Theoretical heterogeneous catalysis, limitations and challenges

Citation for published version (APA):

Document status and date:
Published: 01/01/2007

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
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COMP 229

Selectivity issues in ammoxidation catalysis: MoV(Nb,Ta)(Te,Sb)O System

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Selectivity is assuming ever greater importance in catalysis with the cost escalation of feed stocks. Some forty years ago, we proposed the concept of site isolation, a key requirement to achieve selectivity in oxidation catalysis. This principle is useful in the conceptual design of new selective oxidation catalysts, describing the selectivity behavior of many catalysts, including MoVNbTeO, the currently most efficient propane ammoxidation catalyst. In its optimum form, it is comprised of two crystalline phases, orthorhombic Mo7.8V1.2NbTe0.94O28.9 (M1) and pseudo-hexagonal Mo4.67V1.33Te1.82O19.82 (M2). M1 is the key paraffin activation and ammoxidation phase, its active centers containing all key elements V5+, Te4+, Mo6+, properly arranged to transform propane directly to acrylonitrile. Four Nb5+ centers, each surrounded by five molybdenum-oxygen octahedra isolate the active centers from each other, preventing over-oxidation, leading to high selectivity. Symbiosis between M1 and M2 phases occurs at high propane conversion. Reaction mechanisms for propane ammoxidation are described.

COMP 230

Theoretical heterogeneous catalysis, limitations and challenges

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Two reaction systems will be chosen to discuss theoretically the relation between catalyst structure and catalytic performance. For transition metal catalysis we select for discussion the Fischer-Tropsch reaction that converts synthesis gas into higher hydrocarbons. We will discuss the quantum-chemical aspects of CO activation as well as CH4 formation and C-C bond formation. This catalytic reaction is of interest theoretically, because selectivity strongly depends on choice of metal as well as particle size and shape. Reactivity-free energy relations can be formulated that enable a rational analysis of reactivity trends. A heterogeneous catalytic system with steric constraints is the microporous zeolite. In protonic form these materials are widely used. We will address the question of
the interplay between the reactivity of these protons and the size and shape of zeolite cavity. More recent is the use of reactive cations or cationic clusters to activate hydrocarbons. Chemical interaction between the zeolite channel wall and the cationic systems in the zeolite micropore determine the relative stability of cationic clusters and hence their catalytic activity. This will be discussed for Zn and Ga cationic clusters. Progress in these two topics illustrates the great advances in catalytic science due to access to efficient high quality computer codes as well as hard ware computer performance. The complexity of model systems we can discuss today was unthinkable only ten years ago.

COMP 231

Understanding electrochemical systems from first principles

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 Compared to surface science experiments under UHV conditions, electrochemical systems (such as fuel cells) combine a whole variety of additional effects. These range from the nanostructure of the highly disperse catalyst particles over the presence of the electrolyte and the multi-component environment to the reaction conditions of finite temperature, pressure, and electrode potential. Due to this complexity our knowledge about the ongoing processes is mostly limited to the macroscopic regime. However, nowadays theoretical methods are able to provide a deeper insight into structures and processes at the atomistic level, which together with experiments could lead to a better understanding. Within this talk I will first present theoretical studies on the oxygen reduction reaction (ORR) occurring at the cathode of PEM-fuel cells. Starting with the gas-phase system effects from the reactive surrounding as well as environmental parameters are successively included, finally providing a more realistic description. In order to describe the electrochemical interfaces developing in these systems we formulated the extended \textit{ab initio} atomistic thermodynamics method, which allows calculating \((p,T,\Phi)\)-phase diagrams of electrode/electrolyte-interfaces from first principles. It turned out that the model of a pure and perfect catalyst surface, which is often used to study this reaction, is clearly incomplete. Instead, structure and composition of the catalyst are significantly modified. Afterwards, calculations on alternative catalyst materials (Pt-based alloys and nano-structured Ir) that experimentally show enhanced reaction rates are discussed. We find that the electrode potential is also an important parameter for actively tuning electrode morphologies and nanostructuring.