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Article

Effect of Pd doping on CH₄ reactivity over Co₃O₄ catalysts from density-functional theory calculations

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ABSTRACT

Palladium oxide (PdO_x) and cobalt oxide (Co₃O₄) are efficient catalysts for methane (CH₄) combustion, and Pd-doped Co₃O₄ catalysts have been found to exhibit better catalytic activities, which suggest synergism between the two components. We carried out first-principles calculations at the PBE+U level to investigate the Pd-doping effect on CH₄ reactivity over the Co₃O₄ catalyst. Because of the structural complexity of the Pd-doped Co₃O₄ catalyst, we built Pd-doped catalyst models using Co₃O₄(001) slabs with two different terminations and examined CH₄ reactivity over the possible Pd–O active sites. A low energy barrier of 0.68 eV was predicted for CH₄ dissociation over the more reactive Pd-doped Co₃O₄(001) surface, which was much lower than the 0.98 and 0.89 eV that was predicted previously over the more reactive pure Co₃O₄(001) and (011) surfaces, respectively. Using a simple model, we predicted CH₄ reaction rates over the pure Co₃O₄(001) and (011) surfaces, and Co₃O₄(001) surfaces with different amounts of Pd dopant. Our theoretical results agree well with the available experimental data, which suggests a strong synergy between the Pd dopant and the Co₃O₄ catalyst, and leads to a significant increase in CH₄ reaction rate.

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1. Introduction

Methane (CH₄) is a major component of natural gas and is an important feedstock for the chemical and energy industries. Because of its wide availability, it has been studied extensively for efficient conversion into fuels and chemicals, such as syngas, ethylene, methanol, and aromatics [1–5]. Because of the significant greenhouse effect of CH₄, which is stronger than CO₂, there is significant interest in the efficient combustion of CH₄ at low concentrations to reduce its emission and to minimize its environmental impact. However, under normal conditions, CH₄ is very stable as a result of the high CH₃–H bond energy, which

makes the splitting of the first C–H bond in CH₄ the most difficult step in CH₄ activation. The energy barrier to this splitting is often used as an important gauge for the activity of CH₄-activation catalysts [6,7].

Noble metals and transition-metal oxides have been studied extensively to catalyze CH₄ combustion [8–14]. Palladium (Pd) has been shown to have an excellent catalytic activity for CH₄ combustion. Wang et al. [15] loaded 0.2% Pd on Si(5.2)–Al–O(1100)–550 and measured temperatures at 10%, 50%, and 90% CH₄ conversions (*T*₁₀, *T*₅₀, and *T*₉₀) of 335, 410, and 485 °C, respectively. Jorgensen et al. [16] predicted energy barriers for the first step of CH₄ splitting on Pd(001) and (011)

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surfaces of 0.79 eV and 0.99 eV, where weak CH₄ physisorption was ignored. Neurock, Iglesia, and co-workers [8] predicted energy barriers for the first CH₄ dissociation step over Pd(111), PdO(101), and PdO(100) surfaces of 0.75, 0.64, and 1.35 eV, respectively. However, the high cost of Pd may prevent its industrial application for CH₄ combustion. Cobalt oxide (Co₃O₄) nanocatalysts have been studied extensively for their excellent catalytic activity and because of the much lower price of Co than Pd, and CH₄ combustion was initiated at very low temperatures ($T_{\text{light-off}}$) of 200, 175, and 175 °C for the nanoparticle, nanorod, and nanoplate Co₃O₄ catalysts, respectively [17]. The lowest energy barriers of the first C–H bond splitting of CH₄ were calculated to be 0.98 and 0.89 eV over the Co₃O₄(001) and (011) surfaces [7]. Pd-doped Co₃O₄ (Pd/Co₃O₄) catalysts have been prepared to increase the catalytic activity and to control the cost of the catalytic material [19,20]. Li et al. [21] investigated CH₄ combustion over Pd/Co₃O₄ catalysts, and when doped with Pd by 1% to 10%, $T_{\text{light-off}}$, T_{50} , and T_{100} were reduced significantly from 250 to 170, 360 to 246, and 480 to 300 °C, respectively. Li and co-workers [21] prepared Pd-doped Co₃O₄ catalysts of different shapes, such as nanocubes, nanobelts, and nanosheets, with 1%, 2%, and 5% Pd. Their reactivities were found to increase as nanocube < nanobelt < nanosheet with the same percentage of Pd dopant, and the reactivities also increased with increasing percentage of Pd dopant. Therefore, the Pd dopant has a positive effect on the catalytic activity of the Co₃O₄ catalyst for CH₄ combustion.

The Pd/Co₃O₄ catalysts can be expected to have more complex structures than the Pd and Co₃O₄ catalysts because of the presence of palladium oxide (PdO_x) and Co₃O₄ surfaces and structures in-between. Because CH₄ activation has been investigated by first-principles calculations over different Pd, PdO, and Co₃O₄ surfaces, we have examined the reactivity of the Co₃O₄(001) surface with an atomic Pd dopant, and this approach has been used to study the effect of dopant on different catalysts [22,23]. The Co₃O₄(001) surface was the main nanoparticle- or nanocube-Co₃O₄-catalyst exposed surface. Two surface terminations were considered, and one was predicted to be more stable under O₂-rich conditions [17,24]. Energy barriers for the first C–H bond dissociation of CH₄ were calculated and compared with those calculated previously for the Pd, PdO, and Co₃O₄ surfaces. Results from the first-principles calculations were used to predict the CH₄ reaction rates at different temperatures with different Pd dopant concentrations. These rates were compared with available experimental measurements to determine the effect of Pd dopant on the Co₃O₄ catalyst reactivity.

2. Computational

Periodic density-functional theory (DFT) calculations were carried out with the PBE exchange-correlation functional [25] and the PAW pseudopotentials [26,27], as implemented in the Vienna *ab initio* program (VASP) [28,29]. DFT calculations with an exchange-correlation functional such as PBE in the generalized gradient approximation (GGA) treat strongly correlated systems with difficulty [30–34]. For this reason, we carried out

PBE+U calculations with the approach developed by Dudarev et al. [35], where the energy depends on a single effective parameter of $U_{\text{eff}} = U - J$. We used a U_{eff} value of 3.0 eV for Co and 7.0 eV for Pd, and similar values were used in the literature to treat related systems [8,36].

Default potentials were used for all atoms, and a plane wave kinetic-energy cutoff of 520 eV was used for better accuracy. Bulk Co₃O₄ is anti-ferromagnetic, so we applied spin polarization for all calculations with the correct spin configuration. Gaussian smearing with a width of 0.05 eV was used for the bulk and surfaces. The electronic energy converged to 10^{−5} eV. To calculate the bulk structure of Co₃O₄, a primitive unit cell with a Γ -centered k-point mesh of (5 × 5 × 5) was used. The mesh size was optimized to converge the absolute energy to ~10^{−4} eV. The lattice constant was predicted to be 8.16 Å for the conventional unit cell, which is consistent with previous work, and is slightly higher than the experimental value (8.09 Å) [37]. The calculated magnetic moment of the Co²⁺ ion is 2.65 μ_B , which is also consistent with previous predictions [38], and all are lower than the experimental value by ~0.4 μ_B [39]. Our calculated direct band gaps of bulk Co₃O₄ are 2.32 and 1.66 eV for Γ – Γ and X–X, respectively, which also agrees well with previous predictions [38], although the experimental values have a wide spread [40–43].

Symmetric slab models were first built and optimized for clean Co₃O₄(001) surfaces with two possible terminations denoted as (001)–A and (001)–B. Pd dopant was used to replace one of the Co ions on the relaxed side of the surface denoted as Pd/(001)–A and Pd/(001)–B, which is known to have the highest reactivity for CH₄ dissociation. The Co₃O₄(001) surface is more stable than the other surfaces. The bottom half of the slab was kept fixed at its bulk position, and a vacuum layer of 15 Å was inserted between adjacent slabs. Adsorptions and reactions were allowed only on the relaxed side of the slab. The p(1×1) surface was used with a Γ -centered k-point mesh of (3 × 3 × 1). Transition states were located with the climbing image–nudged elastic band (CI–NEB) approach [44,45]. For transition-state calculations, the force on each relaxed atom converged to 0.05 eV/Å. Vibrational frequencies of the adsorbates were calculated, and zero point energies were included in the final energies.

The dissociation energy (E_r) of CH₄ over the Pd/Co₃O₄ slab surface is defined as:

$$E_r(\text{CH}_4; \text{M-O}) = E(\text{CH}_3\text{-M}; \text{H-O}) - E(\text{CH}_4; \text{M-O}) \quad (1)$$

where the two terms on the right are the total energies of CH₄ adsorbed on the slab surface after and before its dissociation, i.e., the chemisorption and physisorption structures. For the pure Co₃O₄ slab surface, M = Co, whereas for the Pd/Co₃O₄ slab surface, M = Pd. The energy barrier (E_a) of CH₄ dissociation is defined as:

$$E_a(\text{CH}_4; \text{M-O}) = E_{\text{TS}}(\text{CH}_3\text{-M}; \text{H-O}) - E(\text{CH}_4; \text{M-O}) \quad (2)$$

where the first term on the right is the total energy of the transition state for CH₄ dissociation on the slab surface. Details for the calculation of reaction rates will be given in the next section.

3. Results and discussion

3.1. CH₄ dissociation on Pd/Co₃O₄(001) surfaces

As shown in Fig. 1, the p(1×1) (001)–A surface model is composed of Co₈O₁₂, and its surface consists of two penta-coordinated Co^o_{5c}, two tri-coordinated O_{2o,1t}, and two tri-coordinated O_{3o}, where o and t in the superscripts and subscripts denote the octahedral and tetrahedral Co ions, respectively. The p(1×1) Pd/(001)–A surface was arrived at by replacing one Co^o_{5c} with Pd, which lead to an atomic composition of PdCo₇O₁₂, and its surface consists of a penta-coordinated Co^o_{5c}, a penta-coordinated Pd_{5c}, two tri-coordinated O_{1o,1t,Pd}, and two tri-coordinated O_{2o,Pd}. Two distinct Pd–O pair sites can be identified as the Pd_{5c}–O_{1o,1t,Pd} pair site (labeled as the α site), and the Pd_{5c}–O_{2o,Pd} pair site (labeled as the β site).

The p(1×1) (001)–B surface model is composed of Co₁₀O₁₂, and its surface consists of two penta-coordinated Co^o_{5c}, a tetra-coordinated Co^t_{4c}, two tetra-coordinated O_{2o,2t}, and two tetra-coordinated O_{3o,1t}. Similarly, the p(1×1) Pd/(001)–B surface was obtained by replacing one Co^o_{5c} with Pd, which lead to an atomic composition of PdCo₉O₁₂, and its surface consists of a penta-coordinated Co^o_{5c}, a penta-coordinated Pd_{5c}, and a tetra-coordinated Co^t_{4c}, two tetra-coordinated O_{2t,1o,Pd}, and two tetra-coordinated O_{2o,1t,Pd}. Two different Pd–O pair sites are also found, the Pd_{5c}–O_{2t,1o,Pd} pair site (labeled as the α site) and the Pd_{5c}–O_{2o,1t,Pd} pair site (labeled as the β site).

The potential-energy surface for CH₄ dissociation on the pure Co₃O₄(001) surface has been calculated previously by Li and co-workers [7], and by Hu and co-workers [46]. The potential-energy surface for CH₄ dissociation on the Pd/(001) surfaces is shown in Fig. 2. The physisorption energies of CH₄ at the α and β pair sites were calculated to be –0.10 and –0.13 eV on the Pd/(001)–A surface, and –0.08 and –0.13 eV on the Pd/(001)–B surface, so the physisorption of CH₄ on the Pd/(001) surfaces was predicted to be fairly weak. For the Pd/(001)–A surface, the energy barrier for CH₄ dissociation at the α pair site from the physisorption state was predicted to be 0.68 eV, which is lower than that at the β pair site by 0.34 eV, so the α site is much more reactive to CH₄ than the β site. For the

Pd/(001)–B surface, the energy barrier for CH₄ dissociation at the α pair site was predicted to be 1.12 eV, which is lower than that at the β pair site by 0.27 eV.

To understand the structural changes during CH₄ dissociation over the Pd/(001) surface, we list the Pd–O bond distances in the physisorption, transition, and chemisorption states in Table 1. Because of the very weak interaction between CH₄ and the Pd/(001) surface in the physisorption state, the Pd–O bond distance in the physisorption state is essentially the same as that on the clean surface. When CH₄ is split over the Pd/(001) surface, the Pd–O bond length of the Pd–O pair site that is involved directly is elongated, whereas most other Pd–O bond lengths are longer. Thus, the Pd–O bond of the active Pd–O pair site weakens, which can also be attributed to an increase in coordination numbers of the relevant Pd and O atoms. This leads to a strengthening of Pd–O bonds at the diagonal Pd–O pair sites. Various Pd–O bonds on the clean Pd/(001)–B surface are longer than those on the clean Pd/(001)–A surface, which can also be attributed to the higher coordination numbers of the relevant Pd and O atoms and leads to a much-reduced catalytic activity of the Pd/(001)–B surface for CH₄ splitting. Thus, qualitative analyses and quantitative calculations show that the Pd/(001)–A surface is more reactive than the Pd/(001)–B surface. The higher reactivity of the Pd/(001)–A surface than the Pd/(001)–B surface can be explained by coordination numbers of the Pd and O active sites. As shown in Fig. 1, whereas the coordination number of the Pd site is five on both surfaces, that of the O site is three on the Pd/(001)–A surface and four on the Pd/(001)–B surface. Because of the stronger steric effect on the Pd/(001)–B surface, the Pd/(001)–A surface is considerably more reactive.

As mentioned previously, CH₄ dissociation on the pure Co₃O₄(001) and (011) surfaces has been investigated previously by Li and co-workers [7], and by Hu and co-workers [46]. Table 2 compares our calculated reaction energies and energy barriers as defined in Eqs. (1) and (2) with those predicted previously for those on pure Co₃O₄ surfaces. The α pair site has been predicted to be more reactive than the β pair site, and the

Fig. 1. Top and side views of slab models. Surface Co, Pd, and O atoms are shown in blue, cyan, and red, respectively.

Fig. 2. Potential-energy profile of CH₄ dissociation at Pd/(001) surfaces.

Table 1

Pd–O bond lengths (Å) during CH₄ dissociation over Pd/(001) surfaces.

State	Pd/(001)-A				Pd/(001)-B			
	Dis. @ α site		Dis. @ β site		Dis. @ α site		Dis. @ β site	
	Pd–O _α	Pd–O _β	Pd–O _α	Pd–O _β	Pd–O _α	Pd–O _β	Pd–O _α	Pd–O _β
Physisorption state	2.02 ^a	1.98	2.02	1.97 ^a	2.16 ^a	2.14	2.16	2.14 ^a
	2.02	1.97	2.02	1.97	2.16	2.14	2.16	2.14
Transition state	2.03 ^a	1.95	1.97	2.00 ^a	2.25 ^a	2.13	2.14	2.22 ^a
	1.98	1.96	1.98	1.96	2.17	2.18	2.19	2.16
Chemisorption state	2.07 ^a	1.94	1.94	2.05 ^a	2.25 ^a	2.05	2.08	2.28 ^a
	1.99	1.97	1.98	2.00	2.16	2.12	2.22	2.08

^a The bond length for the active Pd–O pair site.

Table 2

Reaction energies (E_r) and energy barriers (E_a) for CH₄ dissociation on the Pd/(001) surfaces, compared with those calculated for the (001) and (011) surfaces of pure Co₃O₄.

Surface	α sites		β sites	
	E_r /eV	E_a /eV	E_r /eV	E_a /eV
Pd/(001)-A	-0.27	0.68	-0.15	1.02
Pd/(001)-B	0.57	1.12	0.91	1.39
(001)	0.27 [7]	0.98 [7]	-0.08 [7]	1.09 [7]
(011)	-0.54 [7], -0.25 [46]	0.89 [7], 0.92 [46]	0.21 [7], -0.03 [46]	1.18 [7], 1.05 [46]

lowest energy barriers of CH₄ splitting over the pure Co₃O₄(001) and (011) surfaces were calculated previously to be 0.98 and 0.89 eV, respectively, which are both higher than that on the Pd/(001) surface of 0.68 eV. Thus, we predict the

Pd-doped Co₃O₄(001) surface to be more active than pure Co₃O₄(001) and (011) surfaces, which is consistent with the experimental results. The catalytic activity of CH₄ combustion was promoted by the Pd dopant for the Co₃O₄ catalysts.

To rationalize the improvement in reactivity by Pd doping of the pure $\text{Co}_3\text{O}_4(001)\text{-A}$ surface, we calculated Bader charges at the M–O (M = Co and Pd) active sites before and after CH_4 dissociation. Bader charges at the Co and O α active sites on the $\text{Co}_3\text{O}_4(001)\text{-A}$ surface were predicted to become more negative by 0.08 |e| and 0.22 |e|, respectively, which is consistent with the fact that the Co–O pair site was reduced upon CH_4 dissociation. Bader charges at the Pd and O α active sites on the $\text{Pd}/(001)\text{-A}$ surface were predicted to become more negative by 0.14 |e| and 0.20 |e|, respectively. Thus, whereas the O site gains a similar number of electrons, the Pd site gains considerably more electrons than the Co site, which is consistent with the higher reactivity of the $\text{Pd}/(001)\text{-A}$ surface than the pure $\text{Co}_3\text{O}_4(001)\text{-A}$ surface.

We can compare the lowest energy barrier for CH_4 dissociation on the $\text{Pd}/(001)$ surface with those calculated previously for different PdO surfaces. The energy barriers for CH_4 dissociation on the $\text{PdO}(001)$ and (101) surfaces were predicted previously to be 1.35 and 0.64 eV [8], which were in fact effective energy barriers from CH_4 in the gas phase and is valid because of very weak CH_4 physisorption on all surfaces, especially at modest to high temperatures. In comparison, we predicted the lowest effective energy barrier on the $\text{Pd}/(001)$ surface to be 0.58 eV (Fig. 2), which is lower than that on the $\text{PdO}(001)$ and (101) surfaces. The effective energy barrier for CH_4 dissociation on the $\text{Pd}/(001)$ surface was also lower than those on the $\text{Pd}(001)$, (011) , and (111) surfaces [8,17]. Thus, the $\text{Pd}/(001)$ surface is more reactive than the pure $\text{Co}_3\text{O}_4(001)$ and (011) surfaces and the different Pd and PdO surfaces, which suggests a synergistic relationship between the Pd dopant and the Co_3O_4 catalyst, and is consistent with experimental observations [21,22].

3.2. Thermodynamic stability of $\text{Co}_3\text{O}_4(001)$ and $\text{Pd}/(001)$ surfaces

Because the $\text{Co}_3\text{O}_4(001)\text{-A}$ and B surface slabs have different atomic compositions, their relative stability is affected by temperature and by the O_2 partial pressure. The relative stability of a surface slab is determined by its surface energy, and for the $\text{Co}_3\text{O}_4(001)$ and $\text{Pd}/(001)$ surface slabs shown in Fig. 1, their surface energies with respect to bulk PdO and Co_3O_4 and gaseous O_2 can be calculated from Eq. (3) [47].

$$\gamma(T, P) = 1/(2A) \cdot \{G_{\text{PdCo}(x-1)\text{O}_y}^{\text{slab}}(T, P, N_{\text{Pd}}, N_{\text{Co}}, N_{\text{O}}) - N_{\text{Pd}}G_{\text{PdO}}^{\text{bulk}}(T) - (N_{\text{Co}}/3)G_{\text{Co}_3\text{O}_4}^{\text{bulk}}(T) - (1/2) \cdot [N_{\text{O}} - (4/3)N_{\text{Co}} - N_{\text{Pd}}] \cdot \mu_{\text{O}_2}(T, P_{\text{O}_2})\} \quad (3)$$

here, $G_{\text{PdCo}(x-1)\text{O}_y}^{\text{slab}}$, $G_{\text{PdO}}^{\text{bulk}}$ and $G_{\text{Co}_3\text{O}_4}^{\text{bulk}}$ are the free energies of the unit cell of the slab and the stoichiometric units of bulk PdO and Co_3O_4 , respectively; N_{Pd} , N_{Co} , and N_{O} are the number of Pd, Co, and O atoms in the unit cell of the slab, respectively; and A is the surface area of the unit cell. For the bulk and the slab, the free energy does not depend strongly on the temperature, and we made the approximation of $G^{\text{bulk}} \approx E^{\text{bulk}}$ and $G^{\text{slab}} \approx E^{\text{slab}}$ [48]. The chemical potential of O_2 as a gaseous molecule was calculated from the expression for an ideal gas given by Herrmann and Heimel [49], and the dependence of chemical potential on the temperature agreed well with that calculated

from the Shomate equation.

$$\mu_{\text{O}_2}(T, P_{\text{O}_2}) = E_{\text{O}_2} + k_{\text{B}}T \ln[P_{\text{O}_2} \lambda^3 / (k_{\text{B}} T)] \quad (4)$$

here, E_{O_2} is the electronic energy of the O_2 molecule, k_{B} is the Boltzmann constant, and λ is given by Eq. (5), where h is the Planck constant and m is the molecular mass.

$$\lambda = h(2\pi m T)^{-1/2} \quad (5)$$

Fig. 3 shows the surface energies of the $\text{Co}_3\text{O}_4(001)$ and $\text{Pd}/(001)$ surface slabs calculated at different temperatures, and for convenience, we set the partial pressure of O_2 as 1 bar, which is sufficiently close to that used in the CH_4 combustion reaction. Relative to bulk PdO and Co_3O_4 , the $(001)\text{-A}$ and $\text{Pd}/(001)\text{-A}$ slabs become increasingly less stable as the temperature increases, whereas the opposite results for the $(001)\text{-B}$ and $\text{Pd}/(001)\text{-B}$ slabs. The $(001)\text{-A}$ slab was predicted to be more stable than the $(001)\text{-B}$ slab below $\sim 350^\circ\text{C}$, whereas the $\text{Pd}/(001)\text{-A}$ slab was calculated to be more stable than the $\text{Pd}/(001)\text{-B}$ surface below $\sim 250^\circ\text{C}$. Compared with the $(001)\text{-A}$ slab, the $\text{Pd}/(001)\text{-A}$ slab is more stable below $\sim 200^\circ\text{C}$, but becomes less stable above this temperature, so the formation of the $\text{Pd}/(001)\text{-A}$ slab from the $(001)\text{-A}$ slab and bulk PdO was predicted to be favorable at a relatively low temperature. The $\text{Pd}/(001)\text{-B}$ slab was calculated to be considerably more stable than the $(001)\text{-B}$ slab within the investigated temperature range, and the formation of the $\text{Pd}/(001)\text{-B}$ slab from the $(001)\text{-B}$ slab and bulk PdO was predicted to be very favorable.

3.3. Simulated reaction rates over Pd-doped Co_3O_4 catalysts

Li and co-workers [22] reported that Pd-doped Co_3O_4 catalysts have a higher catalytic activity than pure Co_3O_4 catalysts for CH_4 combustion, and the percentage of Pd could be as low as 1%. This suggests that the Pd–O site over the Pd-doped Co_3O_4 catalysts is more reactive than the Co–O site on pure Co_3O_4 catalysts, which is consistent with our calculated energy barriers listed in Table 2. For a quantitative comparison between the catalytic activity, we calculated the CH_4 reaction rates over different Pd–O sites of the $\text{Pd}/(001)\text{-A}$ and $\text{Pd}/(001)\text{-B}$ surfaces. The reaction rate can be written as Eq. (6) based on the collision theory [50],

Fig. 3. Surface energies of $\text{Co}_3\text{O}_4(001)$ and $\text{Pd}/(001)$ surface slabs at a standard pressure of 1 bar.

$$r = A\sigma P_M (2\pi mk_B T)^{-(1/2)} \exp(-E_a/(k_B T)) \quad (6)$$

where A is the surface area per active site ($1.66 \times 10^{-19} \text{ m}^2$ for Pd/(001)-A and $1.11 \times 10^{-19} \text{ m}^2$ for Pd/(001)-B), σ is the sticking coefficient for the collision process (~ 1), P_M is the experimental partial pressure of CH_4 in the gas phase ($\sim 1000 \text{ Pa}$) [22], m is the mass of CH_4 molecule, k_B is the Boltzmann constant, and E_a is the effective energy barrier for CH_4 splitting from CH_4 in the gas phase, which is slightly lower than that in Table 2.

Fig. 4 shows that the calculated reaction rates at different Pd-O pair sites over the Pd/(001)-A and Pd/(001)-B surfaces were predicted to follow Pd/(001)-A- α > Pd/(001)-A- β > Pd/(001)-B- α > Pd/(001)-B- β , which is consistent with the sizes of their effective energy barriers. The reaction rates are sensitive to the effective energy barrier. For example, the effective energy barrier is 0.58 eV at the α site on the Pd/(001)-A surface, and it is 0.89 eV at the β site on the same surface. The difference in the reaction rates can be estimated from the difference in their effective energy barriers (ΔE_a) by ignoring the effect of the pre-exponential factor to be $\exp(\Delta E_a/k_B T)$, which is approximately five orders of magnitude at a room temperature of 20 °C. Thus, it is reasonable to consider only the contribution to the total reaction rate at the most active Pd-O pair site when multiple pair sites are available for CH_4 activation, such as the α site on the Pd/(001)-A or Pd/(001)-B surface.

It is expected that a small portion of the Co_3O_4 catalyst surface will be affected by doping with a small amount of Pd, in proportion to the molar percentage of the dopant (X). If we assume that only the most stable $\text{Co}_3\text{O}_4(001)$ surface is present and affected, the total reaction rate can be calculated to be:

$$r = r_{(001)}(1-X) + r_{\text{Pd}/(001)}X \quad (7)$$

where $r_{(001)}$ and $r_{\text{Pd}/(001)}$ are the reaction rates of CH_4 combustion over pure and Pd-doped $\text{Co}_3\text{O}_4(001)$ surfaces.

The calculated reaction rates over the pure and Pd-doped Co_3O_4 surfaces are shown in Fig. 5, which follows the order of (001) < (011) < 1% Pd/(001) < 2% Pd(001) < 3% Pd(001). For the Co_3O_4 surfaces, the order of their reaction rates is consistent with their effective energy barriers, which suggests that the reactivity is dependent primarily on the energy barrier. For

Fig. 4. Calculated reaction rates at different active sites over the Pd/(001)-A and Pd/(001)-B surfaces.

Fig. 5. Simulated reaction rates over pure and Pd-doped Co_3O_4 surfaces.

the Pd-doped $\text{Co}_3\text{O}_4(001)$ surface, the catalytic activity depends quite strongly on the percentage of the dopant. Even with a small amount of dopant (1%), the calculated reaction rate is considerably higher than that over the pure Co_3O_4 surface, and even higher than that over the more reactive (011) surface. At 275 °C, the reaction rates were calculated to be 0.03, 0.11, 0.14, 0.29, and 0.43 mol/s for the (001), (011), 1% Pd/(001), 2% Pd(001), and 3% Pd(001) surfaces. The ratios of the reaction rates of (011), 1% Pd/(001), 2% Pd(001), and 3% Pd(001) over (001) are 3.67, 4.66, 9.67, and 14.33, respectively. These agree well with the experimental ratios in the reaction rates as measured by Li and co-workers [22].

4. Conclusions

First-principles calculations were used to investigate the dissociation of CH_4 over Pd-doped $\text{Co}_3\text{O}_4(001)$ surfaces using two slab models with different terminations. CH_4 physisorption over the Pd-doped $\text{Co}_3\text{O}_4(001)$ surfaces was predicted to be very weak, similar to that over pure $\text{Co}_3\text{O}_4(001)$ surfaces. CH_4 dissociation was predicted to be kinetically preferable at the α Pd-O pair site over the Pd/ $\text{Co}_3\text{O}_4(001)$ -A surface, which is also consistent with that over the pure $\text{Co}_3\text{O}_4(001)$ surface. Pd-doped $\text{Co}_3\text{O}_4(001)$ was predicted to be more reactive to CH_4 than the pure $\text{Co}_3\text{O}_4(011)$ surface, based on comparison with the previously calculated energy barriers. The CH_4 reaction rates over the (001), (011), 1% Pd/(001), 2% Pd/(001), and 3% Pd/(001) were calculated at different temperatures and were found to depend strongly on the exposed facet, the Pd-O or Co-O active pair site, and the percentage of Pd dopant. Our qualitative comparison of the calculated energy barriers and the quantitative comparison of the predicted reaction rates show that the Pd dopant increases the reactivity of the Co_3O_4 catalyst significantly, which is consistent with the experimental observation.

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Graphical Abstract

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Effect of Pd doping on CH₄ reactivity over Co₃O₄ catalysts from density-functional theory calculations

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DFT calculations show that Pd-doped Co₃O₄ catalysts are more reactive for CH₄ dissociation than pure Co₃O₄ catalysts because of the much lower energy barrier and thus the higher estimated reaction rates.

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Pd掺杂对Co₃O₄催化CH₄燃烧反应的影响: 密度泛函理论计算

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摘要: 研究发现, Pd和Co₃O₄催化剂均可有效地催化甲烷燃烧反应, 且Pd掺杂的Co₃O₄催化剂上甲烷反应活性优于单纯的Pd和Co₃O₄催化剂, 可见两者存在明显的协同效应. 然而由于Co₃O₄本身复杂的表面配位环境, 相关理论模拟研究依然较少. 同时, 由于甲烷分子中C–H键有着非常高的键能, 且该分子具有很高的对称性, 导致C–H键活化往往是甲烷选择转化和完全燃烧反应中最困难的一步.

由于Co₃O₄表面电子结构比较复杂, 因此本文基于Co₃O₄(001)晶面的两种不同暴露面来构建和模拟Pd掺杂Co₃O₄表面Pd–O位点的甲烷反应活性. 对于Co₃O₄(001)–A晶面, 暴露面金属离子只有未饱和的八面体Co⁰, 而(001)–B晶面, 还有四面体Co¹. 由于Pd取代Co¹后所形成的Pd/(001)–B面更不稳定, 因而选择了较稳定的Pd替换Co⁰结构模型. 基于第一性原理PBE+U计算的Pd/(001)表面甲烷活化能垒来探讨Pd掺杂对Co₃O₄表面催化活性的影响. 计算表明, 甲烷在Pd掺杂的(001)面上最低解离能垒为0.68 eV, 明显低于在Co₃O₄(001)和(011)面的(分别为0.98和0.89 eV), 表明Pd掺杂的(001)表面催化活性要远高于纯的Co₃O₄(001)和(011)表面.

为了进一步理解Pd掺杂影响Co₃O₄表面甲烷反应活性的原因, 我们计算了反应位点相关原子的Bader电荷. 结果表明, 当CH₃^δ吸附于Pd/(001)–A面Pd位点时, Pd较(001)面上Co位点能从CH₃^δ获得更多电子, 这与Pd较Co有更强的氧化性一致. 我们也对比了(001)–A, (001)–B, Pd/(001)–A和Pd/(001)–B在氧气分压为常压及不同温度下表面能的大小, 并发现在与反应相关的温度区间(001)–A表面较(001)–B表面更为稳定, 同样地Pd/(001)–A表面也较Pd/(001)–B表面更为稳定, 且Pd/(001)–A表面与(001)–A表面稳定性差别不大, 因此Pd单原子掺杂的(001)表面模型在热力学上较为稳定, 且根据计算的能垒, (001)–A和Pd/(001)–A表面对甲烷活化的贡献最大.

为了更好与实验结果对比, 我们构建了简单的动力学模型, 并计算了甲烷在Co₃O₄(001), (011)和1%, 2%, 3%Pd掺杂的Co₃O₄(001)表面的甲烷燃烧速率. 计算表明即使较低量的Pd也可明显提高甲烷燃烧速率, 与实验数据吻合较好, 表明掺杂Pd显著增加Co₃O₄催化甲烷燃烧.

关键词: 四氧化三钴; 钯掺杂; 甲烷燃烧; 密度泛函理论计算; 反应速率; 碰撞理论

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