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The functional interface in catalysis

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Dedicated to Prof. Graham Hutchings on his 70th birthday

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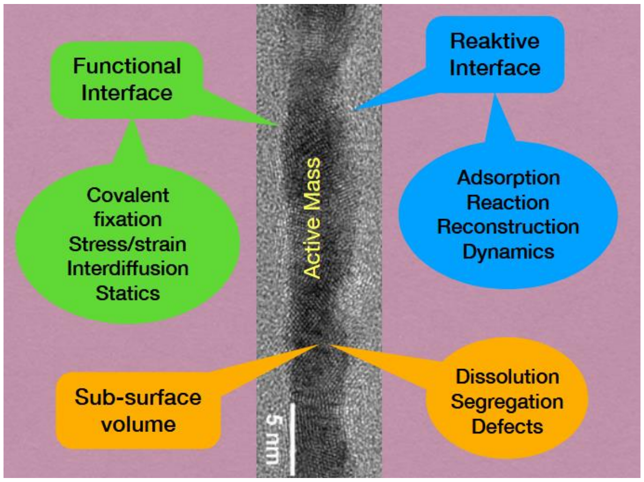
Abstract

This concept paper looks at the “dark side of the moon” in catalysis being the interface between the active mass and its support structure. This “backside” although being not involved directly in the catalytic function is considered a *functional* interface as neither the nanostructure of the active phase nor its real structures can exist without this interface. Both, heterogeneous and self-supported systems exhibit this functional interface. It is suggested to evolve our perception about designing catalysts and pay equal attention to the reactive and the functional interface.



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Introduction

Whenever catalysis comes to performance operation of a given reaction then the material science aspect of the catalyst comes into play. Notably through the enormous progress in theory of catalysis[1-3] we have a rich understanding of active sites representing ensembles of atoms or ions as motif within the active structure or in the extreme case of single atom catalysts[4] (SAC) as one central atom in interaction with ”ligands” from a supporting phase. It is not clear how useful are various discriminations[5] of types of active sites. At the active sites the dominant fraction of energies between interacting reactants and catalyst are exchanged, justifying the focus on the precise electronic and hence structural properties of such sites. It is noted that weaker and long-range interactions add critically to the outcome of catalytic transformations and may explain reaction control in 3 dimensions but are still poorly systematized and not integrated into a complete description of a catalytic transformation. We exclude these for the rest of this discourse. We further exclude molecular catalysts from the discourse where the ligands of the central single atom are molecules themselves. This important large class of systems exhibits multiple forms of reaction-induced transformations and complicated forms of regenerating the active site and are strongly affected by weak interactions within the molecular catalyst and with the environment. Treatment of these catalysts is subject to similar concepts (“universality in catalysis”) but has led to a different field of science that is not easily related to interfacial catalysts except on a very high level of abstraction.

Active sites are small sections of a solid material that is characterized by a bulk phase (mixture) supporting the active phase. In designing or analysing the function of catalysts we usually confine to the interface between reagent phase and the solid surface exposing usually patches of support and active phase. In theory we even omit usually the perimeter between active phase and support and in microkinetic models we ignore the existence of both types of phases and designate active sites with a *. A prominent exception here is the catalytic chemistry of gold[6] where the perimeter between gold nanostructures and oxide or carbon supports is recognized as location of active sites. This may be the case in other systems as well.

The other side of the active phase, the “dark side of the moon” is rarely object of in-depth functional studies. The exception here is the phenomenon of strong metal support interaction or SMSI[7-9] where part of the support overgrows the active phase and such modifies the catalytic function. A semantic issue occurs when we consider SAC[10,11] where there is no distinction possible between reactive and functional interface, at least as long as it exists in its literal form of a “charged atom” [12] and is not collapsed into a nanostructure.

It is well recognized that the functional interface is of utmost importance to the catalytic function of at least the large class of oxide-supported metal nanoparticle systems. In Figure 1 a typical example[13] is shown. The investigation of the atomistic details of the functional interface however remains challenging.[14] The oxide support surface tends to exhibit multiple local structures ("defects") that may serve as chemical anchoring points for nanoparticles and their scattered localisation on the support surface explains the usually irregular distribution of active phase nanostructures over the support. Ordered defects in the support, such as steps or phase boundaries (between support and "binder phases"), are preferred localizations of active nanostructures. An example of how to identify the functional interface,[15] without reverting to PVD-generated model systems,[16,17] was given by chemically synthesized metal nanoparticles deposited onto TiO_2 single crystal supports and annealed to such high temperatures that well-ordered facetted metal particles resulted from a maximization of the metal-support interaction. Structural models for the functional interface were inferred from observing by STM the shape and orientation of the well-facetted metal particles.

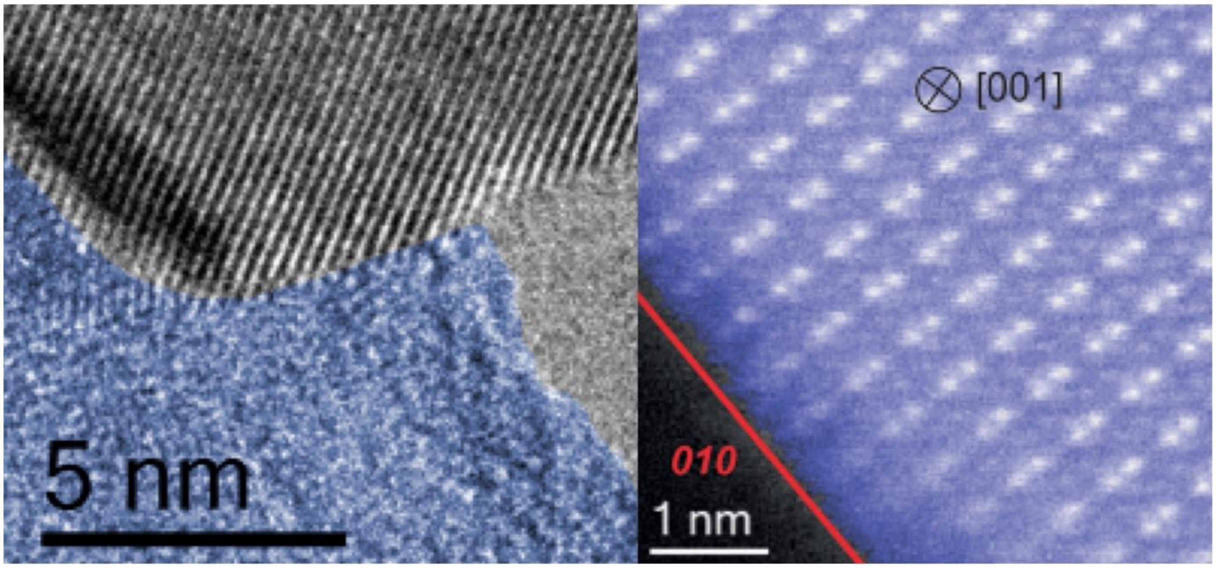


Figure 1. Characteristic situations of active phases on catalysts: (left) a well-facetted, but internally defective Ag nanoparticle (grey) supported on amorphous (blue) alumina[13] generated by calcination of AlO(OH). (Right) highly crystalline MnWO4 imaged along (001) exhibiting characteristic dimers of tungsten (bright) and an active phase[18] of Mn_xO_y forming a film along (010). Here the functional interface is outside of the last row of tungsten dimers.

Bulk catalysts also exhibit such functional interfaces between their active phase and the bulk self-supporting material. Figure 1 reports a typical metal-oxide support system[13] and gives an example[18] of a complex oxide. It hardly ever occurs that the termination of the bulk phase forms the reactive interface with the original structure and composition of the bulk.[19] The notion that the crystal structure motifs from the bulk structure also represent the geometry of active sites[20-22] and control the nature of reaction products[23] is frequently proclaimed to the point that "overlayers" would be detrimental[24] for reactivity. This concept is hard to verify.[25-28] Even the class of refractory perovskite oxides[29] that are used as combustion catalysts for their bulk structural stability form at low temperatures a unique ultrathin termination structure that provides remarkable activity for selective oxidation. Ignoring this structural complexity is one reason for the frequently found "material gap"[30,31] between model and performance catalysis. A particular family of systems where thin overlayers of different structure and composition represent the reactive interface different from its supporting phase are electrocatalysts formed on the surface of metallic electrode materials. The overlayer, in the case of the oxygen evolution reaction in water splitting, is an oxy-hydroxide existing usually only during working conditions and being unidentified if not surface-sensitive *operando* experiments are applied.[32-34]

In this work the term “dynamics” plays an important role. Multiple definitions or understandings attached to this term call for a paragraph of clarification in the present context. “Dynamics” in catalysis designates processes of undirected motion of atoms (or charge carriers) that occur in a steady state of the system. It is stated explicitly that reaching steady state after a change in chemical potential is not covered by the term dynamics and measures are required to ascertain this state (e.g. repetitive changes in chemical potential and observation of possible deviations of steady state following changes in potential). No gradient of energy is required for dynamics. Motion of atoms in gradients of (electro)chemical potential occur frequently as response of the system to the gradient and vanish when the gradient disappears. Motion of atoms can lead to chemical reactions between the atoms (intended for product formation, unintended in the catalyst material) and this from of dynamics is termed “chemical dynamics” in contrast to motion of atoms or molecules without chemical reaction. In condensed phases (solids), motion can also relate to groups of atoms as “structural dynamics” where not a chemical reaction but a re-structuring of the surface or the bulk of the condensed phase is the consequence of dynamics. All forms of dynamics, as well as directed motion, require a driving force in form of energy and relate thus to systems not in their lowest energy state. Dynamics is a reversible process and hence conceptually connected with the catalytic cycle restoring active sites once a single reactant transformation has occurred. In catalysis, structural or chemical transformations occur frequently when changing reaction conditions or when starting a catalytic reaction with a pristine form of catalytic material. These transformations are not dynamical processes, but kinetic responses to the changes in chemical potential - in catalysts they are associated with activation and deactivation of materials.

2. How Catalysts Function

Every interface of a solid material responds in structure and composition to a change in chemical potential of its environment. Heterogeneous catalysts are no exception to this behaviour. Bringing a material from dry air to moist air or increasing the temperature are examples likewise as changing the electrode potential in an electrochemical device. The initial driving force is surface free energy in the system, triggering the nucleation of a phase that is more stable under the changed environmental conditions. Phase transitions result that involve chemical constituents from both the solid and the surrounding phases. Corrosion and passivation of metals in air are prominent examples or the material transformations[35] in electrochemical reactions such as the oxygen evolution reaction. To what extent and how deep into the sub-surface[36,37] such transformations progress, depend on the heterogeneous kinetics of the reaction network involved.

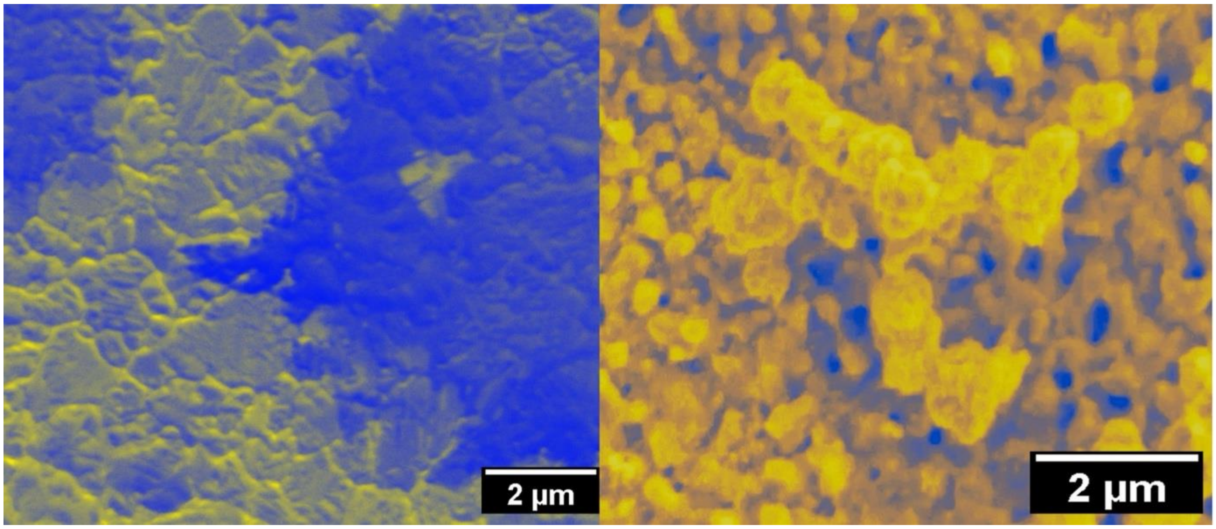


Figure 2. Ni during decomposition of ethylene (*operando* SEM 40 Pa, 913 K) left: after few minutes: yellow Ni oxide in grain boundaries, light yellow Ni metal /Ni oxide patchy surface on the basic structural units (grains), blue carbon deposit. Right; after 60 minute operation; the metal is no longer planar, particles (yellow) have formed in 3 dimensions, the transformation created holes (blue) in the massive Ni sample. (courtesy Dr. Zhuiung Wang, 2011, see also[38])

Figure 2 illustrates this for the case of Ni decomposing hydrocarbons. In early stages of reaction, the mosaic grain structure of the metal is well visible with (native) oxide concentrating in grain boundaries and partly covering the grains. Carbon deposition occurs when the surface oxide film is pre-reduced (Figure 2 left). After extended reaction, the catalyst is massively restructured (Figure 2 right) forming a foam-like morphology with holes deep into the bulk and aggregates of metal covering the formerly flat surface. The size of the basic structural units is not related to the mosaic structure of the initial state of the catalyst.

A prominent example of reaction-induced restructuring with oxide catalysts is the Mars-van Krevelen (MvK) mechanism[39,40] in redox catalysis bringing about structural phase transitions between oxides in different stoichiometries. The activation of ammonia iron[41] for the Haber-Bosch reaction also follows the reaction-induced restructuring pathway.

Orientation and size distribution of the basic structural units in the mosaic structure of the interface are critical descriptors of the kinetics. Nanoscience has taught us that reactivity as function of a size parameter goes through a maximum determined by the fraction of surface atoms and the lattice distortion of a particle. This holds both for mosaic particles of a bulk catalyst and for the active phase particles of a supported catalyst. The structural transformation illustrated in Figure 2 restructures the bulk Ni catalyst autogenously enhancing the nanoscopic organisation of the active phase, and hence optimizing its reactivity. Driving force for this is the dissolution and segregation of carbon (and hydrogen) into the bulk of the metal. In current literature such adaptation of a catalyst material to a change (gradient) in local chemical potential is termed “dynamics”. This is not correct as dynamic phenomena are characterized such that their motion is not following a gradient, but represents a fluctuation in structure without any gradient. The processes illustrated in Figure 2 are not chemical dynamics but represent mesoscopic views of completed phase transitions oscillating[42] between metallic Ni and solid solutions of C, H. An example from electrocatalysis is the poor stability of RuO_2 as OER catalyst induced by the stability of the reactive RuOO* oxyl species that is the desired active site for OER, but as it accumulates when applying oxidising electrical potential it strongly destabilises the whole solid in the electrolyte as consequence of the completed phase transition from RuO_2 to RuOO*.[43]

Synthesis and activation create an active phase on a solid catalytic material that for most performance catalysts takes the form of a thin film supported on a matrix solid which itself can be a nanoparticle. The speciality of catalytic materials comes into play when this active phase is subject to the chemical potential of reactants and products. Then the expected phase transition minimizing the free energy of the active phase does not occur but is kinetically frustrated. This means that the active phase forms nuclei of the under reacting conditions thermodynamically stable phase(es) without being able to grow them. The result is a metastable state of the active phase being in a dynamical state. This dynamical state where fluctuations in geometric structure and chemical composition occur is termed as "chemical dynamics" to discriminate it from dynamical behaviour of matter where no chemical reactions are involved in the motions. Its structure fluctuates between that of the activated phase and the structure of the expected stable phase without gradients in chemical potential. In this state, local configurations are formed that can convert the reagents into the desired products. The catalytic reaction network unfolds. As consequence, the high-energy reactive surface configurations termed "active sites" are destroyed often with the consequence of liberating the adsorbed reaction products. The fluctuating nature of the active phase re-forms the active sites. In this dynamical picture the critical number of active sites is not constant in time and the sites are not prepared during catalysts synthesis. Their nature and abundance is represented by a time-dependent distribution of local structures. The only way to uncover and verify this perception is the *operando* analysis of systems.[32,38,44,45] One finds that the formation of sub-surface species is connected to the generation of active sites and so strongly interferes with the chemisorption processes of reagents, and hence with the productivity of the catalyst.

A notable example for a catalyst where the active sites are pre-fabricated during synthesis is the famous earth alkaline oxide system for oxidative coupling of methane, where clear correlations[46,47] between ordered defects as monoatomic steps and catalytic function exist. Detailed theoretical[48] and experimental[49] studies reveal that a variety of defects can stabilize adsorbed di-oxygen radicals which interact with co-adsorbed methane. The concept of the dynamical catalysts explains here the deactivation process. The reaction products water and CO_2 restructure the earth alkaline oxide surfaces into disordered states where the beneficial specific oxygen-activating step defects tend to vanish and hence the driving force of the dynamics extinguishes itself leaving behind a rough inactive form of the catalyst.

The role of dynamics in porous systems used for sorption and acid-base catalysis is very clear[50] as far as structural dynamics is concerned, but less clear as far as chemical dynamics is studied,[51] where again we meet an intersection with SAC systems. Here the situation is still unclear, but the study of chemical dynamics of these systems poses a substantial challenge to investigation and theory.

Well applicable is the concept of the dynamical active layer concept to bulk catalysts. In this area of catalysis, the term "dynamics" occurred early on,[52] designating only the structural transformation of the pre-catalyst under the chemical potential of the reagents, which in the above context is the "activation" of the catalytic material creating the active phase. The chemical dynamics during operation was not targeted by this analysis. The traditional alkali-vanadate system for sulfuric acid synthesis is the prototype of a so called "supported liquid phase" system where chemical and structural dynamics[53] are essential for correct function. Another vanadate system used for selective butane oxidation to maleic anhydride[19, 54-56] is also prototypical for structural transformation activating a precursor vanadium phosphate into an active pyrophosphate (VPP) phase exhibiting a microscopically discernible active layer that is gradually deactivating into another vanadium phosphate phase. This highly complex interplay of different phases and their disorder variants provides a uniquely selective and productive catalyst for the technical selective oxidation of an alkane hydrocarbon. Its existence is transient in-between reaction-induced phase transformations and its activity is related to the dynamics of structural building blocks, namely dimers of VxOy polyhedra that form active sites for the hydrocarbon oxidation. The complex oxide $MnWO_4$ provides another example,[18] where an activation step that is partly and without intention integrated into the synthesis of the material after suitable thermal treatment brings about a monolayer of Mn-oxide (see Figure 1) that serves as catalyst for propane to propene oxidative dehydrogenation. This example highlights further that the term "structure sensitivity" not necessarily relates to the parent structure of an (oxide) crystal, but rather to its orientation-sensitive reactivity during activation given by the anisotropy of chemical bonds between the constituents. The result is a "structure insensitive" active layer. This work further illustrates that the bulk structural crystallography is with its motifs a poor descriptor[22] of catalytic reactivity, as it was also well documented in the functional elucidation of the VPP system.

It is obvious that an elaborated electronic structure of a catalytic material is required in fulfilling the conflicting requirements of gaining sufficient energy from its instability under reaction conditions to activate the reagents and being able to bind fragments of reactants such that products can form. Chemical specificity is here critical to attain chemo- and regio- selective transformation to products that are often not the thermodynamically preferred ones. These conditions define the compositional and structural requirements of the active phase. As an additional boundary condition, the chemisorbed species must be bonded strongly enough to the active phase that they inhibit the phase formation out of the nuclei at which they were formed. Only then the phase transformation of the catalyst is inhibited as long as the reaction products stay bonded to the active site (kinetically frustrated). Motion of the atoms constituting the active site out of their high-energy configuration leads to liberation of the reaction products and inhibits the crystallisation of the stable phase of the catalyst. The temperature level of the reaction may be limited by this necessary motion more than by the requirements of atomic re-arrangement of the reactants.

In this picture of a functioning catalytic cycle, it approximates the requirements of the local electronic structure of active sites to use theoretically identified local static configurations of a surface as model for active sites and leave them unchanged during the reactant chemical transformation. It was a great success of atomistic theory[1] to be able to describe the dynamics of reactants in a chemical transformation at a static pre-optimized surface structure. The structure of cus-sites in RuO_2 during CO oxidation is a well-known example.[3] The challenge is even larger, as the dynamic surface is likely not empty but covered with (interacting) reagent and product molecules modifying the total electronic structure of the complex between reagents and dynamical active sites, as well as the chemical dynamics of the active phase. It will be highly illustrative to get quantitative insights into these processes once the static theoretical treatment of catalytic reactions is carried forward by molecular dynamical simulations[57] and their quantitative analysis.

Attempts to design solid materials with static representations of active sites inspired by theoretical insight will not lead to catalysts characterised by repetitive performance of the desired chemical reaction per active site, as the critical function of their regeneration is not built into the design. If we consider reactant and product mixtures, then we find often competing chemical properties such as reductive species, oxidative species or strongly complex-forming species. Consequently, we must consider different ways how such species interact with the catalyst containing (for this reason) several chemically different components functioning as catalysts, co-catalysts and promoters. Multi-component oxide catalysts such as the M1 phase,[58,59] the BiMo phases,[60,61] or the silver catalyst for EO synthesis[62] may serve as examples.

The location of this interactions is always the reacting interface. Its composition and local structure will depend on the chemical potential of the reagents. Hence kinetic implications arise from the reaction environment as the chemisorption (and coverages) of species depends on these changes. The feedback loop created such was theoretically evaluated for the case of Cu/ZnO catalysts in methanol synthesis.[63] Under elevated chemical potentials (performance conditions) more drastic phenomena will occur. Fragments of reactants will move below the surface where the sub-surface volume[64] offers space for accepting atoms (hydrogen, oxygen, OH, nitrogen, carbon, to name but a few). Their presence, together with the adsorbates, further changes the electronic structure of the reacting surface.[37,65,66] The adsorbates affect the stability of the sub-surface species with a tendency to segregate back to the reacting interface,[67] creating chemical dynamics[68] perpendicular to the reactive interface. Variation of the chemical potential over a range of oxidizing and reducing values during dissolution and segregation can lead to the formation of novel morphologies of the initial phase, as during dynamic operation the mechanical strain onto the material gets so large that disintegration occurs and multiple small fragments form around an initial material particle.[69] Figure 2 gives an impression of such action where sub-surface carbon and hydrogen species transformed an initially flat Ni surface into a rough 3-dimensional state.

As the kinetics of the dynamic response depends on surface orientation and real structure of the material, such a process can change the dynamics of a given system by the re-structuring of its morphology.[69,70] This provides negative feedback to the restructuring of catalysts following diffusion processes into their sub-surface volume. It keeps the morphology of a system in an intermediate state (rough, stepped, nano-particulates) and inhibits formation of well-ordered large crystals of the respective phase (sintering). An example of this was observed in the reaction of oxygen with hydrogen over Cu nanoparticles.[71] A good way of preventing this process to happen is to build into the catalyst design a series of functional interfaces across the surface. The resulting grain boundary network of a nanostructured volume can effectively extend the lifetime of a complex system against formation of (under reaction conditions) thermodynamically stable chemically simpler compounds. The complexity of mixed oxide systems,[18,26] identified for possibly incorrect mechanistic reasons[72] may be beneficial[22] for this reason. In selective oxidation reactions, the contrast of oxidizing and reducing chemical potential, combined with hydrothermal reaction conditions stemming from the reaction product water, is substantial representing extreme stress on the structural integrity of the catalyst. A prominent case in the realm of metal catalysts is the iron catalyst for ammonia synthesis, where the admixture of highly dispersed oxides is critical[41] for the sustained function and where surely not all components of the promoter “package” affect the elementary steps of the ammonia synthesis.

A classic technical example of a system with lateral and in-depth chemical dynamics is the copper-zinc oxide catalyst for the hydrogenation of CO_x to methanol. Its structural dynamics as variable metal-support interaction controlled by the reactant potential involves simultaneously the reactive and the functional interface. This was discovered in one of the seminal applications of in-*operando* structural studies.[73] Its implications on reactivity was explained by a theory-based kinetic model highlighting the importance of chemical dynamics[63] for catalytic function. The dispute[74] over the nature of the phase transition involving brass or the two-phase system copper metal-zinc (sub) oxide[75] was resolved recently by another in *operando* experiment[76] as being no contradiction, but rather two material options with the chemical potential in combination with the strength of the functional interface (nature of the supporting oxide) discriminating between them. This agrees with the observation of yet another in *operando* study[70] finding that both states can exist with albeit different specific catalytic performances.

Theoretical concepts of describing catalytic reactivity as consequence of differences in the interacting energies of reagents and products provide now tools of considerable predictive power for a range of important chemical processes.[77] The concept focusses on the local electronic structure of the direct interaction between active site and reactants and seems not to require the complex details of having to generate and re-generate these sites through the sequence of events described above. The scope of this extremely valuable approach is to identify lead materials capable of performing the desired reaction, and not to evaluate the kinetic stability of catalysts. Predicted in these studies is the performance under a fixed chemical potential of reactants on static surfaces. Apparent success stories[78,79] of novel catalysts have worked without verifying the material identity under reaction conditions to that of the theoretical prediction. These reports should not be considered as "evidence" against the necessity to consider the systemic nature of catalysis that includes the processes regenerating active sites.

A molecular picture of the regeneration of active sites is that the reaction product coordinates to the nucleus of the stable phase in such a way that growth of the nucleus is (sterically) inhibited. The fluctuating nature of the surface destroys the active sites, liberates reaction products and prevents the growth of the stable phase. Such a picture comes close to the function of molecular catalysts where the coordination of labile, hemi-labile and static ligands controls the operation of a central metal atom. Reversible coordination is associated with conversion whereas irreversible coordination is associated with formation or deactivation of the active site. This is in analogy to the operation of a SAC in the here suggested mode of operation of a heterogeneous catalyst and is compatible to the concept of surface organometallic chemistry.[80]

A striking consequence of this notion for the material science of catalysts is that structural characterisation of either the as-synthesized material or of the post-reaction material cannot give causal information about the active phase or even the active sites. Both data sets are essential to describe the catalyst, but they bracket the information about the reactive structure rather that they directly deliver this important piece of evidence. *Operando* experiments are thus no longer an "extra" to a catalyst study, but merely are indispensable if structure-function relations are to be derived or verified and not only speculated about.

3. The Challenge of Complexity

In material science of catalysis, we are concerned with selecting materials and unit operations of synthesis combining stable solids to a new function providing metastability under reaction conditions. The appropriate designation of this material should be "pre-catalyst". The active phase then can form from this under the participation of reagents. This active phase in contrast to the pre-catalyst exhibits chemical dynamics to retain sustained activity requiring formation and re-formation of the active sites of which we believe to know exactly how they work. We note that in this picture we do not even know the sum formula of the active sites that deviates from that of the pre-catalyst.

From the viewpoint of thermodynamics, the active phase can only function with continuous influx of free energy to maintain the "high energy" reactive steady-state of the system. It is noted that some of the energy required to drive a catalytic reaction is required for this process and not for the molecular transformation. The catalytic system consists of the reagents (educts, products, side products) and their space-time resolved transport properties plus the catalyst consisting of its active phase with the dynamical reactive interface plus its transport properties and of the static support phase. The dimensions of the system are defined such as to accommodate the transport of molecules and energy not only on the molecular level of active sites, but likewise in meso- and macroscales of particles and porous solids up to shaped bodies filling the reactor. Figure 3 illustrates the co-operation of core elements of a catalytic system under steady state reacting conditions.

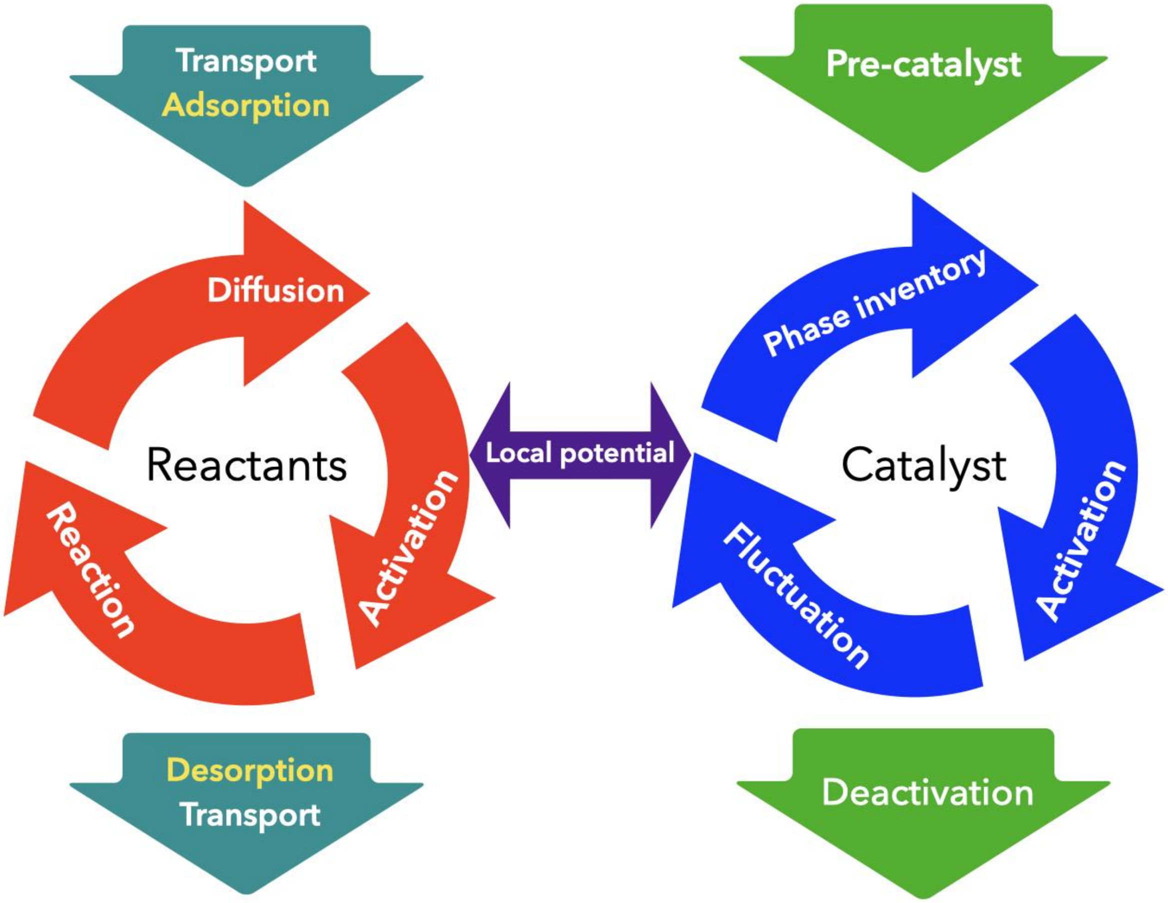


Figure 3. Relevant elements of a catalytic system. Too often the two feedback cycles are studied independently. The local chemical potential forms the coupling element that is responsible for the multi-scale nature of catalytic processes. It is given by composition, pressure, temperature and all their gradients of the mixture of reactants and products.

It is clear from this figure why catalysts cannot be studied outside of their reaction environment and why modifications of the reaction environment will cause a response of the catalytic material. As there are many possible steady states of the system, it is of utmost relevance to couple the two kinetic circles indicated in Figure 3 with the relevant local potential ("*operando* conditions") and not with an arbitrary choice of it ("in-situ" conditions) as for example with a pressure being suitable for surface spectroscopic methods. Important is to note that the coupling local chemical potential is controlled by phenomena at multiple scales such as reactant flow, pressure drops or energy transport and their gradients in the reactor (hot spots), in catalyst grains and in boundary layers close to the active phase. The coupling effect of the local chemical potential on the catalyst material is multi-scale likewise, as it drives the chemical dynamics at the atomic scale and mesoscale phenomena such as restructuring, sintering, segregation and recrystallisation.

We read in the literature that results from molecular catalysis of a reaction such as CO_2 hydrogenation can be used to gain chemical insight in the reaction pathway[81,82] and so generate basic knowledge required for improved or novel[83] interfacial processes. It is only very loosely justified to conclude in a reaction network from one path identified to completely other reaction conditions and catalytic species. There is no substitute to uncover the chemical processes on a given reaction interface and perform these for both the reaction and the catalyst under operation conditions. Nonetheless, extrapolations across the chemical potential and reaction networks are frequently made, leading to diverging hypotheses about catalytic reactions with one consequence being that review work is needed[46,84,85] to order and classify the information.

A representative example for the practice to study catalytic reactions ignoring the complexity of catalytic systems (Figure 3) can be found in a review.[84] In scheme 2 of this work, it is reported that authors claim that homolytic cleavage of water should be part of low-temperature CO oxidation over gold:

$$O_{2ads} + H_2O_{ads} \leftrightarrow OOH^*_{ads} + OH^*_{ads} \qquad (1)$$

It is unlikely that this equilibrium would deliver finite amounts of products if the adsorbent "ads" does not provide charge carriers, i.e. would not be involved in redox processes[86,87] between support and adsorbate. The classical separation between "irreducible" and "reducible" supports may be taken with reservation as any solid even when being a wide-bandgap semiconductor may be modified (thermally, plasma) such that localized charge carriers are available[49] or that adsorbed protons can support molecular oxygen activation into the thermodynamically spontaneous state of superoxide.[86] A detailed search for the corresponding active sites would be needed if there was evidence for reaction 1 to really occur. Ascribing the occurrence of reaction 1 to the same active site as the binding of a CO molecule (the typical * in kinetic equations) is a simplification that does not support the rational design of a catalytic system.

This arbitrarily chosen example illustrates why the synthetic details and pre-history of a catalyst and its support are so immensely important. A new tradition to report in all detail the meta-data of synthesis and activation of catalytic materials[58] would enable the reader and even more so computer algorithms to identify functional patterns in the rich literature dedicated to a relatively small number of reactions. In addition, we need *operando* methods that can identify minority reactive sites on a potentially large area of non-reactive surface. Rigorous execution of this task requires automated and self-analysing algorithms operating *operando* experiments to attain a meaningful number of observations as compared to the more anecdotal description of present experiments. Superficial screening by microscopy (see for example Figures 1 and 2 of this work) or analysing the main features of spectral information will clearly not lead us to these sites.

Multi-method *operando* work[88] sometimes describes the detailed reaction-induced restructuring. In this case, a model copper surface underwent partly irreversible roughening under electro-reductive conditions whereby a large number was created of newly formed undercoordinated step sites. Although adsorbed intermediates were found, the work misses the verification of sustained catalytic operation in the dynamical state described as causal consequence of the well-identified roughening transition.

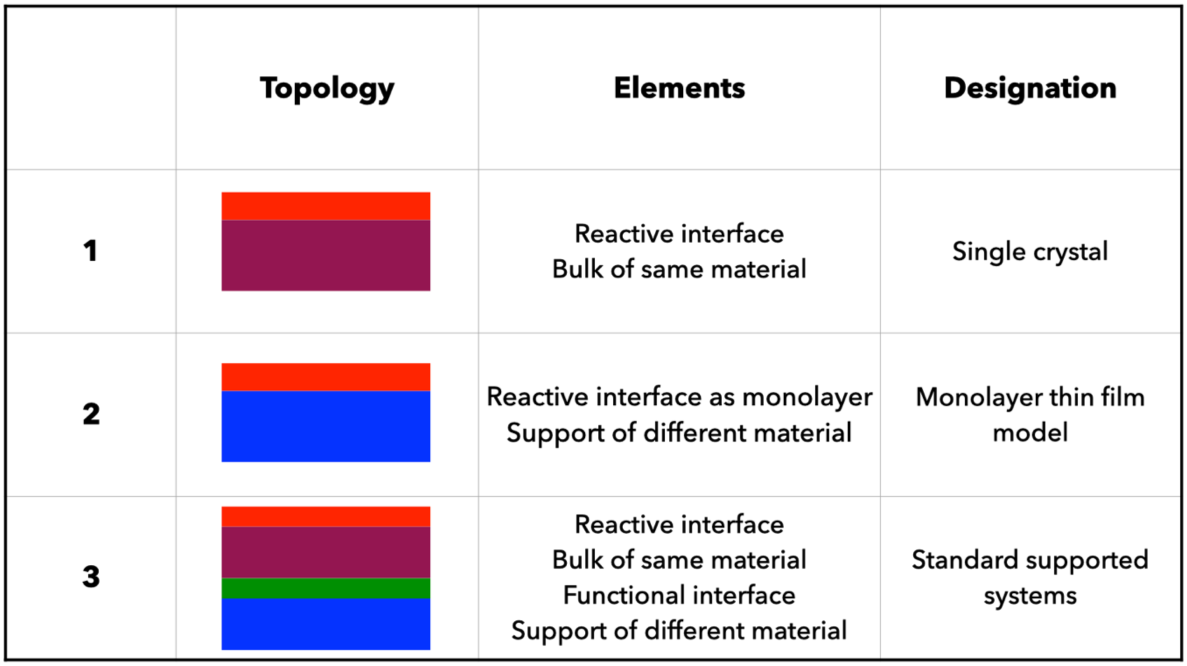
Operando spectro-microscopy[69] did surmount the earlier often acclaimed "gaps"[31,89] in catalyst science and enabled meeting the complexity challenge described here by experiment. Yet we are far away from performing adequate *operando* studies to dismiss bold extrapolations in descriptions of the system function sketched in Figure 3.

Unfortunately, little information exists about the scaling of *operando* results across geometric dimension and pressure/composition spaces, although relevant phenomena[90] can clearly be resolved. Single point studies mostly focus on the observation of structure and composition of reacting catalysts, in many cases not even reporting the details of operation. Great care must be paid to the details of such studies as their conditions ("ambient pressure") and their probes (ionising X-ray radiation or free electrons) can severely interfere with the operating catalytic system. Of equal relevance is the depth of information. Whereas truly surface-sensitive methods are heavily limited in pressure and less in temperature, more robust X-ray scattering techniques are either not truly surface-sensitive or respond only to the coherently ordered fraction of the surface. Even when hard X-ray techniques are applied to nanoparticles with attributed large surface-to volume atom ratio, their results are still far away from true surface sensitivity, notwithstanding the possibility of detecting minority sites in the reacting surface qualifying for active sites. Observing uniform SAC-type catalysts[91] by (N)EXAFS[92a] is the exception to this statement. The broader application of *operando*-spectro-microscopy[69] that can explore parameter spaces rather than stay at single arbitrary points in the reaction parameter space will be a critical feature of future analytical catalysis science. Automation, digitalization and a much more systematic experimental approach than performed today will be needed. Here large-scale facilities have a great responsibility to support individual research teams who cannot cope themselves with the many technical and data-administrative challenges.

The coupling of the reaction cycle with the catalyst dynamics illustrated in Figure 3 can likewise be studied by applying *operando* kinetic experimentation coupled with *operando* determination of the number of adsorbed reactants as function of the local chemical potential. In this way, one can discriminate a change in reaction mechanism with varying chemical potential induced by a change in material properties from a change in site density, induced by either competitive adsorption or the loss of active sites following the change in material properties with changing chemical potential. An illustrative example is found in the following reference[92b] where CO hydrogenation to methane was studied as function of conditions and a loss of active sites was diagnosed with changing hydrogen potential, rather than a change the nature of active sites.

4. The Challenge of Synthesis

More insight into the nature of the functional interface is required if we want to design stable performance catalytic materials. To this end, the methodical developments described above are needed to master the complexity challenge. And even then, the task remains to synthesize the “designed” catalyst. Reproducible recipes and known activation procedures are required for fabrication in a scalable manner. Only then are robust kinetic experiments possible and potential technical exploitations do not require re-designing the whole synthesis procedure for technical unit operations. What we want to synthesize follows from the understanding about the catalytic function in the interpretation of Figure 3. We learn that the dynamic operation requires a higher level of structural complexity than just the interface of an active materials with the reagent phase. Figure 4 exemplifies the gradual evolution of complexity as synthesis target for a functioning catalyst. We confine here the discussion to compact systems and omit the vast area of porous systems exemplified by zeolitic or MOF systems.



	Topology	Elements	Designation
1	🟥 🟪	Reactive interface Bulk of same material	Single crystal
2	🟥 🟦	Reactive interface as monolayer Support of different material	Monolayer thin film model
3	🟥 🟪 🟩 🟦	Reactive interface Bulk of same material Functional interface Support of different material	Standard supported systems

Figure 4. Evolution of structural complexity of active catalysts ranging from model systems to performance systems.

The traditional idea that an extended crystal of the active phase (single crystal approach, **case 1** in Figure 4) should be sufficient to model the function of a catalyst, caused the "gaps" of catalysis science to emerge. This idea is a first approximation to describing catalysis, mainly allowing detailed studies of adsorption phenomena and the response of the top surface structure to the presence of adsorbates.[93] It was already then recognized that the interface responds to the presence of adsorbates. The advent of high pressure experiments[94] allowed the study of restructuring, structure sensitivity and the role of co-catalysts for selected reactions. Little attention was given to the fact that the single crystals were "damaged" or converted into polycrystals with the onset of reactivity. The distinct contribution of surface compounds emerging from reaction of reagents and catalytic material forming, even with metal single crystals was recognized then.[93,95] The price to pay was having to give up the idea of "atomic cleanliness" of reacting surfaces necessary for precise rigorous[96,97] characterization of the reactive interface.

Enhancing the chemical complexity to close the material gap was the aim of studies using systems of **case 2** in Figure 4. They were realized by the advent[16,17,98] of PVD-prepared films of metals on metals and later metals on oxides generated from bulk alloys. This wide class of materials gave a boost to the range of catalytic reactions[17] that were amenable to rigorous surface-science studies. Such systems gave valuable insights in complex reactions, like the dehydrogenation of ethylbenzene to styrene,[99,100] albeit for the price that the model systems lost their integrity at the onset of catalytic reactivity undergoing massive structural and chemical transformations, exactly as described in the previous section. In this sense, the single crystals or ordered thin films were pre-catalysts rather than active phases.

Both the precise experiments conducted with **case 1** systems from Figure 4 and the chemical variability of surface science enabled by **case 2** together laid the foundation for the evolution of theoretical description[1,101,102] of surface reactions.

Sustained catalytic activity is enabled if the interface properties of **case 1** and **case 2** are combined and an appropriate functional interface fixes the sandwich of reactive interface and sub-surface volume to a refractory support as shown in **case 3** of Figure 4. Then the theoretically elaborated surface electronic structure modulated by sub-surface reactivity and combined with its fluctuation to generate and re-generate the active sites can unfold and effect the turnover of reactant molecules many more times than there are active sites present initially.

It is widely assumed that catalyst synthesis involves the generation of a large geometric surface area variant of a thermodynamically fixed phase described by a translational geometric structure[34] and a fixed chemical composition. Consequently, the chemical analysis of a preparation and X-ray diffraction analysis should be lead information for the synthesis. This is a simplistic[26,103] approach and hence the roles of "defects"[18,26] of usually unspecified origin (exception steps) or "surface roughness"[88] are accepted as additional descriptors for synthesis. Unfortunately, little is known on how these morphological features relate to either thermodynamics or kinetics of the pre-catalyst synthesis. Complex recipes and detailed prescriptions for choices of materials and unit operations result from this fragmented knowledge. Working catalysts, even when consisting apparently of only one metallic element such as coin metals, Pd, Pt, Ni just to name but a few, get transformed into metastable structures upon the formation of the active phase from the activated pre-catalyst. This pre-catalyst actually is the material that is generated by catalyst preparation. Examples are Pd dehydrogenation catalysts,[104] the $Cu\delta+$ system in multiple applications[77] or the Cu/Zn alloy system.[76,105] This holds likewise for bulk catalysts as with supported systems where the metal-support interface just adds one more dimension of complexity.

We are aware of this seemingly hypercomplex situation from the results of *operando* studies in combination with careful analysis of the chemical[106] and geometric structures before and after catalytic use. Ideally the whole "value chain" of a catalytic material is amenable to *operando* analysis. Such an experimental approach is hardly ever done[107] although it would provide a maximum of information uncompromised (see Figure 2) by the many unspecified discontinuities in local chemical potential stemming from different experimental conditions of the studies in different stages of the value chain.

5. *Operando* Analysis Precedes and Supports Rational Synthesis

In an ideal world one synchrotron experimental station,[108,109] bringing light for vibrational studies (IR, RAMAN) to the *operando* cell working at chemical potentials of truly near ambient pressure at the same time as X-ray light tuneable between 100 eV and ca. 10 keV were present, would allow such catalyst characterisation. Completion by scattering experiments with hard X-rays focussing on translational and real geometric structure would provide insight about the effects of kinetic and dynamic transformation during the catalyst value chain. Today such information is collected by multiple groups with unrelated materials leading to years of work needed before such a picture emerges.

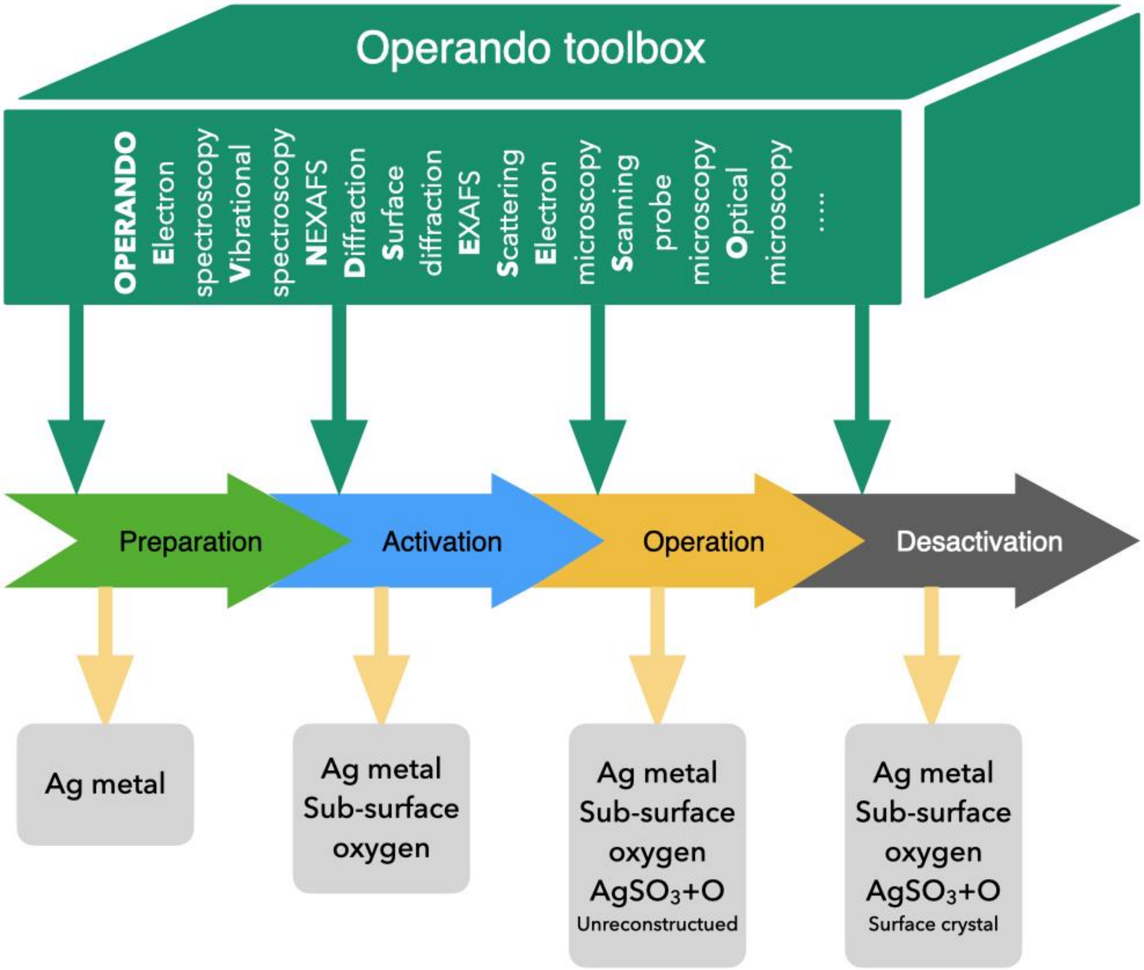


Figure 5. The *operando*-micro-spectroscopy toolbox that is filled by many more tools than indicated on its cover. The central part indicates the value chain of a catalyst to be uncovered using the tools from the box. On the bottom an example is indicated of the formation of the ethylene epoxidation catalyst as discussed in the text.

Figure 5 depicts the situation in which an ecosystem of theory, advanced synthesis, kinetic experimentation and *operando*-spectro-microscopy approaches[106] highlights the complexity challenge. The example of Ag as selective oxidation catalyst for ethylene epoxidation[110-114] is indicated. This reaction is prototypical for the attempts in the ecosystem to solve the riddle of a seemingly simple catalyst for a simple reaction. About 4 decades of intense work was dedicated to this challenge without finding an all-convincing answer. Theory casted doubt[115] on the various explanations and prompted the repetition of careful speciation experiments[116] on various oxygen forms adsorbed on silver. Then, the combination of a rigorous surface science experiment on the working structure of the active Ag and careful *operando* experiments uncovered[116] that the active form of oxygen is not some form of Ag-O species. The Ag-O interaction rather segregates[62] the hitherto unrecognized co-catalyst sulphur to the surface that is dissolved as an impurity in the Ag. There it forms active molecular ("unreconstructed") Ag-SO_3+O species. They produce with high selectivity ethene epoxide as verified[62] experimentally and rationalized by theory. At some point the fluctuating unreconstructed form of the silver sulphate completes the phase transition and forms a reconstructed form of silver surface sulphate that passivates the metal.

In a sufficiently equipped and prepared research ecosystem, we would be able to deliver this type of information within some months of coordinated experimentation. In such a setting, the "hypercomplexity" would become tractable and way better be interlinked with theory. The advances of structural biology may serve as a role model of how modern science can cope with complex systems, with the proviso that an adequate workflow is provided of adapted methodologies. This is well recognised by several coordinated research projects in the world, but their efforts are still sub-critical with respect to the challenge of rational design and realisation of catalytic materials. Given the relevance of catalysis as fundamental science and technology for almost all our technological achievements, it is not easy to understand why the respective communities still fail to arrive at a critical effort and prefer to perform under-complex studies. The emerging digital catalysis science, with its need to rigorously systematize experimental procedures,[58] enables interlinking of multiple experimental data with theory and options of advanced design-of-experiment strategies and may thus facilitate the insight into the value emerging from completion of the knowledge cycle, possibly using reproducible robotic synthesis strategies.

This material-centric approach is essential for catalyst development. It can fortunately be complemented by *operando* kinetic approaches than encompass the transport properties of a catalytic material together with the quantification of the kinetic cycle from Figure 3. Such a "complete experiment" ensures that the likely possibility of different reaction pathways to a product of interest are recognised when the material optimisation may generate chemically different active sites on different catalyst compositions.

6. A novel Concept in Synthesis

Figure 4 creates the impression that catalytic materials may be similar to electronic materials where numerous interfaces between semiconductors and metals create the microelectronic functions. Following this idea, one may recognise the potential of modern thin film technologies in creating interfaces between phases that could not exist under thermodynamic control. However, the 2-dimensional nature of such structures creates a challenge for practical realization where usually the space-time productivity, being a 3-dimensional property, is relevant as opposed to the reactivity per unit surface area. In addition, the postulate to produce sufficient active surface such that realistic kinetic experiments encompassing also higher dimensions of the multi-scale phenomenon catalysis can be conducted, strongly limits the PVD processes of the semiconductor industry as viable approach. Punctual success by chemical synthesis of monolayer oxides on oxide supports[117-119] demonstrates the power of the idea. The universality and reproducibility of PVD processes such as sputter deposition were not utilized in these early attempts.

The thin film approach becomes viable if we consider the synthesis technologies of the photovoltaic industry and science. These methods combine material complexity and physical control of synthesis with access to large areas of functional materials. On a substrate like glass, Si or steel a buffer layer with defined chemical properties can be synthesized via sputter deposition and annealing or via atomic layer deposition. This buffer layer resents one side of the functional interface and can be adequately chosen and prepared (annealing, doping) to provide stable and chemically robust anchoring for the active phase. In addition, abundance and morphology of the active phase can be controlled by sputtering. The minimal abundance is the density of nuclei of its thin film at the transition from a patchy structure to a closed film. At this point, nanoparticles of the active phase cover the buffer layer with high density.

Designing such catalysts follows the concepts of high energy materials being required for good catalytic activity and of the functional interface being pre-requisite for sustained function. It may be expected that the maximum site density where chemical dynamics can evolve with minimum hindrance through collective coupling of atoms, would be the state of the active layer immediately before a continuous thin film forms, in other words where a full coverage occurs of the film nuclei.

Such an approach would allow to freely choose the physico-chemical properties of the bulk support independent from those of the functional interface and from those of the active phase. One could avoid the hard-to-control process of catalyst activation when the pre-catalyst reacts with reagents to form the active phase or where a complex storage phase segregates components to the surface forming the thin film of active phase (see Figures 1 and 2).

This disruptive approach to catalyst synthesis provides the option to assign to the support additional function than just being the inert carrier of an active phase. One function could be to conduct the energetic stimulus (heat, free electrons) directly and exclusively to the active phase. The required use of future green energy in chemical transformations (no more heating with external flames) is greatly facilitated by such a catalyst structure as well as micro-structured or heat exchanger designs of reactors. Novel degrees of freedom in controlling the reactant transport over a planar catalyst structure, with multiple controls of transport patterns (vortex flow, jet flow, flow fields), allow more precise forms of controlling the local chemical potential with its implications for a better control of the entire catalytic system, such as the precise coupling of reactant kinetics with catalyst dynamics unhindered by unnecessary volumes of active phase (see Figure 3).

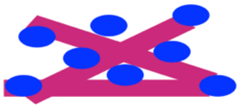
	Mesostructure	**Characteristic**	**Designation**
1		Homogeneous Flat (film) Steps	(1) Single crystal (2) Thin film
2		Active phase nanoparticles on larger support phase	(1) Supported standard catalyst (2) Segregated self-supported
3		Intermixed system of support and active phase	(1) Segregated bulk catalysts (2) Porous supports with nanostructure active phase

Figure 6. Meso-structure of typical non-porous catalysts. The internal structure of the active phase as indicated in Figure 3 is not resolved here.

Figure 6 compares this rather futuristic homogeneous form of a planar catalyst (**case 1**) with the more conventional forms of active phases present as patches of a thin film or as nanoparticles on a support. There, the support (**case 2** and **case 3** in Figure 6) not only carries the active phase but also acts as “mineral spacer” allowing 3-dimensional porous packing of the active layer (**case 1** in Figure 6). This function creates the conventional high volume-density of catalysts. The conventional wisdom, that catalysts perform better when they exhibit higher geometric surface area, stems from the fact that this area is a proxy to the static active site density following from the bulk density of the active phase patches seen in **cases 2** and **3** of Figure 6. If the dynamics of the active phase creates per unit time many active sites and the coupling of the kinetics of reactant transformation and catalyst chemical dynamics becomes highly effective (see Figure 3), then a small geometric surface area and a very small amount of active mass may produce high catalytic performance. A compact realization of a reactor can result with better controlled multi-scale properties for transport of energy and molecules. Such a design revolution would fulfil requirements for a sustainable chemical transformation with minimal use of material and energy resources.

The complexity of systems of **cases 2** and **3** in Figure 6 is illustrated with a synthesis experiment in which a moderately simple functional interface was created from the segregation reaction:

$$2\ AgAlO_2 \rightarrow 2\ Ag + Al_2O_3 + 0.5\ O_2 \qquad (2)$$

Using delafossite[120] as precursor, reductive activation led to nanosized well-facetted Ag particles. In Figure 7 an image gallery is shown of Ag nanoparticles generated by chemical means of impregnation (Figure 7 A,B) or segregation (Figure 7C). In the first two cases, one recognized the small number of suitable sites on the support for holding the active phase Ag metal through the functional interface. It is not accessible for inspection. The rare occurrence of binding sites allows concluding that rather special local chemical situations are required to fix the Ag particles. The segregation technique allowed to uncover this interface detectable as a disordered aluminium oxide thin film (Figure 7C) on the prismatic faces of the hexagonal platelets of the bulk compound.

In Figure 5, the existence of defective local anchor structures in the support phase is not represented as pre-condition for the formation of the functional interfaces. Too little is known about such “defects” of the bulk support phase with respect to chemical composition (nests of OH groups, intentional and unintentional doping by “chemical impurities” in the cation or anion lattices) and extension of these sites (single atom or as large as the active phase patch). Figures 1 and 7 imply that structures without translational order are common sites for the formation of functional interfaces. A possibility to create many binding sites in the buffer layer of the proposed thin film catalysts would be its pre-treatment with a reactive plasma[121] creating a distribution of chemically reactive surface terminations. Subsequent sputtering of the active phase would make use of the reactive sites at the buffer layer and create a homogeneous functional interface. A whole range of chemical interactions across the functional interface might be achieved by selecting various atoms in the plasma treatment. It is noted[13] that none of the catalysts from Figure 7 are useful for ethene selective oxidation because they terminate in oxygen species active in burning the substrate. The origin of the oxygen termination is strain in the metal arising from strong interaction with the support; annealing did remove the strain for the price of destroying the functional interface creating an active and selective ethene oxidation catalyst.[13]

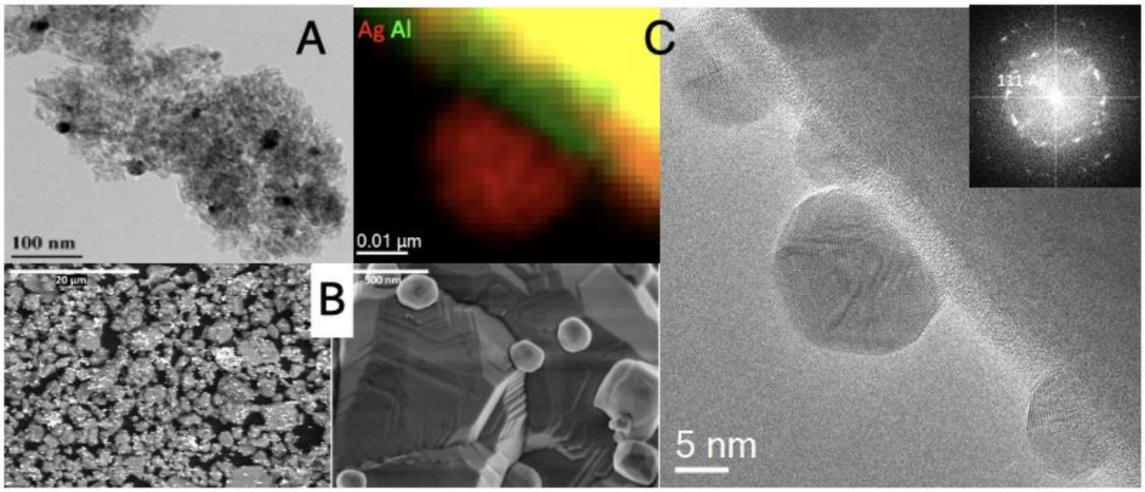


Figure 7: Image gallery of Ag nanoparticles supported on an alumosilicate (A, TEM, black) on a high-temperature annealed α-alumina (B, SEM, bright) and self-supported on platelets of Ag-delafossite (C, TEM, STEM-EDX). For references and details see text.

7. Conclusions

The present paper aims at developing a concept of how to bring together the still fragmented areas of model catalysis and performance catalyst material science. The rigorous understanding of catalysis in the realm of physical chemistry of the phenomenon[122] with its deep and broad quantitative understanding by atomistic modelling[2,77,123-125] forms the reliable foundation required to realize the dream[126-128] about rational design of catalytic processes. Linear extrapolation of non-causal structure-function relations intermixed with chemical intuition and the immense treasure of phenomenological expertise, even augmented with high throughput synthesis and screening, proved to be inadequate for this challenge.

The concept here is to end the fragmented approach towards catalysis in various disciplines of chemistry and physics by practicing that catalysis is a system phenomenon encompassing processes at the atomic scale with the same relevance as processes at meso- and macroscales of space and time.[3,129,130] This system cannot be understood only by increasing the chemical complexity[17] of model systems from extended single crystal surfaces to nanostructures. It is rather suggested (Figure 3) to use as elements of the system "catalytic reaction", two reaction networks describing the molecular transformations of the reactants and the chemical dynamics of the reacting interface. Heterogenous catalysts are no longer treated as static structures brought about by their preparation. Such pre-catalysts undergo transformation into the active phase only in the presence of the mixture of reagents and products at pressure and temperature of operation. The so defined local chemical potential of the reaction environment serves as the coupler generating a steady state of the system. Its action defines the chemical dynamics[131] of the reagents and induces the motion of atoms in the reactive interface. This tries to drive the interface in the low-energy state of a transition into the phase(s) stable in the local potential. In this endeavour, nuclei of the stable phase emerge as high energy configurations of the reactive interface in motion. The presence of the reagents and products is considered to inhibit kinetically the growth of the nuclei of the stable phase (frustration). Continuous attempts of the system to overcome this kinetic barrier to enhanced stability regenerates the active sites and so creates a negative feedback loop against deactivation permitting the sustained action of high energy sites in their catalytic action.

This process is termed the chemical dynamics of the reactive interface. It should be discriminated from the processes designated in the literature as "dynamical behaviour" of catalysts when they undergo restructuring following a gradient in overall chemical potential (electrochemical potential, temperature change, compositional change of the reacting atmosphere) which is actually a kinetic phenomenon of surface chemistry.

Several other feedback loops act in the catalytic system on various scales of time and space. Agents of these loops are: chemisorption of reagents and activated fragments, conversion and selectivity of the reaction network, structure and chemical composition of the functional interface, rigidity and relaxation of the functional interface, transport of energy to and from active sites to the reactor perimeter, transport of reagents to and from the active sites to the reactor perimeter.

The material being capable of performing these multiple tasks needs to be designed and developed by considering these diverse functions. Pre-requisite to this is the verification of the complex function by *operando* spectro-microscopy and adequate performance testing in a parameter field of conditions mapping out the range of local chemical potential where the material is functional. It is noted here that the kinetic parameters available from this testing carry the ambiguity of describing either any one or a combination of the elementary steps in the two constituting reaction networks. The designation of "apparent" kinetic parameters in relation to the desired conversion of reactants is highly appropriate. It is further noted that such synthesis guided by *operando* structural and functional analysis may still not lead to the nature of the active sites as they are likely to be a small aliquot of the reactive interface of transient existence; we need to work with proxies as it was always in analytical catalysis science. *Operando* analysis could end this practice if it were able to simultaneously observe processes at various timescales and sort them into frequent and rare events. Such capability is currently absent to any analytical method but could come into reach when AI-based real-time interpretation of analytical data[132] could be fed back to the operation of spectro-microscopy hardware. Then automated screening with statistically meaningful variation of conditions could map out different classes of processes, one of which is the formation and action of active sites. With the support from appropriate advanced theoretical modelling of dynamical systems the assignment of processes should be possible beyond intuitive approaches.

New in the systems concept is the notion that working catalysts may be designed as patches (nuclei) of a thin film materializing the dynamical reactive interface, the static functional interface and a minimal sub-surface volume required to couple the two interfaces and accommodating atoms that modify the structure of the reacting interface[66,133,134] (alloying or buffering transient species). The volume should be of minimal in thickness to prevent facile crystallisation of stable phases and to accelerate atom diffusion needed to create and operate the active phase. It is noted of course that alternative methods of chemical synthesis and nanoscience may be applied to reach similar representations of catalytic materials. We highlight here the advantages of physical reproducibility, scaling within exact specifications by proven technologies and universality in combination of materials for interfaces and active systems for a design approach encompassing all steps of functional material generation.

The active phase should be deposited by sputtering techniques allowing for precise control of abundance and morphology, as well as offering the chance to activate the phase already during deposition in a reactive atmosphere serving as local chemical potential for the reactive situation. The surface on which the active phase is deposited forms the functional interface and can be prepared and manipulated with the arsenal of the PVD or CVD technologies developed for solar cell manufacture. We suggest using these materials as technology base, as it has solved already the challenge of scaling into very large areas and in converting it into hierarchical functional units (solar panels). A chemical benefit of this approach is that no limit exists in combining material systems (Figure 4) across the functional interface and in using a buffer layer between the physical support and the active phase. This removes many chemical limitations of wet chemical synthesis. Wet chemical synthesis further carries the hard-to-control effect of restructuring the support and hence the functional interface by acid-base chemistry of the solution (dissolution of oxides) in uncontrolled manner during deposition, washing and drying of the pre-catalyst. This results in complicated phenomena during synthetic unit operations and in “dark” recipes aiming at standardising these influences on the desired functional material.

A “flat” thin film catalyst allows controlling the transport of reactants with suitable flow designs at the reactive interface and of energy via the support through the functional interface. Electrical contacts, resistive and inductive heating or photo-stimulation are good options as well as heat exchanger geometries, flow fields or channel structures inside the support. A new era of catalytic materials can result with enhanced integrated functions besides performing the desired chemical transformation. Minimal amounts of active phase, process intensification through dense packing, parallelization through numbering up and technology transfer from the PV industry will together help to make up for the higher cost of such scaled catalytic systems. For catalysis science the material gap between model and performance catalysts vanishes and multi-scale theory can be used directly to design the reaction environment of a system; a “digital twin” of the real catalytic process becomes feasible which includes then options for precise digital control of reaction parameters (avoiding hot spots or explosions, dynamical operation under variable load, in-stationary reaction modes).

These possibilities open finally the chance to develop robotic technologies for synthesis assembling and operating such advanced chemical processes. To exploit these visionary options, it is important that the mode of operation of catalysis science changes and adapts to a digital workflow with open data spaces and pre-competitive cross-industrial cooperation with academia. All these attributes are common to other high-technology operations in physical and biological sciences and can be adapted from there. It may be that catalysis science needs to adapt its *modus operandi* without forgetting their foundation in physical chemistry.

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