Evolution of steady-state material properties during catalysis: oxidative coupling of methanol over nanoporous $Ag_{0.03}Au_{0.97}$

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Activating pretreatments can tune both the surface composition and structure of bimetallic-alloy catalysts. The activation-induced changes in material properties of a nanoporous $Ag_{0.03}Au_{0.97}$ alloy and subsequent evolution under steady-state conditions for CH_3OH oxidation are presented [1]. Initial activation in O_3 forms AgO and Au_2O_3, driving a strong Ag enrichment in the near-surface region, based on AP-XPS and EXAFS analysis. Exposing this oxidized nanoporous $Ag_{0.03}Au_{0.97}$ to an O_2/CH_3OH mixture reduces both the Ag and Au oxides and results in a highly Ag-enriched surface alloy. Both the oxides and the reduced, highly Ag-enriched alloy fully oxidize methanol to CO_2. However, at the reaction temperature (423 K), Ag slowly realloys with Au. Although decreasing, Ag remains enriched (29 at.%) in the top few nanometers under steady-state conditions, and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO were observed with environmental TEM, leading locally to Ag-rich alloys after reduction—critical for O_2 dissociation. DFT calculations indicate that the O on the surface assists in stabilizing the Ag. Moreover, the modest reaction temperature (423 K) is crucial for a stable performance. At higher temperatures, bulk diffusion induces sintering and Ag redistribution, leading to a loss of activity. Material properties determining catalytic activity are dynamic and metastable (kinetically trapped). Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

[1] Zugic, Van Spronsen, Heine, Montemore, Li, Zakharov, Karakalos, Lechner, Crumlin, Biener, Frenkel, Biener, Stach, Salmeron, Kaxiras, Madix, and Friend, *J. Catal.*, **380**, 366–374 (2019)