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Article

Theoretical study of the crystal plane effect and ion-pair active center for C–H bond activation by Co_3O_4 nanocrystals

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ABSTRACT

Methane has attracted extensive interest in recent years due to its potential application as a replacement of oil and a feedstock for valuable chemicals. Due to the large C–H bond energy, the conversion of methane into useful products has been a challenge. In the present study, density functional theory (DFT) calculations were performed to study the activation of the C–H bond of methane on the (001) and (011) planes of Co_3O_4 , which showed that CH_4 activation on Co_3O_4 nanocrystals was fairly easy with only small energy barriers (less than 1.1 eV). Surface Co–O ion pairs are the active site for C–H bond activation, where the two ions provide a synergistic effect for the activation of the strong C–H bond and yield surface Co–CH₃ and O–H species. The Co_3O_4 (011) surface is shown to be more reactive for C–H bond activation than the Co_3O_4 (001) surface, which is consistent with previous experimental results. Our results suggest that methane oxidation on Co_3O_4 nanocrystals has strong crystal plane effect and structure sensitivity and the ion-pair active center plays a significant role in activating the strong C–H bond.

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1. Introduction

Methane is the main constituent in natural gas and it is abundant in nature. The conversion of methane to the more useful methanol or other liquid fuels has attracted extensive interest in energy production and transportation fuels for several decades [1]. Transition metal and metal oxide catalysts have been widely studied in the past decades because of their catalytic properties in alkane transformations [2]. The C–H bond activation is generally the rate determining step (RDS). However, new strategies have still to be developed for the efficient, economical, and direct conversion of methane to more valuable products. The main difficulty is to achieve a highly selective activation of the enormously strong C–H bond, which

has a bond dissociation energy of 4.5 eV [3]. Therefore, the design and synthesis of new catalysts for C–H bond splitting is an important topic in modern chemistry. These catalysts can lead to the economical conversion of methane and other low-carbon alkanes into industrially useful products.

Recently, advances in the research of nanomaterials have given new opportunities for designing and screening well-defined catalysts for catalytic oxidation reactions [4–8]. Reducible metal oxides, due to their distinct redox properties, have been extensively studied for various catalytic reactions such as CO oxidation and alkane oxidation [9–11]. Among these oxides, spinel cobalt oxide (Co_3O_4) has been reported to be a promising transition metal oxide catalyst for methane catalytic oxidation [12–14]. Recently, we reported the controllable synthesis of

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different shapes of Co_3O_4 nanocrystals by a hydrothermal process with a cobalt hydroxide precursor [15,16]. The conversion and temperature-programmed reduction (TPR) results for methane combustion showed that the nanocrystal (112) and (011) planes were much more reactive for methane conversion than the (001) plane. Many previous literature reports have speculated that the high oxidation capacity of the Co_3O_4 surfaces can be attributed to the presence of octahedrally coordinated Co species, which can easily convert between trivalent Co^{3+} and divalent Co^{2+} by the redox process [8,17–22]. However, knowledge about the active sites for methane conversion on Co_3O_4 nanocrystals is still lacking due to its complex surface structure. Therefore the mechanism of C–H bond activation is still not known. Few studies have looked at the crystal plane effect in surface oxidation reactions. Here the crystal plane effect refers to the observation that the different surfaces exposed by Co_3O_4 nanocrystals exhibit different reactivities in CH_4 activation.

In this paper, a comparative density functional theory (DFT) investigation was performed on C–H bond activation at various possible active sites on the Co_3O_4 (001) and (011) surfaces. By comparing the energetics of the different reaction pathways for C–H bond activation, we demonstrated that the activity of C–H bond cleavage exhibited distinct dependence on the exposed crystal plane and active sites. The nature of the high activity of CH_4 conversion on Co_3O_4 nanocrystals is discussed. A microkinetic model was used to analyze the activity at the different sites and to estimate the reaction temperature of C–H bond activation. Our results are consistent with previous experimental observations.

2. Computational details

The theoretical calculations were carried out by using DFT and the DMol3 program (version 4.0) developed by Accelrys, Inc. [23–25]. The generalized gradient approximation (GGA) with the PBE functional was chosen to describe the exchange-correlation effects [26]. The localized double-numerical basis sets with polarization functions (DNP) were used to describe the valence orbitals of the atoms. Relativistic effective core potentials (ECP) were used to replace the core electrons of Co [22,24]. In the geometry optimization, the convergence criterion was set as 1×10^{-4} eV, 1×10^{-3} eV/Å, 5×10^{-3} Å for energy, energy gradient, and geometry, respectively. A Fermi surface smearing of 0.2 eV and a real-space cutoff of 4.5 Å were used. 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. In all the calculations, stoichiometric supercell models 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. The transition states were obtained using the complete LST/QST method, which used a linear synchronous trans-

it (LST) calculation followed by repeated conjugate gradient (CG) minimization and quadratic synchronous transit (QST) maximization until a transition state was located [27]. The convergence criterion for each transition state was set at 0.05 eV/Å. Furthermore, a harmonic vibrational analysis was performed to make sure that the transition state has only one imaginary frequency. The zero point energy (ZPE) was included in all energetics. The structural parameters, magnetic moments, and band gap of bulk Co_3O_4 were first calculated to evaluate the computational methods used in this work. The calculated results of bulk Co_3O_4 listed in Table 1 were close to the experimental data and were also in good agreement with previous computational studies, indicating that the selected exchange-correlation functional and computational approach were appropriate.

The Co_3O_4 (001)-p(1×1) ($a = 5.79$ Å, $b = 5.79$ Å) and Co_3O_4 (011)-p(1×1) ($a = 8.19$ Å, $b = 5.79$ Å) surface slab models cleaved from an ideal bulk spinel structure were used to model the Co_3O_4 planes. Due to the special structure of the spinel lattice, there are two types of surface structure for each plane for different cleaved depths. In the present study, we chose the most stable slab model with the lower surface energy for the (001) and (011) faces, which is shown in Fig. 1. Investigations on the stability of the different surface models can be found in previous theoretical studies [28,29]. There are two types of oxygen ions on each surface, denoted respectively as O^o and O^t in Fig. 1, 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^o are Co^{3+} ions. Both the O^t and O^o ions on the (001) surface are threefold coordinated, while on the (011) surface the O^t ions are twofold coordinated and O^o ions are threefold coordinated.

Table 1

Calculated and experimental data for bulk Co_3O_4 .

Property	This work	Previous work	Exp.
Lattice constant (Å)	8.19	8.17 [20], 8.12 ^a	8.09 [32]
Magnetic moments (μ_B)	2.58/ Co^{2+}	2.63 [28], 2.53 ^a / Co^{2+}	3.02/ Co^{2+} [33]
Electronic gap (eV)	Γ - Γ : 2.20 X-X: 1.82	Γ - Γ : 2.06 [28], 1.67 ^a X-X: 1.75 [28], 1.23 ^a	Γ - Γ : 1.88–2.00 ^b X-X: 1.44–1.52 ^b

^a Calculated data with the DFT + U method [30,31].

^b Gap range from previous experimental studies [32,34–37].

Fig. 1. Surface model of the Co_3O_4 crystal (001) and (011) planes. The ions of the top layers are shown in a ball and stick model. The sublayer Co^{2+} ions are also shown in a ball and stick model. Blue, Co atom; red, O atom.

3. Results and discussion

3.1. CH₄ physisorption on the Co₃O₄ (001) and (011) surfaces

As the Co²⁺ sites are located in the subsurface layer, only the Co³⁺ sites on the surface layer were considered for CH₄ adsorption. The adsorption configurations are shown in Fig. 2. On the (001) and (011) surfaces, the C atom was located at 2.76 Å and 2.57 Å above the surface, respectively. The C–H bond lengths in the adsorption configuration on both surfaces were unchanged with respect to the calculated value for free CH₄ molecule, which was 1.10 Å (close to the experimental value of 1.09 Å), indicating that little interaction existed between CH₄ and the Co₃O₄ surfaces. The CH₄ adsorption energy was calculated using the formula

$$E_{\text{adsorption}} = (E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate}}),$$

where E_{slab} is the energy per surface unit cell of the slab model containing n bulk unit cells, $E_{\text{slab+adsorbate}}$ is the energy of the adsorption complex including those of the relaxed surface and adsorbed CH₄, and $E_{\text{adsorbate}}$ is the energy of the isolated CH₄ molecule. The calculated CH₄ adsorption energies were –0.11 and –0.08 eV for the (001) and (011) planes, respectively, implying that the CH₄ molecule was only weakly physisorbed on the Co₃O₄ surfaces.

3.2. CH₄ → *CH₃ + *H decomposition on Co₃O₄(001) and (011) surfaces

Many previous studies on the CH₄ oxidation mechanism proposed that the first C–H bond activation is the key step for CH₄ conversion [2,38]. Generally, the first C–H bond cleavage can be divided into *CH₃ species binding to one surface site and H* species binding to an adjacent site. As an example, Psogiannakis et al. [38] reported C–H scission accompanied by *CH₃ and *H binding to two adjacent Pt sites. In the present study, the Co₃O₄ surfaces contained both Co ions and O ions. Although CH₄ cannot chemisorb at the surface Co site, we found that CH₄ can be activated at Co–O ion pairs by charge polarization of the C–H bond, leading to the formation of Co–CH₃ and O–H species. To understand the activation nature of the C–H bond on Co₃O₄ nanocrystals, the transition states of the elementary steps were searched using DFT calculations on the Co₃O₄(001) and (011) model surfaces. On each surface, two reaction pathways for C–H bond activation were investigated, for where the proton ended up either on the O^t site or O^o site.

Fig. 2. The calculated CH₄ adsorption configurations.

Table 2

Reaction energies E_r and activation energies E_a for the first C–H bond splitting on the Co₃O₄ (001) and (011) surfaces. Zero point energy is included.

Surface type	E_a at Co–O ^t (eV)	E_r at Co–O ^t (eV)	E_a at Co–O ^o (eV)	E_r at Co–O ^o (eV)
(001)	0.87	0.16	0.98	–0.19
(011)	0.81	–0.62	1.10	0.13

To provide the mechanistic details of the first C–H bond activation, we considered the thermodynamic reaction energies E_r of the C–H splitting and the kinetic barrier energies E_a . The calculated results are shown in Table 2. The positive reaction energy indicated that the oxidation process is endothermic, where a negative value corresponds to an exothermic process following the thermodynamic convention. Despite the high CH₃–H(g) bond dissociation energy (~4.5 eV), the Co₃O₄ nanocrystal surfaces exhibit remarkable reactivity for the first C–H cleavage with rather low barriers (less than 1.1 eV). The geometries of the reactants, transition states (TS), and products at each Co–O pair site are given in Figs. 3 and 4. The bond distances are given in Tables 3 and 4. Compared to the configurations of the reactants, the transition states on both surfaces have a similar configuration transition that accompanies the elongation of the C–H and Co–O bonds and the approaching of the C and Co atoms. Finally, these transition processes led to the production of Co–CH₃ and O–H species. Therefore, it can be inferred that the formation of surface Co–C and O–H bonds decreases the barriers of C–H bond scission and also weakens the surface Co–O bonds.

Table 2 shows that the energy barriers for the first C–H

Fig. 3. Optimized configurations of reactants, transition states (TS), and products on the Co₃O₄(001) surface.

Fig. 4. Optimized configurations of reactants, transition states (TS), and products on the Co₃O₄(011) surface.

Table 3Bond distance of the reactants, transition states (TS), and products on Co₃O₄(001) surface.

Species	$d(\text{C-H})/\text{\AA}$		$d(\text{H-O})/\text{\AA}$		$d(\text{C-Co})/\text{\AA}$		$d(\text{Co-O}^\circ)/\text{\AA}$		$d(\text{Co-O}^\circ)/\text{\AA}$	
	I	II	I	II	I	II	I	II	I	II
Reactant	1.10	1.10	2.57	2.64	2.76	2.76	1.92	1.92	1.91	1.91
TS	1.45	1.50	1.23	1.20	2.10	2.11	1.96	1.92	1.91	1.97
Product	2.62	3.15	0.98	0.98	1.95	1.96	2.03	1.91	1.91	2.01

Pathway I corresponds to the Co–O^t sites and pathway II corresponds to the Co–O^o sites.**Table 4**Bond distance of the reactants, transition states (TS), and products on Co₃O₄(011) surface.

Species	$d(\text{C-H})/\text{\AA}$		$d(\text{H-O})/\text{\AA}$		$d(\text{C-Co})/\text{\AA}$		$d(\text{Co-O}^\circ)/\text{\AA}$		$d(\text{Co-O}^\circ)/\text{\AA}$	
	I	II	I	II	I	II	I	II	I	II
Reactant	1.10	1.10	2.57	2.65	3.13	3.13	1.79	1.79	1.91	1.91
TS	1.45	1.47	1.22	1.23	2.10	2.09	1.99	1.80	1.91	2.01
Product	2.55	2.74	1.00	0.97	1.94	1.96	1.93	1.78	1.89	2.06

Pathway I corresponds to the Co–O^t sites and pathway II corresponds to the Co–O^o sites.

bond activation at the Co–O^t pair are, respectively, 0.11 and 0.29 eV lower than at the Co–O^o pair on the (001) and (011) surfaces, suggesting that the Co–O^t pairs on both the (001) and (011) surfaces are more reactive than the Co–O^o pairs. Therefore, the Co–O^t pairs are the active sites for C–H bond activation on the Co₃O₄ surfaces. In particular, the Co–O^t pairs are expected to be highly active for the C–H bond activation on the (011) surface due to the smaller barrier 0.81 eV and the highly exothermic energy –0.62 eV. For the Co–O^t site, the C–H bond activation is exothermic on the (011) surface and endothermic on the (001) surface, indicating that the C–H scission process on the (011) surface is thermodynamically more favorable (by ~0.78 eV) than on the (001) surface. Concerning the kinetic aspect, however, the barriers on both surfaces are very close, and the entropy contribution may also affect the reactivity.

To understand the interaction of a CH₄ molecule with the active sites on the Co₃O₄ surfaces, Mulliken population analysis was performed on the reactants and products during C–H dissociation. As shown in Table 5, upon CH₃ and H species adsorption, the Co³⁺ ions became less positively charged on both surfaces, indicating that they were reduced to low valent Co ions in the C–H bond activation. Our results also imply that the C–H bond breaking is a heterolytic process (i.e., CH₄ → CH₃^{δ–}(*) + H^{δ+}(*)). This conclusion is in accord with previous speculation that the high oxidation ability of Co₃O₄ originates from the presence of octahedrally coordinated Co³⁺ ions, which become even more oxidizing on the surface due to dangling bonds [8,17–22].

By comparing the C–H bond activation at different Co–O pairs, we found that the different coordination environment for the oxygen ions in the lattice structure is also an essential fac-

tor that affects the activity. For example, the O^t ions on both the Co₃O₄ surfaces are more active than the O^o ions. In other words, the low coordination surface ions contribute to the high activity for methane conversion. Especially, the four-coordinated Co³⁺ ions and two-coordinated O^t ions on the (011) surface are more active than the five-coordinated Co³⁺ ions and three-coordinated O^t ions on the (001) surface. The critical role of the low-coordination oxygen ion on Co₃O₄(011) in catalytic CO oxidation was reported recently by Jiang et al [31].

3.3. Microkinetic analysis

Previously, we reported the experimental results of the catalytic properties of Co₃O₄ nanocrystals with different shape for methane combustion by thermal decomposition [15,16]. CH₄ conversion catalyzed by the Co₃O₄ nanocrystals can occur at a temperature of ~225 °C, and the activity exhibited a significant crystal plane effect: the reaction temperature for CH₄ combustion on the (011) surface was ~25 °C lower than on the (001) surface. To compare the experimental observations with our calculated energetics of the C–H bond activation, we obtained the reaction rate under specific reaction conditions from a microkinetic analysis to see if there is a one-to-one correspondence between C–H bond activation and the CH₄ combustion process on Co₃O₄ nanocrystals.

In the transition state theory, the rate constant is defined as a preexponential (frequency) factor multiplied by a Boltzmann factor [38]:

$$k = A \exp(-E_a/k_B T) = k_B T/h \exp(-\Delta S^\ddagger/k_B) \exp(-E_a/k_B T)$$

In this definition, the preexponential factor *A* is approximately proportional to the temperature, i.e., an elevated temperature will increase the collision frequency between the reactant molecules. This treatment is reasonable for a gas phase reaction because the motion of all the reactants are enhanced with increasing temperature. However, in the present study, the CH₄ molecule reacts with the Co₃O₄ surface via a gas-solid reaction. From a kinetic perspective, the elevated temperature will enhance the desorption of CH₄ and to some extent decrease the probability of its collision with the active site. Therefore, we have modified the rate constant formula by changing the frequency term according to collision theory:

Table 5

Mulliken population of the Co ion on different surfaces before and after the C–H scission.

Active site	$Q_r(\text{Co})/e$	$Q_p(\text{Co})/e$
Co–O ^t on (001)	0.54	0.34
Co–O ^o on (001)	0.54	0.36
Co–O ^t on (011)	0.64	0.38
Co–O ^o on (011)	0.64	0.44

^a Q_r denotes charges of Co ions before C–H scission, and Q_p denotes charges of Co ions after C–H scission.

$$k = \frac{P}{C\sqrt{2\pi mk_B T}} \exp(-\Delta S^\ddagger / k_B) \times \exp(-E_a / k_B T)$$

where P is the partial pressure of CH_4 in the gas phase, m is the mass of CH_4 molecule, and C is the concentration of the active sites per unit area on the surface. Here P was set to equal 2×10^3 Pa to be consistent with our previous study, and C equals $5.9 \times 10^{18} \text{ m}^{-2}$ on the (001) surface and $4.2 \times 10^{18} \text{ m}^{-2}$ on the (011) surface. In this definition, the collision frequency of CH_4 with the surface active sites is described more accurately in the relatively high temperature range, where the elevated temperature has a negative effect on the frequency of CH_4 collision with the surface active sites. A similar treatment for adsorption can be found in a recent study on the microkinetic simulation of temperature-programmed desorption (TPR) on the $\text{RuO}_2(110)$ surface [39].

The estimated rate constants on the different sites on both the Co_3O_4 surfaces are shown in Fig. 5. The order of the rate constants for C–H bond activation, $\text{Co-O}^\text{t}(\text{011}) > \text{Co-O}^\text{t}(\text{001}) > \text{Co-O}^\text{o}(\text{001}) > \text{Co-O}^\text{o}(\text{011})$, was consistent with the order of the calculated energy barriers in Section 3.2. These results implied that the barriers on the Co_3O_4 nanocrystals dominated the activity of C–H bond activation, while the entropy contribution had little effect on the reaction rate of C–H bond activation.

Generally, a range of rate constant of $1\text{--}100 \text{ s}^{-1} \text{ site}^{-1}$ indicates that the reaction processes can be observed in experimental measurements [40]. Therefore, the C–H bond activation on the (011) surface was estimated for $150\text{--}200^\circ\text{C}$, which was not far from the experimental observation that CH_4 combustion occurs at the temperature of $\sim 225^\circ\text{C}$. On the (001) surfaces the reaction temperature at the Co-O^t site was calculated to be $\sim 30^\circ\text{C}$ higher than on the (011) surface, which was consistent with experimental results of CH_4 oxidation reactivity on the different Co_3O_4 nanocrystals [15]. Our results reveal the existence of the crystal plane effect in CH_4 combustion that was observed in our previous experimental study. While we only focused on the first C–H bond activation process, this C–H splitting step is the key step in CH_4 oxidation processes on Co_3O_4 surfaces, as supported by the fact that the reaction temperature of CH_4 combustion in the experiments correlated with the estimated theoretical temperature for C–H bond activation.

Fig. 5. Estimated rate constant at different active sites on the (001) and (011) surfaces.

4. Conclusions

We presented a theoretical study of C–H bond activation on the $\text{Co}_3\text{O}_4(001)$ and $\text{Co}_3\text{O}_4(011)$ surfaces. Two pathways for the first C–H bond cleavage at Co–O pair sites on the two surfaces were studied using DFT calculations with a slab surface model. The surface Co–O pairs are the active sites, where the two ions provide a synergistic effect for the first C–H bond activation to yield surface Co– CH_3 and O–H species. The Co– O^t pairs with O^t bonded to one Co^{2+} ion on the (011) surface are more active for C–H bond activation, with a small barrier of 0.81 eV and an exothermic reaction energy of -0.62 eV. A microkinetic analysis revealed that CH_4 combustion on the Co_3O_4 surface can proceed at $\sim 150\text{--}200^\circ\text{C}$ and exhibited significant dependence on the crystal plane and active sites, consistent with our experimental findings. The low-coordination surface ions are also shown to have high activity for methane conversion. Overall, our microkinetic analysis approach can provide a guide for designing and screening nanocrystal catalysts with high activity and selectivity.

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Graphical Abstract

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Theoretical study of the crystal plane effect and ion-pair active center for C–H bond activation by Co₃O₄ nanocrystals

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Theoretical calculations and a microkinetic analysis of C–H bond activation on Co₃O₄ nanocrystals showed that this occurs on a Co–O ion-pair active center and there is a crystal plane effect and structure sensitivity.

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Co₃O₄纳米晶催化氧化甲烷的理论研究: C–H键活化的晶面效应及活性中心王阳刚^a, 杨小峰^{a,b}, 胡林华^a, 李亚栋^a, 李 隽^{a,*}^a清华大学化学系, 北京100084^b中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023

摘要: 甲烷是一种在自然界中大量存在的原材料, 在取代原油和合成重要化工产品等许多领域具有潜在的应用价值. 然而, 由于CH₄中C–H键的键能特别大(约~4.5 eV), 如何实现甲烷的绿色有效转化在化学化工领域仍然是一个挑战. 本文采用密度泛函理论对Co₃O₄(001)和(011)晶面活化甲烷C–H键的机理进行了理论研究, 得到了如下结论: (1) CH₄的C–H键在Co₃O₄晶面的解离具有很高的活性, 只需要克服大约1 eV的能垒; (2) 与Co²⁺相连的Co–O离子对是CH₄活化的活性位点, 其中两个带正负电荷的离子对C–H解离起着协同作用, 帮助产生Co–CH₃和O–H物种; (3) (011)面的反应活性明显大于(001)面, 与实验的观察一致. 本文的计算结果表明, Co₃O₄纳米晶面对CH₄中C–H键的活化表现出明显的晶面效应和结构敏感效应, Co–O离子对活性中心对于活化惰性的C–H键发挥了关键作用.

关键词: C–H键活化; 甲烷氧化; 晶面效应; 微观动力学分析; 离子对活性中心

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