# DFT insight into the oxygen vacancies formation and CH<sub>4</sub> activation over CeO<sub>2</sub> surfaces modified by transition metals (Fe, Co and Ni)

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## Abstract

The effects of transition metals (Fe, Co and Ni) modification (viz., adsorption, insertion and substitution) of the CeO<sub>2</sub> surfaces on the oxygen vacancy formation and CH<sub>4</sub> activation are studied on the basis of firstprinciples calculations. The results indicate that the hollow, O-O-bridge and Ce-O-bridge sites are the most stable sites for Fe, Co and Ni atoms adsorption on CeO<sub>2</sub> (111) surface, and the double O-bridge, O-top and double O-bridge sites are the corresponding most favorable sites for the CeO<sub>2</sub> (110) surface. Most of the configurations that generated by the transition metals modification of the  $CeO_2$  (111) and (110) surfaces are accompanied by the reduction of  $Ce^{4+}$  to  $Ce^{3+}$ . Based on calculated the subsurface (SS) and sublayer (SL) oxygen vacancies of the CeO<sub>2</sub> (111) surface, the results show that the substitution of transition metals in CeO<sub>2</sub> (111) surface can promote the SS oxygen vacancy formation spontaneously. Whereas, for the SL oxygen vacancy, the transition metal Fe and Ni atoms most stable adsorption on  $CeO_2$  (111) surface can promote it formation spontaneously. For the  $CeO_2$  (110) surface, the substitution of transition metals can facilitate the type of plain (P) and spilt (S) oxygen vacancies formation spontaneously. With respect to the CH<sub>4</sub> activation, the results show that the Co atom substitution in CeO<sub>2</sub> (110) surface can greatly facilitate the first C-H bond activation, and the energy barrier is 0.783 eV, the  $\Delta H$  is -1.458 eV. However, the Co atom substitution in CeO<sub>2</sub> (110) surface with the type of P and S oxygen vacancies is not conducive to the C-H activation. The obtained results could provide new insights into the structural features of transition metals modified  $CeO_2$  at the atomistic level, leading to design more efficient oxygen carriers and to optimize the activation pathways of methane over such catalysts.

*Keywords:* DFT; Transition Metals (Fe, Co and Ni); C-H bond; Oxygen vacancy formation; Methane activation

# **Electronic Supplementary Information (ESI)**

### S1 The Mulliken charge and PDOS of the transition metals modification of CeO<sub>2</sub> (111) surface

S1.1 The Mulliken charge of the transition metals modification of CeO<sub>2</sub> (111) surface

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### Table. S 1

Calculated the Mulliken charge of transition metal (Fe, Co, or Ni), O and the Ce atoms in the transition metals (Fe, Co, or Ni) stable adsorption on CeO<sub>2</sub> (111)  $p(2 \times \sqrt{3})$  surface, respectively. The O and Ce atoms are bond to the transition metal (Fe, Co, or Ni) atoms. The Ce and O atoms are labeled with the number n (1-4) and n (1-5), which are cited in the text as Ce<sub>1</sub>-Ce<sub>4</sub> and O<sub>1</sub>-O<sub>5</sub> [see Fig. S1 (a)]. Magnetic spin moments of reduced Ce and oxidized M ions are  $\mu_{Ce}$ ,  $\mu_M$ .

Adsorption	Location	М	O <sub>1</sub>	O <sub>2</sub>	O <sub>3</sub>	$O_4$	O <sub>5</sub>	Ce <sub>2</sub>	Ce <sub>4</sub>	$\Delta Q_O$	$\Delta Q_{Ce}$	$\Delta Q_{total}$	Valance	$\mu_{Ce}$	$\mu_M$
Metals		(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	Μ		
pure (111)			-0.885	-0.885	-0.885	-0.885	-0.947	1.725	1.725						
	Ce-O-bridge	0.370			-0.865			1.850		0.02	0.125	0.515	Fe <sup>3+</sup>	3×0.960	3.980
	Ce-top	0.318							1.789		0.064	0.382	Fe <sup>2+</sup>	0.895, 0.870	3.330
	hollow	0.366	-0.866	-0.863	-0.863					0.063		0.430	Fe <sup>3+</sup>	0.893, 0.895, 0.932	4.014
Fe	O-O-bridge	0.284	-0.877			-0.876				0.017		0.301	Fe <sup>2+</sup>	2×0.864	3.500
	O-top	0.115			-0.852					0.033		0.148	Fe <sup>0+</sup>	0.160, 0.190	0.115
	$O_d$	0.321					-0.921			0.026		0.347	Fe <sup>2+</sup>	0.880, 0.910	3.210
	Ce-O-bridge	0.144			-0.855			1.857		0.030	0.132	0.306	Co <sup>2+</sup>	2×0.864	2.490
	Ce-top	0.263							1.838		0.113	0.376	Co <sup>2+</sup>	0.798, 0.834	2.520
	hollow	0.349	-0.860	-0.858	-0.858					0.079		0.428	Co <sup>3+</sup>	3×0.863	2.530
Co	O-O-bridge	0.348	-0.856			-0.856				0.058		0.406	Co <sup>3+</sup>	0.891, 0.911, 0.904	2.610
	O-top	0.130			-0.849					0.036		0.166	Co <sup>0+</sup>	1.823	2.023
	$O_d$	0.349					-0.913			0.034		0.383	Co <sup>3+</sup>	0.861, 0.832, 0.795	-2.457
	Ce-O-bridge	0.156			-0.853			1.838		0.032	0.113	0.301	Ni <sup>1+</sup>	0.794	0.000
	Ce-top	0.118							1.975		0.250	0.368	Ni <sup>2+</sup>	0.954, 0.976	0.957
	hollow	0.312	-0.860	-0.852	-0.852					0.091		0.403	Ni <sup>2+</sup>	0.780, 0.892	-1.083
Ni	O-O-bridge	0.117	-0.862			-0.861				0.047		0.164	Ni <sup>1+</sup>	1.719	0.956
	O-top	0.049			-0.862					0.063		0.072	Ni <sup>0+</sup>	1.706	-0.000
	$O_d$	0.326					-0.885			0.062		0.388	Ni <sup>2+</sup>	0.910, 0.893	1.082

### Table. S 2

Calculated the Mulliken charge of transition metal (Fe, Co, or Ni), O and the Ce atoms in the transition metals (Fe, Co, or Ni) stable insertion, and substitution on CeO<sub>2</sub> (111)  $p(2 \times \sqrt{3})$  surface, respectively. The O and Ce atoms are adjacent (bond) to the transition metal (Fe, Co, or Ni) atoms. The Ce and O atoms are labeled with the number n (1-4) and n (1-7), which are cited in the text as Ce<sub>1</sub>-Ce<sub>4</sub> and O<sub>1</sub>-O<sub>7</sub> [see Fig. S1 (c,d)]. Magnetic spin moments of reduced Ce and oxidized M ions are  $\mu_{Ce}$ ,  $\mu_M$ .

Adsorption	pure (111)		Fe		Со		Ni	
Location	insertion	substitution	insertion	substitution	insertion	substitution	insertion	substitution
М			0.807	0.873	0.470	0.527	0.595	0.770
O1	-0.885	-0.885	-0.734	-0.828	-0.838	-0.747	-0.831	-0.758
$O_2$	-0.947	-0.885	-0.783	-0.798	-0.882	-0.771	-0.875	-0.854
$O_3$	-0.963	-0.885	-0.814	-0.798	-0.880	-0.771	-0.875	-0.785
$O_4$	-0.947	-0.947	-0.775	-0.879	-0.831	-0.907	-0.870	-0.896
05	-0.885	-0.947	-0.804	-0.859	-0.904	-0.870	-0.912	-0.832
$O_6$		-0.963		-0.812		-0.866		-0.891
0 <sub>7</sub>		-0.947		-0.879		-0.807		-0.863
Ce <sub>1</sub>	1.725	1.725	1.527	1.154	1.630	1.243	1.730	1.271
Ce <sub>2</sub>	1.725	1.725	1.477	1.542	1.667	1.570	1.660	1.591
Ce <sub>3</sub>	1.725	1.725	1.146	1.254	1.543	1.135	1.643	1.234
$Ce_4$	1.725		1.458		1.515		1.485	
$\Delta Q_O$			0.717	0.609	0.292	0.720	0.264	0.580
$\Delta Q_{Ce}$			-1.292	-1.225	-0.545	-1.227	-0.379	-1.079
$\Delta Q_{total}$			0.232	0.257	0.217	0.020	0.480	0.271
Valance			Fe <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	$\mathrm{Co}^{0+}$	Ni <sup>2+</sup>	Ni <sup>1+</sup>
$\mu_{Ce}$			0.798, 0.896	2×0.804	0.792, 0.850	1.515	0.981, 0.834	0.851
$\mu_M$			3.750	3.840	2.350	-0.850	0.594	0.770



Fig. S 1: (a) CeO<sub>2</sub> (110) p(2×2) surface is modeled by 6-layers; (b) CeO<sub>2</sub> (110) p(2× $\sqrt{3}$ ) surface is modeled by 6-layers. The purple balls respect to the top oxygen atoms, white balls respect to the cerium atom, and red balls respect to the sublayers oxygen atoms, respectively. Region enclosed by dashed line with blue in (a) and (b) represent the fixed layer. The Ce and O atoms are labeled with the number n (1-5) and n (1-8), which are cited in the text as Ce<sub>1</sub>-Ce<sub>5</sub> and O<sub>1</sub>-O<sub>8</sub>, respectively.

From Tables S1 and S2, we we can obviously see that most of the magnetic spin moments of  $\mu_{Ce}$  are ranging from 0.780 to 0.981  $\mu_B$ , excepted that when the the transition metal (Fe, Co, or Ni) adsorbs at O-top site, Ni atom adsorption at O-O-bridge on CeO<sub>2</sub> (111) surface, and Co substitution in CeO<sub>2</sub> (111) surface, after the transition metal (Fe, Co, or Ni) modification of CeO<sub>2</sub> (111) p(2 ×  $\sqrt{3}$ ) surface. The magnetic spin moments of  $\mu_{Ce}$  in all stable modification configurations involved the reduction of Ce ions are close to the ideal magnetic spin moment of Ce<sup>3+</sup> (1 $\mu_B$ ) [1, 2]. This demonstrate, after the transition metal (Fe, Co, or Ni) modification of CeO<sub>2</sub> (111) surface, that the adjacent Ce ions (within the relative to the modification of transition metal (Fe, Co, or Ni) ion), is observed with Ce<sup>4+</sup> reduced to Ce<sup>3+</sup> once again. Our calculated the magnetic spin moments of Co<sup>2+</sup> are ranging from 2.350 to 2.610 for the Co atom modification of CeO<sub>2</sub> (111) surface, this values are consistent with Hu et al. calculated ( $\mu_{Co^{2+}}=2.53\mu_B$ , Ref. [3]).



Fig. S 2: The optimized configurations of Fe adsorb on the CeO<sub>2</sub> (111): (a) Ce-O-bridge, (b) Ce-top, (c) hollow, (d) O-O-bridge, (e) O-top, (f) O<sub>d</sub>, (g) Fe insertion and (h) Fe substitution sites, respectively; The optimized configurations of Co adsorb on the CeO<sub>2</sub> (111): (i) Ce-O-bridge, (j) Ce-top, (k) hollow, (l) O-O-bridge, (m) O-top, (n) O<sub>d</sub>, (o) Co insertion and (p) Co substitution sites, respectively; The optimized configurations of Ni adsorb on the CeO<sub>2</sub> (111): (q) Ce-O-bridge, (r) Ce-top, (s) hollow, (t) O-O-bridge, (u) O-top, (v) O<sub>d</sub>, (w) Ni insertion and (x) Ni substitution sites, respectively; Gray, red and other color spheres represent Ce, O and Fe (or Co, Ni) atoms, respectively.



Fig. S 3: (a) Partial density of states (PDOS) of pure CeO<sub>2</sub> (111), Fe adsorbed on hollow site, Fe inserted into CeO<sub>2</sub> (111), and Fe substituted in CeO<sub>2</sub> (111), respectively; (b) Partial density of states (PDOS) of a single Fe atom, a single Fe atom adsorbed at hollow site, an inserted Fe atom into CeO<sub>2</sub> (111), and a substituted Fe atom in CeO<sub>2</sub> (111), respectively; (c) Partial density of states (PDOS) of pure CeO<sub>2</sub> (111), Co adsorbed on O-O-bridge site, Co inserted into CeO<sub>2</sub> (111), and Co substituted in CeO<sub>2</sub> (111), respectively; (d) Partial density of states (PDOS) of a single Co atom, a single Co atom adsorbed at O-O-bridge site, an inserted Co atom into CeO<sub>2</sub> (111), and a substituted Co atom in CeO<sub>2</sub> (111), respectively; (e) Partial density of states (PDOS) of pure CeO<sub>2</sub> (111), Ni adsorb on Ce-O-bridge site, Ni inserted into CeO<sub>2</sub> (111), and Ni substituted in CeO<sub>2</sub> (111), respectively; (f) Partial density of states (PDOS) of a single Ni atom, a single Ni atom adsorbed at Ce-O-bridge site, an inserted Ni atom into CeO<sub>2</sub> (111), and a substituted Ni atom in CeO<sub>2</sub> (111), respectively.

### *S1.2* The PDOS of the transition metals modification of CeO<sub>2</sub> (111) surface

Aiming at further illustrating the interaction between the transition metals and CeO<sub>2</sub> (111) surface, the partial density of states (PDOS) are calculated. As shown, most of them displays new features between the valance band and conduction band (see the Fig. S3 (a, c, e)) for the most stable modification (adsorption, insertion, or substitution), and other favorable adsorption types are shown in Fig. S4 (a-c). We take the most stable modified configuration (see Fig. S3 (a-f) for an instance and analyze the corresponding PDOS of the transition metals, pure  $CeO_2$  (111) and transition metals modification of  $CeO_2$  (111), respectively. For the Fe atom modification, in Fig. S3 (a and b), the occupied spin up and down states are the Fe-4s state, the occupied spin-up and unoccupied spin-down states that just crossing and splitting the fermi energy corresponds to the Fe-3d state, and the unoccupied spin up and down states are the Fe-3p state, respectively. The highest occupied valence band in Fig. S3 (a) results from O-2p and some contribution from the Ce-4f for pure  $CeO_2$  (111), suggesting Ce-4f/O-2p hybridization [4]. We can obviously see that, compared with the PDOS of the isolated Fe atom in Fig. S3 (b), the adsorption of Fe atom at hollow site on CeO<sub>2</sub> (111) causes the occupied Fe-4s state becoming partially unoccupied, whereas the unoccupied Fe-3p states become partially occupied, and the part of unoccupied Fe-3d state region become larger. This indicates that the electrons on Fe-4s<sup>2</sup> and Fe-3d<sup>6</sup> have been fully and partly transferred, respectively. Simultaneously, there is a new occupied peak corresponding to the Ce-4f states for the Fe/CeO<sub>2</sub> (111) system (see the Fig. S3 (a)), resulted from the charge transferred from the Fe-4s<sup>2</sup> and Fe-3d<sup>6</sup> to the CeO<sub>2</sub> (111) surface, and localized on the Ce-4f states, which leads to three surface Ce atoms are reduced, i.e.  $Ce^{4+} \rightarrow Ce^{3+}$ . This result is in good agreement with the observation by Nolan [5]. The similar phenomenon has been demonstrated for Fe insertion (and substitution) (see the Fig. S3 (a and b)) and other stable adsorption types (see Fig. S4 (a)) in CeO<sub>2</sub> (111) surface. This is indeed consistent with the former Mulliken charge analysis.

For the Co atom modification, in Fig. S3 (c and d), the occupied spin up and unoccupied spin down states are the Co-4s state, the occupied spin-up and unoccupied spin-down states that just crossing and splitting at the fermi energy corresponds to the Co-3d state, and the unoccupied spin up and down states are the Co-3p state, respectively. We can obviously see that the adsorption of Co atom at O-O-bridge site on CeO<sub>2</sub> (111) causes the unoccupied Co-4s almost disappeared, whereas the unoccupied Co-3p states become partially occupied, and the part of unoccupied Co-3d state region become larger, compared with the PDOS of the isolated Co atom in Fig. S3 (d). This indicates that the electrons on Co-4s<sup>2</sup> and Co-3d<sup>7</sup> have been fully and partly transferred, respectively. Concurrently, there is a new occupied peak across the fermi energy, corresponding to the Ce-4f states for the Co/CeO<sub>2</sub> (111) system (see the Fig. S3 (c)), result from the charge transferred from the Co-4s<sup>2</sup> and Co-3d<sup>7</sup> to the CeO<sub>2</sub> (111) and localized on the Ce-4f states, leading to three  $Ce^{4+} \rightarrow Ce^{3+}$  on the surface. The similar phenomenon has been demonstrated for Co insertion (see the Fig. S3 (c,d)) and other stable adsorption types (see Fig. S4 (b)) in CeO<sub>2</sub> (111) surface. It is also in the line with the calculated Mulliken charge result. With respect to the Ni modification, in Fig. S3 (e and f), the unoccupied spin down and occupied spin up states that across fermi energy, are the Ni-4s state, the occupied spin-up and unoccupied spin-down states that just crossing and splitting at the fermi energy corresponds to the Ni-3d state, and the unoccupied spin up and down states are the Ni-3p state, respectively. We are able to tell that the adsorption of Ni atom at Ce-O-bridge site on CeO<sub>2</sub> (111) causes the unoccupied Ni-4s almost disappeared, whereas the unoccupied Ni-3p states become partially occupied, compared with the PDOS of the isolated Ni atom in Fig. S3 (f). This indicates that the electrons on Ni-4s<sup>2</sup> has been transferred to the  $CeO_2(111)$  and localized on the Ce-4f states, with the result of one surface Ce atom is reduced. The similar phenomenon has been demonstrated for Ni insertion (and substitution) (see the Fig. S3 (e and f)) and other stable adsorption types (see Fig. S4 (c), except for Ni adsorption on O-top site) in CeO<sub>2</sub> (111) surface. This is also in good agreement with the former Mulliken charge analysis.



Fig. S 4: (a) Partial density of states (PDOS) of Fe adsorb on Ce-O-bridge site at CeO<sub>2</sub> (111), Fe adsorb on Ce-top site at CeO<sub>2</sub> (111), Fe adsorb on O-O-bridge site at CeO<sub>2</sub> (111), Fe adsorb on O-O-bridge site at CeO<sub>2</sub> (111), respectively; (b) Partial density of states (PDOS) of Co adsorb on Ce-O-bridge site at CeO<sub>2</sub> (111), Co adsorb on Ce-top site at CeO<sub>2</sub> (111), Co adsorb on hollow site at CeO<sub>2</sub> (111), Co adsorb on O-top site at CeO<sub>2</sub> (111), and Co adsorb on O<sub>d</sub> site at CeO<sub>2</sub> (111), respectively; (c) Partial density of states (PDOS) of Ni adsorb on Ce-top site at CeO<sub>2</sub> (111), Ni adsorb on hollow site at CeO<sub>2</sub> (111), Ni adsorb on Ce-top site at CeO<sub>2</sub> (111), Ni adsorb on O-O-bridge site at CeO<sub>2</sub> (111), Ni adsorb on O-O-bridge site at CeO<sub>2</sub> (111), Ni adsorb on O-O-bridge site at CeO<sub>2</sub> (111), respectively; (d) Partial density of states (PDOS) of Fe adsorb on Ce-Ce-bridge site at CeO<sub>2</sub> (110), Fe adsorb on Ce-top site at CeO<sub>2</sub> (110), Fe adsorb on O-O-bridge site at CeO<sub>2</sub> (110), and Fe adsorb on O-top site at CeO<sub>2</sub> (110), respectively; (e) Partial density of states (PDOS) of Co adsorb on O-top site at CeO<sub>2</sub> (110), Co adsorb on Ce-top site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Co adsorb on O-top site at CeO<sub>2</sub> (110), Co adsorb on Ce-top site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Co adsorb on Ce-Ce-bridge site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Ni adsorb on O-O-bridge site at CeO<sub>2</sub> (110), co adsorb on Ce-top site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Ni adsorb on Ce-Ce-bridge site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Ni adsorb on Ce-Ce-bridge site at CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of Ni adsorb on Ce-Ce-bridge site at CeO<sub>2</sub> (110), co adsorb on Ce-top site at CeO<sub>2</sub> (110), co adsorb on O-O-bridge site at CeO<sub>2</sub> (110), and Co adsorb on Ce-top site at CeO<sub>2</sub> (110), respectively; (f) Partial density

# S2 The Mulliken charge and PDOS of the transition metals modification of stoichiometric CeO<sub>2</sub> (110) surface

# S2.1 The Mulliken charge of the transition metals modification of $CeO_2$ (110) surface

### Table. S 3

Calculated the Mulliken charge of transition metal (Fe, Co, or Ni), O and the Ce atoms in the transition metals (Fe, Co, or Ni) stable adsorption on CeO<sub>2</sub> (110)  $p(2 \times 2)$  surface, respectively. The O and Ce atoms are bond to the transition metal (Fe, Co, or Ni) atoms. The Ce and O atoms are labeled with the number n (1-4) and n (1-8), which are cited in the text as Ce<sub>1</sub>-Ce<sub>4</sub> and O<sub>1</sub>-O<sub>8</sub> [see Fig. S1 (b)]. Magnetic spin moments of reduced Ce and oxidized M ions are  $\mu_{Ce}$ ,  $\mu_M$ .

Adsorption	Location	М	O1	<b>O</b> <sub>2</sub>	03	$O_4$	O <sub>5</sub>	0 <sub>6</sub>	O <sub>7</sub>	O <sub>8</sub>	Ce <sub>1</sub>	Ce <sub>2</sub>	Ce <sub>3</sub>	$Ce_4$	$\Delta Q_{0}$	$\Delta Q_{Ce}$	$\Delta Q_{total}$	Valance	$\mu_{Ce}$	$\mu_M$
Metals		(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	М		
pure (110)		-0.849	-0.849	-0.849	-0.849	-0.849	-0.849	-0.849	-0.849	-0.849	1.538	1.538	1.538	1.538						
	Ce-Ce-bridge	0.052											1.670	1.670		0.264	0.316	Fe <sup>2+</sup>	0.873, 0.895	3.470
	Ce-top	0.080										1.588				0.050	0.130	Fe <sup>0+</sup>	0.630	-3.152
Fe	double O-bridge	0.098			-0.801	-0.798			-0.807	-0.802					0.188		0.286	Fe <sup>2+</sup>	0.974, 0.836	2.067
	O-O-bridge	0.233				-0.799			-0.802						0.097		0.330	Fe <sup>2+</sup>	2×0.885	2.076
	O-top	0.457		-0.832											0.017		0.474	Fe <sup>3+</sup>	2×0.947	3.980
	Ce-Ce-bridge	-0.064											1.767	1.667		0.358	0.294	Co <sup>2+</sup>	1.150, 0.970	2.480
	Ce-top	0.181										1.692				0.112	0.293	Co <sup>2+</sup>	1.032, 0.997	2.563
Co	double O-bridge	0.114			-0.791	-0.789			-0.789	-0.790					0.237		0.357	Co <sup>2+</sup>	1.008, 0.873	2.346
	O-O-bridge	0.215				-0.789			-0.790						0.119		0.334	Co <sup>2+</sup>	0.978, 0.936	-1.064
	O-top	0.162		-0.754											0.095		0.257	Co <sup>2+</sup>	0.869, 0.785	2.134
	Ce-Ce-bridge	0.003											1.761	1.761		0.446	0.449	Ni <sup>2+</sup>	0.846, 0.792	1.580
	Ce-top	0.105										1.583				0.045	0.150	Ni <sup>0+</sup>	1.683	0.333
Ni	double O-bridge	0.268			-0.772	-0.770			-0.769	-0.769					0.316		0.584	Ni <sup>2+</sup>	1.003, 0.989	1.964
	O-O-bridge	0.072				-0.801			-0.803						0.094		0.166	Ni <sup>0+</sup>	1.457	0.367
	O-top	0.167		-0.771											0.078		0.245	Ni <sup>1+</sup>	1.116	0.72

### Table. S 4

Calculated the Mulliken charge of transition metal (Fe, Co, or Ni), O and the Ce atoms in the transition metals (Fe, Co, or Ni) stable insertion, and substitution on CeO<sub>2</sub> (110)  $p(2 \times 2)$  surface, respectively. The O and Ce atoms are adjacent (bond) to the transition metal (Fe, Co, or Ni) atoms. The Ce and O atoms are labeled with the number n (1-5) and n (1-6), which are cited in the text as Ce<sub>1</sub>-Ce<sub>5</sub> and O<sub>1</sub>-O<sub>6</sub> [see Fig. S1 (e,f)]. Magnetic spin moments of reduced Ce and oxidized M ions are  $\mu_{Ce}$ ,  $\mu_M$ .

Adsorption	pure (110)		Fe		Со		Ni	
Location	insertion	substitution	insertion	substitution	insertion	substitution	insertion	substitution
Μ			0.645	0.680	0.650	0.641	0.622	0.602
$O_1$	-0.849	-0.849	-0.834	-0.829	-0.793	-0.812	-0.805	-0.832
$O_2$	-0.952	-0.849	-0.938	-0.829	-0.933	-0.812	-0.897	-0.828
$O_3$	-0.952	-0.849	-0.946	-0.829	-0.912	-0.812	-0.897	-0.828
$O_4$	-0.849	-0.849	-0.837	-0.829	-0.819	-0.812	-0.826	-0.832
O <sub>5</sub>		-0.966		-0.946		-0.936		-0.926
$O_6$		-0.966		-0.946		-0.936		-0.926
Ce <sub>1</sub>	1.538	1.538	1.531	1.422	1.523	1.439	1.533	1.456
Ce <sub>2</sub>	1.994	1.994	2.033	1.785	1.871	1.778	1.758	1.866
Ce <sub>3</sub>	2.100	1.994	1.986	1.856	1.998	1.832	2.863	1.866
$Ce_4$	1.994	1.994	1.886	1.832	1.756	1.737	1.732	1.866
Ce <sub>5</sub>		1.994		1.873		1.796		1.866
$\Delta Q_O$			0.047	0.120	0.145	0.208	0.177	0.160
$\Delta Q_{Ce}$			-0.190	-0.746	-0.510	-0.832	-0.690	-0.482
$\Delta Q_{total}$			0.502	0.054	0.285	0.017	0.109	0.280
Valance			Fe <sup>3+</sup>	Fe <sup>0+</sup>	Co <sup>2+</sup>	$\mathrm{Co}^{0+}$	Ni <sup>0+</sup>	Ni <sup>1+</sup>
$\mu_{Ce}$			0.961, 0.823, 0.764	1.442	2×0.935	1.540	1.531	0.975
$\mu_M$			3.445	0.680	2.463	0.641	0.622	1.997

From Tables S3 and S4, we we can obviously see that most of the magnetic spin moments of  $\mu_{Ce}$  are ranging from 0.764 to 1.150  $\mu_B$ , excepted that when the the Fe adsorbs at Ce-top site, Ni atom adsorption at Ce-top and O-O-bridge sites on CeO<sub>2</sub> (110) surface, Fe, Co atom substitution in CeO<sub>2</sub> (110) surface and Ni insertion into CeO<sub>2</sub> (110) p(2 × 2) surface, after the transition metal (Fe, Co, or Ni) modification of CeO<sub>2</sub> (110) surface. The magnetic spin moments of  $\mu_{Ce}$  in all stable modification configurations involved the reduction of Ce ions are close to the ideal magnetic spin moment of Ce<sup>3+</sup> (1 $\mu_B$ ) [1, 2]. This demonstrate, after the transition metal (Fe, Co, or Ni) modification Ce ions (within the relative to the modification of transition metal (Fe, Co, or Ni) ion), is observed with Ce<sup>4+</sup> reduced to Ce<sup>3+</sup> once again. Our calculated the magnetic spin moments of Co<sup>2+</sup> are ranging from 2.346 to 2.563 for the Co atom modification of CeO<sub>2</sub> (110) surface, this values are consistent with Hu et al. calculated ( $\mu_{Co^{2+}}=2.53\mu_B$ , Ref. [3]).



Fig. S 5: The optimized configurations of Fe adsorb on the CeO<sub>2</sub> (110): (a) Ce-Ce-bridge, (b) Ce-top, (c) double O-bridge, (d) O-O-bridge, (e) O-top, (f) Fe insertion and (g) Fe substitution sites, respectively; The optimized configurations of Co adsorb on the CeO<sub>2</sub> (110): (h) Ce-Ce-bridge, (i) Ce-top, (j) double O-bridge, (k) O-O-bridge, (l) O-top, (m) Co insertion and (n) Co substitution sites, respectively; The optimized configurations of Ni adsorb on the CeO<sub>2</sub> (110): (o) Ce-Ce-bridge, (p) Ce-top, (q) double O-bridge, (r) O-O-bridge, (s) O-top, (t) Ni insertion and (u) Ni substitution sites, respectively. Gray, red and other color spheres represent Ce, O and Fe (or Co, Ni) atoms, respectively.



Fig. S 6: (a) Partial density of states (PDOS) of pure CeO<sub>2</sub> (110), Fe adsorbed on double O-bridge site, Fe inserted into CeO<sub>2</sub> (110), and Fe substituted in CeO<sub>2</sub> (110), respectively; (b) Partial density of states (PDOS) of a single Fe atom, a single Fe atom adsorbed at double O-bridge site, an inserted Fe atom into CeO<sub>2</sub> (110), and a substituted Fe atom in CeO<sub>2</sub> (110), respectively; (c) Partial density of states (PDOS) of pure CeO<sub>2</sub> (110), Co adsorbed on O-top site, Co inserted into CeO<sub>2</sub> (110), and Co substituted in CeO<sub>2</sub> (110), respectively; (d) Partial density of states (PDOS) of a single Co atom, a single Co atom adsorbed at O-top site, an inserted Co atom into CeO<sub>2</sub> (110), and a substituted Co atom in CeO<sub>2</sub> (110), respectively; (e) Partial density of states (PDOS) of pure CeO<sub>2</sub> (110), nod a substituted Co atom in CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of a single Ni inserted in CeO<sub>2</sub> (110), and Ni substituted in CeO<sub>2</sub> (110), respectively; (f) Partial density of states (PDOS) of a single Ni atom, a single Ni atom adsorbed at double O-bridge site, an inserted Ni atom into CeO<sub>2</sub> (110), and a substituted Ni atom in CeO<sub>2</sub> (110), respectively.



Fig. S 7: The reduced  $CeO_2$  (110) surfaces, (a) The plane O vacancy (P), and (b) The split O vacancy (S), respectively. The reduced  $CeO_2$  (111) surfaces, (c) The subsurface O vacancy (SS), and (d) The sublayer O vacancy (SL), respectively

### *S2.2* The PDOS of the transition metals modification of CeO<sub>2</sub> (110) surface

Here we take the most energetically favorable stable modified configuration (see Fig. S6 (a-f)) for an instance and analyze the corresponding PDOS of the transition metal atoms, pure CeO<sub>2</sub> (110) surface and modified CeO<sub>2</sub> (110) surface, respectively. From Fig. S6 (a-b), it can be see that its 4s state upon the Fe atom adsorption (at the double O-bridge site) becomes unoccupied and a new peak emerges between unoccupied Ce-4f band bottom and O-2p valance band top, viz, the adsorbed Fe is oxidized whereas the adjacent  $Ce^{4+}$  is reduced to  $Ce^{3+}$ . The phenomenon also appears in the Fe atom insertion into the  $CeO_2$ (110) surface (see Fig. S6 (a-b)) and other stable adsorption types (see Fig. S4 (d), apart from the above mentioned exception). Actually, one can observe two and three neighboring completely reduced Ce ion for Fe atom adsorption at the double O-bridge site and Fe atom insertion into the CeO<sub>2</sub> (110) surface, respectively. For the Co atom modification of  $CeO_2$  (110) surface (see Fig. S6 (c,d)), we can obviously see that the adsorption of Co atom at O-top site on CeO<sub>2</sub> (110) surface causes appearing the unoccupied spin-paired gap state, viz, Co-4s state, whereas the unoccupied Co-3p states become partially occupied, compared with the PDOS of the isolated Co atom in Fig. S6 (d). This indicates that the electrons on Co-4s<sup>2</sup> has been fully transferred to the Ce-4f states, result in a new occupied peak across the fermi energy, corresponding to the Ce-4f states for the Co/CeO<sub>2</sub> (110) system (see Fig. S6 (c)), leading to two Ce<sup>4+</sup> $\rightarrow$  $Ce^{3+}$  on the surface. The similar phenomenon has been demonstrated for the Co atom insertion (see Fig. S6 (c,d)) and other stable adsorption types (see Fig. S4 (e)) on  $CeO_2$  (110) surface. It is also in the line with the calculated Mulliken charge result. With respect to the Ni atom modification, in Fig. S6 (e,f), it is found that the adsorption of Ni atom at double-O-bridge site on CeO<sub>2</sub> (110) surface causes the unoccupied Ni-4s almost disappeared, whereas the unoccupied Ni-3p states become partially occupied, compared with the PDOS of the isolated Ni atom in Fig. S6 (f). This indicates that the electrons on Ni-4s<sup>2</sup> has been transferred to the CeO<sub>2</sub>(110) surface and localized on the Ce-4f states, with the result of two surface Ce atom is reduced. The similar phenomenon has been demonstrated for Ni substitution (see Fig. S6 (e,f)) and other stable adsorption types (see Fig. S4 (f), except for the Ni atom adsorption on Ce-top site, O-Obridge, and Ni insertion into  $CeO_2$  (110) surface, respectively) on  $CeO_2$  (110) surface. This is also in good agreement with the former Mulliken charge analysis.

# S3 Methane adsorption on the transition metals modified $CeO_2$ (110) surface

### Table. S 5

The adsorption energies ( $E_{ads}$ , eV), bond lengths (Å) and net charges (e) for the isolated methane (CH<sub>4</sub>) molecular adsorbed over the CeO<sub>2</sub> (110) surface, the reduced CeO<sub>2</sub> (110) surface, transition metals (Fe, Co and Ni) modification of CeO<sub>2</sub> (110) surface, the reduction of transition metal (Fe, Co and Ni) modification on CeO<sub>2</sub> (110) surface, respectively.

			E <sub>ads</sub> (eV)					Bond length			Net Charge
	$Ce_a$	$Ce_b$	$Ce_c$	$\mathbf{O}_a$	$\mathbf{O}_b$	Μ		(Å)			(e)
CeO <sub>2</sub> (110)	0.131	0.126		0.130	0.041		1.103	1.102	1.102	1.100	0.034
$E_{vac-P}$	0.146	0.147	0.127	0.127	0.126		1.101	1.103	1.103	1.103	0.033
$E_{vac-S}$	0.128	0.121	0.127	0.124	0.113		1.100	1.101	1.102	1.103	0.034
Fe adsorption	2.069	2.046		1.943	1.876	1.632	1.101	1.103	1.103	1.103	0.034
$E_{vac-P}$	0.129	0.123	0.214	0.028	0.033	0.137	1.102	1.104	1.104	1.106	0.041
$E_{vac-S}$	-0.464	-0.484	-0.481	-0.525	-0.561	-0.516	1.101	1.103	1.103	1.102	0.036
Fe insertion	1.784	1.785		1.756	1.726		1.100	1.101	1.102	1.102	0.034
$E_{vac-P}$	0.109	0.113	0.112	0.034	0.114		1.100	1.102	1.104	1.100	0.033
$E_{vac-S}$	0.038	0.078	0.029	0.008	0.111		1.101	1.102	1.102	1.102	0.029
Fe substitution		0.154		0.134	0.069	1.618	1.103	1.104	1.102	1.101	0.017
$E_{vac-P}$		0.150	0.144	0.036	0.149	0.058	1.100	1.102	1.103	1.103	0.049
$E_{vac-S}$		0.155	0.146	0.148	0.161	0.050	1.126	1.103	1.127	1.102	0.046
Co adsorption	0.101	0.141		0.039	0.041	0.059	1.101	1.102	1.103	1.103	0.029
$E_{vac-P}$	0.209	0.222	0.057	0.038	-0.303	-0.212	1.100	1.101	1.101	1.104	0.034
$E_{vac-S}$	0.112	0.113	0.114	0.036	0.048	0.039	1.101	1.102	1.102	1.103	0.038
Co insertion	0.126	0.115		0.100	0.037		1.099	1.102	1.102	1.103	0.034
$E_{vac-P}$	0.126	0.106	0.062	0.025	0.045		1.100	1.102	1.102	1.102	0.036
$E_{vac-S}$	0.125	0.168	0.114	0.050	0.060		1.101	1.104	1.104	1.104	0.032
Co substitution		2.387		1.008	0.899	2.189	1.100	1.101	1.105	1.105	0.055
$E_{vac-P}$		0.873	0.872	0.759	0.795	0.802	1.100	1.102	1.101	1.102	0.046
$E_{vac-S}$		0.880	0.876	0.762	0.853	0.876	1.099	1.103	1.103	1.103	0.046
Ni adsorption	0.149	0.134		0.039	0.401	0.058	1.100	1.103	1.103	1.102	0.034
$E_{vac-P}$	0.111	0.130	0.225	0.528	0.043	0.062	1.101	1.101	1.106	1.107	0.041
$E_{vac-S}$	0.141	0.131	0.005	0.007	0.108	0.069	1.100	1.102	1.102	1.102	0.038
Ni insertion	1.814	1.765		1.735	1.744		1.101	1.104	1.103	1.103	0.033
$E_{vac-P}$	0.187	0.191	0.184	0.062	0.139		1.100	1.101	1.102	1.102	0.034
$E_{vac-S}$	0.111	0.114	0.113	0.134	0.108		1.113	1.103	1.104	1.103	0.024
Ni substitution		1.682		2.326	1.699	2.327	1.102	1.101	1.102	1.104	0.001
$E_{vac-P}$		0.138	0.135	0.136	0.136	0.076	1.099	1.102	1.103	1.103	0.045
$E_{vac-S}$		0.134	0.135	0.072	0.077	0.068	1.067	1.102	1.102	1.103	0.038



Fig. S 8: Total density of states (TDOS) and partial density of states (PDOS) of  $(a_1)$  Free CH<sub>4</sub>,  $(a_2)$  pure CeO<sub>2</sub>(110),  $(a_3)$  the configuration in Fig.S9 (a) and  $(a_4)$  CH<sub>4</sub> in Fig.S9 (a); Total density of states (TDOS) and partial density of states (PDOS) of  $(b_1)$  Free CH<sub>4</sub>,  $(b_2)$  pure CeO<sub>2</sub>(110) with the type of P oxygen vacancy,  $(b_3)$  the configuration in Fig.S9 (b) and  $(b_4)$  CH<sub>4</sub> in Fig.S9 (b); Total density of states (TDOS) and partial density of states (PDOS) of  $(c_1)$  Free CH<sub>4</sub>,  $(c_2)$  pure CeO<sub>2</sub>(110) with the type of S oxygen vacancy,  $(c_3)$  the configuration in Fig.S9 (c) and  $(c_4)$  CH<sub>4</sub> in Fig.S9 (c); Total density of states (TDOS) and partial density of states (PDOS) of  $(d_1)$  Free CH<sub>4</sub>,  $(d_2)$  Co substitution in CeO<sub>2</sub>(110),  $(d_3)$  the configuration in Fig.S10 (d) and  $(d_4)$  CH<sub>4</sub> in Fig.S10 (d); Total density of states (TDOS) and partial density of states (PDOS) of  $(e_1)$  Free CH<sub>4</sub>,  $(e_2)$  Co substitution in CeO<sub>2</sub>(110) with the type of P oxygen vacancy,  $(e_3)$  the configuration in Fig.S10 (e) and  $(e_4)$  CH<sub>4</sub> in Fig.S10 (e); Total density of states (PDOS) of  $(f_1)$  Free CH<sub>4</sub>,  $(f_2)$  Co substitution in CeO<sub>2</sub>(110) with the type of P oxygen vacancy,  $(e_3)$  the configuration in Fig.S10 (e) and  $(e_4)$  CH<sub>4</sub> in Fig.S10 (e); Total density of states (PDOS) of  $(f_1)$  Free CH<sub>4</sub>,  $(f_2)$  Co substitution in CeO<sub>2</sub>(110) with the type of S oxygen vacancy,  $(e_3)$  the configuration in Fig.S10 (e) and  $(e_4)$  CH<sub>4</sub> in Fig.S10 (e); Total density of states (PDOS) of  $(f_1)$  Free CH<sub>4</sub>,  $(f_2)$  Co substitution in CeO<sub>2</sub>(110) with the type of S oxygen vacancy,  $(e_3)$  the configuration in Fig.S10 (e) and  $(e_4)$  CH<sub>4</sub> in Fig.S10 (e); Total density of states (PDOS) of  $(f_1)$  Free CH<sub>4</sub>,  $(f_2)$  Co substitution in CeO<sub>2</sub>(110) with the type of S oxygen vacancy,  $(f_3)$  the configuration in Fig.S10 (f).

Here, we consider the most energetically favorable sites for the clean  $CeO_2$  (110) surface and transition metal modification of CeO<sub>2</sub> (110) surfaces without (or with) formation of P or S oxygen vacancies. The corresponding sites are Ce<sub>a</sub> (see Fig. S9 (a)), Ce<sub>b</sub> (see Fig. S9 (b)), Ce<sub>a</sub> (see Fig. S9 (c)), Ce<sub>b</sub> (see Fig. S10 (d)], Ce<sub>b</sub> (see Fig. S10 (e)) and Ce<sub>b</sub> (see Fig. S10 (f)), respectively. See the TDOS and PDOS (see Fig. S8), CH<sub>4</sub> in the mode of Fig. S9(a) (the TDOS and PDOS are shown in the lift of the first row in Fig. S8), CH<sub>4</sub> in the mode of Fig. S9(b) (the TDOS and PDOS are shown in the middle of the first row in Fig. S8), CH<sub>4</sub> in the mode of Fig. S9(c) (the TDOS and PDOS are shown in the right of the first row in Fig. S8) for the clean  $CeO_2$  (110) surface, the reduction of  $CeO_2$  (110) surface with the type of P or S surface oxygen vacancy catalyst, respectively. Compared to the free CH<sub>4</sub> molecule, the results show that the position of TDOS shifts toward lower energy level. Because of the oxygen vacancy formation is a surface reduction process [6]. It is interesting to note that there is a new occupied peak appeared in the TDOS of pure  $CeO_2$  (110) with the presence of P or S surface oxygen vacancy. The new occupied peak is corresponding to the Ce<sup>3+</sup>. See the TDOS and PDOS of the Co atom substitution in  $CeO_2$  (110) surface without (or with) the presence of P or S surface oxygen vacancy catalyst (see the left of the second row, the middle of the second row and the right of the second row in Fig. S8, respectively), the above mentioned phenomenon is also observed. It is noted that the degree of the position of TDOS toward lower energy level are difference between the CH<sub>4</sub> molecule adsorption on the CeO<sub>2</sub> (110) surface (the reduction of CeO<sub>2</sub> (110) with the presence of P or S surface oxygen vacancies are also included) and the Co atom substitution in CeO<sub>2</sub> (110) surface (the Co atom substitution in  $CeO_2$  (110) surface with two types of oxygen vacancies are also included).



Fig. S 9: The optimized configurations of CH<sub>4</sub> most energetically adsorb on pure CeO<sub>2</sub> (110) surface, the type of P oxygen vacancy and the type of S oxygen vacancy in CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>b</sub> and Ce<sub>a</sub> site (a-c), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Fe adsorption on CeO<sub>2</sub> (110) surface at double O-bridge site, the type of P oxygen vacancy and the type of S oxygen vacancy in Fe adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>c</sub> and Ce<sub>a</sub> site (d-f), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Fe insertion into CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, O<sub>b</sub> and O<sub>b</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Fe insertion into CeO<sub>2</sub> (110) surface, the type of P oxygen vacancy and the type of S oxygen vacancy in Fe insertion into CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, O<sub>b</sub> and O<sub>b</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Fe substitution in CeO<sub>2</sub> (110) surface, the type of P oxygen vacancy and the type of S oxygen vacancy in Fe substitution in CeO<sub>2</sub> (110) surface at Fe, Ce<sub>b</sub> and O<sub>b</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Co adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>b</sub> and O<sub>b</sub> site (j-l), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Co adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>b</sub> and Ce<sub>c</sub> site, the type of P oxygen vacancy and the type of S oxygen vacancy in Fe substitution in CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>b</sub> and Ce<sub>c</sub> site, the type of P oxygen vacancy and the type of S oxygen vacancy in Co adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>b</sub> and Ce<sub>c</sub> site (m-o), respectively.



Fig. S 10: The optimized configurations of CH<sub>4</sub> most energetically adsorb on Co insertion into CeO<sub>2</sub> (110) surface, the type of P oxygen vacancy and the type of S oxygen vacancy in Co insertion into CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>a</sub> and Ce<sub>b</sub> site (a-c), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Co substitution in CeO<sub>2</sub> (110) surface, the type of P oxygen vacancy and the type of S oxygen vacancy in Co substitution in CeO<sub>2</sub> (110) surface at Ce<sub>b</sub>, Ce<sub>b</sub> and Ce<sub>b</sub> site (d-f), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni adsorption on CeO<sub>2</sub> (110) surface at double O-bridge site, the type of P oxygen vacancy and the type of S oxygen vacancy in Ni adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>c</sub> and Ce<sub>a</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni adsorption on CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>c</sub> and Ce<sub>a</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni insertion into CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>c</sub> and Ce<sub>a</sub> site (g-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni insertion into CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>b</sub> and O<sub>a</sub> site (j-i), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni substitution in CeO<sub>2</sub> (110) surface at Ce<sub>a</sub>, Ce<sub>b</sub> and O<sub>a</sub> site (j-l), respectively; The optimized configurations of CH<sub>4</sub> most energetically adsorb on Ni substitution in CeO<sub>2</sub> (110) surface at Ni, Ce<sub>b</sub> and Ce<sub>a</sub> site (m-o), respectively.



Fig. S 11: The optimized configurations of CH<sub>4</sub> dissociative adsorption on CeO<sub>2</sub> (110) surface at O<sub>a</sub> (a), O<sub>b</sub>(k), O<sub>c</sub> (l) sites; The optimized configurations of CH<sub>4</sub> dissociative adsorption on CeO<sub>2</sub> (110) surface with the type of P oxygen vacancy at O<sub>a</sub> (b), O<sub>b</sub> (c), O<sub>c</sub> (m) sites; The optimized configurations of CH<sub>4</sub> dissociative adsorption on CeO<sub>2</sub> (110) surface with the type of S oxygen vacancy at O<sub>a</sub> (d), O<sub>b</sub> (e), O<sub>c</sub> (n) sites; The optimized configurations of CH<sub>4</sub> dissociative adsorption at Co substitution in CeO<sub>2</sub> (110) surface at O<sub>a</sub> (f), O<sub>b</sub>(o), O<sub>c</sub> (p) sites; The optimized configurations of CH<sub>4</sub> dissociative adsorption on Co substitution in CeO<sub>2</sub> (110) surface with the type of P oxygen vacancy at O<sub>a</sub> (g), O<sub>b</sub> (h), O<sub>c</sub> (q) sites; The optimized configurations of CH<sub>4</sub> dissociative adsorption on Co substitution in CeO<sub>2</sub> (110) surface with the type of S oxygen vacancy at O<sub>a</sub> (i), O<sub>b</sub> (j), O<sub>c</sub> (r) sites.

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