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Review

Heterogeneous Catalysis

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Filling the gaps: The understanding of heterogeneous catalysis is built on a standard model of interface catalysis that was developed from surface physics and theory. This model has significant gaps with regards to transferring knowledge yielded to high-performance catalysts, and approaches to fill these gaps are proposed in this Review.

Heterogeneous Catalysis

heterogeneous catalysis
reaction kinetics
surface chemistry

A heterogeneous catalyst is a functional material that continually creates active sites with its reactants under reaction conditions. These sites change the rates of chemical reactions of the reactants localized on them without changing the thermodynamic equilibrium between the materials.

And yet it is only by studying function that we can understand function, so that the kinetic aspect must be allowed to retain its place and assigned its part in the unravelling of the great mystery
C. N. Hinshelwood, 1947

Measure that which is measurable and make measurable that which is not
Galileo Galilei

1. Introduction

References changed to match German version, please check carefully Catalysis is the science and technology of influencing the rates of chemical reactions. A catalyst is a material that changes the path of a chemical reaction without itself being expended. In this way a small amount of catalyst material can convert a large quantity of reactants and this happens preferentially under milder conditions than would be required by the stoichiometric reaction pathway. If more than one reaction product is possible, the catalyst may change the distribution of these products compared to stoichiometric conversion and thereby allow control of the selectivity of a chemical reaction.

In rare cases, the result of a chemical reaction is only one product. Here, an acceleration of the reaction rate and a reduction of the energy expenditure is desirable, if possible all the way down to the thermodynamically determined energy difference between the starting material and product. Typical examples are the synthesis of ammonia from the elements, the oxidation of SO_2 to SO_3, and the oxidation of CO to CO_2. In the majority of reactions, however, several reaction products are possible and an acceleration of the reaction would lead to the favored production of the most thermodynamically stable product. A family of such applications is the total oxidation of hydrocarbons for energy production or the purification of exhaust gases and of water. However, a product is usually sought which is not the most thermodynamically stable and in fact may be less stable than the starting material. The catalyst then has the task of quickly activating the starting materials while slowing the formation of the most thermodynamically favored products and thereby allowing the generation of less-stable products. The latter should not be further activated by the catalyst, although the catalyst must be potent enough to activate the more stable starting materials. Catalysts must also often prevent reactions to end up with the desired products, so the view that catalysts always accelerate reaction rates is, therefore, a misnomer.

This can be seen clearly in Table, where several reactions have been listed in order of standard reaction enthalpy for the desired reactions and for the undesired, but thermodynamically preferred, total oxidation. In all cases, the reaction product is also less stable than the starting material. The Table combines oxidative dehydrogenation, which necessarily produces water, with the oxidation reactions that result with and without compulsory coproducts. The sum of the heats of reaction for total oxidation develop an enormous driving force with increasing molecule size for the overall kinetics and exemplify the directing role of the stability of the compulsory coproducts.

The Table illustrates the large challenges in carrying out these processes in a technologically effective way. This applies of course to the selectivity of the catalyst and also to the reaction engineering, which must be able to safely transport the heat of reaction away while simultaneously allowing its use for other purposes, as one would envision in a sustainable process.

All of the processes in Table, as well as the general case of a chemical reaction, are comprised of several steps, which can occur one after another or in parallel and build a reaction network. With regard to chemical kinetics, every individual step is itself a sequence of more elementary reactions. These are defined by the property that they describe the change of only one chemical bond in the system. The separation of the complete reaction into individual steps enables the description of the entire process in such a way that each step can be integrated into a microkinetic model with its kinetic parameters (stoichiometry, frequency factor, activation energy).[1] Unfortunately, we have only a few of these microkinetic models.[2] In the cases where they do exist, it turns out that the mechanism that is described by a small number of individual steps conceals kinetics which are complex in comparison[3] to the models assumed. It is possible to arrive at the same macrokinetic observations by starting with differing initial parameters and reaction mechanisms. Therefore, it must be assumed that there is no one single analysis of kinetic data with respect to the underlying basic mechanism.[4] It would, however, be useful if some of the basics of physical chemistry were kept in mind during the selection of parameters meant to describe certain observations: the assumption of the production of peroxide from oxygen as a spontaneous reaction without activation energy[1b] would be, for example, worthy of consideration.

If there is no unambiguous relationship between kinetics and mechanism that can be used to predict the conditions for the favorable evolution of a reaction and the nature of the active centers, it may be an exaggeration to expect[5] the design of a catalyst from which a favorable reaction process can be obtained.[6] This includes the case when the catalyst is formally "designed" with the help of a mechanism postulated from the simplified reaction based on formal reaction stoichiometry. This expectation would need to be fulfilled if we, as is freely opined[7] were truly able to tailor a catalyst.

Advances in theoretical chemistry may be able to make inroads into this area. There are many uncertainties in the analysis of catalytic experiments, be they on high-performance catalysts or model systems, as will be discussed in the present Review. Such uncertainties, often reworded as "material gap," "complexity gap", or "pressure gap", make microkinetic analysis[1a,2f,8] even more difficult, which is already encumbered by chronic underdetermination of parameters in its mathematical models. A complete ab initio based model of a chemical reaction[9] with structural and microkinetic components capable of describing[10] the process as a function of the chemical reaction potential at finite temperatures could be a point of reference for proposing catalytic reactions. However, to reach this target, many hurdles must still be overcome in regard to the choice of method[11] and parameters.[12] Nevertheless, it may be expected that the results obtained up until this point[10c,^13] will become an essential part[14] of catalysis science. From an experimental perspective, the calculation of observable characteristics of the resulting catalyst models would be, in addition to the kinetic parameters, very helpful for building a connection between theory and experiment.

Mainly we use mechanistic conceptions for the interpretive basis of kinetic models derived from macrokinetic principles. These data and there numerical adjustment to mathematical models[2i,15] are well-suited to draw conclusions about the parameters of the process, its scaling in other dimensions, and the construction of chemical apparatus within the parameter range of the observations. Considerably more difficult is the use of mechanistic concepts and observations of nonreacting model systems by using the method of microkinetic modeling to predict catalytic behavior during high productivity. This conjunction[16] has been used in special cases[17] with some predictive power for interface processes, however, a general method as used in molecular catalysis is still not found in heterogeneous catalysis.

To proceed to the single desired product in the case of a general reaction with several possible products, the catalysts can be designed towards a specific substrate such that they will react with exactly one component of the reaction network. The result is a very high selectivity and reaction rate because the catalyst must only accelerate a single reaction step. However, a unique catalyst is needed for every individual step of the reaction network that does not proceed spontaneously. Large reaction networks require complex architectures to obtain the necessary variety of catalytic effects in a limited parameter range of reaction requirements. We can also find this principle in nature. Enzymes[18] are complex molecular catalysts that cause mainly one substrate-specific reaction step in the large networks of the chemistry of life. The extreme specificity of the enzymes[19] working together in a common reaction environment results from their complex hierarchical structures that are composed of a limited number of elements and basic motifs. In organometallic catalysis we choose a different path and use catalysts with geometries, which are simple compared to enzymes and attribute their specific reactivity to a very large number of different ligand systems.

Alternatively to substrate specificity, catalysts can also work in a reaction-specific way. They allow a specific sequence of reactions but are constructed in such a way that they bind the starting materials more strongly than the intermediate products. They then release the desired product by breaking the contact between the catalyst and reactant at a specific point in the reaction sequence and leave the network unfinished. This design principle requires precise adjustment of the interaction between the catalyst and reactant so that the interaction itself adapts with the development of the reaction: the nonreactive starting material becomes strongly bound and its conversion diminishes the binding ability of the catalyst. In this case, we speak of "adaptive catalysts" that are often used in the technology of the chemical industry. Clearly defined reaction conditions ensure that the change in the catalyst--substrate interaction achieved through catalyst adaption quickly affects the formation and separation of the chemical bond between the catalyst and reactant.

We recognize that the effect of the catalyst always requires a chemical interaction with the reactant. This interaction must become more specific as more reaction possibilities result from the activation of the starting materials. Here, the notion that a catalyst does not interact with the reactants, even if it does not consume itself, is a misnomer.

This brings us to a further characteristic of catalysts. They are able to carry out their interactions with the reactants several times and can, thus, achieve a super-stoichiometric conversion. The effect of a catalyst is considered to be more potent if the super-stoichiometric conversion factor for the desired product per unit time increases: the catalyst is then described as being "high-performing" or "active." To achieve an observable conversion in a chemical reaction that can be considered a deviation from the chemical equilibrium of the system, the catalyst itself must also exhibit a departure from the chemical equilibrium of its structure. This departure can be firmly ingrained in the structure of the catalyst, in which case it, as a substance, will no longer be in chemical equilibrium. A kinetic stabilization is required if the non-equilibrium state, despite its involvement in chemical processes, is to remain during multiple repetitions of the reaction. We are then dealing with a static catalyst.

Alternatively, the non-equilibrium state can always be reached anew. In this case, we speak of chemical dynamics[21] as the cause of the creation of active states from the structure of a catalyst that remains stable on average. A realization of such systems could be a steady state between two metal--ligand complex formation equilibria fluctuations about a stable average structure or phase changes in bistable regions. Oscillating kinetic behavior[21i,22] in macroscopic systems is a clear indication that these types of dynamic processes play a role in catalysis with molecular as well as solid interfaces.

It is expected that the performance of a catalyst can be correlated to the extent of the deviation of its structure from equilibrium during a catalytic cycle. However, this deviation will affect the stability of the catalyst and also the length of time it remains effectively active. It is, therefore, not possible to use a high-performance catalyst over long periods of time. Both of the desired characteristics stand in contrast to one another with the consequence that one of the most important tasks of creating new catalysts will be formulating the compromise between these important system characteristics.

Incorporating this compromise can be achieved in the context of different architectures. In doing so, the entire material of the catalyst does not have to be activated. It is enough if a high-energy state, or "active center", is formed out of the temporary combination of stable components from the system matrix. In molecular catalysis, the exchange equilibrium between ligands is the characteristic process. In heterogeneous catalysis, we know of processes between reactants and inactive "catalysts precursors" that take place first at critical chemical potentials. They are, therefore, responsible for the existence of "pressure and material gaps" between experiments at low pressures and experiments at normal working reaction pressures.

A small structural instability can be utilized to gain a weak catalytic effect over a long time period. A prototype is the use of an interface formed from the abrupt change in chemical bonds in a solid phase. A stabile molecule, which forms a free coordination site for the substrate through sporadic fluctuations of a solvation shell would be an example of this, as is the dissociation of an ion pair. A much-used alternative is the stabilization of a reactive, local structure in an isolated geometric site on or in a matrix of a carrier structure.[6,^23] This could be, for example, a step on the material surface[2g,24] or a lattice defect[25] in the surface created either spontaneously as a result of the kinetic details of the synthesis or in a planned way by doping the matrix structure.[23d,^26] Interfaces can also serve as carriers for nanostructures or molecular forms of active components. This common variation[27] is very challenging in synthesis[28] and interpretation despite its conceptual simplicity, in part because a non-ambiguous differentiation between the effect of the carrier and the active component on the desired reaction is often not possible. This subject is central in understanding heterogeneous catalysis,[27a,30] as can be seen in the examples of gold catalysis or the use of polyoxometalates,[32] but will not be elaborated upon here.

A further possibility is the use of a structurally dynamic material. Here the fluctuations about a stabile average structure cause the short and random appearances of unstable, active resonance structures. This alternative may be used frequently, although it is seldom purposefully created. Much more often it is the result of chemical dynamics[33] of catalyst precursors under the specific conditions[21a,34] of their use (the author recognizes that the term "chemical dynamics" is used in many different ways in the literature[35] and for this reason it will be further discussed below).

As a fundamental consequence, the search for such active centers cannot be successful if it is performed in the absence of the reactants. Practically speaking, we can only characterize such systems in situ.[36]

Finally, repair mechanisms can be employed to reactivate deactivated local structures through the exchange of damaged elements by means of self-organization. A variation on this would be the exposure of deeper layers of an active substance by separating the damaged over-layers from the underlying material. Catalysts based on carbon[37] are particularly suitable because their oxidation product is gaseous.

We recognize a variety of different functional concepts that we can use to synthesize catalysts. Unfortunately, the identification of these concepts in a given and empirically found catalyst is demanding under high-performance conditions and often has not been done at all. Much more often we use the concept of empirical discovery and interpret its results in terms of the above-mentioned functions. Such a procedure renders knowledge-based targeted modification, impossible.

2. What We Must Investigate

Catalysis needs analysis on several scales of space and time for adequate clarification. The reason for the necessity of consideration on different scales is due to the large multiplier between the events on single molecules, which is of interest as a basis for a mechanistic description, and the chemically observable events themselves in a small laboratory reactor. There we typically observe the behavior of 10^{20} individual reaction processes and wish to describe them by understanding the behavior of single molecules. Two basic challenges appear from this large scaling factor. First, we must account for all of the necessary steps of a reaction that include atomic processes, making and breaking of chemical bonds, and also energy and material transport. Second, with so many parallel processes, a distribution of properties from relevant structures becomes active at every scale. The uniqueness of the link between structure and function at a purely atomic level, therefore, becomes blurred and must be replaced by statistical analysis. Thus, the identification of the "typical" relevant structure for every individual step of the chemical process becomes difficult. Although we have tools with different resolution to analyze structures on different size and times scales, we still suffer from considerable lack of clarity about the conditions under which we observe a reaction. An example of this is the resolution with which we can observe the energetic relationships at the site of a reaction. We can explain well[24b, 38] both experimentally and theoretically phenomena ranging from strong interactions such as forming covalent bonds to weaker interactions such as vibrations of the participating molecules. Dispersive and weaker long-range interactions are less accessible[39] and we tend to ignore them with the argument that they do not contribute significantly to the total energy of a reaction. Figure 1 shows a schematic energy profile during a generalized catalytic reaction and illustrates why this assumption may be incorrect and that the parameter "energy intensity" of a single step is not adequate for a proper assessment of its relevance.

Figure 1 illustrates further that the treatment of the individual steps needed for the conversion of a chemically observable amount of material is split between the disciplines of chemical reaction technology and physical chemistry, although only the description in its entirety[13b, 40] allows the analysis of a catalytic reaction. Furthermore, the Figure shows that regeneration of the active centers is essential for the catalytic function and, therefore, requires even more attention than the conversion of the reactants. Figure 1B contains a rough overview of the space--time dimensions of a heterogeneous reaction, which may be reviewed if the behavior of a macroscopic reactor is to be correlated with the molecular events at the active center.

The practical success of catalysis for the preparation of structural and functional materials[41] as well as for the conversion of energy carriers[42] leads us to believe that we have quantitatively understood the necessary basic concepts. This will allow us to at least predict which optimal possibilities exist for chemical reactions and which materials can be chosen for catalyst production. If we use the enormous body of knowledge on the subject and the rules that have resulted from it, we should be able to fulfill these expectations using "chemical intuition".

However, if we would like to complement this with a knowledge-based physical theory, we are at best at the beginning of such an endeavor. The final goal of the "design" of a catalytic process based on the knowledge of its atomic details, derived for example from a theoretical description, still lies far in the future. It is safe to say at this point that the current state of knowledge will allow us to begin developing the tools to realize these goals at least in small reaction networks.

In Figure 2 such a small reaction network can be found for the activation of oxygen. The network combines the fields of knowledge of biological and technical energy storage with that of fuel cells and of the environmentally friendly synthesis of organic oxidation products. Although the biochemical reaction route seems to be sufficiently clarified,[43] we are still far from a final explanation of the reaction process in electrochemistry.[44] This is most evident in the synthesis[45] of reactive hydrogen peroxide, although the possible reactions are limited. For the case of the activation of CO,[46] a considerably more complex reaction network also offers plenty of opportunity for further clarification. The reaction network for the formal simple activation of methane[2b,i, 47] is truly complex and at this point still without final elucidation. Much of this unsatisfactory state of affairs results from the assumption that the explanation of a reaction mechanism is unique and independent of the conditions and catalysts used. In the framework of static solid catalysts this expectation may be justified although even there the relative abundance of reactants on the surface controlled by the reaction conditions offers multiple pathways of reaction. We will derive, that this view of a static catalyst is only valid as an idealized boundary case. In situations of high performance, catalysts are not static and hence a coupling of their function to the conditions used will exist. This destroys the ideal expectation of a unique mechanistic description of a catalytic reaction. The formal discrepancies in the literature may thus not be contradictions but rather snapshots of one and the same reaction scenario.

Catalysis is a member of the knowledge and technology family of nanoscience.[27c] Despite its empirical maturity,[48] which makes the main part of the (petro)chemical industry possible, the conceptual strength of catalysis is, in contrast, not strongly developed compared to, for example, semiconductor technology.[49] A basic difference is that the function of semiconductors is connected only with the control of their electronic structure, while the chemical and geometric structures remains static. In catalysis on the other hand, we necessarily influence the electronic and geometric structure during every cycle of the reaction. These functional materials must, therefore, exhibit structural plasticity and be able to change at least part of their atomic structure in a reversible way. Here the danger of irreversible structural changes is a hazard that we observe as a loss of performance[50] (deactivation). The normal description that in "catalysis" a previously formed active center must be reactivated as a center of the same kind may be accurate for static centers in the limiting case of small conversion. However, this is no longer correct for dynamic centers that are likely found much more often under high-performance conditions.

Although the investigation of semiconductors under working conditions is possible in many situations, the so-called "in situ" investigation[21h, 51] of catalysts is highly involved and thus rarely performed. Originally, these types of investigations were started[52] to clarify why catalysts are structurally different after use than their initial state.[53] It was soon seen,[21a, 54] however, that this method could achieve much more by offering insight into the reacting systems of catalysis.

Such investigations combine an analysis of geometric or electric structure with the simultaneous proof of catalytic action. From this, significant methodological challenges follow for the identification of structural characteristics under conditions that are unsuitable for the function of the applied method of investigation. Observing bulk or surface structures at high temperatures and pressures of reactants drives the analytical methods to their physical limits. The multiscale characteristics of the behavior of catalysts are very apparent here in the difficulties associated with measuring kinetic data in situ gathered alongside data from correctly dimensioned laboratory reactors. Thus, it is difficult even under in situ conditions to find evidence to clarify the practical function of a chemical process. The results of such experiments have been tested with different methods of measurement[51d, 55] by which complementary properties are observed. It is then expected that the complete set of results will describe a homogeneous picture of the reaction process if no internal contradictions of the findings occur. The author prefers the view, in contrast to the literature, which recommends integrating different in situ techniques into a single experiment,[37e, 56] of combining several independent in situ experiments with kinetic reactor studies and ex situ structure identification. A coherent description of catalyst function that is reached collectively through such a group of experiments offers stronger evidence for the correctness of the described chemical reaction. Today, such studies are rare compared to the many ex situ or "post mortem" studies documented in the literature, in which the nature of the active states must be inferred after the fact.

Unfortunately, there is a differentiation in the literature between "in situ" and "in operando"[36a, 51d, 57] studies, with the latter having the additional requirement of having to be performed under exactly the reaction conditions applied in the technical operation.[57a, 58] From the perspective of the author, it would help all interested parties if a common definition for all such investigations could be found. This definition could be: *in operando investigations identify the geometric or electronic structure of a catalyst under simultaneously documented production of the desired reaction product.*

The validity of this premise is illustrated by an example. The multielement oxide catalyst "M1" is a potent system[59] for the oxidative dehydrogenation of alkanes. However, the reactive phase is not the bulk structure but is rather a termination phase[60] that is produced under reaction conditions. A critical element of the investigation is the question of whether the termination layer is an artifact of the chosen method or whether it is actually the relevant phase at atmospheric pressure with a constitution that is different from the bulk. The corresponding in situ investigations[61] were carried out with NAP XPS (near-ambient pressure X-ray photoelectron spectroscopy) at 25 Pa.

As seen in Table 2, the selectivity for the oxidative dehydrogenation of ethane and propane were obtained in situ and correspond well to experiments performed in a tubular reactor at normal pressure and flux. It can be assumed from this that the active phase has the same chemical constitution, otherwise the selectivity, which is closely linked to the nature of the active centers in complex reaction networks, would be very different between experimental conditions.

3. Catalysis Science, a Basis

Catalysis science today has a fragmented character. Catalysis as a field of knowledge offers systems and processes in a rational way based on molecular concepts and investigates reactions useful for the chemist in the laboratory or for technological purposes. It is defined by extreme diversity, but also through complexity. Next to the small section of research that looks into this complexity, there is a larger part that concentrates phenomenologically on the production of catalysts with desirable properties without an experimentally and theoretically justified molecular basis. The practical success that undoubtedly results from this approach is a proper justification of the procedure. The great variety of catalysts, in particular molecular catalysts, which have been and will be found, is showcased in many issues of this

Journal. The current chemical industry is also largely dependent on this approach. Its success explains the reticence shown by those regularly employing catalysts to expend excess effort for experimental and theoretical functional studies that cannot be justified with plausible clarification beforehand. A "practical" use derived from such studies becomes untenable, mainly because of the amount of effort involved to overcome the experimental complexities. It is one goal of the current Review to show that we are indeed in possession of a concept for escaping this "trap of complexity". The separation into "fundamentalists" and "pragmatists" in catalysis is superimposed on a separation of the field of knowledge of catalysis itself that results from the nature of catalysts. Significant disciplinary differences are found in catalysis with molecular systems, enzymes, and solid interfaces.

We are striving in different ways, and with growing success,[62] to overcome this fragmentation. Dedicated conferences and research networks[63] are a testament to this. Despite this, however, a holistic conception of catalysis remains an enormous challenge. This may be due to the fact that it is still difficult to amass similar know-how in the fields of knowledge of molecular and interface-specific catalysis; in each of the respective fields, the other field is treated in a cursory fashion. The current Review is devoted to the understanding of the characteristics of heterogeneous catalysis with active interfaces which has grown considerably over the last three decades. This is based on a "standard model" of interface catalysis, which was developed from surface science and supporting theory. This model still has significant gaps with regards to transferring knowledge yielded from weakly or nonreactive model systems to high-performance catalysts. These gaps occur, according to the author, from the static comprehension of the catalyst during a catalytic reaction. From this results a substantial difficulty with the utilization of the comprehensive insight provided by the standard model for the targeted synthesis of technical systems. This Review aims to propose a way to bridge the gaps between heterogeneous model catalysis and heterogeneous high-performance catalysis and, for this, conceptual knowledge is taken from molecular catalysis. This Review is not meant to be an introduction to the different fields of catalysis, but reference is indeed made to the fact that the combined fields of catalysis have the same scientific roots. Here a contribution to an interdisciplinary perspective on heterogeneous catalysis is offered. Many elements which are indeed necessary for understanding catalysis as a whole remain cursory here because of the noncomprehensive nature of this Review, for which the author asks the reader for forgiveness.

4. Heterogeneous Catalysis is Systems Chemistry

The new and still somewhat diffuse term "systems chemistry" denotes[64] the efforts to produce new functionalities through self-organization from a library of different components. In contrast to the use of materials of the highest purity in synthesis, mixtures of reactants are used in the preparatively related systems chemistry that self-organize through mutual influence in such a way that novel functions[65] are produced. The minimization of the total energy (thermodynamic library) or dynamic fluctuations (kinetic pantheon) as well as catalytic effects ("catassembler"[64a]) come into play as the driving force. In inorganic chemistry, this procedure has been described somewhat less to date. The production and preservation of dynamic, active centers in catalysts are taken as examples of such systems chemistry. Under catalytic reaction conditions, active centers are created that then produce products and, thereby, disappear. They are then either re-formed or rejuvenated according to the procedures discussed above. Thus, the library of components is a dynamic one. This is immediately clear for molecular complexes used as catalysts. Central atoms, ligands, solvents, and reactants form a library that is organized according to the laws of association and dissociation of complexes.

This is not so immediately clear in heterogeneous systems with initially clearly stable catalyst materials. However, the concept of systems chemistry provides a clue to why the reaction conditions must always be so extreme. It is not about enabling the activation of an organic substrate, but rather about tuning the dynamics of the catalyst so that active centers are produced and held free of reactants and products. Instead of the chemistry of the desired reaction, the chemistry of the active centers dictates the reaction conditions. This explains, for example, the apparent contradiction of the mild reaction conditions of the oxidation of methane in living systems[66] with the drastic conditions that result in heterogeneous catalysis. The high temperatures are necessary to stop the deposition of carbon on metallic catalysts[67] and the decomposition of carbonates or hydroxides on oxidic catalysts. Maintaining the reactive electronic structure of the catalyst[68] requires the high temperatures[47a, 69] and not the stability of the C-H bond.[70]

5. Case Study: MgO as a Catalyst for Methane Activation

The activation of methane to ethane (ethylene) by selective oxidation (OCM) is a "dream reaction" for supplying the chemical industry with raw materials. It is no surprise that many attempts at achieving this are undertaken with heterogeneous catalysis. Figure 3 shows the number of publications and patents over time as well as a summary of the most successful catalysts.[71] We recognize that the problem has not been solved sufficiently, but also that the research community has left the problem essentially unfinished.

Notable is the observation that there seems to be a "universal" limit to the obtainable performance, even though the reaction is not thermodynamically limited. It can be seen further that very different solutions for catalyst chemistry have been found: acidic oxides, basic oxides, mixtures, and halogen components. The assumption can be made that the cause of the "yellow line" in Figure 3 is the complete consumption of oxygen. Thus, the course of the reaction, constrained by the explosiveness of the gas mixture, is responsible for the "universal" limit in Figure 3, with the local chemistry at the active center only being indirectly related through its low selectivity.

The reaction was studied in detail using the catalyst system Li-MgO and from it a general reaction pathway[72] was deduced. However, discussions of this mechanism have led to controversy of late.[47a, 69b] Initiating the debate was the observation, seen already earlier, that MgO[73] itself also exhibits appreciable activity in the OCM. It was shown further that the Li component is leached out of the catalyst[50b, 74] and then acts as a structural modifier.[68a, 75] Independent of this, the basic conception of the mechanism according to Lunsford should be used as a guide. He postulates that the critical reaction is the activation of oxygen into an atomic radical state ($\text{M-O*}^{\text{<M->}}$). This species can activate methane and convert it into a methyl radical and the then deactivated M-OH can react with oxygen in an unknown way to arrive back at the initial state. The presence of alkali components in many OCM catalysts and the high reaction temperatures around 1000 K may lead to the assumption that there may be reactions of alkali hydroxides with oxygen to form alkali suboxides that serve as catalysts. Unfortunately, experiments in matrices[76] and in high-temperature mass spectrometers[77] show that such reactions do not take place practically, at least for Li, which is important in this case. Also no trace of the presence of LiO was found in the relevant model experiments using EPR.[69b] However, this may be different when methane is introduced into the system. In any case, the possibility of a continuous catalytic cycle with LiO is doubtful, even more so if the simultaneous presence of water and CO_2 in the reaction mixture is considered. It can be found for MgO in extensive theoretical treatments[23d, 26, 78] that if this aspect is disregarded, then the substitution of alkaline earth atoms by Li causes a substantial reduction in the activation energy of the OCM and is in a sense similar to electronic doping; this is valid for the doping of the (100) surface as well as for the edge of a step.

Staying with the basic idea of Lunsford's concept that the activation of oxygen is a difficult step, there is only one possibility if the alkali hypothesis is omitted. The electrons necessary for the production of the reduced oxygen species must come directly from the methane. The participation of MgO as an electron donor in a pure or defect form[69b, 78] can also be discounted. We learn from this about the functionality of the catalyst that comes very close to the original conception of catalysis in general: a catalyst is a material that, through its presence, affects a reaction of two components that would otherwise not react. The MgO acts as a "marriage broker" in the Reaction (1) without itself supplying the electrons necessary for the activation of oxygen.

$$CH_4+O_2 \longrightarrow CH_3{}^*+OOH^* \qquad (1)$$

This activation reaction leads to a series of subsequent steps that we will now consider. First of all, there is the process[79] of the initial step. Necessary for this is the adsorption of methane and oxygen on MgO. This can happen in an advantageous way for methane because $Mg^{2+}O^{2-}$ ion pairs exist on the surface that are not fully coordinatively saturated because of the incomplete coordination at the interface. They polarize the symmetric methane molecule and allow adsorption through a C-Mg and H-O interaction. For an isolated MgO^{*+} radical cation,[47a] this interaction would lead spontaneously to the production of the methyl radical. The altered Mg-O binding relationship will occur preferentially on the (100) plane of a crystal surface. This is not enough, however, for a dissociation of the methyl radical because the rather ionic state $Mg^{2+}(CH_3)^-$ provides a substantial stabilization.

The catalytic effect of the MgO step is found in the fact that an oxygen molecule can bind to the formal ion pair. The negative charge moves to the oxygen and the methyl species, is thereby set free and a hyperoxide radical anion is created. This can then accept the proton from the MgO step edge and also desorb into the gas phase at the high reaction temperature of 1000 K, at which point the following reactions make the reaction pathway difficult to interpret. Shown as Equations (2)--(4), the step edge of the MgO (MgO') causes the following reaction without the participation of electrons from the catalyst:

$$O_2+CH_4+MgO'\rightarrow CH_3{*}+MgO\text{-}H+OO{*} \quad (2)$$

$$OO{*}+MgO\text{-}H\rightarrow {*}OOH+MgO' \quad (3)$$

$$ {*}OOH+CH_4\rightarrow CH_3{*}+2\ OH{*} \quad (4)$$

The appearance of the hyperoxide in Equation (2) corresponds to the reacting species in the mechanism of Lunsford.[72] The catalyst[79] makes it possible for all of the necessary elementary reactions[1b] making up the steps (2)--(4) to be temporally decoupled and to proceed with small activation barriers. This is because the fluctuations of the electronic structure at 1000 K can ensure that the appropriate local electron configuration[47a] will occur before the electron transfer takes place. The hyperoxide radical, or its protonated form, can eventually remain on the surface until, as shown in step (4), another methane molecule is activated which should then lead to the fast decomposition of the peroxide into gas-phase OH radicals.

Evidence for this hypothesis was gathered with EPR spectroscopy: the hyperoxide radical could only be found on an activated MgO if methane and oxygen were present. If the catalyst were to activate oxygen on its own, perhaps through F centers, then the hyperoxide radical would also have to arise without the presence of methane. This experiment,[80] documented in Figure 4, also supports the hypothesis that a high temperature is not required for the activation of methane. Furthermore, the complexity of the spectrum shows that there should be several local environments for the hyperoxide radical and that other surface structures are also reactive besides these steps. However, the same reaction pathways may not be followed by all adsorbates, because their local environment is different.

After this heterogeneous catalytic reaction there is a network of subsequent reactions that lead to the observed distribution of the products CO_2, CO, C_2H_4, C_2H_6, and H_2O. A very simple, possible map of the reaction pathways[2b] is shown in Figure 5. Further radicals appear here and it is not clear[1b] whether all reactions take place in the gas phase, perhaps through interactions with the entire surface of the MgO. The complexity of the reaction progression becomes clear and is shown compactly in summed notation in Equation (8):

$$2\ CH_3{*} \rightarrow C_2H_6 \tag{5}$$

$$C_2H_6 + OH{*} \rightarrow C_2H_5{*} + H_2O \tag{6}$$

$$C_2H_5{*} + OH{*} \rightarrow C_2H_4 + H_2O \tag{7}$$

$$\text{Sum (2)--(7): } O_2 + 2\ CH_4 \rightarrow C_2H_4 + 2\ H_2O \tag{8}$$

For the dehydrogenation of the initially produced methane, there are several possibilities in addition to reactions (6) and (7), which are shown here only for formal reasons. This is evident in the reaction network in Figure 5.

To verify the effect of the catalyst as a facilitator in the targeted reaction (8) five samples of highly pure MgO were produced[81] that differed from each other only in their geometrical structure. Trace amounts of foreign elements were detected in all samples, but no relation was found between their presence in ppm amounts and the observed reactivity. In accordance with the idea[3a, 24b, 82] that active centers are characterized mainly through local electronic conditions, the differing morphologies lead to different kinetic rates for the activation of methane. The structural sensitivity[83] of a catalytic reaction observed here and elsewhere, illustrates the particular bonding arrangement at the active centers. From this observation it was realized further that the terraces of the geometric surface of MgO couldn’t be the location of catalysis because there was no correlation between the amount of terraced surface area and activity. This shows that although adsorption is indeed a necessary condition for catalytic activity, it is not a sufficient condition. The active centers relate to surface defects of MgO, the densities of which differ with the preparation method.

The method of selective adsorption with spectroscopic detection was applied to further characterize these defects. Fine details of the local geometric structure can be observed through analysis of the vibration spectra of adsorbed CO an MgO. After 30 years of detailed study[84] we have amassed a catalogue of vibration frequencies that correspond to specific structures, including a value (2147 cm^{-1}) for the monoatomic step edge of the (100) surface. We deduced this classification from the observation that the adsorption of CO at 77 K on the more weakly coordinated terrace sites (2156 cm^{-1}) and multilayer steps (2170 cm^{-1}) are not observed if the sample is thoroughly cleaned of stable[85] O-H groups before adsorption. The more stable bond of CO on a single step (Figure 6A) results from its twofold coordination (Figure 6B). The number of surface defects can be inferred from the quantitative analysis of the intensity of the absorption bands caused by this specific CO adsorption. This number is characteristic of each synthesis product of MgO (extrinsic) and not characteristic of MgO as a material (intrinsic). Figure 6 C shows a HR-TEM image of MgO nano-crystals with atomic resolution. The single and multistep arrangement in the cubic structure can clearly be seen and also that the single step edges are not the most common type of surface defect. Furthermore, it can be clearly seen that the catalytically relevant centers are few in comparison to the total number of centers that are present on the surface and in the bulk of the nanostructured particle. Thus, the identification of active centers becomes the problem of very high analytical sensitivity; active centers are very rare indeed!

From the coadsorption of CO and methane and quantitative analysis of the resulting spectra with infrared spectroscopy, verification was obtained that monoatomic step edges play an important role in reaction processes at least at the beginning of a catalytic reaction during the first 100 h. Figure 6 B shows an IR spectrum of a coadsorption experiment together with a spectrum for pure methane on MgO. CO blocks the monoatomic step edges selectively under the chosen conditions and significantly reduces the adsorption of methane. The number of adsorption sites can be determined from the difference in the spectrum intensities of adsorbed methane. This is then compared with the catalytic activity in a structure--function correlation. A comparison of the IR spectra of adsorbed and free methane demonstrates the polarizing effect of MgO. Finally, a red-shift of 14 cm^{-1} is observed for the C-H stretching mode and the appearance of a symmetry-forbidden symmetric C-H stretching mode at 2897 cm$^{<M->1}$ can be recognized.

A structure--function correlation has been derived (Figure 7) from the combination of targeted synthesis, investigation of catalytic activity free of macroscopic transport barriers, and the investigation of a specific surface defect. We see that the catalytic function of the OCM cannot be correlated to the substance MgO itself but rather to a specific defect structure. Through the combination of information from Figure 6 B and C, we were able to identify the single step edge as a relevant structure.

It is noteworthy that the selectivity of the reaction to the coupling products takes the same course as the activity. It is uncommon that the selectivity of an oxidation reaction increases with increasing conversion, and this can be seen as a strong indication that the reaction pathway is indeed described by Equations (2)--(4). The catalyst activates oxygen in a way that is not independent of methane because it enables the immediate transfer of electrons from the methane to the oxygen. The mechanistic coupling of the surface coverage of both reaction products near the reaction sites does not mean that, in a macrokinetic observation, we should expect equal formal reaction orders or partial pressure dependencies. Relevant is the presence of species at the surface, which is related to the partial pressures by the sticking coefficients under the reaction conditions. The critical relevance of sticking coefficients will be discussed further below.

The deviation from the correlation of the sample (HT) toward lower values and of the sample (C) toward higher values probably indicates the existence of rough terraces in (HT) and especially smooth terraces in (C). Rough surfaces also result during deactivation of the sample. After approximately 250 h, the reaction stabilizes at a low level, although every system is different, and at this point tends to burn more methane. The corrosion caused by the water[86] that develops during the reaction turns the samples into $Mg(OH)_2$, which then becomes dehydrated. The (100) steps are depleted through this process and surfaces[88] with higher indexed steps[85, 87] are produced and can be described with models using (111) steps. Such steps are polar and, therefore, saturated with OH groups.[85] From their topology, shown in Figure 6 C, it can be seen that these terminations contain exposed Mg centers while their environment is heavily screened by the OH groups. Therefore, it can be concluded that a reaction on such rough surfaces will proceed in another way, and we assume that different reaction pathways will result depending on local surface geometry. This also supports the evidence for the differing local environments of the hyperoxide radical (Figure 4). It can not be ruled out that the reorganization of the MgO ion results in accumulation of contaminants at the surface that through activation of oxygen allows redox chemistry on Mg(X)O centers. Despite intensive searches, there has been no evidence for this.

6. The Nature of an Active Center

The long-held and chemically proven notion[89] that oxide surfaces are covered by dissociated water and are, therefore, protected from the chemisorption of other molecules onto the oxide surface was clearly confirmed for MgO through in situ spectroscopy.[90] This was then further corroborated theoretically[85] in combination with model experiments.[91] From these studies we conclude that the reactive centers of MgO for methane activation are blocked in the presence of moisture. This is another reason for the necessary high reaction temperature that, again, has nothing to do with the stability of the C-H bond in methane. There is fierce competition between the dissociative adsorption of methane at an active center and the corresponding reaction with water. This interaction is expressed in Equations (9) and (10):

$$\text{-O-Mg-O-Mg-} + H_2O \rightarrow \text{-O-Mg (OH)}^{-}\text{-O(H)}^{+}\text{-Mg-} \qquad (9)$$

$$\text{-O-Mg-O-Mg-} + CH_4 \rightarrow \text{-O-Mg (CH}_3\text{)}^{-}\text{-O(H)}^{+}\text{-Mg-} \qquad (10)$$

The reaction temperature must be chosen in such a way that all possible active centers are free of dissociated water but must remain low enough that the water from the reaction does not immediately convert MgO into $Mg(OH)_2$. This works poorly in the case of pure MgO and explains the notorious instability of this catalyst in OCM. It has been suggested that this clarification applies equally to many other oxide systems (see

Figure 3), especially if they contain alkali and alkaline earth components.

Monoatomic steps represent outstanding local geometries for reactions where the dissociation of a stable molecule is important. Centers with two free coordination sites are adjacent to centers with one free coordination site and show a slightly larger separation over the diagonal of the step profile than in the more-stable terrace sites. This concept of active centers[3a, 50g, 92] is fundamental in the catalysis of dissociative reactions. However, it should be stressed here that other possibilities for the catalysis of dissociative reactions exist, also on surfaces, which are not redox active. Doping[93] of planar boundary layers with foreign atoms permanently bound into the material matrix represents such a general possibility.

We return now to the discussion of the case study MgO. Figure 8 shows the significant structures of the reaction pathways over steps and isolated centers. It can be seen that both pathways lead to the desired product CH_3*. The subsequent path to CH_3OO* is easier for the isolated center that, according to the reaction network (Figure 5), can easily lead to over-oxidation of methane. This may be the explanation why the initial activity of MgO and of the analogous CaO[26] occurs through the (100) monoatomic step edges and through smooth inactive (100) terraces. As active centers, the steps are too unstable in moist reaction environments. The chemical dynamics of the MgO converts them into rough hydroxylated terminations on which only a common reaction of O_2 and CH_4 on a single Mg center is possible in the absence of heteroatomic doping.

We also see that the determination of the size of the active center is problematic. In both reaction pathways there are different numbers of atoms involved, although always more than one. Here, long-range influences were still ignored despite their mechanistic importance, for example the effect of the polarization of methane on the Lewis acid--base pair Mg-O.

As a consequence of the possibility of remotely manipulating the active center, which was demonstrated through a model experiment,[93] a concept for the promotion[80c] of the reaction was developed. It is advantageous (Figure 8 (2)) to activate the oxygen atom at a center located adjacent to the adsorption center for methane to impede the production of the CH_3OO^* radical. If this is not geometrically possible on MgO in its stationary state, then a foreign atom must help. This would be a redox-active cation[23d, 26, 30d, 94] such as Fe, Mn, or Co in the MgO matrix. However, it is quickly evident that this is problematic because under the reaction conditions the initially isolated cations aggregate to nanoparticles of the promoter oxide that, at high temperatures, are excellent oxidation catalysts for converting methane into CO_2. This undesired consequence of chemical dynamics can be prevented with the following concept. A gold atom on the surface acts as the targeted anchor for oxygen, exactly as in other applications where the perimeter between the gold and its carrier promote the production of activated oxygen.[6, 23d, 26, 30d, 94, 95] A single gold atom that is activated[30d, 93] into a charged state by a transition-metal atom (or a small cluster of atoms) buried under the surface or in the bulk avoids direct contact between a redox promoter and organic molecules and, thereby, prevents their total oxidation.

Completely "unexpectedly", the reference experiments[80c] gave the result that the monoatomic steps are actually active centers: Doping MgO with gold atoms alone caused the activity to drop almost to zero because the gold atoms accumulated almost exclusively on the step edges and made these inaccessible to the reactants. This is an example of a synthetic concept in heterogeneous catalysis. If the reactivity of a dissociative reaction is to be reduced, this can be achieved with atoms that collect preferentially on step edges (gold, lead, tin, sulfur, etc.) and can be carefully controlled by adding only small amounts at a time. Among other uses, this technique is also employed in the catalysis of selective hydrogenation.

7. A Standard Model for Heterogeneous Catalysis

In the last 100 years, vast strides have been made in the general understanding of the function of heterogeneous catalysts. From measurements of the temporal laws governing catalytic reactions we have proceeded to a quantum mechanical based molecular understanding of the elementary steps and a microkinetic description that is able to explain macrokinietic observations. With this we have clarified the "mechanism" of a catalytic reaction.[17] Unfortunately, this approach is only successful for a limited number of reactions and, importantly, we cannot yet explain the reactions crucial to the transformation of our energy systems toward increased sustainability. Although we are apparently in possession of this fundamental understanding in a quantitative form and also have the "standard model" of heterogeneous catalysis,[22d, 24a, 97] we are not able to treat more than a small number of specific cases. With the word "treat" we understand the quantitative explanation of the reaction pathway under high-performance conditions, the development of a resilient structure--function relationship, and the prediction of possible improvements[41e, 98] with experimental verification. This would characterize the ability of a "mature" scientific field and technology to be equal to the task of meeting future challenges with an adequate set of tools.

It has been suggested that certain areas of homogeneous catalysis have already reached this point; however, whether these most impressive results[41a, 99] are an indication of a fundamental understanding or whether they rather shine light on empirical principles of synthetic chemistry will not be elucidated here. In the following, the focus will instead remain on identifying and understanding the causes for the still-deficient state of knowledge in heterogeneous catalysis. The present discussion is not aimed at creating a model that can be understood well in textbooks[100] and original research papers.[97a, 101] We are more interested in the possibilities for further development that can be obtained through consideration of past advancement.

The roots of the standard model can be found in the ideas of Langmuir and Taylor. Both studied typical model reactions, such as the oxidation of CO and H_2 on Pt or the hydrogenation of CO on Ni, and attempted to formulate a "theory of catalysis".[102] Taylor observed an enormous specificity in catalytic effects. The smallest addition of foreign materials or a pretreatment changed the properties of "hydrogenater nickel". As described in the case study of MgO (Figure 6), he was unable to detect any changes with X-ray diffraction,[51k, 103] a typical bulk-sensitive analytical method. He concluded from this that the vast majority of atoms in catalysts have the same geometric arrangement. This should also be the case for the sample surface. However, because the catalytic action of the samples was clearly different, a small minority of atoms must be essential that he could not detect with his analytical method. This minority, which he called "aristocratic atoms",[104] was introduced as active centers. For these, he developed the idea of coordinative undersaturation and postulated that atoms on crystal defects have fewer neighbors than on average in the crystal and, therefore, can be reactive. The catalytic reaction presupposes adsorption, although this does not necessarily lead to a reaction on its own, a result we were able to see in the case study on methane activation. The degree to which this description of active centers is accurate can be seen in Figure 6 C.

In metallic systems, in addition to ordered surface regions with translational symmetry, there are also regions that are rough and jagged, as suggested by Taylor[102] and illustrated in Figure 9. Together with Taylor’s model, copper nanoparticles that are active in methanol synthesis can also be seen in high-resolution aberration-corrected TEM images.[56e, 105]

$$CO_2+3\ H_2 \rightarrow CH_3OH+H_2O \tag{11}$$

$$CO+2\ H_2 \rightarrow CH_3OH \tag{12}$$

A rich variation of defects in the bulk of the nanoparticles ensures that the surface also contains a high density of defects. Strain and foreign atoms in the defects stabilize this high-energy state in "methanol copper" in such a way that it is not lost during the reaction, even under drastic conditions. This was established by a profile analysis from neutron diffraction experiments[106] under reaction conditions. The diffraction profile of such defect-rich systems can be measurably[107] different[51k, 103] from profiles on defect-free samples and can be used for the quantitative and temporally resolved observation of defect reactivity.

A quantitative confirmation[56e] of the Taylor hypothesis was achieved with these data. The results are given in Figure 10. A family of samples of copper nanoparticles supported on ZnO was produced.[105a, 109] The catalytic behavior in methanol synthesis correlated poorly with the "active surface," as determined with N_2O adsorption,[110] but very well with the stacking defect density in the bulk of the 5—10 nm particles. The terminations of twin boundaries and dislocation boundaries on the surface[56e] causes the creation of stabile steps that are apparently an important requirement for copper’s role as an active center in the synthesis of methanol from CO_2 that follows Reaction (11).

The idea that high-energy sites act as active centers for catalytic reactions is generally accepted today. However, there is still a conceptual problem. There are many forms of high-energy sites at an interface: point and extended defects in the bulk and on the surface, contamination, segregation, and morphological defects caused by strain and stress in the active material or induced by the support, as well as changes in the electronic structure at the boundaries of active materials with and without the influence of the support are only several examples of "defects". Their total number is small compared to the total number of atoms arranged with translational symmetry. As the defects have various structural and electronic local properties (see the exact position of the atoms at defect sites in Figures 6 C, 9 and, 10 C) it is an enormous challenge to identify and then classify them all. We also need a method of differentiation because not all types of defects are reactive. The possibilities of advanced catalyst characterization necessary for such classification are, in principle, available today. However, they are seldom used because the costs of such studies, some of which are illustrated here, are still high and their priority is thus lower than that of the empirical search for catalysts.

We should keep in mind that a general quantitative determination of active centers in heterogeneous catalysts is still problematic today. That was also the case in Taylor’s time and has not improved much since then. However, we are now better equipped to estimate the dimensions and challenge of the problem through the available analytical methods and our knowledge of elementary reactions.[22d, 97a] A motivation to proceed further along this path can be seen in the success of syntheses based on models of high-energy centers. These studies[6, 22d, 24a, 111] have contributed significantly to the establishment of the concept of active centers as the basis for the standard model, although there is little experimental evidence for them during catalytic action.

The practical difficulty of an unambiguous determination of the number of active centers during a catalytic reaction also clarifies the paradox of why we cannot adequately specify the most important characteristic of a catalyst: its activity. Although the number of molecules converted per unit time can indeed be easily ascertained, this can only be done relative to the observable quantities mass, volume, or geometric surface area of the catalyst used. The relevant reference value would be the number of active centers in the system, but this cannot be determined. Therefore, the elegant concept of the "turnover frequency (TOF)", which leads us to believe that we can in fact measure the specific activity of a system, is only an idealization with many sources of error resulting from the necessary assumptions of its derivation. The "inventor" of this concept, M. Boudart, commented upon this problem in his publications[101d, 112] but it did not stop him from making use of his idea with "suitable" approximations.

The seemingly understood concept of the TOF is often found in the derivation of the kinetics of catalytic reactions, in the theory of kinetics, and in the comparison of the effectiveness of often very different catalysts. For this reason we will now discuss several approximations. Unfortunately, a vast number of publications, which use TOF values do not state which approximation was used and, therefore, caution must be exercised when comparing reported absolute values. An approximation that is often used for unsupported metal systems is to use the number of surface atoms as the active site count, which results from the surface geometry (TSA for total surface area). In the case of supported metal systems, the reference for the estimation of the number of surface atoms is an area that is measured by chemisorption[113] or electroxidation[114] of a probe molecule, often H_2 or CO (ASA for active surface area). In only a few cases do we have measurements in which the probe molecule is a reactant and conditions for the adsorption measurements can be chosen close to reaction conditions without actually triggering the reaction.[61, 115] This is referred to as an RSA (reactive surface area) characterization. Despite the plurality of methods and further refinements, today we only have approximate methods to determine the upper limit of the number of active centers of a catalyst.

A notable exception to this statement is the determination of the number of active centers in the heterogeneous catalytic metathesis reaction:

$$2\ C_3H_6 \rightarrow C_2H_4 + C_4H_8 \qquad (13)$$

The catalyst is a highly dispersed MoO_x system that in this case[116] was dispersed on SBA15. Reaction (13) is made possible because a prefabricated Mo-CH_2 carbene enters in the reaction cycle. By capturing the carbene with isotope-labeled ethene the number of carbene molecules present under the reaction conditions can be exactly determined to be 1.5 % of the available Mo centers. In further experiments, the generation of the carbene could be verified through a preceding redox reaction of propene with Mo centers that were initially hexavalent, and tetravalent after the reaction. The geometry of the Mo-carbene is not optimally suited for the reaction, as can be concluded from a comparison of the TOF of 0.15 s^{-1} justified for this case with the reference molecular carbene (TOF of 0.9 s^{-1}). In a following study[117] a combination of in situ NEXAFS and simulation of the theoretical spectrum found that the number of active centers is so small only because they are highly geometrically frustrated with respect to the thermodynamically stable Mo(O_4) geometry. This analysis should be one of the most exact experimental determinations of the number and nature of active centers. It was also enabled by the chance occurrence of several favorable circumstances, of which the low necessary temperature was especially significant. Still unexplained are the dynamics of the generation of these centers and how they lead to the target reaction (13), which is apparently impeded compared to purely molecular catalysis.

8. Quantification of the Standard Model

Despite the difficulty in ascertaining the number of active centers, it is still possible to describe quantitatively the kinetics of specific heterogeneous catalysts. At the heart of the concept[24a, 92a, 96a, 111b, 118] lies the idea that a heterogeneous reaction cannot function without the adsorption of the reactants. Therefore, adsorption and its inverse process desorption are central processes in the kinetics of a heterogeneous catalytic reaction. We have I. Langmuir to thank for the quantitative formulation of this concept. In 1922 he published his detailed "Theory of Catalysis"[119] that makes up the central element of the standard model as the "Langmuir--Hinselwood Mechanism (LHM)". Behind the double name there lies a discovery, already known in the 1920s, that the same reaction (H_2+O_2 over platinum) leads to different kinetics at different pressures and that the catalyst has a "memory" of previous treatments.[120] The missing pieces to the universal microkinetics that would later be designated as the "pressure gap" and the "material gap" were known long before the identification of their causes: "*However this may be, the surface on which reaction takes place is not the same at normal pressures as that at the low pressures of the Langmuir experiments.*"[120] It is also noteworthy that Langmuir states at the end of his publication on the theory of catalysis: *"At low temperatures (300 K to 600 K) rather erratic results are obtained for the reaction velocity with mixtures of hydrogen and oxygen, for the velocity depends upon the previous treatment of the platinum."*[119] This observation did not stop him from assuming a constant number of active centers and a relative independence of their function.

The silver catalyst for the oxidation of methanol to formaldehyde[122] (BASF process) and platinum in the oxidation of ammonia to nitrogen[123] (Ostwald process) illustrate drastic examples of the instability of a catalyst surface. The radical change of the bulk of the metal at a 523 K working temperature, that is far below the melting point, can be clearly seen in Figure 11. The underlying processes are not confined to the reacting interface, but rather also span the bulk of the metals and set free dissolved heteratoms. The holes in the sample arise from gas eruptions, whose reactants are transported by bulk chemistry to grain boundaries.

$$(Ag)_n + H_2 \rightarrow Ag_nH \quad (14)$$

$$(Ag)_n + O_2 \rightarrow Ag_nO \quad (15)$$

$$2\ Ag_nH + Ag_nO \rightarrow 3\ (Ag)_n + H_2O \quad (16)$$

The inclusion of hydrogen and oxygen in metals according to Equations (14) and (15) occurs either during the synthesis (nonstoichiometric reduction) or results from the activation of reactants. It is noted that these types of solid solutions with main group elements are also of importance in other areas of applications of metals.[124]

The standard model supplies the kinetic approach of the LHM with a molecular basis by normatively answering the question of how to count active centers. The single-crystal approach[97a, 127] states that the function of the active catalyst can be described by a single crystal of a suitable material and correct surface orientation, including its steps and boundary atoms.[24a, 92a] By using the concept of the TOF,[101d] the absolute number of the centers is no longer necessary. The single crystal and its translationally symmetric structure allow the application of the tools of surface physics before and after the test[24a] in a catalytic reaction. Adsorption and reaction experiments can be quantitatively described[24b, 38] and the structural sensitivity of adsorption and reaction experimentally and theoretically investigated. With this, the elementary steps can be described with observable kinetic constants.

A resulting kinetic model then describes the process of a catalytic reaction with a theoretical ab initio derived mechanism[4a, 16, 128] and quantitative, uniquely determined kinetic constants. For the classical case of the synthesis of ammonia (Stoltze, 1985 #3600), minor corrections for the original kinetic data determined on single crystals resulted from detailed experiments by several groups, but as it turned out, the corrections had no significant influence on the outcome of the simulations.[129] This was because the changes largely compensated each other. From this work it becomes apparent how difficult it is to bring kinetics and mechanisms into agreement; there are often only ambiguous relationships[4b] even when stringent mechanistic predictions prove pertinent in several cases with limited parameter sets.[17] This conceptual approach of linking surface science with theory was first performed for the synthesis of ammonia from the elements. It ended the debate on the reaction mechanism on this one of the most valuable reactions mankind has developed,[130] and marks the end of long efforts in physical chemistry[131] to reach an understanding and clarification of the catalysis of this reaction.[22d]

A simplified schematic description of a heterogeneous reaction is given in Figure 12. It is apparent that the reactant must initially move to the region near the surface (not treated in the model) before being adsorbed there. This mainly spontaneous reaction (1) from Figure 12 brings the molecule in contact with the surface through the formation of a chemical bond (chemisorption). The process must be differentiated from adsorption by dispersive interaction, which is denoted as unspecific adsorption or as physisorption. Often the molecule needs to be further activated, which necessitates a stronger interaction with the catalyst to surmount the activation barrier (see schematic Figure 1 and for example Ref. [22d]). The position of the molecule changes in relation to the surface, which results, for example, in a side-on interaction ((2) in Figure 12). This process of reorientation[2e, 14a, 34b] requires energy. In addition, islands of the reactants can form if strong bonds are present. Such strong adsorbates block the surface for further adsorption and lateral transport.[132] Finally, the molecule must arrive at an active center to achieve dissociation (the step in Figure 12).

At the active center there must be ample room for both products of the dissociation (3). Two activated atoms must come together in order that a reaction can proceed to a product (4). Then there are essentially three possibilities for the resulting reaction, of which only reaction (A) to the products (5) is given by the standard model. Products are formed which leave the surface through desorption. The standard model also provides for the reverse reaction to the starting materials and to their desorption, and with this the chemical equilibrium can be established. The active center and the entire surface are not changed and are, therefore, ready to host another reaction cycle.

It is apparent that many steps are necessary to complete a catalytic reaction cycle even in this simplified picture that is suitable for describing model experiments on single crystals at low pressures. We can see further that the molecules and atoms will have to move on the surface and that for this reason the available free space on the surface is a decisive quantity for the kinetics of the reaction. The involvement of two reactants clearly makes the entire situation more complicated. As soon as we have familiarized ourselves with the fundamentals of the quantitative model we will be able to discuss the questions central to catalyst design: How does the nature of the surface influence the availability of free sites under a given set of reaction conditions?

A classical example for the process shown in Figure 12 is the decomposition of NO on a stepped Ru (0001) surface:

$2\ NO \rightarrow N_2 + O_2$ (17)

Figure 13 shows the result. A monatomic step as localization for the dissociation of NO molecules is evident. The dissociation on the step leads to a distribution obeying a diffusion law for nitrogen atoms (gray squares) and to the nucleation of an oxide phase removed from the step (dark cluster). The conceptual similarity with Figure 12 can be seen. Directly underneath some of the step edge atoms are metal atoms (type I) while underneath other steps the underlying atoms are somewhat more distant. We thus identify two "types" of atomic steps even in this very simple geometric situation. For this reason the oxygen atoms form a row of "oxides" on the type I steps which become contaminated (at 200 K), while the oxygen does not adsorb on the type II steps so that they remain active.

In the standard model we assume a materially unchanged catalyst. In many cases, however, an activated molecule can react irreversibly with the catalyst and modify it. The reaction pathways (B) and (C) in Figure 12 indicate that deposit layers can be formed. Such processes often begin at high-energy centers and a slight deposit layer (approximately 5 % of a monolayer) can completely stop the reaction because steps (3) and (4) in Figure 12 are prevented. Following reaction pathway (C) from Figure 12, an activated atom can also penetrate into the bulk of the catalyst instead of desorbing into the gas phase. The product (7) is a chemically and geometrically modified catalyst that does not fulfill the condition of remaining unchanged throughout the process. Neither reaction pathway (B) nor (C) is considered in the standard model, which leads to the appearance of the "gaps" between model and high-performance experiments.

Model conditions are often chosen so that only a minimal reaction occurs and the possible readsorption of the products can be excluded. Despite this, a modification of the catalyst[133] either during or after the reaction was observed by surface analysis. Remarkably, this change was not taken into account in the quantitative and theoretical treatment. Either the observation was ended after the conversion quantities were still so small that they could be ignored or they were regarded as insignificant. This may be motivated by the difficulty in determining the exact chemical composition and the coordinates of the surface atoms in modified catalysts. The very goal of model experiments is to carry out a catalytic reaction under reactions where the coordinates of the participating atoms are known or can be determined to gain atomically precise insight into the reaction.

The quantitative standard model was derived from the qualitative model shown in Figure 12. This does not need to be completely examined here, as there are textbooks[100, 133a] and publications[134] dealing with the subject. Here, the intention is to discuss simplifications found in the derivation leading to the quantitative picture. With this we identify, at least in part, the source of the gaps between the standard model and experimental results, and we can discuss the application of the model to high-performance systems. We start with the very simple model reaction:

$$A+B+cat.\rightarrow AB+cat. \qquad (18)$$

The first simplification is that the catalyst, "cat.," possesses active centers that react equally with A and B. Thus, there is only one kind of active center that effects both adsorption and reaction. In the introduction we already mentioned the term "structure sensitivity[132d, 132e, 135]" that stands in contrast to the "universality" of active centers in Equation (18). Exceptions to this are reactions whose kinetics depends on the specific adsorption of a single component (A) because the other component (B) adsorbs spontaneously and is easily activated. An important example of this is hydrogen on noble metal surfaces. Here the generation of a single product depends only on the centers that bind and activate (A). This case appears in important reactions of organic hydrogenations, the reduction of nitrogen to ammonia, and the oxidation of SO_2 and CO. Even more kinetically simple are reactions that are catalyzed by solid acids. They obey either Equation (18) or are, like isomerization, formally even more simple ($A + cat. \rightarrow B + cat.$). The actual reaction sequence and the nature of the active centers are, however, extremely complex[136] and are not discussed further here.

The simplification about universal active sites does not apply to many selective reactions. Either the active centers change their chemical reactivity during the reaction (adaptive centers) or there is a set of centers with differing functions, which act together (polyfunctional catalysis). Both cases can be basically described with more-complex Langmuir--Hinshelwood mechanisms (LHMs), but are seldom considered. A simplification restricted to a specific type of active center is also common among catalyst manufacturers if they wish to emphasize the specific characteristics of "single-site" catalysts.[5a, 5c, 62d, 137] Their active centers are "all-rounders" that must be active in many different elementary steps.

We will now formulate a LHM for reaction (18) and consider only the reactions of the starting materials with each other. The intermediate steps of adsorption and activation, which we discussed in Figure 12, appear in Equations (19) and (20).

$$\mathrm{A}+{*}\rightleftharpoons\mathrm{A}{*};\ k_{19}^{+}\ k_{19}^{-} \tag{19}$$

$$\mathrm{B}+{*}\rightleftharpoons\mathrm{B}{*};\ k_{20}^{+},\ k_{20}^{-} \tag{20}$$

$$\mathrm{A}{*}+\mathrm{B}{*}\rightleftharpoons\mathrm{AB}{*}+{*};\ k_{21}^{+},\ \mathrm{k}_{21}^{-} \tag{21}$$

$$\mathrm{AB}{*}\rightarrow\mathrm{AB}+{*};\ K_{22} \tag{22}$$

In this notation the rate constants for the forward and reverse reactions of the elementary steps leading to the generation of the products are given. Desorption of the products in step (22) is presumed to be irreversible and thus becomes kinetically irrelevant. This means that the interaction of the products AB with the catalyst is weaker than that of the products. This is almost always valid for the CO_2 molecule that results from CO oxidation, except if carbonates can be formed.

More problematic is the further assumption that the active centers (*) remain unmodified throughout the reaction and that potentially necessary regeneration steps take place so fast that they are of no kinetic relevance. In the case study of methane activation we saw that this is also applicable, for example, in the case of metallic catalysts for CO oxidation.

However, there is a large and technically relevant class of reactions to which this simplification does not apply. These are the oxidation reactions. Here an oxygen atom is removed during the reaction from what is always a multiatom active center and/or oxide ions become hydroxy groups by accepting protons from the starting material. The regeneration of the active center is seen as rate-determining, while the generation of the product is not assumed to be kinetically decisive. This is, in any case, what is understood with the term "Mars-van Krevelen Mechanism (MvK)". The reverse assumption, that the reoxidation is fast while the product generation is slow,[138] is also described by this acronym. The apparent contradiction can be clarified by observing that the reaction rate is strongly controlled by the concentration of water in the reaction mixture and, therefore, depends on the exact conditions of the measurement, which leads to difficulties in making general statements[139] about the process. A further discussion can be found in Ref. [140]. However, the original publication,[141] from which the process gets its name, does not contain this interpretation. Rather, the authors extended the mechanism in Equations (19)--(22) by an additional step that was justified by the regeneration of the active center.

The LHM approach in Equations (19)--(22) also requires that the stoichiometry with respect to all participating atoms and the exchanged charge equivalents remains unchanged. This will lead to additional reaction steps in the case of more-complex molecules and is the reason why Equations (19)--(22) often describe elementary steps.

Now we will formulate the corresponding reaction rate for every step in the LHM approach in such a way that they are proportional to the total number of active centers. We take from Langmuir’s theory of catalytic reactions[119] that for every participating species, the number of occupied sites on the surface results from the sorption steady state under reaction conditions. For molecular adsorption of A this would be:

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A} \tag{23}$$

while we obtain

$$\theta_B = \frac{\sqrt{K_{B_2} p_{B_2}}}{1 + \sqrt{K_{B_2} p_{B_2}}} \tag{24}$$

for the dissociation of a diatomic molecule. The quantity θ denotes the degree of coverage, and p stands for the pressure or, to be more precise, the chemical potential of the starting materials and products. The constant K specifies the sorption steady state as the quotient of the rate constants for the adsorption and desorption of the material in question.

In some cases setting the pressure or concentration in solution can be equal to the chemical potential, which can lead to significant errors. A drastic example is found in assuming that ammonia can be viewed as molecular nitrogen when describing a reaction of atomic nitrogen. On many surfaces ammonia decomposes easily into nitrogen atoms while molecular nitrogen is much more stable. The effective pressure for a nitridation reaction from either ammonia or from dinitrogen is then different depending on the decomposition constants. Ertl used the term "virtual pressure"[142] to describe this. For the case of Fe_4N[142] 3×10^{-11} bar ammonia has the same effective pressure as 3100 bar dinitrogen at 670 K.

Now we can specify the reaction rates for every partial step. For this we need the additional simplification that we are interested only in the number of reactions per unit time and per active center (TOF) and not in the actual number of centers themselves. This simplification is, however, not absolutely necessary because we can formulate the following equations in such a way that the total number of active centers appears explicitly as a parameter. However, this leads then to the problems of the absolute determination of the active centers described above, which is ignored in many observations involving reaction kinetics. Commonly an approximate value, the number of surface atoms per close-packed metal surface area, is taken for this parameter (ca. 10^{15} cm^{-2}). However, it is possible to formulate this significantly more precisely if an estimate for the number of static active centers is used, for example, the number of step edges.[2g, 96, 130a]

The following set of equations connects the reaction rates for every partial step with the essentially independently determinable coverage of the relevant species.

$$r_{19}=k_{19}^{+}p_{A}\theta^{*}-k_{19}^{-}\theta_{A}$$

$$r_{20}=k_{20}^{+}p_{B}\theta^{*}-k_{20}^{-}\theta_{B}$$

$$r_{21}=k_{21}^{+}\theta_{A}\theta_{B}-k_{21}^{-}\theta_{AB}\theta^{*}$$

$$r_{22}=K_{22}\theta_{\mathrm{AB}}-K_{22}p_{\mathrm{AB}}\theta^{*} \quad (25)$$

From this we see that the knowledge about the degree of coverage of the participating reactants, which can be determined by surface science experiments makes the equation solvable. In this way kinetics can be calculated through experimental results that characterize the sorption of relevant species by using the many different methods of surface science or of other methods in the arsenal of physical chemistry and under many possible reaction conditions.[2e, 3c, 22d, 24a, 143] Then we can verify the reaction mechanism that determines the exact form of the system of Equations (25). After we have identified the reaction mechanism with absolute certainty we can, alternatively, assess the assumption about the nature of the active centers. This is contained in the values for the degree of coverage obtained from the specificity of adsorption/desorption. However, whether we can unambiguously obtain a reaction mechanism from kinetic data has already been called into questioned and is, for example, also discussed using the example of the oxidation of HCl.[50i]

If the sorption characteristics of a reaction system are measured exactly over a range of reaction conditions, it is observed that the degree of surface coverage depends not only on the chemical potential but also on changes in the specific bonding ability of the catalyst with the surface layer. This is closely related to the dynamic of sorption[34b,^144] and necessitates special care during analysis.[145] The result is, also due to this dependence, that the value of the analytical characterization of a reaction mechanism becomes unclear[4b] if a range of reaction conditions (temperature, pressure) is considered and not just one specific combination of these. An instructive illustration for this is a study[146] on the synthesis of methanol from either CO or CO_2 as the carbon source. Under conditions of high performance, the carbon source is CO_2 [Eq. (11)], whereas at a 50 K lower temperature and "differential reaction conditions" CO is the carbon source for methanol [Eq. (12)]. Different intermediates will be found. The controlling factor for this is the surface coverage of water. The analysis is involved in the context of the present discussion as several parallel and consecutive reactions (synthesis of methanol, water gas chemistry) contribute to the net observed conversion. Furthermore, the assumption that all reaction products desorb easily from the surface and that no readsorptions occur in the reaction system is invalid.

Enthalpies of chemisorption as a function of surface coverage can be obtained nowadays[147] with high precision thanks to single-crystal calorimetry. A precise determination of energy data can be related to a precise determination of the surface coverage, including the structure of the adsorbate. The unfortunately very involved and highly tricky experiments are invaluable reference data,[6, 30d, 148] for calibrating concepts and theory of chemisorption. In some cases such data were used to decipher the reaction mechanism along the procedure outlined with Equation (25).

Sorption microcalorimetry on powder samples is noticeably less precise (in the investigation of the degree of coverage) but still applicable to high-performance catalysts. The measurement requires extreme caution and experimental precision,[149] but data for kinetic analyses can be obtained for a large array[150] of systems.

As a rule, however, the necessary observations are not available,[2i] but we have only estimated the corresponding parameters. Quantum mechanical methods in combination with quantitative measurements[151] have been applied with great success in catalysis research to calculate ab initio relevant parameters for elementary step reactions. This has enabled us to establish the solutions to kinetic equations on a new basis.[10c, 152]

Furthermore we know that the sum of all centers must be equal to one. To be able to finally solve the system of Equations (25), we will introduce a series of further simplifications. We will assume that the reacting system is in a stationary state. In this way all surface coverages and reaction rates become independent of time. There is, thus, no chemical dynamics from activation and deactivation of the system. This can be ensured in an experimental setting, but only with great effort. We also assume that adsorbed species do not impede one another or tend toward association (see Figure 12 (2)). Moreover, we exclude the possibility that the active centers differ amongst themselves or when in contact with reactants: the surface is locally homogeneous.

Another significant simplification is that we will not make any statements about the spatial coordinates of the reaction rates in a reactor. The reaction at all positions of a reactor proceeds at the same rate and form the same products because the chemical potential or the sum of the starting materials and products is assumed to be the same everywhere.

This is where chemical process engineering comes into play. Reactors can be planned in such a way that these conditions are nearly fulfilled: such a "stirred-tank reactor" can actually be approximately realized. Much more often, however, in laboratory experiments, its idealized form is assumed as a starting point. The model is applicable in situations with small conversions (differential reaction conditions) so that this simplification can indeed be helpful. This is also the case in many model experiments of surface science. If, however, attempts are made in such experiments to close the pressure gap and achieve high reactions rates, significant complications result with the identification of active surfaces and with the validity of the approximation of homogeneous[153] reaction rates.

These simplifications are, however, not valid in the vast majority of all practical reactors and laboratory experiments aiming at measuring catalytic performances.[13b, 154] Rather, considerable gradients in the chemical potential are present along the typical packed bed of a catalytic experiment. As many reactions have an associated heat exchange, energy flux gradients appear parallel as well as perpendicular to the central axis of the reactor and have a significant effect on the chemical potential. Further complications are the inhomogeneities on the scale of the granular packing ("split solid") as well as of the internal pore structure of the material. Considerable experimental finesse[155] is needed to exclude all of these factors and obtain kinetic data free from their influence. This applies to the synthesis of the samples used that must be homogeneous in structure and reactivity as well as to execution of the experiments themselves. If this is not the case and error-laden data are used for the catalytic analysis using Equation (25), the resulting parameters will be largely inaccurate and also, accordingly, the corresponding conclusions. This situation has resulted in the large "diversity" of "characteristics" described in literature and complicates the contribution from dearly won experimental observations to expanded molecular knowledge.[71] The examples[13a,^156] show that the required quality of work is indeed obtained from a series of reactions in an integrated approach accompanied by the corresponding conclusions that are in accordance with the principles of chemistry and need no "special characteristics" for their interpretation.

The influence of the gradients throughout the reactor will be especially drastic if the reaction proceeds very quickly and with high reaction enthalpy. Partial oxidations are examples[157] of such reactions. Data allowing the calculation of the degree of surface coverage and, therefore, input for mechanistic considerations are obtainable from measurements of profiles of the temperature and material composition in novel profile reactors[51h] or tap reactors. Such data show how far real reactor experiments currently are from the original underlying assumptions. Chemical engineering science is engaged extensively in the quantitative treatment of these effects; it is important to realize for the current work that it is a considerable task to interpret kinetic data from a catalyst in a given reaction for the purpose of supplying a basis for a discourse on molecular processes.

Up until now we have assumed that the catalyst itself does not change during the reaction. A well-known example of this is the catalyst used in ammonia synthesis. However, this is not always the case in the oxidation of CO with oxygen, as was shown spectacularly by Ertl[22d, 158] through the nonlinear behavior of the reaction at low pressures. Nonlinear changes also appear at higher pressures in this reaction, which can even be in part detected as periodic changes of the oxidation state of the catalyst.[159] In the meantime, such significant periodic structural changes[160] have been found in whole series of reactions.

Model conditions are often chosen such that only a minimal conversion is obtained and the readsorption of the products can be ruled out. However, this "plausible" assumption is often incorrect. It influences the analysis of sorption and reaction data as can be seen in the example of the careful analysis of the sorption of dinitrogen on an ammonia catalyst (which would be referred to as a chemically "harmless" case).[4a, 141, 161]

Despite being under "model conditions" a change in the catalyst during or after the reaction was found by surface analysis. A concept central to this is the adsorbate-induced restructuring.[133b,c, 162] By using surface-sensitive methods before and during or after the reaction, it could be established that the surface structure of the catalyst was significantly altered. This has considerable consequences for the adsorption ability (sticking coefficient, geometry of the adsorption centers) and, thus, for the catalytic reaction itself. This observation is a deep-seated concept in the surface science of catalysis and explains, as given above, the necessity of in situ structural investigations. The simplification given earlier that the active and initial states of a catalyst are the same, the latter being well understood, is not applicable in many cases.

9. Case Study of the Dehydrogenation of Ethylbenzene over Iron Oxide

The dehydrogenation of ethylbenzene (EB) to styrene (St) is a large-scale technical reaction for the manufacture of a monomer for polymer synthesis. It takes place using iron oxides as promoters at high temperatures (873 K) with the addition of a 10-fold excess of water vapor. This is an endothermic reaction ($\Delta H_f 298 = +123$ kJ mol^{-1}).

$$C_8H_9 \longrightarrow C_8H_7 + H_2 \qquad (26)$$

The analysis of the role of the catalyst[164] shows that the active phase is a ternary iron potassium oxide ($KFeO_2$) that is metastable under the reaction conditions and becomes Fe_3O_4 and KOH through a complex reaction sequence that may be influenced by promoters. Parallel to this, the reaction suffers from carbon deposits resulting from the polymerization of the products.[165] This reaction is limited by the on-line gasification of carbon with water vapor, which is supported by the potassium promoter.

To decode the complex relationship between the dynamics of catalysis chemistry, the chemistry of unwanted deposits and the actual target reaction, an extensive campaign[166] was mounted for the manufacture and application of planar model catalysts. Another goal was to answer the question of why an "organic" reaction must be carried out under such harsh conditions. Thin single-crystalline films of model oxides were made and characterized structurally.[167] The experiments were used to determine the adsorption parameters of starting material (EB) and product (St) with these samples without problems related to transport limitations. These data enabled an estimate of the actual coverage under reaction conditions, and the results are given in Table 3.

The data show very clearly why the ternary oxide is superior: the potassium is not only a promoter but also an essential co-catalyst that mainly ensures desorption of the product and, thus, access to the active sites in addition to serving many other functions. At the same time a clear and desirable excess of the starting material relative to the product exists on the $KFeO_2$ surface that minimizes not only unwanted polymerization but also improves the reaction rate because the likelihood of contact between the starting material and active center increases.

According to the procedures discussed above it would be important at this point to measure the kinetics of the reaction of a model system experimentally under relevant conditions (atmospheric pressure, 900 K, excess of water vapor). However, this turned out to be a complex challenge that could only be solved after significant methodological developments.[166a,h, 168] The most important results are given in Figure 14. The first step was to build a microreactor[169] from materials that could withstand the conditions of the reaction and enable the transfer of the model sample into the reaction atmosphere. To eliminate transport limitations, a reactor concept was chosen that was able to reach the required temperature by laser heating. The entire apparatus then needed to be integrated into a ultrahigh vacuum (UHV) set-up to be able to perform the necessary structural analysis and manufacture the samples with the required quality. Figure 14 A shows schematically the construction of the microreactor.

It was seen very quickly[166g] that the single-crystalline surface showed no reactivity in the target reaction. We observed[166d] an induction period after which the activity grew strongly. The analysis of the samples after the reaction showed very clearly that the single-crystalline structure was lost and that small and rough oxide islands had formed from the initial thin and flat layers on metal substrates (Pt, Ru) that became covered with carbon during the experiment. LEED images in Figure 14 B give an impression[166a] of the massive reconstruction: after the reaction only the weak reflections of the metal substrate can be seen.

The Fe_3O_4 phase turned out to be completely inactive, although in real samples it is the predominant phase after the reaction; it is a deactivation product. The Fe_2O_3 phase is, on the other hand, very active, as can be seen in Figure 14 C. The initial rates that were observed for the target reaction[170] are approximately 1000 times higher than is measured on technical samples under stationary conditions. The model reaction shows us in a somewhat unexpected way that technical catalysts have still significant potential effectivity in typical tubular reactors even without a phase change away from iron oxide. The reason is probably found in the instability of the active phase at the local chemical potential (too reducing) in the tubular reactor. The measurement in Figure 14 C1 shows that the phase is not stabile and that it develops into a stable permanent state with low activity; in agreement with the results from other groups[171] this was identified as an oxide phase completely covered by carbon. It can be concluded from this that the carbon deposits lead to a modification of the catalyst that, after a short highly active period in the 10-fold excess of water, is composed only of carbon. The instability of the reactor operation that is often observed in practical operation can be clarified as an on-and-off behavior of the catalyst between an oxidic highly active state and a carbon-containing state of low activity.

The product, hydrogen, controls the redox state of the catalyst with the admixture of water working in opposition. This occurs through a reduction of the chemical potential of hydrogen and because the water acts as a source of oxygen through catalytic splitting of water. This oxygen, present in small quantities, does not burn the product St, but instead gasifies the deposited carbon. The high reaction temperature can be explained by two factors. First, the activation of the solid-state reaction for the in situ creation of the metastable iron--potassium phase and second the necessary high reaction temperature for water splitting and the gasification of carbon. The endothermic character of the target reaction does not justify the high temperature.

An extensive amount of new chemistry[37c, 172] results from this picture. It leads to a new concept of active centers for the oxidative hydrogenation of EB to St on nanostructured[173] carbon. By minimizing the transport barriers for material and energy (nonporous catalysts,[171] heat conduction of graphite) a stable performance[172a] and a high selectivity of the reaction could be obtained, even in the presence of large amounts of oxygen. In this reaction, process water does not have to be added and the reaction temperature can be reduced by 300 K.

If a small amount of oxygen is added to the reaction mixture in the dehydrogenation reaction over iron oxide (1:10), then a very stable and high activity[174] is observed (Figure 14 C2) that was found to be reversible by turning the oxygen source on and off. The scale of the addition of oxygen was chosen according to Equation (26), so that hydrogen from the reaction could be burned and the reduction of Fe_2O_3 to Fe_3O_4 was minimized. In this way, the generation of carbon was completely eliminated, with the reasons, not completely[175] understood, being found in the defect structure of the oxide. From Figure 14 D it can be seen that this conclusion from a model system can be reproduced[174] quantitatively on a real-world polycrystalline system (a pressed powder pellet).

Furthermore, it was shown[170b] that the addition of potassium to iron oxide has the same stabilizing effect as the addition of oxygen: the catalyst is significantly more stable against reduction. However, the potassium phase is not stable against hydrolysis and, therefore, loses its effectivity with time, as has often been seen in real-world systems.[164b,c] The beneficial effect of adding steam to moderate the reducing effect of the product water has a simultaneous detrimental effect on the stability of the bulk catalyst phase. Such antagonistic behavior is typical in complex empirical catalyst formulations without a clear understanding of the functional interrelation of the components. The model investigations show that the effect of the potassium can be imitated by the addition of the "co-catalyst" oxygen that eliminates the damaging hydrogen to avoid a destabilization of the main catalyst. The implementation of these model results in a real-world situation that is demanding because transport processes in actual large reactors, discussed above, as well as oxygen dosage in amounts ensuring that organic species are not burned are problems that are not solvable at this time. A completely new development of the reaction process would have to be started and the catalyst would certainly have to be equipped with oxygen storage properties to make it stable against local fluctuations in oxygen partial pressure. An alternative would be the realization of carbon-based catalysts[37b, 176] whose specific activity[173] need, however, to be improved.

The depth of the qualitative and quantitative insight already gained was used to design a microkinetic model[177] of the reaction based on experimental observations. In contrast to earlier attempts that followed the approach given above with an active center of unspecified nature, in this study a model of a catalyst is used that boasts both oxidic as well as carbon-based active centers with the generation of these active centers explicitly taken into account. A verification of the conceptual veracity of this model was obtained by the successful description of the forced change in the catalyst from oxidic to carbon-based through a nonstationary reaction process.

The example shows that valuable, fundamental insight into complicated technical reactions can also be obtained through model experiments. Apart from new knowledge, this insight also provides a rational basis for new fundamental developments. The latter may be motivated by the realization that the current catalysts are lagging far behind the ideal possible performance and lifetimes. However, significant efforts in synthesis as well as in functional verification of the realization of the concept for a given catalyst will be required.

10. Catalysts Are not Static

If we return to our fundamental considerations, we see that the understanding of dynamic proceses in catalysts has been analytically ensured,[21a, 178] but for the most part have not been treated in a general quantitative and theoretical way. The prominent exception, which is widely regarded as such, is the treatment of the dynamics[21i, 158b] of the CO oxidation under the special conditions of a periodically oscillating reaction process. In the general catalysis science no consequences were drawn from this; either the observations were stopped after such small amounts of conversion that the effect of the change was ignored or the dynamics were seen as insignificant. On the other hand, a prominent exception[11a, 21a,f,g,j, 179] to this assertion are the catalysts for partial oxidation that change profoundly[140c] under the conditions of their use and can reversibly offer oxygen from their bulk or surface.[180]

One of the reasons that dynamic effects are so underrepresented in kinetic treatments of heterogeneous catalysis is that the theoretical and quantitative treatment of such changes requires an exact description of the atomic structure of the modified catalyst. This boundary condition has a greater limiting effect than the technical difficulties on the transfer of know-how from model conditions to high-performance conditions in atomically precise catalysis research. However, if this transfer is actually successful, precise analyses grounded in simple facts can be obtained for seemingly complex observations.[6, 14, 30d, 83a,b, 144, 181] It is an invaluable advantage of these studies to be able to greatly simplify the phenomenological diversity of possible explanations, such as "special surface state" or "remote control of the reactivity".[182]

Neglecting structural changes is usually accepted as an approximation, as is limiting the investigations of the reactivity to such an extent that at least no change of the bulk structure occurs. This is not to be confused with the very deliberate adsorption-induced reconstruction[133a] of metal catalysts. Conducting model catalytic studies under the most realistic conditions possible while stopping the chemical dynamics[183] is very well justified by the gain in quantitative insight. However, the results of these studies should not be applied lightly or uncritically to high-conversion catalysis or high-performance catalysts.

Thus, a gap appears in the transfer of knowledge from model experiments to the analysis and also the further development of catalysts with high performance. Such systems correspond weakly to the boundary conditions of model catalysis and their theoretical analysis in the framework of the LHM approach. Therefore, with few exceptions, such as ammonia synthesis,[2j] essentially no general relevance of the results from model experiments can be expected. Two strategies have been developed to close this gap. One approach uses traditional surface science and extends the analytical methods to application under high pressures from several mbar to several hundreds of mbar. For this purpose, typical methods such as atomic force microscopy, sum frequency microscopy, and NAP XP spectroscopy are employed.[24a] Model catalysts in the form of single crystals were used and experiments were developed for their investigation under relatively high "ambient pressures" (200 mbar). Significant structural changes[163a, 184] of the model systems were observed with differing interpretations given.[185] In a well-known case with CO oxidation at high pressures[163, 184c] over Pt crystals it could be shown that the changes were due to the introduction of small amounts of impurities, such as water, through the reaction gases and not because of the pressure of the reactants per se.[153a] However, the observation of the effect of the trace gases was important because it was understood that the stability of the reacting surface is determined by many factors that are often not easy to control. A further uncertainty develops if structural analyses under ideal very clean conditions are to be transferred to less-well-defined environments, for example, during a reaction with high conversion. NAP-XP has developed from a curiosity[186] to a well-established method[187] that is found at many radiation sources around the world as well as in laboratory experiments.[188]

The other approach is to match the reactivity of the model system with that of a realistic high-performance catalyst. For this, formidable challenges must be overcome to deposit nanostructures of the relevant active components in a precise way on well-defined model surfaces of typical catalyst carriers. These include the oxides of Si and Al that are not easy to study with surface-sensitive methods because of their electrically insulating properties. The active components may be either metals or the oxides themselves. This approach was very fruitful for understanding the surface physics and reactivity of "complex" systems such as Pd/Al_2O_3,[6, 181c, 189] Au on diverse carriers[14c, 25a, 31b, 190] or supported vanadium oxides.[161c, 191] Catalytic reactions were observed, such as the oxidation of methanol or the hydrogenation of alkynes, under conditions that permitted an analysis of the structure of the active components. This was possible because the nanostructuring enabled an increase in the reactivity relative to macroscopic crystals of the same substance. An important step is the realization of model systems as thin carriers of an oxide film on an underlying single-crystalline metal carrier with nanostructures as the active component having a very narrow distribution of morphological characteristics.[27a, 181b] It allows the application of scanning probe methods for direct imaging and simultaneously the use of vibrational and electron spectroscopy for the analysis of the chemical structure. The experimental and theoretical application of the knowledge gained from this approach is currently[6, 30d] being extended even further.

11. A Critical Survey: Dynamics in Catalysts

The meaning of the standard model for the development of the understanding of the steps making up heterogeneous catalytic processes[22d, 24a, 192] cannot be underestimated. The core message is that the complete equation of a catalytic reaction can be described by a series of intermediate steps consisting of adsorption, reaction, and desorption. Every intermediate step is characterized by a number of elementary processes with rate constants for the forward and reverse reaction as well as surface coverage. The specificity of the chemistry between the catalyst and the reactant is expressed by the degree of surface coverage. This is typical for the surface termination of a catalyst and is understood as a function of the reaction temperature. A change in the catalyst caused by the reaction beyond the state of being "covered" or "not covered" with differing surface structures[21i, 158b] is excluded. Therefore, no reaction steps are needed for regeneration of the active centers after the catalytic reaction. This theory can, therefore, center on the processes of the desired transformation of the starting materials through transition-state theory as the link between chemistry and molecular elementary processes. The exact chemistry of the catalyst can be disregarded here because the numerical values for sorption and reaction rate constants are encoded with this information.

If calculations are performed for a relevant reaction it is quickly seen that a substantial complexity results from the number of necessary elementary steps. The Equations (25) illustrate a very simplified model situation because in practice nowhere near all of the parameters that are needed can be determined. Instead, they are estimated or critical values are obtained theoretically; experimental measurements can only be used in rare cases. The consequence is that there are many combinations of equations and estimates of parameters that describe an experimentally observed performance of a complete reaction equation. Thus, a kinetic model of a reaction can make a reaction mechanism plausible but not render it a certainty. This does not even apply to the reaction network, that is, for the sequence of complete reaction equations that are possible to arrive at the products from a combination of starting materials. The example of the activation of dioxygen as a very simple reaction, shown in Figure 2, illustrates this well. The seemingly simple example of dimerization of methane to ethene and hydrogen (see Figure 1 and the MgO case study) is a dramatic example of the complexity[2b] of the hidden, underlying reaction network. It is still not completely clarified to this day. Furthermore, the example of the generation of methanol from CO_2 and hydrogen conceals the extensive complexity in a theoretically calculated model[193] of the catalyst Cu/ZrO_2 that treats all the possible reaction pathways.

Here it is of course understandable to not further complicate the situation by relinquishing the concept of a rigid active center that may only be occupied or unoccupied. This assumption[187a] is, however, acceptable for limiting cases with very small conversions and simple reactions that lead to thermodynamically stable products. If the local chemical potential at the site of the active center is increased to the point that conversion rates rise significantly, new reaction possibilities between reactants and the active center appear, as indicated in Figure 12 B,C. The catalyst will then change its surface during conversion, in which case an appropriate regeneration step with corresponding elementary steps must be included. More problematic for the standard model is the case that the catalyst becomes profoundly altered and a new active phase results from the starting phase originally found in the reactor. This new phase may only be stable under the given chemical potential of the reaction and have its own unique surface structure. Under different potential conditions (such as at room temperature in air) it may be metastable and cause the catalyst to decompose or it may bring it back into its original form. Such significant changes appear either for the structure of the active phase[194] or they can also occur in relation to the entire chemical composition.[45b, 51j, 61, 195] We differentiate the cases in which the bonds are formed between reactants and catalyst precursor (for example, hydrides during the reaction with metals[196]) or where the catalyst decomposes and a volatile component is either added[51f, 197] or permanently removed[195a, 198] (this applies for oxides and nitrides). Often complex oxides decompose during this process into thermodynamically stable binary oxides that irreversibly destroys a catalyst. Such processes are very prominent[199] in contaminated, complex oxide phases[200] in partial oxidation while pure-phase materials are significantly more stable[201] against these types of complications.

Figure 15 a summarizes a number of influences that affect the degree of surface coverage----the central quantity for catalysis chemistry in the standard model. It follows from the standard model that the chemical potential and the sticking coefficient are of fundamental importance. However, both are subject to a series of influences that are considered to remain constant or are even ignored as a simplification in the standard model. In addition to the macroscopic variables pressure, the temperature and composition of the reaction mixture (the latter of which does not change in the standard model when viewed as a limiting case with small reaction conversions), the chemical potential is also determined by the reaction conversion and the material and energy transport characteristics of the system. The chemical potential is then dependent on the position, a "local" chemical potential, and the kinetics can no longer be taken to be independent of the exact reaction position ("mean-field approximation").

The phenomena of catalyst dynamics, which are neglected by the standard model, influence the sticking coefficient and the local chemical potential in an integral way. The influences "surface structure" and "molecular dynamics" given in Figure 15 can be corrected by an adaption of the standard model to suitable values of the chemical potential. The effects represented by the yellow boxes in Figure 15 contradict the simplifications in the standard model and the LHM approach and are, therefore, not accounted for. These influences cause a feedback loop between the structure and catalytic activity on the one hand and the local potential on the other. With this they contradict the single-crystal approximation that the catalyst can be investigated essentially independently of its reaction environment and in the form of a model in such a way that relevant parameters for the elementary steps of a kinetic description could be obtained. Unfortunately, this is not applicable in the general case as will now be discussed, and this leads to the insufficient assertiveness of a conventionally determined, self-explanatory prediction of catalytic effectivity. This deficiency in no way means that there is no general physically based concept of heterogeneous catalysis, but rather that the standard model is simply not yet constructed in a general enough way.

After the above discussion, the description of a heterogeneous reaction in its reaction network must also incorporate the reaction of the catalyst with the reactants beyond adsorption and activation. The complexity of the task then increases and it would seem to be necessary to accept the aforementioned simplifications. However, through this the option is given away of making conclusions about the material chemistry of the catalyst from observing its performance. The assumptions about the material character of the active centers used in the standard model and in derived empirical concepts of catalytic reactions are really only speculative and are not based on observations. The case studies of OCM and of EB dehydrogenations may serve as examples. This is a central weakness because the model of the reaction says nothing about the dynamics of the catalyst in the chemical potential of the reactants. In general we do not know the chemical dynamics of the catalyst either at the level of the active center or of the active phase. Regrettably, we are not even in possession of the many material--chemical observations needed to be able to a make an assessment of this chemistry. This situation is in sharp contrast to the insights into reaction pathways of the starting materials and products that we are able to evaluate well with molecular chemistry.

The task is made even more difficult because the local chemical potential is the decisive factor and not the potential of the reactants at the entrance to the reactor. The chemical potential is subject to gradients in a reactor due to the progress of the reaction (macroscopic), transport on the scale of boundary layers of material flow, particles and pores (mesoscopic), and the distribution of active centers in the active phase (microscopic). A similar hierarchy results for the transport of the reaction energy. Both hierarchies, given in Figure 1, determine the local potential.

Unfortunately, this is still not complex enough because the response of a solid body to the local chemical potential is determined through solid-state kinetics. This is dependent on the dimensions of the reacting particle (size, form, material transport mechanism) and is an often ignored motivation for nanochemistry[27c, 37p, 48, 202] in heterogeneous catalysis. The defect chemistry that we sometimes control with promoters, but usually regulate[203] unconsciously with synthesis procedures, explains the molecular dimension of the response of a catalyst to its environment. In semiconductor[204] catalysts, additional size-dependent changes of the electronic structure caused by boundary layers come into play. Their range is often comparable to the size of the particle and, therefore, leads to significant changes in the electronic structure of a working catalyst as compared to a macroscopic sample. In this way the morphology, carrier--metal interaction, and the actual structure of the active phase determine the response of the catalyst to the local potential under reaction conditions. Every deviation from the assumed temporal stability of the fluxes of material and energy complicate the problem even more.

The influence of the complexity of the controlling factors on the events in a reactor is shown in Figure 16. Central to Figure 16 is the cycle of processes (blue) that describes the formation and effectivity of the active centers. The macroscopic variables are colored green and are treated in the standard model and by chemical engineering. They determine the macroscopic effect of a "black box" called a "reactor", in which a targeted conversion takes place. Material chemistry, which transforms the catalyst precursor into active centers and also is responsible for their regeneration (the entire "blue cycle" in Figure 16, is not treated in classical physical catalysis research. Rather the focus is on the chemistry of the conversion of the reactants and leads to the "gaps" in this scientific field. The events become complex because the different steps of this reaction cycle of the catalyst can be controlled by different influential elements.

These factors are themselves not static parameters but rather dynamic processes (yellow in Figure 16). This means that they must be treated as fluctuating with time. A good definition of an influential factor in material chemistry is, therefore, a quantity that fluctuates around its own static mean value. These dynamics are coupled with one another because a superposition of external quantities and the productivity of the catalyst control them simultaneously.

Molecular dynamics[2e, 11b, 130a, 178a] are the most well-understood part of physical catalysis research. They describe the generation and interaction of adsorbed and activated reactants on the sample surface as well as the dynamics of the molecule in the reactant phase.[13b] The field of nonlinear dynamics of catalytic reactions[21i, 205] also belongs to this discussion as it gives us an impression of the power of the feedback loop to modify the events of the reaction beyond the picture derived by the standard model. Here it is new that the dynamics of the reactants during adsorption are not determined by the structure of the catalyst precursor but rather they change with the evolution of their chemical reactions between themselves and with the catalyst precursor and become, therefore, a function of the conversion and of the quality[2e, 24b] of the catalyst precursor. Typical examples are the manifold effects that temperature of the reactants has on their reactivity and the dependence of the reaction rate on the degree of surface coverage (that is actually not included in the LHM approach).

The concept of bonding dynamics that changes an active center into a reactive center through fluctuations is very well known from molecular chemistry and homogeneous catalysis: "ligand-exchange process" and "tautomerism"[206] are the corresponding terms that are well established in chemistry. In this case it is new that these processes, which are defined in molecular chemistry through the reaction system, are also controlled by material chemistry and conversion in a heterogeneous reaction involving a solid that was hitherto considered as "nonreactive". An example of this dynamic could be, according to Equation (27), the fluctuations of a metal--oxygen double bond into a radical structure with single bonds and a reduced metal center.

$$M^{n+}\text{-}O \rightleftharpoons M^{(n+1)+}\text{-}O^{\star} \qquad (27)$$

Such a process illustrates in a straightforward way how adaptive metal centers, acting as redox centers, activate a nonreactive substrate without further activating the product. The formation of an oxyl radical[207] is discussed in the molecular chemistry of oxygen activation and was identified in molecular complexes.

The morphological dynamics that determine the real structure of the catalyst during synthesis and under reaction conditions is well-known from solid-state chemistry and studies on the generation of solid bodies from fluid precursors.[39c, 208] The basis here is the influence of nanochemistry on catalysis.[48] These dynamics describing the assembly of a solid body as a fluctuation about a translationally symmetrical ideal structure is mainly controlled by the synthesis recipe[193b, 209] for the catalyst precursor. Often considered the scientific embodiment of the "black magic" of catalyst synthesis, it actually represents a sequence of completely understandable[109a, 195a, 209f, 210] kinetically controlled chemical processes. Controlling the morphology and defect structure through a variation of synthesis parameters represents yet another wide and only somewhat understood[5c, 118c,211] field of catalyst research.

One of the least well-known areas in catalytic action (Figure 16) is that of chemical dynamics. In this dimension, the chemical composition and the surface structure of a catalyst fluctuate together about the mean value of a basis structure without actually taking on this exact value. This would then be the thermodynamically stable structure (as is often assumed in theory because the atomic coordinates are then fixed). Processes of segregation or deposition, melting of the surface, and the incorporation of atoms under the surface or into the bulk of the bulk phase can all cause these dynamics. The generation of near-surface substoichiometric bonds is normally[212] not observed in a vacuum and can often not be identified with surface spectroscopic methods. Therefore, this has often been erroneously referred to as the "dirty side effect" of bad experiments (that do indeed exist). Nevertheless, it is one of the central mechanisms for generating active phases.

Often the active phases decompose when the chemical potential comes close to the standard potential and leaves behind a modified structure of the catalyst precursor: they are practically "invisible" in analytical methods that are not carried out under reaction conditions. A series of observations of such chemically dynamical systems is reported in Table 4 from our studies.

An example of the essential function of chemical dynamics is the effect of Pd as a hydrogenation catalyst in organic synthesis. The catalytic effect is not only due to the metal but also the hydride-subsurface phase,[189a,b] whose exact stoichiometry[225] determines the reactivity. Without the generation of the hydride phase, Pd[181c] is not effective as a hydrogenation catalyst.

It is notable that the relevant catalysts can also be obtained by impeding chemical dynamics. Examples of this are found in the class of intermetallic compounds[226] that prevent the inclusion of reactants[218] in their bulk by means of stable lattices and, therefore, hinder the action of corresponding reaction-induced modifications on their geometric and electronic structure. For this reason this class of materials is predestined for the development of catalysts supported by theory, which up until now has not been able to incorporate chemical dynamics.

A limiting case where the chemical dynamics are restricted rigorously to the surface, is the possible strong bonding of a reaction product to the catalyst, which leads to self-poisoning. This case of "autoinhibition" is not rare and can result in complex kinetic phenomena such as the well-known rate oscillations[21i] and "compensation effects".[227]

It is also shown in Figure 16 how the dynamic phenomena are connected to each other by control parameters in a feedback loop. This makes it necessary to study catalytic phenomena under reaction conditions as well as with a wider scope of reaction parameters such as structural parameters of the catalyst (defect structures, morphology, nanostructures, size distribution, as examples). This is needed because it may be assumed that different controlling factors affect the observed catalytic behavior in different ways under divergent starting conditions. An instructive example for this is the variation of the activation barrier for the oxidation of propane to propene over a mixed oxide catalyst.[228] This "apparent" constant changes its value by a factor of two if the ratio of water to oxygen is changed while the amount of propane remains constant. We surmise that changes in the sequence of the steps[228b] of the reaction occur because the catalyst modifies its surface chemistry along with the chemical potential of the reactants.

The four governing factors represented in the corners of Figure 16 (purple) control the local geometric and electronic behavior at the site of the active center as well as the influence of material and energy transport. In the standard model these parameters are seen as constant during the reaction at every observed position of the catalyst and are, therefore, not explicitly treated kinetically. The consequences of the reciprocal feedback loop and their effects on the dynamics described in the standard model are, thus, suppressed, thereby resulting in the "material gap" and the "complexity gap" as well as a part of the "pressure gap". A path then opens up for improving the standard model, at least in the choice of the approach, to close these "gaps". This path requires enlarging the scope of elementary steps needed in a microkinetic model by specific reactions between the catalyst and the reactants. Some of them may be considered as being in equilibrium during steady-state operation, but some of them will be irreversible as they describe the maturation of the precatalyst into its active form through the reaction of reactants with the precursor.

We recognize that the description of a working catalyst is not only made difficult by the structural complexity of a catalyst precursor in comparison to a single crystal of the same phase, the latter of which is used to justify the choice of macroscopic single-crystal surfaces[97a, 127] in the development of the standard model. In addition, there is an entire series of dynamics on different scales of space and time that are also influential. This understanding is not new in principle, it was already formulated by Ertl[97a] in a review article. What is new is the insight into how drastic the interplay of dynamics changes a catalyst depending on its reaction environment. The "exact investigation of active centers" required by Ertl in his article is pushed to its limits experimentally and conceptually if states of the catalyst are considered that deliver significant performance in reaction networks. The surfaces are then "flexible," as formulated by Somorjai.[133b] Model systems[111b, 192] fail in their role as samples with known atomic coordinates because they either cannot reach such levels of performance or because they change into undesired, complex systems during the reaction, for example styrene synthesis through dehydrogenation. If the simplifications from the standard model for the analysis of the phenomenon "heterogeneous catalysis" (the "Langmuir period"[111b]) and for the material description of a catalyst[38, 92b, 229] had not been applied, the research in heterogeneous catalysis would still be stuck in the era of black magic and trial and error.

We return now to the types of dynamics that determine the function of a catalyst. They act on different scales of space and time and, according to Figure 17, complete the picture of the "multiscale problem of catalysis" introduced in Figure 1. Also shown in Figure 17 are the charge-carrier dynamics, a universal characteristic of solid-state matter arising from its basic electronic structure. In the form of semiconductor properties from many active phases, these have an important and not yet fully understood effect[80c, 204b] in catalysis because they directly influence the degree of coverage of the reacting surface. This effect cannot be considered to be independent because it is influenced in many ways by the other factors of catalyst function; it acts rather in a combined[51i, 204a] fashion with the other elements of dynamics. In metals the situation is somewhat easier as the bath of free electrons at the Fermi level can be assumed to be a reservoir for redox equivalents required for surface chemical reactions. Thus, the electronic structure of a metallic solid is a critically required, and for many surface processes, sufficient descriptor. This forms one basic ingredient into the success of theory in explaining and even to a certain extent predicting catalytic reactions (see below).

Figure 17 illustrates clearly the large challenges in describing the factors affecting a catalyst and, therefore, also its design. Many different dimensions in space and time require analysis that leads to the demand for diverse analytical methods seldom found in close tandem. Figure 17 demonstrates, therefore, the necessity of cooperation in catalysis research if we desire to reach the level of understanding required to make predictions about the functionality and stability of a system at high performance. This applies to the required combination of synthetic and functional experiments, the modeling of kinetics[2a] and to the theory of chemical reactions.[11a, 13b, 152, 235]

12. The Unified Concept of Catalysis

Let us assume that we have convinced ourselves that the limits of Langmuir’s concept and of the standard model do not allow us to describe the most essential characteristics of the dynamic control of catalyst functionality. Then we can ask anew the question about the common definition of catalytic function common to both the molecular and interface-determined systems. The synthesis of heterogeneous catalysts, according to Figure 6, does not supply the active functional material itself, but rather only the precursor. The active phase then results from the precursor under reaction conditions with participation from the reactants. This finds its parallel in molecular chemistry in a solution of central ions and ligands. In the heterogeneous case, the precursor has the task of making the components of the active phase available and stabilizing their nanostructures to such an extent that, with low activation energy, they display dynamic characteristics leading in turn to active centers. Simultaneously, the precursor, which has now become a matrix, ensures that this dynamic does not turn toward a decomposition of the active phase into a static, thermodynamically stable state that is no longer catalytically active.

One deficit in catalyst research is that we simply do not know enough about these reactions and the mechanisms that control them. This is due to the nature of active phases being thin layers or nanostructures, which are difficult to analyze under normal experimental conditions. In addition, few researchers are interested in the reactivity of nanostructures under the conditions of a catalytic process. One group of special relevance here, the substoichiometric compounds, has only been studied in detail with respect to structural characteristics, while studies of the dynamics of their formation and reactivity are still rare. Active phases also develop through segregation and reconstruction, often induced by chemisorption or the dissolution of reactants in the catalyst. These kinds of processes play an important role in other fields of material science where they are also well-known[124a, 208d, 237] but the transfer to the structures and reaction conditions of catalysts is still missing. An example is the defect chemistry of oxidic materials that is generally very well studied. In electrocatalysts and in oxidic mixed catalysts[238] this defect chemistry is thought to also play a decisive role, but is very hard to observe under reaction conditions. Therefore, despite insistent calls[239] for increased cooperation between these two fields, little progress has been made on this front.

Active centers are generated from the active phase by dynamic processes. These are not continuously present in general but rather result from fluctuations in the material structure and in the chemical bonds of the active phase. They are rare events on the time scale of molecular dynamics (fs--ps), which clarifies the fact why they exist as high-energy states. We may presume that the observed reaction temperature is responsible in many cases for making such uncommon events possible. It is further quite conceivable that the high mean kinetic energy of the system is required both for the generation of active centers and for regeneration of the centers after a successful target reaction. This leads to the energetic control of the dynamics of adsorbate complexes.

It may be speculated whether other forms of energy supply to a catalytic system, such as photoactivation,[240] the generation of electric fields in electrocatalysis[159b, 241] or the stimulation from radicals in plasma catalysis,[242] can also lead to such active centers directly or with a low additional energy input. Much more often the effect on the molecular structure of the reactants[243] by nonthermal energy, induced directly or through the catalyst, is investigated as a central catalyst function. The discussion of "confinement effects",[244] now in vogue again, is an example of this, although here a static catalyst is assumed. The resulting complexity of a connection of such effects with the structural dynamics of active phases will not be discussed here.

The concept that active centers are in general high-energy sites in an active surface phase created during catalyst synthesis is not correct. Rather, the synthesis enables the reaction of the catalyst with the reactants through defects and nanostructures. The result is the creation of the active phase and finally the dynamics of the formation of the active sites. In heterogeneous catalysts that have active centers that are difficult to define geometrically[232, 245] (how many atoms are participating at any one time?) the combination is often found of a defined postsynthesis structure (average composition, particle form, surface orientation, steps) with a dynamic component (segregation, surface-premelted layers, creeping of carrier oxides onto metals, generation of substoichiometric compounds) that is introduced through the reaction conditions.

The general heterogeneous catalyst should be seen as a mixture of static structures and dynamic components that communally result in the active center. The synthesis of the precursors and their chemical properties are as equally important as the dynamics of the active phase. This does not only apply to bulk catalysts, but also to supported catalysts made of a "carrier phase" and an "active material". This partitioning of the structure of the catalyst into two pieces after synthesis is functionally not sustainable because the carrier usually has more than merely a "supporting function", a concept expressed through the term[27c, 29a, 246] "non-innocent support".[247]

In contrast, the discussion up until now shows that a bulk catalyst, such as the systems for ammonia and methanol or the well-known "M1" multielement oxide catalyst,[23a, 201, 209f, 210b, 248] is also not functionally homogeneous, but develops an active surface phase in a sort of "self-support." The processes leading to active centers then take place in this surface phase.

Figure 18 shows some electron microscopy images of prototype structures of metallic catalysts. Although clearly defined structural elements can be seen, these images should not lead to the tempting idea that active centers are visible here. We do not know whether these structures actually carry out the reactions or how their structure under the conditions of electron microscopy is related to that under the conditions of the catalytic reaction. The images call for the methodical development of electron microscopy toward the ability to produce such images under chemically defined conditions so that we will then arrive at a "chemical electron microscopy".

We will now device the picture of a catalyst as being made-up from metallic central atoms that are bound into ligand spheres[246, 249] by carrying out exchange reactions through dynamic processes. The following statement applies respectively for both acid-base catalysts[250] and metal-free catalysts.[251] This picture further applies also to the most important case[211a, 252] of microporous and mesoporous acid-base catalysts (zeolites for example),[253] because the active layer makes up the surface layer of the of pore system. We begin to recognize this from the attempts[254] to unfold this layer and investigate it in detail as a planar model. However, in these systems it is not a bulk matrix that is responsible for the stability of the active phase, but rather the elaborate structure of the active phase itself.[255] The chemical dynamics of such systems is only mentioned here with the descriptive phrases "water vapor treatment" and "chemistry of pore openings". Furthermore, metal-organic frameworks (MOFs) with open network structures,[256] currently being the subject of much study, also belong in this class of matrix-free structure-stabilized active phases. Finally this picture also applies to the group of Lewis acid-base catalysts.[94]

The ligands (counterions) are either present as intentional components or are generated from the reactants and the catalyst precursors (typically OH). The mobility of the molecular system in solution with adjustable chemical potential in an equilibrium of complex formation allows for the processes of chemical dynamics and leads naturally to cycles of the appearance and disappearance of active centers as an "active complex". In the heterogeneous case, this "solution" corresponds to a fluctuating termination layer on solids of approximately 1 nm thickness whose characteristics are determined by the carrier phase. The termination layer is formed during the activation phase of the catalyst under the control of the chemical potential of the reactants.

If we imagine the same basic processes of ligand exchange and redox reactions in this termination layer, as are found in molecular systems, we see that there is no significant difference between molecular and heterogeneous catalysis. The reason is that the actual reactions are not really as "heterogeneous" as the standard model would lead us to believe. Molecular or dissociated water is often produced in heterogeneous reactions and can play the role of a solvent, as can melting of the entire (or parts of) the active layer (for example, main group element oxides), or of additives that are introduced as "promotors". "Supported liquid phases" or "supported ionic liquids" are, therefore, no longer curiosities, but instead illustrate the normal way of how a catalyst operates. However, the thickness of these layers differentiates the systems, and with this we mean mainly layer thicknesses in the monomolecular range and not optically visible layers.

This concept requires the abandonment of the idea of a rigid structure of active surfaces in heterogeneous catalysis described by translationally symmetric atomic arrangements as observable in their non-active states. We sacrifice the concept of analysis of an active structure through isolation in a nonreactive environment and subsequent full physiochemical investigation. Instead we must demand that we will be able to analyze the geometric and electronic structure of the termination layer well enough to develop structural and functional quantifiable pictures of active centers without the application of models. This will not be possible without theoretical contributions achieved in such a way that the structural proposals are made using functional data and spectroscopic findings rather than deriving these characteristics from a predefined structure, as has been done up until this point. In this way we can help circumvent the dilemma of theory wanting to predict reactive non-equilibrium structures by concepts of total energy minimization.

Model investigations receive a new function through this concept. They limit the number of options in the search for active centers through the formulation of hypotheses and the exclusion of certain possibilities. Models of hypothetical active centers can be designed[30d, 83a, 192] and their stoichiometric reactivity[257] as well as the reactivity of the related nanostructures can be subsequently studied under reaction conditions. This does not allow for an unambiguous reconstruction of the reaction, but it is possible in this way to define the stoichiometric elementary steps and significant elements of the material chemistry of the active phase. Also, these can be used to set up boundary conditions for further in situ investigations. Examples for this approach can be found in cooperative works from chemical physics and inorganic chemistry[27a, 46, 80c, 258] that aim to produce catalysts guided by the construction of model systems. Of vast importance here are combined theoretical and experimental investigations of systems with realistic complexity[6, 30d, 191a, 236, 259] that illuminate the reactive and spectroscopic characteristics that serve as landmarks in the examination of reactive systems. An example of this is the evidence of the passive termination of metal oxides with M-O groups[162c, 191b, 260] that only allows chemical reactions after the formation of defects in their dense surface layer. Theoretical[13c, 261] and experimental studies play similar roles for isolated clusters[47a, 194b, 262] and their reactivity; they are able to give information about possible reactions from structures that may be active centers and also give indications about the charge state of these systems.

We then still need analytical access to the atomic details of active surfaces under reaction conditions[13b, 24a, 33b, 51l,m, 108b, 125, 187a,b, 204b, 227, 263] without having to rely on models. The required methods are available to us today as combinations of in situ analytical procedures. Table 5 shows some of the current common methods as well as the limits of their use.

This naturally cursory assessment of the experimental ability of the different methods quickly reveals that despite the enormous arsenal, there is still a critical limitation in their applicability. The powerful methods for the analysis of geometrical and electronic structures are generally not sensitive enough to the termination layer and its dynamics. The extremely surface-sensitive methods using chemical reactions and adsorption with probe molecules are only conditionally suitable to define the investigated structures; theory can be very helpful here to bridge this gap. For example, it can construct geometrical structures that are in agreement with observed vibrational frequencies. The methods that are powerful for the characterization of structures are usually not sensitive enough to give information about the termination layer. However, these methods can identify the transition of the termination phase into unwanted bulk structures and, most of all, the preconditions for their generation through characterization of the carrier structures. If thermochemical methods and time-resolved methods (on the scale of the change of the chemical potential of the reactants, ms to s) are applied in tandem, a picture emerges with options for the generation of the termination layer and its dynamics. The case studies discussed here illustrate this and the importance of the word "combination", used above in connection with the power of the analytical arsenal we in principle have access to today, becomes clear. There is not one overriding method but rather only a combination of methods with their individual abilities (in situ, structural sensitivity to the termination layer, etc.) can be used to solve the problem. All of this also always remains connected with the analysis of the reaction, that is, with kinetics. We are, therefore, not looking for the single "heroic" experiment that delivers ultimate insight but rather the synopsis of many critically analyzed single experiments preformed under precisely defined conditions. And these are all already available to us now. This is what is meant by the statement that today we are able[51j, 56b, 155e,h, 160b, 213, 264] to "look over the shoulder" of a working catalyst without the aid of a model.

It turns out that it is neither negligent nor ignorant to remain with the original simplifications of the standard model and the resulting consequences. For many purposes this makes for a perfectly adequate explanation of catalysis. If, however, the goal is to understand the fundamental nature of the phenomenon of catalysis or acquire the ability to "design" catalysts, then this approach does not suffice and it becomes necessary to re-evaluate the simplifications leading to the standard model. Unfortunately, this has not been done at a desirable level and is the reason why progress remains slight apart from frequent announcements[5c, 7b,c, 37k, 265] and why, when the relationship between costs and output is considered, the impression abounds that empirical catalysis research indeed leads to better results. We can remark that this is not a product of our times. A similar conclusion can be found in other publications and in G. M. Schwabs summary of his *Handbook of Catalysis*,[266] published in 1941.

13. How Did Material Science Arrive at Catalysis?

A fundamental criticism toward knowledge-oriented catalysis research is its weakness in implementing functional insight into new catalysts. The practical success in heterogeneous catalysis is due in most part to process technology, which deals with the macroscopic dimensions of the links connecting the catalyst to reactor, as well as to the reactants, in the way described in Figures 1 and 16. For this, molecular events are largely insignificant. We only really understand this in a limited way with regards to chemical complexity and have until now not been able to furnish the practical catalysis researcher with a robust helping hand in unlocking the material science side of catalysis. This deals with the question of how an optimized catalyst should be designed in terms of composition, structure, and reaction dynamics. Especially the latter has not yet been investigated to a large extent because a structural rigidity is usually assumed, the narrow limitations of which will now be discussed. Furthermore, the molecular processes of activation and deactivation are only understood in exceptional situations[50b,f,j, 54a, 264a, 267] and can, therefore, seldom be treated conceptually.

This analysis does not change fundamentally if the many academic reports on the discovery of new spectacular catalysts are included here. The synthesis of complex nanostructured[268] material has given us a wide range of possible active materials.[211a, 44a, 269] Their function is, however, mostly not understood. They are usually not the result of previous functional considerations and the sustainability of their effects under realistic conversion conditions[244a] is seldom the subject of investigations. We are, therefore, in possession of a rich supply of possibly interesting compounds that can ignite the imagination to construct tailor-made systems. Unfortunately, we do not have efficient methods to prioritize these possibilities according to their effectiveness, other than the laborious cycles of synthesis and functional analysis. A more effective method would enable the selection of those systems whose exact functional characterization would lead past their normal material and structural options in technical catalyst synthesis[5c, 118c, 211b, 270] to conceptually and theoretically based conclusions. Regrettably, the effort involved proves too high a price, especially when it is considered that certain experiments[209g] will most likely not proceed successfully.

We are then charged with the task of proposing a path to a catalytic material that begins by defining the desired function. This is where physical-chemical-oriented catalyst research can be put to use. In this field a concept can be developed through the use of the standard model in the same way that a combination of theory and model experiments[30d] can lead to a knowledge-based approach to new systems. Unfortunately, there have already been many broken promises of success along this road because the complexity of the challenges was underestimated. In particular, only in rare cases was the validity of the selected approach tested with in situ analytical methods so that a fundamental understanding[5c, 80c] of the observed function of the new catalyst could be gained. The catalytic effect is only then a confirmation of the validity of the physical-chemical concept.

This has led to the reservations about physical chemistry in practical catalysis already discussed several times in this Review. The author supports the view that in the cases where empirical research no longer leads to an improvement of a catalytic reaction, the remedy can be provided by the concept of knowledge-based approaches sketched out herein. If this decision were to be made early in the development phase of a chemical reaction, with the knowledge-based approach experiencing repeated use, the associated costs on a case-by-case basis would quickly be reduced. Exemplary of this would be the development of ammonia catalysts.[271] In the history of this field, empirical research methods in the early stages[131] have been combined with knowledge-based approaches[24a, 97a, 127, 130] possible today and led to the expectation[272] that even this system has a large potential for improvement if traditional reaction processes and active materials are taken as a starting point to novel concepts of ammonia synthesis. The level of understanding at this point, suggests the optimum reaction processes possible with the current methods have already been achieved.

A scheme of knowledge-based approaches is sketched roughly in Figure 19. In the center is the elementary reaction, often difficult to investigate, which we wish to be able to control. For reactions that are only to be accelerated, this central reaction becomes a rate-determining step ("rds") in the nomenclature of Boudart.[101c] Unfortunately, there are no shortcuts for a way through all of the stations. As soon as a cycle has been completed and the knowledge gained about the reaction solidified, parallel synthesis and test methods can be employed in a useful way in synthetic peripheral tasks.[273]

This is because the results must then only be sampled randomly as a check of whether the processes are still inside the bounds of the critical elementary reaction.

However, the general case of a reaction with selectivity problems, such as water splitting, the selective hydrogenation of CO/CO_2 to oxygenates or to narrowly distributed hydrocarbon mixtures, or even the selective oxidation of small hydrocarbon materials,[59c] is an even larger challenge than ammonia synthesis. It is high time[42a, 97b] to tackle such challenges in suitably organized projects. The progress made with homogeneous catalysis by carrying out many planned reactions, at least in the laboratory, should provide incentives to attempt to reach a similar goal in heterogeneous catalysis. The present Review aims to show that this is possible in principle and the challenges presented by the complexity of reaching this goal can be met with tools already available today.

However, this appeal is neither original nor is it made for the first time here. The many efforts, for example, those made in the activation of methane,[47a, 95b, 274] may serve as good examples. However, breakthrough success still has not been achieved. Apparently the correct strategy has not been found in the implementation of catalyst development using the knowledge-based approach.

We know today that many historical and current reports attest to the ability of a heterogeneous catalyst to adjust to reaction conditions. Here we speak of chemical dynamics[232, 246, 275] or of a "flexible"[133b] surface and realize that the quantitative characterization of the active centers is an enormous challenge. Without these centers we will hardly be able to formulate a quantitative theory of heterogeneous catalysis with predictive power. The situation in this field, with such phenomenological complexity,[52a, 276] could be helped only by rigorous simplification to arrive at an experimentally verifiable theory of catalysis starting from the empirical-quantitative LHM.

From this model, a theoretical connection can be made to material characteristics[3a, 11, 82, 265e, 277] that a catalyst must display on a molecular level. Therefore, a basis exists for the design of a catalyst[7c, 14e, 23d, 82, 278] if the kinetic details of a reaction are known as a function of the reaction conditions. On the material science side, the electronic structure of the catalyst must be understood in sufficient detail and with chemical accuracy to describe the surface reactivity.

To use the knowledge of how a catalytic reaction proceeds for the identification and optimization of suitable catalysts in material chemistry, we contemplate the following concept, whose derivation can be obtained in text books.[100]

At first we ignore the dynamic nature of catalysts by separating the identification of a suitable catalyst to carry out a reaction from the maximization of the number of active centers per unit surface area. We also break down the choice of material and its activation into different working steps, as shown in Figure 19, which remain closely interlocked, a situation that can be assured through application of a functional analysis of the material synthesis. Systematic findings about the mode of generation and the reaction speeds of the active centers are not accessible to us. In many cases this problem does not become apparent because the critical reaction is the activation of a small molecule on a step or another static high-energy center (see, for example, Figures 7, 8, 12, 16, and 18). The activation of hydrogen, nitrogen, oxygen, and water are typical reactions of this kind. They take place at centers that are generated as static defects after catalyst activation. Different from these are the centers that mediate association reactions and generate more complex molecules against the trend of the reaction where thermodynamically stable products are formed. We know less about this, with the result that the empirical, or even theoretically supported, material chemistry becomes more difficult. A typical field is the selective oxidation of alkanes. Currently only rules derived from practical experience can be used as a guide and we perform work in this field based on the "seven pillars of oxidation catalysis".[279]

Figure 20 illustrates the challenge that appears with the analysis of powerful oxidation catalysts.[280] The surface chemical composition is strongly dependent on the chemical potential of the environment and varies much more then would be allowed from the quite flexible composition of the unit cell structure of the oxide[281] alone: this must be a case of chemically induced segregation.[282] In addition to the heavy Te segregation, a vanadium phase consisting of V^{5+} species also forms in the presence of water vapor. The existence of this phase is directly related to the target reaction[61, 282b] and, interestingly, no changes in the chemical composition of the surface take place during the formation of the phase. The continuous presence of V^{4+} amongst the Nb^{5+} indicates that the bulk structure remains completely stable, in agreement with in situ X-ray structural analysis.[201, 283] The chemical dynamic in this system remains limited to the uppermost termination layer.[60b] In the high-performance system VPO[204b, 222, 284] (vanadium pyrophosphate) this is not the case. Instead, the generation of the active phase[199a, 285] is connected to a complex change of the bulk structure.[286] This complexity long prevented the recognition that in spite of the formally exclusive presence of the V^{4+} species[51d, 287] existing in the VPO structures, the active phase under reaction conditions at 1000 mbar pressure is comprised of V^{5+} [194a, 288] formed by the chemical dynamics of the activation in hot reaction gases. This is an example of an especially difficult form of the pressure gap, because this information was not obtainable at the normal 1 mbar reaction pressure of the in situ analysis with surface analytical methods.[187c, 194a, 289] However, the participation of the V=O bond at the active centers was correctly identified in these experiments and is also supported by earlier studies.[290] High-pressure methods using RAMAN spectroscopy[291] have turned out to be not surface-sensitive enough to detect the active phase whose thickness is only about 1 % of the wavelength of the light used. However, using EXAFS[288] and chemical probes[292] the V^{5+} species was also identified as the catalytically relevant species.

After we have convinced ourselves that the many relevant catalysts of today would be difficult to treat with a knowledge-based approach using our current knowhow, we may turn to a more simple case. We will look at the selective hydrogenation of C≡C bonds (alkynes) to C=C bonds (olefins) over metal catalysts. From Equation (25) and its interpretation, we know that the most essential value for the reaction rate is the surface coverage by reactants. When atomic hydrogen is often found near adsorbed alkynes a high reaction rate[293] will result. As the bonds between alkynes and a metal are significantly stronger than between a metal and alkenes[294] it can be assumed that there is a finite chance it will desorb before it is further hydrogenated by hydrogen to an alkane. There is an established reaction mechanism[10a] and model experiments[147, 181c, 295] that exist for this. The reactions (28) and (29)

$$2\ C_2H_2 + H_2 \rightarrow 2\ C_2H_4 \qquad (28)$$

$$2\ C_2H_4 + H_2 \rightarrow 2\ C_2H_6 \qquad (29)$$

have, furthermore, been studied intensively on a theoretical basis[178b, 296] and serve as case studies for a knowledge-based development of proposed new catalysts. In one theoretical approach a method was introduced[297] where a non-noble metal catalyst could be identified for the reaction of the selective hydrogenation of acetylene. Normally reaction (28) is used selectively to purge an ethylene stream of contamination by acetylene and is accomplished with Pd-Ag alloys.[189b, 296, 298] The problem is to avoid total hydrogenation (29), which destroys the starting material for the polymerization target reaction. With the help of a model, discussed below, a series of alloys with base metals was proposed that can carry out very selective hydrogenation. The data of experimental reproduction are very convincing.[297] However, the products from the synthesis of the catalyst were not checked to determine whether the predicted electronic structure of the alloys was in fact responsible for the observed effect. There is an array of possible explanations for the measurements, the proffered theory[297] being only one of these. Alternatives are based on morphological variations[162a] of the base metals through carrier interactions or selective poisoning of steps on the base metal surfaces, on reactions of a component of an alloy with the carrier, or on a selective capping of the base metal with the alloy component. As these alternatives cannot be excluded, the experiment is not fully able to verify the theory.

These reservations are a consequence of the experiences with the knowledge-based approach from Figure 17. The standard model and the specific model experiments that lead to the theoretical approach sketched above predict that the desired reaction can only proceed under two conditions: first, the active center cannot consist of Pd terraces[294] but rather of isolated Pd atoms. This prevents the dissociation of hydrocarbons, minimizes the reductive effect of hydrogen, and leads to the optimization of the desorption of the target product (site isolation).[14c] Secondly, the generation of subsurface hydrogen must be prevented because this activated form of hydrogen, together with Pd, creates a hydrogenation catalyst[181c] that is unselective[196, 218] in this reaction. In this last study there is classic evidence for the validity of the LHM in the case of hydrogenation.

With this concept it was possible to develop intermetallic compounds[300] into catalysts. The line phases PdGa and Pd_2Ga are both able to keep hydrogen out of their lattice structure[301] and possess terminations[300d, 302] with structures that completely, or nearly completely separate the Pd atoms from one another by forming cagelike motives from Ga and Pd. The strong covalent contributions of the bonds necessary for this special structure also shift the Pd d band to significantly lower energies and effect a modification of the electronic structure. The concept is successful conceptually as well as in reality, for example, with supported nanoparticles, and has led to stable and effective catalysts.[225, 226b]

It turns out when considering the postulated control of the causal relationship between catalyst success and original concept that this is indeed comprehensible[225, 226c, 303, 305] for annealed single crystals and pure samples free of surface oxides.[304] Real nanostructured catalysts and unannealed, crushed bulk samples show, however, another working principle: the generation of a Pd nanostructure protected from sintering by a Ga_2O_3 nanoparticle was observed[226b, 306] as long as it was involved in an acetylene hydrogenation reaction. The high selectivity was achieved by Pd-C subsurface compounds.[196, 225, 299a] These can also cause pure Pd nanoparticles to be highly selective if suitable structuring of the Pd precursor is available to promote their growth along with carbon supports for stabilization.[264f] Properly functioning Pd_2Ga nanoparticles[307] with a stable intermetallic structure can also be produced and utilized[225, 308] on nanocarbon supports. However, if more complex alkynes are to be hydrogenated, the concept does not work well[56c,d] for two reasons. First, the complexing effect of the substrates corrodes the surface and, second, the reactivity of the pristine intermetallic compound cannot compete with the surface-modified Pd systems (Lindlar catalysis) when it comes to substrates that are difficult to hydrogenate.[56d, 309]

several highlights of this development are shown in Figure 21.[300a] By using in situ X-ray diffraction, the generation of PdH was established on nanoparticles supported by nanocarbon[310] along with PdC_x after the reaction. The concept of the modification of Pd surfaces by the generation of intermetallic compounds can be studied on single crystals as well as on polycrystalline systems by determination of the binding energy of the CO probe molecule. In addition to showing how drastically the absorption characteristics (surface coverage) change when Pd metal is converted into an intermetallic compound, Figure 21 B also shows the concept of site isolation. However, this is only the case when tempering is used to achieve a surface termination[304] in which Pd is actually surrounded by Ga. The shift of the Pd d band through the generation of the intermetallic compounds can be easily demonstrated with electron spectroscopy along with the stability against hydrogen.[299a] Electron microscopy can be used to show that the nanoparticles are of similar and homogeneous composition. Their structure corresponds to the bulk phase and the intense interaction binds them so strongly to the carbon that the do not separate even under hydrogenation conditions.

These observations show that it cannot be assumed, even with seemingly straightforward reactions, that the verification of a concept’s function within the framework of a specific model system can be directly transferred to another system. Specifically, from this example we can learn the following lessons, which are also found in a similar form in other fields of nanocatalysis[27c, 311] with metals.

1. The model experiment of a comparison of a Pd nanoparticle with a Pd single crystal showed the importance of the structuring of one and the same material for catalysis.

2. The concept that catalysis is only determined through surface processes must be corrected: subsurface regions of the catalyst can be of decisive relevance if they are brought into the reaction process at critical chemical potential thresholds.

3. The LHM of the standard model was successfully applied to a complex reaction beyond ammonia synthesis and CO oxidation. This forms a solid basis for the general concept of heterogeneous catalytic reactions.

4. Model experiments whose results lead to physically resilient concepts can be used to plan new approaches to synthesis that would likely not have been possible with the planning of mere empirical experiments.

5. The choice of complex materials such as an intermetallic compound can significantly simplify a specific catalytic application. With a good knowledge of the material characteristics a catalytic concept can be accurately implemented.

6. Catalysts are seldom "universal": the transfer of solutions from one reaction to another is only conceivable on an abstract level and as a first approximation.

Here it is worthwhile to dwell a bit longer on the topic of material design for catalysts because we may be able to better understand the ideal "catalyst design". We can take from the standard model that the degree to which the surface is covered by reactants is determined by the material flux and the temperature (together in a reactor with a local chemical potential, see Figures 15 and 16) as well as by a material constant that we call the sticking coefficient. This factor contains the details of the chemical interaction between the reactants and the catalyst. The details of the chemical bonds of interest here are only included implicitly because the derivation of this coefficient is based on the kinetic gas theory[100] of corpuscular interactions and not on explicit chemical bonds. If the sticking coefficient is written in an Arrhenius form

$$S = S_0^{\circ} e^{\frac{-\Delta E_{\mathrm{akt}}}{kT}} \qquad (30)$$

then we may recognize after looking at the value of the activation energy which kind of reactant adsorption we have: there can be weak binding of molecules (0—20 kJ mol<M->1) or strongly activated, dissociative adsorption (40—200 kJ mol<M->1).

The degree of coverage, which is of interesting here, is then given by Equation (31)

$$\theta(t) = 1 - e^{-FS_0(T)t} \qquad (31)$$

Here, *F* is the reactant flux on the surface of the catalyst and *t* is the time. To eliminate this we again use the approximation of the stationary state and recognize that the sticking coefficient and its temperature dependence determine the coverage. The local chemical potential and the chemical nature of the reactants are built into the parameters of the sticking coefficient S_0.

In many cases[263] it is favorable if the surface coverage from different reactants is approximately the same, and is low. Then there is a high probability that the reactants will encounter one another at one of the rare active centers. If the reactants are not too chemically different, a single active phase can fulfill this requirement if the parameters chemical composition, pressure, and temperature are correctly chosen and a highly active catalyst results. It will be much more demanding to choose a material if the reactants are chemically strongly different or if subsequent reaction cascades are necessary for the generation of a product. A "multifunctional" catalyst can be envisioned with one redox function and one acidic function. In contrast to a homogeneous system in which multifunctionality is difficult to integrate into a single active complex, multifunctionality at the surface leads to fewer problems because chemically different groups can co-exist in proximity without influencing each other through directional bonds.

We can choose a middle-of-the-road case with two reactants that are fairly similar. Then, we may assume that we have a descriptor available that allows us to quantitatively describe a family of possible materials. Such a descriptor could be the strength of the interaction between the active phase and an activated reactant. An example could be a metal and a hydrogenation reaction. The descriptor would then be the bond strength between hydrogen atoms and the active phase.

Alternatively, we could take the descriptor to be the bond strength of the molecules that are to be hydrogenated. As a further approximation, the reaction will have only one rate-determining step with one corresponding species. This is often the case for a hydrogenation, although not for an oxidation, if we consider the dehydrogenation and oxygen transfer to be substeps.[152a, 228b, 312] If we suppose that all of the observed active materials carry out the reaction using the same mechanism (often difficult to verify) then we can exploit a general relationship in physical chemistry between the (thermodynamic) strength of a bond between a catalyst and reactant and the height of the energy barrier (kinetic) that must be overcome to complete the reaction. This relationship[3a, 313] states that the barrier and the binding energy are correlated with a schematic representation found in Figure 22.

We now have the necessary tools to choose materials for reactions with a known mechanism (at least with a known rate-determining step). Equations (30) and (31), as well as the discussion on the dynamics of the catalyst, show, furthermore, that this choice is not a constant, but is rather dependent on the reaction conditions. For this reason the search for materials without a parallel consideration of the reaction conditions is not recommended. From this we see again the origin of the cyclic operation of the knowledge-based approach in Figure 19 and postulate that comparing a series of materials under the same test conditions is not sufficient. Only undertaking a very coarse search for large differences in the reaction rates (logarithmic scale in Figure 22) will enable the combination of the important factors into a single constant on the first go around.

This qualitative approach, known in the literature as the "Sabatier Principle",[82, 313a, 314] will be useful first when we have numerical values for the descriptor. The measurement of E_A or E_{Rea} is essentially possible with calorimetry on real systems or on model systems[148a] with well-defined elementary steps. However, this is so costly[147, 149, 150, 151] that attempting to find materials on an empirical basis is preferred.

Here theory has made a novel approach possible. This is due to the now high quality of the description of the surface electronic structure of chemically complex structures. Based on the enormous progress in the theory of molecular processes in catalysis,[3a, 9a, 11, 278c, 315] we are now, with a few curtailments with respect to precision, able to calculate enough numerical values to get a solid idea about many compounds and a large number of relevant reactions. With this information we can make predictions about specific materials, their most advantageous surface structure, and the maximum achievable reaction rate. For the test case of ammonia synthesis[101b, 130a, 316] this was done extensively up to the point of proposing new binary metal compounds[3a, 265e, 277b] with substantial catalytic performance. This achievement was made possible due to the details of the dissociative adsorption of nitrogen on the catalyst being theoretically[96,1 112b, 317] and experimentally[22d, 92b, 130b, 229, 318] very well understood, as are the details of the rate-determining step. The work on the ammonia system has advanced to a degree that there are theoretical predictions stating just how much further this reaction can be developed.[272] These appear rather utopic at this point if the history of the actual development[130b, 131, 271a] of this reaction is regarded in comparison. In theoretical work, however, a very important clue can be found to the method leading to such breakthrough results.

For this we return to Figure 22. It shows that many relevant adsorbates, which may act as possible reactants, have a linear dependence between their heat of formation, and their position in the periodic table of the elements. This is not an accident,[82] but rather it can be explained with C, O, and N atoms using as the bonding mechanism[101b, 319] the interaction of molecular fragments[320] with the d electrons (d band). This is mainly responsible for the bonds in transition elements that are especially relevant in catalysis. The regular shift in the position of the core of the d band,[230a] as well as the band edge, with position in the periodic table (filling of the d shell) explains the change in interaction energies. If this somewhat coarse analysis is refined with input from alloy formation,[7c, 178b, 277c, 278f, 297, 300c, 315c, 321] steps on the surface[24a, 96, 132c] and strain in the unit cell[322] of the metallic catalyst, many new elements are brought into the previously monotone shift of the d band. If this "scaling relation" is investigated to find a series of catalytically relevant fragments over a large number of elements and structures on a catalytic surface, it can be seen[14e, 82] that the scaling relations have similar trends and that the exact structure of the adsorbates has no significant influence on the results. This leads to a certain "universality" in catalysis because one and the same scaling relation applies to several structures. However, if the energy resolution is improved in these relations, it is found that they congregate into groups. Hydrogen stands alone or as a bonding atom of a fragment, it lies far from the universal relation, and defines its own scaling relation. The prediction of catalysts for whole reaction networks, is, therefore, reduced[320, 323] to solving linear equations with numerical values from quantum chemical calculations. These can be stored in a database and used to create new combinations of fragments and materials.[324] Sets of curves or "volcano plots"[9a, 277b] are generated with forms similar to that found in Figure 22: the minimum curve limits the possible performance of the catalyst from that particular set.

If this predicted performance is to be improved, it follows from the theory[272] that the validity of the scaling relations must be rendered untrue. Such a situation will only be found in a set of compounds if it is possible to decouple the activation and reaction of reactants from one another and from the local electronic structure of the catalyst. This can be achieved if a modification of the mode of operation of catalysts takes place that is not found in the models defining the scaling relation. Some of these are dimensionality of the active phase (exact structure, bulk, cluster, thin layers), the spatial morphology of the system (confinement effects), the dynamics of active center formation (static active centers are standard), the reaction environment in which the active material is placed, or the use of nonthermal energy sources mentioned above. These possibilities result from the consideration of Figure 16 that describes the recursive coupling of the entire system "catalytic process" with the active centers.

The methodology of predictions from scaling relations has been applied to diverse and complex systems including the problem of the hydrogenation of acetylene.[296] The result were numerous suggestions[297] for new systems, one of which covered the intermetallic compound PdGa just discussed. This approach was also able to reproduce the verification that the selectivity of this reaction is controlled mainly[196, 325] by the formation of Pd subsurface carbon bonds. The daring presentation of the correlation[297] between selective hydrogenation ability and the monetary value of the catalyst was even risked to predict cost--effect relationships.

A similar and fruitful analysis was undertaken in electrocatalysis.[14e, 44a, 278c, 326] Under the assumption that the catalysts were of a metallic nature, verifiable predictions were made about the composition and structure of electroreduction catalysts (ORRs) for oxygen (see Figure 2). Further experimental support has also been found.[322a, 327] The development of electrocatalysts for hydrogen evolution[278f] was also studied with this method by using a selection of over 700 systems. Notable in this work is the theoretical analysis that also included the stability of the phases against decomposition. An "unexpected" prediction was made of an effective material (a Pt compound) and subsequently experimentally verified. The oxidation reaction of oxygen (OER) was studied on oxides[44, 328] and compared mechanistically with the water splitting found in nature.[44b] The result was the explanation for why no better catalyst than RuO_2 can be found for this reaction although many different systems have been suggested. And this despite the significant overvoltage needed to successfully achieve the reaction with RuO_2 in comparison to the thermodynamic limit of the barrier. Unfortunately missing from this work is information about the nanostructuring and stability[195d, 329] of the system, characteristics that present large experimental[51j,^329a] challenges.

The theoretical design of a catalyst requires the subsequent synthesis of the material in question for its verification as well as knowledge of the composition on mesoscopic and macroscopic scales. This material then needs a functional characterization to show that the theoretical predictions about the active centers are in fact borne out. This has been done in several cases[7c, 265e, 278a,f] if, perhaps, in still a somewhat unrefined manner. However, side effects of the reactivity appeared that influenced the stability of the catalyst in an adverse way and no technical realization has been reported.

There are reservations about continuing along this path of theoretically supported design of catalysts with the current lack of chemical precision.[14e, 82] If the spectrum of the current reports of this approach in the literature is considered, it can be quickly seen that it is not the aim of this theory to provide a highly accurate prediction for one good catalyst: the rates are given on logarithmic scales over several orders of magnitude. In contrast, in real cases we are interested in the effect of a catalyst within a maximum factor of 10, usually, though, within a factor of two. Therefore, this theory of scaling relations may be regarded as a selector that supplies us with material suggestions on the scale of descriptors in Figure 22 (approx. in the middle) in which we can optimistically search for solutions. This approach excludes possibilities that are not relevant as possible solutions and narrows the space of material options for potential hits. At this time the theory utilizes rough structural models, cares hardly for size effects and not at all for chemically complex compound catalysts. The author supports the view that all methods enabling us to distance ourselves from empirical development are important for further progress in catalysis research if we can learn from the observed differences between theoretical and experimental results. There is no one single factor that fundamentally impedes improved precision. One important point is to use helpful information from models to exclude options that will certainly not lead to the goals we have set. The standard for judging on theory-supported catalysis research should not be an immediate technically useful result, or even time-saving compared to a purely empirical approach, but rather the sum of the physics-based conceptual and methodological insight that was gained throughout the process. The value of such findings results when they are utilized in a knowledge-based approach, such as suggested in Figure 19. The time saving will materialize after we have applied this concept to several problems because we can always use the knowledge-based insight ("why has something been observed") again and in a new context. This is not possible in empirical strategies with synthesis tests only because we have no knowledge of the causality of results in new situations.

The most promising route to move catalysis from an empirical science to a design science is the closing of the knowledge gaps that still abound. A sadly all too common denial of its existence shows itself though the proposal of "concepts" based on faulty physical reasoning that are vehemently defended. This does not bring us any closer to our goal. The method of an aesthetic-artistic design of active centers can act as an enrichment of the necessary creativity but is no replacement for the targeted construction based on chemically correct models of the reaction and free from material classes and structural guidelines.[5a,b, 265g] We know the way and possess the basic physical principles but are continuously tempted by the complexity of the kinetics and material chemistry of heterogeneous catalysts to take shortcuts. This results in a mesh of simplifications that impede rather than help the transfer of new knowledge to practical catalytic situations.

The theoretical approach discussed up until now selects materials according to their function based on simplified assumptions of structure and morphology and on neglecting the influence of reaction conditions on the catalyst. This corresponds to the description along the abscissa in Figure 22. To make a contribution to the material science of catalysis with theory, the orthogonal path can also be traversed that runs along the ordinate. In this case we obtain precise and detailed information about the predicted course of the rate-determining step and about the structural details of a chosen catalyst under reaction conditions. From this we can learn much about the constitution and dynamics of a given catalyst. It necessitates an elaborate theoretical apparatus with sufficient "chemical" accuracy that allows quantum mechanical calculations for adequately complex models. Furthermore, a description of thermodynamic functions at finite temperatures and pressures is necessary to construct phase diagrams of the catalyst as a function of the chemical potential of the reactants. This theory[9a, 11b, 152b, 235, 330] emphasizes conceptually the idea of the unity of catalyst and reaction, as described in Figures 12, 16, and 17.

The path to deciphering the systematic behavior of a catalyst step-by-step with the help of theory seems to be very promising at this time.[2g, 13c, 47a, 94, 331] The approach has been applied successfully to, among other procedures, hydrogenation catalysis over noble metals in a very realistic way.[10a,b, 14b,c, 265c, 296, 313b, 332] For methane synthesis a reaction network was also calculated extensively.[146] In these cases, however, rigid assumptions about the nature of the catalyst were made. For the selective oxidation of propane,[152a] a reaction network based on qualitative suggestions[312] was quantified. Here the splitting of the selectivity into partial and total oxidation was described as a function of the redox state of supposed active centers. The result is that a quantitative and experimentally observable[333] descriptor (surface coverage from peroxo species) can be theoretically established for understanding the principles of selectivity control. The resulting development shows how the fields of knowledge of molecular and solid-state catalysis can mutually benefit one another, especially if they become conceptually connected by the bridge of theory.

A further general and instructive example of the success of this theoretical approach is the investigation of CO oxidation over Ru. Starting from extensive experimental investigations[334] a comprehensive theoretical analysis[10c, 11a, 278b, 335] of the reaction was undertaken. One outstanding result for material chemistry is that it became clear with the help of the theoretical approach that the highest reactivity of the system is achieved when the surface does not form any single stable structure. Instead, the surface should lie energetically exactly in the middle between the oxide and metal. This state can be interpreted as a surface oxide and/or a defect state in an oxide film.[156b, 264b] It clarifies in part the contradictory perspectives[334d] on the nature of the active phase and on the oscillations of this reaction[336] that have been found. Clarification is also provided for the result that in the oxidation of methanol over Ru systems the most active state is a surface oxide that, finally adjusting to stationary conditions,[220, 337] forms either from a metal or an oxide precursor.

A further example of the possibilities of theory[9b, 11b] to help interpret complex experimental results is given by the silver/oxygen system used in catalysis for the epoxidation of ethylene and for the partial oxidation of methanol to formaldehyde under different conditions. In this case the results led to a new understanding about the dynamic state of catalysts. Merely the fact that the reactions (32) and (33):

$$2\ C_2H_4 + O_2 \rightarrow 2\ C_2H_4O \qquad (32)$$

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O \qquad (33)$$

lead to two very different products very likely means that silver is able to form different reactive forms from active oxygen. This happens under conditions at which the possibility of a metal oxide phase change can be excluded because of the instability of silver oxide. The system has been extensively studied experimentally.[126b, 179j,k, 187e, 338] Several significant results are summarized in Figure 23.

Under high-vacuum conditions, the system forms a series of reconstructed phases that represent ionic silver strongly interacting with atomic oxygen derived from the dissociation of molecular oxygen below room temperature. As a limit, silver oxide surface phases form up to about 473 K. Above this temperature more weakly bound forms of atomic oxygen exist along with oxygen dissolved under the surface. Above 773 K the latter segregates into a form of strongly bound oxygen localized in the surface. The bulk phase can hold a large amount of oxygen and even acts as a membrane at high temperatures for the removal of oxygen from air. The existence of oxygen dissolved in the metal bulk has been verified many times.[179k, 340] In the example experiment shown in Figure 23 C, oxygen originates from its diffusion deep in the bulk where, after depletion of the subsurface region, new oxygen from the bulk appears through desorption and causes a second desorption maximum. The existence of several different species of atomic oxygen can be seen very clearly in the measurements in Figure 23 as well as in related studies in the literature. They can be separated into nucleophilic and electrophilic forms. Nucleophilic forms are stable, cause the adsorption of organic substrates, and dehydrogenate hydrocarbons. Electrophilic species only result from the interaction of silver with subsurface species. They show only a slight stability, tend to diffuse into the bulk, and cause the transfer of oxygen onto organic, activated substrates such as olefins or alkoxides. The combination of a subsurface layer of oxygen with adsorbed oxygen directly above is especially effective at generating very electrophilic species (see Figure 23 A).

The electronic structure theory of this system was used to construct a phase diagram for the oxygen/silver system for catalytically relevant conditions. The diagram shows the fundamental trends of the structural development in a quantitative way.[341] It is problematic for the theory to represent the bulk species, identified as energetically unfavorable for many states of the system, in comparison to segregation. This is in concurrence with the observation that these states emerge under dynamic oxygen supplies and sufficient temperatures as well as with the application of nanostructured samples. They are metastable against segregation if they are to be isolated under normal conditions. The state in Figure 23 A,d was, however, found to be energetically equivalent to a state similar to that in Figure 23 A,b. Reconstruction and defect formation via oxygen adsorbate phases on silver were found to be in wonderful agreement with experimental results from theory.[339] Furthermore, it was shown that subsurface oxygen can even promote the process of defect generation as a starting point for restructuring and is supported by earlier experiments.[342] In a very early theoretical approach the formation of electrophilic species by the interaction of surface oxygen with subsurface oxygen was found to be significant for the generation of ethylene oxide.[343] This is of interest because the proposal was made before the experimentally water-tight proof of electrophilic oxygen[344] and the dynamics of the silver surface were obtained. The presence of adsorbed oxygen facilitates defect formation in metal, enables extensive structural dynamics, and leads to reconstructions of the surface at mild temperatures. This, on the other hand, has effects on the formation[339] of nucleophilic and electrophilic adsorbate phases.

The reconstruction behavior can, furthermore, be controlled through the formation of alloys. The system Ag-Cu has been reported experimentally[333] as being significantly more selective in ethylene epoxidation than pure silver. This was then attributed to the formation of an alloy. In a later extensive theoretical study[215] it was shown, in conjunction with parallel in-situ photoemission measurements, that it was in fact not an alloy but rather the formation of a thin surface phase of CuO on reconstructed silver. The exact structure and morphology of the silver was found to be sensitive to the chemical potential of the oxygen and a corresponding state diagram was developed. Several proposals[334] for active structures have resulted from this, however, although they are built on a theoretical basis, they were made with consideration of Cu and the structural dynamics of silver.

We can use the example of silver-catalyzed epoxidation of ethene to show that a quantitative description of the kinetics of a catalytic reaction should also contain reaction steps for creating and losing active sites. The interaction of reactants with the silver catalyst should thus be specified more in chemical detail than just using the asterisk symbol for the formation of an adsorbed species [Eq. (34)].

$$Ag+O_2<PRL>AgO_2* \qquad (34a)$$

$AgO_2^* + Ag_{step} \rightarrow 2\ AgO_{nu}^* + Ag$ (34b)

$AgO_{nu}^* + Ag_{sub} \rightleftharpoons AgO_{sub} + Ag_{step}$ (34c)

$AgO_{nu}^* + AgO_{sub} \rightarrow (AgO_{sub})O_{el} + Ag_{step}$ (34d)

$AgO_{nu}^* + Ag \rightleftharpoons AgO_{p4\times4} + Ag_{step}$ (34e)

$6\ AgO_{p4\times4} \rightarrow Ag(111) + 3\ O_2$ (34f)

$6\ Ag_{step} \rightarrow Ag(111)$ (34g)

$AgO_{sub} \rightarrow O_{dis} + Ag_{sub}$ (34h)

$AgO_{sub} + C_2H_4 \rightleftharpoons (AgO_{sub})C_2H_4^*$ (34i)

$(AgO_{sub})C_2H_4^* + (AgO_{sub})O_{el} \rightarrow C_2H_4O_{EO} + 2\ AgO_{sub}$ (34j)

$(AgO_{sub})C_2H_4^* + AgO_{nu}^* \rightarrow C_2H_4O_{AA} + AgO_{sub} + Ag$ (34k)

$C_2H_4O_{AA} + Ag \rightleftharpoons AgC_2H_4O_{AA}^*$ (34l)

$AgC_2H_4O_{AA}^* + 4\ AgO_{nu}^* + 2\ (AgO_{sub})O_{el} \rightarrow$

$2\ CO_2 + 2\ H_2O + 5Ag + 2\ (AgO_{sub})$ (34m)

Besides adsorbed molecular oxygen (AgO_2^*) we find atomic oxygen as nucleophilic species (AgO_{nu}^*), electrophilic species ($(AgO_{sub})O_{el}$), surface oxide ($AgO_{p4\times4}$), and subsurface species (AgO_{sub}) in agreement with the results presented in Figure 23.

The set of Equations (34) describes adsorption (a,b), formation of active oxygen species (c--e) plus the loss of active sites and restructuring of silver (f--h), in addition to the selective (i,j) and nonselective (k--m) oxidation of ethene. The overall combustion reaction is formulated in a rather cursory manner, as many details of this process are not well known. These equations may serve the purpose of understanding how many properties of the reactivity of the catalyst silver with the reactant oxygen except its dissociative activation need to be identified and quantified to arrive at a meaningful description of the target reaction according to the central scheme in Figure 16. We have not yet reached that stage of spending the effort to quantify the reaction parameters of catalyst formation despite that fact that we could do this from our level of analytical capabilities.

Parallel to the progress with theory for catalysis, the chemistry of the synthesis of catalysts must also be further developed.[145] Today we see the refinement and analytical substantiation of conventional synthesis procedures. This has enabled important progress mainly in the homogeneity and scalability of catalytic materials with a considerable deviation from thermodynamic stability leading to good catalytic properties.[109, 209a,c,h, 347] In addition, there is much activity in the synthesis of novel materials[268d, 348] whose potential for use as catalysts is being investigated. This very creative procedure is, however, less compatible with the planned advancement we have attempted to motivate here with theory that begins with a targeted property profile.[244a, 278a, 322a, 327a, 349]

The high specificity of their catalytic effect, which is connected to defects in the bulk structure, generally puts high demands on the synthesis of heterogeneous catalysts. It is not sufficient to only produce a single phase and then test its catalytic activity; along with this a suitable surface structure must also be found. This importance of the specificity of the active catalytic structure,[121] given by the sensitivity of the catalytic reaction to the local electronic structure, is often underestimated. This leads to the view that the synthesis of catalysts is a magical assignment because the usual analytical procedures often cannot differentiate well enough between the local surface structures. The result is that no structural "difference" can be found between substances with different catalytic properties that are chemically otherwise identical.

It should be mentioned at this stage that the multiple approaches for the selection of catalysts with combinatorial synthesis[273a, 350] that the use of chemical composition as the single variable will not, with any surety, result in the expected outcome. With this procedure[351] neither a structurally pure phase[352] nor a uniform and optimized surface structure will be achieved in general. Errors can arise especially with combinatorial optimizations in advanced generations[265a, 353] because the assumption that the catalytic effect is dependent only on the cation composition of the contact mass is incorrect. This does not diminish the value of high-throughput procedures for, as an example, the efficient investigation of the kinetic parameter range of a system[228a] or for material development in a predetermined compositional space.[211a, 354]

The goal for the future planning of synthesis strategies should be to start from the characteristics of the desired active centers. We have learned here that there are essentially two methods of approach for this. One is that either static or dynamic centers can be put to use. In catalytic reactions where a component that is difficult to activate (O_2, H_2, N_2, CO_2, H_2O) is to be converted in dissociated form, using a reactive structure, into a thermodynamically unfavorable product, it is conceivable, as a synthetic approach, to view the combination of both centers as a form of "bifunctionality". To support the concept of such systems that are regularly represented in practice, but often unrecognized in their bifunctionality, the features of both types of centers are given in Table 6. It is evident from this that a significant importance is to be given to the kinetics of the individual production steps[109a, 210a] of the cataylst. In particular, control of the chemical potential of the environment is critical during the steps of thermal treatment such as drying, calcination, and annealing. However, these are often not sufficiently analyzed and controlled, at least in academic synthesis.

A planned synthesis, therefore, needs the basic composition of a matrix phase that must be produced homogeneously and as a pure phase. In the case of complex compounds, however, difficult challenges await[355] to arrive at such phases. This does not only hold for bulk phase catalysts but also for supported systems in which the precursor of the active phase should be brought onto the supporting phase as homogeneously as possible. These challenges are solvable, as exemplified by the synthesis of micro- and mesoporous systems.[62c, 211a, 256a, 356] Furthermore, the chemical dynamics of the material under the planned reaction conditions must also be planned and adjusted. Then nanostructuring must be chosen such that it affects the activation kinetics in a favorable way. Here, stationary active centers must also be provided through the surface structure ("roughening" itself may not be sufficient) and a concept for stabilizing the active phase under the reaction conditions is also necessary. The latter must be achieved, however, without shutting down the dynamics of the process (reduction of the surface area is not enough). Currently there are only few studies that have been conceived in this way.[117, 209f,h] This opens a field for the development of inorganic chemistry[357] that can simultaneously offer multiple properties of a material arising out of its different dimensions.[48, 511, 358]

14. Conclusions

This survey of the current state of heterogeneous catalysis science shows that with the standard model we indeed possess a firm and generalized conceptual basis. The development of a quantum mechanical treatment of the atomic aspects of catalysis based on accurate calculations of the electronic structure of surfaces was triggered by experiments that were qualitatively instructional and quantitatively rigorously carried out. This treatment, with regards to the state of development, is at the same stage as the physiochemical theory of catalysis. A slight hesitation accompanies the use of the word "theory" because an important attribute of this level of maturity of a scientific field, the ability to predict phenomena for the concrete knowledge-based development of catalysts and processes, has not yet been established.

The author apologizies to the readers for the often intentional and unintentional simplification of the presentation. The task in this Review was to demonstrate to the reader the need to allow a degree of chemical complexity to enter into the rigorous world of physicochemical catalysis. Considering catalysis as a rigid gas--solid interfacial problem is only true for the boundary case of minimal reactivity. Synthetic chemistry is more interested in developing catalysis into a state of predicting and designing functional material of considerable complexity for performing effectively the desired task of a chemical transformation. This work should show that bringing together these two views is a central paradigm in "unifying concepts in catalysis".

In the last few decades, three lines of development in catalysis science have led to the expectation that we are on the cusp of moving from a concept of catalysis to a theory of catalysis. One of these lines is the progressing insight that there are no fundamental differences between the subdisciplines of catalysis science. The treatment of heterogeneous catalysts within the concept of dynamic systems marked the first time that the original difference between dynamic active centers in molecular catalysis and static rigidly defined centers in interface analysis fell away. A second line is the swift development of model catalysis away from such static systems toward nanostructured systems. Here the chemical complexity and the dynamic behavior of high-performance catalysts can be described without losing the functional analysis with exactly defined boundary conditions. The third line can be described through the continuing maturity of in situ functional analysis (or operando analysis). Today we are able to decode the function of high-performance catalysts without the use of models and can investigate the structural features of these functions.

These three developments, which have been described and discussed in the current Review, are focused on ascribing dynamic properties to catalytic materials. The dynamics include charge carriers in the electronic structure and atoms in the geometric structure on differing scales in space and time and can, therefore, be understood and quantified through a single characteristic. The task of catalysis to convert measurable quantities of material is a property that plays out on different scales and necessitates for this reason the observation of a large number of physical and chemical phenomena simultaneously.

Viewed historically, we have mastered the challenges of catalysis as system chemistry and multiscale phenomenon by implementing a series of strict boundary conditions and simplifications in the analysis of catalytic systems excluding complexity. These enable the formulation and justification for the standard model. However, to complete the development of the theory of catalysis we must take back several of these boundary conditions and be willing to accept the resulting heightened complexity of the treatment. This is achieved for example by explicitly implementing the dynamics discussed here and integrating them quantitatively into the mathematical description of catalysis as well as qualitatively into the design methods. This should not give the impression that this projection is a new or even an original assertion of this Review. More or less this same requirement is found in many conceptional works on catalysis. In the past it was not conceivable to deal with the complexity of dynamic catalysts and at present it is still inconvenient to do so as the efforts required are still substantial.

At this point the challenge can best be overcome on the theoretical side if the two orthogonally running approaches to theoretical treatments of catalysts were to gather into a single all-encompassing model instead of remaining opposed to one another. In experiments we should mind the following points as a consequence of the insight into the dynamic nature of catalysis:

1. Active centers cannot be premade but are formed during the activation of catalyst.

2. For this reason we must provide materials with the possibility and ability to form dynamic phases. Nanostructuring, chemical and morphological homogeneity, and careful optimization of the activation are to be undertaken for every system and then analytically understood.

3. Catalysts are to be thoroughly characterized before and after the reaction.

4. In situ investigations with complementary methods are not a "luxury" but rather essential parts of the formulating a hypothesis on the function of materials.

5. The development and optimization of the material and reactor as conceptual unit is a prerequisite for the understanding of functionality. The indispensable basis for this is the view of that the investigated transformation is

a network of reactions both between reactants themselves and between the reactants and the catalyst.

6. The chemistry that, starting with solid bodies, makes dynamic systems out of a stabilizing matrix and an active interface is still relatively uncharted. Fundamental knowledge and insight are missing from inorganic chemistry describing the reactivity of nanostructured systems under the conditions of catalytic transformation.

7. Active centers are rare objects in the space--time development of a catalyst and only very small stationary concentrations of them can be expected. The strategy for investigating them must take this into account. We need methods that can unambiguously differentiate tiny regions at an interface from the main phase or from an under layer.

8. Such in situ methods are still scarce. A significant expansion of our analytical palette is still required that can combine atomic resolution with exact chemical identification, surface sensitivity, and in situ capabilities.

9. Testing materials requires an individual optimization of the reaction conditions; the practice of testing entire libraries of materials with universal conditions without parameter variation causes important insight to be lost in the reaction procedure and hampers the identification of possibly new and suitable candidate materials.

10. Concepts for synthesis may be developed along the lines that materials should be made available in scalable

> processes showing a stationary catalytic performance so that they may be kinetically and functionally investigated. Nonscalable systems and mere curious properties are less suitable to help catalysis science progress.

The question may be asked why everything seems to have become so complicated in the end and which simple force is driving all of this complexity. The qualitative answer to this is simple: the driving force is the minimization of the total energy of the system. Catalysts are frustrated because we ensure during synthesis that they cannot reach their minimum energy state as long as they are subject to reaction conditions. Through this we force a state of the material that is not in equilibrium under working conditions. The material's attempt to reach equilibrium sets the dynamics in motion: The reaction conditions allow the heterogeneous system on the surface to begin a process that leads to the thermodynamically stable (deactivated) states via the formation of the active phase. We can cleverly stop this process from causing changes in the termination layer or the nanostructuring that go beyond simply returning to the initial phase. The chemical dynamics of the formation of active centers is for the material an unwanted consequence of its high-energy state as are the occasional macroscopic kinetic oscillations in the failed attempt of the catalyst to stabilize itself. The cyclic process of formation and dissolution of ligand-to-metal bonds in metal-organic catalysis is also an expression of the energetically unstable overall state of a reaction mixture allowing the interchange of different configurations of ligands, reactants, and central atoms. The entire central task of catalysis is, therefore, the generation and stabilization of energetically frustrated systems. The heat of reaction continuously adds new energy to the system and allows the frustrated state to remain, as long as we do not go beyond a critical threshold that will send the system into its stable state that is non-reactive.

The collaborative and interdisciplinary way in which catalysis is currently developing, a trend reflected in the establishment of successful centers for catalysis research, brings us closer to the goal of working in a knowledge-based approach. Each one of us can help with the advancement toward a theory-based science. This happens in our daily work and through the publication of high-quality studies, although two improvements may be suggested. Our colleagues engaged in theoretical work could calibrate their methods with generally accepted test systems with documentation for every case. They may also establish a link to experimental work by calculating observable quantities with their models, again with helpful documentation. On the experimental side we should begin to document the test results of our catalysts in a complete way that can be re-used when needed. A "best practice list" can serve us well for this and should be developed from a central body representing our scientific field. If we can cooperatively create structured documentation using the methods of the internet, we will save ourselves much work while at the same time supporting cooperation. Such initiative has proven to be well worth the effort in other fields of science.

In the end, the observation remains that we have indeed come a long way in fulfilling the demands introduced in the two citations at the beginning of this work. The importance of catalysis as a cross-disciplinary science of chemistry for our discipline and for technological challenges is clear. It should be incentive enough to complete our work and to proceed into the future with a physics-based comprehensive and predictive theory of catalysis that can guide rational synthesis to arrive at suitable catalysis solutions for the challenges in our future.

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Figure 1 Dimensions in catalysis: A) Change in energy (*E*) of a catalytic system with respect to the reaction coordinate (RC) for the basic individual steps: Tm: transport macroscopic, Tp: transport in pores or solvation shells, Ch: chemisorption, AC: activation (dissociation), Re: reaction, De: desorption, dissociation. The energy changes in red denote the impact of the reaction on active centers that are taken here to be adaptive. B) Space--time scales for a heterogeneous catalytic process: blue: the molecular reaction, red: chemical dynamics on the catalyst, green: transport processes of the reactants. The vertical bars indicate often-used terms for the spacial dimensions.

Figure 2 A simple reaction network for the activation of oxygen. Hydrogen and an unnamed electron donor are needed. Red denotes the formal oxidation state -1 and blue the oxidation state -2.

Figure 3 Scientific activities in the oxidative coupling of methane (OCM) as a function of time. In the lower graphic the most successful catalysts are displayed in a conversion--selectivity diagram.

Figure 4 EPR spectra (X band) of MgO after heating in a vacuum at 1073 K. The measurement was performed at 77 K. For spectrum (a), only oxygen (50 mbar) was introduced, whereas for spectrum (b), oxygen and methane were introduced. Three different axial anisotropic environments can be seen for the hyperoxide radical.

Figure 5 Simplified reaction network for the activation of methane over MgO. The double appearance of "CH_3" is for clarity and has no mechanistic purpose.

Figure 6 A) Model of a step in the (100) plane of MgO. The oxygen ions (red) are shown with a realistic size compared to the Mg^{2+} ions (gray). A polar (111) step is displayed in the inset as a comparison. B) IR transmission spectrum of MgO after adsorption of methane (solid line) and after coadsorption of methane and CO (dashed line; measurement temperature 77 K, adsorption pressure 5 mBar). The schemes reflect the bonding arrangement of the adsorbates. C) Aberration-corrected TEM image of a MgO nanoparticle.

Figure 7 Correlation of the consumption rate of methane as well as production rates of the C2 target products with the area of the adsorption bands of the IR spectra of CO at 2147 cm^{-1} resulting from the deconvolution of the complex band forms. Overlap with absorption from other arrangements of CO on MgO defects is responsible for most of the overall error.

Figure 8 Intermediate steps for the activation of methane on MgO: (1) on a free (100) step, (2) on a (111) O-terminated step. The hydroxylation is not shown.

Figure 9 Metal nanoparticles show partially exposed metal atoms. A) Model of active centers[102] from Taylor. B--F) Aberration-corrected TEM images of nanoparticles of copper. B) shows a bare surface. The blurring of the termination atoms is caused by stimulation (motion) during the TEM measurement. C--F) Magnification series on a nanoparticle (region shown in green), showing different varieties of defects in a single particle.

Figure 10 Structure--function relationship for Cu nanoparticles. A) catalytic activity at 483 K (blue) and 523 K (red) in a stationary state for a stoichiometric reaction mixture at 60 bar pressure as [mass methanol/mass catalyst]×Cu surface area in arbitrary units. If the Cu surface were the controlling value, the result would be parallel to the *x*-axis. B) HR-TEM image of the interior of a Cu nanoparticle showing the dislocation in the stacking sequence of the atoms. The red line shows the dislocation of a row of atoms relative to the nominal position through the stacking sequence. C) Stacking errors effect a change in the surface termination of Cu nanoparticles. Three twin boundaries (yellow) change in distinct ways (red: (100), blue: (110), green: (111)). Taken from Ref. [56e].

Figure 11 Catalytic etching in mesoscopic dimensions (in SEM). A--C) Silver in oxidation catalysis. The particles from (A) are completely sintered with one another after 100 h operation during the epoxidation of ethene at 523 K. Picture (B) shows the generation of crystal facets by the transport of bulk atoms: the small bright objects are particles of silicon contamination originally dissolved in the bulk that segregate as oxide. C) A single-crystalline sphere illustrating that catalytic etching is structure-sensitive and does not attack the (111) surface. The bright objects are relocated silver metal. D) Platinum, also after methanol oxidation. See Ref. [126]. Noticeable are the differing orientations of the grains that can be identified through the direction of the visible (111) facets.

Figure 12 Simplified representation of the steps of a heterogeneous reaction according to the standard model. Steps (1)--(4) are shown in a top view of an ordered surface with two types of atoms and a monatomic step. They represent: (1) molecular adsorption, (2) island formation, (3) diffusion to the active center, and (4) dissociation. Steps (5)--(7) are shown as cross-section through the surface. The reactant is a diatomic molecule (blue-green). They represent: Reaction (A) desorption, reaction (B) desorption of a product and generation of a surface bond of the other product, (C) desorption of a product and the generation of a subsurface bond with the other product.

Figure 13 STM image of the decomposition of 0.3 L NO on (0001) Ru at 300 K after 30 min reaction time. The dark line depicts a top view of a monatomic step. From Ref. [130c].

Figure 14 The dehydrogenation of EB to ST. A) Microreactor for the investigation of single crystals. B) LEED images (75 eV) from a Fe_2O_3 (111) surface before and after a reaction at 873 K with EB. C) Changes in the rate of EB consumption over time on a single-crystalline Fe_2O_3 catalyst; (1) only EB with water

(1:10), (2) with EB and oxygen (1:10:0.5). D) As in (C) but with a polycrystalline Fe_2O_3 catalyst (optical image).

Figure 15 Influential factors that control the degree of surface coverage of a material in a heterogeneous reaction in the limiting case of high-performance conversion.

Figure 16 A realistic description of the feedback loop between the material chemistry of a heterogeneous catalyst and its function. The coloring elucidates different levels of chemistry and is clarified in the text.

Figure 17 Different dynamic control elements affect heterogeneous catalyst in different dimensions of space and time. See also Figure 1.

Figure 18 Electron microscopy images of active metal catalysts. The view is of two-dimensional projections of columns composed of rows of atoms. The blurred regions are from structural elements (promotors) not made up from the columns of the main components. A) Iron with promoters for ammonia synthesis, B) copper with ZnO for methanol synthesis. Image (A) shows an iron metal platelet with a [010] orientation that contains many defects and is covered by islands of the promotor oxide (K, Ca, Al) that form a "crust" around the boundary surfaces. The copper particle has formed twin domains and shows several facets and internal lattice defects. It is supported and surrounded by ZnO. The very thin layer in the upper part of the image is graphitic ZnO,[13a] while the mineral spacer in the lower portion of the picture is mainly defect-rich ZnO with a zinc blende structure. The structures were each identified by EELS and by analysis of the Fourier transformations of the lattice. The samples were produced in a nanoreactor and loaded into the microscope under anaerobic conditions.

Figure 19 Scheme indicating a knowledge-based approach to practical catalysis. The arrows show the sequence of tasks that must be completed multiple times to arrive at a sensible solution. The colors represent interdisciplinary cooperation that will be performed most effectively in a team setting. It is important that the steps toward realization are accompanied from the beginning through process technology so that critical parameters of the procedure can be adjusted to the development of the process technology as soon as possible. The common sequential handling of synthesis and testing is unproductive because it only "calls on" the other disciplines when no further immediate improvements in the performance of the reaction can be achieved. The continuous accompaniment of ecological considerations, which is always reacting to the changing eco-social conditions and economic goals with respect to implementation, is not shown.

Figure 20 Development of the active phase on the catalyst $MoVNbTeO_x$ in the reaction of propane with oxygen to acrylic acid. A) The development of the relative cation composition in the bulk and in the termination layer (photoemission at 620 eV kinetic energy) in different reaction environments.[61] B) A selection of morphological data: the needles of the crystal indicate the many steps along the (001) growth axis. Long needles[210b] display a significantly higher selectivity (60 %) with regard to the target product than do the short needles (5 %). C) The effect of water vapor leads to the development of a V^{5+} species in the upper surface layers while the V^{4+} remains in the deeper layers and does not react with water. Over a reaction time of 10 h at 1 mbar reaction pressure the proportion of the V^{5+} phase increases. At the same time the yield of acrylic acid improves. However, the elemental concentration in the segregated termination layer remains unchanged.

Figure 21 Several observations[300a] concerning the use of A) Pd, B) PdGa, and C,D) Pd_2Ga as a catalyst for the selective hydrogenation of C_2H_2 to C_2H_4. A) In situ X-ray powder data (detailed region of the Pd(111) reflections) of approximately 4 nm Pd particles on carbon nanorods: a) fresh catalyst in He at 300 K, b) in 4 % hydrogen at 400 K, c) in 2 % acetylene, 4 % hydrogen at 400 K, d) as in (c) at 503 K, e) in nitrogen at 503 K. The blue lines show reflection positions of pure Pd, the red lines the shift for β-PdH, the intermediate reflections show the generation of PdC_x.[297] B) Temperature-programed desorption of CO on single crystals of Pd and Pt with a (111) orientation and PdGa with two terminations. C) XPS from Pd and Pd_2Ga nanoparticles on carbon nanotubes: a) Pd in 0.2 mbar He, b) Pd_2Ga in 0.2 mbar He, c) Pd_2Ga in 0.2 mbar H_2. No hydride phase is formed for the intermetallic compound. D) TEM and EDX analysis of Pd_2Ga on carbon nanotubes. The TEM image shows the good adhesion of the Pd_2Ga and the EDX analysis the homogeneity of the elemental distribution.[225]

Figure 22 Relationship between the barrier height for the activation of a reactant and the strength of its interaction with a series of active phases (above) and the reaction rate of the corresponding catalytic conversion (below). The relation is shown for two reactants (red, black). The red field denotes the regions of the material descriptor (D_{mat}) in which the reactant is bonded too strongly to the catalyst, the green region shows where the interaction is too weak. E_{rea} is the enthalpy of reaction of the rate determining process, E_{A} is its activation barrier.

Figure 23 Several experimental results for silver as an oxidation catalyst. A) Stages of the interaction of oxygen with silver beginning at ca. 423 K. a) Adsorption and reconstruction, b) surface oxide and facilitated defect formation, c) as in (b) plus electrophilic oxygen through subsurface oxygen integration, d) surface oxide. The process of integration of oxygen into the bulk without the generation of an oxide proceeds much further at ca. 723 K, although only a small amount of adsorbed oxygen is available on the surface. B) XP spectra (O1s) of silver in 0.5 mbar oxygen: bottom: 2 h at 423 K, middle: 30 min at 723 K, top: 5 h at 723 K. C) XPS (O1s) desorption series of oxygen from the state (c) in (B). D) XPS (O1s) from silver particles (100 nm) in oxygen and ethylene (1:2, 0.5 mbar) at 503 K for the given times. E) Correlation of the proportions of the quantities of electrophilic (magenta and dark green in (D)) to nucleophilic (red, light green in (D)) oxygen versus the in situ observed selectivity to ethylene oxide. From Refs. [2b], [339].

Table 1 Thermodynamic data for select catalytic oxidation reactions.

Sratting material	Target product	Mol water per Mol starting material	ΔH_{298} target product	ΔH_{298} Total oxidation

CH_3OH	CH_2O	1	-311	-675
C_2H_4	C_2H_4O	0	-438	-1323
C_3H_6	C_3H_4O	1	-365	-1959
i-C_4H_8	C_4H_6	1	-242	-2522

Table 2 Selectivities of an M1 catalyst at different pressures.[a]

Selectivity [%]	25 Pa	1000 Pa
Oxidation of ethane		
C_2H_4	98	97
CO	2	1
CO_2	1	2
Oxidation of propane		
C_3H_6	51	64
CO	19	8
CO_2	29	11

[a] Temperature 673 K, stoichiometric feed, flux 9000 GHSV at 1000 Pa.

Table 3 Some parameters[164a, 164f] for the sorption of ethylbenzene (EB) and styrene (St) on single-crystal model catalysts.[a]

Surface	E_{des} St	E_{des} EB	θ EB [%]	θ St [%]	θ St/ θ EB
Fe_3O_4 (111)	118	86	92	100	250
Fe_2O_3 (111)	73	64	37	29	0.8
$KFeO_2$ (111)	65	65	25	6	0.2

[a] The desorption energy is given in kJ mol^{-1}. The degree of surface coverage was obtained with a reactant pressure of 100 mbar at a reaction temperature of 900 K.

Table 4 Examples of chemical dynamics in heterogeneous catalysts. The references cite sources in the literature that provide context.

Reaction	Basisphase	Active phase	Reference
ammonia synthesis	Fe	$Fe_{18}N_{1-x}$	[213]
formaldehyde synthesis	Ag	$Ag_{sub}O$	[214]
formaldehyde synthesis	Cu	$Cu_{sub}O$	[215]
methanol synthesis	Cu	$Cu_{sub}O+ZnO_{gr}$	[56e]
ethylene epoxidation	Ag	$Ag_{sub}O+O$	[216]
ethylene epoxidation	$AgCu_x$	$Ag_{sub}O+CuO_{1-x}$	[217]
selective hydrogenation	Pd	$Pd_{sub}C$	[218]
selective hydrogenation	PdGa	Pd@PdGa	[56d]
selective hydrogenation	Pt	C@Pt	[219]

formaldehyde synthesis	RuO_2	$Ru_{sub}O$	[220]
CO oxidation	Ru, RuO_2	$Ru_{sub}O$	[221]
styrene synthesis DH	Fe_3O_4	$KFeO_2$	[164a]
styrene synthesis DH	Fe_2O_3	$C@Fe_3O_4$	[170b]
styrene synthesis ODH	C	$C_xH_yO_z$	[37e]
butane to MSA	VOP_2O_7	$V_xO_y+H_3PO_4$	[222]
butane to MSA	$V_2O_5 \times H_2O$	V_xO_y	[223]
propane to acrylic acid	$MoNbVTeO_x$	$V_xO_y+TeO_2$	[224]
propane to CO	NiO	$Ni_{sub}O$	[160b]

Table 5 Some of the approaches used today and their limitations.

Method	In situ capability	Investigated catalyst characterist
physisorption	no	surface, morphology
chemisoprtion, temperature-programmed desorption	limited	reactive centers, quantitative, qu
microcalorimetry	limited	heat of sorption
vibrational spectroscopy	yes	structure and bonding geometry of phases

optical spectroscopy	yes	electronic structure of active pha adsorbate Phases
photoelectron spectroscopy	yes	quantitative surface analysis, dep profiles, adsorbate phases, surfac electronic structure
ion scattering	no	composition and structure of the o layers
X-ray absorption	yes	electronic structure of active pha adsorbate phases and geometrical s of active phases
scanning tunneling microscopy	yes	morphological structure and dynami mesoscopic scale
X-ray microscopy	yes	morphology, chemical structure, to mesoscopic, analysis
transmission electron microscopy	limited	atomic structure of active phases, structural dynamics, chemical comp and electronic structure with atom resolution
X-ray scattering	limited	translationally symmetric geometri structure of bulk and surface (lim real structure, defects
neutron scattering	yes	real structure and defects of the phases

inelastic scattering of X-rays and neutrons	yes	adsorbate phases under harsh react conditions (pressure, temperature)
thermal Aanalysis	limited	chemical dynamics, adsorbates, pha
magnetic resonance	limited	structure and dynamics of active p adsorbates

Table 6   Several properties of active centers.

Property	Static center	Dynamic center
sormation	during synthesis	in contact with reactants
activation	not necessary	matrix during initial activation, active sites contnuously
structure	static, observable	dynamical, "amorphous"
composition	similar to bulk phase	no relation to bulk phase
existence	always as high-energy site	stochastic as a rare event
effect	splitting of small molecules	formation of sensitive molecules
regeneration	through desorption	through molecular dynamics

component of	the bulk phase	a termination layer different from the bulk phase (matrix)
realization	steps, lattice defects, doping	two-dimensional layer or islands, semiconductor properties defined through under layer

Prof. Robert Schlögl (born Feb. 23, 1954 Munich) studied chemistry and completed his PhD at Ludwig Maximilians University in Munich. After postdoctoral research at Cambridge and Basle and a professorship at the University Frankfurt, he became a director at the Fritz Haber Institute of the Max Planck Society in Berlin in 1994. In 2011 he was appointed founding director of the Max Planck Institute for Chemical Energy Conversion in Mülheim a.d. Ruhr. His research mainly focuses on inorganic chemistry, heterogeneous catalysis, nanostructures, material science for chemical energy conversion, and concepts for sustainable energy supply and storage.