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Book review

Shustorovich E. (ed) (1991) Metal-Surface Reaction Energetics. Theory and applications to heterogeneous catalysis, chemisorption, and surface diffusion. VCH Publishers, New York, 232 pp.

For a detailed microscopic understanding of catalytic processes at metal surfaces such as adsorption, diffusion or reaction mechanisms it is necessary to know the energetics that control these processes: Adsorption and desorption energies, adsorbate-adsorbate interactions, energies of reactive intermediates, activation barriers for elementary steps of complex reactions at surfaces, etc. Some of these quantities are not easily accessible to experiment, and it is hoped that theory may provide both qualitative models and reliable numerical methods for estimating them.

The present book reflects the current status of the theory of reaction energetics at metal surfaces. It is divided into five chapters, i.e. five review articles written by different authors, about fifty pages each. The first chapter by Per E. M. Siegbahn and Ulf Wahlgren contains an account of rigorous quantum chemical *ab initio* cluster calculations for the adsorption of atoms and small molecules on metal surfaces, in particular on Ni(100) and Cu(100). A careful discussion of the problems connected with these calculations, such as 3*d* relaxation effects, different correlation contributions and cluster convergence as well as the presentation of several examples illustrates the predictive power of the *ab initio* methods, but also their difficulties and limitations. In the second chapter by Jay B. Benziger just the opposite approach is taken: Adsorption energies and reaction enthalpies are estimated from purely empirical thermodynamic data. For this purpose, the bond-order conservation approach based on Morse potentials (BOC-MP) as proposed by Shustorovich some years ago has proven to yield fairly reliable estimates with errors of only a few kcal/mol in favorable cases.

The other three chapters are dedicated to applications, i.e. to theoretical investigations of different processes at metal surfaces which are based on potential energy surfaces or reaction energetics as – in principle – provided by the methods described in the first two chapters. Roger C. Baetzold summarizes conceptual aspects of diffusion processes of adsorbed species on metal surfaces. This chapter covers both experimental techniques and data and theoretical methods, e.g. trajectory calculations and Monte Carlo simulations. The bond-order conservation principle is invoked as a simple means to estimate diffusion barriers and parameters for adsorbate-adsorbate interactions. In the chapter by David Halstead and Stephen Holloway several examples are presented in which the time dependent Schrödinger equation is solved for the dissociative chemisorption of diatomic molecules, mostly H_2, at metal surfaces. The question how the properties of the underlying potential energy surface influence reaction probabilities, sticking coefficients etc. is discussed in a way quite similar to the discussion of elementary gas phase reactions some twenty years ago by Polanyi. In the last chapter by Alexis T. Bell again the bond-order conservation approach is applied to calculate reaction energetics which are then used to discuss the kinetics and possible reaction mechanisms for some heterogeneously catalyzed reactions of practical interest.

All five chapters are written by very competent and active workers in their fields and present the current status of the respective subjects very thoroughly and clearly. The book suffers slightly from the typical defect of collections of review articles: The selection of the topics seems quite accidental. For instance, as far as the calculation of reaction energetics is concerned, there are at present four types of approaches: *ab initio* calculations, semi-empirical methods, density functional theory, and purely phenomenological estimates. But only the first and the last of these possibilities are reviewed in the first two chapters.

Nevertheless, the book can be recommended to all workers in the field of molecule-surface interactions. It contains a lot of valuable up-to-date information and gives an excellent, though not complete, overview about the contributions of modern theory to the investigation of surface reactions. Complicated formalisms are completely avoided, therefore the book is useful not only for the theorist, but even more so for the experimentalist.

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