Electronic Supplementary Information

Mechanisms and selectivity of methanol oxidation reaction on $PtRuM_3$/C-MWCNTs (M = Fe, Co) electrocatalysts

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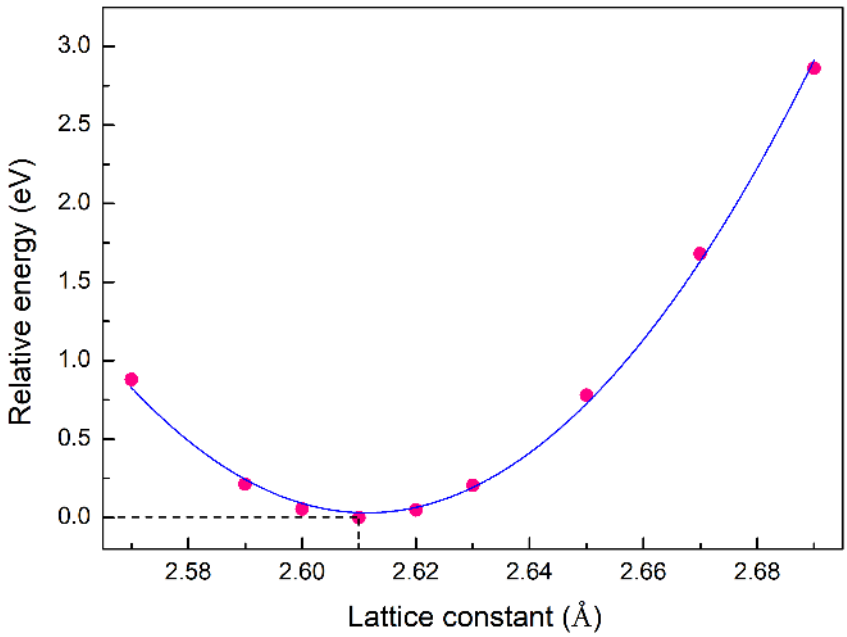

Fig. S1 The relative energy, compared to that of the minimum point, is a function of the lattice constant of $PtRuM_3$/C-MWCNTs (M = Fe, Co) substrates. Both substrates have the same optimized lattice constant of 2.61 Å.

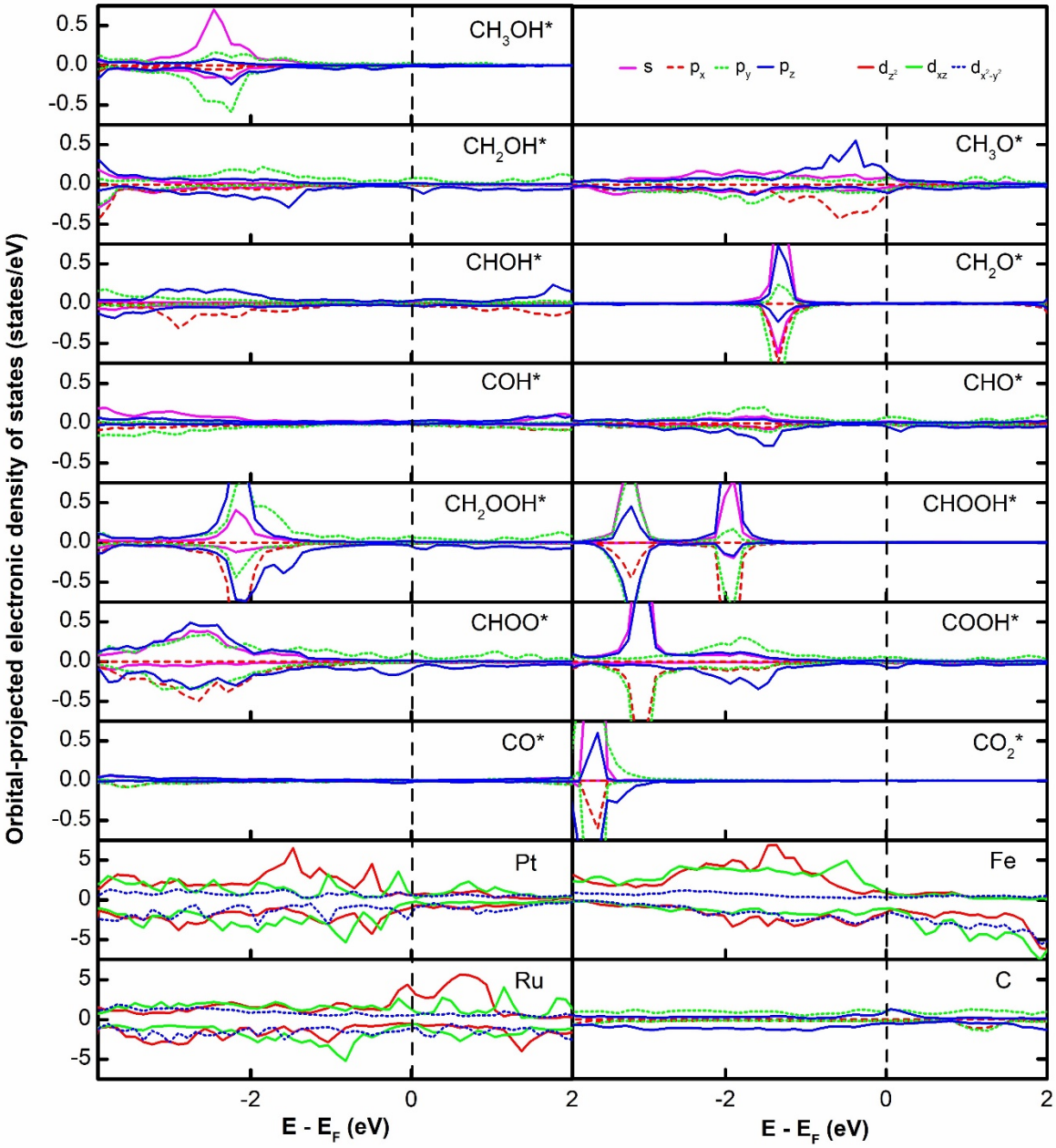

Fig. S2 The orbital-projected electronic density of states for the systems of the $PtRuFe_3$/C-MWCNTs substrate and the adsorbed intermediate: d_{xz} is identical to d_{yz}, and d_{xy} is identical to $d_{x^2-y^2}$.

Table S1 The distances from the nearest atom (carbon atom/oxygen atom) of adsorbate molecules to the surface ($d_{ads\text{-}sur}$), the adsorption energy (E_{ads}), zero-point energy (*ZPE*), and total energy (E_{total}, equals E_{ads} plus *ZPE*) of the intermediates on the $Pt_1Ru_1M_3$ (M = Fe, Co) substrates. The adsorption sites: T = the top of a Pt atom, B = the bridge of two Pt atoms, and H = the hollow with an underneath Ru atom.

Molecule	Radical	$d_{ads\text{-}sur}$ (Å)		E_{ads} (eV)		*ZPE* (eV)		E_{total} (eV)	
		M = Fe (site)	M = Co (site)	M = Fe	M = Co	M = Fe	M = Co	M = Fe	M = Co
Methanol	CH_3OH^*	2.76 (T)	2.66 (T)	-0.078	-0.097	1.375	1.379	1.297	1.282
Methoxy	CH_3O^*	2.18 (T)	2.11 (T)	-1.184	-1.243	1.061	1.060	-0.123	-0.183
Formaldehyde	CH_2O^*	2.96 (T)	3.06 (T)	-0.032	-0.029	0.721	0.724	0.689	0.695
Formyl	CHO^*	2.35 (T)	2.31 (T)	-1.943	-1.912	0.470	0.471	-1.473	-1.441
Carbon monoxide	CO^*	2.22 (T)	2.16 (T)	-1.066	-1.068	0.203	0.205	-0.863	-0.863
Hydroxymethyl	CH_2OH^*	2.50 (T)	2.51 (T)	-1.596	-1.576	1.109	1.106	-0.487	-0.470
Hydroxymethylene	$CHOH^*$	1.94 (B)	1.88 (B)	-3.419	-3.543	0.800	0.801	-2.619	-2.742
Isoformyl	COH^*	1.50 (H)	1.44 (H)	-3.593	-3.462	0.492	0.492	-3.101	-2.970
Hydroperoxymethyl	CH_2OOH^*	2.48 (T)	2.46 (T)	-1.637	-1.387	1.162	1.171	-0.475	-0.216
Formic acid	$CHOOH^*$	2.95 (T)	3.07 (T)	-0.023	-0.034	0.902	0.901	0.879	0.867
Carboxyl	$COOH^*$	2.39 (T)	2.38 (T)	-1.900	-1.920	0.616	0.616	-1.284	-1.304
Formate	$CHOO^*$	2.32 (T-T)	2.29 (T-T)	-1.933	-2.072	0.611	0.615	-1.322	-1.457
Carbon dioxide	CO_2^*	3.32 (T-B)	3.43 (T-B)	0.032	0.010	0.316	0.316	0.348	0.326

Table S2 The thermodynamic barrier (eV) of the intermediate steps on the $PtRuM_3$ (M = Fe, Co) substrates at the applied potential U = 0 V, the pressure of 1 bar, and the temperature of 300 K. The thermodynamic barrier of the rate-limiting step is marked by bold font. The pathway corresponding to the highest thermodynamic barrier is presented in parentheses.

Intermediate step	$PtRuFe_3$	$PtRuCo_3$
$CH_3OH + H_2O \rightarrow CH_3OH^* + H_2O$	**0.417 (Path1)**	0.376
$CH_3OH^* + H_2O \rightarrow CH_3O^* + 1/2H_2 + H_2O$	**0.950 (Path3)**	**0.901 (Path3)**
$CH_3OH^* + H_2O \rightarrow CH_2OH^* + 1/2H_2 + H_2O$	0.176	0.230
$CH_3O^* + 1/2H_2 + H_2O \rightarrow CH_2O^* + H_2 + H_2O$	-0.388	-0.283
$CH_2OH^* + 1/2H_2 + H_2O \rightarrow CH_2O^* + H_2 + H_2O$	0.386	**0.388 (Path1)**
$CH_2OH^* + 1/2H_2 + H_2O \rightarrow CHOH^* + H_2 + H_2O$	0.401	0.277
$CH_2O^* + H_2 + H_2O \rightarrow CH_2OOH^* + 3/2H_2$	**2.737 (Path4)**	**2.958 (Path4)**
$CH_2O^* + H_2 + H_2O \rightarrow CHO^* + 3/2H_2 + H_2O$	-0.465	-0.378
$CHOH^* + H_2 + H_2O \rightarrow CHO^* + 3/2H_2 + H_2O$	-0.480	-0.267
$CHOH^* + H_2 + H_2O \rightarrow COH^* + 3/2H_2 + H_2O$	-0.191	0.056
$CH_2OOH^* + 3/2H_2 \rightarrow CHOOH^* + 2H_2$	-2.942	-3.192
$CHO^* + 3/2H_2 + H_2O \rightarrow CHOOH^* + 2H_2$	0.260	0.144
$CHO^* + 3/2H_2 + H_2O \rightarrow CO^* + 2H_2 + H_2O$	-0.511	-0.609
$COH^* + 3/2H_2 + H_2O \rightarrow CO^* + 2H_2 + H_2O$	-0.800	-0.932
$CHOOH^* + 2H_2 \rightarrow CHOO^* + 5/2H_2$	0.229	0.112
$CHOOH^* + 2H_2 \rightarrow COOH^* + 5/2H_2$	-0.010	-0.087
$CO^* + 2H_2 + H_2O \rightarrow COOH^* + 5/2H_2$	**0.761 (Path2)**	**0.666 (Path2)**
$CHOO^* + 5/2H_2 \rightarrow CO_2^* + 3H_2$	-0.667	-0.623
$COOH^* + 5/2H_2 \rightarrow CO_2^* + 3H_2$	-0.428	-0.424