Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Effects of surface oxygen vacancy on CO_2 adsorption and its activation towards C_2H_4 using metal (Cu, Pd, CuPd) cluster-loaded TiO_2 catalysts: A first principles study

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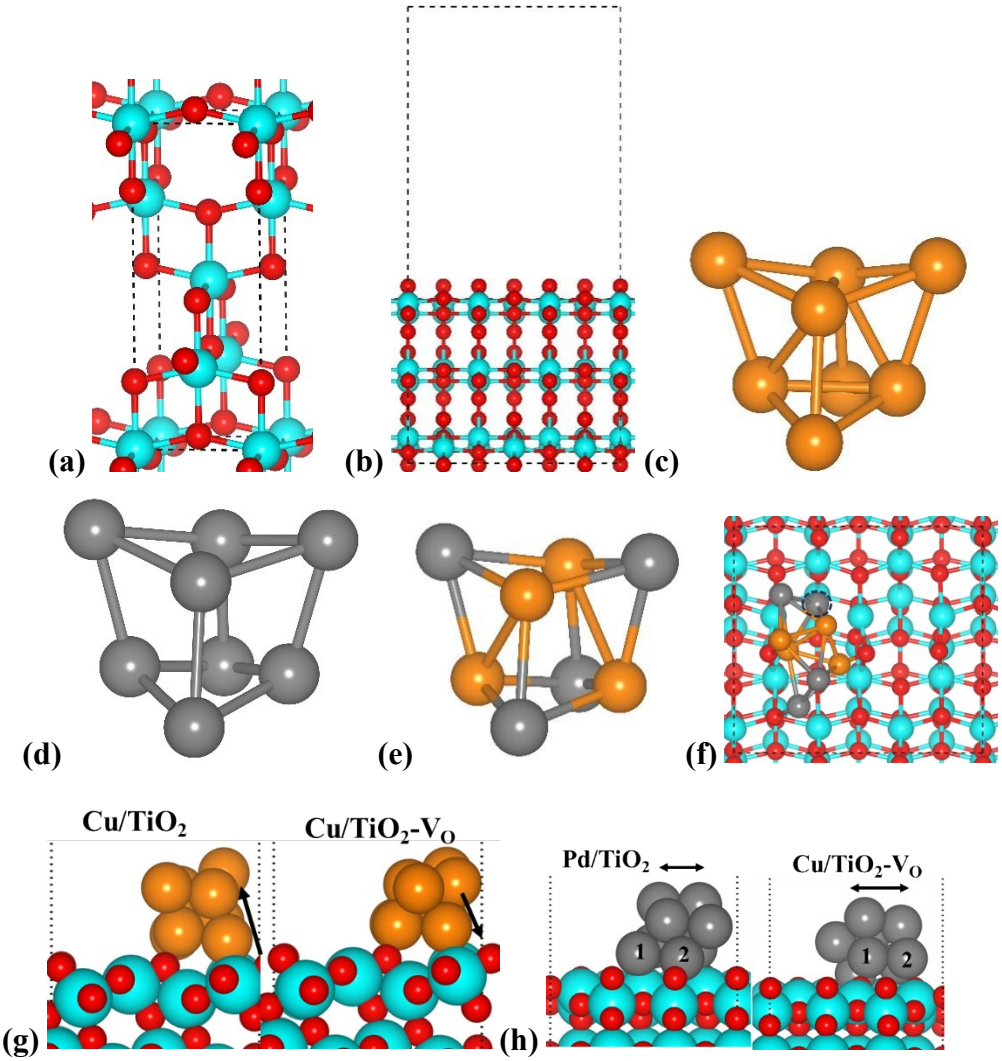

Fig. S1: The optimized geometries of (a) TiO_2 (b) clean TiO_2(101) facet (c) Cu_8 (d) Pd_8 (e) Cu_4Pd_4

(f) CuPd/TiO_2-V_O, where one Pd occupies the V_O, (g) Cu/TiO_2 with and without oxygen vacancy and (h) Pd/TiO_2 with and without oxygen vacancy. The cyan, red, orange and gray represent Ti, O, Cu and Pd, respectively.

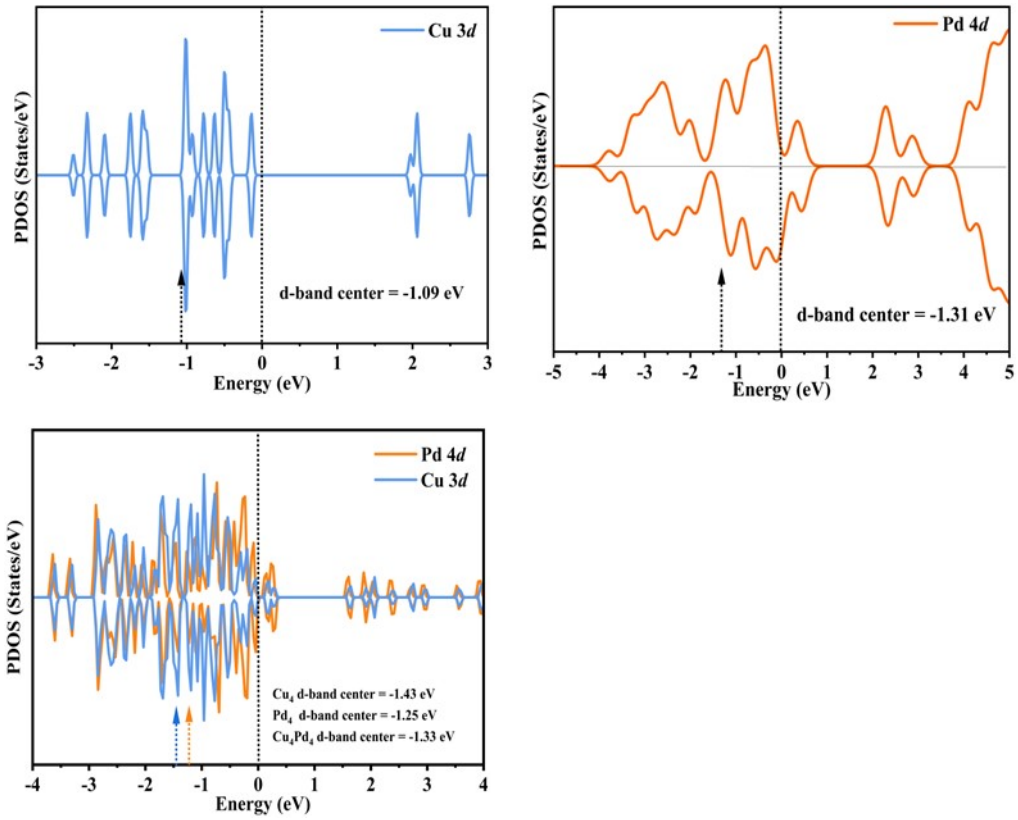

Fig. S2: The d-orbitals over (a) Cu_8 (b) Pd_8/ and (c) Cu_4Pd_4 clusters.

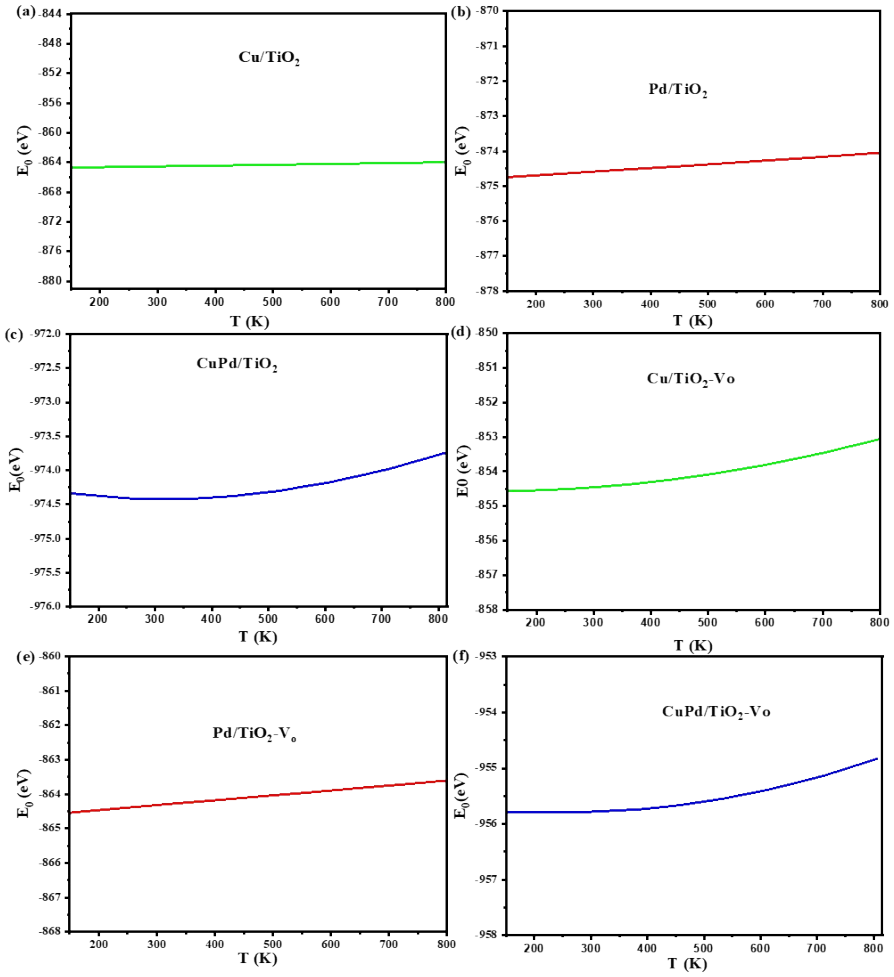

Fig. S3: Results of the ab intio molecular dynamics (AIMD) simulation at 1000K showing the variation of the energy and temperature.

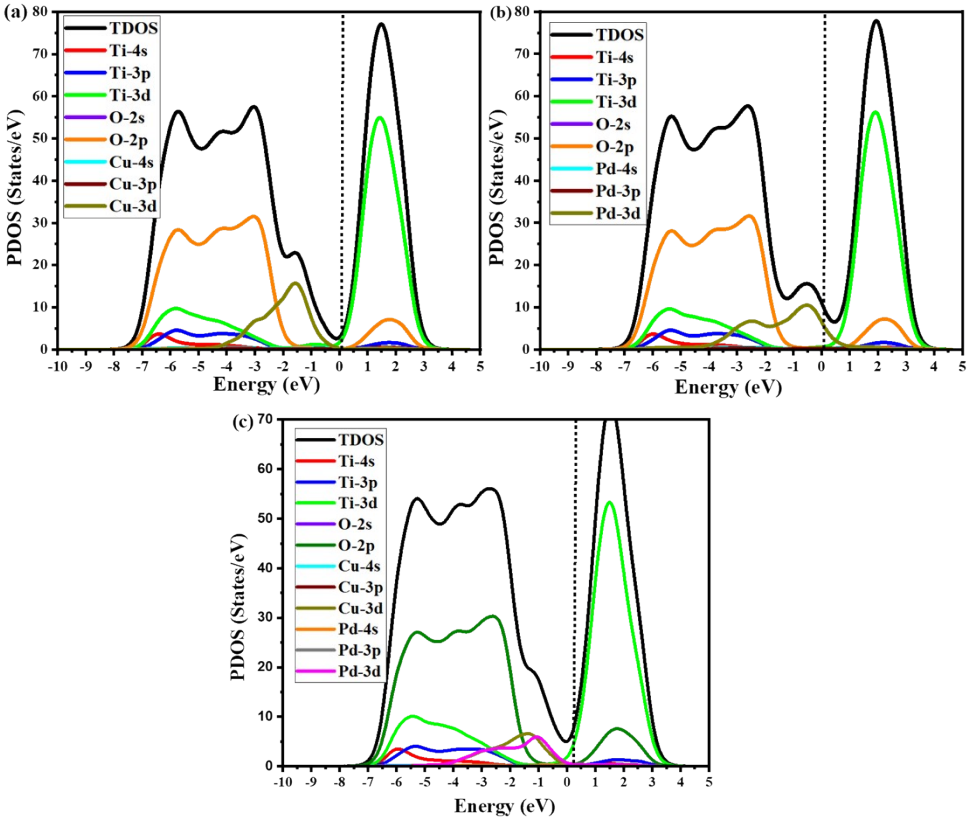

Fig. S4: The calculated TDOS and PDOS of (a) Cu/TiO_2-V_O, (b) Pd/TiO_2-V_O and (c) CuPd/TiO_2-V_O.

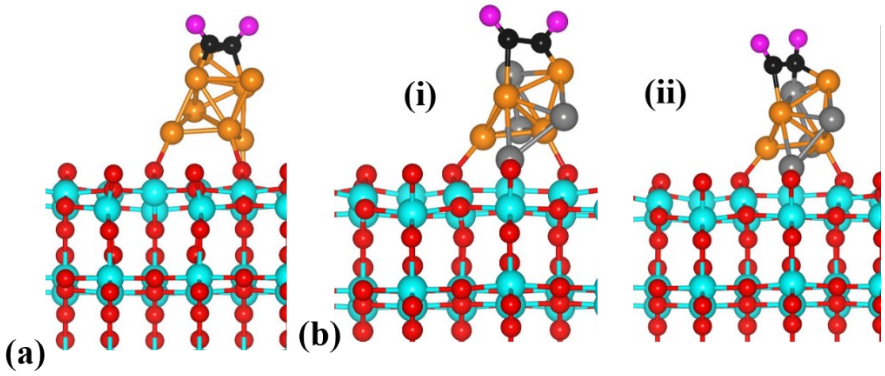

Fig. S5: The insertion of CO molecules before the optimization at the (a) Cu-Cu sites of the Cu/ TiO_2-V_O (b) (i) Cu-Cu, (ii) Cu-Pd sites of the CuPd/ TiO_2-V_O, where cyan, red, orange and gray represent Ti, O, Cu and Pd, respectively. The pink and black balls represent the O and C atoms of the CO_2 molecules, respectively.

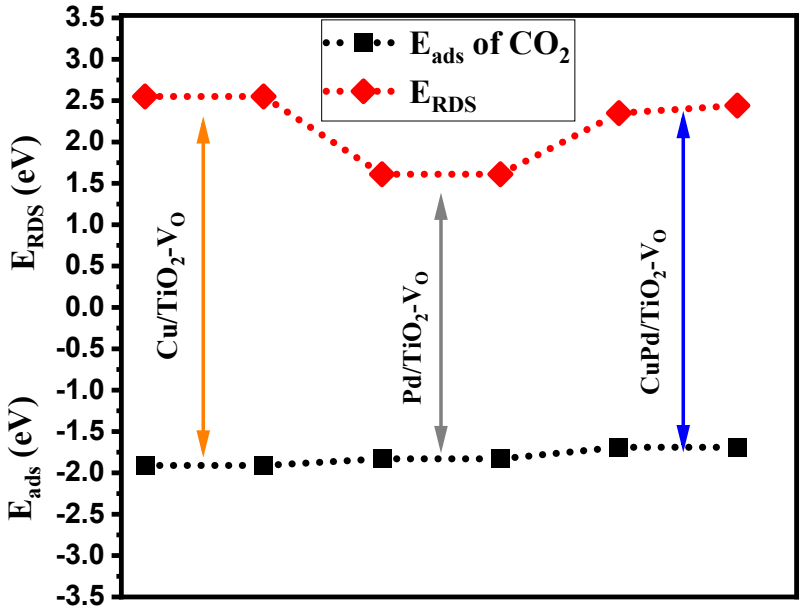

Fig. S6: The relation between adsorption energy of CO_2 molecule and energy barrier of the rate-determining step (RDS) during the C-C coupling reaction at the M/TiO_2-V_O (M= Cu, Pd, CuPd) interfaces.

Fig. S7: The reaction mechanism of C-C coupling on the M/TiO_2 and M/TiO_2-V_O (M= Cu, Pd, CuPd) catalysts.

$$* + CO_2 \rightarrow CO_2*$$

$$CO_2* + \frac{1}{2}H_2 \rightarrow COOH*$$

$$COOH* + \frac{1}{2}H_2 \rightarrow H_2O + CO*$$

$$CO* + CO \rightarrow OCCO*$$

Fig. S8: The hydrogenation of OCCO to C_2H_4 on the M/TiO_2 and M/TiO_2-V_O (M= Cu, Pd, CuPd) catalysts.

$$OCCO* + \frac{1}{2}H_2 \rightarrow C_2O_2H* + H_2O$$

$$C_2O_2H* + \frac{1}{2}H_2 \rightarrow C_2O* + H_2O$$

$$C_2O + \frac{1}{2}H_2 \rightarrow C_2OH*$$

$$C_2OH^* + \frac{1}{2}H_2 \rightarrow C_2OH_2^*$$

$$C_2OH_2^* + \frac{1}{2}H_2 \rightarrow C_2OH_3^*$$

$$C_2OH_3^* + \frac{1}{2}H_2 \rightarrow C_2OH_4^*$$

$$C_2OH_4^* + \frac{1}{2}H_2 \rightarrow C_2H_3^* + H_2O$$

$$C_2H_3^* + \frac{1}{2}H_2 \rightarrow C_2H_4^*$$

Table S1: Zero-point energy (ZPE) and entropy (TS) corrections used to calculate free energies of reactants, products, and reaction intermediates at reaction temperature 573 K.

	Cu/TiO_2						Pd/TiO_2					
	Perfect		Defect		Top		Perfect		Defect		Top	
	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS
CO_2*	0.307	0.532	0.293	0.500	0.292	0.694	0.313	0.595	0.295	0.523	0.298	0.523
CO_2H*	0.607	0.661	0.616	0.577	0.604	0.551	0.627	0.487	0.605	0.562	0.610	0.718
CO*	0.1811	0.373	0.193	0.315	0.182	0.373	0.195	0.501	0.194	0.301	0.186	0.355
OCCO*	0.363	0.753	0.433	0.729	0.372	0.886	0.409	0.761	0.410	0.719	0.400	0.575
C_2O_2H*	---	---	0.680	0.882	---	---	0.746	0.791	0.728	0.776	0.714	0.655
C_2O*	---	---	0.306	0.578	---	---	0.319	0.592	0.309	0.457	0.307	0.529
C_2OH*	---	---	0.516	0.414	---	---	0.607	0.589	0.603	0.492	0.589	0.630
C_2OH_2*	---	---	0.903	0.595	---	---	0.857	0.537	0.905	0.550	0.889	0.746
C_2OH_3*	---	---	1.228	0.690	---	---	1.20	1.559	1.205	0.616	1.202	0.789
C_2OH_4*	---	---	1.446	0.496	---	---	1.510	0.846	1.390	0.629	1.503	0.714
C_2H_3*	---	---	---	---	---	---	1.068	0.472			1.08	0.542
C_2H_4*	----	---	---	---	---	---	1.395	0.604			1.385	0.656
	$CuPd/TiO_2$						CO_2		CO		H_2	
	Perfect		Defect		Top							
	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS	ZPE	TS
CO_2*	0.324	0.507	0.438	0.503	0.290	0.636	0.308	0.396	0.087	0.166	0.270	0.400
CO_2H*	0.628	0.612	0.611	0.624	0.602	0.715	---	---	---	---	---	---
CO*	0.199	0.265	0.191	0.363	0.186	0.472	---	---	---	---	---	---
OCCO*	0.431	0.708	0.424	0.758	0.37	0.67	---	---	---	---	---	---
C_2O_2H*	0.735	0.785	0.745	0.761	---	---	---	---	---	---	---	---
C_2O*	0.311	0.544	0.331	0.508	---	---	---	---	---	---	---	---
C_2OH*	0.580	0.579	0.602	0.534	---	---	---	---	---	---	---	---

C_2OH_2*	0.905	0.614	0.905	0.631	---	---	---	---	---	---	---	---
C_2OH_3*	1.21	0.655	1.07	0.690	---	---	---	---	---	---	---	---
C_2OH_4*	1.53	0.73	1.42	0.697	---	---	---	---	---	---	---	---
C_2H_3*	1.098	0.54	---	---	---	---	---	---	---	---	---	---
C_2H_4*	1.38	0.66	---	---	---	---	---	---	---	---	---	---

Table S2: The calculated Gibbs free energies (G) and energy barriers (ΔG) involved in hydrogenation of OCCO to C_2H_4. All energies have been calculated in unit of eV.

Adsorbate	**Pd/TiO_2**		**$CuPd/TiO_2$**		**Cu/TiO_2-V_O**		**Pd/TiO_2-V_O**		**$CuPd/TiO_2$-V_O**		**$(Pd)_{top}/TiO_2$-V_O**	
	G	**ΔG**	**G**	**ΔG**	**G**	**ΔG**	**G**	**ΔG**	**G**	**ΔG**	**G**	**ΔG**
CO_2*	-1.53	---	-1.14	---	-1.91	---	-1.83	---	-1.69	---	-1.22	---
CO_2H*	0.82	**2.35**	0.28	**1.42**	0.64	**2.55**	-0.22	**1.61**	0.66	**2.35**	-0.41	0.81
CO*	-0.93	---	-1.13	---	0.68	0.04	0.086	0.13	-0.44	---	-0.90	---
***COCO**	-1.23	---	0.25	1.38	-1.76	---	-0.84	---	-1.45	---	0.35	**1.25**
***C_2O_2H**	-0.13	1.10	0.02	---	0.74	**2.50**	0.34	**1.18**	0.32	**1.77**	0.25	---
***C_2O**	-0.25	---	-0.11	---	-0.45	---	-0.19	---	-0.40	---	0.28	0.03
***C_2OH**	-0.74	---	-1.12	---	-0.66	---	-1.44	---	-0.60	---	-1.90	---
***C_2OH_2**	-0.03	0.71	-0.80	0.32	-1.28	---	-1.38	0.06	-1.16	---	-1.54	0.36
***C_2OH_3**	-1.11	---	-0.50	0.30	-0.70	0.58	-0.43	0.95	-1.20	---	0.01	**1.55**
***C_2OH_4**	0.33	**1.44**	-0.005	**0.49**	---	---	---	---	---	---	-0.28	---
***C_2H_3**	-0.22	---	0.24	0.24	---	--	---	---	---	---	0.304	0.58
***C_2H_4**	-0.65	---	-0.77	---	-0.50	0.20	-1.80	---	-1.54	---	-0.93	---