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Author(s)	LU, Bang
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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　LU Bang

学 位 論 文 題 名

Elucidation of Structure-Activity Relationship in Heterogeneous Catalysis by *in situ*/*operando* Surface Science Techniques

(*in situ*/*operando* 表面科学手法による不均一触媒構造活性相関の解明)

Catalysts play a critical role in industrial chemistry since they can increase the rate of chemical reactions. Most of the industrial catalysts consist of active metal species that are highly dispersed on powdery oxide supports and the catalytic performance largely depends on the morphological and electronic states of the active metal species. Therefore, it is important to characterize them at the atomic level to elucidate the "structure-activity relationship" for the development of further active catalysts. However, since the powdery catalysts are "ill-defined" with polycrystalline and microporous structures, it is hard to obtain an accurate structure. Using single-crystal surfaces can solve this problem by providing "well-defined" surfaces and applying the ultra-high vacuum (UHV) surface science techniques, which are mainly electron probe techniques, give an atomic-level understanding of the surface processes in heterogeneous catalysis. The catalytic reaction does not occur without reactants (i.e., UHV condition). Thus, the development of *in situ*/*operando* surface science techniques, where surface characterization is carried out under working conditions, is highly demanded to unravel the surface chemical processes on the model catalysts under realistic reaction conditions.

In this work, firstly I used single-crystal surfaces to investigate the surface processes of plasma-assisted catalysis. Then I analyzed the 3-dimensional structure of Cu species on an α-Al_2O_3(0001) single crystal by polarization-dependent total reflection fluorescence (PTRF)-XAFS. Finally, I developed an *in situ*/*operando* surface science technique, which is named "*operando* (PTRF)-XAFS technique", to obtain the structure-activity relationship in heterogeneous catalysis.

The first chapter of the dissertation is the introduction. The second chapter describes experimental methods. It mainly includes the details of the development of the *operando* PTRF-XAFS technique and the construction of an integrated UHV system for the preparation and multiple characterizations of model catalyst surfaces.

The third chapter describes the investigation of surface processes of plasma-assisted catalysis by surface science techniques. An XPS study on Co(0001) surface found that the adsorption of nitrogen species occurred when the surface was exposed to the electron cyclotron resonance (ECR) N_2 plasma at room temperature while no nitrogen adsorption without the plasma. They can be further hydrogenated to ammonia at RT by exposure to the H_2 plasma. The corresponding kinetics and mechanism study was carried out on the Co(0001) surface.

In the fourth chapter, the 3D structure of Cu atoms on an α-Al_2O_3(0001) single-crystal surface at low coverage (9.7×10^{13} /cm^2) was studied in the UHV conditions using the newly developed *operando* PTRF-XAFS cell to test its performance on XAFS measurements. The PTRF-XANES spectra in both s- and p-polarizations showed the formation of monovalent Cu species. Furthermore, an iterative method using FEFF code to simulate PTRF-EXAFS spectra based on a real-space model structure suggested that the Cu species was atomically dispersed and stabilized by the surface oxygens of the α-Al_2O_3(0001) surface.

The fifth chapter focuses on an *operando* study of a Pt/α-Al_2O_3(0001) model catalyst during the CO oxidation reaction using the batch-type *operando* PTRF-XAFS cell. The cuboctahedral Pt clusters consisting of 147 Pt atoms were found to be the main species under the CO oxidation reaction condition at 493K. Its corresponding turnover frequency (TOF) of CO_2 formation was determined to be 0.06 s^{-1} based on the structure determined by the *operando* PTRF-XAFS and the simultaneous activity measurements using the quadrupole mass spectrometry (QMS).

In the sixth chapter, I found there were two temperature regimes in the activation energies towards CO oxidation on the Pt/α-Al_2O_3(0001) by using the flow-type cell. The *in situ* PTRF-XAFS measurements were applied to reveal the origin of two different activation energies.

The seventh chapter is the general conclusions of the work. I have successfully developed a novel *operando* PTRF-XAFS technique to reveal the well-defined catalyst surface structure to unravel the surface processes. Consequently, my Ph.D. work has opened a new horizon of *operando* surface science in the heterogeneous catalysis field.