Catalyst Design: Scaling from UHV Models to Operating Conditions

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Studies of oxygen-assisted coupling of methanol on single crystal gold were used to reveal the catalytic cycle responsible for the oxygen-assisted coupling of alcohols to form their corresponding ester. This reaction is initiated by adsorbed oxygen atoms - so-called “active” oxygen. These model studies correctly predict the patterns of reactivity observed under catalytic conditions over nanoporous gold catalysts at 1 atm and 100-150 °C. To understand more precisely the connection between the UHV studies and the reactor performance, fast, metered, pressure pulses of methanol were passed over a small amount of the catalyst at 100-150 °C (TAP reactor) over a wide range of prescribed oxygen coverages, and the transient responses of the products utilized to determine the product selectivity. The dependence of the selectivity on oxygen coverage and temperature were assessed using rate constants obtained from the studies in UHV in combination with theoretical computations. Regression of the transient response information using the mechanism obtained from UHV reproduced the selectivity patterns precisely with modest adjustments to the rate constants. Differences in selectivity with respect to steady flow reactor results at 1 atm and 150 °C were observed, however. These differences were explained entirely by a pressure effect, the origin of which is the variation in the surface concentration of adsorbed methoxy due to the kinetics of the elementary steps of the mechanism. When adjusted from the TAP conditions to 1 atm pressure, the mechanistic analysis accounts for the reactor performance exactly. The relationship between these kinetic studies and the mechanistic determinations from the model studies will be discussed.

Figure 1. Selectivity contours for increasing reactant pressure (methanol) at varying active oxygen coverage on npAu catalysts from mechanistic analysis and fundamental rate constants

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