Supporting Information—

Designing for Selectivity: Weak interactions and the competition for reactive sites on gold catalysts

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Methanol Oxidation:

Methanol oxidation on O/Au(111) and its reaction mechanism has been studied previously in ultra high vacuum and is well understood.[1] As a point of both calibration and comparison to the ethanol and trifluoroethanol oxidations, we address it in our current work. This data for methanol oxidation on 0.1 ML O/Au(111) (Fig S1) was collected in close proximity to the data for both ethanol and trifluoroethanol, ensuring as similar of experimental conditions as possible. Of note for this work are the lower temperature of CO_2 production from formate in comparison to CO_2 from acetate or trifluoroacetate, as well as the low temperature of formaldehyde formation, which must be present in order to form methylformate. Also note the small excess oxygen peak in m/z=32 just over 500 K.

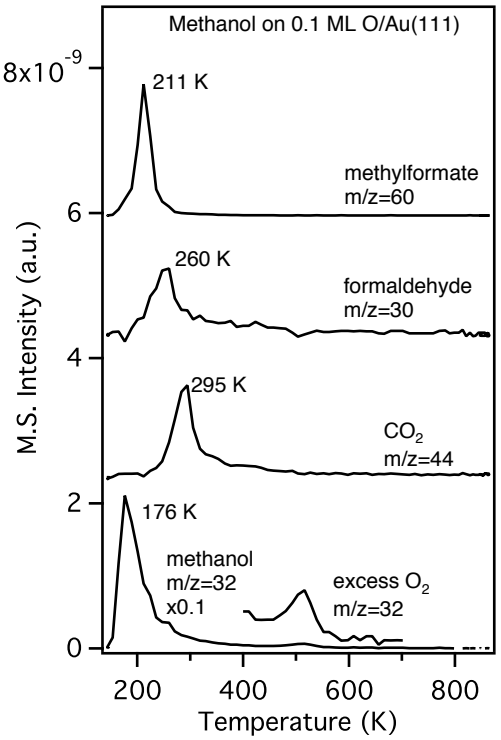

Figure S1: Oxidation of methanol on 0.1 ML O/ Au(111). The methanol was dosed in excess at 120 K, and the heating rate was 5 K/s. The m/z traces have been corrected for fragmentation and ionization cross-section, and then the multiplication factor was applied so that all products could be seen.

Additional experimental details:

Temperature programmed reaction spectroscopy (TPRS), which has been described in detail elsewhere,[2] was done in an ultra high vacuum chamber with a base pressure of ~ $2x10^{-10}$ torr using a triple filter Hiden quadrupole mass spectrometer (HAL-Hiden/3F). The heating rate in all experiments was 5 K/s. To prevent electron-stimulated reactions from taking place due to the mass spectrometer filament, a bias of -100 V was applied to the sample during TPRS experiments. The gold (111) single crystal was cleaned by argon ion sputtering and annealing to 900 K, followed by multiple oxidation cycles using ozone until no CO_2 desorbed from the surface. Ozone was generated using a commercial ozone source (LG-7 CD Laboratory Ozone Generator).

Approximately 15 g/Nm^3 ozone in oxygen was constantly flowed through a gas line from which the ozone was dosed, creating adsorbed atomic oxygen on the surface. Each day, the ozone dose was calibrated using a reference saturation coverage of 1.1 ML. Alcohols were dosed using a direct doser and doses were always done in excess to ensure equilibrium on the surface.

To identify the products in each case, a rigorous method of quantitative TPRS was applied, which accounts for the mass fragments of all the species.[3] The product identities were deciphered using fragmentation patterns from neat samples or the NIST database when neat samples were unavailable. To calculate the yield for each product, the ionization cross section, quadrupole transmission and detection coefficients, and fragmentation patterns were taken into account. The ionization cross sections for the fluorinated compounds were not known, but were estimated using an additive model of 0.35 Å^2 per fluorine atom substitution. This number was calculated using average experimental values at 70 eV from Bart et al.[4] Other literature sources have varying values, as low at 0.1 Å^2 per fluorine.[5-7] However, these were usually for the maximum total ionization cross section, which occurs at a different eV for the fluorinated compounds vs. the perhydrido compounds. Therefore, in this case the experimental values were given preference. This results in a conservative calculation of the amount of fluorinated compounds, as to not over-estimate the selectivity of the cross-coupling reactions. Changing the ionization cross section calculation to use 0.1 Å^2 per fluorine does not dramatically change the results. The original ionization cross sections for the alcohols, aldehydes, and esters were calculated using the method from Hudson et al.[8]

Calculation details:

A quantitative measurement for the relative stability of alkoxides on the surface was obtained by measuring the equilibrium constant between pairs of alkoxides and an ambient phase of known composition. In order to do this, a mixture of two alcohols of known composition was dosed on oxygen-covered gold at a low oxygen coverage such that all the oxygen was consumed and excess alcohol remained; it was assumed that equilibrium was reached on the surface, according to Scheme 1. Then the surface was heated, and the species leaving the surface were measured by quantitative temperature programmed reaction spectroscopy. Molecularly adsorbed species desorb intact, and each alkoxy species were identified and quantified on the basis of their well-known product distributions and temperatures. The selectivities and equilibrium constants were then computed over a range of ambient compositions, using the same method as previous work. [3] The selectivities are calculated on a per-alcohol basis.

CO_2 to alcohol calculation using acetate data was deemed unneccesary and complicating. One could argue that a CO_2 should equal 0.5 alcohol, and one could also argue that a CO_2 should be 1.61 alcohol, given experimental data that 62% of the carbons from an acetate molecule become CO_2, as seen previously.[9] This would then imply that the number of CO_2's should be multiplied by 1.61 to give how many alcohols were transformed into CO_2. However, it is not clear whether the CF_3 acetate will have the same combustion product distribution, and if it is quite different, then one CO_2 could be as little as 0.5 of an acetate, the rest becoming CF_3 or other products. Therefore, we chose to leave the approximation of 1 CO_2= 1 alcohol for our selectivity calculations. When changing it one way or the other, only minor changes in selectivity and equilibrium constant were observed.

The error in the measurements can be introduced several ways, including calculations of the fragmentation correction, estimation of the ionization cross section, and deconvolution of various fragments. As stated in the main text, at most, we estimate error bars of 2.9±1 and 0.38±0.1. We arrived at this estimate by using different values for ionization cross-section and fragmentation correction and comparing them. To minimize error, deconvolution of fragments was done by hand.

References:

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