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Electronic Supplementary Information

Chemical Original and Catalytic Activity of Coinage Metals: From Oxidation to Dehydrogenation

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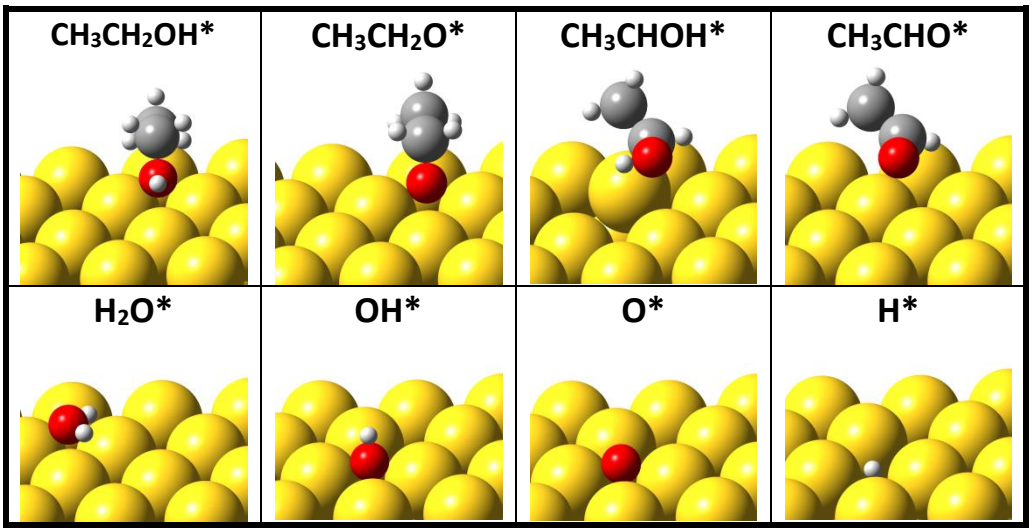

Fig. S1 Side views of optimized structures of CH_3CH_2OH*, CH_3CH_2O*, CH_3CHOH*, CH_3CHO*, H_2O*, OH*, O* and H* on Au(111). Yellow, grey, red and white spheres are represented as Au, C, O and H atoms. The corresponded top views are shown in Fig. 1b.

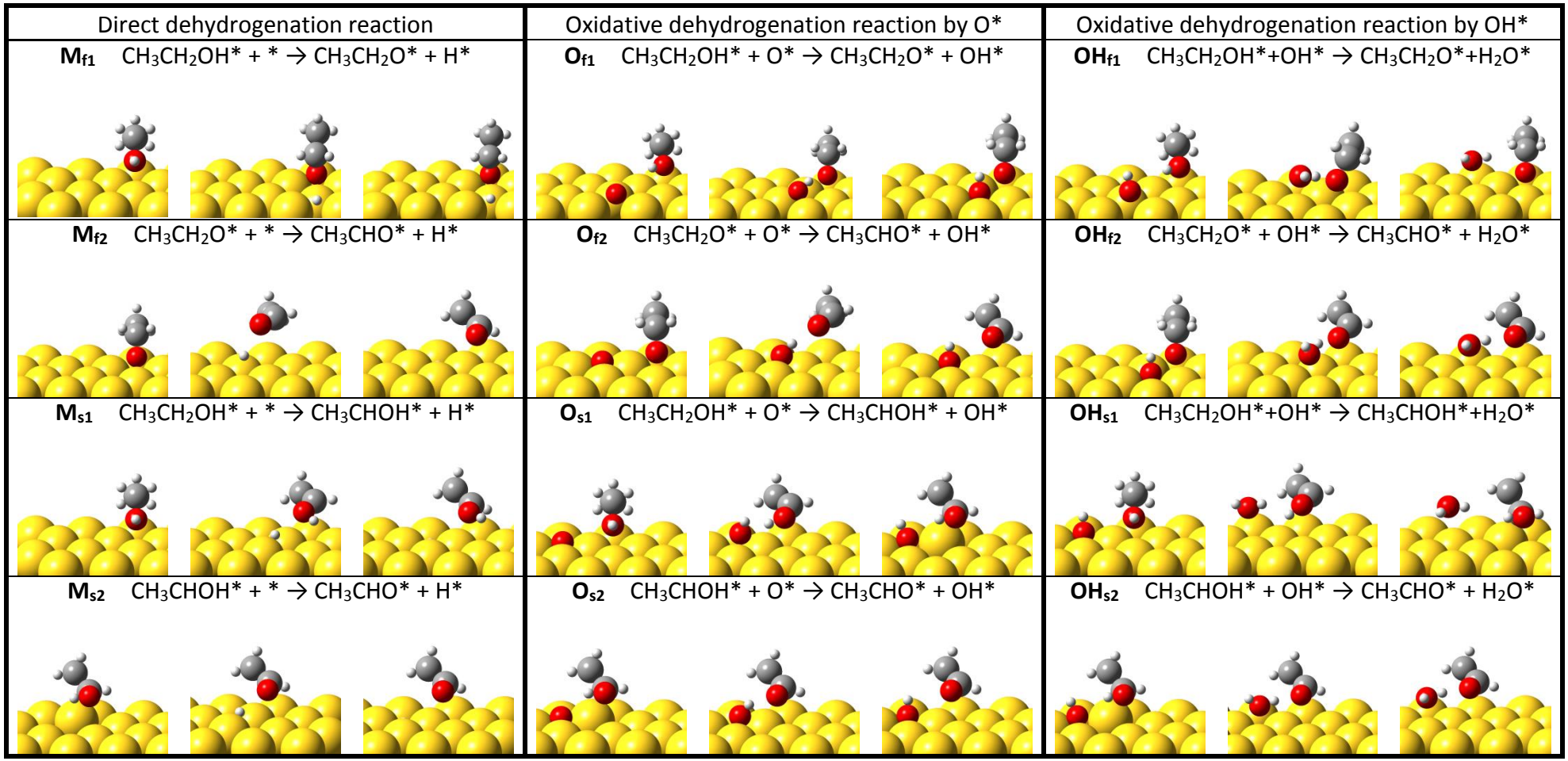

Fig. S2 Side views of optimized structures of the local minimums and transition states for the four steps in the direct dehydrogenation reaction and oxidative dehydrogenation reactions by O* and OH* on Au(111). Yellow, grey, red and white spheres are represented as Au, C, O and H atoms, respectively. The corresponded top views are shown in Fig. 2.

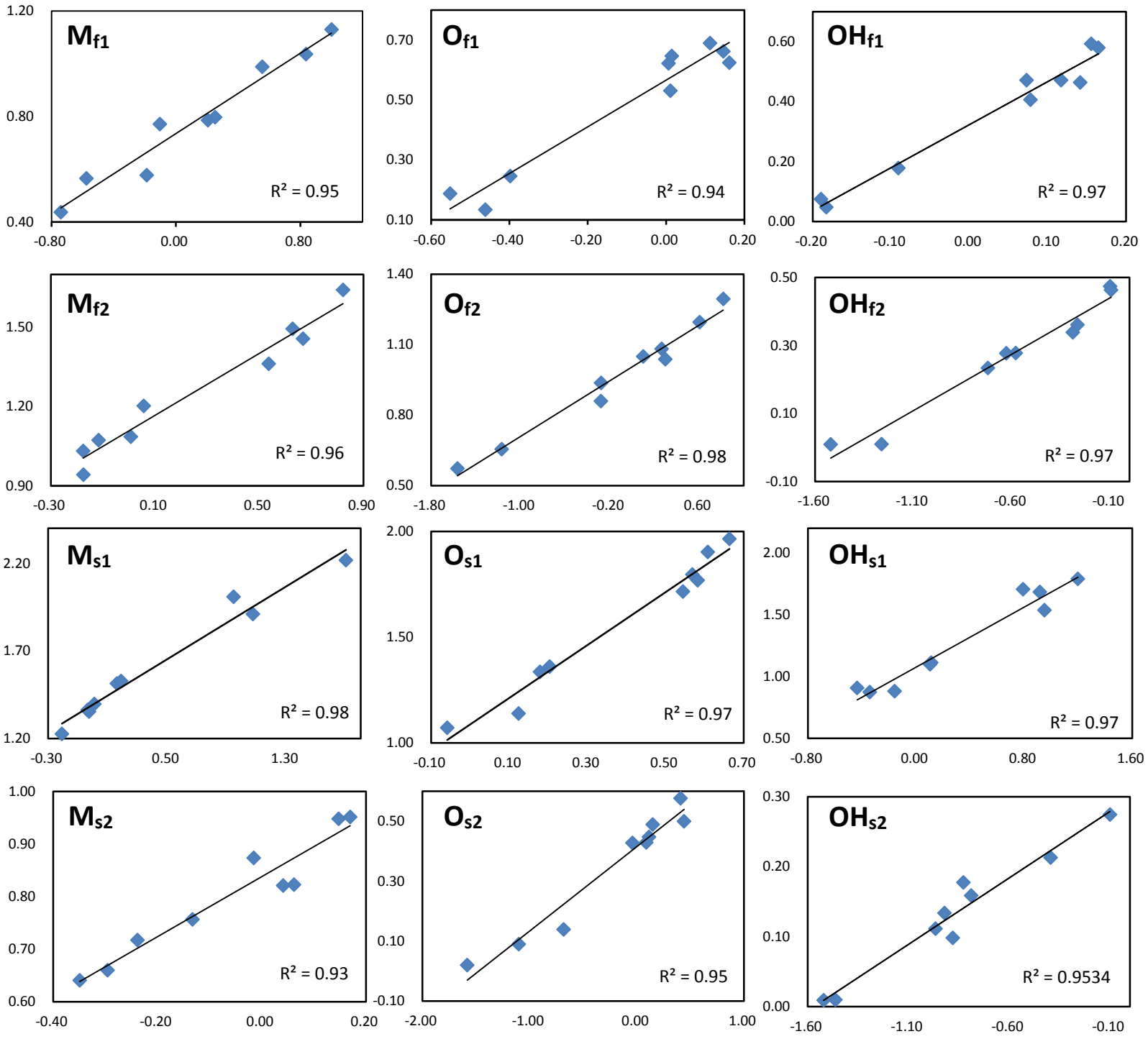

Fig. S3 Plots of activation energy (*Ea*) against reaction energy (*ΔE*) in the BEP relation for the 12 elementary steps in listed Table 2 on the TM surfaces

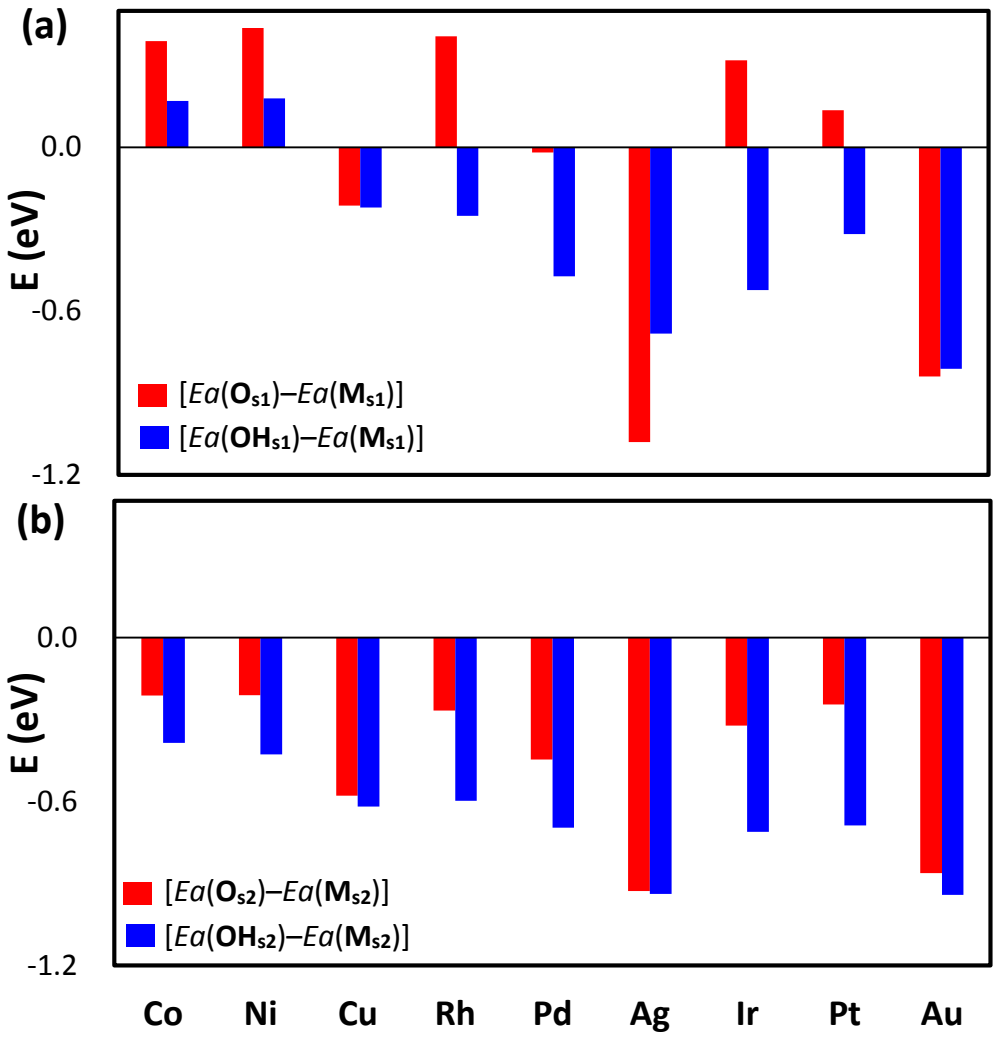

Fig. S4 (a) *Ea* differences between the oxidative and direct dehydrogenation reactions for **s1**, [*Ea*(**O**$_{s1}$)–*Ea*(**M**$_{s1}$)] and [*Ea*(**OH**$_{s1}$)–*Ea*(**M**$_{s1}$)] in red and blue bars, respectively. (b) *Ea* differences between the oxidative and direct dehydrogenation reactions for **s2**, [*Ea*(**O**$_{s2}$)–*Ea*(**M**$_{s2}$)] and [*Ea*(**OH**$_{s2}$)–*Ea*(**M**$_{s2}$)] in red and blue bars, respectively.

Table S1. ΔE differences between the oxidative and direct dehydrogenation reactions for **f1**, [ΔE(**O**$_{\mathbf{f1}}$)– ΔE(**M**$_{\mathbf{f1}}$)], and **f2**, [ΔE(**O**$_{\mathbf{f2}}$)– ΔE(**M**$_{\mathbf{f2}}$)], on the (111), (100), (110) and (211) surfaces of coinage metals.

	[ΔE(**O**$_{\mathbf{f1}}$)– ΔE(**M**$_{\mathbf{f1}}$)]	[ΔE(**O**$_{\mathbf{f2}}$)– ΔE(**M**$_{\mathbf{f2}}$)]
Cu(111)	-0.45	-0.72
Cu(100)	-0.37	-0.54
Cu(110)	-0.30	-0.68
Cu(211)	-0.83	-0.85
Ag(111)	-1.30	-1.84
Ag(100)	-1.26	-1.74
Ag(110)	-1.22	-1.75
Ag(211)	-1.57	-1.91
Au(111)	-1.40	-1.62
Au(100)	-1.40	-1.58
Au(110)	-1.79	-1.56
Au(211)	-2.05	-1.90

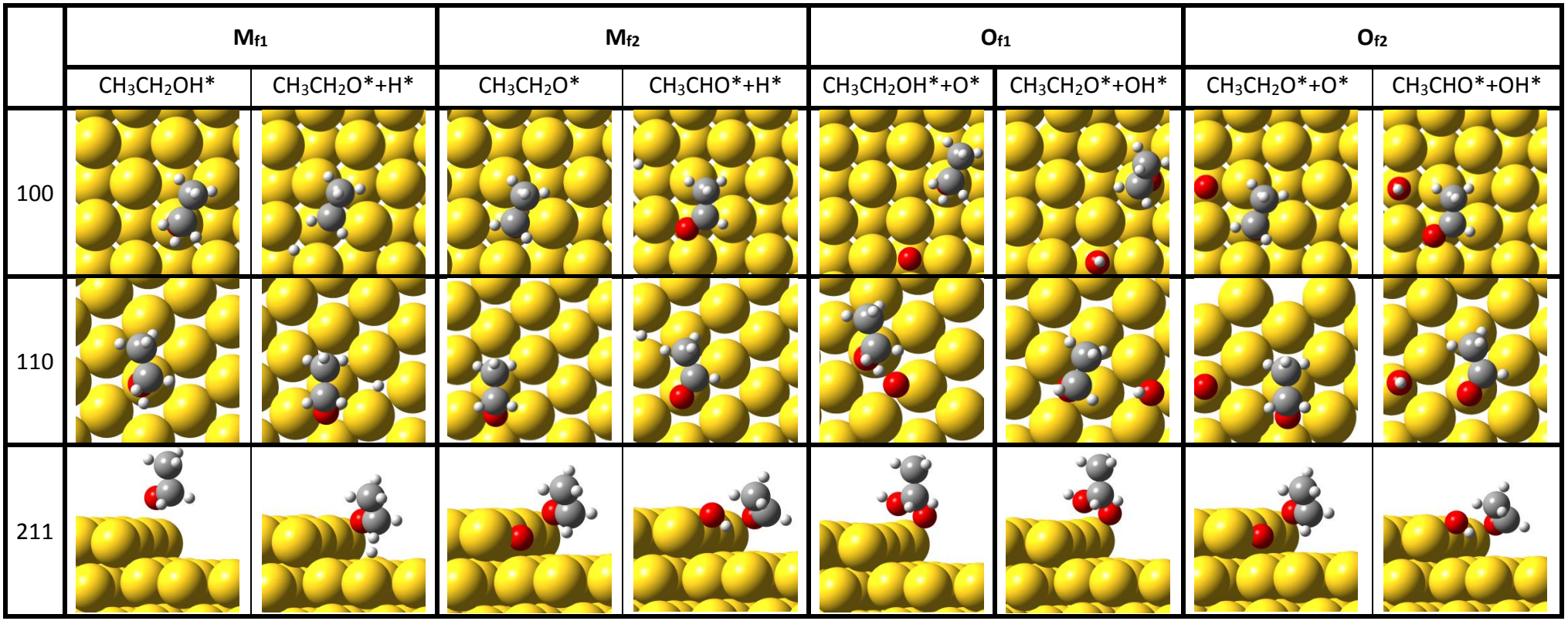

Fig. S5 Optimized structures of the reactants and products in the direct dehydrogenation reaction (**M_{f1}** and **M_{f2}** steps) and oxidative dehydrogenation reaction by O* (**O_{f1}** and **O_{f2}** steps) on Au(111). The corresponded reaction energies (ΔE) are listed in Table S1. Yellow, grey, red and white spheres are represented as Au, C, O and H atoms, respectively.

Table S2. Adsorbate Effect, the Energetic Differences between the Two Adspecies Separating Infinitely and Co-adsorbing on the TM surfaces, in **Mx**, **Ox** and **OHx** steps.

	Co	Ni	Cu	Rh	Pd	Ag	Ir	Pt	Au
$E_{ads}(CH_3CH_2O^*) + E_{ads}(H^*) - E_{ads}(CH_3CH_2O^*+H^*)$	-0.07	-0.04	-0.01	-0.04	-0.06	-0.02	-0.08	-0.11	-0.09
$E_{ads}(CH_3CHO^*) + E_{ads}(H^*) - E_{ads}(CH_3CHO^*+H^*)$	-0.10	-0.13	-0.02	-0.07	-0.12	-0.03	-0.12	-0.12	-0.06
$E_{ads}(CH_3CHOH^*) + E_{ads}(H^*) - E_{ads}(CH_3CHOH^*+H^*)$	-0.07	-0.08	-0.07	-0.05	-0.07	-0.07	-0.06	-0.05	0.00
$E_{ads}(CH_3CH_2OH^*) + E_{ads}(O^*) - E_{ads}(CH_3CH_2OH^*+O^*)$	-0.09	-0.05	-0.04	-0.09	-0.14	0.08	-0.07	-0.15	0.06
$E_{ads}(CH_3CH_2O^*) + E_{ads}(OH^*) - E_{ads}(CH_3CH_2O^*+OH^*)$	-0.14	-0.13	-0.08	-0.15	-0.15	-0.08	-0.14	-0.18	-0.07
$E_{ads}(CH_3CH_2O^*) + E_{ads}(O^*) - E_{ads}(CH_3CH_2O^*+O^*)$	-0.14	-0.15	-0.14	-0.13	-0.18	-0.18	-0.02	-0.15	-0.20
$E_{ads}(CH_3CHO^*) + E_{ads}(OH^*) - E_{ads}(CH_3CHO^*+OH^*)$	-0.15	-0.19	-0.06	-0.17	-0.18	-0.02	-0.18	-0.16	0.02
$E_{ads}(CH_3CHOH^*) + E_{ads}(OH^*) - E_{ads}(CH_3CHOH^*+OH^*)$	-0.10	-0.10	-0.04	-0.18	-0.14	0.02	-0.20	-0.16	0.03
$E_{ads}(CH_3CHOH^*) + E_{ads}(O^*) - E_{ads}(CH_3CHOH^*+O^*)$	-0.06	-0.06	0.00	-0.07	-0.13	0.12	-0.05	-0.17	0.11
$E_{ads}(CH_3CH_2OH^*) + E_{ads}(OH^*) - E_{ads}(CH_3CH_2OH^*+OH^*)$	-0.15	-0.18	-0.12	-0.11	-0.07	-0.02	-0.10	0.09	-0.02
$E_{ads}(CH_3CH_2O^*) + E_{ads}(H_2O^*) - E_{ads}(CH_3CH_2O^*+H_2O^*)$	-0.17	-0.20	-0.09	-0.10	-0.07	-0.03	-0.06	-0.12	-0.03
$E_{ads}(CH_3CHOH^*) + E_{ads}(H_2O^*) - E_{ads}(CH_3CHOH^*+H_2O^*)$	-0.18	-0.15	-0.10	-0.11	-0.14	-0.04	-0.17	-0.13	-0.03
$E_{ads}(CH_3CHO^*) + E_{ads}(H_2O^*) - E_{ads}(CH_3CHO^*+H_2O^*)$	0.05	0.06	0.10	0.11	0.02	0.17	0.14	0.10	0.15

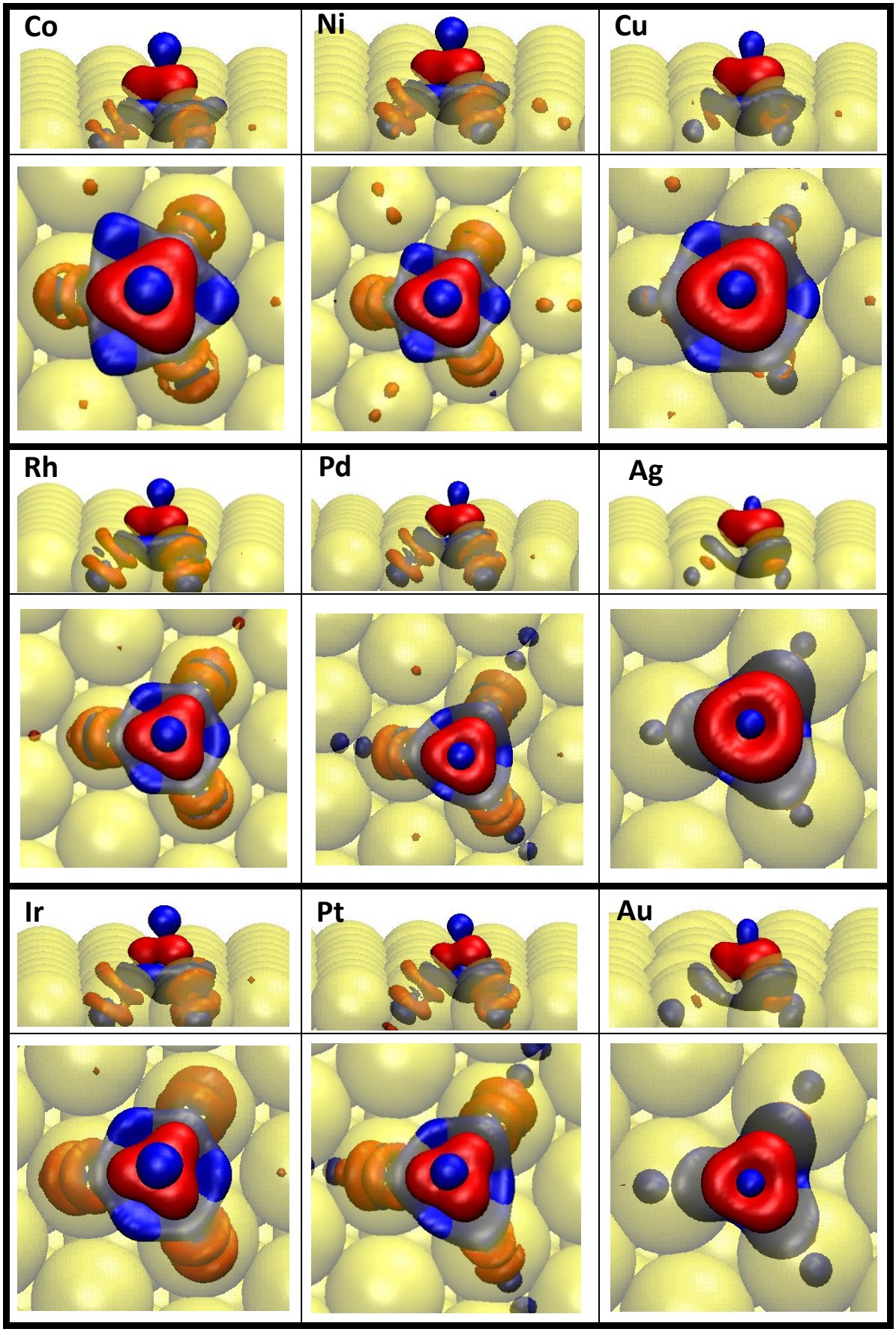

Fig. S6 Induced charge rearrangement of OH* on the TM surfaces in side and top views. Red and blue isosurfaces indicate depletion and addition of 0.03|e|/Å ^{3}, respectively, referenced to the separated systems. TM atoms are marked in transparent yellow sphere.