Supporting Information

Identity of the Most and Least Active Sites for Activation of the Pathways for CO₂ Formation from the Electro-oxidation of Methanol and Ethanol on Platinum

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1. Partial CO Stripping

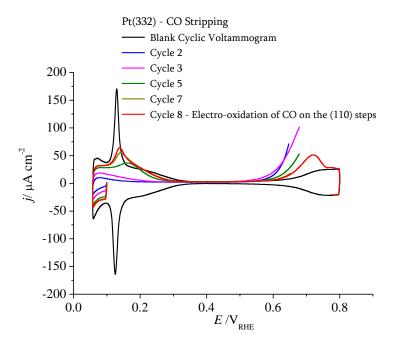


Figure SI 1. Successive voltammograms recorded at $0.05~V~s^{-1}$ during the electro-oxidation of a CO adlayer on Pt(332) in $0.1~M~HClO_4$.

2. Reactivity of Stepped Pt Surfaces Toward Electro-oxidation of Alcohols as Monitored by Cyclic Voltammetry

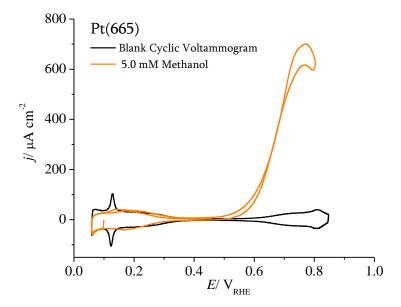


Figure SI 2. Electro-oxidation of 5.0 mM methanol on Pt(665) in the presence of 0.1 M HClO₄. Data recorded at 0.05 V s^{-1} .

3. Electro-oxidation of Alcohols on Stepped Pt Single Crystal Surfaces with the (110) Steps Marked with ¹³CO_{ads} as Monitored by *in situ* FTIR Spectroscopy

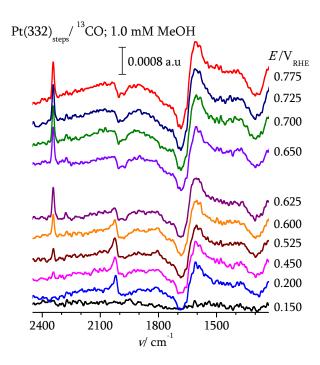


Figure SI 3. Spectra for the electro-oxidation of methanol (1.0 mM) on a Pt(332) stepped surface with the (110) steps previously and selectively decorated with $^{13}CO_{ads}$. The series of spectra (200 interferograms at resolution of 8 cm $^{-1}$) was acquired from 0.050 to 0.800 V_{RHE}, in intervals of 25 mV (only some selected spectra are shown). The reference spectrum was acquired at 0.100 V_{RHE}.