

Density Functional Theory and Experimental Surface Science as Complementary Methods for Interfacial-Structure Elucidation and CO₂-Reduction Studies

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April 17, 2023



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DATE RECEIVED:
February 11, 2017

DOI:
10.15200/winn.148679.90448

ARCHIVED:
February 11, 2017

KEYWORDS:
DFT, Surface Science, Surface Structure, CO₂ Reduction, Adsorption

CITATION:
Alnald Javier, Density Functional Theory and Experimental Surface Science as Complementary Methods for Interfacial-Structure Elucidation and CO₂-Reduction Studies, *The Winnower* 4:e148679.90448, 2017, DOI: 10.15200/winn.148679.90448

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Surface science techniques such as scanning tunneling microscopy (STM), high-resolution electron energy loss spectroscopy (HREELS) and electrochemistry along with computational methods based on density functional theory (DFT) can be employed as complementary methods in determining the interfacial structure of molecules adsorbed on metal surfaces. As an example, the surface geometry, configuration and position of quinone-based, aromatic and simple molecules such as hydroquinone [1], hydroquinone sulfonate [2,3], benzene [4], 2,3-dimethylhydroquinone [5], sulfuric acid [6] and atomic hydrogen [7] adsorbed on bulk Pd and Pd thin-film surfaces have successfully been identified utilizing this technique. This scheme is extremely essential especially in ascertaining structure-composition-function relationships of surface-modified materials and in establishing methods for surface-structure elucidation for surface-reaction mechanistic studies. This approach is also important in studying self-assembled monolayers of species used for electrocatalysis, for instance, iron hydrogenase enzyme analogs immobilized on Au electrode surfaces used for the electrocatalysis of hydrogen gas formation [8-11] in an effort to discover better H₂-evolution catalysts.

Theory and experimental surface science may also be employed in CO₂-reduction studies particularly on the discovery and development of novel heterogeneous catalysts for the reduction of CO₂ to hydrocarbons, alcohols and other oxygenates that are used as fuels. The discovery of Au-on-W near-surface alloy [12] and NiGa alloy [13,14] as alternative CO₂-reduction electrocatalysts was achieved utilizing this approach.

Understanding the CO₂-reduction mechanism can provide clues as well on how the product yield and selectivity can be improved and should assist in the search for the ideal electrocatalyst. Hence, empirical investigations that aid in the elucidation of the mechanism of CO₂ reduction to methane, ethylene and ethanol on a Cu electrocatalyst surface were pursued as a supplementary approach to theory by reducing theoretically proposed reduction intermediates in a differential electrochemical mass spectrometry (DEMS) system and comparing the reduction product distribution [15-20].

Finally, a parallel implementation of electrochemical STM and DEMS was assembled to determine the *operando* surface structure of Cu responsible for the selectivity towards the formation of ethanol from CO₂ reduction [21-26]. It is therefore vital to obtain insights from theory to rationalize this behavior and consequently allow the prediction of the surface structure necessary to produce a certain product.

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