

The interaction between hydrogen and MoS₂ basal planes studied by near-ambient pressure XPS and DFT calculations

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Molybdenum disulfide (MoS₂) has attracted much attention for many kinds of applications such as field-effect transistors, optoelectronic devices, gas sensors, and catalysts. In particular, the MoS₂ surface is a reaction field for various catalytic processes involving hydrogen [1]. However, the active sites for these catalytic reactions are considered to be the edge sites of MoS₂ surface or the defect sites, since the ideal basal plane is inert for various molecules including molecular hydrogen. Therefore, enhancing the reactivities of the MoS₂ basal plane is desired for improving the catalytic activities as well as gas sensor efficiencies.

Formation of sulfur vacancies on the basal plane is one of the promising methods to change the intrinsic properties and activities of the MoS₂ basal plane. However, the electronic states of the sulfur vacancies are not fully understood, particularly for quantitatively describing the core level shifts with the sulfur vacancy formation. We measured the electronic states of the MoS₂ basal plane during annealing in hydrogen by near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) [2]. Above 600 K, the XPS spectra of the Mo 3d and S 2p core levels showed significant changes: the appearance of low binding energy components and the decrease in the intensity ratio of S 2p core level to Mo 3d core level. These results indicated the low energy components were related to the sulfur vacancy formation. Using density functional theory (DFT) calculations, we obtained the absolute energies of core levels for the model MoS₂ surfaces including hydrogen atoms and sulfur vacancies. Our calculated core level shift can quantitatively explain the observed binding energy shifts.

Furthermore, we have demonstrated a new method to activate the MoS₂ basal plane for hydrogen molecules by deposition of Pd atoms on the basal plane [3]. Since Pd nanoparticles on oxide surfaces are known to be sites for hydrogen spillover, where the hydrogen atoms dissociated on the Pd atoms migrate onto the support materials, we investigated the corresponding process on the Pd deposited MoS₂ surface by NAP-XPS and temperature-programmed desorption spectra. These spectra indicated that the dissociation of molecular hydrogen and the adsorption of atomic hydrogen occur on the Pd-deposited sites on MoS₂, and thereafter hydrogen atoms spillover onto the MoS₂ surface as shown in Fig. 1.

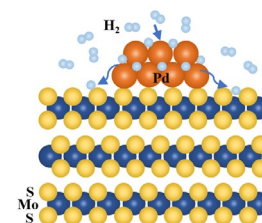


Fig. 1. A schematic image of Pd atoms deposited MoS₂ surface.

[1] J. Mao *et al.*, *Frontiers of Physics*, **13**, 138118 (2018).

[2] F. Ozaki, S. Tanaka *et al.*, (in preparation). [3] F. Ozaki, S. Tanaka *et al.*, *Applied Surface Science*, **593**, 153313 (2022).