Supporting information for "A New Reduction Mechanism of CO Dimer by Hydrogenation into C_2H_4 on Cu(100) Surface: A Theoretical Insight into Kinetics of Elementary Steps"

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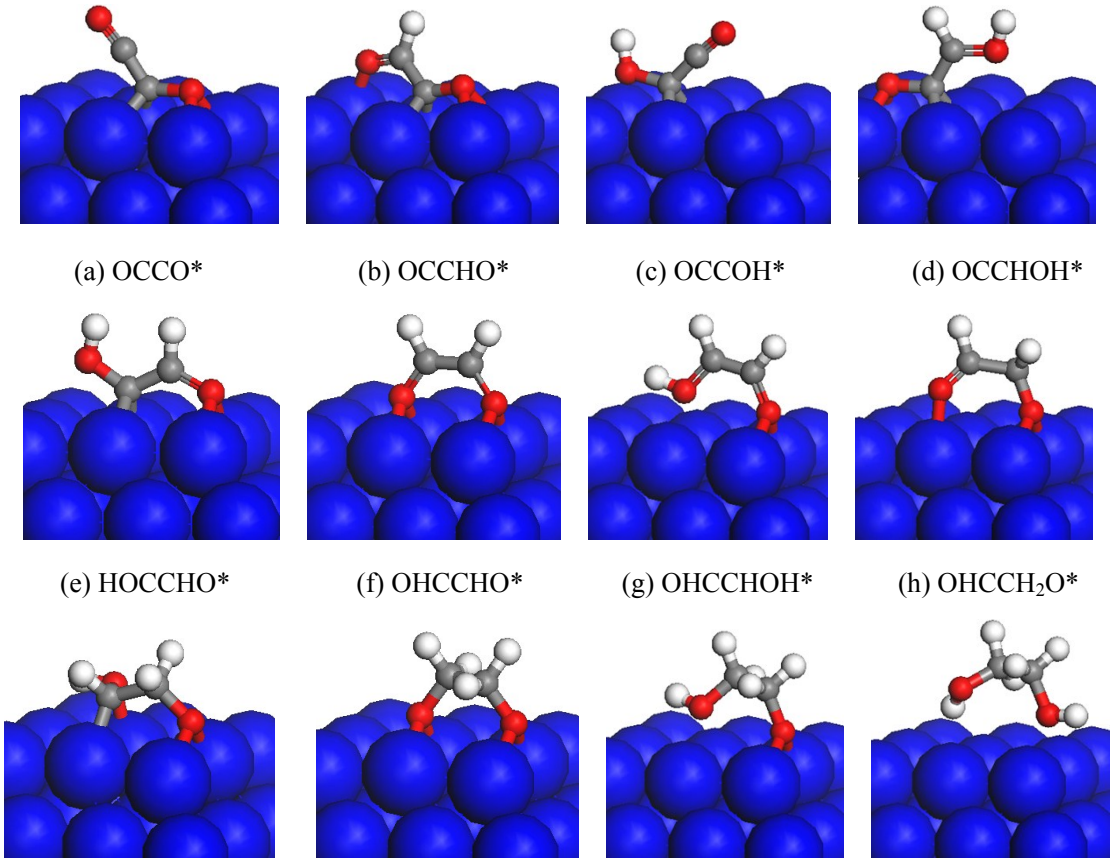
1. Adsorption energies and geometry structures of various possible adsorption intermediates on Cu(100)

The adsorption energies and geometry structures of preferred adsorption configurations for various possible reaction intermediates on Cu(100) are given in Table S1 and Figures S1, respectively. The adsorption energy (E_{ad}) of various possible reaction intermediates "A" was calculated according to $E_{ad}(A) = E(\text{slab-A}) - E(\text{slab}) - E(A)$, where E(slab-A), E(slab) and E(A) refer to the total energy of a slab with an adsorbed intermediate "A", the total energy of a slab, and the total energy of the free "A" respectively.

Table S1. Adsorption energies of the most stable structure of various possible adsorbed intermediates (E_{ad}, eV) on Cu(100)

Adsorption States	E_{ad}(eV)
OCCO	-1.83
OCCHO	-1.62
OCCOH	-3.85
OCCHOH	-1.15
HOCCHO	-3.30
OHCCHO	-1.64
OHCCHOH	-1.31
$OHCCH_2O$	-2.63

$HOHCCH_2O$	-0.34
$OHCCH_2OH$	-0.19
OH_2CCH_2O	-2.33
HOH_2CCH_2O	-2.51
HOH_2CCH_2	-1.43
HOH_2CCH_2OH	-0.23



(a) OCCO* (b) OCCHO* (c) OCCOH* (d) OCCHOH*

(e) HOCCHO* (f) OHCCHO* (g) OHCCHOH* (h) $OHCCH_2O$*

(i) $HOHCCH_2O$* (j) OH_2CCH_2O* (k) HOH_2CCH_2O* (l) HOH_2CCH_2OH*

Fig. S1. The preferential adsorption configurations of the most stable adsorption state of partial reaction intermediates in reduction mechanism of CO dimer on Cu(100).

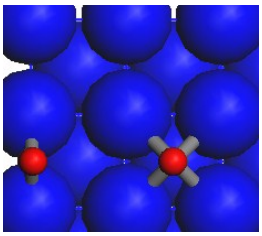
2. Co-adsorption energies and geometry structures of various possible co-adsorption intermediates on Cu(100)

The co-adsorption energies and geometry structures of preferred adsorption configurations for various possible co-adsorption intermediates on Cu(100) are given in Table

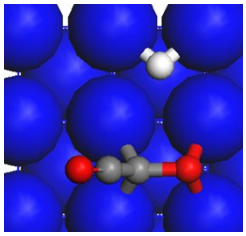
S2 and Figures S2, respectively. The co-adsorption energy between intermediates "A" and "B" was calculated according to $E_{co\text{-}ad}(A, B) = E(slab\text{-}A, B) - E(slab) - E(A) - E(B)$, in which $E(slab\text{-}A, B)$ refers to the calculated total energy of the slab with co-adsorbed "A" and "B".

Table S2. Co-adsorption energies of the most stable structure of various possible co-adsorbed intermediates ($E_{co\text{-}ad}$, eV) on Cu(100)

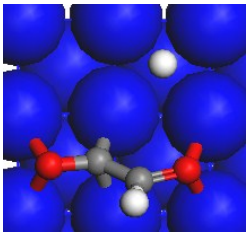
Co-adsorption States	$E_{co\text{-}ad}$(eV)
(CO+CO)*	-1.69
(CCO+O)*	-8.71
(OCCO+H)*	-4.23
(OCCHO+H)*	-4.12
(OHCCHO+H)*	-4.07
(OHCCH+O)*	-6.01
($OHCCH_2O$+H)*	-5.09
(OH_2CCH_2+O)*	-8.83
(HOH_2CCH_2O+H)*	-4.95
(H_2CCH_2OH+O)*	-6.89
(OH_2CCH_2+OH)*	-6.95
(H_2CCH_2+2OH)*	-6.95



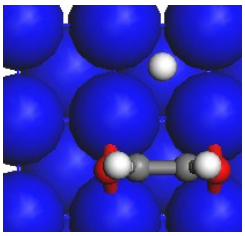
(a) (CO+CO)*



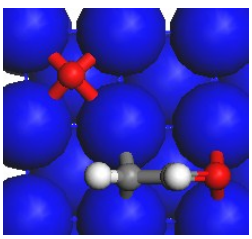
(b) (OCCO+H)*



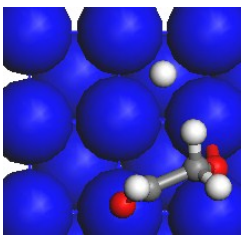
(c) (OCCHO+H)*



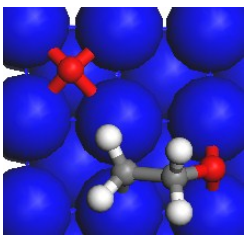
(d) (OHCCHO+H)*



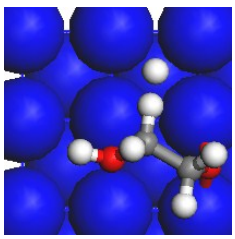
(e) (OHCCH+O)*



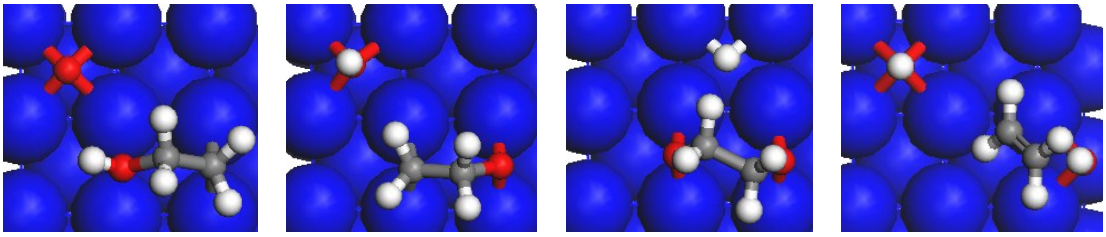
(f) ($OHCCH_2O$+H)*



(g) (OH_2CCH_2+O)*



(h) (HOH_2CCH_2O+H)*



(i) (H_2CCH_2OH+O)* (j) (OH_2CCH_2+OH)* (k) (OH_2CCH_2O+H)* (l) (H_2CCH_2+2OH)*

Fig. S2. Geometrical structures of the most stable co-adsorption site of partial reaction intermediates in reduction mechanism of CO dimer on Cu(100).