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# Effect of Doped Metals Rh, Pd, and Cu over the IrO<sub>2</sub>(110) Surface: Improving C<sub>2</sub> Selectivity during Oxidative Coupling of Methane

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on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces to explore catalysts with high activity and  $C_2$  hydrocarbon selectivity. A pure  $IrO_2(110)$  surface exhibits high activity, but the  $C_2$ selectivity is low because  $O_2$  is easily adsorbed and dissociated to form  $O_{ad}$ , which will lead to the formation of the byproduct CO. Therefore, the catalytic performance of  $IrO_2(110)$  surfaces doped with second metals (Rh, Pd, and Cu) was investigated. The results show that the doping of Cu and Pd is detrimental to the adsorption and dissociation of  $O_2$  and inhibits the formation of  $O_{ad}$ . However,



Rh doping has no obvious effect. Additionally, charge analysis shows that the doping of metals reduces the transfer of charge from the catalyst surface to the adsorbed  $O_2$  compared to the pure  $IrO_2(110)$ , which results in the relatively weak adsorption and high dissociation energy of  $O_2$ . Moreover, the analysis of reaction rate constants also shows that the dissociation rate of  $O_2$  on Cu/  $IrO_2(110)$  at the same temperature is much lower than that on  $IrO_2(110)$ , Rh/IrO<sub>2</sub>(110), and Pd/IrO<sub>2</sub>(110) surfaces. It can be seen that the doping of Cu can improve the  $C_2$  hydrocarbon selectivity of the  $IrO_2$  catalyst.

## 1. INTRODUCTION

Natural gas, one of the three major fossil energy sources, compared with coal and oil, has abundant reserves and is relatively inexpensive.<sup>1,2</sup> Methane, the principal component of natural gas, has potential value as a raw material to produce high-value-added chemicals.<sup>3–5</sup> Over the past few decades, extensive research has been concentrated on the conversion of methane to alcohols or higher hydrocarbons.<sup>6,7</sup> Oxidative coupling of methane (OCM) is one of the most desirable approaches in the direct conversion of methane into C<sub>2</sub> hydrocarbons.<sup>1,8,9</sup>

However, the low  $C_2$  yield of OCM has long limited its economic feasibility.<sup>1,10</sup> The main reason is that highly efficient catalysts with high methane conversion and  $C_2$  hydrocarbon selectivity have not been developed.<sup>11</sup> Methane is a highly symmetric and nonpolarized molecule, and the C–H bond dissociation energy is as high as 4.55 eV.<sup>12</sup> Therefore, methane activation usually requires high temperatures. However,  $C_2$ hydrocarbon products have a higher reactivity than methane under high temperature conditions, which inevitably leads to the formation of the undesirable product  $CO_x$  and resulting in low  $C_2$  hydrocarbon selectivity.<sup>13</sup> Generally, OCM requires a relatively high temperature (>873 K), while the separation of byproducts from products needs to be carried out at low temperatures (less than 373 K).<sup>5,14</sup> Hence, a higher one-way yield of the  $C_2$  hydrocarbon is required to reduce energy consumption. Consequently, the development of a low-temperature OCM catalyst to achieve simultaneously high methane conversion and high  $C_2$  hydrocarbon selectivity is important to the industrial application of OCM.

Recently, researchers found that the  $IrO_2(110)$  surface can activate the C–H bond of methane at temperatures as low as 150 K.<sup>15–18</sup> The capability of the  $IrO_2(110)$  surface to promote methane activation at low temperatures indicates the possibility of developing  $IrO_2$ -based catalysts to specifically transform methane to high-value-added chemicals. Although the  $IrO_2$  catalyst has a high catalytic activity for methane conversion, the principal products of methane conversion are CO,  $CO_2$ , and  $H_2O$ .<sup>15</sup> Whether the second metal doping can improve the C<sub>2</sub> hydrocarbon selectivity of the OCM reaction is worth studying.

The metal Pd doping into the  $CeO_2$  lattice provides a coordination environment for  $Pd^{\delta+}$  species, which makes the oxidation states of  $Pd^{2+}$  and  $Pd^{4+}$  alternate expediently, thus

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producing highly reducible sites suitable for methane activation.<sup>19</sup> In addition, methane also can be selectively activated and directly converted over a heterogeneous single-atom catalyst. The single-atom Rh doped into the  $ZrO_2$  surface could activate methane under mild conditions and convert methane to ethane with O<sub>2</sub> in the gas phase below 573 K.<sup>20</sup> Compared with pure CeO<sub>2</sub>, Cu-doped CeO<sub>2</sub> increases the formation energy of oxygen vacancies and promotes the dissociation adsorption of methane but weakens the stability of CH<sub>3</sub>\* + H coadsorption.<sup>21</sup> The regulation of the catalytic performance of metal oxide catalysts toward methane has been derived from different kinds of metal cations.<sup>22</sup>

Moreover, understanding the role of surface oxygen atoms in the OCM reaction is of great significance for studying the mechanism of OCM reaction and improving the C2 hydrocarbons' selectivity on the  $IrO_2(110)$  surface. Rutile  $IrO_2(110)$ exposes 5-fold coordinated iridium atoms (Ir<sub>cus</sub>) and 2-fold coordinated oxygen atoms (O<sub>br</sub>), which occupies a bridging site relative to two underlying iridium atoms in the IrO<sub>2</sub> lattice. At room temperature, O2 is adsorbed and dissociated effectively on the surface of  $IrO_2(110)$  and produces oxygen atoms (O\_{ad}) adsorbed on the top of  $\mathrm{Ir}_{\mathrm{cus}}^{23-26}$  Some studies showed that the activity of the O<sub>br</sub> atom in promoting the C-H bond activation of methane is similar to the O<sub>ad</sub> atom, and the  $O_{ad}$  atom promotes methane oxidation to carbon dioxide on the  $IrO_2(110)$  surface.<sup>26,27</sup> Furthermore, the reaction with CH<sub>2</sub> self-coupled to form ethylene and the reaction with CH<sub>2</sub> and O<sub>ad</sub> to form CH<sub>2</sub>O are competitive reactions on the  $IrO_2(110)$  surface. Then,  $CH_2O$  is easily converted to  $CO_2$ which has a great influence on the selectivity of ethylene.<sup>11,26</sup> Therefore, it is necessary to increase the barrier for O2 dissociation because this can inhibit the formation of O<sub>adv</sub> which will lead to the formation of the byproduct CO, so as to improve the ethylene selectivity of the  $IrO_2(110)$  surface.

In this work, we will focus on the single metal atom (Rh, Pd, and Cu) doped in the  $IrO_2(110)$  surface to improve the  $O_2$ dissociation energy as well as reduce the energy barrier of ethane formation and then improve  $C_2$  hydrocarbons. For this purpose, an extensive density functional theory (DFT) study will be applied to explore the mechanism of OCM reaction on pure  $IrO_2(110)$  surface and single metal atom (Rh, Pd, and Cu) doped  $IrO_2(110)$  surfaces.

#### 2. COMPUTATIONAL DETAILS

2.1. Computational Methods. All of the periodic planewave DFT calculations were carried out with the Vienna Ab initio Simulation Package (VASP).<sup>28,29</sup> The Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) was used as the exchange-correlation potential,<sup>30</sup> and 400 eV was set as the plane-wave cutoff energy. The Monkhorst–Pack mesh k-point<sup>31</sup> of  $7 \times 7 \times 11$ for the bulk of IrO2 was used, and the Monkhorst-Pack kpoint of  $2 \times 3 \times 1$  for IrO<sub>2</sub>(110) and M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces was applied. The convergence of states near the Fermi level was improved by SIGMA = 0.2 eV. The convergence criterion of geometry optimization on the force was 0.03 eV/Å, and the energy was  $1 \times 10^{-5}$  eV. Transition states (TSs) were searched by the climbing-image nudged elastic band (CI-NEB) $^{32,33}$  and the dimer method.<sup>34</sup> The saddle point between the known reactants and products was obtained using the CI-NEB method.35,36 The forces of the structure optimization of TSs by the dimer approach on all atoms were less than 0.05 eV/Å.<sup>37</sup> Then, the calculation of the

vibrational frequency further proved that TSs had only one imaginary frequency.

The atomic substitution energy  $(E_{\rm sub})$  of the doping surface is defined as

$$E_{\rm sub} = E_{\rm M/IrO_2} + E_{\rm Ir} - E_{\rm M} - E_{\rm IrO_2}$$
(1)

where  $E_{M/IrO_2}$ ,  $E_{Ir}$ ,  $E_{M}$ , and  $E_{IrO_2}$  represent the energies of the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surface, the Ir atom, the M atom, and the IrO<sub>2</sub>(110) surface, respectively. The smaller the  $E_{sub}$ , the easier the Ir atom is to be replaced.

The binding energy  $(E_b)$  of the doping surface is defined as

$$E_{\rm b} = E_{\rm M/IrO_2} - E_{\rm M} - E_{\rm IrO_2 - Ir_v}$$
 (2)

where  $E_{M/IrO_2}$ ,  $E_M$ , and  $E_{IrO_2-IrO_v}$  are the total energies for the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu), the isolated M (M = Rh, Pd, and Cu) atom, and the clean IrO<sub>2</sub>(110) surface with an iridium vacancy, respectively.

The calculation formula of the d-band center is shown as follows

$$\varepsilon_{\rm d} = \frac{\int_{-\infty}^{+\infty} E\rho_{\rm d}(E) dE}{\int_{-\infty}^{+\infty} \rho_{\rm d}(E) dE}$$
(3)

where  $\rho_d$  indicates the density of states projected onto the dband of the top two layers of IrO<sub>2</sub>(110), Rh/IrO<sub>2</sub>(110), Pd/ IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110) surfaces and *E* is the energy of the d-band.

The adsorption energies  $(E_{ads})$  of reaction molecules adsorbed on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces are calculated using the equation

$$E_{\rm ads} = E_{\rm adsorbate/substrate} - E_{\rm adsorbate} - E_{\rm substrate}$$
(4)

where  $E_{adsorbate/substrate}$ ,  $E_{adsorbate}$ , and  $E_{substrate}$  are the total energies of the adsorption system, the isolated adsorbate, and the substrate, respectively.

The activation energy  $(E_a)$  and the reaction energy  $(\Delta E)$  are calculated by the following formulas

$$E_{\rm a} = E_{\rm TS} - E_{\rm IS} \tag{5}$$

$$\Delta E = E_{\rm FS} - E_{\rm IS} \tag{6}$$

where  $E_{IS}$ ,  $E_{TS}$ , and  $E_{FS}$  are the total energies of the reactant, the TSs, and the product, respectively. The smaller the  $E_a$ , the more advantages the reaction will have.

**2.2. Surface Models.** The lattice parameters calculated for bulk IrO<sub>2</sub> are a = 4.50 Å, b = 4.50 Å, and c = 3.18 Å (Table S1). The results agree well with the experimental value.<sup>38</sup> Pure IrO<sub>2</sub>(110) and M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) models were developed by a  $p(3 \times 1)$  periodic slab with a = 9.56 Å and b = 6.36 Å, and 12 atomic layers were used. In addition, the model size test is shown in Figure S1 and Table S2. A 15 Å vacuum region was added to separate the slabs in the perpendicular direction. In the process of geometry optimization, the lowest three layers were kept fixed, and the top nine layers and species were relaxed. For M/IrO<sub>2</sub>(110) surfaces, one of the surface Ir<sub>cus</sub> atoms was substituted by an M (M = Rh, Pd, and Cu) atom.<sup>39</sup> The top and side views of IrO<sub>2</sub>(110) and M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces are shown in Figure 1.



Figure 1. Top and side views of the optimized configurations of the  $M/IrO_2(110)$  surface and the corresponding active sites. Green, blue, and red balls denote M (M = Rh, Pd, and Cu), Ir, and O atoms, respectively.

## 3. RESULTS AND DISCUSSION

**3.1. Stability of M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) Surfaces.** The relationship between M (M = Rh, Pd, and Cu) atoms and the  $IrO_2(110)$  surface is discussed by the electronic structure analysis, and partial density of states (pDOS) for the M (M = Rh, Pd, and Cu) atom on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces and the Ir atom on the  $IrO_2(110)$  surface, as well as Rh, Pd, Cu, and Ir single atoms in the gas phase, is shown in Figure 2. The curve shape of pDOS of the Ir atom on



**Figure 2.** Partial density of states (pDOS) for the M (M = Rh, Pd, and Cu) atom on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces and the Ir atom on the  $IrO_2(110)$  surface and Rh, Pd, Cu, and Ir single atoms. The black dotted line, blue line, and red line represent the Fermi level and pDOS of the doped M atom and the M single atom (M = Rh, Pd, and Cu), respectively.

the  $IrO_2(110)$  surface is broadened noticeably compared with the gas-phase Ir atom. Moreover, the curve shape of pDOS of the M (M = Rh, Pd, and Cu) atom on the M/IrO\_2(110) (M = Rh, Pd, and Cu) surface is broadened significantly compared with the gas-phase M (M = Rh, Pd, and Cu) atom, which is similar to that of the pure IrO\_2(110) surface. This indicates that the M (M = Rh, Pd, and Cu) atom is stably doped into the IrO\_2(110) surface. At the same time, below the Fermi level, the height of occupied states' peak decreases, also suggesting that M (M = Rh, Pd, and Cu) atoms interact with the IrO\_2(110) surface. In addition, the  $E_{sub}$  values of Rh/ IrO\_2(110), Pd/IrO\_2(110), and Cu/IrO\_2(110) surfaces are 0.55, 3.52, and 2.84 eV, respectively. It is indicated that the ease of Rh, Pd, and Cu atoms doped on the surface of IrO<sub>2</sub>(110) is Rh > Cu > Pd. Also, the  $E_{\rm b}$  values of Rh/IrO<sub>2</sub>(110), Pd/IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110) surfaces are -7.32, -4.36, and -5.03 eV, respectively. In addition, we also calculated the energy barrier for the migration of the doped M (M = Rh, Pd, Cu) atom separated from the M/IrO<sub>2</sub>(110) (M = Rh, Pd, Cu) surface to the gas phase, which are 3.39, 1.92, and 3.06 eV, respectively. These large migration energies mean that these surface dopants are stable on the surface rather than segregate during reaction. It is indicated that Rh/IrO<sub>2</sub>(110), Pd/IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110) surfaces are stable.

**3.2. OCM Reaction on the Pure IrO<sub>2</sub>(110) Surface.** *3.2.1.*  $CH_4$  Dissociation on the  $IrO_2(110)$  Surface. The dissociation of methane (CH<sub>4</sub>) on the pure  $IrO_2(110)$  surface  $Ir_{cus}$ -O<sub>br</sub> sites is calculated and compared with the literature.<sup>11,27</sup> The structures of the initial state (IS), transition state (TS), and final state (FS) as well as the reaction activation energy and reaction energy of the CH<sub>4</sub> dissociation reaction of each step can be seen in Figure 3. According to the



Figure 3. Potential energy diagram and configurations of initial states, transition states, and final states for  $CH_4$  dissociation to C and 4H on the  $IrO_2(110)$  surface. The unit of bond length in all structure diagrams is Å.

calculation results, the adsorption energy of CH<sub>4</sub> on the IrO<sub>2</sub>(110) surface is -0.46 eV (the value is -0.41 eV as reported by Tsuji et al.).<sup>27</sup> The activation energy and reaction energy of the CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub> + H reaction are 0.41 and -1.17 eV, respectively. These energy values agree with the previous literature. The activation energy and reaction energy of the CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub> + H reaction in the literature of Pham et al. are 0.30 and -1.09 eV, respectively.<sup>11</sup> Then, the activation

energies of the  $CH_3 \rightarrow CH_2 + H$  reaction, the  $CH_2 \rightarrow CH + H$ reaction, and the  $CH \rightarrow C + H$  reaction are 0.78, 1.39, and 0.34 eV, respectively. Based on the calculated results, the  $IrO_2(110)$  surface has a powerful active methane capability. In the process of methane dissociation, the activation energies of  $CH_4 \rightarrow CH_3 + H$  and  $CH_3 \rightarrow CH_2 + H$  are relatively lower and the  $CH_2 \rightarrow CH + H$  reaction has the highest energy barrier, so  $CH_2$  and  $CH_3$  are important  $CH_x$  species. It provides a guarantee for the subsequent C-C coupling reaction to generate the  $C_2$  hydrocarbon.

3.2.2.  $C_2$  Hydrocarbon and Byproduct  $CO_2$  Formation. Next, we studied the reaction of coupling of  $CH_x$  (x = 2, 3) on the pure  $IrO_2(110)$  surface. It is widely accepted that OCM includes a surface-mediated C-H activation step followed by radical reaction in the gas phase. However,  $CH_3^{\bullet}$  can also adsorb on the catalyst surface when the catalyst has a strong adsorption of  $CH_3^{\bullet}$ .<sup>40,41</sup> The surface of  $IrO_2(110)$  has strong chemical adsorption for  $CH_3$ , and its adsorption energy is -2.71 eV. Hence, the  $CH_3$  coupling reaction occurs on the  $IrO_2(110)$  surface rather than in the gas phase. As shown in Figure 4, the activation energy and reaction energy of the  $CH_3$ 



**Reaction coordinate** 

**Figure 4.** Potential energy diagram and configurations of initial states, transition states, and final states for  $CH_3 + CH_3 \rightarrow C_2H_6$  and  $O_2 \rightarrow O$  + O on the  $IrO_2(110)$  surface. Red balls represent lattice oxygen. Yellow balls represent adsorbed oxygen. The unit of bond length in all structure diagrams is Å.

+ CH<sub>3</sub> → C<sub>2</sub>H<sub>6</sub> reaction are 2.40 and 0.52 eV, respectively. (In the report of Pham et al., the values are 2.90 and 0.79 eV, respectively.)<sup>11</sup> Moreover, two CH<sub>2</sub> spontaneously generate ethylene without overcoming the energy barrier. Based on the calculated results, ethylene is the main C<sub>2</sub> hydrocarbon product on the IrO<sub>2</sub>(110) surface.

Oxygen is the commonest oxidant in the process of OCM. Then, the adsorption and dissociation of  $O_2$  on the pure  $IrO_2(110)$  surface were studied. The adsorption energy of  $O_2$  on the pure  $IrO_2(110)$  surface is -1.81 eV. As shown in Figure 4, the activation energy for the decomposition of  $O_2$  is only 0.28 eV and the reaction energy is -0.03 eV. On the pure  $IrO_2(110)$  surface, the adsorption energy of CH<sub>4</sub> is much lower than that of  $O_2$  (-1.81 vs -0.46 eV), and the dissociation energy of  $O_2$  is lower than that of CH<sub>4</sub> (0.28 vs 0.41 eV). Therefore, in the OCM reaction system, the formation of the  $O_{ad}$  atom is inevitable on the pure  $IrO_2(110)$  surface.

Then, the reactions of  $CH_x$  (x = 2, 3) with the  $O_{ad}$  atom to form  $CH_xO$  (x = 2, 3) species were studied (Figure 5).  $CH_3$ 



**Figure 5.** Potential energy diagram for the formation and dissociation of  $CH_xO$  on the  $IrO_2(110)$  surface.

and CH<sub>2</sub> react with the O<sub>ad</sub> atom to form CH<sub>3</sub>O and CH<sub>2</sub>O, respectively. The activation energy of the CH<sub>3</sub> + O  $\rightarrow$  CH<sub>3</sub>O reaction is 1.38 eV. For CH<sub>2</sub> + O  $\rightarrow$  CH<sub>2</sub>O, the CH<sub>2</sub> and O<sub>ad</sub> atom adsorbed on two adjacent Ir<sub>cus</sub> atoms, spontaneously generating CH<sub>2</sub>O without overcoming the energy barrier. Then, the activation energy of CH<sub>2</sub>O dehydrogenation to CHO is only 0.30 eV and the activation energy of CHO dehydrogenation to CO is 0.70 eV. Subsequently, CO reacts with another O<sub>a</sub> atom to produce the byproduct CO<sub>2</sub> with an energy barrier of 0.77 eV. It can be seen that O<sub>2</sub> is easily dissociated on the surface of IrO<sub>2</sub>(110) to form O<sub>ad</sub> atoms only with the activation energy of 0.28 eV. The self-coupling of CH<sub>2</sub>O to ethylene and the reaction of CH<sub>2</sub> with O<sub>ad</sub> to CH<sub>2</sub>O are

	IrO <sub>2</sub> (110)	Rh/IrO <sub>2</sub> (110)		Pd/IrO <sub>2</sub> (110)		Cu/IrO <sub>2</sub> (110)	
species	Ir site	Ir site	Rh site	Ir site	Pd site	Ir site	Cu site
$CH_4$	-0.46	-0.43	-0.32	-0.35	-0.02	-0.29	-0.02
CH <sub>3</sub>	-2.71	-2.66	-2.22	-2.51	-2.03	-2.40	-1.11
CH <sub>2</sub>	-4.22	-4.16	-3.37	-4.00	-2.43	-3.95	-1.45
CH	-4.78	-4.75	-3.44	-4.66	-2.66	-4.71	

Table 1. Adsorption Energies of  $CH_x$  (x = 1-4) Species at the  $Ir_{cus}$  Site and the M Site on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) Surfaces

both barrierless processes, and they are competitive reactions. However, the CH<sub>2</sub>O is likely converted to the byproduct CO<sub>2</sub>, which leads to the decrease in C<sub>2</sub> selectivity. Hence, one can see that inhibition of O<sub>2</sub> dissociation and further oxidation of CH<sub>x</sub> are key to improving C<sub>2</sub> selectivity. Therefore, the second metals Rh, Pd, and Cu were doped on the surface of IrO<sub>2</sub>(110) to explore their effects on CH<sub>4</sub> dissociation, formation of C<sub>2</sub> species, and O<sub>2</sub> adsorption and dissociation.

3.3. M(M = Rh, Pd, and Cu)-Doped IrO<sub>2</sub>(110) Surface on OCM Reaction. 3.3.1. CH<sub>4</sub> Dissociation on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) Surfaces. First, the adsorption and dissociation of  $CH_x$  (x = 1-4) at the M (M = Rh, Pd, and Cu) site on the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surface were studied, and relative information are shown in Table 1 and Figure S2. On Rh/IrO<sub>2</sub>(110) and Pd/IrO<sub>2</sub>(110) surfaces, the adsorption energies of  $CH_x$  (x = 1-4) at the Ir<sub>cus</sub> site are larger than that at the Rh or Pd site. On the  $Cu/IrO_2(110)$  surface, the adsorption energies of  $CH_x$  (x = 2-4) at the Ir<sub>cus</sub> site are -3.95, -2.40, and -0.29 eV, respectively, and at the Cu site they are -1.45, -1.11, and -0.02 eV, respectively. We can find that the adsorption energies of  $CH_x$  (x = 1-4) species at the  $Ir_{cus}$  site are larger than that at the M site on the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surface. Hence, the dissociation of methane on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces is similar to that on the pure  $IrO_2(110)$  surface.  $CH_x$  (x = 0-4) species are adsorbed on the Ir<sub>cus</sub> atom instead of doped atoms, and the dissociated H atom is adsorbed on the O<sub>br</sub> atom. On  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces, the activation energy of  $CH_2 \rightarrow CH + H$  (1.37, 1.32, and 1.35 eV, respectively) is much higher than the  $CH_4 \rightarrow CH_3 + H$ reaction (0.42, 0.41, and 0.42 eV, respectively) and the  $CH_3 \rightarrow$  $CH_2$  + H reaction (0.77, 0.75, and 0.74 eV, respectively). Thus,  $CH_2$  and  $CH_3$  are important  $CH_x$  species. Based on these results, the doping of Rh, Pd, and Cu metals has no significant negative effect on the dissociation process of CH<sub>4</sub>, compared with the pure  $IrO_2(110)$  surface. Reaction activation energy and reaction energy of the CH<sub>4</sub> dissociation reaction and the appropriate structures on  $Cu/IrO_2(110)$ , Rh/  $IrO_2(110)$ , and Pd/IrO<sub>2</sub>(110) surfaces can be seen in Figures 6, S3, and S4, respectively. In addition, it is well-known that the  $Ir_{cus}$  sites on the  $IrO_2(110)$  surface are very reactive toward oxygen. Dissociation of  $CH_4$  to  $CH_3$  and H on  $O_a$ -Ir $O_2(110)$ and  $O_a$ -M/Ir $O_2(110)$  (M = Rh, Pd, and Cu) surfaces has been studied, and the relative information is shown in Figure S5. It can be obtained that the O<sub>a</sub> atom located on the neighboring Ir<sub>cus</sub> site has no significant effect during the C-H activation of methane.

Furthermore, once one C–H bond in methane is broken, another methane C–H activation is required for water generation via the interaction with OH species and then water desorption.<sup>12</sup> Three cases are used to study the effects of the first hydroxyl group (from the first C–H activation) on the second C–H activation, and the relative information is shown in Figure S6. We can find that the first hydroxyl group (from the first C–H activation) has negative effects on the second C–H activation. On pure  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces, the energy barrier of the second methane interacting with the  $O_{br}H$  species to produce  $H_2O$  is higher than that of the first methane interacting with the  $O_{br}$  atom to produce the  $O_{br}H$  species. This means that the  $O_{br}H$  species. This means that the  $O_{br}H$  species. Then, the difficulty of desorption of  $H_2O$  from the four surfaces follows the trend of  $IrO_2(110) = Rh/IrO_2(110)$  (1.02 eV) > Pd/IrO\_2(110) (0.77 eV) > Cu/IrO\_2(110) (0.44 eV). The relevant structures as well as the reaction activation energy and reaction energy are shown in Figure 7.

3.3.2. C-C Coupling Reaction on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) Surfaces. We subsequently investigated the C-Ccoupling reaction on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces, and the corresponding results are summarized in Figure 8. On M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces, activation energies for the formation of  $C_2H_6$  by coupling two  $CH_3$  adsorbed on the top sites of  $Ir_{cus}$  and M (M = Rh, Pd, and Cu) are 1.90, 1.76, and 0.75 eV, respectively. The activation energy of  $CH_3 + CH_3 \rightarrow C_2H_6$  on the pure  $IrO_2(110)$  surface is 2.40 eV. The doping of Rh, Pd, and Cu reduces the activation energy of  $CH_3$  self-coupling to  $C_2H_6$ . The reason is that the adsorption energy of  $CH_3$  on Ir and M (M = Rh, Pd, and Cu) atoms follows the trend of Ir(-2.70 eV) > Rh(-2.22)eV) > Pd(-2.03 eV) > Cu(-1.10 eV) on the IrO<sub>2</sub>(110) and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces. It can be seen from the TS1 geometry of Figure 8 that CH<sub>3</sub> adsorbed on the M (M = Rh, Pd, and Cu) atom is desorbed and coupled with CH<sub>3</sub> adsorbed on the Ir<sub>cus</sub> atom. Therefore, as the adsorption energy of CH<sub>3</sub> on Ir, Rh, Pd, and Cu atoms gradually decreases, the activation energy of C<sub>2</sub>H<sub>6</sub> formation reduces. On Cu (100), (111), and (211), CO–CO coupling is facile to realize, which is conducive to the formation of C<sub>2</sub> products.<sup>42</sup> Moreover, the Pd catalyst is one of the important catalysts for the formation of the C–C bond in organic chemistry.<sup>43</sup> These are consistent with the results that Pd and Cu doping can reduce the energy barrier of the coupling reaction of CH<sub>3</sub> to  $C_2H_6$ . For the coupling reaction of two  $CH_2$  to  $C_2H_4$  on M/  $IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces, two CH<sub>2</sub> are adsorbed on the adjacent  $Ir_{cus}$  atom and the M (M = Rh, Pd, and Cu) atom, respectively, and then spontaneously form C2H4 without overcoming the energy barrier. Based on the calculated results, C<sub>2</sub>H<sub>4</sub> is the main C<sub>2</sub> hydrocarbon product on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces.

3.3.3.  $O_2$  Adsorption and Dissociation on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) Surfaces. Next, the adsorption and dissociation of  $O_2$  on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces were studied. The structures of IS, TS, and FS for the  $O_2 \rightarrow O + O$  reaction and the reaction activation energy and reaction energy can be seen in Figure 8. On the Rh/IrO<sub>2</sub>(110) surface, the adsorption energy of  $O_2$  is -1.47 eV, which is

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Cu/IrO<sub>2</sub>(110)



Figure 6. Potential energy diagram for  $CH_4$  dissociation to C and 4H on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces and configurations of initial states, transition states, and final states on the  $Cu/IrO_2(110)$  surface. The unit of bond length in all structure diagrams is Å.

stable in the bridge site of  $Ir_{cus}$ -Rh. On M/IrO<sub>2</sub>(110) (M = Pd and Cu) surfaces, O<sub>2</sub> is adsorbed on the  $Ir_{cus}$  top site via an O

atom, and the adsorption energies of  $O_2$  are -1.00 and -0.86 eV, respectively. The adsorption of  $O_2$  on the  $RuO_2(110)$ 



Figure 7. Potential energy diagram for  $H_2O$  formation and desorption on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces and relevant structures. The unit of bond length in all structure diagrams is Å.

surfaces was -1.27 eV.<sup>44</sup> In contrast, the adsorption energy of  $O_2$  on the Cu/IrO<sub>2</sub>(110) surface is lower. On M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces, the decomposition of O<sub>2</sub> into two  $O_{ad}$  atoms is accompanied by activation energies of 0.76, 1.18, and 1.75 eV, respectively, and reaction energies of 0.27, 1.07, and 1.69 eV, respectively. On the pure  $IrO_2(110)$ , the adsorption energy of  $O_2$  is as high as -1.81 eV, and the energy barrier for  $O_2$  dissociation is only 0.28 eV. Doping of M (M = Rh, Pd, and Cu) atoms reduces the adsorption energy of  $O_2$ and increases the dissociation energy of  $O_2$  in order of M being Rh, Pd, and Cu. The reason is that configurations of  $O_2$ adsorption on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces are various. As such, previous studies found that Cu doping can reduce the adsorption energy of O<sub>2</sub> on the Al(111) surface,<sup>45</sup> and Pd-based catalysts weakly combine with the atomic oxygen.<sup>46</sup> It can be seen from the O<sub>2</sub> geometry of Figures 8, S7, and S8 that the distances between the left O atom and Rh, Pd, and Cu atoms are 2.135, 2.881, and 3.234 Å, respectively. On the pure  $IrO_2(110)$  surface, the distance between the left O atom and the  $\mathrm{Ir}_{\mathrm{cus}}$  atom is 1.875 Å. The distance follows the sequence of O-Cu > O-Pd > O-Rh > O- $Ir_{cus'}$  which is consistent with the increasing order of the  $O_2$ dissociation energy.

While the barrier for  $O_2$  activation is higher on the Cu–Ir pair site, there are still available Ir–Ir sites that are not affected significantly by the presence of Cu. Hence, we next studied a higher concentration of dopants to see how additional Cu would affect the properties of the Ir–Ir pair site. In this section, we build a 2Cu-doped IrO<sub>2</sub>(110) surface, that is, a  $p(5 \times 1)$ periodic IrO<sub>2</sub>(110) slab; the two interphase surface Ir<sub>cus</sub> atoms were substituted by one Cu atom. On the 2Cu-doped IrO<sub>2</sub>(110) surface, the adsorption configuration and the corresponding adsorption energy of O<sub>2</sub> molecules at different adsorption sites are shown in Table S3. It can be found that the most stable adsorption site of O<sub>2</sub> is the Ir–Ir bridge site and the adsorption energy is -1.37 eV. The adsorption energy of O<sub>2</sub> on the pure IrO<sub>2</sub>(110) surface is -1.88 eV. Therefore, additional Cu can also reduce the adsorption energy of O<sub>2</sub> at the Ir-Ir site. As shown in Figure S9, the energy barrier of the  $O_2 \rightarrow O + O$  reaction on the pure  $IrO_2(110)$  surface is similar to that on the 2Cu-doped  $IrO_2(110)$  surface. As a result, additional Cu has little effect on O2 dissociation at the Ir-Ir site. It can be obtained from the above analysis that on the 2Cu-doped  $IrO_2(110)$  surface,  $O_2$  is easily absorbed at the Ir-Ir site rather than at the Ir-Cu site. In addition, O2 is easily dissociated into O<sub>a</sub> atoms at the Ir-Ir site. Next, we studied the initial dissociation of methane on the 2Cu-doped  $IrO_2(110)$  surface adsorbed with an  $O_a$  atom. As shown in Figure S10, the activation energy of the  $CH_4 \rightarrow CH_3 + H$ reaction is 0.47 eV, which is only 0.05 eV higher than that on the  $Cu/IrO_2(110)$  surface. In addition, for the coupling reaction of two  $CH_2$  to  $C_2H_4$  on the 2Cu-doped  $IrO_2(110)$ surface adsorbed with an O<sub>a</sub> atom, two CH<sub>2</sub> are adsorbed on the adjacent Ir<sub>cus</sub> atom and the Cu atom, respectively, spontaneously forming C<sub>2</sub>H<sub>4</sub> without overcoming the energy barrier, rather than reacting with O<sub>a</sub> to form the CH<sub>2</sub>O species.

Furthermore, we also investigated the stability of the added surface Cu. The migration energies of the two doped Cu atoms segregated from the 2Cu-doped  $IrO_2(110)$  surface are 3.05 and 3.19 eV, respectively. These large migration energies mean that the added surface Cu is stable and difficult to segregate from the 2Cu-doped  $IrO_2(110)$  surface.

**3.4.** Selectivity of  $C_2$  Hydrocarbon on Pure and M-Doped IrO<sub>2</sub>(110) Catalysts. On IrO<sub>2</sub>(110) and M/ IrO<sub>2</sub>(110) (M = Rh, Pdm and Cu) surfaces, coupling of two CH<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> is a barrierless process, and the activation energy of two CH<sub>3</sub> coupling to C<sub>2</sub>H<sub>6</sub> is higher than that of CH<sub>4</sub> dehydrogenation to CH<sub>3</sub> and CH<sub>3</sub> dehydrogenation to CH<sub>2</sub>. Moreover, the activation energy of CH<sub>3</sub> dehydrogenation to CH<sub>2</sub> on the IrO<sub>2</sub>(110) surface is 0.78 eV, and the energies on the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces are all within 0.04 eV. On surfaces of IrO<sub>2</sub>(110), Rh/IrO<sub>2</sub>(110), Pd/ IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110), the activation energy of CH<sub>3</sub> coupling to C<sub>2</sub>H<sub>6</sub> gradually decreased from 2.40 to 0.75 eV.



Figure 8. Potential energy diagrams for  $O_2 \rightarrow O + O$ ,  $CH_3 + CH_3 \rightarrow C_2H_6$ , and  $CH_2 + CH_2 \rightarrow C_2H_4$  on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces, and configurations of initial states, transition states, and final states on the Cu/IrO<sub>2</sub>(110) surface. Red balls represent lattice oxygen. Yellow balls represent adsorbed oxygen. The unit of bond length in all structure diagrams is Å.

The activation energy of CH<sub>3</sub> dehydrogenation to CH<sub>2</sub> is similar on the four surfaces and lower than the activation energy of CH<sub>3</sub> coupling to C<sub>2</sub>H<sub>6</sub> on the corresponding surface. In addition, the byproduct CO is formed by continuous dehydrogenation of CH<sub>2</sub>O, which is obtained by the reaction of the O<sub>ad</sub> atom with CH<sub>2</sub>. Therefore, the differential value between the activation energy of O<sub>2</sub> dissociation to O<sub>ad</sub> and the activation energy of CH<sub>3</sub> coupling to C<sub>2</sub>H<sub>6</sub> is used as the qualitative evaluation index of C<sub>2</sub> hydrocarbon selectivity. As shown in Figure 9, on the IrO<sub>2</sub>(110) surface, the activation energy of CH<sub>3</sub> + CH<sub>3</sub>  $\rightarrow$  C<sub>2</sub>H<sub>6</sub> is 2.40 eV, and the difference between them is -2.12 eV. On M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces, the activation energies of  $O_2$  dissociation reaction are 0.76, 1.18, and 1.75 eV, respectively, the activation energies of  $CH_3 + CH_3 \rightarrow C_2H_6$  are 1.90, 1.76 and 0.75 eV, respectively, and the differences between the activation energies of the two reactions are -1.14, -0.58, and -1.00eV, respectively. This indicates that the doping of Rh, Pd, and Cu can improve the selectivity of the  $C_2$  hydrocarbon in different degrees compared with the pure  $IrO_2(110)$  surface, among which the effect of Cu doping is the best.

**3.5. Reaction Rate Constant Analysis.** Based on the calculation of potential energy, we further estimated the reaction rate constants of key elementary reactions in the four



**Figure 9.** Activation energies of  $CH_3 + CH_3 \rightarrow C_2H_6$ ,  $O_2 \rightarrow O + O$ , and  $CH_2 + CH_2 \rightarrow C_2H_4$  reactions and  $C_2$  hydrocarbon selectivity on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces.

systems. The formula of rate constants for the key elementary reactions step is as follows  $^{47}$ 

$$k = \nu_i \exp\left(\frac{-\Delta E_a}{RT}\right) \tag{7}$$

where  $\nu_i$  is the pre-exponential factor,  $E_a$  is the ZPE-corrected energy barrier, and T is the temperature. The formula of the pre-exponential factor  $\nu_i$  is as follows<sup>47</sup>

$$\nu_{i} = \frac{k_{\rm B}T}{h} \frac{\prod_{i=1}^{3N} \left[ 1 - \exp\left(-\frac{bf_{i}^{1S}}{k_{\rm B}T}\right) \right]}{\prod_{i=1}^{3N-1} \left[ 1 - \exp\left(-\frac{bf_{i}^{1S}}{k_{\rm B}T}\right) \right]}$$
(8)

where  $f_i^{IS}$  is the vibrational frequency at the IS and  $f_i^{TS}$  is the vibrational frequency at the TS. Additionally,  $k_B$  is the Boltzmann constant.  $\Delta E_a$ , the activation energy with the zero-point correction, is calculated as follows<sup>48</sup>

$$\Delta E_{\rm a} = (E_{\rm TS} - E_{\rm IS}) + \Delta Z P E_{\rm barrier} \tag{9}$$

$$\Delta ZPE_{\text{barrier}} = \left(\sum_{i=1}^{\text{vibration}} \frac{hf_i}{2}\right)_{\text{TS}} - \left(\sum_{i=1}^{\text{vibration}} \frac{hf_i}{2}\right)_{\text{IS}}$$
(10)

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where points to zero-point energy revision of the reaction activation energy, h is Planck's constant, and  $f_i$  is the vibration frequency.

The IrO<sub>2</sub> catalyst had a good catalytic capability for methane activation in the range of 150-515 K.18 The reaction rate constants of key elementary reactions at different temperatures are calculated (Tables 2, S4, and S5). On the  $IrO_2(110)$ surface, the rate constants of O<sub>2</sub> dissociation and two CH<sub>3</sub> coupling to  $C_2H_6$  are 7.77  $\times$  10<sup>4</sup> to 3.05  $\times$  10<sup>10</sup> and 1.79  $\times$  $10^{-67}$  to  $5.47 \times 10^{-11}$  in the range of 150–550 K, respectively. On M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces, the rate constants of O<sub>2</sub> dissociation are in the range from  $2.14 \times 10^{-11}$ to  $1.44 \times 10^{6}$ ,  $2.80 \times 10^{-26}$  to  $5.70 \times 10^{1}$ , and  $1.89 \times 10^{-45}$  to  $2.99 \times 10^{-4}$ , respectively, and the rate constants of two CH<sub>3</sub> coupling to  $C_2H_6$  are in the range of 1.14  $\times$  10<sup>-49</sup> to 4.86  $\times$  $10^{-6}$ ,  $2.13 \times 10^{-45}$ , to  $4.73 \times 10^{-5}$  and  $2.38 \times 10^{-12}$  to  $7.26 \times 10^{-12}$  $10^4$ , respectively. It can be seen that the reaction rate constants of O<sub>2</sub> dissociation follow the trend of  $IrO_2(110) > Rh/$  $IrO_2(110) > Pd/IrO_2(110) > Cu/IrO_2(110)$ , and the reaction rate constants of two CH<sub>3</sub> coupling to C<sub>2</sub>H<sub>6</sub> follow the trend of  $Cu/IrO_2(110) > Pd/IrO_2(110) > Rh/IrO_2(110) > IrO_2(110).$ Moreover, the  $O_2$  dissociation rate on the Cu/IrO<sub>2</sub>(110) surface is far lower than that of  $CH_3$  coupling to  $C_2H_{6}$ , but the dissociation rate of O<sub>2</sub> on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces is much higher than that of  $CH_3$ coupling to  $C_2H_6$ .

**3.6. Electronic Structural Property Analysis.** An electronic analysis of the  $O_2$  adsorption and the transition state structures of the CH<sub>3</sub> coupling reaction on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces has been carried out to improve the understanding on the impact of metal dopants (Rh, Pd, and Cu) on preventing  $O_{ad}$  and promoting the formation of ethane. Here, the electronic interactions involved in the related atoms by plotting the projected density of states (pDOS) diagrams have been analyzed, as shown in Figures 10 and S11. Zhi et al.<sup>49</sup> also studied the effect of

Table 2. Rate Constants (s<sup>-1</sup>) of Key Primitive Reactions on  $IrO_2(110)$  and  $Cu/IrO_2(110)$  Surfaces at Different Temperatures (K)

surface	reaction	150	250	350	450	550
IrO <sub>2</sub> (110)	$CH_4 \rightarrow CH_3 + H$	$1.16 \times 10^{3}$	$8.53 \times 10^{6}$	$4.01 \times 10^{8}$	$3.52 \times 10^{9}$	$1.44 \times 10^{10}$
	$CH_3 \rightarrow CH_2 + H$	$3.13 \times 10^{-9}$	$8.50 \times 10^{-1}$	$2.62 \times 10^{3}$	$1.84 \times 10^{5}$	$3.32 \times 10^{6}$
	$\mathrm{CH}_2 \to \mathrm{CH} + \mathrm{H}$	$9.96 \times 10^{-29}$	$3.26 \times 10^{-12}$	$3.22 \times 10^{-5}$	$2.11 \times 10^{-1}$	$5.01 \times 10^{1}$
	$CH \rightarrow C + H$	$4.13 \times 10^{3}$	$2.39 \times 10^{7}$	$8.34 \times 10^{8}$	$5.31 \times 10^{9}$	$1.57 \times 10^{10}$
	$CH_3 + CH_3 \rightarrow C_2H_6$	$1.79 \times 10^{-67}$	$6.90 \times 10^{-36}$	$1.30 \times 10^{-22}$	$1.99 \times 10^{-15}$	$5.47 \times 10^{-11}$
	$O_2 \rightarrow O + O$	$7.77 \times 10^{4}$	$1.46 \times 10^{8}$	$2.96 \times 10^{9}$	$1.33 \times 10^{10}$	$3.05 \times 10^{10}$
	$CH_3 + O \rightarrow CH_3O$	$1.59 \times 10^{-32}$	$1.66 \times 10^{-15}$	$2.44 \times 10^{-7}$	$3.99 \times 10^{-3}$	$1.95 \times 10^{0}$
	$CH_2O \rightarrow CHO + H$	$7.77 \times 10^{4}$	$3.34 \times 10^{8}$	$4.69 \times 10^{9}$	$1.57 \times 10^{10}$	$2.75 \times 10^{10}$
	$\rm CHO \rightarrow \rm CO + \rm H$	$1.39 \times 10^{-6}$	$6.88 \times 10^{1}$	$1.10 \times 10^{5}$	$5.50 \times 10^{6}$	$5.75 \times 10^{7}$
$Cu/IrO_2(110)$	$CH_4 \rightarrow CH_3 + H$	$1.43 \times 10^{2}$	$1.86 \times 10^{6}$	$1.08 \times 10^{8}$	$1.05 \times 10^{9}$	$4.59 \times 10^{9}$
	$CH_3 \rightarrow CH_2 + H$	$9.72 \times 10^{-8}$	$6.84 \times 10^{0}$	$1.19 \times 10^{4}$	$6.09 \times 10^{5}$	$6.31 \times 10^{6}$
	$CH_2 \rightarrow CH + H$	$8.89 \times 10^{-27}$	$6.57 \times 10^{-11}$	$2.42 \times 10^{-4}$	$1.07 \times 10^{0}$	$1.99 \times 10^{2}$
	$\mathrm{CH} \to \mathrm{C} + + \mathrm{H}$	$7.00 \times 10^{1}$	$2.15 \times 10^{6}$	$1.56 \times 10^{8}$	$1.51 \times 10^{9}$	$5.83 \times 10^{9}$
	$CH_3 + CH_3 \rightarrow C_2H_6$	$2.38 \times 10^{-12}$	$9.56 \times 10^{-3}$	$6.66 \times 10^{1}$	$5.82 \times 10^{3}$	$7.26 \times 10^{4}$
	$O_2 \rightarrow O + O$	$1.89 \times 10^{-45}$	$1.40 \times 10^{-22}$	$6.90 \times 10^{-13}$	$1.41 \times 10^{-7}$	$2.99 \times 10^{-4}$
	$CH_3 + O \rightarrow CH_3O$	$2.78 \times 10^{-19}$	$4.14 \times 10^{-7}$	$6.55 \times 10^{-2}$	$5.04 \times 10^{1}$	$3.46 \times 10^{3}$
	$CH_2O \rightarrow CHO + H$	$2.50 \times 10^{-17}$	$5.27 \times 10^{-6}$	$2.47 \times 10^{-1}$	$2.46 \times 10^{3}$	$2.27 \times 10^{3}$
	$\rm CHO \rightarrow \rm CO + \rm H$	$4.19 \times 10^{8}$	$1.21 \times 10^{10}$	$3.76 \times 10^{10}$	$5.73 \times 10^{10}$	$6.44 \times 10^{10}$



Figure 10. Projected density of states (pDOS) for O<sub>2</sub> adsorption on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces.

dopant Zr on the formation of  $CH_4$  using pDOS. When  $O_2$  is adsorbed on the  $IrO_2(110)$  surface, the relative strong interaction between the  $O_2$  molecule and the  $IrO_2(110)$ surface mainly comes from the mixing between the O 2p and Ir 5d orbitals due to the large overlap. Similarly, the  $O_2$  molecule and the  $Rh/IrO_2(110)$  surface interaction mainly comes from the mixing between the O1 2p and Rh 4d orbitals and the O2 2p and Ir 5d orbitals. Significantly, the interaction between the former is weaker than the latter. In addition, on the Pd/  $IrO_2(110)$  surface, similar results were obtained, and the narrower overlap between the O1 2p orbital as the atom adjacent to the doped metal and the 2p orbital of the O2 atom gradually decreased. In Figure S11, on  $IrO_2(110)$ , Rh/  $IrO_2(110)$ , Pd/ $IrO_2(110)$ , and Cu/ $IrO_2(110)$  surfaces, the overlap between the 5d orbital of the Ir atom adjacent to the doped metal and the 2p orbital of the C2 atom increases gradually. We can find that the interaction between the M atom and the O1 or C1 atom is weak, but it significantly affects the interaction between the adjacent Ir atom and the O2 atom or C2 atom. The dopant metal site does not act as the active site of the methane dissociation reaction but affects the O2 adsorption and CH<sub>3</sub> coupling reaction of the adjacent Ir<sub>cus</sub> site.

It is obvious that the doping of Rh, Pd, and Cu has an effect on the electronic structure properties rather than the geometry structure. We analyze the d-band structure of monolayers on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces (Figure 11). The d-band centers of surface  $IrO_2(110)$ , Rh/  $IrO_2(110)$ , Pd/ $IrO_2(110)$ , and Cu/ $IrO_2(110)$  monolayers are



**Figure 11.** Partial density of states (pDOS) for surface  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) monolayers of  $IrO_2(110)$ , Rh/ $IrO_2(110)$ , Pd/ $IrO_2(110)$ , and Cu/ $IrO_2(110)$  surfaces. (The vertical solid line represents the location of the Fermi level, and the vertical dotted line represents the location of the d-band centers.).

-3.79, -3.77, -3.72, and -3.51 eV, respectively, indicating that the closer the center of the d-band is to the Fermi level,



Figure 12. Differential charge density of  $O_2$  adsorption on M/Ir $O_2(110)$  (M = Rh, Pd, and Cu) surfaces. Yellow and blue shaded regions represent the charge gain and charge loss, respectively.

the more instrumental it is in the coupling reaction of  $CH_3$  to  $C_2H_{6\prime}$  and the more detrimental it is to the dissociation of  $O_2$ .

Furthermore, the essential reasons for the different catalytic performances of Rh, Pd, and Cu atoms doped  $IrO_2(110)$ surface are analyzed from the microscopic point of view. The Bader charge and differential charge on  $IrO_2(110)$  and M/  $IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces are calculated. The differential charge density on  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces is shown in Figure S12. The results are indicative of the electron transfer between the M (M = Rh, Pdm, andCu) atom and  $IrO_2(110)$ , and the charges gather at the interface. Moreover, the Bader charge analysis makes it clear that the total charge transfers from Rh, Pd, and Cu atoms to  $IrO_2(110)$  are 1.28, 1.09, and 1.13*e*, respectively. Consequently, the results of electronic and structural properties show moderate amounts of charge transfer between the M (M = Pd)and Cu) atom and  $IrO_2(110)$  and a charge region at the interface of  $M/IrO_2(110)$  (M = Pd and Cu) catalysts, which improves the  $C_2$  hydrocarbon selectivity of the OCM reaction.

To understand the effect of the  $IrO_2(110)$  doped metal M single atom (M = Rh, Pd, and Cu) on the dissociation of  $O_2$ , we analyzed the differential charge density of  $O_2$  adsorption on M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surfaces (Figure 12). The results are indicative of the electron transfer between the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surface and the  $O_2$  molecule. Moreover, Bader charge analysis makes it clear that the total charge transfers from  $IrO_2(110)$ , Rh/IrO<sub>2</sub>(110), Pd/IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110) to the O<sub>2</sub> molecule are 0.48, 0.41, 0.30, and 0.29e, respectively. Bader charge analysis shows that the M/IrO<sub>2</sub>(110) (M = Rh, Pd, and Cu) surface transferred less charge to the O<sub>2</sub> molecule than pure IrO<sub>2</sub>(110), which can cause weak adsorption of the O<sub>2</sub> molecule; consequently, doping Rh, Pd, and Cu can inhibit the dissociation of O<sub>2</sub> and further hinder the formation of CO.

**3.7. Effect of Doped Second Metals on the IrO**<sub>2</sub>(110) **Surface on the OCM Reaction.** According to our calculation on IrO<sub>2</sub>(110), the second metal M (M = Rh, Pd, and Cu) doped IrO<sub>2</sub>(110) surface maintains the high activity of methane activation compared with that on the pure IrO<sub>2</sub>(110) surface. The formation of CH<sub>3</sub> and CH<sub>2</sub> is more favorable than that of CH. Therefore, CH<sub>3</sub> and CH<sub>2</sub> species participate in the coupling reaction to generate the C<sub>2</sub> hydrocarbon (C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>).

On the pure  $IrO_2(110)$  surface,  $CH_2$  coupling to ethylene is a spontaneous reaction without overcoming the energy barrier. However, the formation of  $CH_2O$  via the reaction of  $CH_2$  with  $O_{ad}$  is also no energy barrier. The reaction with  $CH_2$  selfcoupling to form ethylene and the formation of  $CH_2O$  are competitive reactions.  $CH_2O$  leads to the generation of the byproduct CO, which reduces the selectivity of the  $C_2$  hydrocarbon. However, the production of the  $O_{ad}$  atom via  $O_2$  dissociation is a key step to CH<sub>2</sub>O formation. On the pure IrO<sub>2</sub>(110) surface, the activation energy for the decomposition of  $O_2$  is only 0.28 eV, which will provide the  $O_{ad}$  atom for the CH<sub>2</sub>O species. However, Rh, Pd, and Cu doped in the IrO<sub>2</sub>(110) surface can inhibit the formation of the  $O_{ad}$  atom with  $O_2$  decomposition energy barriers of 0.76, 1.18, and 1.75 eV, respectively. Among these, Cu is the most effective to prevent the formation of the  $O_{ad}$  atom, which is expected to hinder the generation of CH<sub>2</sub>O species and improve the selectivity of the C<sub>2</sub> hydrocarbon.

Moreover, the microkinetic analysis shows that the  $O_2$  dissociation rate on  $Cu/IrO_2(110)$  at the same temperature is much lower than that on  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh and Pd) surfaces. Additionally, charge analysis implies that the Cu doping reduces the transfer of charge from the catalyst surface to the adsorbed  $O_2$  compared to the pure  $IrO_2(110)$  surface, which results in the relatively weak adsorption and high dissociation energy of  $O_2$ . These results further show that Cu doping is beneficial to improve the selectivity of the  $C_2$  hydrocarbon on the  $IrO_2(110)$  surface.

## 4. CONCLUSIONS

In this study, the reaction mechanism of the OCM reaction is calculated over the  $IrO_2(110)$  and  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces by the DFT method. Our results show that the initial activation energy of  $CH_4$  to  $CH_3$  on the  $IrO_2(110)$ surface is 0.41 eV, and the activation energies on Rh/ IrO<sub>2</sub>(110), Pd/IrO<sub>2</sub>(110), and Cu/IrO<sub>2</sub>(110) surfaces are all within 0.01 eV. In the process of methane dehydrogenation to  $CH_x$  (x = 0-3),  $CH_3$  and  $CH_2$  are the major  $CH_x$  species. The doping of Rh, Pd, and Cu metals has no negative effect on the catalytic activity of the  $IrO_2(110)$  surface. That is, M/  $IrO_2(110)$  (M = Rh, Pd, and Cu) surfaces have a high methane conversion activity similar to the pure  $IrO_2(110)$ surface. Moreover, on IrO<sub>2</sub>(110), Rh/IrO<sub>2</sub>(110), Pd/  $IrO_2(110)$ , and  $Cu/IrO_2(110)$  surfaces, the O<sub>2</sub> adsorption energy decreases and the dissociation energy barrier increases. This indicates that the Cu-doped  $IrO_2(110)$  catalyst is not conducive to the adsorption and dissociation of O<sub>2</sub> and inhibits the formation of  $O_{ad}$ , which is beneficial to the byproduct CO. Furthermore, the activation energy of  $CH_3 + CH_3 \rightarrow C_2H_6$  on the  $IrO_2(110)$  surface is 2.40 eV, and the energies on Rh/  $IrO_2(110)$ , Pd/ $IrO_2(110)$ , and Cu/ $IrO_2(110)$  surfaces are 1.90, 1.76, and 0.75 eV, respectively. It shows that doping Cu reduces the activation energy of CH3 coupling to C2H6. Additionally, charge analysis shows that the  $M/IrO_2(110)$  (M = Rh, Pd, and Cu) surface transferred less charge to the  $O_2$ 

molecule than pure  $IrO_2(110)$ , which results in the relatively weak adsorption of  $O_2$ . Furthermore, the reaction rate constant analysis also shows that the  $O_2$  dissociation rate on Cu/  $IrO_2(110)$  is much lower than that on  $IrO_2(110)$ , Rh/  $IrO_2(110)$ , and Pd/ $IrO_2(110)$  surfaces at the same temperature. In general, Cu/ $IrO_2(110)$  does not merely exhibit a high activity but also is highly selective to the  $C_2$  hydrocarbon, which can be used as a potential catalyst for the OCM reaction. Future work examining processes such as diffusion would be important to fully understand how CH<sub>x</sub> species transfer to the dopant metal.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c04670.

Lattice parameters of the  $IrO_2$  crystal structure;  $CH_4$ adsorption and C–H bond cleavage on  $IrO_2(110)$ surfaces with different cell sizes; potential energy diagram and configurations of IS, TS, and FS for  $CH_4$ dissociation at the M site on M/IrO\_2(110) (M = Rh, Pd, and Cu) surfaces; configuration structures for  $CH_4$  and O<sub>2</sub> dissociation on Rh/IrO\_2(110) and Pd/IrO\_2(110) surfaces; rate constants (s<sup>-1</sup>) of key primitive reactions on Rh/IrO\_2(110) and Pd/IrO\_2(110) surfaces at different temperatures; and differential charge density of M/ IrO\_2(110) (M = Rh, Pd, and Cu) surfaces (PDF)

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#### Notes

The authors declare no competing financial interest.

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