Supporting Information

Strategies To Improve the Activity While Maintaining the Selectivity of Oxidative Coupling of Methane at La_2O_3: A Density Functional Theory Study

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Table S1. Calculated lattice parameters of bulk La_2O_3 and the O_v formation energies at the La_2O_3(001) and Sr/Ce-La_2O_3(001) surfaces using the PBE and HSE06 functionals.

	Lattice parameters		
Bulk La_2O_3	PBE	HSE06	Experimental [1]
	a = b = 3.920 Å	a = b = 3.939 Å	a = b = 3.939 Å
	c = 6.093 Å	c = 6.136 Å	c = 6.136 Å
	O_v formation energies		
	PBE	HSE06	
La_2O_3(001)	6.60 eV	6.65 eV	
Sr/Ce-La_2O_3(001)	4.18 eV	4.28 eV	

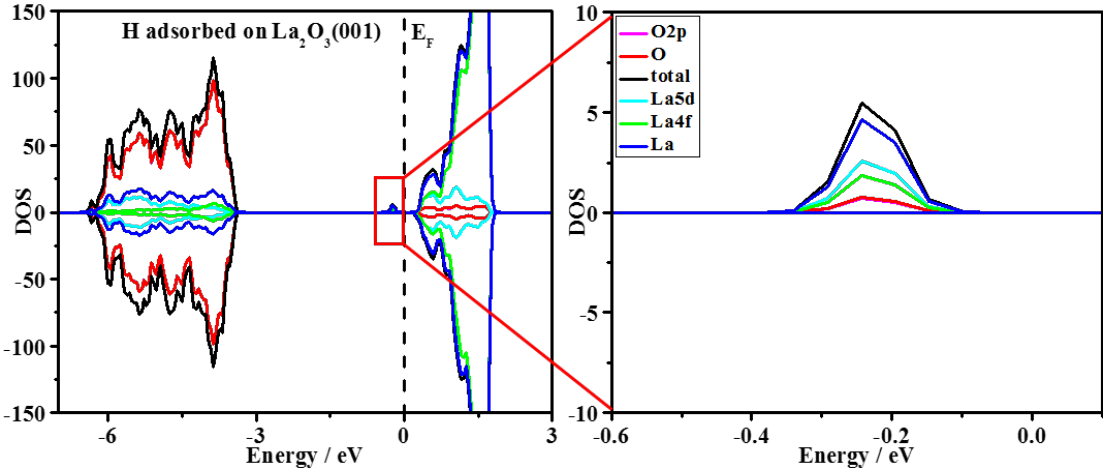

Figure S1. Calculated DOSs of the La_2O_3(001) surface with adsorbed H.

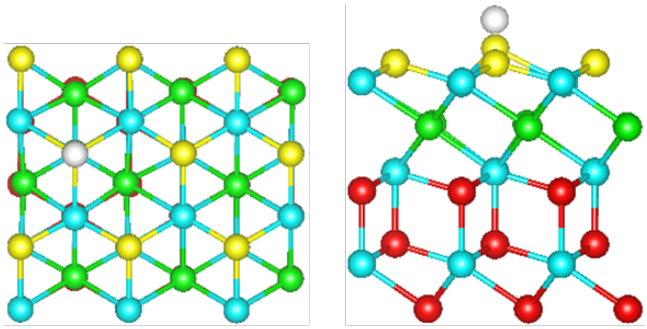

Figure S2. Calculated structures and the spin-polarized charge densities of H adsorption on the $La_2O_3(001)$ surface with the electron being delocalized in the system.

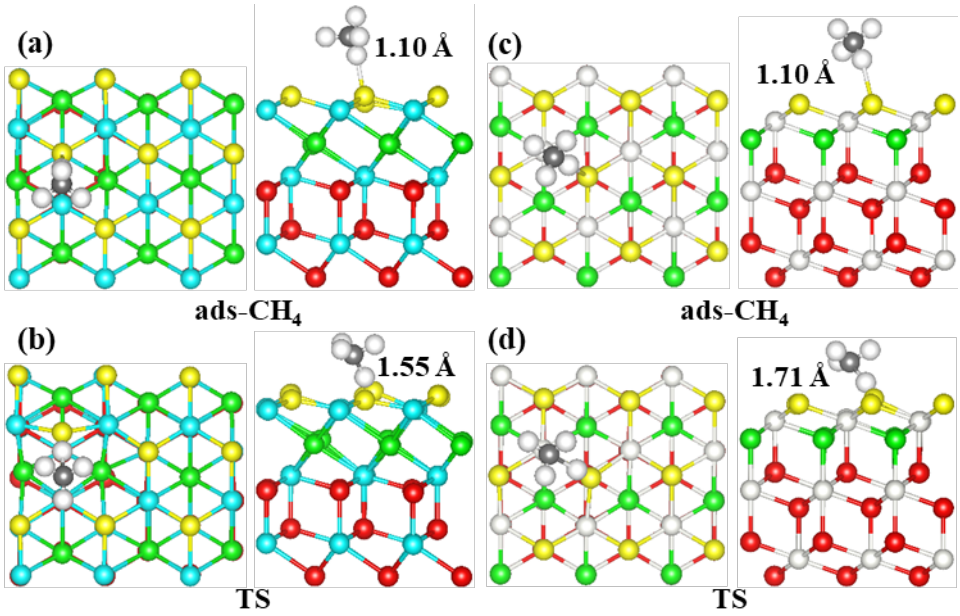

Figure S3. Calculated structures and the corresponding spin-polarized charge densities of (a, c) adsorbed methane and (b, d) transition states for their dissociation at the (a, b) $La_2O_3(001)$ and (c, d) $CeO_2(111)$ surfaces.

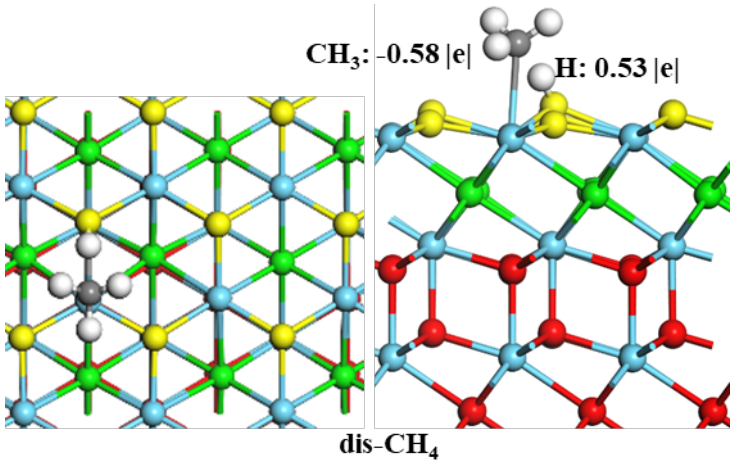

Figure S4. Calculated Bader charges of the dissociated methane on the $La_2O_3(001)$ surface.

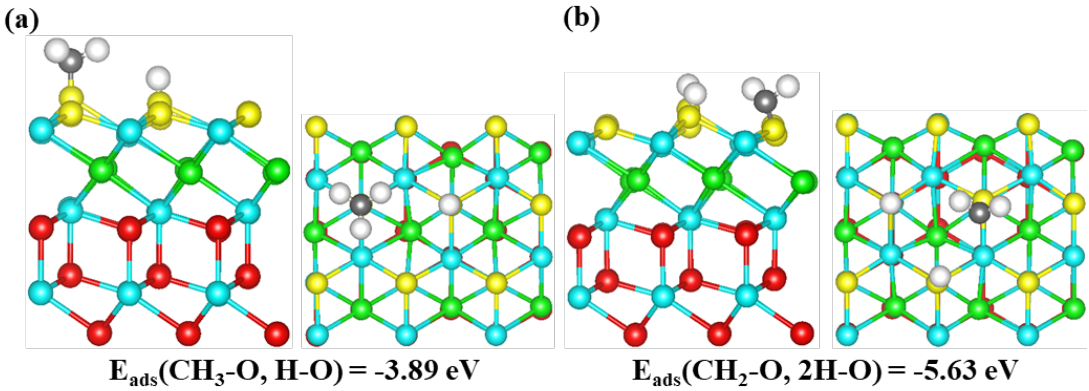

Figure S5. Calculated structures and the corresponding spin-polarized charge densities of the $La_2O_3(001)$ surface with dissociative adsorbed methane: (a) methyl group on O site and (b) further dissociated methyl.

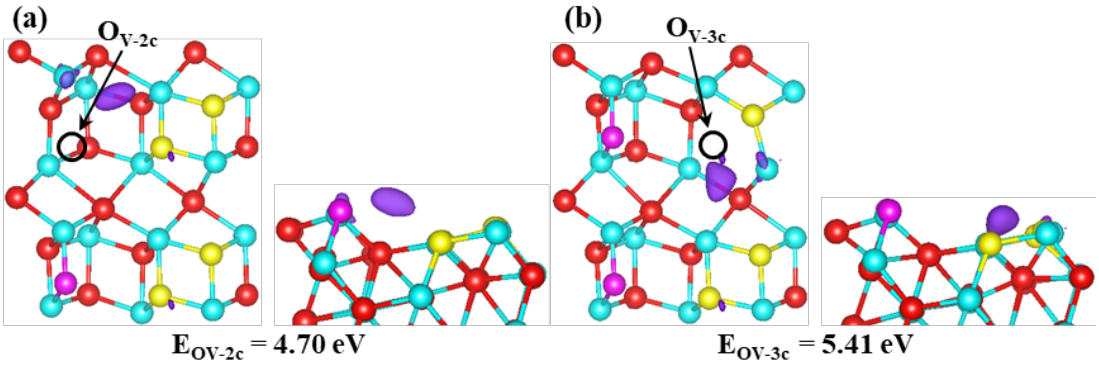

Figure S6. Calculated structures and the corresponding spin-polarized charge densities of the $La_2O_3(210)$ surface with an oxygen vacancy formed by removing one (a) O_{2c} or (b) O_{3c}.

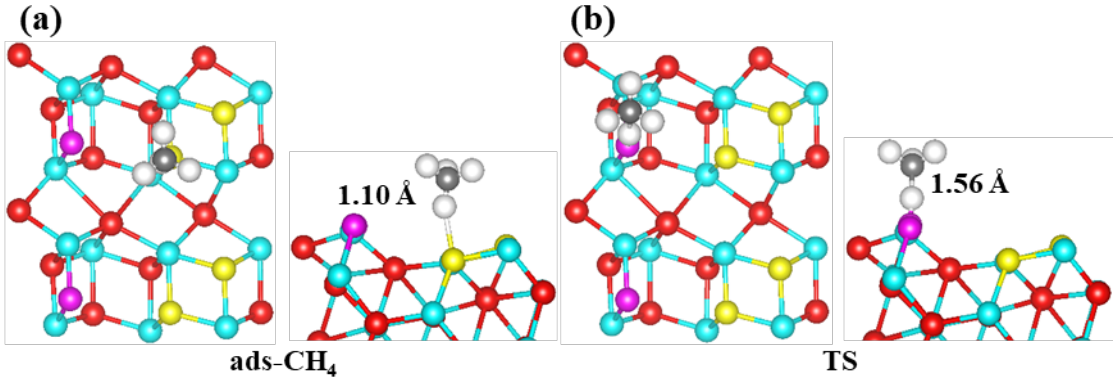

Figure S7. Calculated structures and the corresponding spin-polarized charge densities of (a) the adsorbed methane and (b) its dissociation transition state on the $La_2O_3(210)$ surface.

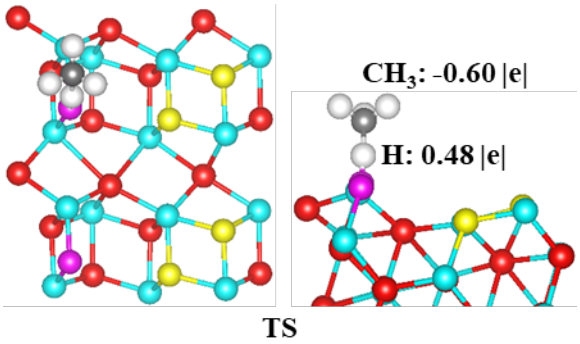

Figure S8. Calculated Bader charges of the dissociated methane on the $La_2O_3(210)$ surface.

Table S2. Calculated Bader charges of Ce cations at different surfaces and sites, including the $CeO_2(111)$ with and without an O_v on the surface, Ce-$La_2O_3(001)$, Sr/Ce-$La_2O_3(001)$ with and without one adsorbed hydrogen.

Ce cations	Ce^{4+}		Ce^{3+}		
	$CeO_2(111)$	Sr/Ce-$La_2O_3(001)$	$CeO_2(111)$ with a surface O_v	Ce-$La_2O_3(001)$	Sr/Ce-$La_2O_3(001)$ with H
Bader charge / |e|	+2.39	+2.29	+2.06	+2.04	+2.05

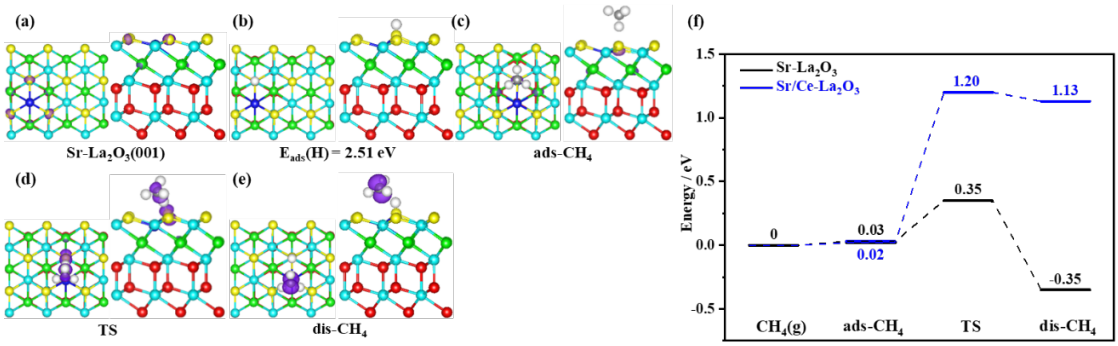

Figure S9. Calculated structures and the corresponding spin-polarized charge densities of the (a) Sr-La_2O_3(001) surface and those with (b) adsorbed H or (c) methane molecule, as well as the (d) transition state and (e) intermediate state of methane dissociation. The energy profiles of methane dissociation on the Sr-La_2O_3(001) and Sr/Ce-La_2O_3(001) surfaces were also presented (f).

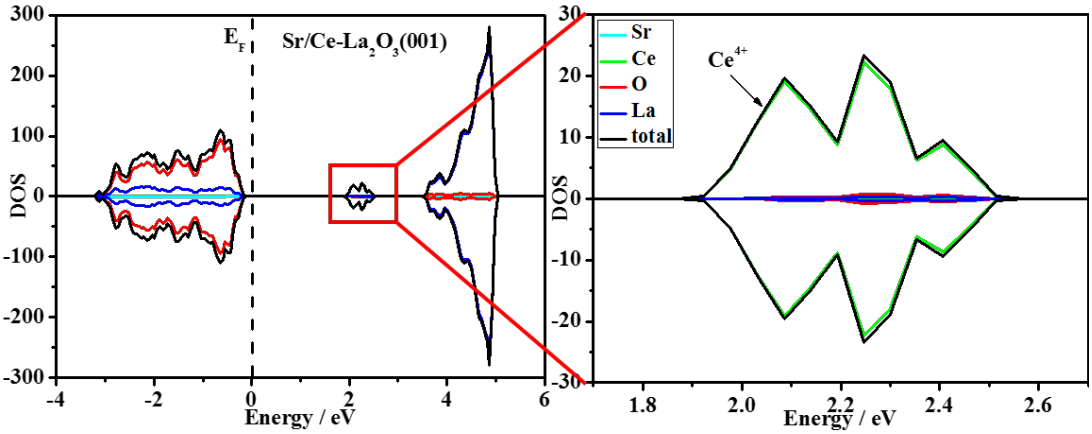

Figure S10. Calculated DOSs of the Sr/Ce-La_2O_3(001) surface.

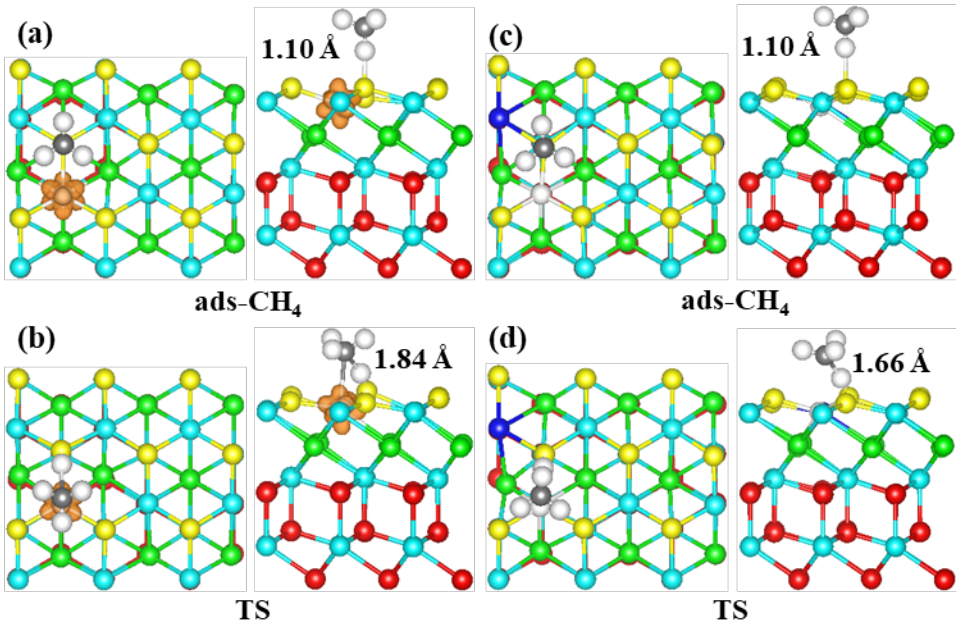

Figure S11. Calculated structures and the corresponding spin-polarized charge densities of (a, c) adsorbed methane and (b, d) its dissociation transition states on the (a, b) Ce-La_2O_3(001) and (c, d) Sr/Ce-La_2O_3(001) surfaces.

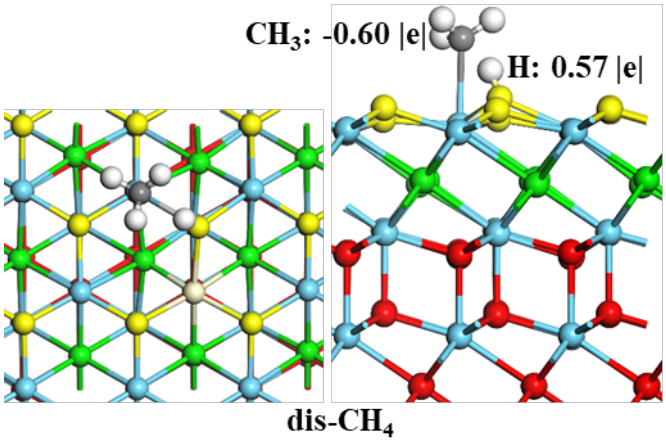

Figure S12. Calculated Bader charges of methyl group and hydrogen adsorbed on the Ce-La_2O_3(001) surface.

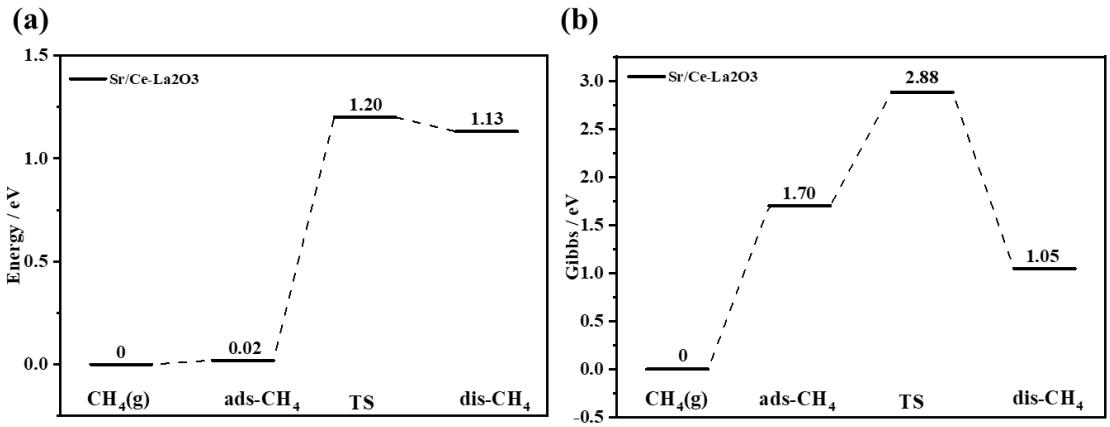

Figure S13. Calculated energy profile of methane dissociation with (a) the enthalpy changes and (b) the Gibbs free energies at the 873 K on the Sr/Ce-La_2O_3(001) surface.

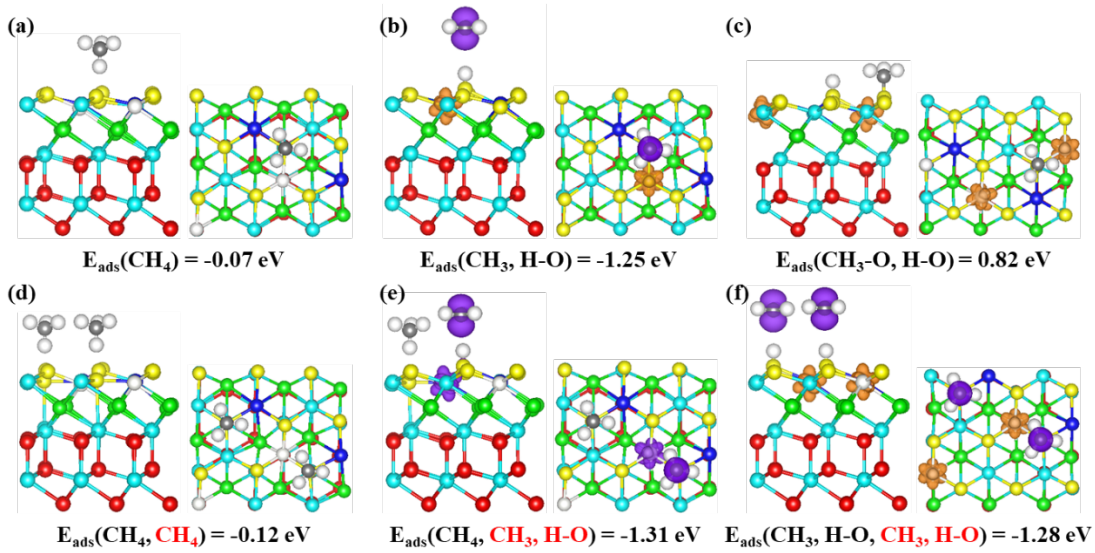

Figure S14. Calculated structures, adsorption energies and the corresponding spin-polarized charge densities of the methane molecule in the absence (upper row) or presence (bottom row) of a neighboring methane molecule on the 2(Sr/Ce)-La_2O_3(001) surface.

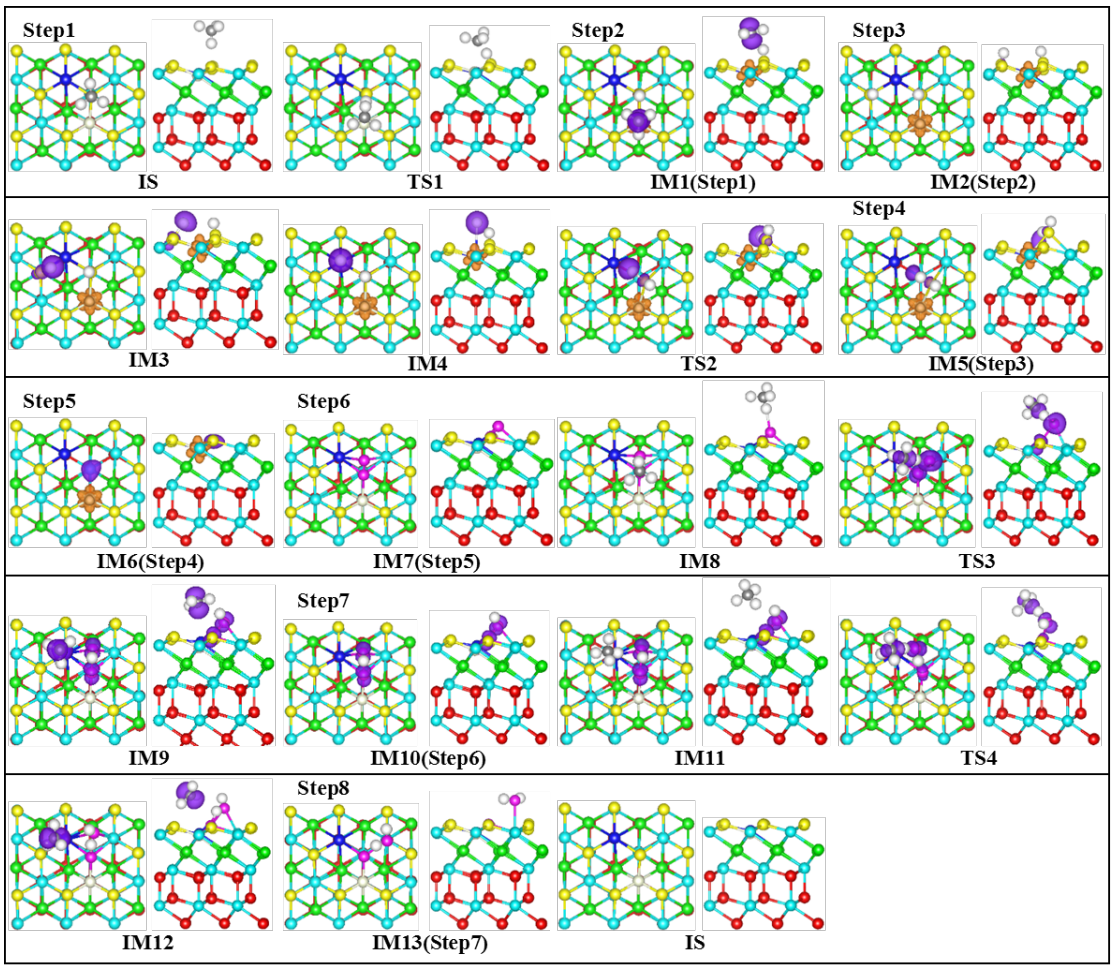

Figure S15. Calculated structures and the corresponding spin-polarized charge densities of the key species within the complete OCM reactions on the Sr/Ce-La_2O_3(001) surface.

References

(1) Zhou, W.; Jefferson, D. A.; Liang, W. Y. Surface Atomic Imaging of La_2O_3 and La_2CuO_4. *Surf. Sci.* **1989**, 209, 444–454.