

Heterogeneous Catalysis – An Interdisciplinary Approach

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Abstract: Catalysis is a powerful method for developing chemical processes that make efficient use of energy and raw materials and have minimal impact on the environment. The main emphasis of our research lies in advancing the scientific basis for the design of efficient heterogeneous catalytic processes for fine chemical synthesis and the abatement of pollutants. Present research activities are briefly reviewed.

Keywords: Catalyst design · Environmental catalysis · Fine chemicals · *In situ* characterization · Theoretical modeling

Introduction

The main emphasis of our research lies in heterogeneous catalysis. Our interests cover the full gamut of heterogeneous catalysis from fundamentals to reaction engineering. The principal target is to improve the scientific basis for rational design of heterogeneous catalytic systems. For this purpose we use a highly interdisciplinary approach which combines solid-state chemistry, physical chemistry and reaction engineering knowledge. Our group is composed of chemists and chemical engineers, an ideal combination to cope with the many facets of catalysis research. For a detailed discussion of our research strategy the reader is referred to previous accounts [1]. The research activities within our group can be divided into five branches: catalyst materials, *in situ* characterization of catalytic systems, reaction engineering, catalysis for the synthesis of fine chemicals, and environmental catalysis. All these areas are strongly interdependent as illustrated in

Fig. 1. Studies of the interrelationship between structural and chemical properties of solid materials and their catalytic properties are at the origin of the design of new catalysts. *In situ* characterization (characterization of catalysts in the working state) and theoretical modeling are

applied to gain the information necessary for a rationally guided catalyst design. Research in reaction engineering is mainly concerned with the optimization of the interplay between chemical reaction and mass- and heat transfer in the catalytic system. The ultimate goal of these con-

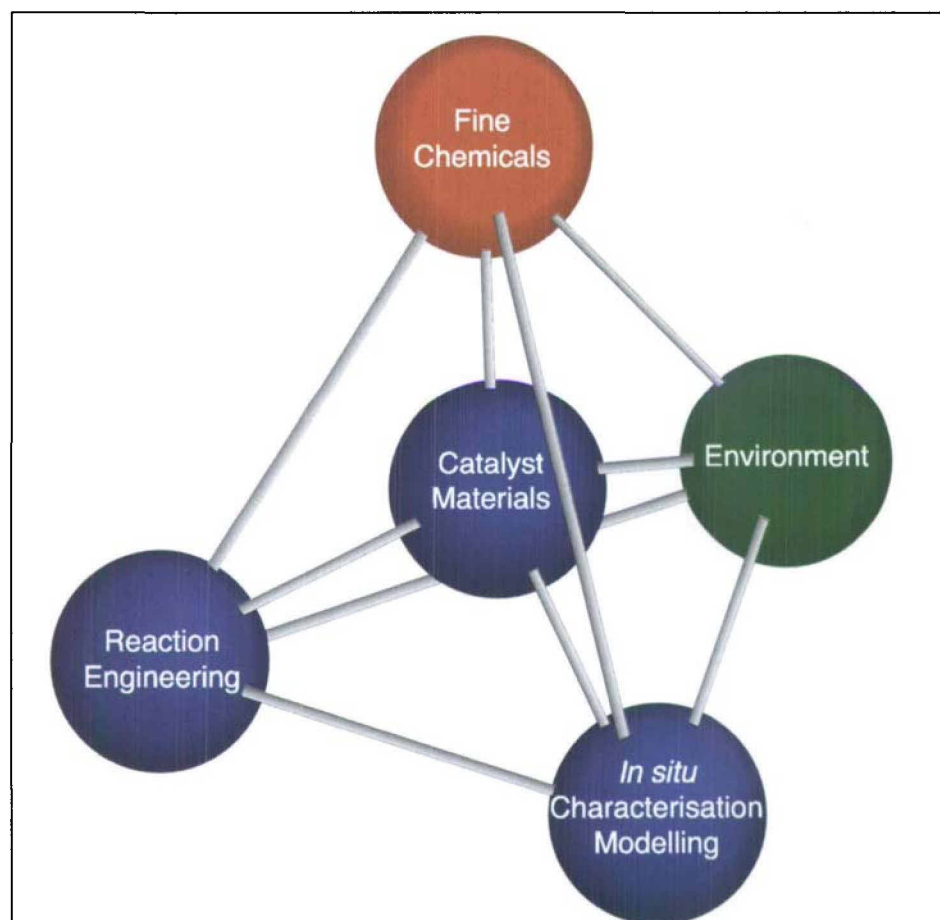


Fig. 1. Major directions of research and their interdependence

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certed efforts is the development of new efficient catalytic systems for the production of fine chemicals and application in environmental catalysis. Here, a brief survey of the research activities of our group in the past two years is provided. For detailed information on the projects and for acquiring some knowledge on the world-wide state of research in the covered fields the reader is referred to the pertinent recent publications and references therein.

Catalyst Materials

The efficiency of a catalytic process in general greatly depends on the performance of the catalyst, rendering the development of efficient catalytic materials one of the foremost challenges in catalysis research. Studies on the relation between structural and chemical properties of solid materials and their catalytic behavior are at the origin of this endeavor. Model catalysts with well-defined structural and chemical properties serve for elucidating structure-activity relationships. *In situ* spectroscopy is applied to gain important knowledge concerning mechanism and pathway of reactions. Where possible the experimental studies are complemented by theoretical calculations aimed at elucidating the structure of interaction-complexes relevant to the catalytic pathway. Altogether this results in a rationally guided catalyst design, which is generally more efficient than the classical empirical (trial and error) approach.

Materials under consideration range from various metal oxides and metals to organic-inorganic hybrid systems. A survey of applied materials can be found in previous reports of our research activity [1]. Catalyst materials of current interest include: grafted mixed oxides [2a], sol-gel derived mixed oxides modified by organic groups [2b], organic-inorganic hybrid materials [2c], supported metal catalysts with controlled particle size [2d,e], flame-made mixed oxide nanoparticles [2f], and supported metal catalysts, modified with chiral auxiliaries [2g].

In situ Characterization and Modeling

The final goal of catalyst characterization is to understand the catalyst in its working state, which we pursue by *in situ* characterization techniques, such as vibrational spectroscopy [3a], X-ray ad-

sorption near edge spectroscopy [3b], cyclic voltammetry [3c], and pulse thermal analysis combined with mass spectrometry [3d] or FTIR. Most recently, considerable effort has been made to investigate solid-liquid interfaces using attenuated total reflection infrared spectroscopy (ATR-IR) which probes the region at and near the interface [3e]. This method is successfully applied to unravel the structure of chiral modifiers adsorbed on metal catalysts used in chiral catalysis [3f]. Fig. 2 shows an example of this effort, the adsorption of cinchonidine (CD) on supported platinum measured at different surface coverages. Cyclic voltammetry is used to uncover the state of metal surfaces during redox processes [3c], such as the oxidation of alcohols in the liquid phase. Pulse thermal analysis combined with spectroscopic techniques has been developed in our laboratory to a powerful tool for the *in situ* characterization of reactant-induced changes in the bulk properties of catalysts during reaction. Another *in situ* technique which has been integrated recently in our research is the video monitoring of the phase behavior of the reaction mixture in high pressure reactions, which is particularly important in understanding reactions in supercritical fluids. For this purpose a special high pressure cell has been constructed [3g]. A new cell which should allow *in situ* ATR-IR and transmission IR measurements under higher pressure is presently under construction.

Theoretical calculations have been instrumental in gaining a better understanding of the structure of feasible transition states and reaction pathways, particularly in cases where spectroscopic methods were not applicable. The theoretical tools employed include *ab initio*, semi-empirical and force field methods, depending on the complexity of the catalytic system. A field where theoretical calculations have been particularly rewarding is enantioselective hydrogenation on chirally modified metal catalysts [3h,i]. The theoretical calculations have provided approximate structures of feasible diastereomeric transition states formed upon interaction of the reactant with the chiral modifier.

For illustration, Fig. 3 depicts the structure of diastereomeric interaction complexes proposed for the enantioselective hydrogenation of trifluoroacetophenone. These structures predict the stereochemical outcome of the asymmetric hydrogenation and afford a valuable guide for the design of new efficient chiral modifiers [2g][3h].

Reaction Engineering

Present research in reaction engineering is mainly concerned with the application of supercritical fluids in catalytic reactions and the preparation of new catalyst materials. Supercritical fluids have attracted attention as media for chemical reactions because of their unique properties [4a]. Their physical and transport properties such as diffusion coefficients, viscosities, and densities typically fall between those encountered in gases and liquids. Another attractive feature is that many of their properties are strong functions of pressure and temperature near the critical point. These features can be beneficially applied in the design of chemical processes which are efficient and environmentally benign. Our research aims at gaining some fundamental insight into how the supercritical state of a reactant or solvent can affect the performance of a heterogeneous catalyst. For this purpose various catalytic reactions are studied in supercritical media [4b-e]. *In situ* monitoring of the phase behavior and spectroscopic investigation of the molecular interactions are key for understanding catalytic reactions under these conditions. Fig. 4 illustrates the effect of the transition from a two-phase to a single supercritical phase system for the semihydrogenation of phenylacetylene.

Environmental Catalysis

Our research in environmental catalysis concentrates on NO_x removal from mobile and stationary combustion sources and the synthesis of chemicals using CO₂ as C₁-building block. Research on NO_x removal from mobile combustion sources aims at developing three-way catalysts with improved dynamic behavior [5a] and catalysts for lean-burn engines which operate with excess oxygen (air-fuel ratios = 25:1). Platinum metals [5b] in combination with components for NO_x storage are applied to remove NO_x by hydrocarbons in the presence of excess oxygen. The work aims at elucidating the mechanism and the crucial structural requirements of catalysts for efficient NO_x removal under lean conditions. The selective catalytic reduction (SCR) of NO_x by NH₃ has been a topic of interest for more than a decade. Present activities focus on increasing the activity and stability of SCR catalysts [5c]. In parallel several reactions relevant for environmental catalysis, such as CO [2e] and NH₃ oxidation are studied systemati-

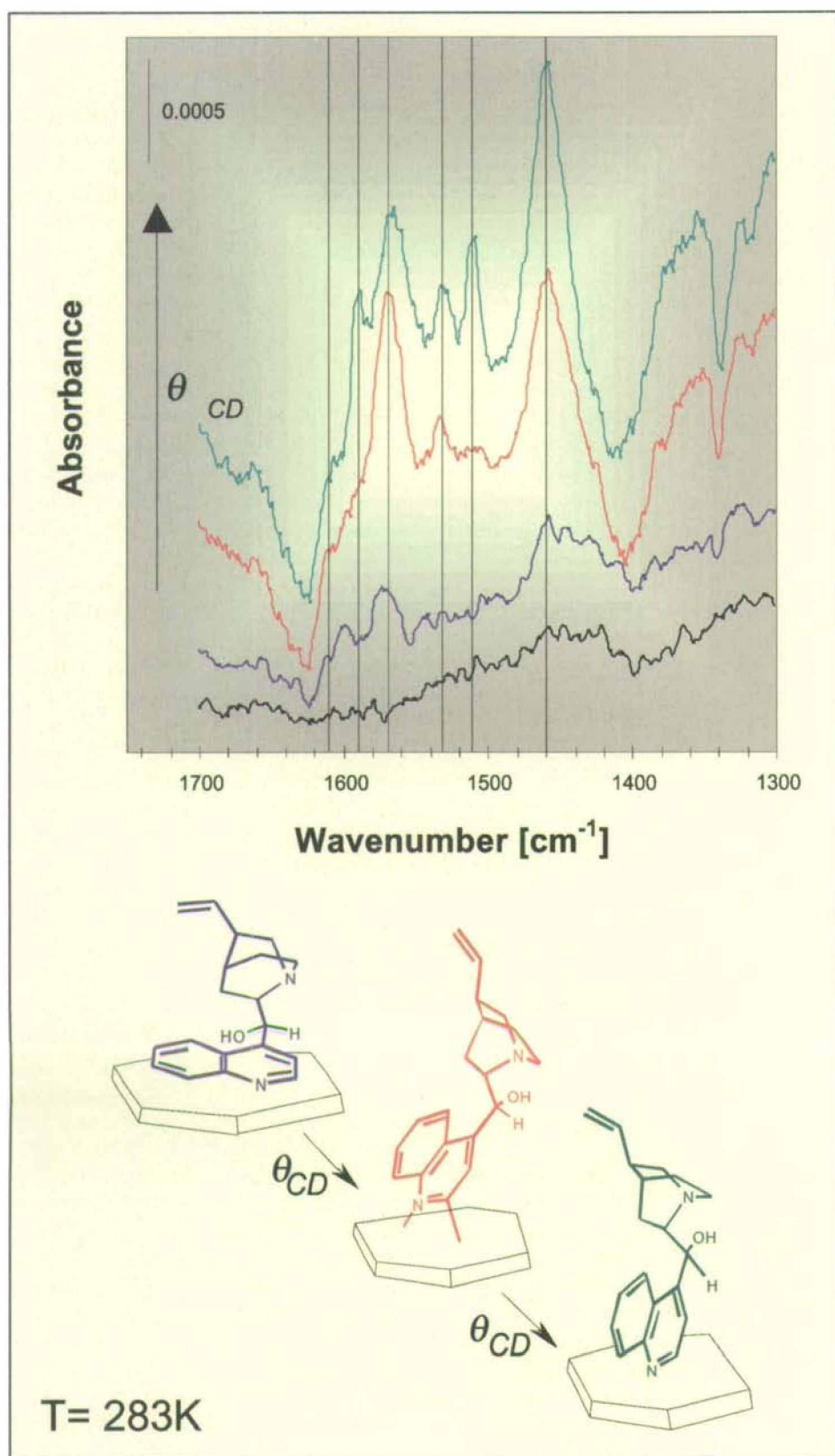


Fig. 2. Adsorption of cinchonidine used for chiral modification of supported platinum catalyst studied by ATR-IR spectroscopy in a specially designed flow cell. Spectra taken at different coverage (θ_{CD}) of the platinum surface indicate a change from preferential flat adsorption via π -bonding at low coverage to a tilted species bound via nitrogen lone pair at higher coverage. Note that all three species coexist at high coverage.

cally on model-type and technical catalysts.

Catalysis is a promising approach to CO_2 fixation. Substituting the presently used toxic C_1 feedstocks, CO and COCl_2 , by non-toxic, easy to store, transport, and handle CO_2 is an attractive challenge, which can greatly contribute to environmentally benign production of various chemicals. The aim is to extend the scope

of chemicals which can be synthesized from CO_2 using heterogeneous catalysts. Particularly attractive are heterogeneous catalytic processes that make use of supercritical CO_2 as reactant and solvent. This solvent-free reaction design has been successfully demonstrated for the synthesis of formic acid derivatives [5d] and carbamates [5e] from CO_2 . Catalyst development and mechanistic studies are

central interests. A survey of our activities in this field is given in the references [5f].

Fine Chemicals

Heterogeneous catalysis affords interesting opportunities for environmentally benign production of fine chemicals and

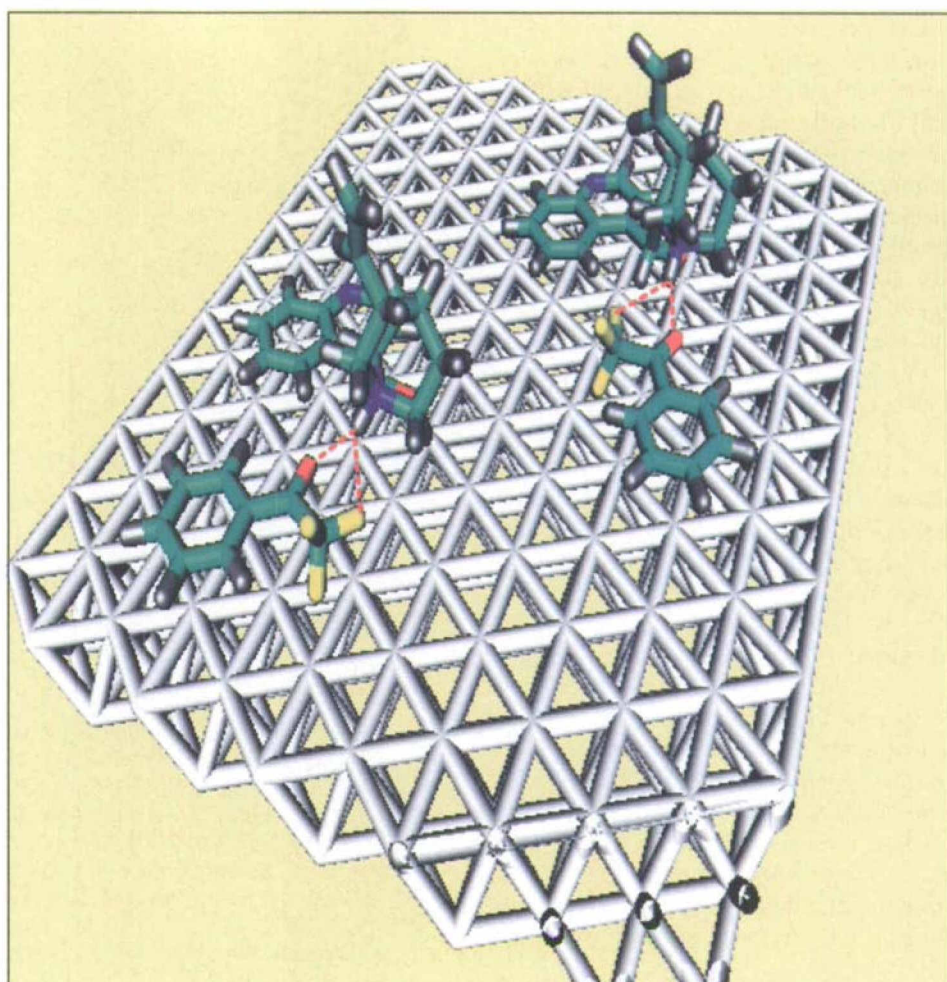


Fig. 3. Structures of diastereomeric interaction complexes between reactant (trifluoroacetophenone) and chiral modifier (cinchonidine) adsorbed on platinum surface calculated by *ab initio* methods. The pro-(*R*) complex, resulting in the (*R*)-product (2,2,2-trifluoro-1-phenyl-ethanol) is shown on the left side and the pro-(*S*) complex on the right side. The hydrogen bond interaction (marked by dashed lines) is decisive for enantiodiscrimination. C is green, fluorine is yellow, O is red, N is blue, hydrogen is gray and platinum is white.

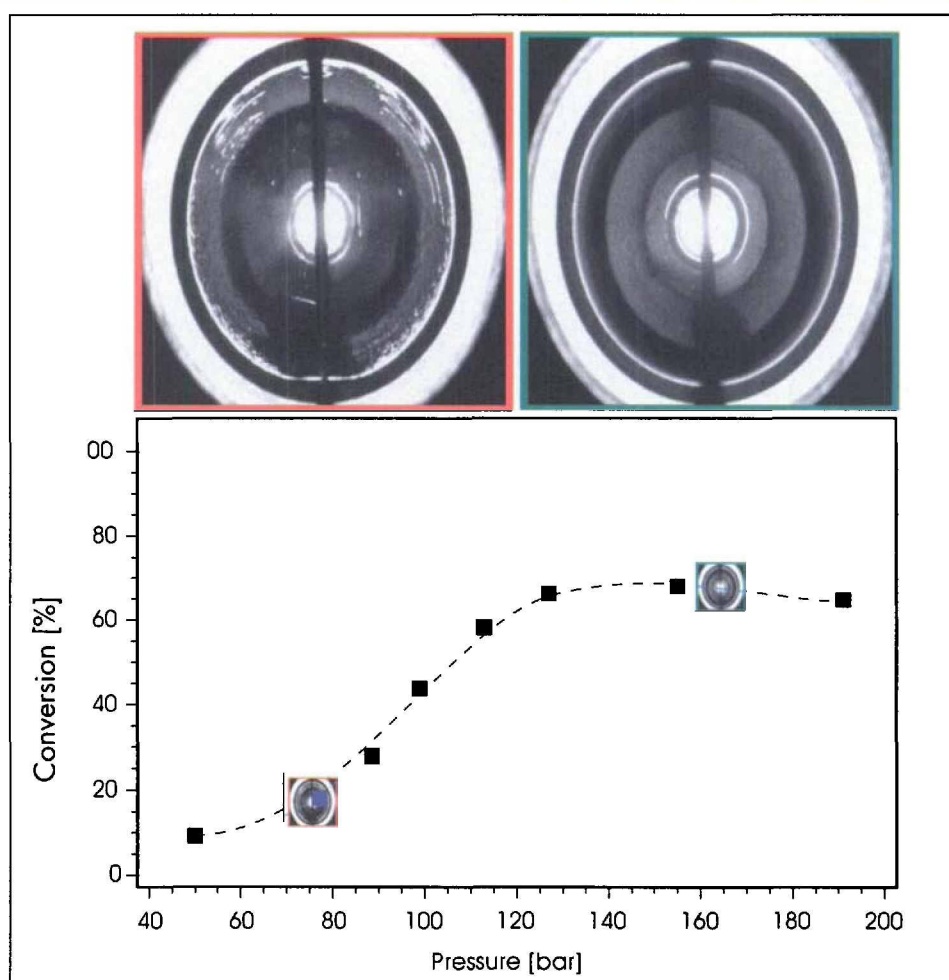


Fig. 4. Hydrogenation of phenylacetylene to styrene in supercritical CO_2 catalyzed by glassy Pd-Zr alloy. Role of phase behavior on catalyst performance. Transition from two-phase region to homogeneous supercritical phase is accompanied by drastic increase in conversion. On top, the phase behavior as revealed by *in situ* video monitoring is presented.

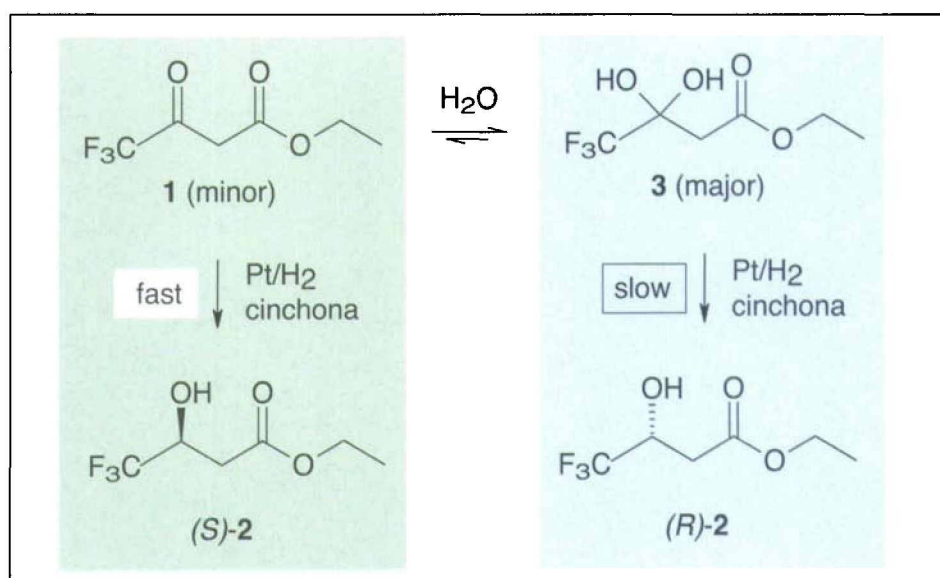
pharmaceuticals. The principal aim is to extend the scientific basis that industry needs for developing new environmentally friendly and economic catalytic processes. Generally this comprises the simultaneous consideration of reaction mechanism, catalyst design, solvent-reactant interaction, mass- and heat transfer, and reactor design. Understanding of the interrelationship of these crucial factors is at the origin of successful development of efficient catalytic processes. Emphasis is placed on answering the question of how chemo- and stereoselectivity in the catalytic system is controlled. An example of this research is illustrated in the Scheme, which shows the interdependence of competing reaction pathways controlling the achievable enantioselectivity in the hydrogenation of an activated ketone. Present research activities embrace the enantioselective hydrogenation of various organic compounds on platinum metals chiralily modified by chiral auxiliaries (modifiers) [4d,6], the chemo- and stereoselective epoxidation of olefins on titania-silica based mixed oxides with alkylhydroperoxides [7], oxidation of primary and secondary alcohols by oxygen in supercritical CO₂ [4c], amination of alcohols and polyols in supercritical NH₃ [4b], and the stereoselective semihydrogenation of triple bonds on glassy metal catalysts [4e].

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