

Preface

The definition of materials is quite different in chemistry and physics. That is, a group of materials or compounds having novel functional or chemical properties are considered new materials in chemistry. From this point of view, the surface of a solid is quite interesting as a material, because chemical properties depend on the crystal planes; a different crystal plane has different chemical properties. For this reason, the property of solid materials known to us is that of their surface, and no one knows the real chemical property of the solid material itself.

If we consider a two-dimensional material such as graphene, graphite, and MoS_2 , their surface is a one-dimensional edge. The different chemical property of a one-dimensional edge, the surface, is revealed by breaking it from that of the parent material. Graphite and MoS_2 are very stable materials chemically and thermally, but with their one-dimensional edge formed by breaking, the surface of two-dimensional materials provides active new materials. In fact, the edge of MoS_2 becomes an active catalyst as shown in this book.

If the surface formed by breaking provides a new chemical material, the reaction of surface atoms would provide additional new materials, although these could not be removed from the bulk. According to this idea, the numerous phenomena taking place on the surface are responsible for the new materials which can exist only in the two- or one-dimensional space. Some of these materials are passive, but some of them have unique reactivity in chemical reactions and catalysis, even though these materials can exist only on a specific surface. An additional important feature of the new materials is that the chemical reaction dynamics are restricted in two- or one-dimensional space as discussed in this book.

About 100 years ago, the first scientific page of catalysis in metals was opened. At that time, a metal surface was imagined to be an array of atoms like a chess-board. In the last 50 years, the remarkable development of vacuum technology and electronics has enabled us to detect feeble currents and to elucidate the inherent properties of the surface of solid materials. However, most work has focused on the crystal structure and the electronic structure of the surface in relation to those of solid materials, which are well rationalized by the band structure and the lattice energy calculations in relation to those of solid materials. However, it can be said

that little study has been done from a view point that the surface comprises new chemical materials, although metal clusters are recognized as new material.

This book throws some light on the surface as a realm of unexplored interesting materials existing on the solids. The following passage from Roald Hoffmann in *Solids and Surfaces—A Chemist's View of Bonding in Extended Structures* is relevant.

A surface—be it of metal, an ionic or covalent solid, semiconductor—is a form of matter with its own chemistry. In its structure and reactivity, it will bear resemblance to other forms of matter: bulk, discrete molecules in the gas phase and various aggregated states in solution. And it will have differences. Just as it is important to find the similarities, it is also important to note the differences. The similarities connect the chemistry of surfaces to the rest of chemistry, but the differences make life interesting (and make surfaces economically useful).

The present book is composed of two parts: “Dynamic Chemical Processes on Metals” and “Dynamics of Chemical Reactions in Catalysis.” Part I illustrates various unusual chemical processes on metal surfaces regulated by two-dimensional freedom, but the characteristic reactions of surface atoms are difficult to anticipate. When Cu(100) and Cu(110) surfaces are exposed to O₂ at room temperature, O₂ molecules dissociate into O(a) atoms on either a Cu(100) or Cu(110) surface. The O(a) atoms are stabilized by forming a minimum size of $c(2 \times 2)$ domains (made by several O atoms) on a Cu(100) surface, whereas O(a) atoms on a Cu(110) surface undergo reaction with surface Cu atoms and one-dimensional (–Cu–O–) strings are formed on a Cu(110) surface, referred to as “quasi-compounds” in this book.

To understand real catalysis, we must know the dynamic chemical processes on the surface. As discussed in Part II, it has been accepted that the kinetic equation of catalytic reaction depends on the rate determining the slow steps of the reaction, but the intrinsic activity of the surface as a catalyst depends on the steady concentration of active compounds formed on the surface.

The role of promoting materials is quite important in practical catalysis, but it remains an awkward common problem in catalysis. In Part II, Chap. 10, Sects. 10.4 and 10.5, the role of promoting materials in selective oxidation of CO in excess H₂ on metals is carefully discussed. It could be said that the cooperation of different functional materials over the same surface is a big advantage of heterogeneous catalysis. If efficient cooperation of two or more materials in a series of connected reactions could be designed, this would be the golden key to attaining a high-performance catalyst, as discussed in Sects. 10.4 and 10.5. In this sense, this book will be a good guide not only for the reader interested in the basic chemistry of solid surfaces but also for the reader anticipating the surface to be new materials and having an invaluable idea for designing high-performance catalysts.

Dynamic Chemical Processes on Solid Surfaces

Chemical Reactions and Catalysis

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