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Article

Multi sites vs single site for catalytic combustion of methane over $\text{Co}_3\text{O}_4(110)$: A first-principles kinetic Monte Carlo study

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ABSTRACT

Single-atom catalysts have been applied in many processes recently. The difference of their kinetic behavior compared to the traditional heterogeneous catalysts has not been extensively discussed yet. Herein a complete catalytic cycle of CH_4 combustion assuming to be confined at isolated single sites of the $\text{Co}_3\text{O}_4(110)$ surface is computationally compared with that on multi sites. The macroscopic kinetic behaviors of CH_4 combustion on $\text{Co}_3\text{O}_4(110)$ is systematically and quantitatively compared between those on the single site and multi sites utilizing kinetic Monte Carlo simulations upon the energetic information from the PBE + U calculation and statistic mechanics. The key factors governing the kinetics of CH_4 combustion are disclosed for both the catalytic cycles respectively following the single-site and multi-site mechanisms. It is found that cooperation of multi active sites can promote the activity of complete CH_4 combustions substantially in comparison to separated single-site catalyst whereas the confinement of active sites could regulate the selectivity of CH_4 oxidation. The quantitative understanding of catalytic mechanism paves the way to improve the activity and selectivity for CH_4 oxidation.

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1. Introduction

Single-atom catalysis (SACs) [1] has become the most active new frontier in heterogeneous catalysis field in recent years [2–6]. The most important structure feature of SACs contributing to catalytic activity and selectivity is the isolated atoms dispersed on the support, which could be analogical to homogeneous catalysts [7]. In general, the high ratio of exposed individual atoms is possible to provide uniform active sites and maximize the catalytic efficiency compared to heterogeneous catalysts consisting of various active sites [8]. With the great

advances in synthetic methodologies, a large number of single-atom catalysis (SACs) has exhibited excellent performances for various chemical reactions [9–12]. Interestingly, when we gaze at the typical metal oxide surface, it could be found that the surface is alike the combination of a series of single metal atom center coordinated with oxygen anions. Moreover, it is worth noting that for the SACs, the bonding capacity of single atom may limit its application in the complicated reaction.

The catalytic combustion of methane (CH_4) [13–15] is a complex process which should include four steps of dehydrogenation and two C–O coupling elementary steps at least. It is a

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vital alternative to the conventional thermal combustion processes of coal and oil [16] for energy production. However, as a major component of natural gas, CH₄ is also a greenhouse gas, which has as much as 28 times more potent than carbon dioxide (CO₂) [17]. Accordingly, its highly efficient combustion could relieve the greenhouse effect due to exhaust emission [18–20]. To meet the lower level of methane emission requirement in stricter environmental standards such as the Euro-VI standard for natural gas vehicles (NGV), there are urgent requirements for high activity catalysts to maintain high combustion rates for the abatement of methane emissions in the NGV exhaust [21]. In order to achieve high activity and thermal stability for catalytic combustion of methane, extensive studies have been done and various catalysts have been developed by scientists, such as supported palladium oxides [22] and rhodium oxides [23] catalysts. Cargnello et al. recently reported a modular Pd@CeO₂ nanoparticles on functionalized Al₂O₃ that could achieve both catalytic activity below 400 °C and thermal stability up to 850 °C [24]. Nevertheless, due to the high cost, sintering and susceptibility to poisoning of noble metal catalysts, cobalt-based spinel oxides, e.g. Co₃O₄, which are treated as alternatives also exhibit excellent catalytic performance for methane combustion [25–28]. Recently, Hu et al. [29] investigated a complete catalytic cycle for methane combustion on the Co₃O₄(110) surface based on first-principles calculations. It is found that the cooperation of multiple sites on Co₃O₄ surface may play an important role in promoting methane combustion over Co₃O₄ surfaces. Yet the effect of multi-site on CH₄ combustion activity just lies on the energetic analysis from density functional theory (DFT) calculations. Still, it is not easy to intuitively comprehend the importance of the cooperation between multiple active sites for the overall catalytic activity compared to SACs-like separated single active site.

Kinetics simulation as an efficient approach linking macroscopic and microscopic properties of catalytic systems [30–33] could be used to analyse complex catalytic system quantitatively. Over the last few years, kinetic Monte Carlo (kMC) simulation based on DFT calculations has been widely used in heterogeneous catalytic reactions and biomolecular reactions [34–42]. As kMC simulations intrinsically take all the location information and diffusion issues into account, it is an effective way to describe the single- or multi-site effect of heterogeneous catalysis quantitatively.

In this paper, to quantitatively understand the kinetic influence of the interplay of multi site for the catalysis, the reaction mechanism through multi active sites is systematically compared with that constrained at the single active site for the CH₄ combustion over Co₃O₄(110) utilizing first-principle kMC simulation. First, we explore a complete CH₄ combustion cycle on an ideal isolated single active site on Co₃O₄(110) surface. Based on the energetic data from DFT calculations, we then perform kMC simulations for both two types of catalytic cycles of CH₄ combustion on Co₃O₄(110) respectively through single and multiple active sites. By the virtue of kinetic calculations, we manage to quantitatively analyze the effect of the interplay of multiple active sites for the activity and selectivity of CH₄ oxidation. Furthermore, the key factors governing the kinetic activi-

ties are also disclosed, which may help to improve the catalytic activity of spinel-type cobalt oxide catalysts for CH₄ oxidation.

2. Computational details

2.1. DFT calculations

All the spin-polarization calculations in this work were performed using the Perdew-Burke-Ernzerh (PBE) generalized gradient approximation (GGA) functional under the framework of density functional theory (DFT) in Vienna *ab initio* Simulation Package (VASP) [43–46] with the employment of a plane wave basis set [47]. The projector-augmented-wave (PAW) pseudopotentials [48] with the cores of 1s 2p, 1s, and 1s for Co, O, and C, respectively, were utilized to describe the valence-core interactions. A plane-wave kinetic energy cutoff of 500 eV was set for the expanded plane wave basis-set. As for the strong correlation between the electrons in partially occupied 3d orbitals of Co, the on-site Coulomb repulsion correction term of *U* within the Hubbard scheme (PBE+*U*) was applied in the 3d electrons of Co. The effective *U*_{eff} value, namely *U*–*J*, was set to 2.0 eV, which has been demonstrated to well simulate the properties of Co₃O₄ such as the band gap, lattice constant, and magnetic moment in previous work [28,49–52]. Van der Waals interactions were determined by the BJ-damped variants of the Grimme's D3 approach [53,54]. The Brillouin-zone integration was performed on Monkhorst-Pack grids with a 2 × 3 × 1 mesh where a Gaussian-smearing approach with $\sigma = 0.05$ eV is used during the ionic optimization.

The Co₃O₄(110) surface was modeled using a stoichiometric slab with of a *p*(2×1) unit cell, which was based on the antiferromagnetic bulk Co₃O₄ with normal spinel structure (*a* = 8.124 Å). Each periodic slab contains eight layers of Co-O plane and separated by a vacuum space of approximately 15 Å. Co₃O₄ surface may have two different terminations [55–57]. We investigated the stabilities of the two terminations of the Co₃O₄(110) surface in our previous work [29]. The (110)-A termination exposes two types of cobalt cations (Co²⁺ and Co³⁺) and one type of oxygen anion (3-fold coordinated oxygen anion, O_{3c}), whereas the (110)-B termination has only one type of cobalt cation (Co³⁺) and two types of oxygen anions (2-fold coordinated oxygen anion O_{2c} and 3-fold coordinated oxygen anion O_{3c}). The (110)-B termination which has a lower Gibbs surface energy under the work conditions was utilized in the work. For the spin configuration of the slab, we used the anti-ferromagnetic configuration from the subsurface to the bottom layer of the slab model. It is consistent with the bulk properties. For the surface layer, the spin of the unsaturated Co_{4c} was opposite to the spin of Co²⁺ in the subsurface. The same spin configuration has also been confirmed as the most stable configuration for the Co₃O₄(110) in previous work [58]. Top and side views of the Co₃O₄(110) surface structure is displayed in Fig. 1(a). Modeling details can also be found in our previous work [29]. In this work, we treat a O_{3c}-Co³⁺-O_{2c} as a single active site on Co₃O₄(110) surface as labeled in Fig. 1(a) by black dashed square.

All the geometry structures of adsorption intermediates

Fig. 1. $\text{Co}_3\text{O}_4(110)$ surface (a) and transition state structures of the first C-H activation (b), C- O_{2c} coupling on multi sites (c), and C- O_{3c} coupling on single active site (d). Co, O_{2c} , O_{3c} , H, C atoms and lattice O in sublayer are shown in blue, pink, magenta, white, gray, and red colors, respectively. In addition, in the top view of the structures, the atoms at the top layer and sublayers are illustrated by ball-and-stick and stick models, respectively, and the rest of the atoms are given by line models.

were optimized using a force-based conjugate gradient algorithm until the forces on all the relaxed atoms were below $0.05 \text{ eV}/\text{\AA}$. During the geometry optimization, the bottom four Co-O layers were fixed while the top four Co-O layers and adsorbates could be relaxed. The transition states (TS) in reactions were searched with a constrained optimization scheme [59] and the convergence of forces was set to $0.05 \text{ eV}/\text{\AA}$. It was achieved when all the forces on atoms vanished and the total energy was a maximum along the reaction coordination but a minimum with respect to the rest of the degrees of freedom (namely saddle point). Each TS was further verified as a first-order saddle point with only one imaginary vibrational frequency and the corresponding vibrational mode along the reaction coordination on the basis of a numerical vibrational frequency analysis.

2.2. Kinetic Monte Carlo simulation

For the kinetic Monte Carlo simulation of CH_4 combustion process on $\text{Co}_3\text{O}_4(110)$, we implemented a simulation code based on the VSSM kMC method [34,60–62]. To overcome the stiff problem introduced by the fast species diffusion on surface and accurately describe its influence on the kinetics, the fast species redistribution (FSR) algorithm [63] was adapted in our code where the fast diffusion species are redistributed within feasible space under quasi-equilibrium assumption during kMC iteration. For the surface grid modeling of $\text{Co}_3\text{O}_4(110)$, Co, O_{3c} , O_{2c} sites and O vacancy are all explicitly modeled in a 30×30 two-dimensional grid with periodic boundary condition enabled. In simulation process, surface adsorbate coverages and turnover frequencies (TOF) were calculated from statistical

time averages [39]. The steady state was detected based on exponentially weighted moving average (EWMA) protocol [64–66] where the tolerance range parameter L was set to 6 and the decay parameter λ of EWMA was 0.05. The convergence criterion $p_c = 0.05$ was chosen to ensure enough kMC sampling in our work. The degrees of rate control (X_{RC}) for elementary reaction i were calculated directly using the formula in the definition [30,32,67] based on numerical differentiation:

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}$$

where r refers to the reaction rate, the partial derivative is obtained through keeping the rate constant, k_i , for the other steps ($j \neq i$) and each equilibrium constant, K_i as constants. All kinetic Monte Carlo simulations were implemented upon free energy landscape [68,69]. The free energy was calculated based on the total energy from DFT calculations with the thermodynamic correction. The calculation process is as follows:

$$G = E + \int C_P dT - TS$$

where G , E and C_P refer to the chemical potential (partial molar Gibbs free energy), electronic energy and heat capacity, respectively. The entropy term can be expressed as the sum of the translational, rotational, vibrational and electronic contributions as to:

$$S = S_t + S_r + S_v + S_e$$

And finally, the intrinsic zero-point energy (ZPE) corrections can be included to finally obtain:

$$G = E + \int C_P dT - T(S_t + S_r + S_v + S_e) + \text{ZPE}$$

For the case of solids and adsorbates, some approximations can be assumed: (1) $S_e \approx 0$ at the fundamental electronic level; (2) Translational and rotational motions can be neglected, therefore, $S_t \approx 0$ and $S_r \approx 0$. In this sense, all the entropy contributions come from vibrations: $S = S_v$. Similarly, translational and rotational contributions to the heat capacity are neglected. Therefore, Gibbs free energies for the different states have been calculated as to:

$$G = E + \int C_P dT - TS_v + \text{ZPE}$$

In this paper, all energetic data reported are free energy after correction under the reaction conditions of $T = 450 \text{ }^\circ\text{C}$, $P(\text{CH}_4) = 0.01 \text{ bar}$, $P(\text{O}_2) = 0.2 \text{ bar}$, $P(\text{CO}_2) = 0.01 \text{ bar}$, and $P(\text{H}_2\text{O}) = 0.02 \text{ bar}$. The original DFT calculated total energies and details of kinetic parameters calculation methods are shown in the Supporting Information.

3. Results and discussion

3.1. Catalytic cycle of CH_4 complete oxidation on single active site

The complete catalytic cycle and possible reaction network of CH_4 combustion on the $\text{Co}_3\text{O}_4(110)$ surface has been explored via multi-site mechanism in the total energy landscape in our previous work [29]. The optimal reaction route of CH_4 complete oxidation following the optimal multi-site mechanism can be summarized as: $\text{CH}_4 \rightarrow \text{CH}_3(\text{Co}) \rightarrow \text{CH}_3\text{O}_{2c} \rightarrow \text{CH}_2\text{O}_{2c} \rightarrow \text{O}_{2c}\text{CH}_2\text{O}_{2c} \rightarrow \text{O}_{2c}\text{CHO}_{2c} \rightarrow \text{O}_{2c}\text{CHO}(\text{Co}) \rightarrow \text{CO}_2$. Each adsorbate bonded with Co^{3+} is denoted with (Co) throughout this work.

^a In the reaction expressions, (Co) and (g) denote Co site and gas phase, respectively. vac(O_{3c}) is O_{3c} vacancy. This notation is used throughout all reaction expressions in this work.

Table 2

Calculated free reaction barriers ($\Delta^\ddagger G$) and free reaction energies (ΔG) of the elementary steps involved in the catalytic cycle of CH₄ combustion on Co₃O₄(110) multi active sites under the reaction conditions of $T = 450\text{ }^\circ\text{C}$, $P(\text{CH}_4) = 0.01\text{ bar}$, $P(\text{O}_2) = 0.2\text{ bar}$, $P(\text{CO}_2) = 0.01\text{ bar}$, and $P(\text{H}_2\text{O}) = 0.02\text{ bar}$.

Reaction	$\Delta^\ddagger G$ (eV)	ΔG (eV)
CH ₄ (g) → CH ₃ (Co) + HO _{2c}	1.80	0.77
CH ₃ (Co) → CH ₃ O _{2c}	0.82	-0.91
CH ₃ O _{2c} → CH ₂ O _{2c} + HO _{2c}	0.70	-0.15
CH ₂ O _{2c} → HCHO(g) + vac(O _{2c})	—	0.31
CH ₂ O _{2c} → O _{2c} CH ₂ O _{2c}	—	-1.00
O ₂ (g) + O _{2c} CH ₂ O _{2c} → O ₂ (Co) + O _{2c} CH ₂ O _{2c}	—	0.02
O _{2c} CH ₂ O _{2c} + O ₂ (Co) → O _{2c} CHO _{2c} + OOH(Co)	0.64	-0.41
O _{2c} CHO _{2c} + OOH(Co) → O _{2c} CHO(Co) + OH(Co)	—	-1.54
O _{2c} CHO(Co) + OH(Co) → CO ₂ (g) + H ₂ O(Co) + vac(O _{2c})	0.84	-0.68
O ₂ (g) + vac(O _{2c}) + 2HO _{2c} → H ₂ O(Co)	0.45	-2.44
H ₂ O(Co) → H ₂ O(g)	0.0	-0.30

cle on single active site (in Fig. 2(b)), we can find that the first C-O coupling step has the highest effective free energy barriers (2.26 eV). This indicates that the first C-O coupling step may be the key step with the greatest impact on the entire cycle. However, when analyzing the elementary reactions separately, we can find that the maximum free energy barrier is 1.80 eV for

the first C-H breaking step. Therefore, it is difficult to quantitatively analyze the properties of the whole catalytic cycle from the energy profile alone. Furthermore, so far we have obtained both catalytic pictures about methane combustion cycles on both single and multiple active sites over Co₃O₄(110) based on PBE+*U* calculations. Nevertheless, it is still not enough for quantitative comparison of the effects of single and multiple sites to catalytic oxidation activities. In the following parts, we will perform kinetic analysis on different catalytic cycles using kinetic Monte Carlo (kMC) simulation for the further analysis.

3.2. Kinetic Monte Carlo simulation for CH₄ combustion

In this section, we performed kinetic analysis utilizing kMC simulations for both CH₄ combustion catalytic cycles on single active sites and multi active sites of Co₃O₄(110) surface. The calculated free energetic data used for kMC simulations for single-site and multiple-site cases are listed in Table 1 and Table 2, respectively. All kMC simulations were performed at the typical temperature of complete conversion of the methane ($T = 450\text{ }^\circ\text{C}$, $P(\text{CH}_4) = 0.01\text{ bar}$, $P(\text{O}_2) = 0.2\text{ bar}$, $P(\text{CO}_2) = 0.01\text{ bar}$, $P(\text{H}_2\text{O}) = 0.02\text{ bar}$). Table 3 shows the simulated steady-state coverages of different adsorbates on three different sites (O_{3c},

Fig. 3. Optimized structures of transition states and intermediates in catalytic cycle of CH₄ combustions on limited single active site on Co₃O₄(110) surface. Co, O_{2c}, O_{3c}, H, C atoms and lattice O in sublayer are shown in blue, pink, magenta, white, gray and red colors, respectively. In addition, the atoms at the top layer and sublayers are illustrated by ball-and-stick and stick models, respectively, and the rest of the atoms are given by line models.

Table 3

Simulated steady-state coverages (ML) of different adsorbates on three different sites (O_{3c} , O_{2c} , and Co) on $Co_3O_4(110)$ surface for catalytic cycle on multiple active sites^a.

	O_{3c}	Co	O_{2c}
vac	0.0	0.0	4.40×10^{-3}
H	2.74×10^{-4} (HO_{3c})	0.0	6.50×10^{-2} (HO_{2c})
CH_3	0.0	4.08×10^{-5}	1.61×10^{-3} ($O_{2c}CH_3$)
$-CH_2-$	0.0	0.0	1.69×10^{-7} ($O_{2c}CH_2O_{2c}$)
CH_2	0.0	0.0	3.28×10^{-8} (CH_2O_{2c})
O_2	0.0	2.75×10^{-2}	0.0
OH	0.0	6.67×10^{-5}	0.0
CHO	0.0	0.0	1.92×10^{-8} ($O_{2c}CHO$)
O	0.0	2.73×10^{-2}	0.0
OOH	0.0	3.44×10^{-5}	0.0
*	9.99×10^{-1}	9.45×10^{-1}	9.29×10^{-1}

^a All species expressions in the first column do not include lattice O. For example, H on O_{3c} is equivalent to HO_{3c} . OCH_2 on O_{3c} is $O_{3c}CH_2O(Co)$. Symbol * represents empty surface site. This notation is used throughout all the coverage result tables in this work.

Co, and O_{2c}) for CH_4 combustion cycle on multi active sites. Apart from the unoccupied sites, the surface H(O_{2c}) is the dominant species that has the maximum coverage (6.50×10^{-2} ML) on the surface. The coverage of CH_3 species is secondly to H(O_{2c}) (1.61×10^{-3} ML) on O_{2c} site, which is consistent with the observations in experiments [28]. From the surface coverage results, it is clear from Table 3 that the C containing species are mainly located at the Co and O_{2c} site. Therefore, compared with the O_{3c} site, the active O_{2c} site plays a more important role in the CH_4 complete oxidation with the help of cooperation of multiple sites on $Co_3O_4(110)$ surface. The simulated turnover frequency (TOF) towards CO_2 is $5.57 \times 10^{-3} s^{-1}$ following the optimal mechanism. HCHO is a possible by-product from the surface reaction. It has a lower yield of $7.18 \times 10^{-4} s^{-1}$. However, since 450 °C is above the ignition point of HCHO (300 °C), the generated HCHO would be rapidly burned to completely form CO_2 as well. In order to identify the rate-determining steps, we calculated event frequencies for each elementary reaction in the CH_4 combustion cycle and the degree of rate control ($X_{RC,i}$) of elementary step i [30,32] as displayed in Fig. 4 using kinetic Monte Carlo simulation. It is clear that most of the elementary steps reach the quasi-equilibrium, namely the reversibility of forward and reverse step is close to 1, except for the first C-H bond breaking, the first C-O coupling, the second C-O coupling and HCHO desorption. The further degree of rate control analysis discloses that the first C-H bond activation step possesses the greatest X_{RC} value, indicating that the first C-H activation is the rate-determining step for the catalytic cycle of CH_4 combustion on multi active sites.

To intuitively comprehend the effects of multi active sites on the catalytic activities, we also calculated kinetic properties of CH_4 combustion cycle confined at the single site of $Co_3O_4(110)$ surface as the reference. The simulated surface coverages of different adsorbates on three different sites are listed in Table 4. In the single active site case, as the active O_{2c} site is passivated by H species, the major active sites for CH_4 combustion turn to Co and O_{3c} . As shown in Fig. 5, different from the multi-site case, only HCHO is generated with a low rate of $3.98 \times 10^{-6} s^{-1}$, indicating that HCHO rather than CO_2 is the main product for

Fig. 4. Statistics of elementary reaction event occurrence in multi-site catalytic cycle, showing the number of events per site per time for the forward (blue bar) and reverse (yellow bar) steps. The degree of rate control (X_{RC}) for each elementary step is labeled on the top of each bar. The red one is the maximum of X_{RC} value indicating a rate-determining step in catalytic cycle.

CH_4 combustion over the $Co_3O_4(110)$ surface if the reaction cycle is limited on the single active site. Although gaseous HCHO is also rapidly converted to CO_2 under the reaction conditions, the turnover frequency is still much lower than that following the multi-site mechanism. This suggests that the single active site has extremely low activity for oxidation of CH_4 . Moreover, interestingly, forward and reverse elementary event frequencies in Fig. 5 show that the first C-H activation step is almost equilibrated following the single-site mechanism. This indicates that it may be not the rate-limiting step for CH_4 combustion cycle anymore if following this mechanism. This is proved by the further degree of rate control results. The X_{RC} value of the first C-H activation step is 0.11 which is significantly less than 0.97 of the first C-O coupling. This indicates that the first C-O coupling instead of the first C-H breaking step becomes the greatest limitation to the overall catalytic oxidation activity if following single-site mechanism. Hence, it is demonstrated from the reverse side that the cooperation of multi sites could effectively ease the deep dehydrogenation and C-O coupling for methane combustion over $Co_3O_4(110)$ but is

Table 4

Simulated steady-state coverages (ML) of different adsorbates on three different sites (O_{3c} , O_{2c} , and Co) on the $Co_3O_4(110)$ surface for catalytic cycle on single active sites.

	O_{3c}	Co	O_{2c}
H	0.0 (HO_{3c})	0.0	5.55×10^{-4} (HO_{2c})
CH_3	1.64×10^{-11} (CH_3O_{3c})	5.55×10^{-4}	0.0
O_2	0.0	6.0×10^{-12}	0.0
OOH	0.0	2.76×10^{-11}	0.0
CH_2	3.35×10^{-15}	0.0	0.0
OCH_2	2.03×10^{-13} ($O_{3c}CH_2O(Co)$)	8.65×10^{-10}	0.0
*	9.99×10^{-1}	9.99×10^{-1}	9.99×10^{-1}

Fig. 5. Statistics of elementary reaction event occurrence in single-site catalytic cycle, showing the number of events per site per time for the forward (blue bar) and reverse (yellow bar) steps. The degree of rate control (X_{RC}) for corresponding elementary steps are labeled on the top of each bar. The red one is the maximum of X_{RC} value indicating a rate-determining step in catalytic cycle.

unable to facilitate the first C-H bond activation.

By virtue of kMC simulation, the effect of active sites and kinetic behaviors of CH₄ complete oxidation on the Co₃O₄(110) surface can be analyzed quantitatively. By comparing the final overall turnover frequencies of different cycles, it can be found that the CH₄ catalytic combustion rate following the multi-site mechanism would be more than 3 orders of magnitude higher than that confined at the separated single site. It indicates the synergistic effect of multi active sites could promote the catalytic activity substantially. From the statistical results of surface coverage and adsorbate distribution on different sites (O_{3c}, O_{2c}, and Co) for two different cases, it is found that O_{2c} and Co are the major active sites of multi sites catalytic cycle, while O_{3c} and Co are main reaction sites for single site oxidation cycle. It could be attributed to the fact that the multi sites could assist the rapid transfer of H species on the Co₃O₄(110) surface to prevent the passivation of active two-coordinated O sites (O_{2c}). However, on the isolated single active site, once the O_{2c} is occupied by H and blocked, the less active O_{3c} has to be the reaction site. Consequently, it is the CH₃* and O_{3c} coupling that becomes the rate-determining step for the methane combustion. This significantly limits the whole reaction activity. It suggests that the fast removal of H on O_{2c} by the assistance of multi sites could switch the C-O_{3c} coupling to C-O_{2c} coupling to enhance the activity of CH₄ oxidation. In addition to species migration, the space limitation broken by multi sites could also provide more possibilities for the surface intermediates to reach more stable structures. With the assistance of two neighboring O_{2c} sites, the CH₂O_{2c} could be reconstructed to more stable O_{2c}CH₂O_{2c} structure where C atom switches from *sp*² hybridization to *sp*³ hybridization. The C-O bonding could be therefore

changed from the double bond to single bond, promoting the surface Co-O bonding and consequently promoting the intermediate stability. This kind of intermediate stabilization allows the reaction to proceed towards the complete combustion to CO₂ rather than the selective oxidation to HCHO. Vice versa, the CH₄ confined at the single active site can only be oxidized to HCHO selectively. Therefore, from the quantitative kinetics comparisons between CH₄ complete oxidation cycles on single site and multi sites, we can find that the cooperation of multi active sites could not only avoid rapid passivation of single sites but also facilitate to form more stable intermediate to promote methane complete combustion substantially. In other words, it also indicates that it is possible to efficiently regulate the selectivity of CH₄ oxidations by confining the active sites to form separate sites. Nevertheless, the kMC simulation results also disclose that the conversion of methane is possible to be weakened due to the confined and isolated active sites.

4. Conclusions

In summary, based on the quantitative comparative results from the first-principles kinetic Monte Carlo simulation on single active sites and multi active sites, we find that the cooperation of multi active sites in Co₃O₄(110) could substantially promote the activity of the methane oxidation compared to single active sites. The selectivity of the surface oxidation would be changed as well. The complete oxidation product of CO₂ could be yielded following the multi-site mechanism while the gaseous HCHO would be produced following the single-site mechanism over the Co₃O₄(110) surface. The synergistic effect of multi active sites mainly originates from: (1) providing space for species migration to avoid rapid passivation of single sites, and (2) providing more possibilities for surface intermediates to reach more stable structures. The confinement of separated single active sites can only selectively catalyze CH₄ oxidation to generate gaseous HCHO if not considering the rapid direct combustion of HCHO to CO₂ in the gas phase under the reaction conditions. Consequently, from the other side, it sheds light on the fact it is of great significance to confine active sites in the catalyst surfaces for the selective oxidation of CH₄.

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Graphical Abstract

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Multi sites vs single site for catalytic combustion of methane over $\text{Co}_3\text{O}_4(110)$: A first-principles kinetic Monte Carlo study

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Systematical first-principles kinetic Monte Carlo simulations of CH_4 combustion on $\text{Co}_3\text{O}_4(110)$ show that the cooperation of multi active sites can promote the activity of complete CH_4 combustions substantially in comparison to separated single-site catalyst whereas the confinement of active sites could regulate the selectivity of CH_4 oxidation.

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Co₃O₄(110)表面甲烷催化燃烧中的单位点和多位点性能对比: 第一性原理动力学蒙特卡洛研究

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摘要: 近年来, 单原子催化剂已经被广泛应用于化学反应过程中, 但有关单原子催化与传统多相催化在催化动力学上的差异尚缺少深入研究. 作为天然气的主要成分, 甲烷(CH₄)也是一种有害的温室气体. CH₄催化燃烧可以有效降低天然气汽车尾气中CH₄排放, 减小温室效应. 除了传统的贵金属催化剂, Co₃O₄等钴基尖晶石氧化物也在CH₄催化燃烧上展现出良好性能. 最近, 基于第一性原理计算的理论研究结果表明, Co₃O₄(110)表面多位点的协同作用能够提升CH₄完全燃烧的催化活性. 然而, 相关结论是基于密度泛函理论计算所获得的能量图景上取得的半定量结果. 定量确定多活性位点之间的协同作用, 以及多位点与单位点催化在催化动力学上的影响仍然相当困难. 本文通过在位库伦校正的密度泛函理论计算从自由能量图景上模拟了限阈在Co₃O₄(110)表面孤立的单活性位点上的CH₄催化燃烧反应机制, 并与通过多活性位点机制发生的催化循环进行了全面对比. 基于PBE+*U*计算获得的能量信息并结合统计力学, 我们采用动力学蒙特卡洛方法定量地模拟对比了遵循单位点机制和多位点机制时Co₃O₄(110)表面CH₄催化燃烧过程的动力学.

通过动力学蒙特卡洛模拟定量比对在多活性位点或限阈的单活性位点上的Co₃O₄(110)表面CH₄催化燃烧转化频率, 我们发现CH₄在多位点上协同催化燃烧的速率比类均相单位点催化燃烧过程高出3个数量级以上. 这表明多活性位点的协同作用可以显著提高催化活性. 通过进一步的控速步骤敏感度分析可知, 当反应限于单位点时, CH₄活化后产生的H将占据表面二配位晶格O, 使得CH₃中间体只能与相对惰性的三配位晶格O发生C–O耦合反应, 该步骤极大地限制了整体催化反应活性. 而在多个位点的协助下, 二配位晶格O上H迅速迁移, 使得CH₃可迅速与活性的二配位晶格O发生耦合反应, 从而增强CH₄的催化氧化活性. 多位点不仅可以促进表面物种迁移, 还可以为表面中间体提供更多位点空间, 提升其达到能量更稳定结构的可能性. 这种中间体稳定化作用也促使CH₄氧化反应朝着完全氧化成CO₂的方向进行, 而不是选择性氧化成HCHO. 因此, 通过单位点和多位点CH₄催化燃烧的动力学量化对比, 我们可以发现, 多活性位点的协同合作不仅可以避免活性位点的快速钝化, 而且可以形成更稳定的中间体促进CH₄的深度氧化. 这也表明可以通过对催化剂表面活性位点空间限域程度的调控实现CH₄氧化选择性的调控. 本文工作提供了甲烷催化氧化机理的定量化分析和理解, 为进一步改善CH₄催化氧化活性和选择性提供了重要的理论基础.

关键词: 甲烷燃烧; 密度泛函理论; 单原子催化; 多位点; 单位点; 尖晶石钴氧化物; 动力学蒙特卡洛

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