Adsorption-Driven Surface Segregation of the Less Reactive Alloy Component

Counterintuitive to expectations and all prior observations of adsorbate-induced surface segregation of the more reactive alloy component (the one forming the stronger bond with the adsorbate), we show that CO adsorption at elevated pressures and temperatures pulls the less reactive Cu to the surface of a CuPt near-surface alloy. The Cu surface segregation is driven by the formation of a stable self-organized CO/CuPt surface alloy structure and is rationalized in terms of the radically stronger Pt–CO bond when Cu is present in the first surface layer of Pt. The results, which are expected to apply to a range of coinage (Cu, Ag)/Pt-group bimetallic surface alloys, open up new possibilities in selective and dynamical engineering of alloy surfaces for catalysis.

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