Supporting Information

Water Gas Shift Reaction Mechanism and Activity on Single Atom Alloy Al_1/ Cu (111) Surface

Yun Bai, Dongxu Tian*

School of Chemistry, Dalian University of Technology, No.2 Linggong Road, Dalian City, Liaoning Province, P. R. China, 116024

Table S1. H_2O adsorption and dissociation data on M_1/Cu (111) (M = Ga, Al, Be and Cu) surfaces.

	Cu (111)	Ga_1/Cu (111)	Al_1/Cu (111)	Be_1/Cu (111)
$E_{ads\text{-}H_2O}$ (eV)	-0.43	-0.29	-0.58	-0.63
$d_{HO\text{-}H\text{-}IS}$ (Å)	0.98	0.98	1.01	0.99
$\Theta_{(H\text{-}O\text{-}H)}$ (°)	104.86	104.64	116.57	107.28
$d_{HO\text{-}H\text{-}TS}$ (Å)	1.48	1.53	1.40	1.38
ΔE_a (eV)	1.13	1.07	0.67	0.51
Freq (cm^{-1})	1263.29i	1044.65i	1177.69i	1206.93i

Table S2. The reaction mechanism and the RDS and reaction energy barrier for WGSR on representative catalysts.

System	Mechanism	RDS	Activation energy	Ref.
Ir_1/FeOx	redox	H* + H* → H_2*	3.45	1
Ir_1/FeOx	redox	CO* + O* → CO_2*	1.52	1
Cu/α-MoC	carboxyl	H_2O* → H* + OH*	0.96	2
CuB	carboxyl	H_2O* → H* + OH*	1.16	3
Pt_1/FeOx	carboxyl	H migration from O to Pt	1.29	4
Cu (211)	carboxyl	H_2O* → H* + OH*	0.94	5
Pt (111)	carboxyl	H_2O* → H* + OH*	0.88	6
Au (100)	carboxyl	H_2O* → H* + OH*	1.53	7
Cu_{29}	carboxyl	H_2O* → H* + OH*	0.93	7
Au_{29}	carboxyl	H_2O* → H* + OH*	1.29	7
Pt/TiO_2	redox	CO_2* → CO_2(g)	0.91	8
Pt_1@$Ti_3C_2S_2$	redox	OH* → H* + O*	1.12	9
aNi@TiO_{2-x}	redox	H_2O* → H* + OH*	0.35	10
K/Cu (111)	carboxyl	H_2O* → H* + OH*	1.08	11
K/Cu (100)	carboxyl	H_2O* → H* + OH*	1.06	11

References

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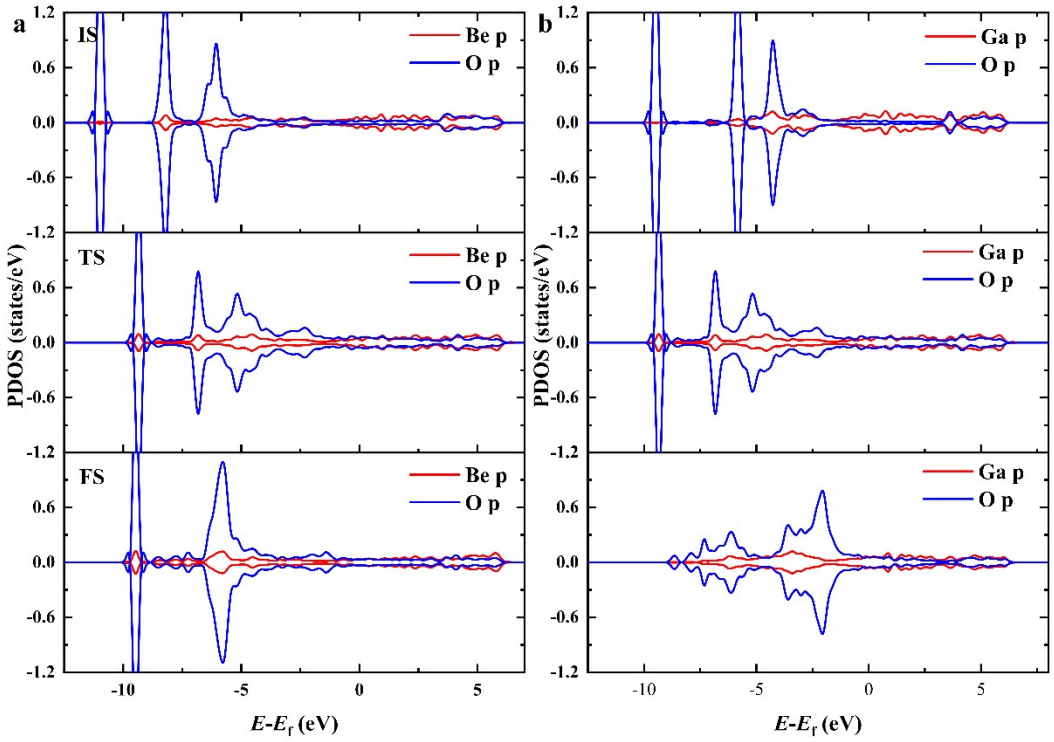

Figure S1. The PDOS plots for H_2O adsorption states(IS), dissociation transition states (TS) and final states(FS) on the M_1/Cu (111) (M = Be and Ga).

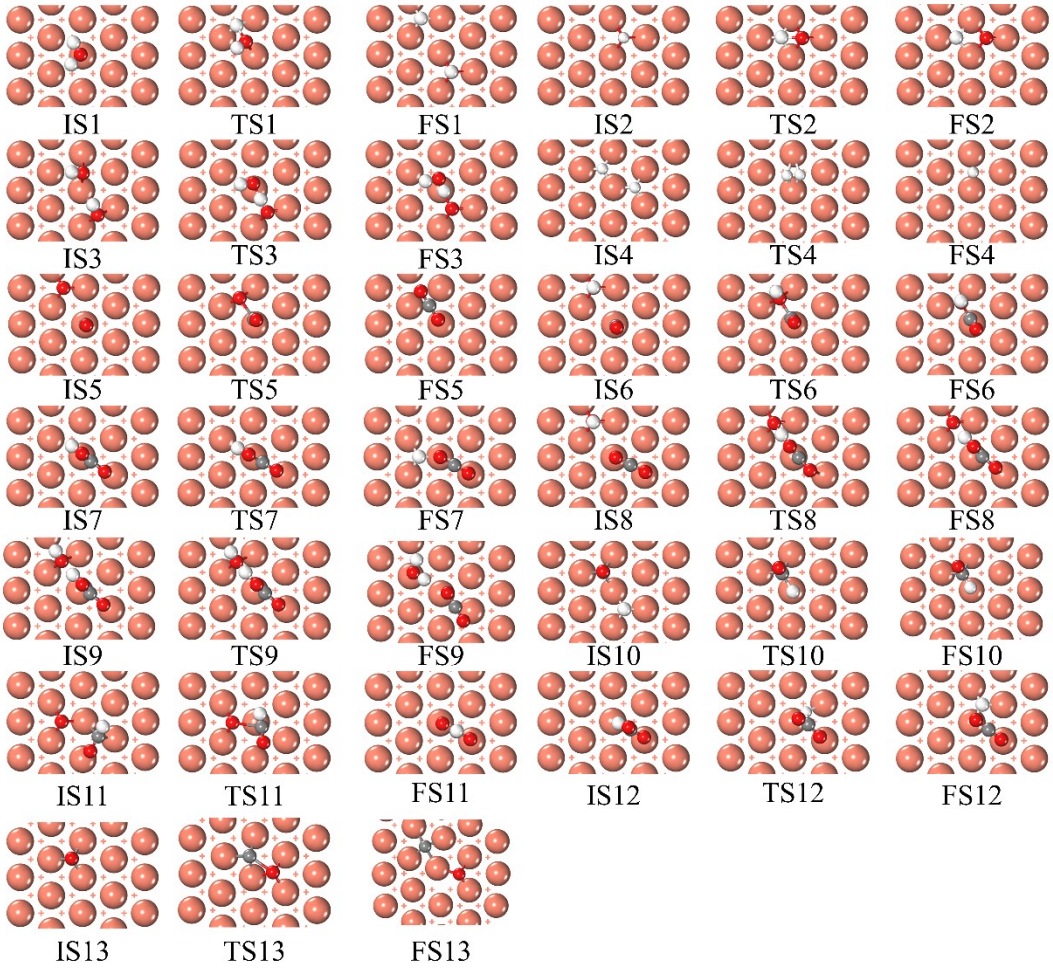

Figure S2. Initial state (IS), transition state (TS), final states (FS) of the reaction of each radical of WGSR on Cu (111).

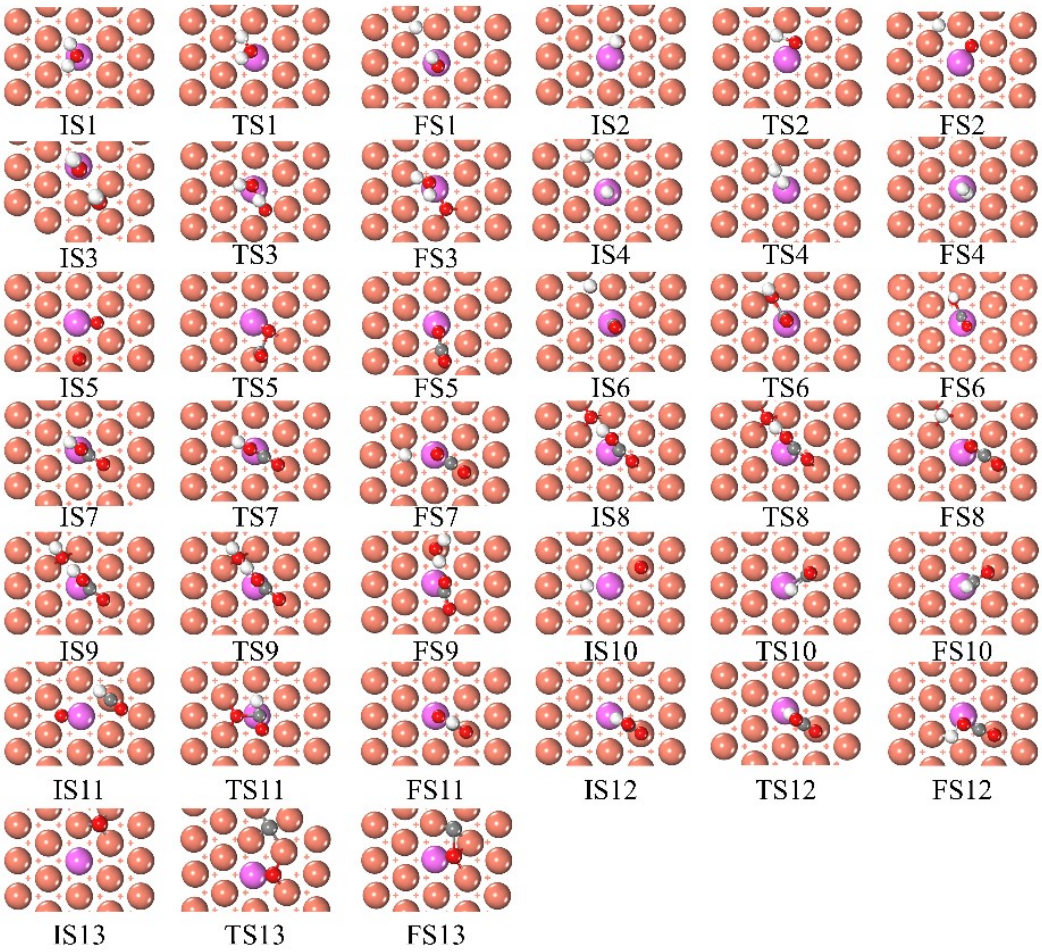

Figure S3. Initial state (IS), transition state (TS), final states (FS) of the reaction of each radical of WGSR on Al_1/Cu (111).

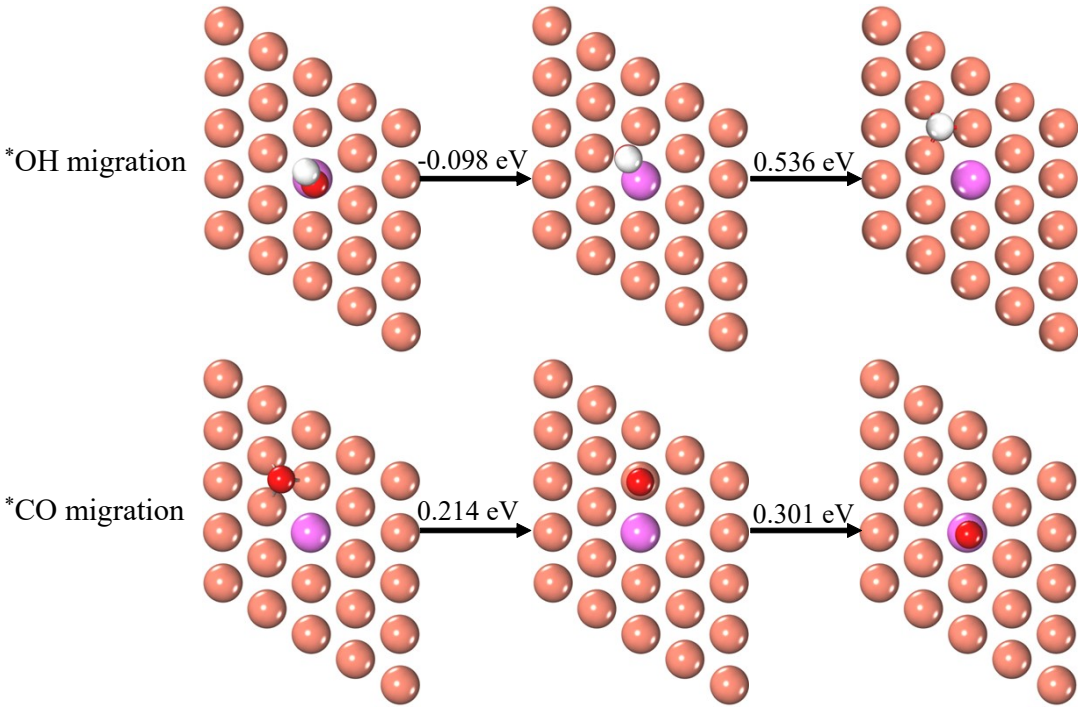

Figure S4. OH migration from the Al top site to the hollow site and CO migration from the Cu hollow site to the Al top site.