Support information

Theoretical Insight in Electrocatalytic CO_2 Reduction on Palladium-Copper Alloys: Metal ratio and Reaction Mechanism

Minmin Xing Ling Guo* Zijun Hao

a. Key Laboratory of Magnetic Molecules & Magnetic Information Materials Ministry of Education, Shanxi Normal University. Linfen, China, 041004.

b. The School of Chemical and Material Science, Shanxi Normal University, No. 1, Gongyuan Street, Linfen, China, 041004.

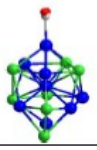
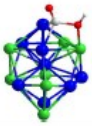
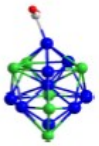
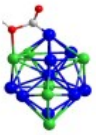
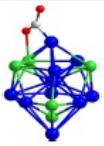
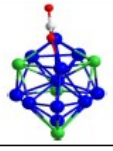
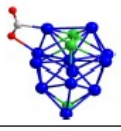
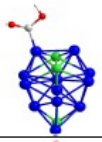
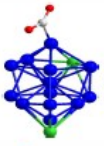
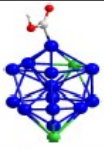
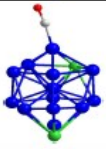
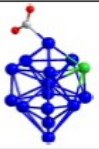
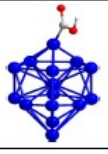
Intermediates	CO_2	COOH	CO
Pd_8Cu_7			
Pd_9Cu_6			
$Pd_{10}Cu_5$			
$Pd_{11}Cu_4$			
$Pd_{12}Cu_3$			
$Pd_{13}Cu_2$			
$Pd_{14}Cu$			
Pd_{15}			

Figure S1. The structure of an intermediate different from the CO_2RR to CO. Pd atoms are in blue, Cu atoms in green, O atoms in red, H atoms in white, and C atoms in gray.

Computational Method and Details of Adsorptions Energies (E_{ads})

$$E_{ads} = E_{total} - E_{substrate} - E_{adsorbate} \quad (6)$$

E_{total} is the total energy of the adsorbate–substrate system in the equilibrium state. $E_{adsorbate}$ and $E_{substrate}$ are the total energy of the free adsorbate and substrate in the gas phase, including cluster, hydrocarbon respectively. The $E_{adsorbate}$ of the reaction intermediates is sum of electronic and thermal energies through the frequency calculation as a separate small molecule for the reaction intermediates ($C_xH_yO_z$).

$$E_{ads} = E_{C_xH_yO_z - Pd_{10}Cu_5} - E_{Pd_{10}Cu_5} - E_{C_xH_yO_z} \quad (6\text{-}1)$$

For example, the adsorption energy of CH_4 adsorbed on $Pd_{10}Cu_5$ can be expressed as:

$$E_{ads} = E_{CH_4 - Pd_{10}Cu_5} - E_{Pd_{10}Cu_5} - E_{CH_4} \quad (6\text{-}2)$$

And the adsorption energy of CHOH adsorbed on $Pd_{10}Cu_5$ can be expressed as:

$$E_{ads} = E_{CHOH - Pd_{10}Cu_5} - E_{Pd_{10}Cu_5} - E_{CHOH} \quad (6\text{-}3)$$

Table S1. Table S1. Adsorption energies of Reactants, Intermediates, and Products on the $Pd_{10}Cu_5$ surfaces. The unit of E_{total}, $E_{substrate}$ and $E_{adsorbate}$ is Å, the unit of adsorption energies is eV.

	E_{total} (Å)	$E_{substrate}$ (Å)	$E_{adsorbate}$ (Å)	E_{ads} (eV)		E_{total} (Å)	$E_{substrate}$ (Å)	$E_{adsorbate}$ (Å)	E_{ads} (eV)
CO_2	-2436.99	-2248.59	-188.38	-0.60	CH_2CHO	-2401.59	-2248.59	-152.94	-1.84
COOH	-2437.56	-2248.59	-188.87	-2.69	$HCCH_2O$	-2401.56	-2248.59	-152.87	-2.65
CO	-2361.83	-2248.59	-113.18	-1.85	CH_2CHOH	-2402.19	-2248.59	-153.55	-1.32
C	-2286.53	-2248.59	-37.71	-6.48	CH_2CH_2O	-2402.17	-2248.59	-153.58	0.08
CH	-2287.19	-2248.59	-38.40	-5.52	$CHCH_2OH$	-2402.15	-2248.59	-153.42	-3.77
CH_2	-2287.77	-2248.59	-39.04	-3.83	HCCHOH	-2401.55	-2248.59	-152.88	-2.26
CH_2O	-2362.96	-2248.59	-114.34	-0.82	CH_3CHOH	-2402.76	-2248.59	-154.11	-1.61
CH_2OH	-2363.54	-2248.59	-114.87	-2.07	CH_2CH_2OH	-2402.75	-2248.59	-154.09	-2.03
CH_3	-2288.41	-2248.59	-39.74	-2.33	CH_2OCHO	-2476.72	-2248.59	-228.06	-1.97
CH_3O	-2363.43	-2248.59	-114.87	0.65	CH_2OCO	-2476.15	-2248.59	-227.51	-1.22
CH_3OH	-2364.13	-2248.59	-115.52	-0.61	CH_2OHCHO	-2477.33	-2248.59	-228.70	-1.19
CH_4	-2288.99	-2248.59	-40.40	-0.18	CH_2OHCO	-2476.75	-2248.59	-228.07	-2.63
CHO	-2362.39	-2248.59	-113.71	-2.60	CHOCHO	-2476.17	-2248.59	-227.52	-1.66
CHOH	-2362.93	-2248.59	-114.25	-2.69	CHOCO	-2475.60	-2248.59	-226.91	-2.78
COH	-2362.34	-2248.59	-113.63	-3.12	CHOHCHO	-2476.71	-2248.59	-228.09	-0.96
CCO	-2399.84	-2248.59	-151.04	-5.89	CHOHCO	-2476.15	-2248.59	-227.50	-1.69
CH_2CO	-2401.02	-2248.59	-152.39	-1.27	CH_2COH	-2401.56	-2248.59	-152.89	-2.21
CH_3CH_2O	-2402.75	-2248.59	-154.10	-1.48	CCH_2O	-2400.97	-2248.59	-152.16	-6.01
CH_3CH_2OH	-2403.36	-2248.59	-154.75	-0.67	HCCOH	-2401.00	-2248.59	-152.32	-2.57
CH_3CHO	-2402.19	-2248.59	-153.58	-0.70	CCHOH	-2400.99	-2248.59	-152.19	-5.92
CH_3CO	-2401.62	-2248.59	-152.95	-2.32	CCHO	-2400.41	-2248.59	-151.65	-4.69
COCO	-2474.98	-2248.59	-226.28	-2.98	CH_3COH	-2402.18	-2248.59	-153.49	-2.87
COCOH	-2475.54	-2248.59	-226.87	-2.19	CCOH	-2400.35	-2248.59	-151.63	-3.62
HCCO	-2400.43	-2248.59	-151.73	-3.07	CH_2COH	-2401.55	-2248.59	-152.89	-1.97
HCCHO	-2401.03	-2248.59	-152.25	-5.24					

Table S2. Comparison of calculated adsorption energies (in eV) for $C_xH_yO_z$ on $Pd_{10}Cu_5$ with respect to previous theoretical studies.

Adsorbate	$Pd_{10}Cu_5$ PBE	Pd–PdCu(111)[1] PBE	Cu–PdCu (111)[1] PBE	$Pd_6Cu_3(111)$[2] PW91
CO_2	-0.60	-0.42	-0.20	−0.17
COOH	-2.69	-3.08	-2.47	−2.03
CO	-1.85	-1.96	-1.84	−1.33
CH_3OH	-0.61			−0.40
CH_2OH	-2.07			−1.96
CH_2O	-0.82			−0.30
CHO	-2.60			−2.50

1. J. Mater. Chem. A, 2016, 4, 4776–4782.

2. J. Phys. Chem. C 2017, 121, 26287−26299.