Towards synthetic fuels via electrocatalysis - DTU Orbit (04/10/2019)

Towards synthetic fuels via electrocatalysis: Electrochemical CO2 Reduction

The storage of electricity in chemical bonds in form of fuels is a promising route for leveling the intermittent production of renewable energy. The present PhD thesis is concerned with the electrocatalysis of CO2 reduction in aqueous media at ambient conditions, as an alternative process to Fischer-Tropsch fuel synthesis.

The thesis encompasses electrochemical CO2 and CO reduction on pure metals consisting of polycrystalline copper and gold, as well as the bimetallic catalysts consisting of copper overlayers on platinum single crystals and bulk and surface alloys of gold-cadmium.

By roughening the surface of polycrystalline copper in a low buffer capacity electrolyte, we favoured the selectivity towards ethylene rather than methane production. We show trends between the selectivity towards CO, CH4 and C2H4.

By depositing monolayers of copper onto platinum single crystals, we tuned the reactivity of copper by modifying the tensile strain. However, the overlayers appeared to be unstable under reaction conditions, due to the strong interaction of CO with platinum.

We investigate the reduction of CO2 to CO on polycrystalline Au in neutral media. On the basis of our observations, we propose that the coverage of the adsorbed *CO under reaction conditions is significant. This suggests the existence of two types of adsorbed *CO, whereby the weakly bound *CO could be the reactive intermediate for CO evolution. We also carried out the reduction of CO on roughened Au in alkaline media, which yielded trace amounts of formaldehyde and methanol. The observation that adsorbed, strongly bound *CO is not reduced further, suggests the existence of additional kinetic barriers.

Guided by the theoretical models, we followed a strategy of alloying to break the existing scaling relations between the key CO2 reduction intermediates. Density functional theory calculations suggested Au3Cd should possess respectable stability, and higher catalytic activity than Au for CO evolution and CH3OH. However, extensive CO2 electrolysis measurements on gold-cadmium bulk and surface alloy exhibited lower activities for CO evolution, relative to Au. Despite the promising predictions about low overpotentials based on DFT calculations, CO electrolysis in alkaline media on cadmium alloyed gold surfaces revealed negligible activity for CO reduction. We hypothesise that adsorbate induced rearrangements of the surface take place, possibly involving segregation of elements and thus loss of active sites, analogous the copper-platinum system. The most likely candidates for these adsorbates are *CO and *H under reaction conditions and possibly *OH and *OCHO* at more positive potentials. Similar to Au, trace amounts of methanol and formaldehyde were observed as products of CO reduction. Our results point towards the need to design a catalyst surface that is stable under reaction conditions, where reactive intermediates cannot restructure the active sites.

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