VIII-T Nanoscale Characterization of Heterogeneous Catalyst Surfaces

Heterogeneous catalysis occurs on a surface of a solid catalyst. Active centers for heterogeneous catalysis commonly consist of clusters of several surface atoms, and thus a long-range order of surface atoms is not normally required. Therefore, when using precious metals as catalysts, nanometer-scale superfine particles are commonly employed in order to increase its surface area and to decrease the amount of catalysts. This introduces difficulties in characterizing the catalyst surfaces and their active centers, because characterization techniques of solid surfaces at nanometer-scale are not well established. Here we mainly used scanning probe microscopes, in conjunction with other surface characterization techniques, to characterize catalytically active centers as well as the nature of catalyst-support interactions.

VIII-T-1 Monte Carlo Simulation of Pyridine Base Adsorption on Heulandite (010)

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Adsorption of pyridine base molecules (pyridine and α-, β- and γ-picolines) on a surface of a natural zeolite, heulandite (010), was examined by Monte Carlo simulations. Two types of adsorption areas were identified on heulandite (010) bound by surface OH arrays, and each area showed different influence on the adsorption and orientation for pyridine base molecules. The presence of methyl group and its position within the adsorbed molecule also influenced its adsorption characteristics. For pyridine adsorption, molecular dynamics simulation was also performed. The results were compared with existing experimental data obtained through atomic force microscopy.

VIII-T-2 Apparent Local Structural Change Caused by Ultraviolet Light on a TiO_2 Surface Observed by Scanning Tunneling Microscopy

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An apparent local surface structural change at nano-scale was observed by scanning tunneling microscopy on a TiO_2 surface upon irradiation with ultraviolet (UV) light. This phenomenon was reversible with UV light irradiation, and was interpreted to be due to the local accumulation of photoexcited states. This is the first real-space observation of inhomogeneous local charge distribution under UV light irradiation at nanoscale on a semiconductive photocatalyst surface, which may help identify the photocatalytic active sites and elucidate their reaction mechanisms.

VIII-T-3 Electronic Structure Change on TiO_2 Surface due to UV Light Irradiation

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Photocatalysts have been paid extensive attentions for their environmental as well as energy applications. Although each photocatalytic processes may be different in terms of their kinetics and surface reactions involved, they are all initiated with the photoexcitation of TiO_2 electrons, the process commonly understood and explained by the so-called band model which assumes an infinite array of crystallographic lattice points. In contrast, catalytic reactions involved in photocatalysis are highly local in nature: some reactant may need particular local arrangements of atoms that are present on the catalyst surface, and others may need particular local electronic states of the surface atoms to provide unique adsorption or reaction sites. Despite this gap that exist in between the two descriptions involved in heterogeneous photocatalysis (band model and local catalysis), no efforts to address and bridge this gap are known to the authors. The present report is the first of such attempts, and examines the local electronic characters of TiO_2 surface upon UV-light illumination by means of scanning tunneling microscopy (STM).

VIII-T-4 In Situ Observations of Tetraamineplatinum (II) Hydroxide Adsorption from Its Aqueous Solution on Heulandite (010) Surface by Atomic Force Microscopy

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Adsorption of tetraamineplatinum (II) hydroxide, a Pt catalyst precursor, from its aqueous solution on a (010) surface of a natural zeolite heulandite was observed, in situ, by atomic force microscopy (AFM). The Pt complex exhibited certain adsorption habits on the surface, frequently forming a short chain along the zeolite *a* axis, separated by three times the *c* unit cell length in the *c* direction. Possible adsorption sites on the surface were identified and discussed. The present work constitutes the first in situ atomic-level observation of a liquid-phase preparation process of supported metal catalysts.

VIII-T-5 Defect Creation on Rutile TiO_2 (110)-(1x1) Surface due to Light Irradiation Observed by Scanning Tunneling Microscopy

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Laser light irradiation created atomic-scale structures on rutile TiO_2 (110)-(1×1) surface, the number of which increased with irradiation time. The created bright structures appear to be cross-shaped, each bridging two titanium [001] rows, and having dark areas in the front and in the back. The structure is interpreted as an oxygen deficiency on the (1×1) surface, and the one of the dark spots around the structure as the oxygen atom displaced from its original position. The structure often appears as a pair aligned along [1-10] direction, which could be viewed as a local (2×3) structure.

VIII-T-6 Crater Structures on a Molybdenite Basal Plane Observed by Ultra-High Vacuum Scanning Tunneling Microscopy

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Atomic structure of a natural molybdenite (MoS_2) single crystal basal plane was examined by ultra-high vacuum scanning tunneling microscopy (UHV-STM). After high-temperature (473 K) resulfidation, numbers of crater structures with diameters ranging from 6 to 8 nm were observed. Atomic structures within these craters were continuous from the surrounding terrace, with no step structures at the rims of the craters. Atoms in the bottom of the craters showed higher corrugations compared to the terrace atoms, indicating perturbed electronic states in the craters. Its implication in hydrodesulfurization activity over MoS_2 basal plane is discussed.