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Material Science for catalysis: Quo vadis?

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Dedicated to Professor Josef Breu on the occasion of his 60th birthday

The scientific work of the laureate of this special issue Josef Breu can be characterized as functional material science of nanostructures with emphasis on layered materials and functional polymers. A central theme is the creative utilization of self-organisation effected in reduced dimensions. His work targets selected application areas amongst which catalysis is prominent. The range of applications is, however, much wider as his scientific achievements address the concepts of functional material synthesis. The author focusses here on the relevance for catalysis. This is justified besides the competence of the author by the critical need in catalysis science for intelligent synthetic concepts leading to dynamical materials.

The following bibliographic data may characterize the work of the laureate. Using the web of science, we find that from 292 analysed papers 94 deal with layered materials and 21 with catalysts as application. In Figure 1 we see the assignment of the 292 papers to the core topics within the web of science systematics.

The figure clearly illustrates that Josef is developing generic concepts and cannot be attached to a single community. In this way he follows the classical tradition that chemistry as a science develops its own agenda independent of the fact that its results can be used or are needed by other disciplines. The Figure further evidences that chemical synthetic work is "multidisciplinary" on one side and may be characterized likewise as "material science". The difference between synthetic chemistry and material science should be that in chemistry reactions and reactivity are objects of curiosity whereas in material science one tries to cast a set of pre-defined properties into a material by rational synthetic methods. Both fields of activity require serious efforts in characterization giving the field of "physical chemistry" a large weight in the work of Josef Breu. He applies a broad range of spectroscopic, microscopic and scattering methodologies to determine the overall structure and in particular the interaction between various components in his materials. It is beyond the scope of this short text to deeply analyse novelty and value of the chemical concepts developed and applied by Josef to arrive at his elegant and surprising solutions of chemical questions. It is however common to the research areas of Josef that self-organisation plays a central role in the realization of materials. In particular, the possibilities that open up in the interlayer space between layered templates figure up as central feature in his fields of activity.

From the viewpoint of heterogeneous catalysis, the following examples are of particular interest as they may not occur within the realm of conventional catalyst synthesis methods. In a recent study[1] Josef and team successfully managed to "bottle" model catalysts consisting of an interface between a metal (Pd) and a monolayer of silicate (hectorite). Such systems were found to be active in CO oxidation merely as they inhibit the auto-poisoning of the reaction[2] by strongly bound CO. In an elegant synthesis approach the work paves the way to prepare metal and alloy nanostructures separated by a silicate template of only one monolayer thickness. This allows according to the authors for a detectable ionic interaction between the silicate layer charge and a counter charge sitting on the metal nanoparticles. There is no fundamental reason not to combine several metal nanostructures and create well-arranged heterometallic systems with a clear particle distance or to vary the layer charge of the silicate and thus modify the metallicity of the metal nanoparticles.

Metal nanoparticles in controlled space and relative distance to each other play the key role in an elegant synthesis of Pt nanostructures embedded in a sphere of polyelectrolyte brushes bound to polystyrene beads. The particles were first synthesized as Pt–Au alloys and upon oxidative dealloying from gold recrystallized into single metal nanoparticles still firmly held in the polyelectrolyte network. Well-facetted albeit surface-defective Pt nanostructures remained fixed in the polymer network without sintering and well accessible for hydrogenation reactions in aqueous solution. Such systems are well better suited for demanding catalytic processes in water or protic solvents as compared to conventional carbon-supported Pt catalysts. The same technique of fixing homogeneous nanoparticles here of Au–Pd composition in the polyelectrolyte network of brushes allowed a systematic study[4] of the catalytic activity in aqueous phase hydrogenation as function of the

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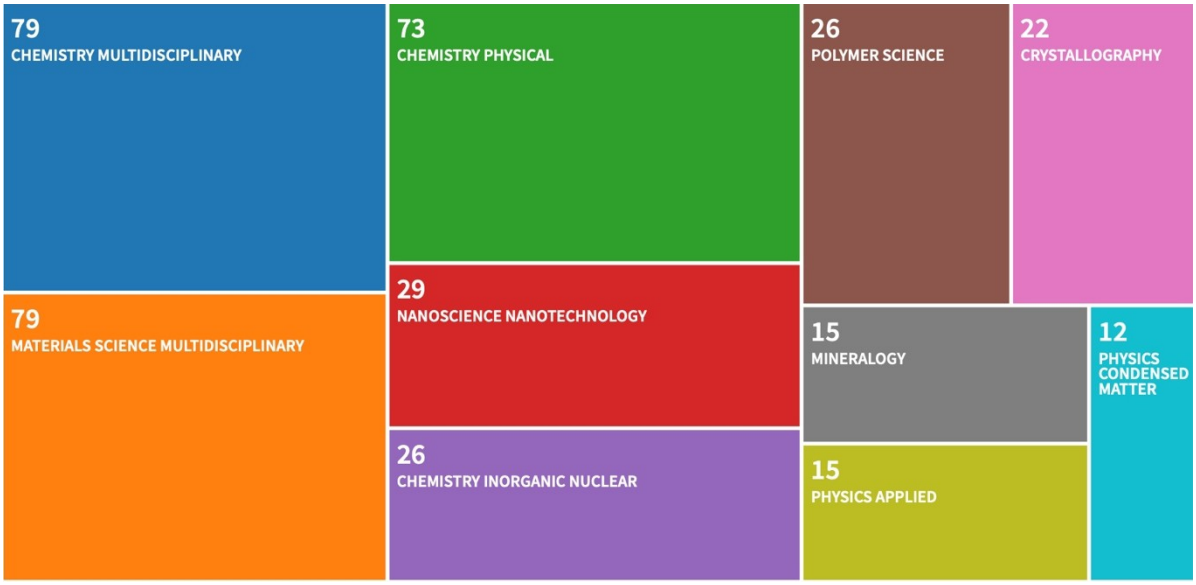

Figure 1. The topical breakdown of the scientific work of Josef Breu following the systematics of web of science (2021).

alloy composition without changing the size or distribution of the particles. A clear compositional maximum was rationalized in terms of an early systematic study of the system by DFT calculations. The work is relevant due to the clear experimental separation of size effects and compositional effects that is difficult to achieve with more conventional realizations of Au–Pd nanoalloys.

In another polymer-inorganic synthesis approach[5] a well-defined pathway to ordered mesoporous oxy-carbides of molybdenum was developed. In a hexagonal phase of a block-copolymer the precursor structure of a molybdenum hetero-polyacid (Mo Keggin) was dispersed under retention of the hexagonal arrangement of the tubular polymer structure. By employing a rational definition of a heat treatment protocol, it was possible to retain the precursor structure into an oxy-carbide without the formation of MoO_3 nanocrystals which would be the thermodynamically stable phase besides carbon yielding a low-surface area binary mixture with little catalytic value. The synthesis protocol gains now renewed interest in the search for highly active systems for ammonia reforming a test reaction that was already applied in the original work.

If in a broader sense we ask where future trends in catalysis material science may be found it is surely the need to better control interfacial properties between the various components of heterogeneous catalysts being the active dynamical surface, its sub-surface regime, the matrix of the "active phase", its support and auxiliary formulation components. Such control was well achieved in the examples discussed here from the work of Josef Breu and team. The fact that in catalytic processes not only the strong direct local interactions between substrate and active site but in addition a range of weaker interactions between reagents and reagent-catalyst together control the local chemical potential and its variation in time[6] requires this wider attention to all components of a catalyst under conditions of performance catalysis[7] far apart from an equilibrium situation. The chemical contrast in support and active phase used in the approaches of the Breu team allowed for a controlled pre-fabrication of the interfacial structure that could be transferred by a variety of activation procedures into working catalysts. A take-home message is that the "support" should not be chosen as a stable material onto which active phases may be "grafted". Rather, a co-condensation approach may be chosen using at least one reactive component capable of condensing with the other components into a homogeneous nanostructured precursor.

A central issue in the selection of active phases is the role of crystallinity and long-range order of materials in contrast to "rough" or "amorphous" structures. The former tend to be stable and are structurally well-defined[8] whereas the latter may be "reactive"[9] and more appropriate for difficult reactions. Without doubt the former calls is suitable for fundamental studies that imply the need to know where the atoms are in space. The latter allow for the embodiment of modern trends like "single atom catalysis"[10,11] or "high entropy catalysis"[12] where isolated species or statistical mixtures are the target of synthesis. The debate as to which of the two prototypes are more valuable goes back to the dispute about the nature of active sites that are either regular as on crystalline surfaces[13] ("Langmuir-type") or isolated "aristocratic"[14] local configurations on a non-translational surface ("Taylor-type"). The Breu work tends to emphasize the value of ordered active nano-structures for catalysis. The author takes the view that both classifications do not meet the really active sites that cannot be probed also today with all the operando techniques that we have developed. The reason is that performance catalysts are

dynamical systems. Active catalysts are at least at their termination layer (the surface plus the sub-surface regime) existing under reaction conditions in a state of structural fluctuation. The reason and the necessary energy for this come from the fact that the correctly chosen reaction conditions drive the termination layer into a phase transition (e.g., from metal to oxide, oxide to carbide or nitride, or from an oxide to its sub-oxide). The function as catalytic material comes from the property that this phase transition is kinetically frustrated e.g., the process stops at the nucleation phase of the transformation phase. Interactions with supports or "templates", compositional complexity ("impurities and promoters") or structural defects generated during synthesis are typical synthetic means to generate the frustrated phase, often unintentionally. Here one recognises the relevance of controlled synthetic concepts as developed by Josef that can provide the kinetic barrier of the phase transition under reaction without impeding the fluctuation of its active surface.

The continuing attempt of the system to overcome the kinetic hindrance and to reach thermodynamic stability is the process that regenerates the active sites as elements of the fluctuating termination layer. In such a picture there are no pre-defined active sites and there is little room for translational ordering. But there is of course need for a well-defined local order and for structure-directing self-organization that should not be involved in the catalytic process to preserve the overall catalyst structure against reaching the thermodynamic minimum of separated components all in long-range ordered forms (segregated and sintered) Intercalation in all its forms is a highly valuable principle in such a scenario and hence it becomes clear that the intelligent combination of structural flexibility and stable templating is a powerful concept to high-performance catalysts. The work of Josef Breu has indicated this direction and shown recipes of realization of a variety of chemically different systems. In this way he is strongly contributing to the grand challenge of finding design concepts of catalytic materials. The catalysis community is happy that skilled inorganic chemists like Josef use their toolboxes of combing local dynamics and mesoscopic integrity ("stability") and pave the way to better controlled systems by dedicated and scalable synthesis methods.

Conflict of Interest

The authors declare no conflict of interest.

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