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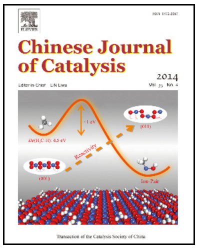

Article

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-CH_3 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.

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 transit (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.

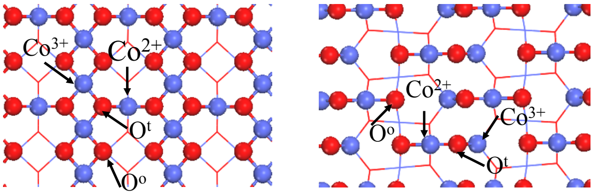
The Co_3O_4(001)-p(1×1) (a = 5.79 Å, b = 5.79 Å) and Co_3O_4(011)-p(1×1) (a = 8.19 Å, b = 5.79 Å) surface slab models cleaved from an ideal bulk spinel structure were used to model the Co_3O_4 planes. Due to the special structure of the spinel lattice, there are two types of surface structure for each 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.

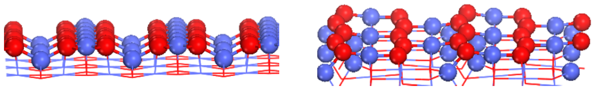
Property	This work	Previous work	Exp.
Lattice constant (Å)	8.19	8.17 [20], 8.12[a]	8.09 [32]
Magnetic moments (μ_B)	2.58/Co^{2+}	2.63 [28], 2.53[a] /Co^{2+}	3.02/Co^{2+} [33]
Electronic gap (eV)	Γ-Γ: 2.20 X-X: 1.82	Γ-Γ: 2.06 [28], 1.67[a] X-X: 1.75[28], 1.23[a]	Γ-Γ: 1.88–2.00[b] X-X: 1.44–1.52[b]

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

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



(a) Top view-(001) (c) Top view-(011)



(b) Side view-(001) (d) Side view-(011)

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.