Revealing the CO_2 conversion towards sustainable energy sources at the reducible metal-oxide interface probed with ambient pressure X-ray photoemission spectroscopy

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In the last decade, global climate change has brought unprecedented national threats such as wildfires, floods, drought, and desertification worldwide (*1*). Those disasters are no longer minor issues that a small group of individual leadership would resolve. Our collective intelligence clearly recognizes that excessive carbon dioxide (CO_2) emissions cause the global warming effect due to its highly inactive characteristic in the atmosphere. So, extensive international efforts have been conducted to capture and utilize greenhouse gases, and recent advances in clean energy technologies will play a vital role in the future accomplishments of the “net zero carbon by 2050”. In the surface science realm, we have focused on the revealing CO_2 activation process over well-defined model catalysts with considering the pressure and material gaps issues. Notably, one of the emerging techniques at the synchrotron facility, ambient pressure X-ray photoemission spectroscopy (AP-XPS) (*2*), is unveiling the momentous reaction steps of CO_2 dissociation and sequentially formed intermediate species at the gas-solid interface. The collected chemical bonding or binding information probed with AP-XPS provides critical evidence for understanding CO_2 activation progress towards the methane or methanol productions at the molecular level. In this talk, I will discuss *in situ/operando* surface catalysis studies of CO_2 conversion over metal or metal-oxides model catalysts under ambient pressure conditions. In particular, I will highlight the physical behavior of the vicinal copper (Cu) surface and Cu-based zirconium oxides interfaces during CO_2 dissociation at ambient pressures. The characterized real-time morphology analysis results on a Cu(997) surface point out that the adsorbate-induced geometric alterations at step-edge sites are involved in the highly enhanced CO_2 activation phase, which is a significant difference from the Cu(111) surface consisting of wide terrace morphologies. These features will be compared to the previously observed physicochemical properties of platinum and rhodium model catalysts, elucidating the nature of the discrepancy of metallic-bonding strength between Cu and Pt. The vital role of adsorbate intermediates at step and terrace sites of the catalyst surface could also be discussed regarding changes in electronic structures. Finally, from the fundamental understanding, we can approach the complex interface structures such as zirconium-deposited reducible oxides (*3*) to investigate the catalytic CO_2 bond-breaking and atomic oxygen transport at the metal-oxide interface. Our systematic *in situ/operando* surface characterizations will shed light on the novel catalyst design and clean energy conversion technology advances in the future.

References

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2. J. Kim, H. Choi, D. Kim, J. Y. Park, Operando Surface Studies on Metal-Oxide Interfaces of Bimetal and Mixed Catalysts. *ACS Catal.* **11**, 8645-8677 (2021).
3. N. Rui *et al.*, CO_2 Hydrogenation to Methanol over Inverse ZrO_2/Cu(111) Catalysts: The Fate of Methoxy under Dry and Wet Conditions. *J. Phys. Chem. C* **126**, 14479-14486 (2022).

Short Biography

Dr. Kim is a research staff at the Chemistry Division of Energy and Photon Sciences Department, Brookhaven National Laboratory (BNL), United States. He received his Ph.D. in Energy, Environment, Water, and Sustainability (Major: Chemical Physics of Solid Surfaces) from the Korea Advanced Institute of Science and Technology (KAIST). He worked as a postdoctoral associate at the Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), South Korea, and at the Department of Chemistry, Massachusetts Institute of Technology (MIT). He joined a research group (Catalysis: Reactivity and Structure, Group Leader: Dr. Jose A. Rodriguez) at BNL in 2021 to pursue the atomic-scale surface catalysis phenomena by employing various *in situ/operando* characterization techniques. He has been dedicated to the long-standing topic in surface science: "*Bridging the Pressure and Materials Gaps*", and he explores the geometric and electronic structures of metal-oxide model surfaces and C1 chemistry by surface science tools (Synchrotron-based X-ray Photoemission Spectroscopy; XPS, Scanning Tunneling Microscopy; STM, Infrared Reflection-Absorption Spectroscopy; IRRAS, Low-Energy Ion/Electron Scattering; LEIS, and High-Resolution Electron Energy-Loss Spectroscopy; HREELS). Dr. Kim and colleagues are conducting clean energy-related research projects for reducing greenhouse gas emissions with its mineralizations, and they have intense international collaborations to investigate the catalytic reaction intermediates using synchrotron-based AP-XPS, ARPES, and LEEM/XPEEM at National Synchrotron Light Source-II (United States), Advanced Light Source (United States), Synchrotron SOLEIL (France), and Photon Factory (Japan).

Selected Publications

[1] N. Rui et al., "CO_2 Hydrogenation to Methanol over Inverse ZrO_2/Cu(111) Catalysts: The Fate of Methoxy under Dry and Wet Conditions", *JPCC* **126** (2022), 14479-14486.

[2] J. Kim et al., "Operando Surface Studies on Metal-Oxide Interfaces of Bimetal and Mixed Catalysts", *ACS Catalysis* **11** (2021), 8645-8677.

[3] J. Kim et al., "How Rh surface breaks CO_2 molecules under ambient pressure", *Nature Communications* **11** (2020), 5649.
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[4] T.-S. Kim et al., "Catalytic Synergy on PtNi Bimetal Catalysts Driven by Interfacial Intermediate Structures", *ACS Catalysis* 10 (2020), 10459-10467.

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Research Highlights

[1] "*Operando study of catalytically active interfacial metal-oxide nanostructure*"
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