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Article

Theoretical studies of CO oxidation with lattice oxygen on Co_3O_4 surfaces

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ABSTRACT

Low-temperature CO oxidation has attracted extensive interest in heterogeneous catalysis because of the potential applications in fuel cells, air cleaning, and automotive emission reduction. In the present study, theoretical investigations have been performed using density functional theory to elucidate the crystal plane effect and structure sensitivity of Co_3O_4 nano-catalysts toward catalyzing CO oxidation. It is shown that the surface Co–O ion pairs are the active site for CO oxidation on the Co_3O_4 surface. Because of stronger CO adsorption and easier removal of lattice oxygen ions, the $\text{Co}_3\text{O}_4(011)$ surface is shown to be more reactive for CO oxidation than the $\text{Co}_3\text{O}_4(001)$ surface, which is consistent with previous experimental results. By comparing the reaction pathways at different sites on each surface, we have further elucidated the nature of the crystal plane effect on Co_3O_4 surfaces and attributed the reactivity to the surface reducibility. Our results suggest that CO oxidation catalyzed by Co_3O_4 nanocrystals has a strong crystal plane effect and structure sensitivity. Lowering the vacancy formation energy of the oxide surface is key for high CO oxidation reactivity.

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1. Introduction

Recent advances in nanotechnology have provided new opportunities for designing and screening well-defined catalysts [1–4]. Catalytic performance has been reported to strongly depend on particle size and shape. Because of their prominent redox properties, reducible metal-oxide nanocrystals have been extensively studied for catalyzing various important reactions such as CO oxidation and alkane oxidation [5–15]. Among these oxides, spinel cobalt oxide (Co_3O_4), an important semiconductor material, has been extensively studied [7–12] and found to be particularly effective in catalyzing many important

reactions such as CO oxidation, N_2O decomposition, and low-temperature methane conversion. The shape and plane structure of Co_3O_4 nano-catalysts have been found to play essential roles in controlling catalytic reactivity and selectivity. For example, Li and coworkers [7] effectively synthesized different shapes of Co_3O_4 nanocrystals and found that the nanocrystal (112) and (011) planes were much more reactive than the (001) plane in catalyzing methane decomposition. Later they demonstrated that the nanocrystal (011) planes are more active than (001) planes for CO oxidation [8]. The temperature-programmed reduction experiments further showed that the (011) planes had stronger reducing properties than the

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(001) planes. Similarly, Xie *et al.* [3] reported that oxidation of CO catalyzed Co_3O_4 nanocrystals at temperatures as low as -78°C . Density functional theory (DFT) calculations have also been carried out to understand the structure sensitivity of Co_3O_4 nanocrystals [16–21]. Generally, the high oxidation reactivity of Co_3O_4 planes is attributed to the presence of octahedrally coordinated Co species that can easily convert between Co^{3+} and Co^{2+} via a redox process. However, knowledge about the active sites for catalytic oxidation reactions on Co_3O_4 nanocrystals is still elusive because of their complex surface structure. Taking CO oxidation as an example, Broqvist *et al.* [16] reported that CO could adsorb at Co^{3+} sites on the $\text{Co}_3\text{O}_4(110)$ surface and then move toward the oxygen ion to form a CO_2 complex. Xu *et al.* [17] and Jiang *et al.* [18] proposed that low-coordinate O sites were responsible for CO oxidation on Co_3O_4 planes. However, Pang *et al.* [19] concluded that both Co^{3+} and O^{2-} sites controlled the catalytic activity of CO oxidation. These somewhat contradictory results indicate that it is necessary to obtain a clear understanding of the active sites and the nature of high reactivities of Co_3O_4 nanocrystals.

In this work, a DFT investigation has been performed to compare CO oxidation at various possible active sites on $\text{Co}_3\text{O}_4(001)$ and (011) surfaces. By comparing the energetics of the different reaction pathways for CO oxidation activation, we have demonstrated that the activity of CO oxidation exhibits distinct dependence on the exposed crystal plane and active sites. We propose that the nature of this structural sensitivity originates from the reducibility of the surface sites. This viewpoint provides a potential scheme to design and screen well-defined catalysts. Our results are consistent with previous experimental observations.

2. Computational details

All the calculations were performed using DFT methods as implemented in the Dmol3 package developed by Accelrys, Inc. [22–24]. The exchange-correlation potential is described by the generalized-gradient approximation (GGA) with the spin-polarized exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) [25]. The localized double-numerical basis sets with polarization functions (DNP) were used to describe the valence orbitals of the atoms, whereas relativistic effective core potentials (ECP) were employed for replacing the core electrons of Co [23,26]. A Fermi smearing of 0.2 eV and a real-space cutoff of 4.5 Å were used. All the slabs were periodically repeated with a vacuum spacing of 15 Å between the images in the direction perpendicular to the surface. Two-dimensional Brillouin integration was performed with an $8 \times 8 \times 8$ k-point mesh for the bulk crystal and a $4 \times 4 \times 1$ k-point mesh for the slabs. Larger k-point meshes were also tested and the total energy showed nearly converged behavior. In the geometry relaxation calculations, the spin-polarization Kohn-Sham formalism was used for the self-consistent field (SCF) iterations and molecular symmetry was not enforced. The convergence criteria were set as 1×10^{-4} eV, 1×10^{-3} eV/Å, and 5×10^{-3} Å for energy, energy gradient, and geometry, respectively. In all calculations, stoichiometric supercell models were used. The

method is found to correctly reproduce the structural parameters, magnetic moment, and band gap of the bulk Co_3O_4 , indicating that the selected exchange-correlation functional is appropriate. See our recent study for details [6]. The transition states were obtained using the Complete LST/QST method [27] with a force criterion of 0.05 eV/Å. Vibrational analysis was further performed to ensure that each transition state had only one imaginary frequency. The zero point energy (ZPE) was included in all energetics. Surface slab models cleaved from the bulk crystal were used to model the $\text{Co}_3\text{O}_4(001)$ and (011) planes, as shown in Fig. 1. Each slab consists of four atomic layers, where the two bottom layers were held fixed during optimization while the top two layers were allowed to relax. We note that there are two types of surface structure for each plane based on different cleavage depths. The one with the lower surface energy was chosen for the (001) and (011) planes. Discussions on the stability of the different slab models can be found in previous theoretical studies [6,16,28,29].

3. Results and discussion

3.1. CO adsorption on the $\text{Co}_3\text{O}_4(001)$ and (011) surfaces

We first consider CO adsorption on the Co_3O_4 surfaces. The optimized adsorption configurations and the corresponding distances are shown in Fig. 2. Three possible sites denoted as Co, Co– O° , and Co– O^t on each surface are considered for CO oxidation. Only CO molecules with C-coordination are considered to interact with each surface, which is propitious to approach the surface and subtract the lattice oxygen to form CO_2 . At Co sites, the CO is found to adsorb perpendicularly to the Co–O bond. The distances between the C and the Co atom range from 1.826 to 1.920 Å. At the Co–O pair site, CO adsorption leads to the formation of a nonlinear O–C–O species at each surface, where the C atom binds to both the lattice Co ion and the oxygen ion. The C–Co and C–O distances are 1.88–1.96 and 1.27–1.35 Å, respectively. In all cases, both C–O bond and Co–O bonds are lengthened, relative to the clean surface and the gas molecule. This can be attributed to the highest occupied molecular orbital (HOMO) 5σ of the CO transferring additional charge to the surface Co ion, thus weakening both C–O and Co–O bonds

Fig. 1. Surface models for $\text{Co}_3\text{O}_4(001)$ and (011) . The ions of the top layers are shown in a ball and stick model. Blue, Co atom; red, O atom. On each slab, there are two types of oxygen ions (O^t and O°), which differ in the way they are bonded in the lattice structure. O^t is bonded to one Co^{2+} ion and 1–3 Co^{3+} ions, while all atoms near O° are Co^{3+} ions. Both the O^t and O° ions on the (001) surface are threefold coordinated, while on the (011) surface the O^t ions are twofold coordinated and the O° ions are threefold coordinated.

Fig. 2. Possible adsorbed configurations of CO molecule on Co_3O_4 surfaces.

[16,17]. Mulliken population analysis confirms that the surface Co ions become less positively charged by $\sim 0.3e$ on both surfaces.

The CO adsorption energy is further considered to elucidate the interaction between CO and the substrate. It is calculated according to the formula $E_{\text{ads}} = E_{\text{CO@slab}} - E_{\text{slab}} - E_{\text{CO}}$, where E_{slab} is the energy of the surface slab, $E_{\text{CO@slab}}$ is the energy of the surface slab with CO adsorbed, and E_{CO} is the energy of the isolated CO molecule. The calculated adsorption energies for each configuration are summarized in Table 1. On the (001) surface, CO can strongly adsorb at Co sites with a high adsorption energy of -1.10 eV, but only weakly adsorbs at Co–O pair sites with lower adsorption energies at Co–O pair sites. On the (011) surface, the adsorption energies at Co, Co–O $^\circ$, and Co–O t sites are -1.14 , -1.15 , and -0.72 eV, respectively, which indicates competitive adsorption at different sites.

3.2. CO oxidation with the lattice oxygen

CO oxidation on a Co_3O_4 substrate or other transition metal oxides is generally reported to follow the Mars–van Krevelen (MvK) mechanism, where CO molecules react with the lattice oxygen ions and gaseous O_2 molecules replenish the oxygen defects [3,30–33]. Both experimental and theoretical studies have suggested that lattice oxygen abstraction by CO is crucial for CO oxidation [3,18–21,30,31]. Especially, Jiang *et al.* [20] also proposed that the CO reaction with lattice oxygen ions was the rate limiting step, and that the O_2 molecule could easily dissociate without a barrier between two neighboring oxygen vacancies. Therefore, in the present study we focus on the oxidation of CO with the lattice oxygen ion and aim to elucidate the structure sensitivity and crystal plane effect.

Table 1
The adsorption energies (E_{ads}) at Co, Co–O $^\circ$, and Co–O t sites.

Surface	E_{ads}/eV		
	Co	Co–O $^\circ$	Co–O t
(001)	-1.10	-0.01	-0.29
(011)	-1.14	-0.72	-1.15

Table 2

Barriers for adsorbed CO configuration change from Co to Co–O sites.

Surface	E_{a}/eV	
	Co $\rightarrow$ Co–O $^\circ$	Co $\rightarrow$ Co–O t
(001)	1.17	0.84
(011)	1.08	1.00

On the basis of the adsorption energies, CO is highly energetically favorable to adsorb at the Co site. To achieve oxidation of CO with the lattice oxygen ion, a configuration change of CO moving from the Co site to the Co–O site is necessary. The diffusion barriers are calculated and are listed in Table 2. It is found that all the barriers for the configuration change are relatively high (more than 0.8 eV), indicating that the process has a room temperature reactivity based on the estimation of transition state theory. These results also imply that at very low temperatures such as -78 °C [3], adsorbed CO species at Co sites do not substantially contribute to the formation of CO_2 and thus have no direct relation to the reported crystal plane effect. In contrast, adsorption at the Co site could hinder further adsorption of CO at the Co–O site because the Co site is already occupied.

We further consider the formation of CO_2 directly from adsorbed CO at Co–O sites. The reaction pathways and transition states are shown in Fig. 3. The processes can be outlined in three steps: (1) the gas CO molecule adsorbs at a Co–O pair site; (2) the adsorbed CO species interacts with the lattice oxygen ion, forming an adsorbed CO_2 species; (3) a CO_2 molecule desorbs into the gas phase. On the (001) surface, the adsorbed CO species only need to overcome small barriers to form CO_2 , with 0.24 eV at the Co–O $^\circ$ ion-pair site and 0.70 eV at Co–O t pair site. This is in contrast with the scant reactivity of the (001) surface reported by the experimental results. Further, the adsorption energies on the (001) surfaces are very small (<0.3 eV) at Co–O sites, which implies that at realistic conditions, CO desorption will strongly affect CO coverage on the surface and thus significantly decrease the rate of CO_2 formation.

This scenario changes when we consider the (011) surface. The CO molecule can easily bind to a Co–O $^\circ$ or Co–O t pair site with a high adsorption energy. At the Co–O t site, adsorbed CO can easily abstract a lattice oxygen to form CO_2 after overcoming a small barrier of 0.26 eV. CO oxidation is expected to be difficult at the Co–O $^\circ$ pair site as the barrier for CO_2 formation is very high (0.95 eV), especially when considering the low reaction temperature in the experiments [3].

According to the calculated energy pathways, all the adsorbed CO_2 species can easily desorb into the gas phase because of the small desorption energy (<0.3 eV), which indicates that the observed crystal plane effect is mainly determined by CO adsorption and oxygen subtracting steps. The adsorption steps determine the coverage of CO at the ion-pair active site on the surface, and the subtracting step controls the degree of difficulty for the formation of CO_2 species. In conclusion, the lower adsorption energy (more negative) and the smaller barrier for subtracting the lattice oxygen ion lead to a high reactive surface for CO oxidation.

Assuming that the number of Co–O pair sites on each sur-

Fig. 3. The pathways and energies for CO oxidation with the lattice oxygen ion.

face is identical, the relative coverage of CO can be determined by a Boltzmann distribution via the formula $\exp(-E_{\text{ads}}/RT)$. Since the adsorption energies at the Co^{3+} site on (001) and (011) surfaces are very close (-1.10 vs -1.14 eV), the relative coverage at the Co-O site has a similar reference value, i.e. $\exp(-E_{\text{ads}}(\text{Co})/RT)$, and will not largely be affected by the selective occupancy of CO at the Co site. Based on the transition state theory, the rate for the oxygen subtracting step can be expressed by $A\exp(-E_{\text{a}}/RT)$. As a result, the relative reactivity at different reactive sites can be expressed by $A\exp(-(E_{\text{ads}}+E_{\text{a}})/RT)$. The pre-exponential factor A for each surface is estimated by $(k_{\text{B}}T/h)\exp(\Delta S^\ddagger/k_{\text{B}})$, where $\Delta S^\ddagger$ is the change of entropy between the reactant and the transition state, and the temperature T is set to 200 K according to the experimental temperature [3]. The calculated pre-exponential factors for (001)-Co-O^o, (001)-Co-O^t, (011)-Co-O^o, and (011)-Co-O^t are 4.9×10^{14} , 1.8×10^{14} , 5.9×10^{14} , and $9.8 \times 10^{14} \text{ s}^{-1}$, respectively; because these values are all quite similar to each other, this indicates that there is a negligible entropy effect on the rate constant. It was also previously reported that the entropy contribution had little effect on the reaction rate of C-H bond activation over the Co_3O_4 surface [6].

Therefore, we chose the energy level of the transition state ($E_{\text{TS}} = E_{\text{ads}} + E_{\text{a}}$) for the CO_2 formation as an indicator of the reactivity of CO oxidation, which can be approximately considered as the apparent activation energy relative to the initial state of gas-phase CO. By comparing E_{TS} at different sites, we can easily obtain the reactivity order: (011)-Co-O^t >> (001)-Co-O^o > (011)-Co-O^o > (001)-O^t. This indicates that the exposed Co-O^t site on the (011) surface exhibits the highest activity for CO oxidation.

Various studies attributed the high oxidation capacity of the Co_3O_4 surface to the presence of octahedrally coordinated Co^{3+} ions [7,8,34]. While it is demonstrated in our present study that both (001) and (011) surfaces contain exposed Co^{3+} ions, they have significantly different reactivity for CO oxidation. This implies that simply attributing reactivity to the presence of exposed octahedral Co^{3+} is not always correct because the ex-

posed surface Co^{3+} ions have different lattice environments. The real active site for CO oxidation is not the Co site, but instead is the Co-O pair site, which is consistent with our recent study on C-H activation on Co_3O_4 nanocrystals [6]. In light of these results, one can speculate that low-coordination surface ions contribute to the high activity for CO oxidation. For example, four-coordinate Co^{3+} ions and two-coordinate O^{t} ions on the (011) surface are more active than the five-coordinate Co^{3+} ions and three-coordinate O^{t} ions on the (001) surface. As CO oxidation with the lattice oxygen ion abstraction leads to oxygen vacancy formation, and both CO adsorption and oxygen vacancy formation cause reduction of the surface, correlation between the vacancy formation energy and reactivity is expected. The vacancy formation energy is defined as $E_{\text{vf}} = E_{\text{v}} + 1/2E_{\text{O}_2} - E_{\text{slab}}$, where E_{v} , E_{O_2} , and E_{slab} are the energies of the oxygen-defect surface, O_2 molecule, and stoichiometric surface, respectively. Based on this definition, the vacancy formation energy represents the strength of O ion binding to the environmental lattice. The energy levels of the transition states and the oxygen vacancy formation energies are listed in Table 3. One can conclude that there is a positive correlation between the two values. That is, the easier the oxygen ions are to remove, the more reactive the surface. For example, the Co-O^t ion in the Co_3O_4 (011) surface that has the lowest vacancy formation energy is found to be the most reactive site for CO oxidation. This accords with previous theoretical research on the importance of low-coordinate oxygen ions in catalytic CO oxidation [20]. Our results indicate that exposed Co^{3+} ions are not the direct factor that affects the reactivity; instead, the bonding

Table 3

Comparison between the transition state energies and the vacancy formation energy of lattice oxygen.

Co-O site	E_{TS}/eV	E_{vf}/eV
(001)-Co-O ^t	0.41	3.51
(011)-Co-O ^o	0.25	3.32
(001)-Co-O ^o	0.21	3.07
(011)-Co-O ^t	-0.89	2.46

scheme of surface Co and O ions in the lattice structure that affect the reducibility of Co ions might determine the reactivity. Our results show that lowering the vacancy formation energy via popular methods such as controllable synthesis of specific planes or metal doping in the lattice is promising for higher CO oxidation reactivity.

4. Conclusions

We have performed a theoretical study of CO oxidation with the lattice oxygen ions on $\text{Co}_3\text{O}_4(001)$ and $\text{Co}_3\text{O}_4(011)$ surfaces by using density functional theory. It is found that CO oxidation exhibits significant dependence on the crystal plane and active sites, consistent with previous experimental findings. Surface Co–O ion pairs are found to be the active sites for CO oxidation. Co–O⁺ pairs with O⁺ bonded to one Co^{2+} ion on the (011) surface are the most active site for CO, with a small barrier of 0.26 eV. The reactivity of Co_3O_4 surfaces is correlated with the vacancy formation energy. The nature of the high reactivity of low-coordination oxygen ions is attributed to their weak binding to the substrate lattice. As a result, low-coordination surface ions have high activity for CO oxidation.

Generally speaking, the ultimate goal of catalysis design is to understand the nature of the catalytic active site and tailor the catalyst from the atomic level, achieving high reactivity and optimizing economization of the catalysts [35]. Singly dispersed atoms anchored on metal-oxide surfaces have recently been reported to exhibit robust stability and significant catalytic activity [33,36,37]. This type of catalyst is referred to as a single atom catalyst (SAC) and has become a potential solution to reduce usage of expensive noble metals in catalytic industries. The current study furthers our understanding of this class of catalysts by revealing that the ion-pair active center (IPAC) that naturally exists on the cobalt oxide surface provides a synergistic effect in catalyzing CO oxidation, where the cation contributes to the CO adsorption and the anion facilitates CO_2 formation. Recent theoretical work [6,38] also demonstrates that Pd–O pairs on the Pd surface and Co–O pairs on the Co_3O_4 surface can effectively activate C–H bonds synergistically. These results imply that effective creation of dispersed ion-pair active centers on the support (metal or metal oxide) might be vital for screening and designing nanocrystal catalysts with high activity and selectivity.

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Graphical Abstract

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Theoretical studies of CO oxidation with lattice oxygen on Co_3O_4 surfaces

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Theoretical studies reveal that the reactivity of CO oxidation on Co_3O_4 nanocrystals exhibits significant crystal plane effects and structure sensitivity, and has a positive correlation with the surface reducibility.

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Co₃O₄纳米晶表面晶格氧催化氧化CO的理论研究

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摘要:近年来, 纳米科学技术的迅速发展给催化领域, 特别是多相催化带来了新的机遇和挑战. 科学家们开始着眼于在纳米尺度上对催化剂结构和催化性能进行表征、控制和设计. Co₃O₄作为一种重要的半导体金属氧化物材料, 由于其优异的氧化还原性质, 在锂电池、气体传感器以及多相催化领域得到了十分广泛的应用. 最近, 研究者发现Co₃O₄纳米晶在催化CO低温氧化和CH₄活化等一系列重要反应中表现出显著的反应活性和晶面效应, 表明有效设计和合成特定的高活性、高选择性的纳米晶面, 对催化领域的发展将具有十分重要的意义. 因而, 从原子层面对纳米晶所表现出的这种高活性和晶面效应进行深入解释, 将为高效催化剂设计提供重要指导.

低温CO氧化作为一种重要的催化反应在燃料电池、空气净化与汽车尾气处理中具有重要的应用价值. 本文采用密度泛函理论对Co₃O₄纳米晶催化CO氧化反应的机理、晶面效应以及结构敏感性进行了理论研究. 首先, 研究了CO在Co₃O₄(001)和(011)表面Co, Co–O^o和Co–O^t三种不同位点的吸附扩散行为, 发现CO在Co位点表现出较强的吸附行为, 但这种吸附构型需要克服很高的能垒(~1 eV)才能转变到Co–O离子对位点, 在低温下这种转变将不可能发生, 因此我们推断CO在Co位点的吸附对Co₃O₄催化CO氧化的晶面效应没有显著影响. 接着, 对CO在Co–O离子对位点抽提晶格氧生成CO₂的反应机理进行了研究. 我们发现, (011)表面Co–O^t位点可以较强地吸附CO(吸附能–1.15 eV), 并十分容易夺取晶格氧离子(能垒0.26 eV), 具有很低的势能面, 因而其CO氧化活性明显大于(001)面.

为了更清楚地理解这种晶面效应和结构敏感效应的本质, 我们提出将CO₂形成步的过渡态在反应路径上的能级作为反应活性指标. 这种活性指标兼顾考虑了CO在Co–O氧位点的吸附覆盖度和CO₂形成步的反应能垒, 可以近似理解为反应的表现活化能. 据此我们得出, Co₃O₄不同表面不同晶格位点催化CO氧化的反应活性顺序为: (011)–Co–O^t >> (001)–Co–O^o > (011)–Co–O^o > (001)–Co–O^t. 由于CO吸附和CO₂形成步都涉及到表面被还原的过程, 我们因此发现CO催化氧化活性的高低与表面晶格氧位点的可还原性具有正相关性. 这种表面不同位点的还原性可以直接通过对空穴形成能的计算获得, 降低表面氧空穴的生成能将有利于提高CO氧化的活性.

催化设计的终极目标是在对催化活性位点的本质及反应机理深入认识的基础上在原子层面对催化剂进行可控设计, 从而实现催化剂材料的高效、经济的利用. 本文研究表明离子对活性位点是Co₃O₄纳米晶催化CO氧化反应的活性位点, 其中阳离子负责对CO的吸附, 阴离子则负责CO₂的形成过程, 这种协同作用实现了Co₃O₄纳米晶的高反应活性. 我们相信, 寻找有效的方法在催化剂表面增加离子对位点活性中心的数目是一种实现高性能催化剂设计的途径.

关键词: 一氧化碳氧化; 四氧化三钴; 晶面效应; 离子对活性中心

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