

# Moving Frontiers in Transition Metal Catalysis: Synthesis, Characterization and Modeling

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Nanosized transition metal particles are important materials in catalysis with a key role not only in academic research but also in many processes with industrial and societal relevance. Although small improvements in catalytic properties can lead to significant economic and environmental impacts, it is only now that knowledge-based design of such materials is emerging, partly because the understanding of catalytic mechanisms on nanoparticle surfaces is increasingly improving. A knowledge-based design requires bottom-up synthesis of well-defined model catalysts, an understanding of the catalytic nanomaterials “at work” (operando), and both a detailed understanding and a prediction by theoretical methods. This article reports on progress in colloidal synthesis of transition metal nanoparticles for preparation of model catalysts to close the materials gap between the discoveries of fundamental surface science and industrial application. The transition metal particles, however, often undergo extensive transformations when applied to the catalytic process and much progress has recently been achieved operando characterization techniques under relevant reaction conditions. They allow better understanding of size/structure–activity correlations in these systems. Moreover, the growth of computing power and the improvement of theoretical methods uncover mechanisms on nanoparticles and have recently predicted highly active particles for CO/CO<sub>2</sub> hydrogenation or direct H<sub>2</sub>O<sub>2</sub> synthesis.

## 1. Introduction

A series of steps are required in different disciplines to design, synthesize, and optimize performance of catalysts in a rational way.<sup>[1]</sup> By now, a plethora of interesting nanostructures, high throughput testing systems, theoretical approaches, and characterization techniques are known. Synthetic strategies and a wealth of structural insights have been reported for model systems including single crystals, defined clusters, and nanoparticles (NPs).<sup>[1b,c,2]</sup>

To understand heterogeneous catalysts, reaction mechanisms have been studied on single crystal surfaces of transition metals.<sup>[3]</sup> However, these studies are typically carried out under conditions different from the catalytic reaction (e.g., in ultrahigh vacuum) and some important catalyst features are not considered (e.g., the specific electronic and geometric structures of small particles with a high density of low coordinated atomic sites). In order to elucidate the role of particle characteristics in catalytic reactions, metal clusters have been deposited on thin films and investigated in catalytic reactions.<sup>[4]</sup> This is particularly interesting to study the fundamental role

of ultrasmall clusters with sizes from the single atom level to 1–2 nm, but the amount of catalyst is limited to the nanogram range and the conditions under which the catalytic reactions may be carried out are restricted.<sup>[5]</sup> To bridge the discoveries of fundamental surface sciences and industrial application, powder model catalysts with defined particle size are important. As closer mimics of real catalysts, catalysts derived from colloidal transition metal NPs are thus particularly interesting.<sup>[6]</sup>

Nevertheless, in many cases the most active catalyst structures are not those that have been directly synthesized, but those that evolve during exposure to the conditions of the catalytic reaction.<sup>[7]</sup> To understand the performance of a catalytic material, it is thus important to establish in situ and operando characterization techniques to get in-depth insight into reaction conditions, also at elevated pressures and temperatures.<sup>[8]</sup>

Moreover, the enormous increase in computing power together with the development of computational tools has been exploited to predict structure–function relations and to compute energy landscapes of heterogeneous reactions.<sup>[9]</sup> Nevertheless,

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the rational design of practical catalysts that can operate in specific processes under certain reaction conditions is still challenging. Besides some exceptions, only a few studies report on structure–function relations with a detailed insight into the nature of the active sites and their role in facilitating the reaction in question.<sup>[10]</sup> On the other hand, the experimental design of catalysts with improved function has also failed in reactions predicted by theory since generic synthetic strategies for catalysts in a performance-optimized form are lacking.

The multitude of aspects relevant for knowledge-driven catalyst design requires multiple iterative steps of experiment (synthesis, performance, operando characterization, and reaction engineering) and theory (elementary reaction mechanism, modeling, and simulation) in integrative approaches over the different disciplines across all time and lengths scales. Moreover, tools capable of handling the enormous data volumes generated by these knowledge-based processes will be needed to analyze the data and build up applied materials libraries, such as the Novel Materials Discovery (NOMAD) Laboratory<sup>[11]</sup> and the Materials Genome Initiative in materials science or CatApp for heterogeneous catalysis.<sup>[12]</sup>

Herein, we discuss the progress made and expected in the tailor-made synthesis of nanoscale catalytic materials, characterization methods for working catalysts under relevant reaction conditions, and theoretical modeling of catalytic surfaces and reactions. A special emphasis is paid to the direct synthesis of hydrogen peroxide from hydrogen and oxygen in liquid phase and the syngas-to-dimethyl ether (STD) and the related methanol synthesis process in *gas phase*.

## 2. Synthesis of Tailored Catalysts at the Nanoscale

Supported transition metal particles are among the most relevant catalysts currently applied in the field of heterogeneous catalysis. Due to the large industrial production scales, even small improvements of the overall catalytic performance or a decrease of (noble) metal content have significant economic and ecologic impact.<sup>[13]</sup> The size and morphology of the catalyst particles (typically transition metal NPs)<sup>[14]</sup> and their synergy with the support (typically a metal oxide)<sup>[15]</sup> are the most important factors determining a catalysts performance. In early work, catalytic reactions on metal catalysts where the reaction rate (as the number of reagent transformations for one active center per unit time, i.e., the turnover frequency (TOF)) depended on the metal NP size were classified as structure-sensitive, while those reactions which did not reveal size dependence were called structure-insensitive.<sup>[16]</sup> Intimate NP–support interactions may result in considerable changes of the physical properties and the catalytic performance which is particularly relevant for small NP sizes (below 1 nm).<sup>[15c]</sup> Significant efforts have been devoted to achieve an in-depth understanding of the electronic and geometric factors originating from size, shape, and support effects.<sup>[17]</sup> Likewise, the targeted synthesis of size- and shape-selected catalysts is highly desirable, while the conventional methods for catalyst preparation such as impregnation and (co)precipitation usually lead to poorly defined particles with large or asymmetric size and shape distributions. Since the catalytic performance of a given material is often dominated by



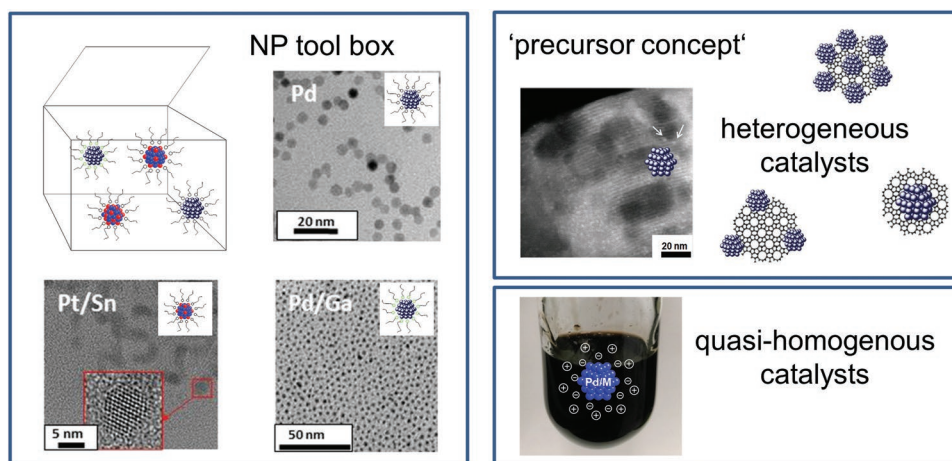
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**Figure 1.** Transition metal NPs provide well-defined building units for the preparation of model catalysts: 1) as colloidal sols in quasihomogeneous catalysis or 2) after deposition on a metal oxide support in heterogeneous catalysis. Adapted with permission.<sup>[18c,20]</sup> Copyright 2018, Elsevier.

only a few specific sites that are particularly active, such structural inhomogeneities may conceal the genuine catalytically active species of the catalyst. Examples include ligand-stabilized transition metal colloids that have been demonstrated to act as quasihomogeneous catalysts in the organic or aqueous phase in various catalytic reactions (**Figure 1**).<sup>[18]</sup> In the so-called “precursor concept,” colloidal NPs have been deposited on a support and used as well-defined precursors for the manufacturing of heterogeneous model catalysts.<sup>[15d,19]</sup> In general, the catalytic performance of heterogeneous catalysts is often highly sensitive to details of the synthesis protocol, one factor which may have contributed to inconsistencies in the literature.<sup>[15d]</sup> In the “precursor concept,” the separation of NP synthesis and deposition in individual steps diminishes the contribution of the support on NP formation and vice versa.

Thus, the NPs provide well-defined building units that allow independently addressing the influencing catalyst parameters of the transition metal NPs and the metal oxide support.<sup>[21]</sup>

Thanks to improvements of colloidal NP synthesis, the development of transition metal NPs has extensively advanced over the past decades and allows for carefully tailoring various structural characteristics (such as size, shape, and composition).<sup>[2b,22]</sup> Major breakthroughs have been achieved using various methods of chemical (co)reduction and (co)decomposition of metal precursors in solution in combination with kinetic control of (over) growth rates (e.g., by facet-selective capping) and site-specific dissolution (e.g., by etching or galvanic replacement).

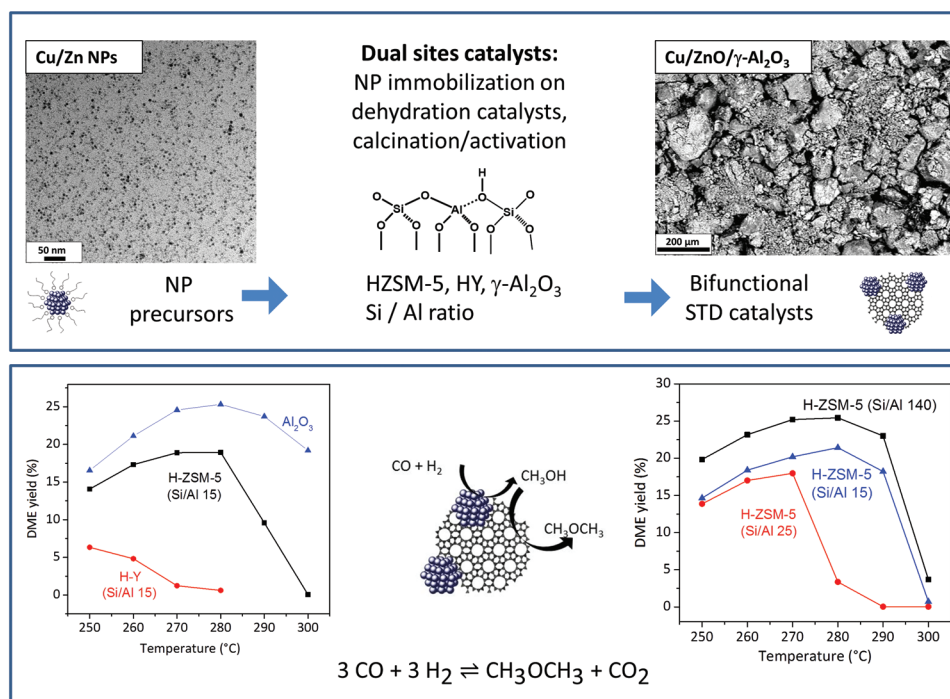
Organometallic compounds, for example, have been shown to serve as a reducing agent and as a stabilizer for NPs at the same time.<sup>[19]</sup> Both the reduction of transition metal ions and the control of particle nucleation and growth processes are then brought about by the same reagent (i.e., termed as “reductive stabilization”). Recently, small Cu/Zn-based NPs have been obtained by reacting Cu(acac)<sub>2</sub> with Et<sub>2</sub>Zn.<sup>[21,23]</sup> The reaction was suggested to proceed via a transmetallation reaction where the as-formed Cu-alkyl intermediates further decompose to yield a zerovalent Cu core surrounded by a layer of stabilizing Zn-containing species. In general, this reaction concept is versatile and provides different types of NP building blocks (e.g., Cu/Zn-, Pd/Ga-

and Pd/Zn-based NPs) which already demonstrated good performance as the methanol active component in bifunctional catalysts for the syngas-to-dimethyl ether process (**Figure 2**).<sup>[20a]</sup>

High sintering resistance was achieved for monomodal, size-selected clusters by suppressed Ostwald ripening, elucidating the importance of a narrow NP size distribution.<sup>[24]</sup> Decrease in the NP size is not only accompanied by an increase in the total number of surface atoms but also by the increase in atoms with low-coordination numbers at vertex and edge sites.<sup>[16b]</sup> These sites may reveal altered catalytic properties.<sup>[25]</sup> Meanwhile, synthesis techniques for nanocrystals also allow distinct morphology control with selective crystal facet exposure. For transition metal nanocrystals, facet-dependent catalytic properties have been elaborated in a large number of catalytic reactions.<sup>[17f]</sup> The (111) facets of Pd nanooctahedra, for example, were shown to be more favorable with respect to H<sub>2</sub>O<sub>2</sub> selectivity and reaction rate than the (100) facets of Pd nanocubes in the direct synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>[26]</sup> Even multimetallic nanocrystals ranging from transition metal polyhedra to nanoframes with three dimensional catalytic surfaces have been prepared recently via colloidal approaches and used as catalysts for oxygen reduction reaction.<sup>[17c,27]</sup> Nanocrystals with concave and high-index facets are highly interesting for catalytic application due to their high density of low-coordinated atoms, steps, edges, and kinks. However, the synthesis of these complex structures remains challenging since their formation is not favored by thermodynamics owing to the higher energy compared to their convex and low-index counterparts.<sup>[28]</sup>

Recently, particular interest has also been devoted to the synthesis of multimetallic NPs with core-shell, Janus-type, solid-solution or intermetallic composition.<sup>[29]</sup> Due to synergistic effects, modified electronic and/or geometric surface structures, high catalytic activities, and selectivities have been achieved in chemical reactions even if one of the constituents was less or inactive.<sup>[18c,30]</sup> Surface strain due to lattice mismatch between metals in multimetallic NP structures may further be employed to engineer sorption energies of molecules and boost catalytic performance.<sup>[31]</sup> Alloying Pd NPs with Au, Ag, or Sn, for example, has been addressed to overcome the selectivity problem in direct H<sub>2</sub>O<sub>2</sub> synthesis to induce the increase in H<sub>2</sub>O<sub>2</sub>





**Figure 2.** Immobilization of Cu/Zn-based NPs on solid acids yields dual site STD catalysts with close proximity of active sites for methanol synthesis and dehydration. Catalytic tests demonstrate that DME yield depends on various materials parameters, including loading of Cu/Zn NPs and type of solid acid. Adapted with permission.<sup>[21]</sup> Copyright 2018, Elsevier. Adapted with permission.<sup>[23]</sup> Published by the RSC.

selectivity.<sup>[32]</sup> Recently, promotional effects have been reported for bimetallic AgPt nanooctahedra prepared by a hydrothermal procedure.<sup>[33]</sup> In some cases, intermetallic NP are formed in situ under conditions of catalyst activation or chemical reaction via reaction of the metal NPs with a metal containing capping agent or the (reducible) metal oxide support.<sup>[20a,34]</sup> Particularly, alloying the early with late transition metals in individual NPs has remained challenging due to the large differences in their reduction potential.<sup>[35]</sup> Despite numerous recent developments, more accurate control over nucleation and growth processes is needed for multimetallic NPs since catalytic performance is highly sensitive to atomic ordering (i.e., random alloy vs intermetallic compound) even if the overall composition and stoichiometry are exactly the same.

In chemical synthesis, NPs are typically capped by surface adsorbates, which control particle nucleation and growth and stabilize the NPs against agglomeration. A wide variety of stabilizing agents have been utilized, including polymers (e.g., poly(vinylalcohol) (PVA)), surfactants (e.g., hexadecyl-2-hydroxyethyl-dimethyl ammonium dihydrogen phosphate (HHDMA)), proteins, or small ligands with high binding affinity for the transition metal (e.g., phosphines, thiols, and amines).<sup>[18a,b,30,36]</sup> Surface properties of colloidal NPs also affect their adsorption behavior and spatial distribution on the metal oxide support which is another important factor in catalysis.<sup>[37]</sup> The protecting shell has been removed from supported NPs by solvent extraction or thermal degradation. In some approaches, the NPs were stabilized directly by solvent molecules (termed “capping-agent free” methods).<sup>[18c,38]</sup> Ionic capping agents in aqueous solution may offer further ease of capping agent removal, but these

procedures face future challenges for high-level control of NP size and structure. Surface adsorbates itself may also lead to steric hindrance, electronic interfacial effects, and act as a poison to selectively block sites on the NP surface, boosting selectivity in various catalytic reactions.<sup>[2a,22e,39]</sup> PVA ligands adsorbed on Pd NPs, for example, have been reported to impede O–O bond rupture on Pd in the direct synthesis of H<sub>2</sub>O<sub>2</sub> from hydrogen and oxygen significantly increasing the selectivity toward H<sub>2</sub>O<sub>2</sub>.<sup>[32,40]</sup> Ligand leaching and successive NP agglomeration, however, resulted in the rapid decrease in selectivity.<sup>[40a]</sup> For Pd@HHDMA NPs, the crucial role of HHDMA ligands was highlighted in the direct H<sub>2</sub>O<sub>2</sub> synthesis, increasing the energetic barrier for the two side reactions (overhydrogenation and H<sub>2</sub>O<sub>2</sub> decomposition) to water and thus H<sub>2</sub>O<sub>2</sub> selectivity.<sup>[41]</sup>

Although there have been significant advancements toward precise NP synthesis, catalytic mechanisms at NP surfaces have not yet been entirely understood. NPs often undergo extensive transformations when applied to the reaction conditions of the catalytic process, creating unique catalytic sites in situ at the NP surface and perimeter. NP interactions with the metal oxide support and the reactive gases at elevated temperatures and pressures induce chemical (re)ordering which may change the morphology and surface crystal facets, phase segregation, or selective oxidation affecting the overall catalytic performance.<sup>[42]</sup>

While the production of NPs with selected size, shape, and composition is possible and the necessary synthetic approaches are emerging, many challenges and opportunities have remained for their catalytic application. The synthesis of NP with nonequilibrium shapes or the controlled introduction of surface lattice strain and defects offers promising routes for

catalyst design. The improvement of thermal and chemical stability is still an important topic, and it would be useful to map stable core–shell configurations and intermetallic systems depending on NP size, size distribution, shape, and support material under conditions of catalytic application. Conceptual analogies between the chemistry of organic molecules and multicomponent NPs have been proposed to control synthesis through both mechanistic understanding and empirical insights.<sup>[43]</sup> However, the mechanistic guiding principles of NP nucleation and growth are often not well understood at an atomic level. Therefore, insights into NP formation and active site motifs under operando conditions as well as advancements of computational-assisted investigations (e.g., DFT calculations of reaction mechanisms and microkinetic modeling of surface reactions) have a great significance for future design and preparation of novel types of NPs as well as for the prediction of their catalytic performances.<sup>[44]</sup>

### 3. In Situ/Operando Characterization Techniques

The design of nanoscale transition metal catalysts and their characterization (Section 2) plays a key role in developing next generation catalysts. However, often the structure of the as-prepared NPs and active sites changes during activation and exposure to the reaction conditions.<sup>[7c,8b]</sup> Supported NPs may change their size, shape, oxidation state,<sup>[45]</sup> and composition<sup>[46]</sup> also under dynamic reaction conditions.<sup>[47]</sup> The transition metal NPs respond to the surrounding atmosphere and hence, they should usually be considered as “precursors.” The difficulty of predicting these changes necessitates the use of operando characterization techniques to measure the structure of the NPs as well as to track changes occurring under relevant reaction conditions. Preferentially, the reaction conditions including fluid and heat properties should mimic the real reactor including sometimes harsh reaction conditions (temperatures up to 1000 °C, pressures up to 200 bar). Only a few characterization methods are able to reliably probe the catalysts under these conditions: X-ray-based techniques are particularly interesting as they can penetrate a (high pressure) catalytic reactor, but also UV–vis, Raman, infrared and Mößbauer spectroscopy or neutron diffraction provide helpful complementary tools.<sup>[48]</sup>

Commonly used X-ray techniques are X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and the more advanced photon-in/out-techniques (X-ray emission spectroscopy (XES), high energy resolution fluorescence detected XAS (HERFD-XAS), and resonant inelastic X-ray scattering (RIXS)).<sup>[7d,8h,48,49]</sup> They provide information about crystalline and amorphous phases, small clusters and even single site species, but they are bulk sensitive and probe over the whole catalyst sample. Therefore, also ambient pressure X-ray photon–electron spectroscopy (XPS) has been developed as a more surface sensitive technique to provide in situ information,<sup>[50]</sup> and local probing techniques like in situ/environmental TEM (ETEM)<sup>[51]</sup> have been advanced. They cannot be used under real reaction conditions, but provide useful complementary information.<sup>[51a,52]</sup>

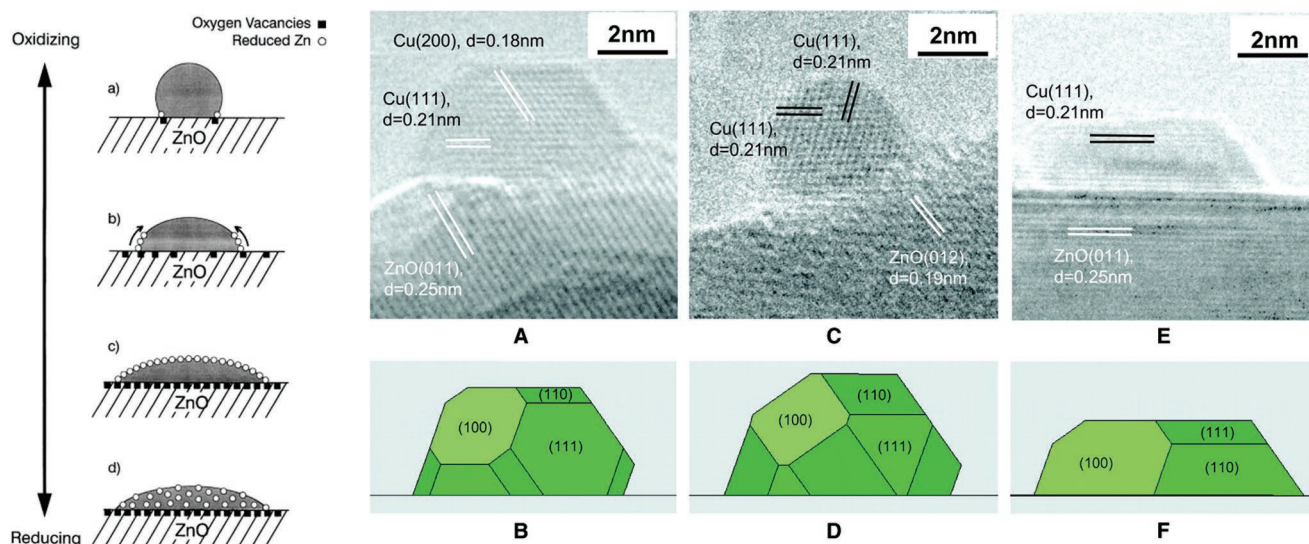
With respect to transition metal NPs, XAS in terms of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) and related techniques (XES,

HERFD-XAS, and RIXS) are particularly useful since they are sensitive to all atoms of the particular element irrespective of the cluster/particle size.<sup>[49b,53]</sup> They probe electronic structure of absorber atoms, their coordination number/geometry and the nature of their nearest neighbor atoms. This knowledge, in turn, allows to detect alloy formation, to evaluate crystal structures of NPs and, in some cases, also to reveal their size and shape. As XAS is the technique of choice to measure working catalysts in an almost noninvasive way (i.e., it does not influence the target reaction), a dedicated beamline has been built at the KIT synchrotron source in Karlsruhe.<sup>[54]</sup> Due to its importance, further XAS facilities<sup>[55]</sup> with infrastructure established for in situ/operando catalysis research include Synchrotron Catalysis Consortium (US),<sup>[56]</sup> SuperXAS at Swiss Light Source and Swiss-Norwegian beamlines at European Synchrotron Radiation Facility (ESRF),<sup>[57]</sup> DUBBLE<sup>[58]</sup> and BM23<sup>[59]</sup> beamlines at ESRF, and SAMBA and ROCK beamlines<sup>[60]</sup> at the SOLEIL synchrotron.

The significance of such studies is highlighted here for the two examples, i.e., transition metal NP-catalyzed methanol/DME synthesis and direct H<sub>2</sub>O<sub>2</sub> synthesis.

For both methanol and DME synthesis, the copper particles are typically formed during activation. This system was also one of the first examples where the influence of reaction conditions on the shape of catalyst particles was studied. Using in situ XAS, reversible changes of the Cu coordination number were found which was explained by the dynamic change of the Cu NP shape between disk-like, flat Cu particles with a large Cu–ZnO interface to more round-shaped Cu NPs with a decreased Cu–ZnO interface (**Figure 3**).<sup>[61]</sup> The spreading is induced by the higher reduction potential of the reaction gas mixture and the formation of vacancies (due to reduced Zn) leading to a better wetting of the Cu NPs. This conclusion was later directly visualized using in situ TEM (**Figure 2**).<sup>[51a]</sup> Nevertheless, many mechanistic questions are still under debate, e.g., the role of Zn/ZnO migration on the Cu particle, the formation of surface or bulk CuZn alloys or the influence of oxidized Cu/Zn species.<sup>[10b,62]</sup>

In situ or environmental TEM can only be applied in the mbar pressure range. In order to really derive structure–activity relationships, higher pressures are needed to monitor the product online. In contrast, XAS may be used at realistic process pressures, with the upper pressure limit defined only by the used in situ cell. Recently, we performed operando XAS at elevated pressure during DME synthesis on NP-derived Cu/Zn- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cu/Zn-HZSM-5 catalysts (**Figure 2**).<sup>[21]</sup> Similar to the Cu–ZnO methanol catalysts, metallic Cu NPs with highly defect and partially reduced, amorphous ZnO are the essential part of the active catalyst. In this case, the colloidal, Cu/Zn-based NPs were used as precursor for the methanol active component and immobilized directly on the solid acid dehydration catalyst. Alternatively, also core@shell Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>@ZSM-5 catalysts have been used.<sup>[63]</sup> Again X-ray techniques are excellent tools, namely to uncover the hierarchical structure.<sup>[51c,64]</sup> Using synchrotron-based micro X-ray fluorescence, micro XRD, and scanning transmission X-ray microscopy computed tomography (CT), the evolution of Cu/ZnO and zeolite components were analyzed in a single catalyst grain during calcination, reduction, and under DME synthesis conditions.<sup>[63]</sup> The X-ray CT allowed to identify a metastable Cu<sup>+</sup> phase at the core–shell



**Figure 3.** Left: Schematic model for the a) nonwetting, b) wetting of the Cu NPs on the ZnO support, c) surface alloying, and d) bulk alloy formation due to severe reduction. Right: In situ TEM images of a Cu–ZnO catalyst and the corresponding Wulff constructions of the Cu NPs imaged in A,B) 1.5 mbar 3:1 H<sub>2</sub>/H<sub>2</sub>O; C,D) 1.5 mbar H<sub>2</sub>; and E,F) 1.5 mbar 95:5 H<sub>2</sub>:CO. Left: Reproduced with permission.<sup>[61]</sup> Copyright 2018, Elsevier. Right: Reproduced with permission.<sup>[51a]</sup> Copyright 2018, AAAS.

interface. The next step forward will be true operando CT measurements.

Operando techniques are also extensively used to study bimetallic catalysts. For instance, in situ XRD and XAS were ideal tools to follow transformation of Ni and Ga nitrate precursors to Ni<sub>5</sub>Ga<sub>3</sub> alloy NPs which provide active catalysts in methanol synthesis.<sup>[65]</sup> Formation of Pd<sub>2</sub>Ga alloyed nanoparticles and their stability could be monitored during STD at ambient<sup>[9]</sup> and high pressures.<sup>[20a]</sup> Operando XAS during STD at 20 bar showed moderate changes in the coordination environment of Pd possibly attributed to sintering and/or dealloying of the PdGa nanoparticles.<sup>[20a]</sup>

Another challenging area is the operando characterization of transition metal NPs in liquid phase catalytic reactions, especially if high pressures are additionally employed. The direct H<sub>2</sub>O<sub>2</sub> synthesis from H<sub>2</sub> and O<sub>2</sub> (see also Section 2) is one of the examples. To safely provide O<sub>2</sub> and H<sub>2</sub> at high pressure is crucial to increase the amount of dissolved gas in the liquid phase. Only this strategy allows obtaining detectable concentrations of H<sub>2</sub>O<sub>2</sub> in the effluent stream. In order to realize such operando studies a new concept of an in situ setup in which H<sub>2</sub> and O<sub>2</sub> are dissolved at high pressures in separate solvent streams has been introduced.<sup>[66]</sup> This avoids mixing in the gas phase allowing safe measurements. Combined with an in situ cell designed for XAS measurements at Pd K edge at high pressures (10 bar, further developed to 100 bar) the structure of Pd NPs producing quantitative amounts of H<sub>2</sub>O<sub>2</sub> was uncovered. Here, the formation of an  $\alpha$ -PdH<sub>x</sub> hydride structure with surface-chemisorbed O has been observed which deviated significantly from the as-prepared catalysts (Figure 4).

While recent years have shown the development of in situ and operando techniques that are now more often being used to characterize working catalysts, there are still plenty of challenges ahead. A particular focus lies on the development of

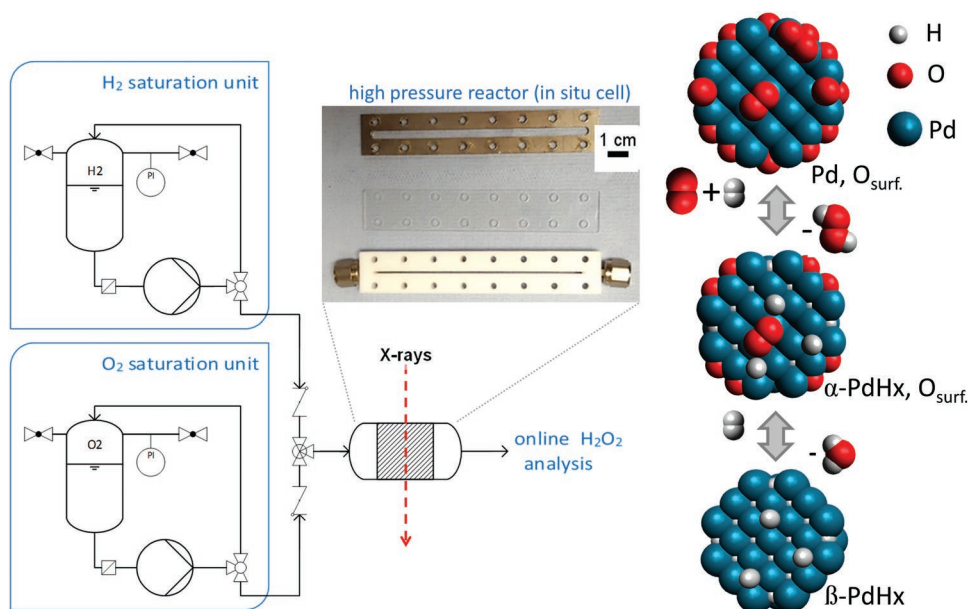
combined techniques. Specially designed in situ XAS cells,<sup>[66]</sup> for example, allow for simultaneous Raman measurements due to transparent windows, thus providing valuable complementary information, e.g. on the structure of (oxidized) metals, the extent of core–shell particles,<sup>[52]</sup> or the presence of organic surfactants derived, e.g., from colloidal preparation techniques (see above). Moreover, Raman spectroscopy also allows detecting important surface intermediates during reaction conditions. Other technique combinations profiting from synergies between the employed methods include but are not limited to XAS-XRD<sup>[7c,67]</sup> and XAS-SAXS,<sup>[68]</sup> XAS-DRIFTS<sup>[69]</sup> and XAS-ATR IR,<sup>[70]</sup> and XAS–UV–vis.<sup>[71]</sup>

The obtained information on the structure of the active catalyst provides insight into the reaction mechanism at the atomic scale and is a key to improve and validate theoretical modeling efforts of reactions on surfaces (see below). In combination with theory, suggested structures from DFT calculations can be directly evaluated with respect to structures derived from EXAFS spectra<sup>[72]</sup> and theoretical calculation of spectra enhance the interpretation of XANES and XES spectra.<sup>[73]</sup> Another promising approach is modulation excitation spectroscopy (MES). When coupled, e.g., with XAS<sup>[73b,c]</sup> or XRD,<sup>[74]</sup> important information about minor changes on the catalyst surface could be revealed that would not be detectable by conventional X-ray techniques. Finally, operando spectroscopy does not only link up to synthesis to follow the evolution of the catalyst under reaction conditions, but it can also be directly used to study the formation of NPs by colloidal synthesis<sup>[18d,75]</sup> or even hydrothermal reaction conditions.<sup>[76]</sup>

## 4. Theory

Theoretical calculations, typically based on density functional theory (DFT), have become an important field in catalysis





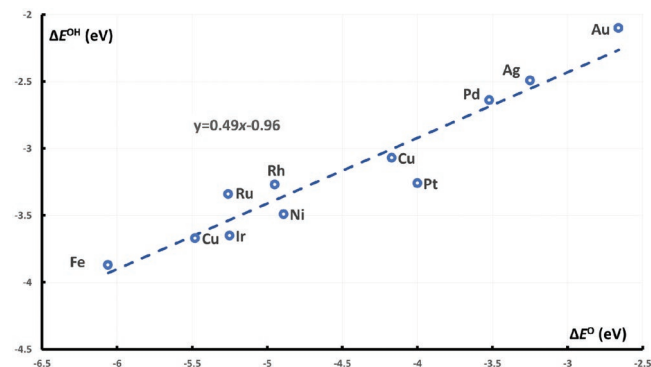
**Figure 4.** Left: Scheme of the setup for operando studies of the direct  $\text{H}_2\text{O}_2$  synthesis at high pressure and a photo of the reactor cell used at pressures up to 10 bar. Right: Dynamic transformations of Pd NPs under conditions of direct  $\text{H}_2\text{O}_2$  synthesis revealed using operando XAS at high pressure. Reproduced with permission.<sup>[66]</sup> Copyright 2018, ACS.

in the past years. They are now routinely used to calculate adsorption energies and to elucidate reaction mechanisms on transition metal surfaces.<sup>[77]</sup> The insight obtained from these calculations can be used to further understand and develop structure-reactivity relations, that is connecting structural motifs of surfaces—typically consisting of a few atoms—to a specific catalytic activity and selectivity. While the error related to the use of DFT for transition metal surfaces (commonly 0.2 eV or more)<sup>[78]</sup> prevents the simulation of highly accurate reaction rates (since the error goes into the exponent of the rate constant), trends between various active site motifs or different surfaces are usually well described.<sup>[79]</sup> The reactivity of surfaces is typically described with Sabatier's principle, where the optimal catalyst is found by a well-balanced binding of the intermediates. Importantly, the magnitude with which the interaction between a transition metal surface and an intermediate changes is related to the change for other intermediates through so-called scaling relations.<sup>[80]</sup> Examples are, e.g., the finding that the binding energy of chemisorbed hydroxyl ( $\text{OH}^*$ ) scales linearly with the binding energy of oxygen ( $\text{O}^*$ ) (Figure 5). The slope of the scaling can be rationalized through simple bond counting arguments, which in this case sums to 0.5 (OH forming one bond, while atomic O forms two).

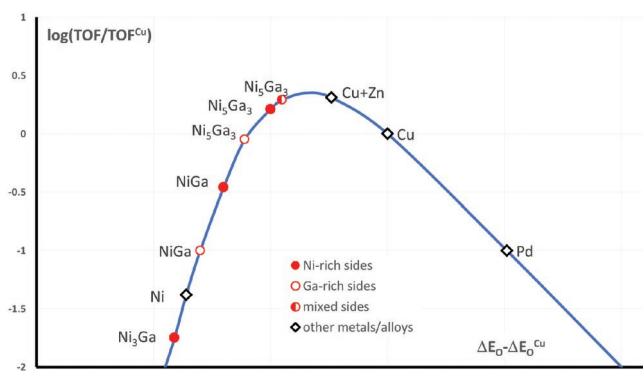
Importantly, these scaling relations typically reduce the large number of parameters (adsorption energies<sup>[80]</sup> and transition states<sup>[81]</sup>) describing a reaction mechanism on a surface to only a few. This approach has been used to describe the activity and selectivity for the direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  as a function of only one descriptor, the oxygen binding energy.<sup>[82]</sup> Another example is given by investigations targeting the development of new  $\text{CO}_2$  to methanol catalysts. Using extensive DFT calculations in conjunction with scaling relations and microkinetic modeling allowed constructing an

activity volcano where the activity is given as a function of only one descriptor (Figure 6).<sup>[83]</sup> This analysis corroborates the fact that a Cu/Zn surface is more active in  $\text{CO}_2$  hydrogenation compared to pure copper catalysts, as Zn increases the binding of oxygen and thus moves the oxygen binding energy closer to the optimum.<sup>[62c]</sup> Importantly, the reduction of the parameter space to, in this case, one descriptor allows for the fast computational screening of new catalysts leads. Using the activity volcano shown in Figure 6 led to the identification of highly active NiGa catalysts for the hydrogenation of  $\text{CO}_2$  to methanol via computations.<sup>[83]</sup> Operando spectroscopy proved that indeed in many cases the corresponding alloys form but may also be partly transformed, e.g., resulting in surface segregation (cf. Section 3 and, e.g., ref. [84]).

Despite of remarkable success in the in silico design of new catalyst materials, there is still ample need to improve



**Figure 5.** Adsorption energies of OH intermediates ( $\Delta E^{\text{OH}}$ ) with respect to adsorption energies of atomic O ( $\Delta E^{\text{O}}$ ) on the stepped surface on various transition metals. Reproduced with permission.<sup>[80]</sup> Copyright 2007, APS.

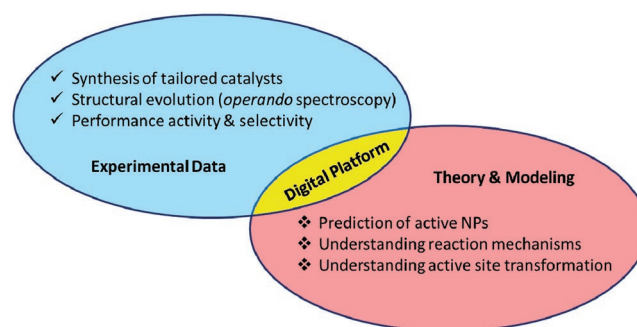


**Figure 6.** Turnover frequency as a function of the oxygen adsorption energy ( $\Delta E_O$ )  $\Delta E_O$ , relative to Cu(211). Reproduced with permission.<sup>[83]</sup> Copyright 2014, Springer Nature.

the theoretical models. While it will still be unfeasible for the foreseeable future to go beyond density functional theory, there is a strong focus on improving its accuracy, with the best GGA functionals now having errors below 0.2 eV.<sup>[78,85]</sup> On the other hand, most models of how a catalytic surface facilitates a reaction are still rather simplistic. Here an improvement of the theoretical description implies a move toward more complex models together with the spectroscopic and structural information presented in Section 3. These include the consideration of coverage effects,<sup>[86]</sup> reaction mechanisms over multiple active sites and inclusion of diffusion limitations where appropriate. An example is the direct H<sub>2</sub>O<sub>2</sub> synthesis in liquid phase. Improved models need to include solvent effects (since specific solvation of intermediates on the surface could lead to their stabilization),<sup>[87]</sup> the effect of promoters (e.g., an understanding of how acids, halide ions, etc. influence the selectivity for direct H<sub>2</sub>O<sub>2</sub> synthesis)<sup>[88]</sup> that might not only poison the surface but also influence the electronic structure of the catalytic site. Furthermore, improved models need to target the effect of the support material,<sup>[89]</sup> the particle size<sup>[90]</sup> and possible structural disorder that might change over time.<sup>[91]</sup> Since an increase in complexity concurs with an increase of the computational effort, there is an additional focus on the development of faster methods. These are often based on new developments in the field of machine learning,<sup>[77d,92]</sup> parameterization,<sup>[93]</sup> and genetic algorithms.<sup>[94]</sup>

## 5. Conclusions and Outlook

In recent years, numerous examples have shown the progress made in the development of tailor-made transition metal catalysts, operando studies to track the “fate” and evolution of these NPs during the catalytic reaction, and an understanding of the reaction mechanisms on the specific surfaces of catalytic materials using theoretical models. In the “precursor concept,” colloidal transition metal NPs are combined with specific support materials and thus provide well-defined building units for model catalysts, which may not only help to elucidate the role



**Figure 7.** Facets that are expected to move the frontiers in transition metal catalysis to the next step. Here, a digital platform connecting experimental data and theory/modeling will play a crucial role.

of a specific catalytic material but also link fundamental catalytic studies on single crystal surfaces or clusters deposited on those surfaces to real world catalysts. NP-based model catalysts also prove to be suitable for experimentally studying the results of DFT simulations as the high degree of size and shape uniformity is difficult to be achieved by conventional wet impregnation or (co)precipitation. In addition, operando characterization techniques are particularly important to rationalize the structural transformations of the catalytic NPs at the nanoscale and to identify active site motifs occurring under reaction conditions. Models provided by DFT calculations can be directly validated with EXAFS data and spectroscopic information from high-resolution XANES and XES data. This provides a basis for further in-depth theoretical investigations that now have even started to reveal the kinetics of structural changes of such catalytic NP clusters. With the tremendous progress made in these fields in recent years, we expect that the three areas will increasingly interconnect and benefit from each other. The prerequisite for this will be a common data platform (Figure 7) that combines the experimental data (as a result of material synthesis, catalyst testing, and operando characterization) with the theoretical modeling (prediction of novel and active NPs and their evolution under reaction conditions, identification of active site motifs, and description of reaction mechanisms), preferably similar to the digital platforms emerging now in the field of materials science. This digital turn or “digitalization in catalysis,” which has recently also been discussed intensively in the literature<sup>[1d]</sup> and at the GECATS day,<sup>[95]</sup> may move the frontiers in transition metal catalysis further toward the goal of a more rational catalyst design.

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## Conflict of Interest

The authors declare no conflict of interest.



## Keywords

density functional theory, operando characterization, nanoparticles, synthesis, theoretical calculations

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