Supplementary Information

First-Principles Study on the Selective hydrogenation of the C=O and C=C bonds of Acrolein on the Pt-M-Pt (M=Pt, Cu, Ni, Co) Surfaces

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1,Free energy corrections

Harmonic approximation has been adopted for the calculation of free energy calculation as in ref.^{1,2}. The free energy surface calculated with approximation agrees well with the results for CO_2 reduction on Cu. The approximation has also been widely used in other work. In this work, the vibration frequencies are calculated with VASP. The substrates are frozen during the calculation of the vibration frequencies of the adsorbate. The HarmonicThermo module implanted in ASE (atomic Simulation Environment) package was used to calculate the free energy correction with the vibration frequencies. The zero point energy, enthalpy and entropy contribution are included as :

$$G = E_{DFT} + ZPE + \int C_p dT - TS$$

in which E_{DFT} is the electronic energy calculated with VASP, ZPE is the zero-point energy, Cp is the heat capacity, S is the entropy contribution, and T is the temperature. Gas-phase molecules are treated as ideal gases. Its free energy correction was calculated with the IdealGasThermo module in Atomic Simulation Environment (ASE). All free energy corrections were calculated at the normal condition. The symmetry number of the gas-phase molecules H₂, Acrolein, ally alcohol and propanal is 2, 1,1,1 because they belong to the $D_{\infty h}$, C_s, C₁ and C₁ point group.

2 Structures of the intermediates

Fig. S1-S3 show the structures of TS1, IS2, TS2 and FS1 for 1, 2-addition, 4, 3-addition and 3, 4addition on the Pt-M-Pt surfaces. Note that IS2 in the manuscript means AH^*+H^* . The H* is adsorbed far away from AH^* , which is why it is not shown in the figures. The Pt-X (X = C, O) distances for all structures are summarized in Table S1-S3. In Fig.S1-S3, when the Pt-X distance is smaller than 2.5 Å, a bond is shown between Pt and X atoms in the corresponding structures. Namely, in the discussion, a "bond" simply means the distance between Pt and X is smaller than 2.5 Å, which is about 1.25 times of the sum of the radius of Pt and X.

For 1, 2-addition, the structures of TS1, IS2, TS2, and FS1 on the four surfaces are similar, though the structure of adsorbed acrolein in IS1 on the Pt(111) surface (Figure 1) is different from that on the bimetallic surfaces. One major difference is that the number of Pt-X bond is smaller on Pt-Co-Pt surface for TS1, IS2, and TS2, suggesting a weaker interaction between Pt-Co-Pt and the adsorbate. On the other hand, the smaller Pt-X distances (Table S1) on pure Pt surface suggests that the interaction between pure Pt and the adsorbate is much stronger.

For 4, 3-addition and 3, 4-addition(Fig.S2-S3), the structures of TS1, IS2, TS2 and FS1 on the pure Pt surface are significantly different from those on the bimetallic surfaces. More Pt-X bonds are formed on the pure Pt surface. For example, in the FS1, there are two Pt-X bonds on the pure Pt surface but none on the bimetallic surfaces. On the other hand, for both 4, 3-addition and 3, 4-addition, the structures of TS1, IS2, TS2 and FS1 resembles much to each other on the bimetallic surfaces(Fig.S2-S3).



Fig.S1 Structures of TS1, IS2, TS2, FS1 for 12-addition on the Pt-M-Pt surfaces for M=Pt, Cu, Ni, Co from up to down

1, 2-add	М	Pt-O	Pt-C2	Pt-C3	Pt-C4
TS1	Pt	3.071	2.701	2.171	2.1
	Cu	2.929	2.507	2.515	2.149
	Ni	3.147	2.845	2.257	2.143
	Со	3.275	2.83	2.869	2.255
IS2	Pt	2.906	2.113	2.174	2.096
	Cu	3.367	2.202	3.089	2.174
	Ni	3	2.162	2.293	2.135
	Со	3.305	2.248	3.033	2.2
TS2	Pt	3.119	3.048	2.156	2.089
	Cu	3.281	3.178	2.382	2.122
	Ni	3.202	3.155	2.328	2.142
	Со	3.31	3.198	2.724	2.203
FS1	Pt	3.041	3.554	2.141	2.104
	Cu	3.389	3.592	2.169	2.129
	Ni	3.379	3.531	2.192	2.142
	Со	3.343	3.519	2.212	2.154

Table S1, Pt-X distance in TS1, IS2, TS2, FS1, on Pt-M-Pt surfaces for 1,2-addition



Fig.S2 Structures of TS1, IS2, TS2, FS1 for 4, 3-addition on the Pt-M-Pt surfaces for M=Pt, Cu, Ni, Co from up to down

4, 3-add	М	Pt-O	Pt-C2	Pt-C3	Pt-C4
TS1	Pt	2.1	2.191	2.128	2.286
	Cu	3.298	3.238	2.266	3.148
	Ni	2.813	3.187	2.591	3.498
	Со	2.565	3.225	2.747	3.673
IS2	Pt	2.081	2.227	2.117	3.34
	Cu	2.472	3.078	2.155	3.611
	Ni	2.297	3.077	2.208	3.644
	Со	2.299	3.091	2.229	3.554
TS2	Pt	2.086	2.246	2.92	3.428
	Cu	2.954	3.22	2.45	3.582
	Ni	2.353	3.083	2.445	3.534
	Со	2.327	3.113	2.487	3.652
FS1	Pt	2.059	2.163	3.324	3.585
	Cu	4.343	3.412	4.106	4.093
	Ni	3.982	3.299	3.93	3.94
	Со	4.918	3.365	4.032	4.062

Table S2, Pt-X distance in TS1, IS2, TS2, FS1, on Pt-M-Pt surfaces for 4, 3-addition



Fig.S3 Structures of TS1, IS2, TS2, FS1 for 3, 4-addition on the Pt-M-Pt surfaces for M=Pt, Cu, Ni, Co from up to down

3, 4-add	М	Pt-O	Pt-C2	Pt-C3	Pt-C4
TS1	Pt	2.105	2.138	2.332	2.083
	Cu	3.895	3.186	3.247	2.343
	Ni	3.616	2.985	2.557	2.137
	Со	3.651	3.031	2.738	2.186
IS2	Pt	2.088	2.146	3.173	2.103
	Cu	3.804	3.046	3.471	2.107
	Ni	3.777	3.073	3.451	2.122
	Со	4.44	3.158	3.558	2.133
TS2	Pt	2.091	2.128	3.149	2.256
	Cu	3.941	3.12	3.631	2.288
	Ni	4	3.13	3.607	2.288
	Со	3.94	3.118	3.592	2.296
FS1	Pt	2.059	2.163	3.324	3.585
	Cu	4.343	3.412	4.106	4.093
	Ni	3.982	3.299	3.93	3.94
	Со	4.918	3.365	4.032	4.062

Table S3, Pt-X distance in TS1, IS2, TS2, FS1, on Pt-M-Pt surfaces for 3, 4-addition

3. The magnetic moments of the atom in the Pt-Ni-Pt and Pt-Co-Pt model

Each Ni/Co atom bring two/three unpaired electron to the model. The Magnetic moment from is not localized at Ni/Co atom but spill over to other Pt atoms. Magnetic moment of each atom from Bader analysis³ is summarized in Table S4.

	1 st -layer Pt	2 nd layer atom	3 rd -layer Pt	Bottom-layer Pt	
Pt-Ni-Pt	0.32	0.94	0.45	0.27	
Pt-Co-Pt	0.35	2.06	0.45	0.24	

Table S4 Magnetic moments(μB) of the atoms in a Pt-M-Pt 1x1 surface unit cell

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- 3 W. Tang, E. Sanville, G. Henkelman, J. Phys. Condens. Matter 2009, 21, 084204.