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Article

Sr-doping effects on La_2O_3 catalyst for oxidative coupling of methane

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ABSTRACT

Density-functional theory calculations were carried out to study the strontium (Sr)-doping effect on methane activation over a lanthanum-oxide (La_2O_3) catalyst for the oxidative coupling of methane (OCM) using the cluster model. Eight Sr-doped La_2O_3 cluster models were built from pure La_2O_3 clusters that were used previously to model the La_2O_3 catalyst. These form two distinct categories, namely, those without a radical character ($\text{LaSrO}_2(\text{OH})$, La_2SrO_4 , $\text{La}_3\text{SrO}_5(\text{OH})$, and $\text{La}_5\text{SrO}_8(\text{OH})$) and those with a radical character (LaSrO_3 , $\text{La}_2\text{SrO}_4(\text{OH})$, La_3SrO_6 , and La_5SrO_9). The potential-energy surface for CH_4 activation to form a CH_3 radical at different Sr–O and La–O pair sites on these Sr-doped La_2O_3 clusters was calculated to study the Sr-doping effect on the OCM catalytic activity. CH_4 physisorption and chemisorption energies, and activation barriers, and CH_3 desorption energies were predicted. Compared with the pure La_2O_3 clusters, in general, the Sr-doped La_2O_3 clusters are thermodynamically and kinetically more reactive with CH_4 . For the Sr-doped La_2O_3 clusters without the radical character, the Sr–O pair site is more reactive with CH_4 than the La–O pair site, although a direct release of the CH_3 radical is also highly endothermic as in the case of the pure La_2O_3 clusters. In contrast, for the Sr-doped La_2O_3 clusters with a radical character, the activation of CH_4 at the oxygen radical site and the release of the CH_3 radical are much easier. Thus, our calculations suggest that the Sr dopant prompts the OCM catalytic activity of the La_2O_3 catalyst by providing a highly active oxygen-radical site and by strengthening the basicity of the M–O pair site, which leads to lower CH_4 activation energies and lower CH_3 desorption energies.

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1. Introduction

Methane is a major component of natural gas and is used extensively by industries to produce fuels and valuable chemicals. Methane conversion is carried out mainly via indirect routes by its transformation to synthesis gas ($\text{CO} + \text{H}_2$) via highly endothermic reforming reactions and followed by fur-

ther conversion to fuels and chemicals via the highly exothermic Fischer-Tropsch synthesis reaction. To reduce capital costs and energy consumption, direct routes such as the oxidative coupling of methane (OCM) reaction have been studied extensively for the efficient conversion of methane into fuels and chemicals [1–6]. Over the past three decades, many OCM catalysts have been developed, although the commercialization of

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the OCM process has not been achieved because of the limited product yield and high reaction temperature [7].

La_2O_3 -based catalysts exhibit an excellent catalytic activity and thermal stability towards the OCM reaction [8–12]. Deboy and co-workers [10,13,14] published a series of research studies on Sr-doped La_2O_3 catalyst, and found that the yield of C_2 hydrocarbons could reach 20% with a C_2 hydrocarbon selectivity of 69%. Choudhary and co-workers [15] studied a series of Sr-doped rare-earth metal oxides (La, Ce, Pr, Ne, Sa, Eu, Ga, Dy, Er, and Yb), and found that the Sr-doped La_2O_3 catalyst exhibited the best catalytic performance. Bailer and co-workers [16] claimed that La_2O_3 or samarium(III) oxide catalysts doped with Ca, Sr, or Ba were the most active OCM catalysts of the irreducible metal oxide catalysts. Zhu and co-workers [17] found that the hybrid Sr-doped La_2O_3 nanofiber catalysts exhibited a superior catalytic performance for the OCM reaction over conventional Sr-doped La_2O_3 spherical catalysts, where the CH_4 conversion rate and C_2 selectivity reached 35% and 47% at 500 °C with the hybrid La_2O_3 catalyst doped with 8.6 wt% Sr and at an initial ignition temperature of only ~500 °C.

In our previous studies, we performed density-functional theory (DFT) and coupled-cluster [18] calculations using the cluster models, $(\text{La}_2\text{O}_3)_n$ ($n = 1, 2, 3$), to investigate the reactivity of CH_4 at the $\text{La}^{3+}\text{--O}^{2-}$, $\text{La}^{3+}\text{--O}_2^{2-}$, and $\text{La}^{3+}\text{--CO}_3^{2-}$ acid–base pair sites [19–21]. We predicted that the $\text{La}^{3+}\text{--O}^{2-}$ acid–base pair site would be significantly more reactive than the other two pair sites, and that its acid–base properties, especially its CO_2 chemisorption energy, correlate well with its CH_4 reactivity [22]. Our studies suggest that the $\text{La}^{3+}\text{--O}^{2-}$ acid–base pair site, especially that located at the surface steps or corners with low coordination numbers, is a potential active site for CH_4 activation in the OCM reaction, which is consistent with a recently proposed mechanism for Li-doped MgO catalyst from a combined experimental and computational study [23].

We carried out extensive DFT calculations to investigate CH_4 reactivity with eight Sr-doped La_2O_3 clusters derived from the parent La_2O_3 clusters by replacing a La atom with a Sr atom. These neutral Sr-doped La_2O_3 clusters fall into two categories, those in a closed shell without radical character ($\text{LaSrO}_2(\text{OH})$, La_2SrO_4 , $\text{La}_3\text{SrO}_5(\text{OH})$, $\text{La}_5\text{SrO}_8(\text{OH})$) and those in an open shell with radical character (LaSrO_3 , $\text{La}_2\text{SrO}_4(\text{OH})$, La_3SrO_6 , La_5SrO_9). Similar to our previous studies, the OH group in these clusters was used to balance the charge. Similar to the pure La_2O_3 clusters, these Sr-doped La_2O_3 clusters can be considered to be effective models for the low coordination sites at the surface steps and corners on the La_2O_3 -based catalysts. Potential-energy surfaces for CH_4 activation and CH_3 radical formation over these Sr-doped La_2O_3 clusters were calculated, and were compared with our previous results for pure La_2O_3 clusters to elucidate the Sr-doping effect.

2. Computational approach

The Sr-doped La_2O_3 catalyst was modeled with two distinct classes of molecular clusters, the closed-shell neutral clusters of $\text{LaSrO}_2(\text{OH})$, La_2SrO_4 , $\text{La}_3\text{SrO}_5(\text{OH})$, and $\text{La}_5\text{SrO}_8(\text{OH})$, and the open-shell neutral clusters of LaSrO_3 , $\text{La}_2\text{SrO}_4(\text{OH})$, La_3SrO_6 ,

and La_5SrO_9 , which were derived from the stoichiometric pure La_2O_3 clusters of La_2O_3 , $\text{La}_3\text{O}_4(\text{OH})$, La_4O_6 , and La_6O_9 used previously to model the pure La_2O_3 catalyst. The OH group was used to balance the charge, because the catalyst could be expected to carry no charge and a positive or negative charge would have a significant and artificial influence on CH_4 physisorption and the dissociation energies. The former class can be considered to be stoichiometric mixed Sr–La oxide clusters, where the Sr, La, and O atoms exist in their formal +2, +3, and –2 oxidation states. The latter class was formed by the direct substitution of a La atom with a Sr atom, and because of the lower valency of Sr compared with La, an electron hole (or an oxygen-centered radical) was generated, which led to open-shell clusters.

Equilibrium geometries and vibrational frequencies were calculated at the DFT level with the B3LYP hybrid exchange–correlation functional [24]. Geometry optimizations for the minima were carried out with the Berny algorithm [25], whereas transition states were located with the synchronous transit-guided quasi-Newton algorithm [26] and confirmed by intrinsic reaction-coordinate calculations [27,28]. Geometry optimizations were performed in the redundant internal coordinates [29,30], where all the atoms in the clusters were fully relaxed. The aug-cc-pVDZ basis set for H, C, and O [31,32], the MWB28 pseudopotential-based basis set in segmented contraction for La [33,34], and the aug-cc-pVDZ-PP pseudopotential-based basis set for Sr [35,36] were used; this combination of basis sets will be denoted aVDZ. Analytic harmonic vibrational frequencies were calculated to verify the nature of the stationary states and to obtain zero-point energy corrections. Our previous studies [22] suggest that the energy barriers calculated at the B3LYP/aVDZ level are usually lower than the CCSD(T)/aVDZ values with a mean absolute deviation of 0.026 ± 0.017 eV, so the B3LYP/aVDZ method is reasonably accurate to predict these energy barriers, although care must be taken when comparing very small energy differences.

The DFT calculations were carried out with the Gaussian 09 program package [37]. Molecular visualization was done using the AGUI graphics program of the AMPAC program package [38]. Calculations were performed on our Xeon-based Lenovo computing cluster and the computing cluster at the Shanghai Advanced Research Institute.

3. Results and discussion

3.1. Sr-doped La_2O_3 cluster structures

Structures of the clusters used to model the Sr-doped La_2O_3 catalyst are shown in Fig. 1. For $\text{LaSrO}_2(\text{OH})$, each of the La and Sr atoms is bonded with two equivalent bridge O atoms and one bridge OH group, which leads to one distinct La–O pair site and one distinct Sr–O pair site for CH_4 activation. For La_2SrO_4 , each of the two equivalent La atoms and the Sr atom is bonded with three bridge O atoms, which leads to three distinct La–O pair sites and three distinct Sr–O pair sites. For $\text{La}_3\text{SrO}_5(\text{OH})$, each of the two equivalent La atoms is bonded with three bridge O atoms, and each of the unique La and Sr atoms is

Fig. 1. Structures of Sr-doped La_2O_3 clusters.

bonded with two bridge O atoms and one bridge OH group, which leads to four distinct La–O pair sites and one distinct Sr–O pair site. The $\text{La}_5\text{SrO}_8(\text{OH})$ contains three similar La atoms, which are each bonded with four bridge O atoms, and two similar La atoms and one Sr atom, which are each bonded with three bridge O atoms and one bridge OH group. This arrangement leads to many more distinct La–O pair sites and two distinct Sr–O pair sites.

For LaSrO_3 , each of the La and Sr atoms is bonded with three equivalent bridge O atoms, which leads to one distinct La–O pair site and one distinct Sr–O pair site for CH_4 activation. For $\text{La}_2\text{SrO}_4(\text{OH})$, one La atom and the Sr atom are bonded with three bridge O atoms, and the other La atom is bonded with an additional terminal OH group, which leads to three distinct La–O pair sites and three distinct Sr–O pair sites. For La_3SrO_6 , each of the La and Sr atoms is bonded with three bridge O atoms, which leads to two distinct La–O pair sites and one distinct Sr–O pair site. For La_5SrO_9 , each of the La and Sr atoms is bonded with four bridge O atoms, which leads to many more distinct La–O pair sites and one distinct Sr–O pair site. Thus, the number of distinct La–O pair sites and that of the distinct Sr–O pair sites depends strongly on the cluster size and symmetry.

Because of the odd number of electrons in the last four clusters in Fig. 1, one unpaired electron exists in these clusters, so we show their calculated electron spin density in Fig. 2, which is centered on one or more oxygen sites. For LaSrO_3 , the electron spin density is distributed equally on two equivalent O sites. For $\text{La}_2\text{SrO}_4(\text{OH})$ and La_3SrO_6 , the electron spin density is located on one O site only, which lies between the Sr and La sites. For La_5SrO_9 , the electron spin density is distributed mainly on two O sites, a bridge O between the two La and one Sr site and the central O, although the latter is not expected to react with CH_4 because of steric hindrance.

Fig. 2. Electron spin density on Sr-doped La_2O_3 clusters at the B3LYP/aVDZ level.

3.2. CH_4 activation over stoichiometric mixed-oxide clusters

We examined the reactivities of the stoichiometric mixed La–Sr-oxide clusters with CH_4 , which are compared with the corresponding stoichiometric pure La-oxide clusters. Our previous studies have shown that the La–O acid–base pair sites over the stoichiometric La_2O_3 clusters were quite active for CH_4 activation and led to the formation of a La– CH_3 bond and an OH group [19]. Each of these stoichiometric clusters has an even number of electrons, which results in a spin multiplicity of one, and thus the stationary states involved in its reactions with CH_4 are closed-shell species with the same spin multiplicity. With CH_3 radical desorption, each resulting clusters has an odd number of electrons, which leads to a spin multiplicity of two, and so spin conservation is always enforced in these calculations.

Fig. 3 shows the potential-energy surface for CH_4 activation by the smallest mixed La–Sr-oxide cluster, $\text{LaSrO}_2(\text{OH})$, which has two distinct active sites, the La–O and Sr–O pair sites, and both can activate CH_4 . Physisorption of CH_4 at these two pair sites is fairly weak, with physisorption energies of -0.06 and -0.08 eV at the La–O and Sr–O pair sites, respectively. These values are slightly more negative than that of -0.03 eV for the La–O pair site on La_2O_3 [19]. The energy barriers for CH_4 activation from the physisorption state at the La–O and Sr–O pair sites were predicted to be 0.87 and 0.73 eV, which leads to the formation of La– CH_3 and Sr– CH_3 bonds, respectively. These sites have a lower energy barrier than that of 0.91 eV at the La–O pair site on La_2O_3 [19], and so the reactivity of $\text{LaSrO}_2(\text{OH})$ with CH_4 was predicted to be higher than that of La_2O_3 . The chemisorption energies of CH_4 from the physisorp-

Fig. 3. Potential-energy surface for CH_4 activation at the La–O (red) and Sr–O (green) pair sites on $\text{LaSrO}_2(\text{OH})$ and La_2SrO_4 at 0 K in eV.

tion state at the La–O and Sr–O pair sites were calculated to be 0.04 and 0.11 eV, which were compared with that of –0.24 eV for the La–O pair site on La_2O_3 [19]. The exothermicity for La_2O_3 occurs mostly because of the conversion of a bridge OH group into a terminal OH group, which was not predicted for $\text{LaSrO}_2(\text{OH})$. La–CH₃ and Sr–CH₃ bond breakage to form the CH₃ radical was predicted to require significant energy of 2.07 and 2.02 eV, respectively. These energies are lower than that of 2.19 eV, which is required to break the La–CH₃ bond in the case of La_2O_3 [19]. Because of the high energy that is required to break the M–CH₃ bond, we also considered the possibility of further hydrogen transfer from the CH₃ group that is adsorbed at the La site, which was predicted to be slightly lower in energy than that adsorbed at the Sr site. Hydrogen transfer from the CH₃ group to the remaining bridge O site to form the CH₂ group and a bridge OH group was predicted to be endothermic by 1.92 eV with an energy barrier of 2.33 eV, so it is less favorable than direct desorption of the CH₃ group with an endothermicity of 2.07 eV. Thus, deep dehydrogenation of the CH₃ group was predicted to be less likely to occur than its direct detachment.

Fig. 3 also shows the potential-energy surface for CH₄ activation by the La–O and Sr–O pair sites on La_2SrO_4 . As mentioned previously, three distinct La–O pair sites and two distinct Sr–O pair sites exist, and we have calculated the potential-energy surfaces for CH₄ activation at these M–O pair sites. The three distinct La–O pair sites share the same La atom, but differ in the O atom. The energy barriers from the physisorption state for CH₄ activation at these La–O pair sites were predicted to be 0.88, 0.89, and 0.98 eV, and among them, that shown in Fig. 3 has the lowest energy barrier, where the H atom is transferred to the bridge O shared by a La atom and a Sr atom. The chemisorption energies of CH₄ from the physisorption state at these three La–O pair sites were calculated to be 0.50, 0.63, and 0.48 eV, respectively, so CH₄ chemisorption is quite endothermic. Breaking the La–CH₃ bond in the corresponding chemisorption structures requires a significant amount of energy of 1.84, 2.12, and 2.10 eV, respectively. In contrast, the energy barriers from the physisorption state for CH₄ activation at the two Sr–O pair sites were predicted to be 0.61 and 0.93 eV, and that shown in Fig. 3 has the lowest energy barrier, where the H atom is transferred to the bridge O shared by a La atom and a Sr atom. The chemisorption energies of CH₄ from the physisorption state at these Sr–O pair sites were calculated to be 0.53 and 0.91 eV, so CH₄ chemisorption is also very endothermic. Sr–CH₃ bond breakage in the corresponding chemisorption structures requires a significant amount of energy of 1.85 and 1.83 eV, respectively. The energy barriers for CH₄ activation from the physisorption state at all the La–O and Sr–O pair sites on La_2SrO_4 are considerably lower than those on $\text{La}_3\text{O}_4(\text{OH})$ of ≥ 1.13 eV [19], so La_2SrO_4 is more reactive with CH₄ than $\text{La}_3\text{O}_4(\text{OH})$. This result is consistent with the higher reactivity of all the La–O and Sr–O pair sites on $\text{LaSrO}_2(\text{OH})$ than La_2O_3 .

Fig. 4 shows the potential-energy surface for CH₄ activation by the La–O and Sr–O pair sites on $\text{La}_3\text{SrO}_5(\text{OH})$. As mentioned previously, four distinct La–O pair sites and one distinct Sr–O pair site exist, and we have calculated the potential-energy

Fig. 4. Potential-energy surface for CH₄ activation at the La–O (red) and Sr–O (green) pair sites on $\text{La}_3\text{SrO}_5(\text{OH})$ and $\text{La}_5\text{SrO}_8(\text{OH})$ at 0 K in eV.

surfaces for CH₄ activation at most of these M–O pair sites. The energy barriers from the physisorption state for CH₄ activation at two of these distinct La–O pair sites were predicted to be 0.88 and 1.10 eV, and among these, that shown in Fig. 4 has the lower energy barrier, where the H atom is transferred to the bridge O shared by a La atom and a Sr atom. The chemisorption energies of CH₄ from the physisorption state at these two La–O pair sites were calculated to be 0.14 and 0.66 eV, respectively, so CH₄ chemisorption is quite endothermic. La–CH₃ bond breakage in the corresponding chemisorption structures requires a significant amount of energy of 2.27 and 1.72 eV, respectively. In contrast, the energy barrier from the physisorption state for CH₄ activation at the unique Sr–O pair site was predicted to be 0.82 eV, where the H atom is again transferred to the bridge O shared by a La atom and a Sr atom. The chemisorption energy of CH₄ from the physisorption state at the Sr–O pair site was calculated to be 0.62 eV, so CH₄ chemisorption is also very endothermic. Sr–CH₃ bond breakage in the corresponding chemisorption structures requires a significant amount of energy of 1.80 eV. The energy barriers for CH₄ activation from the physisorption state at all the La–O and Sr–O pair sites on $\text{La}_3\text{SrO}_5(\text{OH})$ are considerably lower than that on La_4O_6 of 1.16 eV [19], so $\text{La}_3\text{SrO}_5(\text{OH})$ is more reactive with CH₄ than La_4O_6 .

Fig. 4 shows the potential-energy surface for CH₄ activation by the La–O and Sr–O pair sites on $\text{La}_5\text{SrO}_8(\text{OH})$. As mentioned previously, as many as ten distinct La–O pair sites and two distinct Sr–O pair sites exist, and we have calculated the potential-energy surfaces for CH₄ activation at all these M–O pair

sites. The energy barriers from the physisorption state for CH₄ activation at the ten distinct La–O pair sites were predicted to be as low as 0.80 eV and as high as 1.02 eV, and among them, that shown in Fig. 4 has the lower energy barrier, where the H atom is transferred to one of the bridge O atoms shared by two La atoms and a Sr atom. The chemisorption energy of CH₄ from the physisorption state for this La–O pair site was calculated to be 0.39 eV, so again, CH₄ chemisorption is quite endothermic. Breaking the La–CH₃ bond in the corresponding chemisorption structure requires a significant amount of energy of 2.23 eV. In contrast, the energy barrier from the physisorption state for CH₄ activation at the two distinct Sr–O pair sites was predicted to be 0.87 and 0.92 eV, and that in Fig. 4 has the lower energy barrier, where the H atom is also transferred to one of the bridge O atoms shared by two La atoms and a Sr atom. The chemisorption energy of CH₄ from the physisorption state at this Sr–O pair site was calculated to be 0.78 eV, so CH₄ chemisorption is also very endothermic. Sr–CH₃ bond breakage in the corresponding chemisorption structure requires a significant amount of energy of 1.86 eV. The lowest energy barriers for CH₄ activation from the physisorption state at the La–O and Sr–O pair sites on La₅SrO₈(OH) of 0.80 and 0.87 eV are considerably lower than that on La₆O₉ of 0.96 eV [19], so La₅SrO₈(OH) is also more reactive with CH₄ than La₆O₉.

3.3. CH₄ activation over non-stoichiometric mixed-oxide clusters

We now investigate the reactivities of the non-stoichiometric mixed La–Sr-oxide clusters with CH₄. Each of these non-stoichiometric clusters has an odd number of electrons, which results in a spin multiplicity of two, and thus the stationary states involved in its reactions with CH₄ are open-shell species with the same spin multiplicity. Upon CH₃ radical desorption, stoichiometric clusters are formed with a spin multiplicity of one, so spin conservation is also enforced in these calculations.

Fig. 5 shows the potential-energy surface for CH₄ activation by the smallest LaSrO₃ cluster to form the CH₃ radical. Similar to the La–O and Sr–O pair sites on the stoichiometric LaSrO₂(OH) cluster shown in Fig. 3, those on the non-stoichiometric LaSrO₃ cluster can also activate CH₄. The physisorption energies of CH₄ at the La–O and Sr–O pair sites on LaSrO₃ were calculated to be –0.03 and –0.07 eV, respectively, which is comparable with those of –0.06 and –0.08 eV on LaSrO₂(OH). The energy barriers from the physisorption state at these pair sites on LaSrO₃ were predicted to be 0.87 and 0.77 eV, respectively, which are also comparable with those of 0.87 and 0.73 eV on LaSrO₂(OH). The chemisorption energies from the physisorption state at these pair sites on LaSrO₃ were calculated to be 0.19 and –0.22 eV, which are compared with those of 0.04 and 0.11 eV on LaSrO₂(OH). The most significant difference lies in the desorption energies of the CH₃ species from the La and Sr sites after CH₄ chemisorption, which were predicted to be less than 0.15 eV for LaSrO₃, and much lower than those of 2.07 and 2.02 eV for LaSrO₂(OH). In fact, the CH₃ species was predicted to be unbound at the La site, which suggests it can attach only

Fig. 5. Potential-energy surface for CH₄ activation at the La–O (red) and Sr–O (green) pair sites, and at the oxygen radical (blue) site on LaSrO₃ at 0 K in eV.

weakly to the Sr site.

In addition to the La–O and Sr–O pair sites, the oxygen site on LaSrO₃ has a radical character, so it can also activate CH₄ without the assistance of the M site, as shown in Fig. 5. The physisorption energy of CH₄ at the oxygen radical site is very low at –0.03 eV, whereas the energy barrier from the physisorption state is only 0.34 eV, which is much lower than those at the La–O and Sr–O pair sites on LaSrO₃ and LaSrO₂(OH). Therefore, LaSrO₃ prefers to activate CH₄ at its oxygen radical site. This transition state also differs from those at the La–O and Sr–O pair sites in that the CH₃ species has a nearly planar structure and is a leaving group, compared with the usual pyramidal structure when it is transferred to the M site. Upon CH₄ activation at the oxygen radical site, the CH₃ radical is already formed with a favorable chemisorption energy of –0.11 eV, although it may re-adsorb at the Sr site with a low adsorption energy of –0.15 eV.

Fig. 6 shows the potential-energy surface for CH₄ activation by La₂SrO₄(OH). We have calculated the energy barriers from the physisorption state for CH₄ activation at one La–O pair site (0.94 eV), two Sr–O pair sites (0.86 and 0.98 eV), and three oxygen radical sites (0.11, 0.42, and 0.72 eV), and those at the oxygen radical sites were predicted to be the lowest, which is consistent with our predictions for LaSrO₃ in Fig. 5. The energy barriers and the chemisorption energies (–0.51, –0.17, and 0.14 eV) from the physisorption state for CH₄ activation at the different oxygen radical sites were found to differ significantly. The oxygen radical site between the La and Sr atoms is the most reactive, whereas that at the center of the cluster is the least reactive, partially because of the steric effect. Among them, only part of the potential-energy surfaces were shown in Fig. 6 with a relatively low energy.

Fig. 7 shows the potential-energy surface for CH₄ activation by La₃SrO₆. We have calculated the energy barriers from the physisorption state for CH₄ activation at one La–O pair site (1.00 eV) and one oxygen radical site (0.22 eV), and that at the

Fig. 6. Potential-energy surface for CH_4 activation at the La–O (red) and Sr–O (green) pair sites, and at the oxygen radical (blue) site on $\text{La}_2\text{SrO}_4(\text{OH})$ at 0 K in eV.

oxygen radical site was predicted to be much lower. The chemisorption energy from the physisorption state for CH_4 activation at this oxygen radical site was found to be -0.29 eV. Thus, the oxygen radical site between the La and Sr atoms is also very reactive.

Fig. 7 shows the potential-energy surface for CH_4 activation by La_5SrO_9 . We have calculated the energy barriers from the physisorption state for CH_4 activation at two La–O pair sites (0.87 and 0.98 eV) and one oxygen radical site (0.22 eV), and that at the oxygen radical site was predicted to be the lowest. The chemisorption energy from the physisorption state for CH_4 activation at this oxygen radical site was found to be -0.30 eV. Thus, the oxygen radical site between two La and one Sr atoms is also very reactive. Among them, only part of the potential-energy surfaces was shown in Fig. 7 with a relatively low energy.

3.4. Sr-doping effect on CH_4 reactivity with La_2O_3 catalyst

Because of the very weak physisorption of CH_4 on the La and mixed La–Sr-oxide clusters, its effect on the CH_4 reactivity can be ignored, because at modest to high reaction temperatures CH_4 will not be physisorbed. In Table 1, we list the energy barriers and chemisorption energies for CH_4 activation at the La–O, Sr–O, and $\text{O}^\bullet$ sites on these clusters without considering the effect of CH_4 physisorption. Also listed are the desorption energies of the CH_3 radical from the La or Sr site after CH_4 activation at the La–O or Sr–O pair site, and for the $\text{O}^\bullet$ site, the CH_3 radical was considered to be released directly into the gas phase. These energetics correspond with the most favorable pathways that are judged by the size of the energy barrier.

A comparison in Table 1 shows that for a given cluster, the

Fig. 7. Potential-energy surface for CH_4 activation at the La–O (red) pair site and at the oxygen radical (blue) site on La_3SrO_6 and La_5SrO_9 at 0 K in eV.

energy barrier for CH_4 activation follows $\text{O}^\bullet \ll \text{Sr–O} < \text{La–O}$, if any or all of these sites are available to activate CH_4 , although some exceptions exist, for example, the La–O pair site on $\text{La}_5\text{SrO}_8(\text{OH})$ was predicted to be more reactive with CH_4 than the Sr–O pair site. For clusters with the same number of metal atoms, the energy barrier to CH_4 activation at the La–O pair site was predicted to follow the order of stoichiometric La–Sr–O < non-stoichiometric La–Sr–O < stoichiometric La–O, whereas that at the Sr–O pair site was found to follow the order of stoichiometric La–Sr–O < non-stoichiometric La–Sr–O for the limited data set. The oxygen radical site in the non-stoichiometric La–Sr–O cluster is more reactive than either the La–O or Sr–O pair site.

From the calculated CH_4 chemisorption energies, CH_4 dissociation at the La–O or Sr–O pair site on the stoichiometric La–O and La–Sr–O clusters was predicted to be quite endothermic except for the clusters with only two metal atoms. CH_4 dissociation at the different sites on the non-stoichiometric La–Sr–O clusters was predicted to be mostly exothermic.

For CH_4 dissociation at the La–O or Sr–O pair site on the stoichiometric La–O and La–Sr–O clusters, the resulting CH_3 species was predicted to be attached strongly to the metal site, so direct desorption of the CH_3 radical by breaking the M– CH_3 bond requires a significant amount of energy from 1.8 to 2.4 eV. Therefore, the direct formation of a CH_3 radical can only occur at very high reaction temperatures. Regardless of the active site

Table 1

Energy barriers and chemisorption energies for CH₄ activation at the La–O, Sr–O, and O· sites, and CH₃ desorption energies from the M sites calculated at the B3LYP/aVDZ level (0 K in eV).

Cluster	Energy barrier			Chemisorption energy			Desorption	
	La–O	Sr–O	O·	La–O	Sr–O	O·	La	Sr
La ₂ O ₃ [19]	0.88	—	—	–0.27	—	—	2.19	—
La ₃ O ₄ (OH) [19]	1.10	—	—	0.37	—	—	2.41	—
La ₄ O ₆ [19]	1.07	—	—	0.68	—	—	2.14	—
La ₆ O ₉ [20]	0.92	—	—	0.68	—	—	2.29	—
LaSrO ₂ (OH)	0.81	0.65	—	–0.02	0.03	—	2.07	2.02
La ₂ SrO ₄	0.85	0.54	—	0.47	0.46	—	1.84	1.85
La ₃ SrO ₅ (OH)	0.84	0.77	—	0.10	0.57	—	2.27	1.80
La ₅ SrO ₈ (OH)	0.77	0.82	—	0.36	0.73	—	2.23	1.86
LaSrO ₃	0.84	0.70	0.31	0.16	–0.29	—	—	0.15
La ₂ SrO ₄ (OH)	0.90	0.79	0.04	–0.34	–0.29	–0.58	0.12	0.07
La ₃ SrO ₆	0.95	—	0.16	–0.21	—	–0.35	0.12	—
La ₅ SrO ₉	0.83	—	0.18	–0.34	—	–0.34	0.09	—

for CH₄ dissociation over the non-stoichiometric La–Sr–O clusters, the CH₃ radical can form readily because of the very low CH₃ desorption energy of ≤ 0.15 eV for the clusters that were investigated.

Our discussion suggests that the non-stoichiometric Sr-doped La₂O₃ cluster that is formed by the substitution of one La atom with one Sr atom in the stoichiometric La₂O₃ cluster is the most reactive with CH₄ because of its odd number of electrons and its radical character. After the reaction with one molecule of CH₄, this cluster is transformed into a stoichiometric Sr-doped La₂O₃ cluster with an even number of electrons and no radical character, which is much less reactive than CH₄ compared with the non-stoichiometric Sr-doped La₂O₃ cluster with a radical character. Nevertheless, it is still much more reactive than the stoichiometric La₂O₃ cluster, most likely because of the enhanced basicity that results from the Sr dopant. Its further transformation in the catalytic OCM reaction can be expected to involve a reaction with O₂ in the gas phase, which will be investigated in our future work. In general, because CH₄ activation is regarded as the rate-determining step in the catalytic OCM reaction, our calculations suggest that the Sr dopant can enhance the catalytic activity of the La₂O₃ catalyst for the OCM reaction significantly, which is consistent with previous experimental findings [10,13–17].

Our previous DFT and coupled-cluster calculations have shown that the reactivity of CH₄ with the La–O pair site can be correlated positively with its basicity [22], and thus, the enhanced reactivity of the stoichiometric Sr-doped La₂O₃ cluster over the pure La₂O₃ cluster can be attributed to the increased basicity, which is also consistent with the experimental studies. The basicity of a metal-oxide catalyst is usually correlated with its CO₂ chemisorption energy [21,22], which can be determined experimentally using the temperature-programmed desorption (TPD) of CO₂ [39,40]. Choudhary and co-workers [41] have measured the surface basicity and acidity of alkaline-earth-promoted La₂O₃ catalysts by CO₂-TPD, and found that Sr-doped La₂O₃ catalysts contain a larger number of strong basic sites with the best activity and selectivity for the OCM reaction. Zhu and co-workers [17] used temperature pro-

grammed desorption of CO₂ to characterize their La₂O₃ and Sr-doped La₂O₃ catalysts, and found that the La₂O₃ catalyst that was doped with 8.6 wt% Sr was more basic and also more reactive than the pure La₂O₃ catalyst. These experiments suggest that the Sr-doped La₂O₃ catalyst has a stronger basicity and a higher catalytic activity for the OCM reaction than the pure La₂O₃ catalyst, which is consistent with the above discussion based on our calculations. To verify the applicability of our previously found linear correlation between CH₄ reactivity and CO₂ chemisorption energy, we calculated the CO₂ chemisorption energies at the La–O and Sr–O pair sites on LaSrO₂(OH) to be –1.60 and –1.45 eV at 0 K, respectively, which should be compared with that at the La–O pair site on La₂O₃ of –1.50 eV [21]. Table 1 shows the predicted energy barriers for CH₄ activation at the La–O and Sr–O pair sites on LaSrO₂(OH) of 0.81 and 0.65 eV, respectively, whereas those at the La–O pair site on La₂O₃ were calculated to be 0.88 eV. Thus, the more negative CO₂ chemisorption energy at the La–O pair site on LaSrO₂(OH) than that on La₂O₃ can be correlated with its lower energy barrier for CH₄ activation. However, the CO₂ chemisorption energy at the Sr–O pair site on LaSrO₂(OH) was predicted to be lower than the La–O pair sites on LaSrO₂(OH) and La₂O₃, although its energy barrier for CH₄ activation was found to be the lowest. This may suggest that our previously found linear equation between these two properties applies only to CH₄ activation at the La–O pair site, and the coefficients of the linear correlation may also depend on other factors, such as the metal identity.

4. Conclusions

Four stoichiometric mixed La–Sr-oxide clusters, LaSrO₂(OH), La₂SrO₄, La₃SrO₅(OH), and La₅SrO₈(OH), and four non-stoichiometric mixed La–Sr-oxide clusters with a radical character, LaSrO₃, La₂SrO₄(OH), La₃SrO₆, and La₅SrO₉, were used as models for the Sr-doped La₂O₃ catalyst in the OCM reaction. CH₄ activation at distinct La–O and Sr–O pair sites and at the oxygen radical (O·) site on these mixed La–Sr-oxide clusters was investigated by DFT calculations, and the reactivities of these clusters were compared with those of the pure La₂O₃

clusters from our previous studies. In general, for a given cluster, the energy barrier for CH₄ activation follows the order of O << Sr–O < La–O, so CH₄ dissociation was predicted to be highly preferable at the oxygen radical site. For the stoichiometric mixed La–Sr-oxide clusters without the oxygen radical site, the energy barrier for CH₄ activation at the La–O pair site was also predicted to be lower on the mixed-oxide clusters than that on the pure La₂O₃ clusters. Thus, the Sr dopant can enhance the activity of the La₂O₃ catalyst significantly for CH₄ activation in the OCM reaction by providing a highly reactive oxygen radical site and by enhancing the reactivity of the non-radical M–O (M = La, Sr) acid–base pair sites. The latter can be attributed to an increase in basicity of the pair site, as the basicity has been shown to increase the OCM activity of the La₂O₃ catalyst experimentally and theoretically.

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References

- [1] C. Hammond, S. Conrad, I. Hermans, *ChemSusChem*, **2012**, 5, 1668–1686.
- [2] P. Tang, Q. J. Zhu, Z. X. Wu, D. Ma, *Energy Environ. Sci.*, **2014**, 7, 2580–2591.
- [3] A. I. Olivos-Suarez, Á. Szécsényi, E. J. M. Hensen, J. Ruiz-Martinez, E. A. Pidko, J. Gascon, *ACS Catal.*, **2016**, 6, 2965–2981.
- [4] B. L. Farrell, V. O. Igenegbai, S. Linic, *ACS Catal.*, **2016**, 6, 4340–4346.
- [5] C. Karakaya, R. J. Kee, *Prog. Energy Combust. Sci.*, **2016**, 55, 60–97.
- [6] W. Taifan, J. Baltrusaitis, *Appl. Catal. B*, **2016**, 198, 525–547.
- [7] U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, *ChemCatChem*, **2011**, 3, 1935–1947.
- [8] K. Otsuka, K. Jinno, A. Morikawa, *J. Catal.*, **1986**, 100, 353–359.
- [9] T. Jiang, J. J. Song, M. F. Huo, N. T. Yang, J. W. Liu, J. Zhang, Y. H. Sun, Y. Zhu, *RSC Adv.*, **2016**, 6, 34872–34876.
- [10] J. M. Deboy, R. F. Hicks, *J. Catal.*, **1988**, 113, 517–524.
- [11] V. R. Choudhary, S. A. R. Mulla, B. S. Uphade, *Ind. Eng. Chem. Res.*, **1998**, 37, 2142–2147.
- [12] P. Huang, Y. H. Zhao, J. Zhang, Y. Zhu, Y. H. Sun, *Nanoscale*, **2013**, 5, 10844–10848.
- [13] J. M. Deboy, R. F. Hicks, *Ind. Eng. Chem. Res.*, **1988**, 27, 1577–1582.
- [14] J. M. Deboy, R. F. Hicks, *J. Chem. Soc., Chem. Commun.*, **1988**, 982–984.
- [15] V. R. Choudhary, S. A. R. Mulla, V. H. Rane, *J. Chem. Technol. Biotechnol.*, **1998**, 71, 167–172.
- [16] T. Baidya, N. van Vegten, R. Verel, Y. Jiang, M. Yulikov, T. Kohn, G. Jeschke, A. Baiker, *J. Catal.*, **2011**, 281, 241–253.
- [17] J. J. Song, Y. H. Sun, R. B. Ba, S. S. Huang, Y. H. Zhao, J. Zhang, Y. H. Sun, Y. Zhu, *Nanoscale*, **2015**, 7, 2260–2264.
- [18] R. J. Bartlett, M. Musial, *Rev. Mod. Phys.*, **2007**, 79, 291–352.
- [19] Y. Lei, C. Q. Chu, S. G. Li, Y. H. Sun, *J. Phys. Chem. C*, **2014**, 118, 7932–7945.
- [20] C. Q. Chu, Y. H. Zhao, S. G. Li, Y. H. Sun, *J. Phys. Chem. C*, **2014**, 118, 27954–27960.
- [21] C. Q. Chu, Y. H. Zhao, S. G. Li, Y. H. Sun, *J. Phys. Chem. C*, **2016**, 120, 2737–2746.
- [22] C. Q. Chu, Y. H. Zhao, S. G. Li, Y. H. Sun, *Phys. Chem. Chem. Phys.*, **2016**, 18, 16509–16517.
- [23] K. Kwapien, J. Paier, J. Sauer, M. Geske, U. Zavyalova, R. Horn, P. Schwach, A. Trunschke, R. Schlögl, *Angew. Chem. Int. Ed.*, **2014**, 53, 8774–8778.
- [24] A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648–5652.
- [25] X. Li, M. J. Frisch, *J. Chem. Theory Comput.*, **2006**, 2, 835–839.
- [26] C. Peng, H. B. Schlegel, *Israel J. Chem.*, **1993**, 33, 449–454.
- [27] P. Hratchian, H. B. Schlegel, *J. Chem. Phys.*, **2004**, 120, 9918–9924.
- [28] H. P. Hratchian, H. B. Schlegel, *J. Chem. Theory Comput.*, **2005**, 1, 61–69.
- [29] P. Pulay, G. Fogarasi, *J. Chem. Phys.*, **1992**, 96, 2856–2860.
- [30] C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.*, **1996**, 17, 49–56.
- [31] T. H. Dunning Jr., *J. Chem. Phys.*, **1989**, 90, 1007–1023.
- [32] R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, *J. Chem. Phys.*, **1992**, 96, 6796–6806.
- [33] X. Cao, M. Dolg, *J. Mol. Struct.: Theochem.*, **2002**, 581, 139–147.
- [34] M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.*, **1989**, 90, 1730–1734.
- [35] H. Li, H. Feng, W. Sun, Y. Zhang, Q. Fan, K. A. Peterson, Y. Xie, H. F. Schaefer III, *Mol. Phys.*, **2013**, 111, 2292.

Graphical Abstract

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Sr-doping effects on La₂O₃ catalyst for oxidative coupling of methane

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Sr dopant in a La₂O₃ catalyst can enhance its reactivity with CH₄ significantly by providing a highly reactive oxygen radical site, in addition to increasing the basicity and thus the reactivity of the non-radical metal–oxygen acid–base pair site.

- [36] I. S. Lim, H. Stoll, P. Schwerdtfeger, *J. Chem. Phys.*, **2006**, 124, 034107.
- [37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, **2009**.
- [38] AMPAC 9, 1992–2008 Semichem, Inc. 12456 W 62nd Terrace-Suite D, Shawnee, KS 66216.
- [39] Z. Wang, G. Zou, X. Luo, H. Liu, R. Gao, L. Chou, X. Wang, *J. Nat. Gas Chem.*, **2012**, 21, 49–55.
- [40] W. Jeon, J. Y. Lee, M. Lee, J. W. Choi, J. M. Ha, D. J. Suh, I. W. Kim, *Appl. Catal. A*, **2013**, 464–465, 68–77.
- [41] V. R. Choudhary, V. H. Rane, S. T. Chaudhari, *Appl. Catal. A*, **1997**, 158, 121–136.

铈掺杂对氧化镧催化甲烷氧化偶联反应的影响

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摘要: 甲烷氧化偶联反应(OCM)是天然气直接转化利用的重要途径之一。该反应通过甲烷和氧气在催化剂作用下进一步将甲烷直接转化为乙烯等具有高附加值的产品, 避免了涉及高能耗过程的合成气间接路径, 不仅有可能减少中间副产物的生成, 还有可能大大提升整个过程的能源利用效率。因此, 研究OCM反应具有十分重要的实际意义。目前氧化镧基催化剂具有良好的催化活性、产物选择性和热稳定性, 但在OCM反应中产品收率仍未能达到工业应用的要求, 因而近几十年来高效OCM催化剂的研发一直是研究热点。实验发现, 铈掺杂氧化镧催化剂具有更为优异的催化性能, 主要表现在具有比纯氧化镧催化剂更高的催化活性和产物选择性, 但对于铈掺杂的影响机制仍然缺乏系统的理论研究。目前普遍认为, 甲烷活化是OCM反应的第一步, 也是决速步, 这主要是由于C-H键活化需要越过很高的能垒, 因此往往需要很高的温度。本文主要采用团簇模型, 通过密度泛函理论计算来研究OCM反应中铈掺杂对氧化镧催化剂上甲烷活化性能的影响及其作用原理。

本文构建了八种铈掺杂的氧化镧团簇作为该催化剂模型, 可分为没有自由基性质的团簇($\text{LaSrO}_2(\text{OH})$, La_2SrO_4 , $\text{La}_3\text{SrO}_5(\text{OH})$, $\text{La}_5\text{SrO}_8(\text{OH})$)和具有自由基性质的团簇(LaSrO_3 , $\text{La}_2\text{SrO}_4(\text{OH})$, La_3SrO_6 , La_5SrO_9)。我们计算了甲烷在这些铈掺杂氧化镧团簇上Sr-O和La-O酸碱对位点以及氧自由基活性位点上的活化机制, 以研究铈掺杂对OCM反应活性的影响, 并与我们前期计算的纯氧化镧团簇上甲烷活化性能进行了对比。通过计算甲烷在不同铈掺杂氧化镧团簇上的物理和化学吸附能、活化能垒以及甲基自由基的脱附能, 发现铈掺杂氧化镧团簇上的甲烷活化在热力学和动力学上都要比纯氧化镧团簇上更为有利。对于具有相同金属原子数目的团簇, 甲烷在La-O上活化的能垒大小为: 化学计量比的La-Sr-O团簇 < 非化学计量比的La-Sr-O团簇 < 化学计量比的La-O团簇; 而甲烷在Sr-O上活化的能垒大小依次是: 化学计量比的La-Sr-O团簇 < 非化学计量比的La-Sr-O团簇。给定一个铈掺杂氧化镧团簇, 甲烷在不同活化位点上的活化能垒大小通常是: $\text{O} \cdot \ll \text{Sr-O} < \text{La-O}$, 其中无论何种性质的铈掺杂氧化镧团簇, 甲烷在Sr-O上的反应活性要高于La-O上的, 而对于具有自由基特征的铈掺杂氧化镧团簇, 甲烷更容易在氧自由基位点上发生解离。此外, 对于没有自由基特征的铈掺杂氧化镧团簇, 甲基自由基的脱附如同纯氧化镧团簇一样是强吸热过程。相反, 对于具有自由基特性的铈掺杂氧化镧团簇, 甲基自由基的脱附则十分容易。

由此可见, 铈掺杂促进氧化镧催化剂上OCM反应活性主要有以下两个原因: (1) 通过掺杂可以提供具有自由基特性的氧活性位点, (2) 对于非自由基性质的团簇, 可以增强金属-氧对位点的碱性和甲烷反应活性, 从而有效降低了甲烷的活化能垒和甲基自由基的脱附能。

关键词: 甲烷活化; 甲基自由基产生; 团簇模型; 密度泛函理论; 铈掺杂; 氧化镧

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