Design of In-House Ambient Pressure X-ray Photoelectron Spectrometer and Ambient Pressure High Temperature Scanning Tunnelling Microscope for Operando Studies of Catalysts

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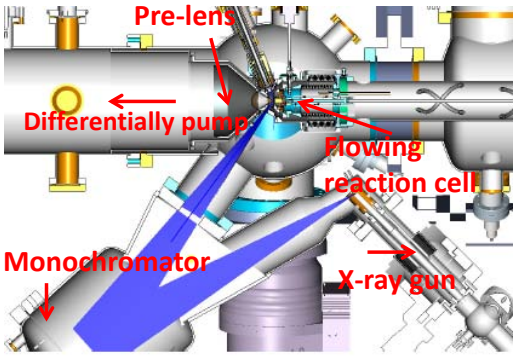
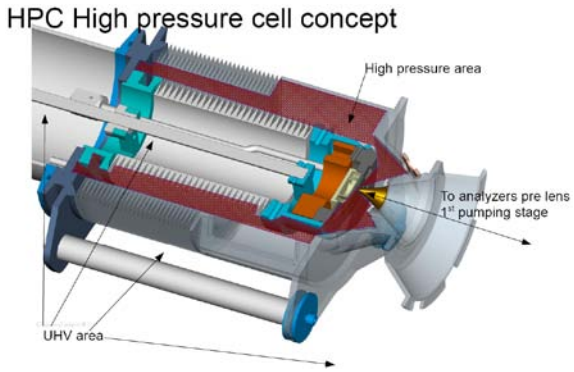
Introduction and Objectives

In reactive environments (reactive gases or liquids), the surfaces of most materials are likely to restructure their geometrical and electronic structure. Such changes have profound effects on the functions and properties of materials. In these cases, the structures and compositions of the material surfaces in a reactive environment in which they function are different largely from those characterized in high vacuum (HV) or ultrahigh vacuum (UHV), the operational environment of most of conventional electron-based surface analytical techniques. The difference between the HV or UHV condition of samples *during characterization* and the ambient or high pressure conditions of catalysts *during catalytic reactions* results in a gap in the studies of heterogeneous catalysis, typically called a pressure gap. This difference was revealed in recent years by using in-situ spectroscopy and microscopy[1, 2]. One of the spectroscopy techniques is the synchrotron-based ambient pressure XPS. A few synchrotron-based ambient pressure XPS systems have been installed



(a)



(b)

in recent years. To increase the availability of this technique, we proposed to design an ambient pressure XPS using monochromated Al Kα in 2010. One objective is to make the AP-XPS technique available in research groups. In addition, to visualize surface structure of the model catalysts under reaction conditions an ambient pressure high temperature scanning tunneling microscope (APHT-STM) was proposed to design.

Results and Discussion

I will present a successful design of a new ambient pressure XPS which we have finished recently. As it uses in-house X-ray source, monochromated Al Kα, we termed it in-house ambient pressure XPS (AP-XPS). The success of this design has made this technique available for any individual research groups. Fig. 1a shows configuration of this in-house AP-XPS system. Another feature of this AP-XPS is the integration of a flowing reaction cell into the setup of X-ray sources and pre-lens, which allows collecting photoelectrons from catalyst surfaces when catalysis is performed in a reactor working in a flow mode. Such a feature makes it offer surface chemistry of catalysts under catalysis conditions compatible to these micro flowing reactors of by catalysis groups. Fig. 1b schematically presents the concept of a flowing reactor. This system can examine surfaces of catalysts up to a condition of 550°C of a sample in a gaseous environment of 25 Torr. I will discuss the evolution of oxidation state of oxide and bimetallic catalysts under reaction conditions including methane oxidation and CO_2 reduction we have performed.

Another technique we developed for operando studies of catalyst surfaces under reaction condition and during catalysis is the ambient pressure high temperature scanning tunneling microscopy (APHT-STM). The feature of this new design is the separation of STM room from the reaction cell by using a dome. This design allows minimizing thermal drift and remaining the temperature of the STM scanning tube and coarse approaching motor at room temperature when catalysis is performed on a model catalyst at high temperature at ambient pressure in reaction cell. I will present the observed structural evolution of model catalysts under reaction conditions.

Reference

(1) M. Salmeron and R. Schlogl, *Surface Science Reports* **2008**, *63*, 169-199
(2) Tao, F. et al. Science **2011**, *327*, 850-853.