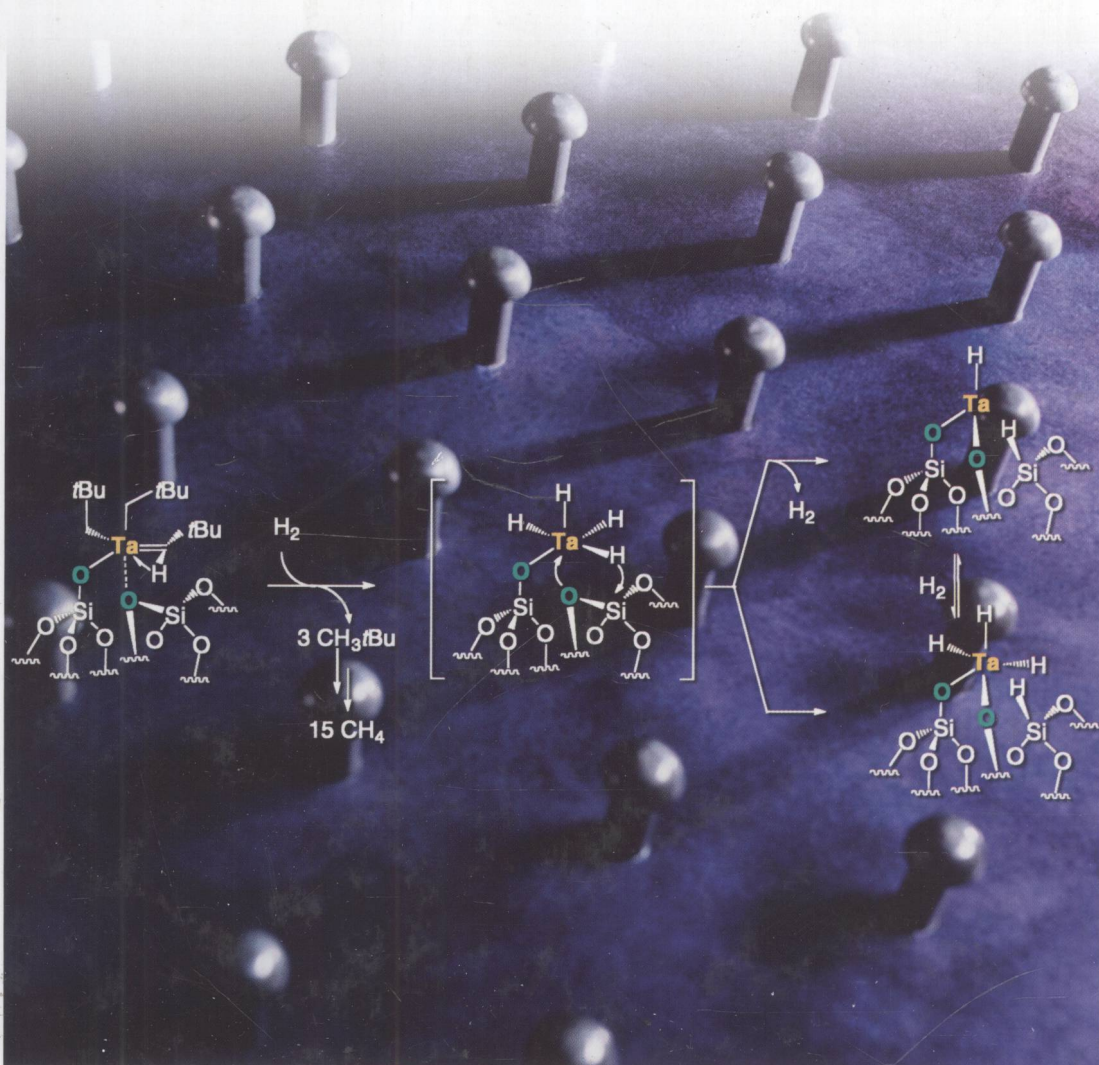


Edited by Jean-Marie Basset, Rinaldo Psaro,
Dominique Roberto, Renato Ugo

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Modern Surface Organometallic Chemistry



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Edited by

*Jean-Marie Basset, Rinaldo Psaro,
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Preface

Catalysis is the number one technology in chemical industry and petroleum refining. In the future one may reasonably expect that catalysis will be among the leading solutions for meeting the new global and intimately related challenges of environment and energy. The advantages of catalytic processes are due to the relatively mild reaction conditions, their cost efficiency, and their environmentally friendly character.

Nevertheless, even if it has probably the longest history, heterogeneous catalysis, which is the most commonly used among all the catalytic tools (the other ones being homogeneous and enzymatic), still suffers from many drawbacks. Sometimes it is not selective enough, which increases evolution of products involved in green house effects (like CO₂, NO_x or particles), sometimes it requires high temperatures which is energy demanding, sometimes its lifetime is too short which is not economical, sometimes its regeneration procedures are difficult if not impossible.

Some of the reasons for these drawbacks are inherent to the “heterogeneous” character. The multiplicity of active sites in terms of surface and bulk structure and their low concentration prevent the easiness of achievement of a reliable structure-activity relationship, a necessary step for improvement of existing catalysts or even for a predictive approach for new catalytic reactions. Despite all these drawbacks, heterogeneous catalysis remains the most applied solution for one simple reason: catalyst separation from reagents or reaction products is usually easy which renders industrial processes more easily achievable.

A predictive approach to the design of heterogeneous catalysts is now slowly emerging due to the spectacular progresses made recently in the synthesis of new and structurally well defined materials. The nano-control of active sites via a pluridisciplinary approach is one of the ways to address this issue of predictive performances of catalysts. It is now possible to achieve the rational design and synthesis of well defined supports with the expected structure, acidity, porosity or shape in the field of oxides, or zeolites, carbon based materials or even of pluri-metallic particles of given size, shape and composition. But the synthesis of

materials, which are more and more defined from the atomic level to the nano level and finally to the centimetric level, is often not enough to warranty the required catalytic activity, selectivity, and lifetime. These new materials are most of the time a support of the metallic active site.

It is one of the reasons why the field of “*surface organometallic chemistry*” has been developed. This field concerns the grafting of organometallic or coordination compounds onto a reactive surface. By surfaces we mean those of simple oxides (from mesoporous materials up to zeolitic materials), those of metals (from unsupported nanoparticles to supported ones, up to single crystals), those of carbon (from carbon black to naphthenes to carbon nanotubes), those of carbides, nitrides, etc. Probably the surfaces of oxides are the most commonly used. The grafting of organometallic compounds onto these oxides aims at the synthesis of “single site” catalysts. In principle the detailed knowledge of the surface organometallic chemistry, that is the structure and chemical behaviour of the active site which results from a careful structural determination, leads to elucidation of elementary steps of heterogeneous catalysis and a structure-activity relationship can be achieved in several cases. Therefore a new generation of catalysts, controlling new and selective catalytic reactions and relevant improvements of existing catalysts, have been discovered on these materials. Such knowledge of the catalytic materials greatly benefited from the precision with which in situ and ex situ methods of structural and chemical characterization coming from advanced surface science and molecular chemistry may be carried out on such single sites (in situ IR, in situ ^1H , ^{13}C NMR, 2D NMR, EXAFS, Surface Microanalysis, determination of the stoichiometry of surface reactions, molecular models of the surface sites).

This book wants to analyze many aspects of this “*modern catalytic and surface chemistry by design*”. The reaction with surfaces of metal oxides or some specific silicates of “*organometallic compounds*” has been extended to “*coordination compounds*”. The types of metals cover not only “*transition metals with a variety of d electronic configurations*”, but also “*lanthanides and actinides*” or “*non transition metals*”. The types of surfaces have been extended to those of “*supported or unsupported metals or metal nanoparticles*”. Metallic nanoparticles of given size and composition, prepared by their “*synthesis in mesoporous materials*” or “*on simple oxides by carbonyl decomposition*”, have been broadly covered. The concept of metallic single site has been extended to “*building block approaches*” and “*immobilisation of homogeneous catalysts*”. A “*broad range of catalytic reactions*” such as those related to “*energy, raw materials and environment*” but also those involving more sophisticated aspects such as “*hydrosilylation and enantioselective reactions*” have been extensively covered. We have shown in this book how the molecular approach to silica-supported organometallic chemistry through the synthesis and investigation of “*silsesquioxanes based organometallic molecules*” is the basis of good models of the behaviour and structure of organometallic single sites on oxides but is also the origin of a family of catalysts on their own. The facile and selective “*Surface-mediated organometallic syntheses*” in particular of metal carbonyl clusters, a domain

of intense research which results directly from surface organometallic chemistry, has been fully described.

We thank the authors for their excellent efforts and their willingness to mould their contributions to our conception of the book.

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