Abstract:

X-ray techniques play an important role for gaining the fundamental understanding needed to tailor novel catalysts for CO2 reduction reaction (CO2RR), by providing chemical and structural information of catalytic surfaces. We have utilized surface-sensitive soft X-ray techniques to investigate the interaction of metal catalytic surfaces with electrolytes and/or gases (H2O and/or CO2) under in situ/operando conditions at the Advanced Light Source (ALS). This poster reports our work on AP-XPS for studying (i) CO2 adsorption on Cu and Ag surfaces to understand the initial atomic level events for CO2 electrocatalysis on the metal catalysts, (ii) CO2 adsorption on Ag/Cu alloys to provide the basis for developing improved catalysts electrolyte/solid catalytic surfaces.

Introduction

The discovery of new electrocatalysts that can efficiently convert CO2 into fuels require a complete atomistic understanding of the adsorption and activation mechanisms. Despite numerous experimental and theoretical studies, there remain considerable uncertainties in understanding the role of catalyst surface structure and chemistry on the initial steps of CO2 reduction reaction (CO2RR) activity and selectivity. To provide this experimental information, we used Ambient Pressure X-ray photoelectron spectroscopy (APAXPS).

Team

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Outlook

- Developing and optimizing synchrotron X-ray methods for characterizing CO2RR reaction, together with the theory
- Comparison of the CO2 interaction with different metal surfaces, and understanding the effects in multi-metallic surfaces
- Utilizing the knowledge for designing multi-metallic catalysts for high product selectivity

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AP-XPS Studies on the Initial Stage of the CO2 Reduction Reaction on Metal Catalyst Surfaces

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Characterizing CO2 reduction reaction using synchrotron X-ray techniques

Catalytic mechanism

Adsorbed molecules: Structure Adsorbed sites

Probing the solid-gas interface

Ambient Pressure (AP)-XPS @ BL 9.3.2

Advanced Light Source

CO2 Adsorption on Cu Surfaces

The result provides insights on how COx adsorbates interact with different metal surfaces, and also provides a baseline knowledge of how to interpret the AP-XPS data for metal alloys.

CO2 Adsorption on Ag Surfaces

Adding H2O and CO2 then leads to O¼CO3−2, H3O+, and HCO3−/OH−.

Surface D promotes the formation of the surface adsorbate.

Surface oxygen coverage determined the surface adsorbates coverage.

Pre-surface oxygen coverage determined the surface adsorbates coverage.

CO2 Adsorption on AgCu Surfaces

Sublayer O goes to surface O without energy barrier on Ag, interacts with g CO2 to form a chemisorbed O¼CO3−2 species.

Sublayer O goes to surface O without energy barrier on Ag, interacts with g CO2 to form a chemisorbed O¼CO3−2 species.

Surface reconstruction induced by gas adsorption

Comparison of the CO2 Adsorption on Cu and Ag Surfaces

Comparison of the CO2 Adsorption on AgCu Surfaces

CO2 adsorption on AgCu mixture (Ag:Cu = 2.4 : 1 nm surface), 0.7:1:1 mixture (3.6 nm surface)

Surface reconstruction induced by gas adsorption

Cu content on the surface increases after the CO2 adsorption (transition of subsurface Cu surface Cu)

Adsorbates on AgCu have different geometrical and electrical structure, in comparison to the Cu or Ag surfaces.

The synergic effect between Ag and Cu initiates the evolution of bi-metallic surface under gas adsorption and further alters gas adsorption configurations.

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