Near-Surface Imaging of Multicomponent Gas Phase above a Catalyst Surface During Methanol Oxidation

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In catalysis science, *operando* experiments are essential to generate fundamental knowledge for practical catalysis conditions. We have built an optically accessible catalytic flow reactor for *operando* measurements using *in situ* optical probes, and *ex situ* mass spectrometry probes that enable detection of free radicals and reactive intermediates. We have applied these diagnostics to partial oxidation of methanol (CH_3OH) catalyzed by polycrystalline Ag and methanol conversion over Pd-based catalysts in collaboration with researchers at UC Davis. We demonstrate gas-phase measurements of major and minor species above the Ag catalyst using 1-D Raman scattering, laser-induced fluorescence (LIF) imaging of formaldehyde (CH_2O), and universal species mapping with molecular beam mass spectrometry. Imaging of CH_2O shows growth of a steady boundary layer as the flow of CH_3OH and O_2 in N_2 progresses over the Ag surface. As CH_3OH is oxidized, the resulting CH_2O diffuses into the boundary layer. LIF imaging reveals variations in product distributions and provides a measure of catalytic activity as a function of reactant mixture, catalyst temperature, and localized deactivation. Raman scattering measurements provide maps of temperature and composition. Mass spectrometry detects species sampled by a quartz nozzle with a 50μm orifice diameter. Near-surface molecular beam mass spectrometry enables simultaneous detection of all species using a gas sampling probe. Detection of gas-phase free radicals, such as CH_3 and CH_3O, and of minor products, such as acetaldehyde, dimethyl ether, and methyl formate provides insights into catalytic mechanisms of methanol oxidation. In particular, we detected methoxymethanol (CH_3OCH_2OH) over Pd-based catalysts, which is a rarely observed and reactive C_2 oxygenate that has been proposed to be a critical intermediate in methyl formate production. The combination of these optical and mass spectrometry techniques provides a detailed picture of the coupling between the gas phase and surface in heterogeneous catalysis.