Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Different Effects of Water Molecules on CO Oxidation in Different Reaction Mechanisms

Shan Ping Liu, Ming Zhao, Guo En Sun*, Wang Gao* and Qing Jiang

Table S1. Reaction barriers and reactive energies of the corresponding reactions for the OCOO pathway with PBE method.

System / Reactions / Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+O_2*→OCOO*	1.82	1.31	1.00	0.46
OCOO*→ CO_2+O*	\	-1.97	\	-1.50
O*+CO→O* +CO*	\	-1.82	\	-1.76
O*+CO*→CO_2*	0.93	-0.92	0.62	-0.88

Table S2. Reaction barriers and reactive energies of the corresponding reactions for the OCOO pathway with PBE+TSsurf method.

System / Reactions / Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+O_2*→OCOO*	1.79	1.45	1.11	0.62
OCOO*→ CO_2*+O*	1.76	-2.66	1.27	-2.69
CO_2*+O*→CO_2+O*	\	0.74	\	0.60
O*+CO→O* +CO*	\	-2.53	\	-2.32
O*+CO*→CO_2*	0.93	-0.85	0.65	-1.16

Table S3. Reaction barriers and reactive energies of the corresponding reactions for the O_2 dissociation pathway with PBE+TSsurf method.

System / Reactions / Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
O_2*→O*+O*	1.25	-0.85	0.99	-0.88
O*+O*+CO→O*+O*+CO*	\	-2.13	\	-2.55
O*+O*+CO*→O*+CO_2*	1.47	-1.06	1.09	-0.88
O*+CO_2*→O*+ CO_2	\	0.89	\	0.58
O*+CO→O*+CO*	\	-2.36	\	-2.42
O*+CO*→CO_2*	0.98	-1.14	0.81	-1.23

Table S4. Reaction barriers and reactive energies of the CO*+O*→CO_2* process for the different systems with different reactants concentration by using PBE method.

System / Concentration — Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+ O*	0.93	-0.65	0.62	-1.25
2CO*+ O*	0.88	-0.76	0.63	-1.35
CO*+2O*	0.97	-1.06	0.76	-1.62
2CO*+2O*	0.66	-1.53	0.57	-1.83

Table S5. Reaction barriers and reactive energies of the CO*+O*→CO_2* process for the different systems with different reactants concentration by using PBE+TSsurf method.

System / Concentration — Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+ O*	0.94	-0.62	0.63	-1.18
2CO*+ O*	0.87	-0.74	0.64	-1.28
CO*+2O*	1.04	-0.98	0.75	-1.47
2CO*+2O*	0.66	-1.46	0.62	-1.66

Table S6. Reaction barriers and reactive energies of the corresponding reactions for the CO+OH pathway with PBE method.

System / Reactions — Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+OH*→COOH*-*cis*	0.56	0.19	0.55	0.18
COOH*-*cis*→COOH*-*tra*	0.42	-0.16	0.56	0.04
COOH*-*tra*→CO_2*+H*	0.74	0.47	0.76	0.52

Table S7. Reaction barriers and reactive energies of the corresponding reactions for the CO+OH pathway with PBE+TSsurf method.

System / Reactions — Energy (eV)	Pt(221)		Pt(221)/7H_2O	
	E_a	E_r	E_a	E_r
CO*+OH*→COOH*-*cis*	0.56	0.18	0.57	0.18
COOH*-*cis*→COOH*-*tra*	0.39	-0.19	0.62	0.07
COOH*-*tra*→CO_2*+H*	0.77	0.44	1.00	0.19

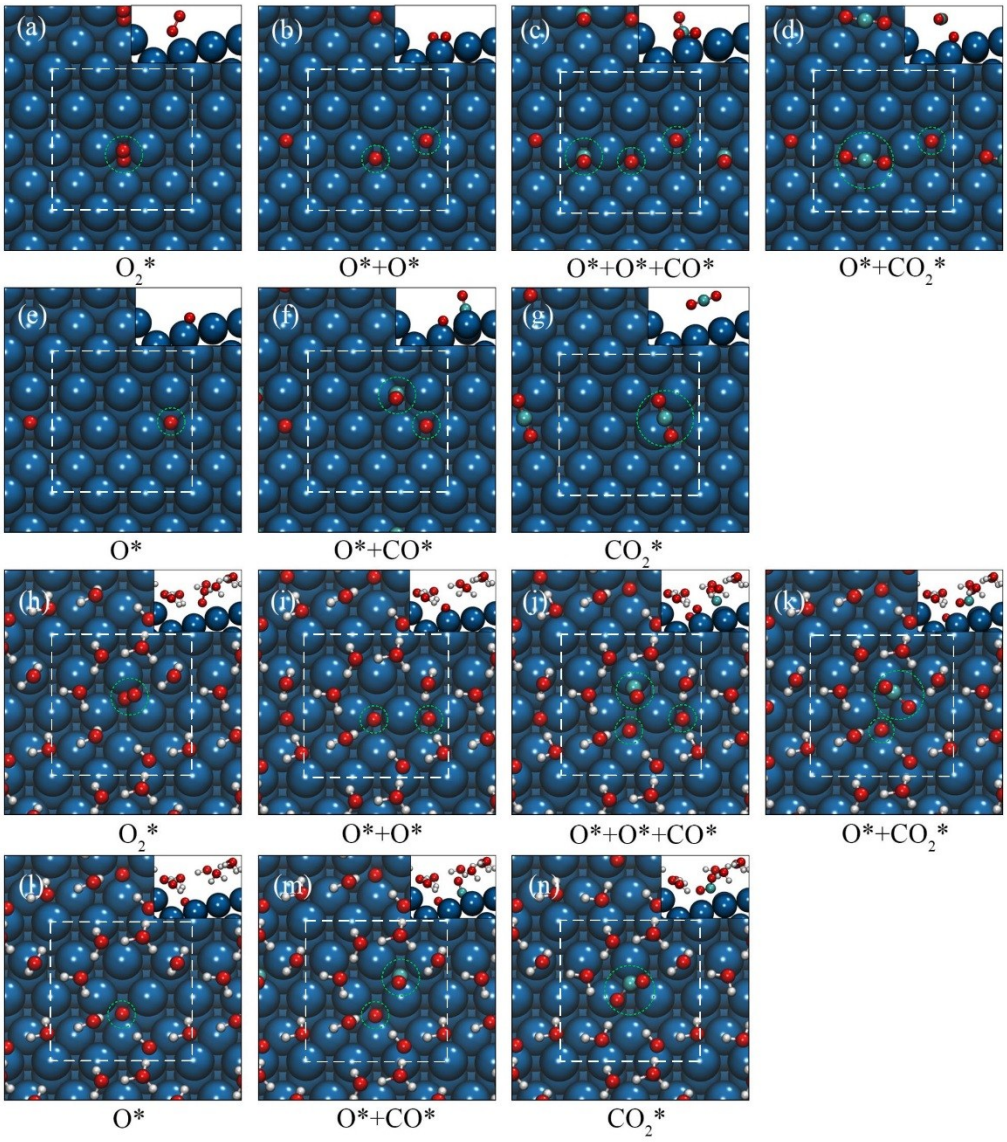

Figure S1. Configurations of the intermediates for O_2 dissociation pathway on Pt(221) (a-g) and Pt(221)/7H_2O (h-n). All the intermediates are marked out with green circles.