L3.2 Establish understanding of the relationships between CO2RR electrocatalyst activity, selectivity, structure and composition using in situ and operando methods.

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

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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 CO_2 electroreduction 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 (APXPS)** .

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

Acknowledgments

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Results, Highlights, and Accomplishments

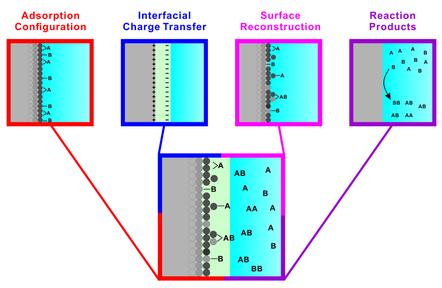
Characterizing CO2 reduction reaction using synchrotron X-ray techniques

Catalytic mechanism

Catalyst:
Surface distribution
Electronic structure

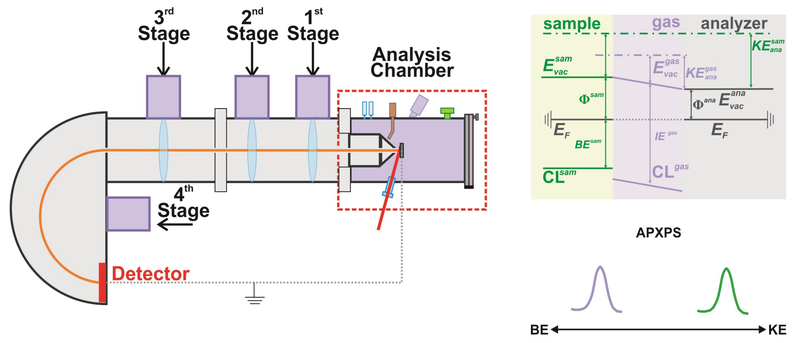
Adsorbed molecules:
Structure
Adsorbed sites

Probing the solid-gas interface!



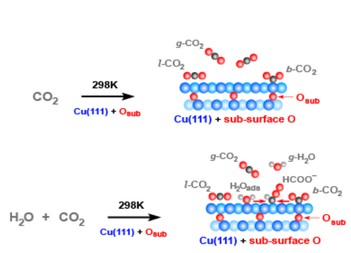
Ambient Pressure(AP)-XPS @ BL 9.3.2, Advanced Light Source

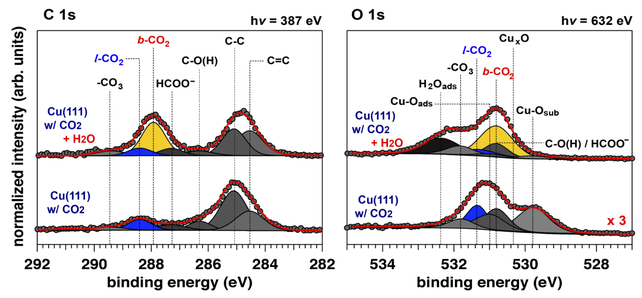
In situ/Operando AP-XPS at ALS



Soft X-rays is used for the AP-XPS studies of gas (CO2 and/or CO2+H2O)/catalyst interfaces.

CO2 Adsorption on Cu Surfaces





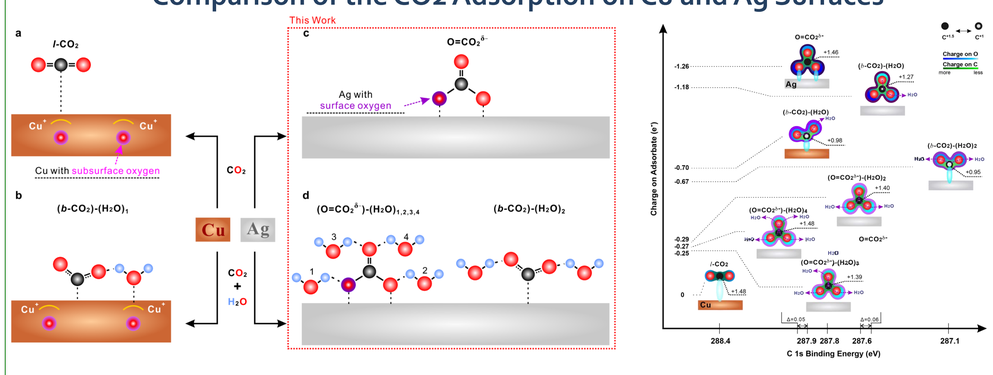
	Structure	Predicted δO_{ads} and δO_{sub}
DFT	¼ MLE O_{ads}	δO_{ads}=−2.2 eV
DFT	¼ MLE O_{sub}	δO_{sub}=−1.3 eV
DFT	¼ MLE O_{ads} + ¼ MLE O_{sub}	δO_{ads}=−0.3 eV; δO_{sub}=−1.5 eV
APXPS	0.06 MLE O_{ads} + 0.08 ML O_{sub}	δO_{ads}=−0.4 eV; δO_{sub}=−1.6 eV

- Presence of **physisorbed CO_2** (*l*-CO_2) at 298 K under the pressure > 150 mTorr.
- Differences in C 1s peak, between Cu under CO_2 vs Cu under CO_2/H_2O mixture.
- CO_2 peak shift under the presence of H_2O (**chemisorbed CO_2,** *b*-CO_2).
- Surface suboxide + H_2O likely play an important role in the early stage of the reaction

The result provides insights on how to design improved carbon dioxide reduction catalysts. Similar analysis will be pursued for alloys to generalize our observation on the CO2 adsorption.

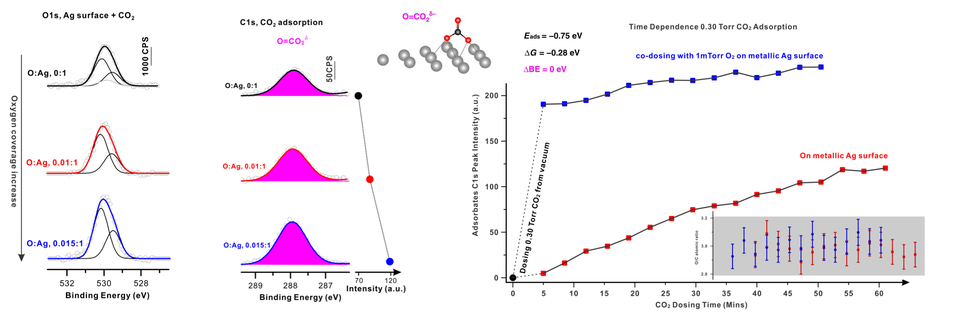
Collaboration w/ B. Goddard, Favaro et al. PNAS 2017, 114 (26) 6706

Comparison of the CO2 Adsorption on Cu and Ag Surfaces

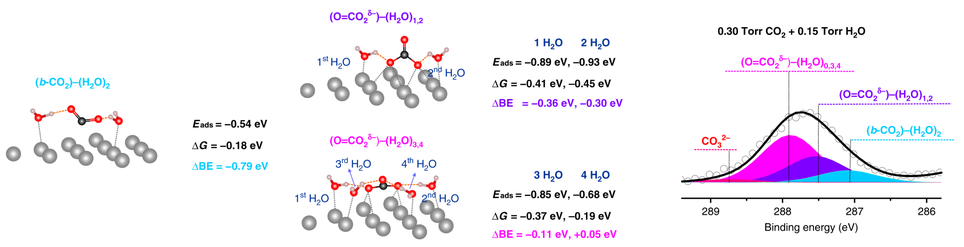


- Oxygen plays an essential role to induce reactions involving CO_2 and H_2O on Ag and Cu surfaces, but the consequences for each metal are dramatically different.
- Different catalyst surfaces modify the CO2 adsorption and activation process.

CO2 Adsorption on Ag Surfaces



- ✓ Pre-surface oxygen coverage determined the surface adsorbates coverage



- ✓ Adding H_2O and CO_2 then leads to (O=$CO_2^{\delta-}$)-(H_2O)$_{1-4}$ and (*b*-CO_2)-(H_2O)$_2$

- Dramatic different C 1s spectra observed on Ag *vs.* on Cu
- *l*-CO2 and *b*-CO2 are not stable on Ag surface
  Surface O promotes the formation of the surface adsorbate
- Sublayer O goes to surface O without energy barrier on Ag, interacts with *g*-CO_2 to form a chemisorbed O=$CO_2^{\delta-}$ species.

The result provides insights on how CO2 and CO2+H2O interact with different metal surfaces, and also provides a baseline knowledge of how to interpret the AP-XPS data for metal alloys.

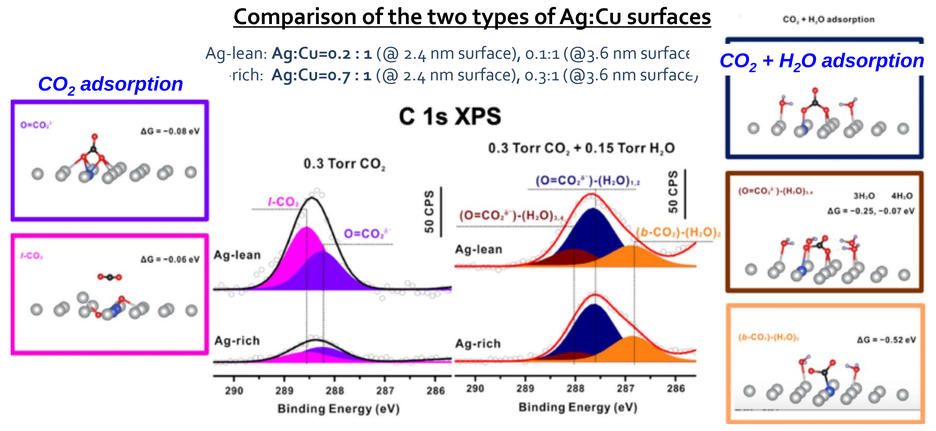
Ye et al. Nature Comm. 2019, 10, 1875

CO2 Adsorption on AgCu Surfaces

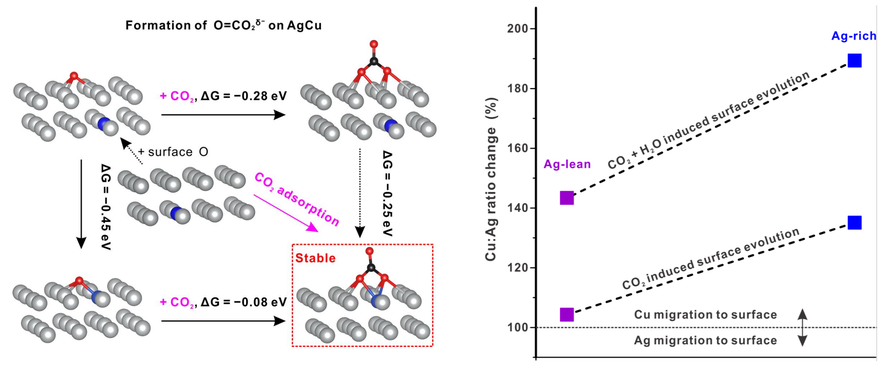
We have studied how the CO2/H2O interactions changes when two different metals are co-located on the surfaces, with **silver-copper (AgCu)** as the material platform. We used AP-XPS and quantum mechanics to examine the processes of CO2 adsorption and activation on AgCu as exposed to CO2 (and H2O) at 298 K, in the similar manner we studied Cu and Ag monometallic systems.

Comparison of the two types of Ag:Cu surfaces

Ag-lean: **Ag:Cu=0.2 : 1** (@ 2.4 nm surface), 0.1:1 (@3.6 nm surface
-rich: **Ag:Cu=0.7 : 1** (@ 2.4 nm surface), 0.3:1 (@3.6 nm surface)



Surface Reconstruction Induced by Gas Adsorption



- Cu content on the surface increases after the CO2 adsorption (transition of subsurface Cu to surface Cu)
- Adsorbates on AgCu have different geometrical and electrical structure, in comparison to the Cu or Ag surfaces.
- The synergy effect between Ag and Cu initiates the evolution of bi-metallic surface under gas adsorption and further alters gas adsorption configurations

The CO_2 adsorption on AgCu bimetallic surface is tuned by the synergy between Ag and Cu, providing a new insight for manipulating the alloy surface to achieve selectivity and activity.

Ye et al. ACS Applied Mater. & Interfaces. 2020, 12, 22, 25374