule is elongated to 1.29 Å, which is longer than that of free O$_2$ (1.23 Å) and similar to O$_2$ adsorption individually (1.31 Å). Based on the Mulliken analysis, the O atom as an intermediate has similar atomic charges to the individual adsorbed O$_2$ molecule, which further confirms the strong chemical adsorption.
Figure 4. The potential energy profile of the first step of HCHO oxidation together with the structures of TSs and FSs on Co$_3$O$_4$ (110) surface. The unit of bond lengths are Å.

We first considered the E-R mechanism on the Co$_3$O$_4$ (110) surface. The first element reaction is the contact of O$_2$ with HCHO to form CH$_2$O$_2$ and an O atom. If gaseous O$_2$ is contacted with HCHO pre-adsorbed on the surface, there will be no conversion into CH$_2$O$_2$ and O due to the lack of a transition state. Whereas, if HCHO in the gaseous phase is contacted with surface pre-adsorbed O$_2$, it will convert into CH$_2$O$_2$ and an O atom. However, the activation energy can reach as high as 5.51 eV. Therefore, the E-R mechanism was excluded from consideration. Subsequently, the L-H mechanism and MvK mechanism were investigated in detail. From the co-adsorption of HCHO and O$_2$ on the Co$_3$O$_4$ (110) surface to the CO$_2$ and H$_2$O production, HCHO would lose two H atoms and gain one O atom for the formation of CO$_2$. Meanwhile, O$_2$ would lose one O atom and gain two H atoms for the formation of H$_2$O. Based on these two mechanisms, the corresponding activation barriers and reaction energy of all possible elementary reactions involved in HCHO oxidation have been listed in Table 2.

2.2.1. The Possible First Step of HCHO Oxidation

According to Table 2, all reactions on Co$_3$O$_4$ (110) surface are represented by Rn-m ($n = 1$–$5$; $m = 1$–$10$). The reactions from R1-1 to R1-4 represent four possible initial steps when HCHO and O$_2$ co-adsorb on Co$_3$O$_4$ (110) surface. Figure 4 presents the potential energy profiles of possible pathways of the four possible initial steps together with transition states (TSs) and final states (FSs) on the Co$_3$O$_4$ (110) surface.

R1-1 goes through TS1-1 to form CH$_2$O$_2$ and O. Firstly, HCHO adsorbs at hollow site, and O$_2$ adsorbs on the top Co$^{3+}$ site with the O–O bond length of 1.31 Å. Then, one O atom tends to get close to the C atom of HCHO with the O–O distance extending to 3.50 Å. In the final state, the O–O distance is lengthened to 4.69 Å and becomes broken, forming CH$_2$O$_2$ with two O atoms connecting on two Co$^{3+}$ sites, and the remaining O atom is adsorbed on another Co$^{3+}$ site. The activation barrier and reaction energy of this elementary reaction are 4.73 eV and 1.47 eV, respectively. For R1-2, O$_2$ can dissociate into two O atoms through TS1-2, where the O–O distance is elongated to 2.07 Å. In the final state, the O–O distance is lengthened to 2.76 Å and broken, forming two O atoms co-adsorbed on the Co$^{3+}$ site. The activation barrier and reaction energy of this elementary reaction are 2.22 eV and 1.71 eV, respectively. R1-3 and R1-4 are reactions of HCHO dissociation into HCO and H atom,
and the difference is whether the H atom adsorbs on the Co$_3$O$_4$ (110) surface or combines with O$_2$ to generate OOH. In TS1-3, one H atom of HCHO tends to combine with O$_2$ to form OOH with the C-H bond elongating to 1.32 Å and O-H bond shortening to 1.61 Å. In the final state, HCO adsorbs on the hollow site and OOH adsorbs on the Co$^{3+}$ site. The activation barrier and reaction energy of this elementary reaction are 0.52 eV and $-1.64$ eV, respectively. In TS1-4, the C-H distance is elongated to 2.29 Å from 1.11 Å of the adsorbed HCHO. In the final state, HCO adsorbs on the hollow site with the H atom adsorbing on the Co$^{3+}$ site. The activation barrier and reaction energy are 1.05 eV and $-3.07$ eV, respectively.

Table 2. All possible elementary reactions with the corresponding activation barriers ($E_a$/eV) and reaction energies ($\Delta E$/eV) involved in HCHO oxidation on Co$_3$O$_4$ (110) surface.

| Reactions | Co$_3$O$_4$ (110) Surface | $E_a$/eV | $\Delta E$/eV |
|-----------|---------------------------|--------|-------------|
| R1-1      | HCHO + O$_2$ → CH$_2$O$_2$ + O | 4.73  | 1.47       |
| R1-2      | HCHO + O$_2$ → HCHO + O + O | 2.22  | 1.71       |
| R1-3      | HCHO + O$_2$ → HCO + OOH | 0.52  | $-1.64$   |
| R1-4      | HCHO + O$_2$ → HCO + H + O$_2$ | 1.05  | $-3.07$   |
| R2-1      | HCOO + O$_2$ + OOH → HCOO + O + OH + O$_{\text{latt}}$ | - | 0.16 |
| R2-2      | HCOO + O$_2$ + OOH → HCOO + H + OOH | 1.25 | $-0.60$ |
| R2-3      | HCOO + O$_2$ + OOH → HCOO + H + OOH | 2.24 | $-2.55$ |
| R2-4      | CO$_2$ + H + OH → CO$_2$ + H$_2$O | 1.09  | 0.48       |
| R3-1      | HCO + O$_{\text{latt}}$ + OOH → CO + O$_2$ + OOH | 4.26  | $-2.78$   |
| R3-2      | CO + O$_{\text{latt}}$ + H + OOH → CO$_2$ + O$_2$ + H + OOH | 2.02  | 1.59       |
| R3-3      | CO$_2$ + O$_2$ + OOH → CO$_2$ + O$_2$ + H + O$_{\text{latt}}$ | 1.16  | $-1.77$   |
| R3-4      | CO$_2$ + H + OH → CO$_2$ + H$_2$O | 1.40  | 0.48       |
| R3-5      | CO + O$_{\text{latt}}$ + H + OOH → CO + CO$_2$ + OOH | 5.36  | 1.84       |
| R3-6      | COOH + O$_2$ + OOH → COOH + CO$_2$ + OOH | 1.80  | $-2.39$   |
| R3-7      | COOH + O$_2$ + OOH → CO$_2$ + H + O$_{\text{latt}}$ | 1.24  | 0.84       |
| R3-8      | COOH + O$_2$ + OOH → CO + COOOH | 1.62  | $-1.70$   |
| R3-9      | CO + O$_{\text{latt}}$ + HOOH → CO$_2$ + O$_2$ + HOOH | 1.85  | 0.86       |
| R3-10     | CO$_2$ + O$_2$ + HOOH → CO$_2$ + O$_2$ + O$_{\text{latt}}$ + H + OH | 1.00  | $-2.12$   |
| R4-1      | HCO + O$_{\text{OH}}$ → HCO + O + OH | 0.68  | 0.21       |
| R4-2      | HCO + O$_{\text{OH}}$ → HCOO + OH | 4.05  | $-0.65$   |
| R4-3      | HCOO + O$_{\text{OH}}$ → CO$_2$ + H + OH | 2.24  | $-2.55$   |
| R4-4      | CO$_2$ + H + OH → CO$_2$ + H$_2$O | 1.09  | 0.48       |
| R4-5      | HCO + O$_{\text{OH}}$ → HCOOH + O | 1.11  | 0.04       |
| R4-6      | HCOOH + O$_{\text{OH}}$ → HCOOH + O | 2.05  | $-0.84$   |
| R4-7      | HCOOH + O$_{\text{OH}}$ → HCOOH + OH | 0.76  | 0.16       |
| R4-8      | HCOOH + O$_{\text{OH}}$ → HCOOH + OH | 2.24  | $-2.55$   |
| R5-1      | HCO + O$_{\text{OH}}$ → CO + H + OOH | 0.98  | 0.37       |
| R5-2      | CO + H + OOH → CO + H + O + OH | 4.26  | $-2.78$   |
| R5-3      | CO + H + O$_{\text{OH}}$ → CO + O$_2$ + OH + H | 6.20  | $-0.55$   |
| R5-4      | CO$_2$ + OH + H → CO$_2$ + H$_2$O | 1.09  | 0.48       |
| R5-5      | CO + H + O + OH → COOH + O + H | 2.30  | 0.12       |
| R5-6      | COOH + O + H → CO$_2$ + H + OH | 4.68  | $-0.67$   |
| R5-7      | HCOOH + O$_{\text{OH}}$ → CO + HOOH | 1.62  | $-1.70$   |
| R5-8      | CO + HOOH → COOH + OH | 0.52  | $-1.63$   |
| R5-9      | COOH + OH → CO$_2$ + H$_2$O | 1.24  | 0.84       |

The case where HCHO obtains the O$_{\text{latt}}$ for CH$_2$O$_2$ formation is also considered. However, the formed CH$_2$O$_2$ still adsorbs with the O atom filling the (O$_{\text{OH}}$), and the configuration is no different with HCHO adsorbing on the pristine surface similar to the final state of R1-1, thus this reaction is not considered. Through comparing the activation barrier and reaction energy, it is found that R1-3 of HCO and OOH formation is the most favorable reaction with the absolutely low activation barrier. Moreover, R1-3 is exothermic, indicating this step is not only thermodynamically but also kinetically favored. It is worth mentioning...
that although R1-4 is the most exothermic, its activation barrier is much higher than that of R1-3, which is kinetically hindered. Thus, the first step of HCHO reacting with O₂ is in favor of forming HCO and OOH on the Co₃O₄ (110) surface, and the subsequent pathway of HCHO oxidation is considered starting from HCO and OOH.

In order to investigate why O₂ comfortably accepts one H atom for OOH formation, the PDOS and charge density difference is displayed in Figure 5. The energy levels of Co minority α-spin d orbitals and O₂ π* orbitals are well matched, leading to partial occupation of the formed d-π*orbitals. While the strong spin polarization provides large exchange stabilization energy for the majority β-spin orbitals, resulting in Co β-spin d-orbitals with energy levels about 1.0 eV lower than the π* orbitals of O₂. Therefore, no conspicuous interaction of β orbitals is observed, indicating that only the α π* orbitals of O₂ are partially occupied, which forces O₂ to be of a radical nature, and active for hydrogenation. When O₂ is hydrogenated to OOH, one electron transfers from the H atom to the β π* orbitals of O₂, and both α and β DOS of Co 3d orbitals overlap with OOH’s π* orbitals, which further weakens the O–O bond. Therefore, the enhanced interaction and larger occupation of the π* orbitals in OOH leads to a lower O–O bond order, which is responsible for the lower dissociation barrier than that for O₂.

![Figure 5. Electronic structure analysis. (a) Projected electronic density of states (PDOS) and schematic illustrations of 3D orbitals of Co on Co₃O₄ (110) surface, 2p-orbitals of the O₂ gas molecule, and their interaction within Co₃O₄-O₂ configuration. (b) PDOS and schematic illustrations for Co₃O₄-OOH interaction configuration. As the O₂ and OOH adsorb on a Co top site, the PDOS displays this Co atom and O₂/OOH. (c,e) The charge density difference of O₂ and OOH adsorb on Co₃O₄ (110) surface, respectively. (d) O₂ molecular orbitals.

2.2.2. HCHO Catalytic Oxidation Mechanism on Co₃O₄ (110) Surface from HCO and OOH

MvK Mechanism

The corresponding elementary reactions are revealed in Table 2, where the reactions related to MvK mechanism are marked R2-ν and R3-ν. The adsorbed HCO can react with O₅ to generate HCOO and Oᵥ, followed by the OOH dissociation into OH and an O atom, and O atom filling Oᵥ to restore the surface (R2-1). Subsequently, CO₂ is formed by OH oxidation through C-H breaking away from HCOO (R2-2), and H atom migration to OH to produce H₂O (R2-3). Another alternative reaction path is described below: HCO first dehydrogenates into CO (R3-1), which can pick up O₅ to form CO₂ and
O\textsubscript{v} (R3-2). Then, OOH is dissociated into OH and an O atom, which fills O\textsubscript{v} to restore O\textsubscript{latt} (R3-3). Meanwhile, OH combines with H atom to form H\textsubscript{2}O (R3-4). In addition, O\textsubscript{latt} can also adsorb H atom from HCO dehydrogenation to form COOH (R3-5), which is further oxidized to CO\textsubscript{2} and H\textsubscript{2}O by OOH, accompanied by the recovery of O\textsubscript{v} to O\textsubscript{latt} (R3-5 and R3-7). It is worth mentioning that the H atom of HCO can also transfer to OOH for CO and HOOH formation (R3-8). Then, CO can be oxidized by O\textsubscript{latt} (R3-9), and the formed O\textsubscript{v} can be restored by an O atom produced from the HOOH decomposition, accompanied by the formation of H\textsubscript{2}O (R3-10). Therefore, four possible routes account for the MvK mechanism.

The potential energy profile and possible reaction paths of TSs and FSs on Co\textsubscript{3}O\textsubscript{4} (110) surface are shown in Figures 6 and 7. The difference in line color indicates different paths. As shown in Figure 6, after HCO and OOH co-adsorption, HCO is more favorable for connecting to O\textsubscript{latt} to form HCOO than dissociating into CO and H atom, because the dissociation barrier of 4.26 eV is much higher than that of HCOO formation with almost no activation barrier. Even so, the CO path is still considered, because concerning the catalytic cycles, one transition state does not determine the kinetics. The determining states are not necessarily the highest transition state and the lowest intermediate state. The condition that TOF-determining transition state (TDTS) and the TOF-determining intermediate (TDI) must maximize the energetic span, thus the determining states may be different from the extreme state of the energy profile. After HCOO formation via the oxidation of O\textsubscript{latt}, the following oxygen vacancy filling, dehydrogenation and OH combining with H atom for H\textsubscript{2}O generation go through TS2-1, TS2-2 and TS2-3, and their activation barriers are 1.25 eV, 2.24 eV and 1.09 eV, respectively. For the paths of CO capturing O\textsubscript{(110) surface are shown in Figures 6 and 7. The difference in line color indicates different

\[\text{HCO} + \text{OOH} \rightarrow \text{HCOO} + \text{O} + \text{OH} \]

\[\text{TS2-1} -0.22 \quad \text{TS2-2} 0.16 \quad \text{TDI} \]

\[\text{HCOO} + \text{O} + \text{OOH} \rightarrow \text{HCOO} + \text{O} + \text{OH} \]

\[\text{TS2-3} -3.51 \quad \text{CO}_2 + \text{OH} + \text{H} \]  

\[\text{CO}_2 + \text{H}_2\text{O} -4.14 \]

\[\text{HCO} + \text{O}_2^* \]

\[\text{HCHO} + \text{O}_2^* \]  

\[\text{HCO} + \text{OOH} \]

\[\text{HCOO} + \text{O}_2 + \text{OH} \]

\[\text{HCOO} + \text{OH} \]

\[\text{HCOO} + \text{O} + \text{OH} \]

\[\text{TS1-3} 0.52 \quad \text{TS2-1} -1.64 \quad \text{TS2-2} -1.48 \quad \text{TS2-3} -2.07 \quad \text{TDTS} \quad \text{TDI} \]

\[\text{CO}_2 + \text{OH} + \text{H} (1) -4.60 \]

\[\text{CO}_2 + \text{H}_2\text{O} -4.14 \]

\[\text{Reaction coordinate} \]

\[\text{Relative energy/eV} \]

\[\text{Figure 6.} \] The potential energy profile of HCHO oxidation based on MvK mechanism through HCO grabbing O\textsubscript{latt} together with the structures of TSs and FSs on Co\textsubscript{3}O\textsubscript{4} (110) surface.
As for the catalytic cycles, the TDTS for blue, red, green and purple line marked reaction paths are TS2-2, TS3-1, TS3-5, and TS3-9, respectively. Their corresponding TDI are $\text{HCOO}^{+} + \text{OH}$, $\text{HCOO}^{+} + \text{O}_V + \text{OOH}$, $\text{CO}^{+} + \text{H} + \text{OOH}$ and $\text{CO}^{+} + \text{HOOH}$, respectively. As the TDTS comes after the TDI, according to formula (5a), the $\delta E$ for these four reaction routes are 2.24 eV, 4.26 eV, 5.36 eV, and 1.85 eV, respectively, which means that the efficiency of the catalytic cycles of the purple line marked reaction path are satisfactory. In short, irrespective of whether considering single route or catalytic cycles, the specific reaction paths representing the MvK mechanism are described below: firstly, two H atoms of HCHO continuously transfer to O$_2$, forming CO and HOOH. Then, CO grabs O lattice to generate CO$_2$, and HOOH dissociates into two OH groups with one of them occupying O$_V$, and its H atom moves to another OH for H$_2$O formation.

**Figure 7.** The potential energy profile of HCHO oxidation based on MvK mechanism through CO grabbing O$_{\text{lat}}$ together with the structures of TSs and FSs on Co$_3$O$_4$ (110) surface.

Starting from the reaction of CO + H + OOH (R3-2, R3-5), CO binds to O$_{\text{lat}}$ for CO$_2$ formation through TS3-2 and binds to lattice OH for COOH formation through TS3-5 with the activation barrier of 2.02 eV and 5.36 eV, respectively. The two reaction steps are endothermic with reaction energies of 1.59 and 1.84 eV, respectively, suggesting the combination of CO with lattice OH for COOH formation is blocked kinetically and thermodynamically. The following O$_V$ filling by OOH dissociation through TS3-3 and TS3-6 exhibits the activation barrier of 1.16 eV and 1.80 eV, respectively, which are different from that of R2-1, indicating that OOH dissociation is affected by co-adsorbents. As for the reaction of OH combining with H atom (TS3-4) and the reaction of H atom of COOH transferring to OH for H$_2$O formation (TS3-7), their activation barriers are 1.40 eV and 1.24 eV, respectively. Starting from the reaction of CO+HOOH, CO reacts with O$_{\text{lat}}$ to produce CO$_2$, and HOOH dissociates into two OH groups. One OH occupies O$_V$, the other
OH reacts with H atom to produce H₂O. The activation barrier for these three elementary reactions (R3-9, R3-10, R2-3) are 1.85, 1.00, and 1.09 eV, respectively. Through comparing the four reaction paths, the purple line in Figure 7 is the most preferable as the maximum activation barrier of 1.85 eV is much lower than other three paths with the maximum barrier of 4.26 eV.

As for the catalytic cycles, the TDTS for blue, red, green and purple line marked reaction paths are TS2-2, TS3-1, TS3-5, and TS3-9, respectively. Their corresponding TDI are HCOO + OH, HCOO + Oᵥ + OOH, CO + H + OOH and CO + HOOH, respectively. As the TDTS comes after the TDI, according to formula (5a), the δE for these four reaction routes are 2.24 eV, 4.26 eV, 5.36 eV, and 1.85 eV, respectively, which means that the efficiency of the catalytic cycles of the purple line marked reaction path are satisfactory. In short, irrespective of whether considering single route or catalytic cycles, the specific reaction paths representing the MvK mechanism are described below: firstly, two H atoms of HCHO continuously transfer to O₂, forming CO and HOOH. Then, CO grabs Oᵥ to generate CO₂, and HOOH dissociates into two OH groups with one of them occupying Oᵥ, and its H atom moves to another OH for H₂O formation.

**L-H Mechanism**

The difference between the L-H mechanism and the MvK mechanism is that the ROS binding to carbon intermediates are derived from surface adsorbed oxygen species, rather than Oᵥ. The specific reactions related to the L-H mechanism are marked R4-n and R5-n in Table 2. Starting from HCO and OOH absorbed on Co₃O₄ (110) surface, the O-O bond of OOH dissociates into OH and O atom (R4-1), which can bind to HCO for HCOO (R4-2) or HCOOH formation (R4-5). HCOO can be oxidized by OH to produce CO₂ and H₂O (R4-3 and R4-4); whereas HCOO combines with O atom to form HCOO and OH (R4-6 and R4-7), which in turn react to produce CO₂ and H₂O (R4-8). In addition, HCO can be dehydrogenated to form CO (R5-1). The O-O bond of OOH decomposes into OH and O atom (R5-2), the former combines with CO to form CO₂ (R5-3) and the latter combines with H atom to form H₂O (R5-4). Moreover, OH can also combine with CO to form COOH, which is subsequently converted into CO₂ (R5-5 and R5-6). The H atom from HCO dehydrogenation can bind to OOH for HOOH formation (R5-7). It reacts with CO to form COOH and OH (R5-8), which are finally converted to CO₂ and H₂O (R5-9). Therefore, five possible routes account for the L-H mechanism.

The potential energy profile and possible reaction pathways of TSs and FSs on the Co₃O₄ (110) surface are shown in Figures 8 and 9. As shown in Figure 8, HCO follows the L-H mechanism to grab surface adsorbed oxygen species via two reaction paths. After HCO and OOH co-adsorption, O–O bond of OOH is broken to form an O atom and OH adsorbed on Co³⁺ site through TS4-1. The dissociation barrier is 0.68 eV and the reaction energy is 0.21 eV. In TS4-2, an O atom approaches HCO, and the C-O bond length is shortened from 3.36 Å to 1.98 Å; In TS4-5, OH rotates and moves to HCO, and the C-O distance is shortened from 3.13 Å to 2.11 Å. The activation barrier of the two transition states are 4.05 eV and 1.11 eV, respectively, and the reaction energies are −0.65 eV and 0.04 eV, respectively, indicating that the combination of HCO to OH is kinetically feasible. This is against that of the MvK mechanism, in which HCO preferentially combines with Oᵥ, suggesting that the lattice oxygen species and adsorbed oxygen species possess different electronic properties that affect their reaction capability. In addition, for transition states (TS4-6, TS4-7, and TS4-8) through which HCOOH is converted to CO₂ and H₂O, their energy barriers are lower than those through HCOO paths (TS4-3 and TS4-4), indicating that the route starting from HCO combining with OH is preferable.
of 1.24 and 0.84 eV, respectively. Comparing to R5-6 with dehydrogenation of COOH with the H atom adsorbed on the O atom, H atom prefers to be close to OH, which is similar to the fact that the H atom of HCO prefersentially reacts directly with the OOH rather than bond with the surface absorbed O atom.

In conclusion, among five reaction paths, the light blue line marked route in Figure 9 is the most favorable, because the maximum energy barrier is much lower than that of other four paths. In Figure 8 and 9, the TDTS and TDI marked in different colors represent different paths of TDTS and TDI. As the TDTS comes after the TDI for the five routes, according to formula (5a), the $\delta E$ for these five routes are 4.26 eV, 2.29 eV, 6.57 eV, 5.16 eV, and 1.65 eV, respectively, which means that the efficiency of catalytic cycles of the light blue line marked path is satisfactory. Therefore, the optimal reaction path of the HCHO oxidation process is as follows: two H atoms of HCHO are successively transferred directly to O$_2$ to form HOOH. Subsequently, the O–O bond of HOOH is broken to generate two OH. One OH binds to CO to form COOH, whose H atom further combines with another OH to finally generate CO$_2$ and H$_2$O.

As revealed in Figure 9, another three possible reaction paths start with the dehydrogenation of adsorbed HCO to form CO, which further follows the L-H mechanism to grab surface adsorbed oxygen species. The H atom generated by the dehydrogenation of HCO can be combined with lattice oxygen through TS5-1, whose activation barrier and reaction energy are 4.26 eV and 2.78 eV, respectively. The H atom can also be combined with OOH through TS5-7 to form HOOH, whose activation barrier and reaction energy are 1.62 eV and $-1.70$ eV, respectively. In this reaction, the C-H distance is elongated to 1.49 Å along with the H-O distance shortened to 1.28 Å. Therefore, it can be inferred that H atom preferentially bonds with OOH rather than other locations on the surface after cleaving away from HCO. Starting from the reaction of CO + H + OOH, the O–O bond of OOH ruptures again through TS5-2, whose activation barrier and reaction energy are 0.98 eV and 0.37 eV, respectively. CO can react with O atom to form CO$_2$ via TS5-3 or OH to form COOH via TS5-5. Their activation barriers are 6.20 eV and 2.30 eV, respectively, and their reaction energies are $-0.55$ eV and 0.12 eV, respectively. This suggests that the CO reaction with OH is more preferable than O atom, which is consistent with the HCO reaction with OH or O, further indicating that surface adsorbed OH is an important ROS. The following COOH dehydrogenation by O atom via TS5-6 may be prevented by the high activation barrier of 4.68 eV. Starting from the reaction of CO+HOOH, CO can directly capture OH from HOOH for COOH formation via TS5-8 with the activation barrier as low as 0.52 eV. Meanwhile, the O–O distance is elongated 2.28 Å and C-O distance is shortened to 2.24 Å. This reaction step is also kinetically favored with reaction energy of $-1.63$ eV. The H atom
of COOH can transfer to OH through TS5-9 with the activation barrier and reaction energy of 1.24 and 0.84 eV, respectively. Comparing to R5-6 with dehydrogenation of COOH with the H atom adsorbed on the O atom, H atom prefers to be close to OH, which is similar to the fact that the H atom of HCO preferentially reacts directly with the OOH rather than bond with the surface absorbed O atom. In conclusion, among five reaction paths, the light blue line marked route in Figure 9 is the most favorable, because the maximum energy barrier is much lower than that of other four paths.

In Figures 8 and 9, the TDTS and TDI marked in different colors represent different paths of TDTS and TDI. As the TDTS comes after the TDI for the five routes, according to formula (5a), the δE for these five routes are 4.26 eV, 2.29 eV, 6.57 eV, 5.16 eV, and 1.65 eV, respectively, which means that the efficiency of catalytic cycles of the light blue line marked path is satisfactory. Therefore, the optimal reaction path of the HCHO oxidation process is as follows: two H atoms of HCHO are successively transferred directly to O2 to form...
HOOH. Subsequently, the O–O bond of HOOH is broken to generate two OH. One OH binds to CO to form COOH, whose H atom further combines with another OH to finally generate CO₂ and H₂O.

2.2.3. Comparison of HCHO Catalytic Oxidation through MvK and L-H Mechanism

Starting from HCHO and O₂ co-adsorption, the most favorable reaction paths that belong to MvK and L-H mechanism are shown in Figure 10 and Scheme 1. Two H atoms of HCHO transfer to O₂ continuously for CO and HOOH formation are the first two favorable steps. For MvK mechanism, CO grabs O₁₉₈ to generate CO₂ firstly. The maximum activation barrier is 1.85 eV in this reaction path. The subsequent steps are the O–O bond of HOOH breaking and O vacancy filling by O atom of OH. Finally, H atom move to another OH for H₂O formation. For L-H mechanism, COOH is formed through CO drawing OH from HOOH, and then H atom of COOH is taken away by another OH for CO₂ and H₂O formation. The maximum activation barrier of this reaction path is 1.65 eV, corresponding to the second H atom of HCHO dehydrogenation, which is slightly lower than that of MvK mechanism. Therefore, the highest energy barriers to overcome for the MvK and L-H mechanisms are similar, making both mechanisms feasible. The δE of the two paths correspond exactly to the activation barrier, suggesting that the catalytic cycle through the two mechanisms are equivalent to some extent. It is worth noting that due to the relatively strong exotherm of the reaction, HCHO cannot be oxidized smoothly at room temperature if the energy released in the previous cycles cannot be fully utilized for subsequent cycles. In addition, the maximum δE cannot be affected by the reaction energy according to formula (5b), resulting in TDTS appearing after TDI in all possible paths through MvK and L-H mechanism.

Figure 10. Potential energy diagram for the most favorable pathways of HCHO catalytic oxidation through the MvK and L-H mechanism.
Scheme 1. Elementary reaction steps of HCHO catalytic oxidation based on MvK and L-H mechanism on Co$_3$O$_4$ (110) surface.

3. Computational Details

3.1. Surface Models

Co$_3$O$_4$ has a spinel structure (Fd3m) which contains half-filled octahedral sites with Co$^{3+}$ cations and tetrahedral sites with Co$^{2+}$ cations. For the Co$_3$O$_4$ (110) surface, it bears two different terminations, usually denoted as the A and B terminations: the (110)-A termination exposes two types of cations (Co$^{2+}$ and Co$^{3+}$) and one type of anion (three-fold coordinated O$_{3c}$), whereas the (110)-B termination has only one type of cation (Co$^{3+}$) and two types of anions (two-fold coordinated O$_{2c}$ and three-fold coordinated O$_{3c}$). Chen et al. [31] have reported the curves of Gibbs surface energy of these two terminations against oxygen chemical potential and found that the terminal B surface possessed a lower Gibbs surface energy in oxygen-rich conditions. Considering the oxygen chemical potential under the common work conditions of HCHO oxidation ($P_{O_2}/P_0 = 0.2; T = 300-330$ K), the (110)-B termination was energetically more stable than the (110)-A termination. Therefore, the (110)-B termination was chosen to model the catalyst surface. We simulated symmetric slabs with an odd number of five layers, for which the total dipole moment was zero. This slab was stoichiometric and symmetric along the surface normal plane. The p($2 \times \sqrt{3}$) supercell slabs were utilized for Co$_3$O$_4$ (110)-B surface, which can be seen in Figure 1. The bottom two Co-O layers are fixed. Whereas the topmost three Co-O layers and the adsorbates are fully relaxed in all calculations.

3.2. Computational Details

All the calculations were performed in the framework of the density functional theory (DFT) by using the Cambridge Sequential Total Energy Package (CASTEP) in Material Studio 8.0 of Accelrys. The generalized gradient approximation (GGA) was chosen to represent the exchange-correlation potential in the formulation of the Perdew–Burke–Ernzerhof (PBE) [32]. Owing to the magnetic properties of Co, all calculations were spin-polarized...
with an energy cutoff of 380 eV. The Brillouin zone was sampled by a $2 \times 2 \times 1$ k-points grid generated via the Monkhorst-Pack procedure [33]. The geometry optimization was converged when the energy differences between two electronic optimization steps were smaller than $10^{-5}$ eV, and the forces for ions were less than 0.05 eV/Å. For the transition state (TS) search calculations of all elementary reactions in HCHO oxidation process, the complete LST/QST was adopted for search protocol, and the convergence tolerance of RMS convergence resorted to 0.25 eV/Å. In order to further confirm that the transition from reactant to product went through a transition state structure, the obtained transition state from TS search will be further checked via TS confirmation. The output of a TS confirmation calculation is another trajectory document, which follows the Intrinsic Reaction Path (IRP) as discussed in reaction paths.

The adsorption energy of all reactants, intermediates, and product species can be calculated through the following formula:

$$E_{\text{ads}} = E_{\text{species/slab}} - E_{\text{species}} - E_{\text{slab}}$$  \hspace{1cm} (1)

where $E_{\text{species/slab}}$ represents the total energy of Co$\text{O}_4$(110) surface adsorbing certain species, $E_{\text{species}}$ represents the energy of sole species, $E_{\text{slab}}$ represents the slab energy of Co$\text{O}_4$(110) surface.

Based on the calculation results, all the adsorption energies are negative. Therefore, we take absolute values to compare the adsorption energies of different surface species.

The desorption time ($\tau$) was calculated through the following formula:

$$\tau = \frac{1}{Ae^{\frac{E_{\text{des}}}{k_B T}}}$$  \hspace{1cm} (2)

where $A$ is bond vibration frequency in the range of 1012 Hz, $k_B$ is the Boltzmann constant ($8.63 \times 10^{-5}$ eV/K) and $T$ is the room temperature of 298.15 K. $E_{\text{des}}$ is the desorption energy.

For a reaction such as $R$ (reactant) $\rightarrow$ $P$ (product) on catalyst surface, the activation barrier ($E_a$) and reaction energy ($\Delta E$) were calculated according to the following formulas:

$$E_a = E_{\text{TS}} - E_R$$  \hspace{1cm} (3)

$$\Delta E = E_P - E_R$$  \hspace{1cm} (4)

Where $E_R$ and $E_P$ are the total energies of the adsorbed reactant and product, respectively, and $E_{\text{TS}}$ represent the total energies of the transition state.

The energetic span ($\delta E$) model was also employed to elucidate the efficiency of the catalytic cycles. According to the literature, there were only two states to determine $\delta E$, namely determining transition state (DTS) and determining intermediate state (DIS), the smaller the energy span, the faster the reaction. $\delta E$ is shown as:

$$\delta E = \begin{cases} 
T_{\text{TDT$S$}} - I_{\text{TDL}}, & \text{if TDT$S$ appears after TDI (a)} \\
T_{\text{TDT$S$}} - I_{\text{TDL}} + \Delta E_r, & \text{if TDT$S$ appears before TDI (b)}
\end{cases}$$  \hspace{1cm} (5)

4. Conclusions

DFT calculations have been performed to investigate possible HCHO catalytic oxidation paths on pristine Co$\text{O}_4$(110) surface for comparisons of different reaction mechanisms. In addition, the maximum $\delta E$ is calculated to state the catalytic cycle. The following results were obtained. HCHO and O$_2$ prefer to co-adsorb on the Co$\text{O}_4$(110) surface. The transfer of the H atom of HCHO to O$_2$ for HCO and OOH formation represents the first preferable step rather than O$_2$ dissociation. The electron property of PDOS analysis further suggests that only the $\alpha \pi^*$ orbitals of O$_2$ are partially occupied, forcing O$_2$ to be of a radical nature, which is active for hydrogenation. HCO is further prone to transfer its H atom to OOH to generate CO and HOOH. Regarding the MvK mechanism, through CO grabbing O$_{\text{latt}}$, CO$_2$ is produced and the O vacancy is filled by one OH group originating from HOOH.
bond breakage. Meanwhile, the H atom approaches in close proximity to OH to form H$_2$O.

For the L-H mechanism, CO obtains one OH from HOOH, then COOH gives an H atom to another OH for the formation of CO$_2$ and H$_2$O. Comparing the maximum activation barrier and $\delta E$, both the MvK and L-H mechanism are found to be feasible. Lattice oxygen in the MvK mechanism and surface OH in the L-H mechanism are both key ROS for oxidation of CO intermediates, and the catalytic cycle is almost equivalent.

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