

Robert Schlögl*

Interfacial catalytic materials; challenge for inorganic synthetic chemistry

<https://doi.org/10.1515/znb-2022-0070>

Received April 26, 2022; accepted May 17, 2022;

published online May 30, 2022

Abstract: Interfacial catalysts are indispensable functional materials in the energy transformation. The traditional empirical search strategies reach their potential. Knowledge-based approaches have not been able to deliver innovative and scalable solutions. Following a short analysis of the origin of these shortcomings a fresh attempt on the material challenge of catalysis is proposed. The approach combines functional understanding of material dynamics derived from operando analysis with digital catalysis science guiding the exploration of non-linear interactions of material genes to catalytic functions. This critically requires the ingenuity of the synthetic inorganic chemist to let us understand the reactivity of well-defined materials under the specific conditions of catalytic operation. It is the understanding of how the kinetics of phase changes brings about and destroys active sites in catalytic materials that forms the basis of realistic material concepts. A rigorous prediction and engineering of these processes may not be possible due to the complexity of options involved.

Keywords: energy chemistry; functional interface approach; surface science.

Dedicated to Professor Martin Lerch on the occasion of his 60th birthday.

1 Introduction

The energy transformation and the geopolitical destabilisation as hallmarks of the economic developments in the second decade of the century demand novel approaches in catalytic chemistry. This science and technology have to provide solutions for transporting and storage of a large fraction of the global energy demand within a geographically diversified international market. Water is converted for this purpose with regenerative energy into hydrogen and

derivative energy carriers from which oxidation regains energy for end applications. Optimized catalysts are required for electrically or thermally stimulated processes operating robustly with very high selectivity. The utilization of noble metals is practically excluded for the scale of demand and for geopolitical reasons. Cyclic operation with respect to carbon and all mineral components of these processes is demanded for qualifying as “sustainable”. An impression about the scale of such catalytic operation follows from the estimate that possibly 30% of the global energy demand will have to be converted to energy carrier molecules. This amounts to about 40,000 TWh equivalent to about 10,000 world-scale (100 MW_{th}) power stations.

Figure 1 illustrates the system design for sustainable energy supply that is independent from localization and timing as it can store and transport all energy quantities required. The shaded area encompasses critical elements requiring catalytic processes. From top to bottom one can see that the oxidation states of the energy carrier atoms being carbon and nitrogen are reduced by storing regenerative energy. Energy is liberated by combustion or dehydrogenation of the energy carriers. This mode of operation has led to the designation [1] of chemical energy conversion (CEC)-based energy systems as “chemical batteries”.

Such requirement poses a massive challenge on chemical industry and its catalytic technologies. The underlying science has now to prove that its maturation from an empirical “black magic” into a knowledge base can deliver design concepts and materials fulfilling the high expectations. The traditional approaches have failed to deliver [2] suitable answers within the last half century when enormous efforts with already substantial success were put into the chemistry of energy-relevant “petrochemical” [3] reactions.

The present text briefly recalls the pathways taken so far and tries to identify the conceptual weaknesses. It then suggests a generic solution for finding novel functional interfaces for energy-related reactions. Signature roles of material synthesis and importance of phase-pure reference materials will be elucidated.

2 Terminology

In the review process of this work, it was criticised that the terminology would be imprecise and misleading with

*Corresponding author: Robert Schlögl, Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim a.d. Ruhr, Germany; and Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany, E-mail: acsek@fhi-berlin.mpg.de

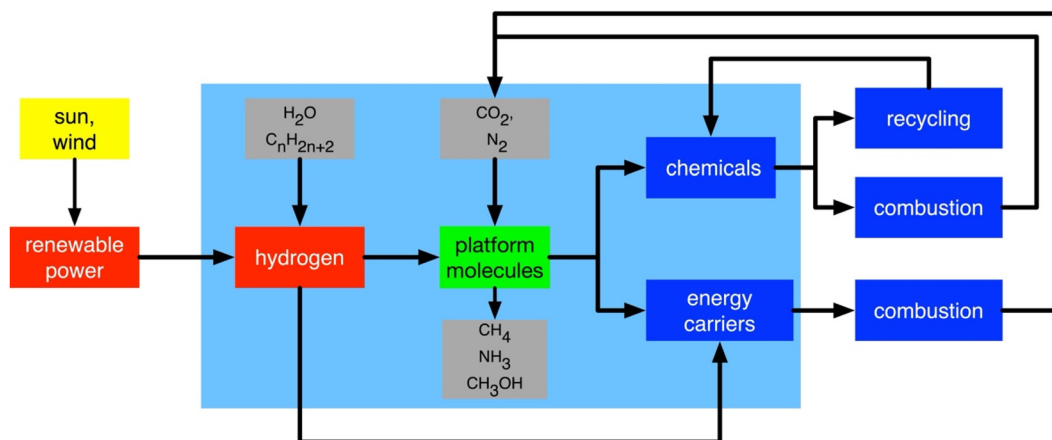


Figure 1: Generic scheme of energy supply using the concept of chemical batteries. The shaded area designates the processes requiring catalysis as critical science and technology.

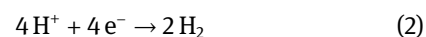
respect to physicochemical rigor. This is correct. It is an intention of this work to help to bridge the gap between physical chemistry and the emerging energy science. There many disciplines besides physical chemistry have created a terminology that is well understood there but at variance with the traditional meanings. Examples are “renewable electricity” and “renewable energy” or the elements of the “*Farbenlehre*” of molecular energy carriers such as “green hydrogen”. The custom to define energy requirements in terms of the power required such as “1 GW of hydrogen” is of course not correct in terms of physical chemistry. In energy science many of these terms are still unprecise in their definitions as for example the rules for the essential life cycle analysis are not standardised. Nonetheless, the present work uses such terminology and hopes to contribute to the mutual tolerance required to bridge the terminology gap.

3 Energy chemistry

Few chemical reactions of small molecules provide the material basis of sustainable energy cycles which transform primary renewable electricity in molecular energy carriers that retain the volatile energy in unlimited amounts for infinite times. With such chemical batteries the essential defossilization can be realized as to minimize climate change [4] and still support the socio-economic well-being of mankind. It is important to understand that unlike with fossil energy sources (coal, oil and gas) such chemical batteries are no energy sources but energy carriers. The common energy source for all sustainable molecular energy carriers is always the solar radiation, usually converted

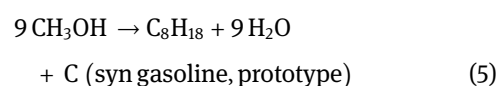
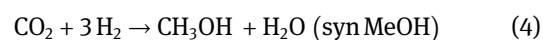
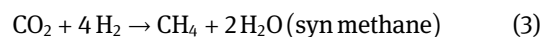
by PV or wind mills into primary electricity termed “renewable”.

The primary molecular energy carrier is hydrogen. It is available from water splitting, that transfers electrons from oxide ions to protons that are reduced to molecular hydrogen [4]. Two catalysts for oxide oxidation and proton reduction are required. It is noted that the difficult half reaction is the oxide oxidation providing the electrons needed to generate hydrogen from protons.



Most technical embodiments of these reactions are electrocatalytic. Here catalysts need to be bifunctional [5]. They must allow for stoichiometric amounts of electron flow as well as for adsorption and reaction of water and its dissociation products OH^- and H_3O^+ . Complex metal-semiconductor systems [6, 7] are in operation. Alternative concepts for water splitting use plasma catalysis or thermochemical reactions to perform reactions (1) and (2). Catalysis is essential to minimize the excess energy required to drive the kinetics of these endothermic processes.

As the physical properties of di-hydrogen hamper facile storage and transport, it will be useful to derivatize hydrogen into synthetic fuels [4] by CEC that may be identical or similar in their application profiles to fossil energy sources.





Nickel, copper, aluminosilicate microporous materials and iron are typical catalysts suitable for these reactions.

It is not the purpose of this text to enumerate the many bottlenecks in applying the existing catalysts for large-scale energy transformations. Some hints may suffice being stability against trace impurities or sustainability against water formation in high-temperature reduction of CO₂, coke deposition or nitride formation in dehydrogenation reactions to motivate the critical need [2] for improving our catalytic processes. Incremental empirical optimization has been performed over decades on these reactions and has come to an end of its potential. What is needed now is the knowledge-based approach to the kinetic optimum of these reactions.

4 The surface science approach

The advent of surface science in the 1960 years transformed [8] catalytic chemistry that found all the systems mentioned above by trial-and-error into a rigorous physical [9] and quantitative [9, 10] science. It allowed the application of quantum chemical theory and microkinetic modelling [11, 12] and led to the rational explanation of the mode of operation [13–15] of the metal-based catalytic processes enumerated above. The generalization of the theoretical description [16, 17] of catalytic reactions [2, 18–21] further allowed to predict the maximal performances of given catalysts [21] or to predict novel catalytic materials that were also found to be active [2] once they were synthesized.

All these successes, accomplished on a variety of reactions including ammonia synthesis and CO oxidation as prototypes for hydrogenation and oxidation reactions, make us believe that we now have a firm conceptual understanding of what catalysts do [9, 10, 16, 17] and what they are [22, 23]. *Catalysts are functional materials that expose rare high energy sites [24, 25] at the interface to a reactant phase as single [26, 27] or few-atom sized entities that enable molecular transformations. These sites are either not altered or regenerated during operation and thus allow multiple executions of molecular transformations.* Eventually the material “de-activates” and loses the ability to execute molecular transformations. The action of a catalyst modifies the way of the reactants [28, 29] through the energy hypersurface created by the multiple interactions between the molecules with the catalyst surface; consequently the product distribution changes with the action of a catalyst and also with the specific type of the catalysts [28–33] (“selectivity”). Chemical transformations form complex networks [34] of elementary reactions (a process

in which the reaction coordinate of the system is changed in only one dimension) of which a catalyst changes at least one reaction (rate-determining step).

The fact that a catalytic interface offers a platform for reactants to meet and rearrange [34–36] in exchange with the “active” sites greatly affects the energy barriers and so changes the kinetics of chemical transformations. Catalysts cannot change the thermodynamic boundaries of chemical processes representing the ultimate limit of performance.

Catalysis science attempts to maximize the abundance and lifetime of active sites as part of a matrix called “active mass” giving together rise to maximal productivity that is required for the world-scale applications in energy chemistry. The active mass comprises the embodiment of a catalyst usually supported on a seemingly inert carrier with high geometric surface area for maximizing the number of active sites per unit mass. The active mass is selected such the local electronic structure at an active site with respect to the molecular structure of reagents and products allows for a maximum surface coverage [37–40] of reactants and simultaneously for a minimum coverage of products. The performance of catalyst can thus be described as a set of sorption processes [29] or coverages of activated surface intermediates that is traced back through quantum chemistry [16, 41, 42] to the nature of the chemical bonds in the reactants and in the active site.

5 Weaknesses of the concept

This highly convincing rigorous concept [43] did not lead to any rationally designed novel catalyst of practical relevance despite multiple calls [14, 44]. The origins are manifold. A whole set of deficits concerns the considerations for the necessary transport of molecules and energy to and from the active sites. This very important aspect is neglected in molecular scale descriptions [41, 45] of active sites and their interactions with (few) reactant molecules. The large body of literature on this subject being central to chemical engineering is not followed here except mentioning that for these reasons the mesoscopic dimensions and macroscopic shapes of catalyst materials are equally important than is the local electronic structure [46] of active sites.

An even more fundamental deficit considers the stability of the systems. Catalysis requires the active sites to perform the catalytic reaction many times. The high energy site must not lose its local energy and must not undergo irreversible binding with reaction intermediates or products. Such processes running aside of the desired catalytic conversion are frequently not considered in material design concepts. This is because of the immense parameter space

opening for such unwanted reactions of active sites the exact chemical nature and structure [47, 48] of which is rarely known. Reactive sites are typically modelled by relaxed static geometries derived from translational crystal terminations with adsorbates. The surface science approach thus covers only a fraction [49–51] of the chemical reactivity of the system. One example is the usual neglect of the reaction of an activated molecular fragment with the active mass by subduction below the surface and formation of a “surface compound”. Although it is known today that such static approximations are not realistic only limited attempts have been made to develop alternatives such as molecular dynamics description [45]. The results and predictions from static surface science cannot be extrapolated to “high pressure” with the intention to describe the performing catalyst system. This weakness is termed “science gap” and caused much disappointment amongst practitioners of catalysis.

6 Other concepts

Recognizing these weaknesses led to other conceptual approaches. An early attempt was on designing single active sites and placing them into well-defined 3-dimensional porous environments. Their structure and function were to be investigated by bulk-sensitive methods such as NMR (Nuclear Magnetic Resonance) and EXAFS (Extended X-ray Adsorption Fine Structure). The success [23, 52–54] of this concept was however, limited likely due to the narrow synthetic options.

An alternative concept of combinatorial catalysis was first to postulate that atomic complexity must be removed. The inherent complexity of understanding atomistic details of catalyst-reactant interactions were considered as intractable. It was rather suggested that by statistical methods and high-throughput experimentation [55–57] it should be possible to find the global material optimum for a given catalytic problem. This approach failed [58] despite impressive examples of optimization of complex transition metal oxide catalysts [59] mainly because the phase space of inorganic materials is not continuous and hence the underlying structure-function relation is not continuous and smooth. Both mathematical conditions are pre-requisites for predicting the functioning of the concept by interpolation between experiments.

7 A fundamental alternative idea: structural dynamics

Based on the observation that all catalysts deactivate by a change in structure or by the deposition of reactants or

products [60] the idea arose [61–63] that catalysts are not static and that the fundamental paradigm of surface science that only the exact knowledge of static atomic positions would allow rigorous understanding [43] may not cover fully the function of catalysis [61–63]. This paradigm is the central distinction between the science branches of interfacial (rigid structures) and molecular (liquid) catalysis. Could it be that this distinction is misleading? Surely, it is not useful for obtaining high-energy sites atop of a solid interface that it melts, as then the surface energy would be greatly reduced. But between a liquid interface and a rigid interface is the intermediate situation of dynamical re-arrangement. This intermediate state is known to occur during phase formation where a solid has to form first nuclei of the new phase before it can grow into an extended new phase. During this nucleation process the constituents of a solid attempt new configurations being high in energy. The resulting nucleation barrier is well known in phase formation. The driving force for such structural dynamics of a working catalyst (for this reason it can only be studied in operando) is the interaction of the reactants with the catalyst surface. At low chemical potential (pressure times sticking probability) adsorption and desorption processes of reactants occur leaving the surface largely unaffected (with minor structural adaptations called reconstructions). At high chemical potential (high pressure, performance conditions) the reactants can penetrate under the surface and begin the formation of a new phase. This was well observed [64] experimentally. Such processes bring about the nuclei that can act as high energy sites in catalysis. These reduce their energy by either growing into the under reaction conditions more stable catalyst phase or by transforming and desorbing reagents. The transformation of reagents must not lead to irreversible displacements of the atoms involved in the active site resulting in sintering or compound formation, both being origins of de-activation.

The successful catalyst exposes a dynamical surface on its way to a phase transition imposed by the reactants and operation conditions of pressure and temperature. Its completion is inhibited by kinetic frustration. It is achieved by multiple effects such as the lack of geometric space for growing nuclei into crystals of the low-energy phase, (roughness of the active surface) by strain and stress caused by interaction with the underlying interfaces or by enhancing chemical complexity with foreign ions inhibiting the formation of translational order like in glasses.

In such a picture it is clear that neither the translational bulk or surface structure alone nor the local electronic structure alone can describe sustained catalytic action that includes the regeneration of the active sites. To speed up

structural dynamics (stochastic fluctuations of the local structure) by melting is no solution for site regeneration, as the free motion of the catalyst components reduces the extra energy gained with dynamic fluctuations with respect to the surface free energy of the crystalline compound. Well-ordered surfaces are not good for structural dynamics as then the activation barrier for collective movement of atoms allowing the formation of sub-surface nuclei is too high (hence the experimental observation required kinked steps in [64]).

The successful catalytic material is thus a nanostructured active mass bound to a rigid support ensuring long-term integrity of the material. This can be achieved either by self-support of a crystalline core carrying a nanostructured shell or by anchoring nanostructured active catalyst mass onto a dedicated support material with no own catalytic function. In many cases this clear distinction of active mass and inactive support is oversimplified and cooperation of the two phases is observed rendering the overall optimization a complex task. The usefulness of chemical complexity in the active mass by the addition of promoters finds one explanation as it serves as kinetic “frustrater” against attaining a larger crystallite of the high energy phase required by the thermodynamics of the working systems. The combination of atoms in compounds (alloys, multinary oxides, oxy-nitrides [65, 66] etc.) create the electronic structure of a material. Complexity allows [20, 67] to tailor the electronic structure into states distinct from those of constituents and to take care of the matching between electronic structures of catalyst and reactants. Such matching decides over the strength of interaction between reactants and catalyst (and of products) and controls hence the relative coverage of species and such the reaction kinetics of the catalytic transformation. This idea forms the core of the “Nørskov approach” [2, 68] of designing catalysts by quantum chemical modelling. It is however also the kiss of death to the stability of the catalytic system working at the brink of a phase transition; segregation and phase separation are the responses of activated complex materials if they are not stabilised by appropriate chemical bonding between its constituents (e.g. intermetallic compounds vs statistical alloys [69]).

8 Role of inorganic chemistry

The combination of elements required for achieving adequate activation of reagents and simultaneously facilitated desorption of the reaction products leads to chemical compound of enormous compositional and structural complexity. An example is a MoVNbTeO_{3-x} compound [70]

as excellent catalyst for the selective oxidation of propane. It is barely possible to determine the structure of such compounds. Next to nothing is known about the thermal and chemical reactivity of such phases [47, 71]. As it is likely impossible to theoretically predict the phase space of reaction products between reagents and catalytic material, it is difficult to gain realistic insight into the electronic structures and stability conditions of working catalysts. Even the seemingly simple case of a metal like copper and oxygen [6, 72, 73] poses substantial challenges when transient compound formations and heterogeneities in distribution of phases become relevant [74, 75].

It would thus be of utmost relevance if inorganic chemistry could establish pathways of reactivity of classes of compounds under conditions of catalytic actions. These are usually characterized by the simultaneous presence of oxidative and reductive species and often complicated by the additional action of water. Under such conditions relatively little is known about the reactivity even when well-known oxides are concerned [76]. This area of chemical science is presently only weakly active, possibly because it is not clear how important it is to establish reactivity patterns of solids under the complex conditions of catalysis. Extrapolations about reactivity taken from the traditional literature that studied compound reactivity in either oxidizing or reducing atmospheres if specified at all (“temperature of decomposition” as example) are not reliable, leading to the difficulty that little can be stated about the existence of phases and decomposition products of performance catalysts. As “reactivity” is a kinetic phenomenon, it is essential to perform such studies over a variety of embodiments of a compound differing in real structure and morphology to account for the effects of nanostructure. Evidently, phase integrity of each of such samples is critical requiring a whole range of synthetic techniques to be applied in the synthesis of even only one compound. Catalysis science would be greatly helped if synthetic inorganic chemistry would engage more in such studies the results of which being not only beneficial for catalysis but also for the general understanding of the interplay between thermodynamics and kinetics in solid state chemistry of real-world compounds.

9 Functional interface approach

Returning to the generation of novel catalytic systems this text describes a novel approach catering for many requirements of a stable and active performance catalyst. It begins with selecting a material suitable for activating the reactants (element or simple compound). It then avoids

classical multi-promotion by adding further elements in mostly unknown phase relation to the base active mass and nano-structuring the bulk of the material (morphology, pore structure, immobilisation on supports) being the main tools of catalyst development. The new approach tailors the reactivity of the base catalyst reactivity by engineering of the functional interface between the active material and its support (hetero-structure or self-support). Targets are to simultaneously maximise the energy difference between activated and stable phase, to maximize the energy content of the active sites and to minimize the success of the phase growth. The design goal is optimizing the conditions for a frustrated transition into the state stable under reaction conditions.

In Figure 2 the mode of operation of such a catalyst is indicated in a diagram relating the energy of the material to the reaction coordinate of the constituting atoms of both the catalyst and the reagents that form together the reaction ensemble. A non-catalytic material undergoes nucleation and growth of the phase stable under reaction condition (blue, red, purple points in Figure 2). Catalytic materials deviate to point A (green) and find a chance to regenerate by avoiding the growth of the stable phase.

The approach respects the real structure of active materials. It requires a for catalysis new concept of materials that allow constructing solid-solid interfaces outside of the limitations of phase diagrams. One suitable technology is thin film synthesis as applied in solar cell production and other large-area thin film applications. Such an approach is scalable to the still required large areas of 2-dimensional materials. It assumes that the much higher geometric surface areas of conventional catalysts may not be needed as the uniformity of the interfaces would provide a higher density of active sites under dynamical conditions than on conventional systems. The approach further honours the often-neglected role of the “functional interface” between the support and the active phase. By varying the thickness of the multiple layers, it is further possible to involve or exclude the action of the sub-surface range of the active phase.

Figure 3 illustrates the concept. Any solid crystal terminates in a reconstructed version [77, 78] of the translational bulk structure. When allowing surface irregularities, segregated components and the action of a reactive environment to enhance the complexity of the system suitable for performing a catalytic reaction [79–82] then a series of

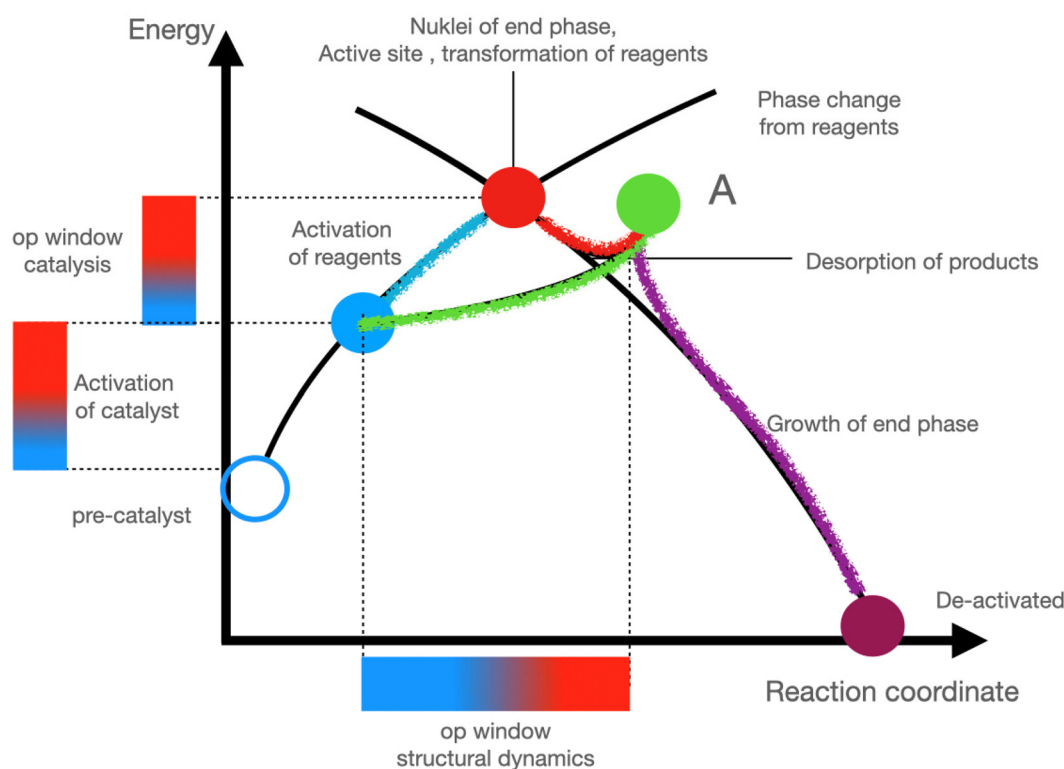


Figure 2: Diagrammatic representation of the energetic situation of the reaction ensemble on a catalyst under performance operation conditions. The black lines denote the course of potential energies: uprising the metastable situation of the catalyst with reagents, down rising the energy gain through growth of the stable phase. The catalyst needs first activation (in the reaction or in a special run-in phase) to reach the window of operation. Fluctuations in the structure of the reaction ensemble will lead to reagent activation, transformation and desorption. The momentary structure of the ensemble at point A decides if de-activation (purple) or regeneration (green) occurs.

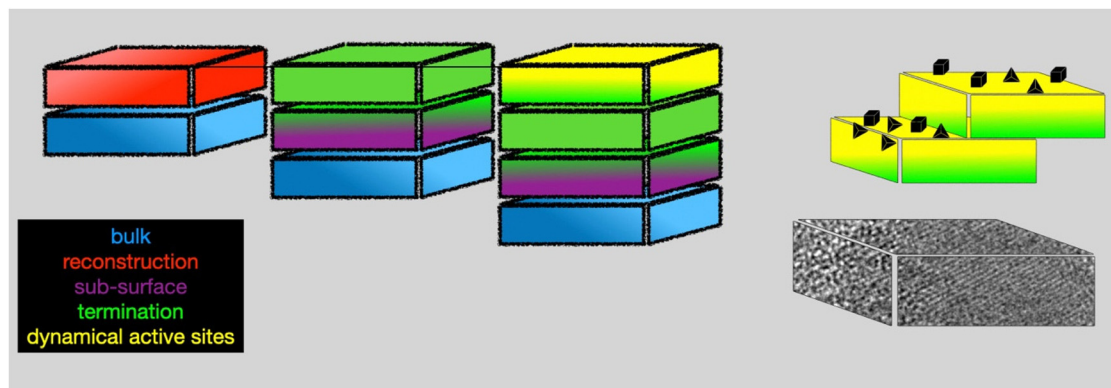


Figure 3: The functional interface approach. Crystalline solids (blue) exhibit increasingly complex termination structures if reactive conditions are allowed to gradually act upon the initially bare frozen situation. The blurred interface in the TEM (Transmission Electron Microscopy) image (right bottom) illustrates the relation between the schematic components and the real situation. The reality of polycrystalline materials is enhanced further in complexity by the presence of steps and of segregated components or co-catalysts (schematized in the top right object, co-catalysts as black particles).

atomically sharp and diffuse interfaces constitutes the “near surface” of a material. The near-surface volume is represented in Figure 3 as stack of thin slabs with finite volumes. Instead of letting this structure emerge when bringing a pre-catalyst into the reactive environment, the functional interface approach aims at pre-defining the reactive structure for catalytic action. In this way the chemical complexity may be reduced by omitting not required chemical elements and structures (such as promoters or the bulk of an active mass). Theory is no longer forced to search descriptions of the activation procedure in the complex reaction space of possible interactions of all components, but can concentrate on the mesoscopic structure of the reactive complex. In this way a leading function of theory seems possible in which structure-function correlations in many dimensions from simulations and experimental observations are merged [83] (“digital catalysis”). The combination of deposition, (reactive) annealing and plasma treatments [31] being all accessible in modern thin-film synthesis instrumentation allows a wide range of processes and thus of structures to be realized in reproducible and automated fashion. Additional methods of ALD (Atomic Layer Deposition), CVD (Chemical Vapor Deposition) and their plasma-assisted versions further enhance the option space.

It is pointed out that this approach goes far beyond the thin-film techniques applied in earlier applications [84] of catalyst developments where the sheer compositional variability was the target of the approach. In the functional interface approach the composition of the system is pre-determined and the design of the interfaces in the surface-near region of the solid is the target of the synthesis. These interfaces exist in all forms of solid catalysts but are usually excluded from a synthetic approach that deals with the

requirement of the outermost solid-fluid interface between “catalyst” and “reactant”. The approach was inspired but is not a copy of the thin film synthesis technology performed in the preparation of model compounds [10, 43, 85] for catalysis. In these applications the rigorous control over the atomic details of atomically sharp interfaces between phases is the target. Resulting are surfaces with static and precise atomic structures under conditions of chemisorption and model reactions. These systems require extremely skilful preparation procedures both for the substrate acting as structural template for the film and of the film being grown under mildly reactive conditions to arrive at the desired well-controlled termination of the system. The results of such studies are of great informative value when designing functional interfaces. The systems themselves are usually not reactive enough for performance applications, have stability problems and cannot be scaled to areas suitable for rigorous kinetic investigations.

Scientifically the functional interface approach leads to catalysts with verifiable performance in a version such that all inner interfaces of the system can be analytically accessed. This is extremely demanding in performance bulk-surface or supported nanostructured systems. In addition, the physical support needed for the thin film stack can be used for various purposes not available in conventional catalysts. Besides a precise control of the solid-fluid phase interaction by mesoscopic patterning (flow pattern design) and the realization of short or pulsed contact times of the reagents in reactors with low pressure drop, the support can carry probes for elucidating interface properties (conductivity, local temperature). The fabrication of “chemical semiconductor” devices such as chemical diodes allowing to use charge carriers for stimulating

reactions or harvesting chemical energy is feasible and has been demonstrated [14]. In addition, the support can be used for electrical and time-programmed heat supply being of particular relevance in endothermic reactions. All energy-related chemical battery loading processes are of that type and would benefit from a maximal effective all-electrical energy supply that is to be stored in the target product.

The pre-condition to such approaches is however a solid understanding of the phase space available to the components of the system. Only then a meaningful selection is possible in a knowledge-based manner of compounds, interface descriptors and synthesis strategies. Here theory is needed in a broader sense than only focussing on quantum-chemical atomistic descriptions of reaction ensembles. Multi-scale approaches allowing the realistic representation of fluctuations by molecular dynamics is a pre-requisite to understand the structural and compositional handles in the reaction ensemble. The description must not only focus on the desired reaction but encompass the full option space of reactions when catalyst and reagents are activated in the reaction conditions. Techniques of machine learning and interpolation between pre-existing knowledge points will be needed. Here massive deficits of inorganic chemical input into theory are stated that need to be removed by interdisciplinary cooperation between theory and experiment. In addition, theory needs also to develop effective ways of data analysis based upon the clean data and FAIR approaches [83] as background information for informed design of experiment strategies. These strategies encompass both synthesis and test protocols. Such a wide understanding of a “package approach” of theory (termed “digital catalysis”) is currently emerging. In combination with computational spectroscopy [86] enabling operando experimentation to deliver rapidly relevant structural information it is feasible that a true “design” of catalytic interfaces may become possible.

This short outlook into development perspectives of interfacial catalysis highlights the potential of overcoming prohibitive complexity in designing catalysts by a knowledge-based approach. For this it is needed to leave the working hypothesis that only the time-independent knowledge of the positions and interactions of all atoms in the reactive complex between active site and all essential adsorbates and fragments can result in a design approach. A concept of reactive ensembles between reagents and catalyst being in a fluctuating state driven by the attempt of the catalyst to reduce its high energy state of reaction conditions by a phase change retains conceptual rigor of atomistic theory coarse-grained into a mesoscopic description of functions over supra-molecular dimensions. The

“science gap” in catalysis is resolved when the static choice of the structure of the reaction ensemble is augmented by trajectories of reaction following from structural fluctuations existing only under reaction conditions.

The historically limited success of the co-operation between solid state chemistry and interfacial catalysis being inferior to the situation with molecular catalysts and coordination chemistry can be much enhanced if the respective roles of the two sciences are constructively exploited. The prevailing idea of chemistry having to provide high-energy structures inaccessible by conventional catalyst synthesis approaches is of limited value, as catalysis requires both high energy sites and stable regeneration functions. A contribution of conceptual inorganic chemistry would be most needed in catalysis science. It should consist in defining reaction scenarios of inorganic materials subject to reagent mixtures and conditions of performance catalytic applications. Then knowledge of reactive behaviour will replace speculation from phase diagrams of proxy components from the reaction mixture. Uncovering of novel metastable compounds is of interest for both sciences and refined structural concepts within the realm of mesoscopic pictures (cluster descriptions of inorganic materials as example [87]) for describing the inevitable “defective structures” likely being identified are still a challenge for rigorous structural inorganic chemistry.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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