Electronic Supplementary Information

Carboxylic Acid Formation by Hydroxyl Insertion into Acyl Moieties on Late Transition Metals

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Table S1. Adsorption energies E_{ads}(X) of various adsorbates X (kJ mol^{-1}).

		OH	Acetyl	Propionyl	Acetic acid	Propionic acid
3*d*	Fe	–380.1	–269.0		–46.1	
	Co	–326.6	–188.5		–35.0	
	Ni	–306.7	–197.7		–38.3	
	Cu	–287.5	–122.1		–18.8	
4*d*	Ru	–322.0	–230.7	–229.1	–56.0	–50.8
	Rh	–278.0	–233.0		–47.0	
	Pd	–238.5	–209.9	–204.8	–38.7	–38.4
	Ag	–238.9	–79.2		–13.9	
5*d*	Os	–302.3	–242.7		–56.6	
	Ir	–258.6	–242.0		–46.4	
	Pt	–225.0	–225.4	–224.2	–38.8	–37.8
	Au	–173.7	–117.0		–10.7	

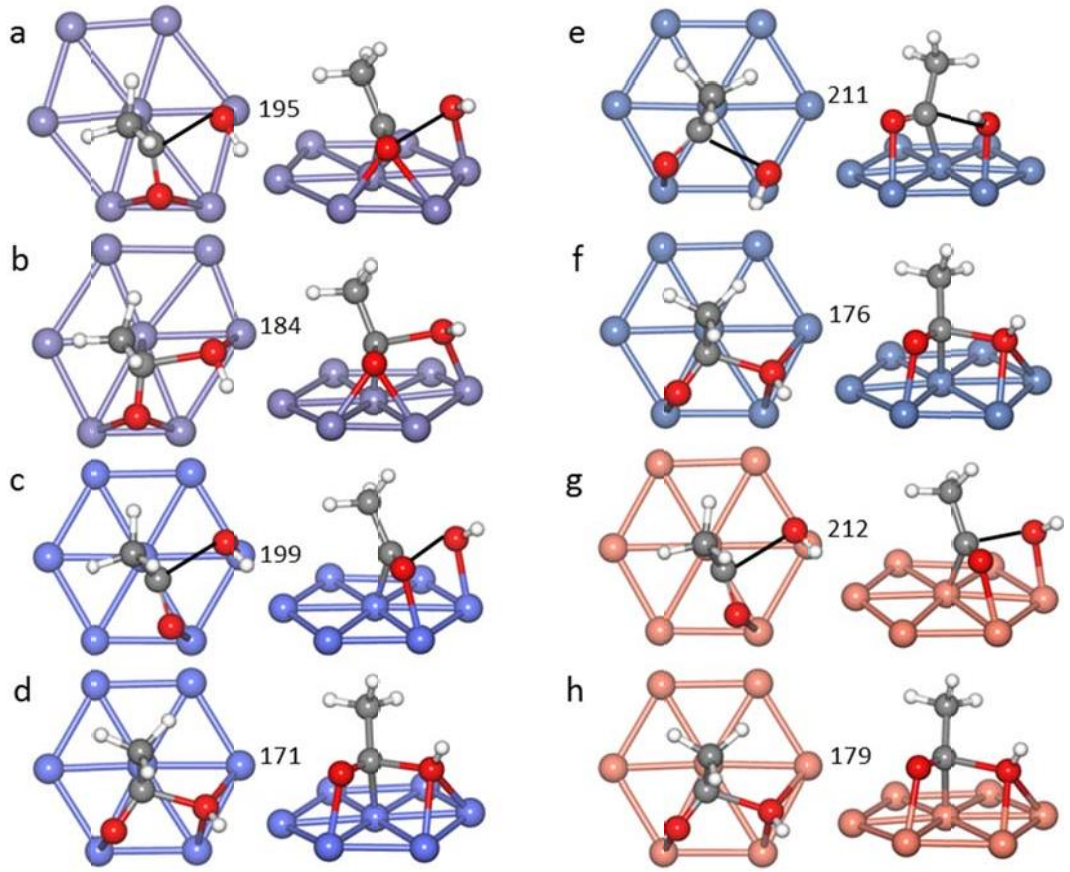

Figure S1. Sketches of the TS geometries of the OH insertion into an adsorbed acyl moiety on various metal surfaces (top and side views). C_1-O_2 distances in pm. a –acetyl/Fe; b – acetyl/Co top; c – acetyl/Co bridge; d – acetyl/Ni bridge; e –acetyl/Cu top; f – acetyl/Cu bridge.

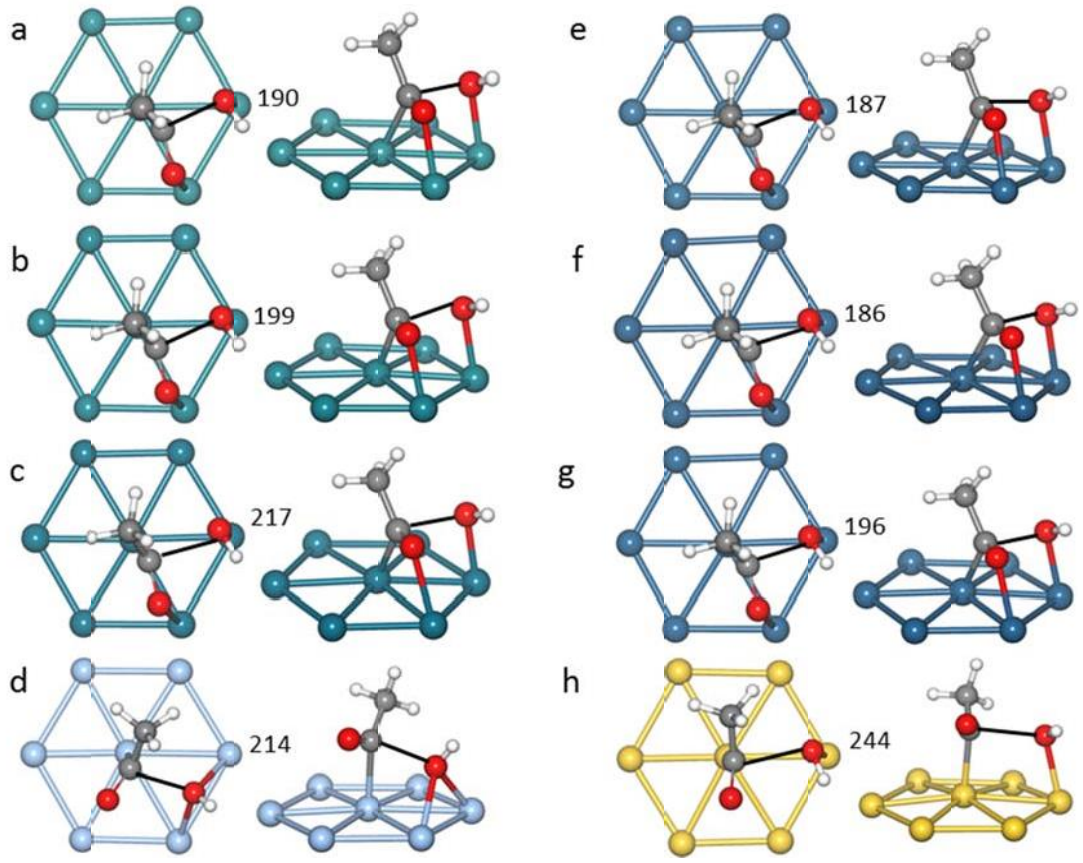

Figure S2. Sketches of the TS geometries of the OH insertion into an adsorbed acyl moiety on various metal surfaces (top and side views). C_1-O_2 distances in pm. a –acetyl/Ru; b – acetyl/Rh; c – acetyl/Pd; d – acetyl/Ag; e – acetyl/Os; f – acetyl/Ir; g – acetyl/Pt; h – acetyl/Au.

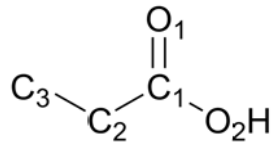

Figure S3. Atom labels for an acid, for the example of propanoic acid.

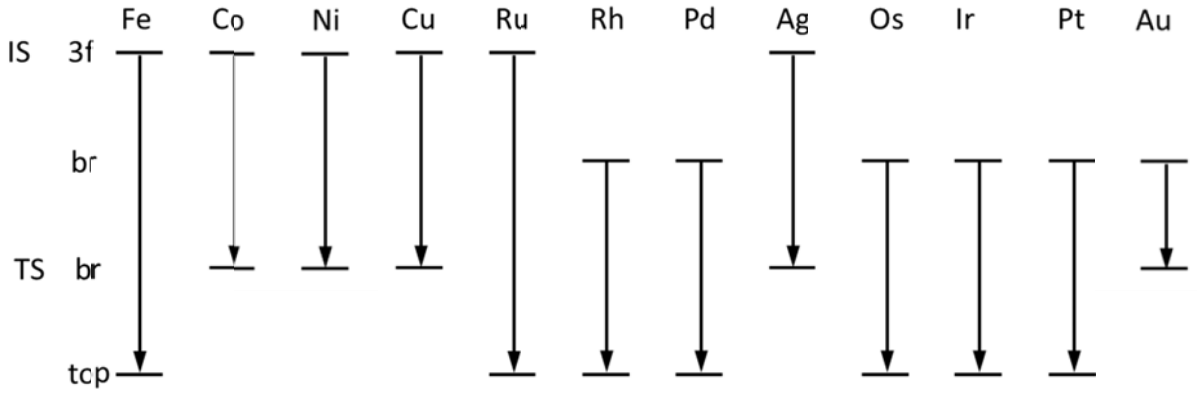

Figure S4. Overview of the change of adsorption site of the OH group in the IS and TS structures on the metals studied. 3f – hollow site, br – bridge site, top – top site.

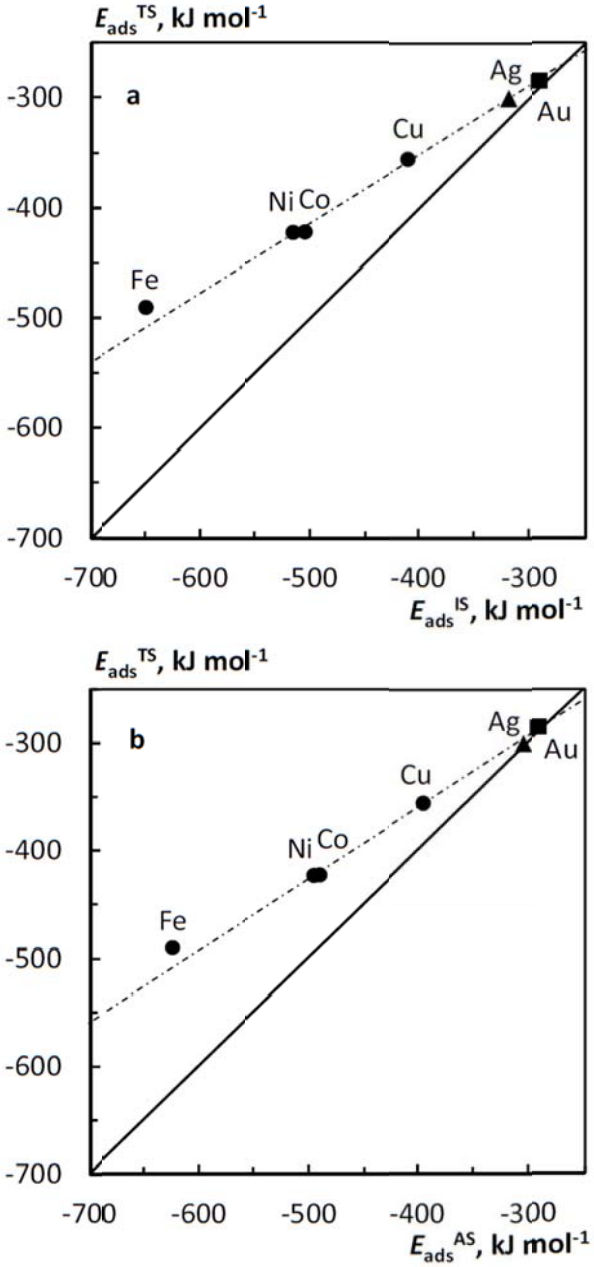

Figure S5. (a) BEP relation of the adsorption energies, E_{ads}^{IS}, of the initial states vs. the corresponding adsorption energies, E_{ads}^{TS}, of the bridge TSs. The regression line (dashed) from a least-squares fit, excluding Fe, reads: $E_{ads}^{TS} = 0.63 \times E_{ads}^{IS} - 119.1$ (kJ mol^{-1}), R^2 = 0.98. (b) Similar BEP relation, but plotted against the adsorption energy, E_{ads}^{AS}, of the activated precursor states. Regression line (dashed, excluding Fe): $E_{ads}^{TS} = 0.67 \times E_{ads}^{AS} - 94.0$ (kJ mol^{-1}), $R^2 = 1.00$. In this case, mean absolue error MAE = 4 kJ mol^{-1}.

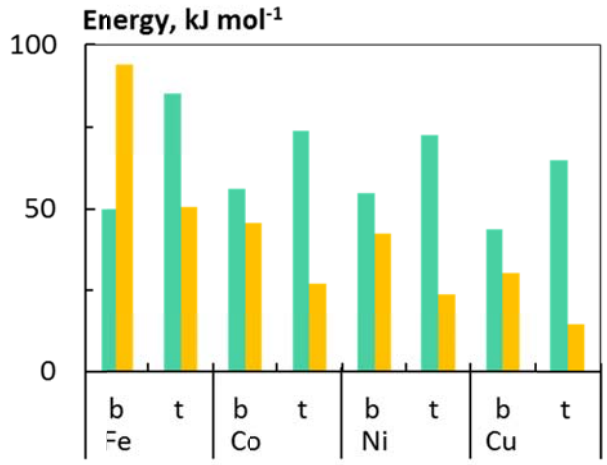

Figure S6. Preparation energies of OH, E_{prp}(OH) (green), and acetyl, E_{prp}(RCO) (yellow), of bridge (b) and top (t) TSs on 3*d* metals.

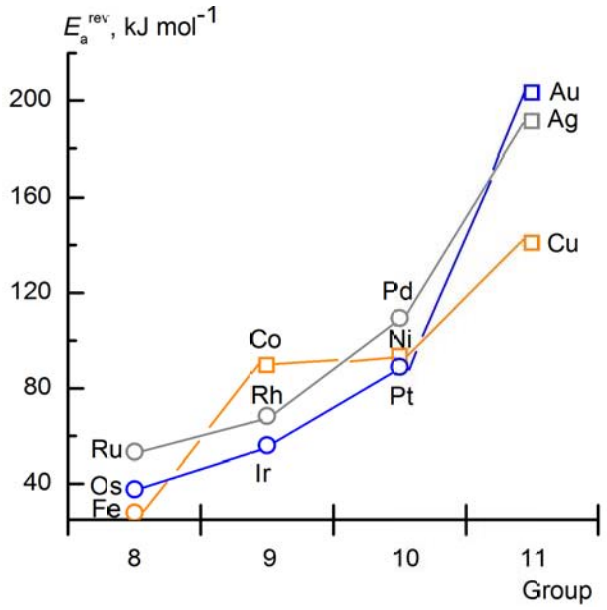

Figure S7. Activation energies E_a^{rev} of the backward reaction, i.e., C-OH dissociation, for the metals under study. Circles and squares denote top and bridge TS structures, respectively. The lines are a guide for the eye.