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Defects in metal exsolution catalysts: a double-edged role in nanoparticle activity and stability

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Abstract

Metal exsolution—the precipitation of metal nanoparticles from host oxides—holds potential for the design of oxide-supported metal catalysts, relevant for a broad range of applications. In oxides, defects give rise to a wide variety of functional properties that are essential for the performance of oxide-based catalysts. In addition, the nanoparticle exsolution behaviour is closely linked to the defect structure of oxides. Consequently, defect engineering has been established as a strategy to tailor exsolution catalysts, primarily in terms of key morphological nanoparticle properties such as the nanoparticle surface density, typically used as a measure to quantitatively evaluate and compare the exsolution behaviour in oxides. For this purpose, the defect structure of exsolution-active host oxides is often deliberately modified. Moreover, defects may evolve in response to the reducing exsolution reaction conditions, leading to altered functional properties of oxide supports upon exsolution. As a result, defects in exsolution-active oxides mediate nanoparticle properties and support properties under reaction conditions, rendering the control of catalytic performance in exsolution catalysts challenging. In the present perspective paper, I aim to discuss the critical role of defects in metal exsolution synthesis, addressing their impact on nanoparticle and support properties that mediate catalyst activation and degradation processes.

1. Tailored nanoparticle and support properties for high-performance catalysts

Oxide-supported metal nanoparticles constitute an important class of catalysts for energy conversion technologies. For a given combination of support and metal composition, nanoparticle properties such as particle size may be considered among the most relevant levers for tuning a catalyst's performance toward a targeted reaction [1]. Here, a common objective lies in synthesizing small nanoparticles with a high surface particle density and with uniform dispersion, leading to a high number of catalytically active triple-phase boundaries and a large surface-to-volume ratio of the metal [2, 3].

Beyond these morphological factors, the catalytic activity may be directly linked to the particle size, where a larger fraction of atoms occupy surface sites with lower coordination in smaller nanoparticles, frequently associated to increased catalytic activity [4–6]. Size-dependent charge-transfer between metal nanoparticles and oxide supports may further cause a modified electronic structure and chemical state with the potential of modifying catalytic activity [7, 8], on which basis a 20-fold increase in activity of ceria-supported platinum for the production of hydrogen was demonstrated [9, 10]. The success of this catalyst design strategy relies on strong metal-support interactions and size-control of Pt clusters, which is directly coupled to the electronic properties and defect structure of the oxide support.

The function of oxide supports in catalysis, therefore, goes beyond providing an electronically and/or ionically conductive backbone for catalytic metals, where modulating catalytic behaviour through particle–support interactions is of major interest in the field of catalysis [1, 11]. The control of nanoparticle and support properties as well as particle–support interactions under operational conditions, however, remains challenging beyond the model system level.

2. Catalyst design by metal exsolution reactions

Metal exsolution reactions have been demonstrated to yield excellent results in the synthesis of supported nanoparticles, achieving high nanoparticle densities and uniform dispersion, even in porous oxides with complex microstructures. The concept describes the precipitation of a metal phase from reducible cations initially incorporated in a host oxide. Metal exsolution reactions are induced when the temperature and oxygen partial pressure are sufficient to turn the change in Gibbs free energy ΔG negative for the metal oxide to metal phase transition as depicted for binary oxides by the Ellingham diagram [12], and observed empirically to be transferable to complex host structures such as perovskite oxides.

Initially recognized for performance increases in catalytic converters [13] and in solid oxide cells [14], exsolution was only fully recognized as a powerful synthesis method after demonstration of its controllability with respect to the nanoparticle yield by tuning the defect structure of host oxides [15]. Since then, the synthesis of oxide-supported metal nanoparticle catalysts by metal exsolution reactions has gained considerable momentum, with researchers exploring an ever-growing range of host compositions and structures [16] for a wide variety of catalytic target reactions, with particular focus on energy applications [17].

Imperfections in the crystal lattice of exsolution-active host oxides are essential in mediating the exsolution and nanoparticle growth dynamics. Accordingly, the fundamental understanding of exsolution synthesis has grown hand in hand with an improved understanding of how defects contribute to shaping the exsolution behaviour of reducible cations in oxides. Consequently, defect engineering to control nanoparticle properties has emerged as a major area of interest in the exsolution community. In view of this development, I aim to map out the complexities involved in controlling the properties of exsolution catalysts in this perspective paper, with particular focus on the role of defects in exsolution-active host oxides. Notably, transmission electron microscopy, combined with advanced sample preparation protocols, has enabled direct resolution of defect structures that are otherwise highly challenging to study. This approach has significantly advanced the understanding of defect interactions in exsolution catalysts, particularly for extended defect structures, whereas point defects typically remain elusive in the relevant concentration regimes.

After a brief literature review, one focal point of the discussion will be the essential role of defects for the morphological properties of exsolved nanoparticle catalysts, e.g. by defect-mediated coarsening, which can pose a major challenge in the development of efficient catalysts for applications at elevated temperatures [18, 19]. As nanoparticle properties typically are the focus of attention in evaluating the design of exsolution catalysts, less attention is paid to defect-induced (dys) functionality of the oxide support that evolves from the initial host oxide during the reaction. Therefore, defect-governed property changes of host oxides serving as functional supports for exsolved nanoparticles are briefly addressed. The discussion focuses on perovskite oxides, which are to date the most widely used host oxide structure in exsolution synthesis, although certain aspects discussed here may be transferable to other host oxide structures, which are gaining increasing significance.

3. Defect interactions shape nanoparticle properties in metal exsolution catalysts

Defects can be present in host oxides in a broad range of concentrations, either deliberately engineered or inadvertently forming in response to the conditions applied during oxide synthesis or under exsolution reaction conditions. I aim to briefly outline selected examples of defect interactions in exsolution-active perovskite oxides that are decisive for the nanoparticle characteristics, with the main goal of providing a concise overview of the topic. The important impact of defects on the properties of exsolved nanoparticle populations and the respective oxide is schematically illustrated in figure 1, depicting a considerable interplay between different types of defects and a close interconnection with the exsolution behaviour of reducible cations. For organizational clarity, the discussion is structured with respect to the defect dimensionality (0D, 1D, 2D and 3D defects), addressing their influence on four principal aspects of metal exsolution reactions discussed in the literature, i.e. phase stability/cation release, mass transfer of reducible dopants toward the surface, nanoparticle nucleation, and coarsening. While it is fair to assume that some of these processes may become more relevant at earlier stages of exsolution reactions (e.g. nucleation) and others remain relevant also at later stages of the reaction (e.g. coarsening), the division into separate processes is mainly intended to facilitate a more systematic discussion. Defects that are engineered into host oxides, or that form in the oxide under harsh reduction treatments, further impact the functional properties of the oxide support. Here, both the nanoparticle properties and support properties determine the catalytic performance of exsolution catalysts, often dynamically evolving under reactions conditions.

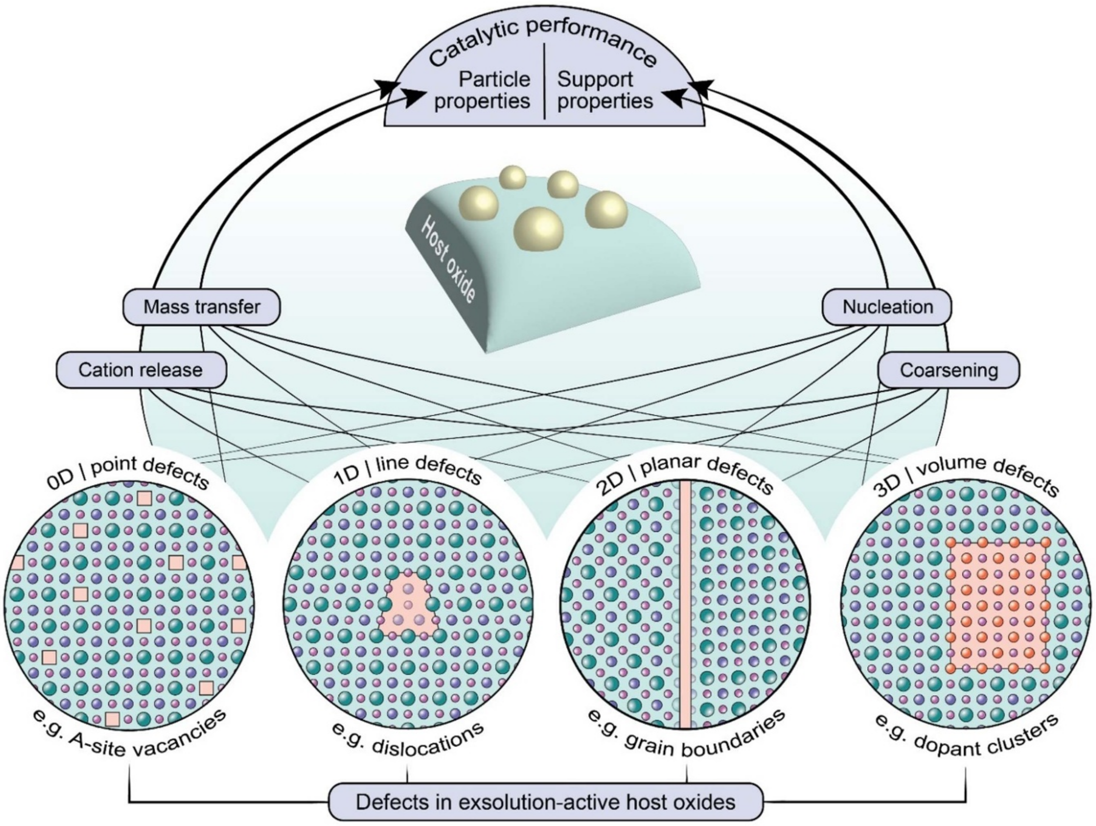

Figure 1. Schematic defect interactions during metal exsolution from host oxides. Defects of different dimensions (0D, 1D, 2D, 3D) have been identified to influence exsolution reactions on various levels including the release of reducible cations from the host oxide, the bulk mass transfer toward the surface, the nucleation of metal nanoparticles as well as the nanoparticle coalescence dynamics under reaction conditions. In this way, defects play a key role in shaping the properties of the exsolved nanoparticle population. In addition, the defect structure is decisive for the functional properties of the oxide support and modulates particle–support interactions, such as charge transfer processes that mediate catalytic performance. Defects are highlighted by orange shading, where defect sites and associated interfaces are heavily simplified in structure for schematic illustration.

3.1. 0D | point defects

Point defects are the most widely studied type of defect in exsolution-active oxides. A-site cation deficient host oxides are commonly applied as parent materials to facilitate nanoparticle exsolution of B-site metals. The effect of *A-site cation vacancies* has been associated to the destabilization of the perovskite oxide phase. Here, A-site deficient host oxides are expected to provide for a favourable energetic landscape for the release of B-site cations, which is accompanied by the formation of a (more) stoichiometric host oxide structure [15].

Moreover, *oxygen vacancies* have been demonstrated to play a crucial role in exsolution reactions, where a high oxygen ion mobility, typically scaling with the oxygen vacancy concentration [20, 21], has been shown to be correlated to a fast exsolution dynamics [22, 23]. Additionally, surface oxygen vacancy pairs [24, 25] and clusters [25] were identified to serve as preferential nucleation sites for metal nanoparticles under reaction conditions. Both A-site vacancies and oxygen vacancies further promote B-site exsolution due to modifications in cation segregation energies, facilitating mass transport of dopants to the oxide surface [26, 27]. Importantly, the concentrations of oxygen and cation vacancies are strongly modulated in space charge regions that are associated with oxide surfaces (and other defects such as dislocations [28] and grain boundaries [29]). The space charge potential and defect concentrations respond dynamically with respect to the oxygen partial pressure with considerable implications for the dopant mass transport kinetics at the solid–gas interface. Here, space charge may act as an additional barrier for exsolution, where the kinetics of exsolution reactions are influenced by electrostatic interactions between charged ionic species and the surface potential as well as the modified oxygen exchange behaviour [23, 30].

Point defects have been further identified to shape the coarsening resistance of exsolved nanoparticles. For instance, large concentrations of A-site vacancies were suggested to facilitate interdiffusion between metal nanoparticles and the oxide support, and were proposed to promote nano-socketing, thereby enhancing the thermal stability of the catalyst [31]. In addition, oxygen vacancies have been proposed to impact the thermal stability of exsolved nanoparticles, linked to the nature of metal–oxygen (M–O) bonds at the interface between metal nanoparticles and the oxygen sublattice of the support [23]. Here, oxophilic metals tend to form strong bonds with oxygen and are less stable on supports with large concentrations of oxygen vacancies due to a lower average number of M–O bonds, correlated to a larger chemical potential and accelerated coarsening dynamics of the nanoparticles (see section 4.1).

Another example of point defects modifying the exsolution behaviour in oxides is the influence of *redox-stable co-dopants* correlated to the unit cell volume of the host lattice and the associated elastic strain fields [32] presumably linked to the size mismatch between host and dopant cations [33] or co-doping of charged defects that modify the nature of the surface space charge potential [23, 30].

While point defects influence material properties homogeneously, higher-dimensional defects—discussed in the following sections—typically modulate material characteristics locally. For instance, structural, chemical or electronic changes linked to a dislocation, grain boundary or secondary phase inclusion usually lead to defect interactions that are somewhat laterally confined to the respective defect site.

3.2. 1D | line defects

Recent studies report on an interplay of *dislocations* with reducible dopants in exsolution reactions. Here, the nucleation of dislocations in host oxides has been described to be correlated with nanoparticle exsolution under thermal reduction, where the authors hypothesize about a mass transfer mechanism for reducible metal cations that involves dislocation propagation [34]. The study suggests a strong correlation between the emergence of dislocations with mixed edge- and screw components and nanoparticle exsolution at the oxide surface.

Investigations of exsolution from deliberately dislocation-engineered host oxides present evidence of a direct association between dislocation cores and a lower threshold of $\sim$10% of the total number of investigated exsolved nanoparticles [35]. The study indicates that asymmetric strain fields of dislocations and electrostatic interactions of charged acceptors with the dislocation core charge may influence dopant accumulation along dislocation cores, resulting in a correlation between the dislocation and nanoparticle sites.

In addition to altered distributions of acceptor dopants, space charge fields associated with dislocations may cause altered concentration distributions of oxygen vacancies [28], where the changes in point defect populations may have an additional impact on the exsolution behaviour. For instance, in Ni-doped strontium titanate, a considerable depletion of oxygen vacancies is expected in the vicinity of dislocations, potentially stabilizing oxophilic metal nanoparticles by lowering the oxygen vacancy concentrations at the particle–support interface. Moreover, dislocations may be related to a decreased energy barrier for nucleation facilitating nanoparticle formation at dislocation sites [36].

3.3. 2D | planar defects

Since the primary interest in the field of exsolution is surface functionalization, the properties of *surfaces* as planar defects arising from lattice truncation, are highly relevant in shaping the exsolution behaviour. For example surface reconstructions can suppress or delay dopant mass transport toward the surface to a significant extent [15, 37] and even chemical changes limited to the atomic surface termination layer has been demonstrated to cause differences in the nanoparticle density and size [30]. Also a clear dependency of the nanoparticle properties on the crystal surface orientation has been demonstrated, where contributions of anisotropic bulk diffusion [31, 38] and differences in the interfacial energy have been pointed out [39, 40]. It is worth noting that after continuous thermal reduction treatments, the highest surface particle density of exsolved nanoparticles and the smallest nanoparticle size has been consistently found at (111) perovskite oxide facets [37, 39, 40], which coincides with the fact that AO_3-terminated (111) perovskite facets provide for the highest surface density of oxygen anions. Here, a larger density of M–O bonds at the nanoparticle–support interface hence may contribute to a larger thermal stability and slower coarsening dynamics [23] of nanoparticles at (111) facets.

Grain boundaries are another highly relevant planar defect present in exsolution-active oxide ceramics with strong impact on the properties of exsolved nanoparticle populations. Various examples in the literature highlight increased densities of exsolved nanoparticles close to grain boundaries [41–46]. Here the grain boundary chemistry and structure can be complex, often featuring a larger solubility for dopants relative to the bulk [47, 48], where strain fields [49, 50] and space charge [29] may further contribute to the segregation of dopants to grain boundaries. For instance, increased lattice site occupancy of Fe at grain boundaries in $SrTi_{1-x}Fe_xO_{3-\delta}$, a popular exsolution-active oxide, has been demonstrated across a broad range of compositions from the near dilute case (2 at% Fe on the B-site) and for the highly substituted case (25 at% Fe on the B-site) [51], demonstrating a considerable impact of grain boundaries on the distribution of reducible cations.

Furthermore, *anti-phase boundaries*, that may compensate for large A-cation/B-cation off-stoichiometries in perovskite oxides in the form of rock-salt type intergrowth layers have been proposed to influence the exsolution behaviour [52]. The authors show that reducible cations may be locally enriched at designated areas in the host oxide, where they point out that the characteristic anti-phase boundary structure may allow for facile mass transport along the defects, which has been previously demonstrated for the case of fast strontium diffusion in strontium titanate under an applied electric field [53].

In this context it may be worth mentioning that in the special case of epitaxial composite thin films, engineered *heterointerfaces* have been proposed to provide of fast exsolution pathways in comparison to bulk materials [54].

3.4. 3D | volume defects

While perovskite oxides are highly adaptive in terms of composition, large dopant or defect concentrations may promote defect association and clustering, leading to cation inhomogeneities and phase separation. Dopant clustering was demonstrated to influence metal exsolution, e.g. with respect to the mass transport dynamics and the coarsening behaviour, particularly relevant for exsolution-active oxides with dopant concentrations approaching the solubility limit [55, 56]. While separated phases may be present in the form of coherently embedded clusters in the perovskite oxide matrix [55], dopant clusters tend to preferentially form in the vicinity of higher dimensional defects, where increased concentrations of segregated cations are commonly detected. For instance, considerable accumulation of reducible cations along dislocation cores (see section 3.2), may in some cases result in the crystallization of separated phases [35]. Moreover, reducible cations often accumulate with increased tendency at grain boundaries [57]. On this basis, modified exsolution concepts have been demonstrated, using grain boundary phases as reservoirs for significant concentrations of reducible dopants and with potentially increased exsolution kinetics along grain boundary interfaces [58].

In addition, exsolution-active host oxides are commonly synthesized with a large A-site cation deficiency (see section 3.1). While it was demonstrated that certain perovskite oxide compositions such as $La_{0.4}Sr_{0.4}TiO_{3-\delta}$—a prime example for host oxides in exsolution catalysts—form stable solid solutions under a broad range of redox conditions [59], A-site cation deficiency can be accommodated only to a limited extent in the form of vacancies in other perovskite oxides [60]. Here, large concentrations of A-site vacancies may destabilize the perovskite structure, promoting the formation of B-site cation-rich clusters and separated phases in host oxides.

For example, in strontium titanate, first indications of a TiO_2 excess phase become evident for a strontium deficiency of only 0.5 mol% [61]. In contrast, A-site deficiencies up to 20 mol% are commonly used in oxides employed for exsolution synthesis, likely causing a certain degree of cation inhomogeneity and dopant clustering in a variety of host oxide compositions. Reports about limited effects of A-site deficiency on the exsolution behaviour in some materials may be related to limitations in accommodating such large degrees of off-stoichiometry in the form of cation vacancies [55, 62]. Importantly, indications for an increased tolerance with respect to A-site deficiency has been detected for Nb-doped $SrTiO_{3-\delta}$ [63], suggesting an increased solubility of B-site excess in donor-doped host oxides, widely applied in exsolution catalysts.

Moreover, secondary phases may be deliberately added to exsolution catalysts to manipulate the exsolution behaviour, e.g. by accelerating the oxygen exchange kinetics via deposited Pt nanoparticles at the surface of exsolution-active oxides [64]. Similar effects may be expected to come into play during exsolution of multi-metallic nanoparticles, where metals of different reducibility are typically exsolved with different dynamics. In Cu– and Fe– co-doped oxides, a seeded growth mechanism has been proposed to occur, with a decreased energy barrier for the exsolution of iron dopants that are less readily reduced [65]. Furthermore, the deposition of secondary phase oxide surface layers onto exsolution-active oxides has been demonstrated to alter surface space-charge effects and the correlated exsolution behaviour [30].

In the broadest sense, nano-sockets [31] might as well be considered volume defects, where three-dimensional features with similar stoichiometry to the oxide support form at the particle–support boundary. In many cases, these features lead to a considerable stability enhancement of supported nanoparticles (see section 4.1).

Moreover, pores that constitute 3D defects in oxide supports have been shown to influence the coarsening behaviour of supported metal catalysts [66].

It is worth noting that it may be challenging to detect dopant clusters and secondary phases of finite size finely dispersed within the perovskite main phase. Especially in highly porous oxides, a large interfacial and surface area allows to accommodate excess dopants, whereas dopant inhomogeneities will become more obvious in dense oxide samples. Consistently, laboratory-based x-ray diffraction, serving as a standard technique to investigate phase purity, often fails to detect dopant inhomogeneities. However, nanoscale phase separation and dopant inhomogeneities in exsolution-active oxides may become evident through faint secondary signatures or by a certain degree of asymmetry in the main diffraction peaks [55, 67–70], while the lack of such indicators is typically not sufficient to confirm that dopant inhomogeneities are absent on the nanoscale [59, 71, 72].

Here, it needs to be considered that the defect structure of oxides can be highly material specific and depends on the processing conditions applied during synthesis. For instance, the presence of defects such as dopant clusters is typically influenced by thermodynamic and kinetic aspects. While the solubility of dopants in host oxides plays a major role, kinetic limitations during oxide synthesis also impact phase purity and cation homogeneity in conventional powder synthesis [51], in advanced non-equilibrium sintering techniques, e.g. affecting grain boundary chemistry [73], or in non-equilibrium epitaxial growth often used for the synthesis of thin film model systems [55, 74, 75].

4. Challenges for property control in exsolution catalysts

In the previous discussion, examples of defect interactions in exsolution synthesis have been presented, highlighting the considerable complexity of the broad parameter space influencing exsolution behaviour. While defect engineering may be used to tailor nanoparticle properties with the goal of tuning catalytic functionalities, defects are also involved in mediating degradation processes of supported nanoparticle catalysts. In the following, I want to address nanoparticle coarsening and defect-governed dysfunctionality in oxide supports in more detail.

4.1. Nanoparticle coarsening

Thermally activated coarsening promotes nanoparticle growth and typically leads to the degradation of catalytic performance under operational conditions by a loss of the active surface area, and potentially, by altering the electronic structure of supported nanoparticles over time. As depicted schematically in figure 2(A), coarsening processes are thermodynamically driven by the difference in chemical potential for nanoparticles of different size [19], where the larger chemical potential of smaller nanoparticles is rooted in the lower average coordination of the metal atoms [76].

Metal exsolution has been suggested as a convincing concept to address the issue of nanoparticle coarsening. Here, a study demonstrating nano-socketing provided a compelling example of exsolved nanoparticles that grow highly oriented with respect to the host lattice and partially submerged into the surface of the support, correlated to an enhanced thermal stability and coking resistance as compared to a reference catalyst synthesized by deposition of nanoparticles via thermal evaporation [31]. This demonstration of stability enhancement likely contributed to the perception of socket-formation generally being linked to the exsolution synthesis route as well as exsolved nanoparticles being not affected by coarsening. Notably, the socketing effect has been repeatedly confirmed for a variety of material compositions, but it can be observed that it manifests with considerable variability in socketing depths across different material systems. Furthermore, the expected benefits of socketing for enhancing the thermal stability of catalytic nanoparticles are often not explicitly demonstrated, despite being commonly implied.

Frequent observations of decreasing nanoparticle densities in exsolution catalysts after treatments with increasing reduction temperatures or with increasing reduction times challenge the widely accepted assumption that exsolved nanoparticles will fully withstand coarsening [30, 40, 77–81]. In addition, reports on socket formation for particles fabricated by dewetting of metal films cast doubt on socketing as an exsolution-specific feature [40, 82]. Here, similarities between socketing and ridging need to be considered. The latter is described as a process linked to the reconstruction of phase boundaries as a consequence of minimizing interfacial energy, which determines the wetting behaviour upon thermodynamic equilibration [83, 84].

On the other hand, recent studies have shown that exsolved nanoparticles may exhibit limited socketing behaviour in certain materials, while at the same time showing considerable differences in their coarsening resistance linked to the defect chemistry of the respective host oxide [23, 56]. The origin lies in a strong influence of the oxygen sublattice in oxide supports on the thermal stability of particle–support interfaces, impacting the coarsening behaviour of supported nanoparticles. Importantly, my discussion builds substantially on the work of C T Campbell and colleagues serving as a basis for further elaboration (please refer to e.g. [6]).

Considering a situation where socket formation is negligible, the chemical potential of supported nanoparticles depends on the defect chemistry of the oxide, decisive for the nature of the particle–support interface. In the case of non-noble metals (with oxophilic character), bonds between metal atoms with oxygen anions of the oxide support (M–O) stabilize the interface and lower the chemical potential of the supported particles. As illustrated in figures 2(B) and (C), a large concentration of oxygen vacancies leads to

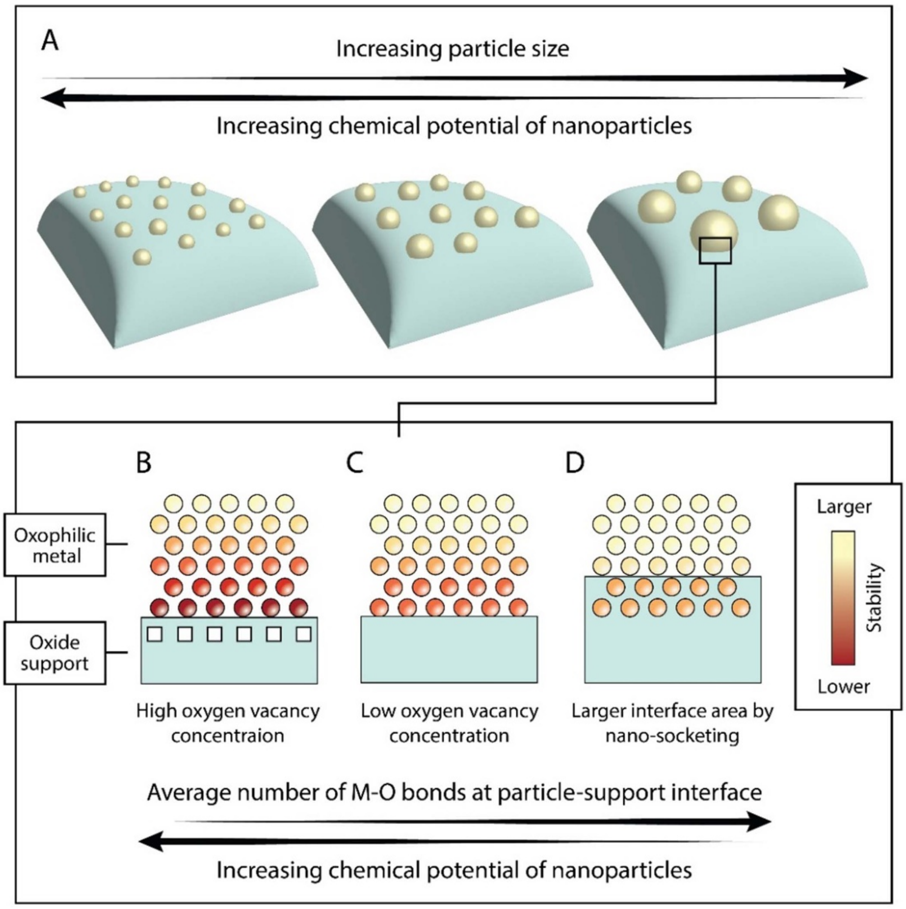

Figure 2. Schematic illustration depicting the influence of nanoparticle size and support properties for the chemical potential of supported nanoparticles with oxophilic character. (A) The chemical potential increases with decreasing nanoparticles size. (B)–(D) Metal nanoparticles are stabilized to a different degree when supported on oxide supports, depending on the interface properties that are largely influenced by the oxides' defect structure. In a simplified picture, a larger average number of M–O bonds between metal atoms and oxide anions of the support lead to a decreasing chemical potential and increased thermal stability of nanoparticles. (B) A large oxygen vacancy concentration decreases the average number of M–O bonds, leading to a decreased thermal stability. (C) A low oxygen vacancy concentration leads to an increased number of M–O bonds and increased thermal stability. (D) Nano-socketing of nanoparticles is correlated to an increased interfacial area between nanoparticles and oxide support, leading to an increased number of M–O bonds and enhanced thermal stability (often correlated to large A-site vacancy concentrations in host oxides).

a lower average number of stable M–O bonds at the particle–support interface related to an increased chemical potential [85], which has been shown to be correlated to coarsening by Ostwald ripening processes and highly dynamic particle migration of exsolved nanoparticles [56]. Vice versa, noble metals may be stabilized on supports with a large concentration of oxygen vacancies [9, 86], as has been further demonstrated by size-control of (deposited) Au nanoparticles by controlling the oxygen vacancy concentration at oxide surfaces applying an electrochemical potential [87].

Nano-socketing has been shown to be associated with an increased thermal stability of supported nanoparticles, which can be rationalized by an increased interfacial area between nanoparticles and oxide supports, increasing the number of M–O bonds. The finding that socketing proceeds subsequent to the nucleation and growth of nanoparticles in a sequential manner, however, introduces a temporal dimension to socketing processes [81] implying that nano-socketing may be effective in mitigating nanoparticle coarsening during the later stages of nanoparticle exsolution and growth. Over the course of longer reduction times, nanoparticle sockets may evolve for certain materials, increasing the interfacial area between nanoparticles and the support phase (figure 3(D)), associated with a decrease in the chemical potential. Notably, the thermal stability of the interface must be expected to be influenced by the defect structure of the oxide (e.g. the oxygen vacancy concentration) also when nano-sockets are formed. Given the structural anchorage at the oxide support, nano-sockets may be additionally associated with an increased energy barrier for particle migration, resulting in a slower coarsening dynamics by mitigating particle migration and coalescence. However, it is unlikely that nanoparticle socketing can fully suppress Ostwald ripening, i.e. net positive mass transport via ionic diffusion from smaller to larger particles.

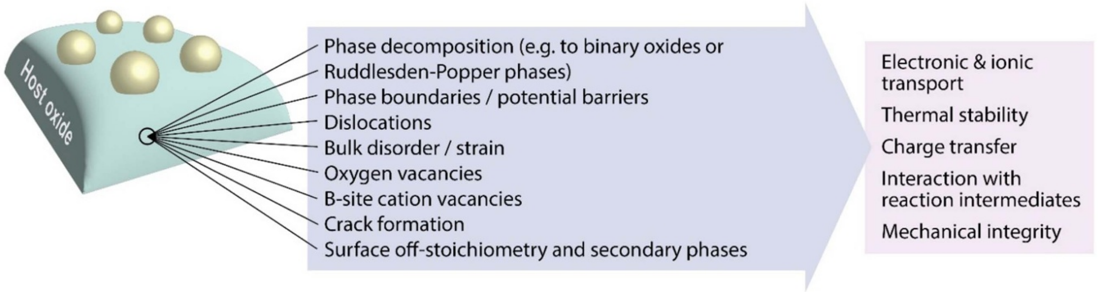

Figure 3. Selected examples of defect formation in host oxides, related to altered functional properties and potentially correlated to the degradation of catalytic performance.

The interface properties of exsolved nanoparticles and the respective oxide support hence directly impact their chemical potential and coarsening behaviour, relevant particularly for exsolution catalysts that do not show distinct socketing behaviour. In general, however, a major impact on particle growth and coarsening during early stages of exsolution reactions is expected, where nanoparticle sockets have not yet developed. Here, the particular role of the oxygen sublattice of oxide supports has been recognized, especially for the stability of small metal clusters and nanoparticles [19, 85], while the impact of the support properties may lose significance for increasing particle sizes. This is consistent with direct evidence reported by Jennings *et al* for exsolved nanoparticles following a random-walk diffusion behaviour in the initial stages of nanoparticle exsolution, indicating high mobility on the oxide support. Moreover, studies on the kinetics of coarsening of exsolved nanoparticles find an increase in the growth law exponent for later stages of exsolution reactions, which may point towards increasing thermal stability of exsolved nanoparticles after development of nano-sockets under continuous thermal reduction [40]. Therefore, size-control of metal clusters and small nanoparticles ($<$5 nm in diameter) highly relevant for catalysis, must be expected to remain challenging via exsolution reactions.

Consequently, control of the defect chemistry of host oxides can be used as a strategy to lower the nanoparticle coarsening dynamics [23]. Importantly, it was pointed out that spill-over effects may mitigate the detrimental effects of particle growth associated to the shrinkage of triple phase boundary lengths if the nanoparticle surface density remains within the decay length of the spill-over process, which should be taken into account when optimizing nanoparticle surface densities in exsolution catalysts [88]. Moreover, indications that larger nanoparticles may be decisive in electrochemical performance improvements in certain exsolution catalysts need to be considered, emphasizing the need to tune nanoparticle properties in view of the targeted application and depending of the respective material system [89].

4.2. Phase decomposition & lattice disorder of host oxides

Under continuous thermal reduction, point defect concentrations in the host oxide adjust with respect to the oxygen partial pressure, where oxygen and cation vacancies are formed in the oxide lattice upon exsolution of reducible dopants. Increasing point defect concentrations may induce the formation of higher dimensional defects, originating from partial phase decomposition and impacting the functional properties of the oxide support (figure 3). Therefore, particularly, exsolution reactions driven in host oxides with limited redox stability may be associated with severe lattice disorder and extended defect structures present in the oxide support.

Here, nanoparticle exsolution may affect the bulk and surface properties of oxides beyond the decoration with metal nanoparticles. For instance, the near-surface region of exsolution oxides, serving as the main reservoir for metal dopants during exsolution of surface nanoparticles, becomes strongly depleted from reducible metal cations [23, 79, 90], which may be directly linked to an altered functionality of the electrochemical interface. Furthermore, structural and stoichiometric changes of oxide surfaces associated with exsolution reactions have been detected in the form of a considerable enrichment of host cations, e.g. titanium enrichment at the surface of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ [90]. Although less pronounced, surface enrichment of titanium has been also reported to accompany Ni exsolution in the case of $SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-\delta}$ under similar annealing conditions [91]. Here, minor changes in surface stoichiometry may cause a change in the electronic structure of the oxide as the work function in strontium titanate is sensitive to small changes in the oxygen and cation stoichiometry [92, 93].

While the near-surface region becomes depleted from metal cations by surface nanoparticle exsolution, metal cations in the oxide bulk typically remain immobilized in the form of buried metal nanoparticles, causing disorder in the oxide lattice [39, 55, 79, 94, 95]. As a result, elastic strain fields, associated with a high density of internal particle-oxide interfaces have been demonstrated to affect ionic transport in oxides [55, 79]. The exsolution of bulk nanoparticles has also been reported to be linked to the nucleation of dislocations [34], which are typically accompanied with local variations of point defect concentrations potentially affecting electronic properties and ionic transport within oxide supports.

In oxides with increasingly large concentrations of doped or substituted reducible cations, the probability for detrimental secondary processes increases. For example, the exsolution of Fe in $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ and $SrTi_{0.3}Fe_{0.7}O_{3-\delta}$ or Ni exsolution in $LaNiO_{3-\delta}$ has been reported to be correlated to redox instability of the respective host oxide lattice and associated to severe bulk decomposition [46, 96–98]. In these cases, the host oxide may undergo a partial phase transition toward the Ruddlesden–Popper structure [96, 97], further associated to the formation of cracks impacting mechanical integrity [97]. Moreover, severe decomposition and formation of a variety of oxide decomposition compounds has been reported [96]. Here, exsolution reactions render oxide supports highly complex with respect to structure and composition. Similar effects may be expected for metal exsolution from stoichiometric oxides, often accompanied by the formation of A-site rich phases, which may lead to lattice distortions and disorder [62].

It is worth noting that the formation of defects, lattice disorder or even phase decompositions formed under exsolution conditions may be in some cases beneficial for the catalytic properties of the nanocomposites. For example, oxygen vacancy formation in oxides may influence charge transfer between the nanoparticles and the support [99], which could, in principle, lead to increased catalytic activity. Given the complexity of detecting small oxygen vacancy concentrations [100], this observation emphasizes nicely how small changes in defect concentration may cause fundamental changes in catalytic properties. The controlled phase transition of host oxides during exsolution reactions further has been reported to improve electrochemical performance in certain material systems [101–103], e.g. when employing Ruddlesden–Popper parent oxides [102]. Moreover, bulk exsolution has been demonstrated as an approach to engineer strain fields and associated oxygen ion transport properties [79] or for tuning electronic and magnetic properties in oxides [104].

5. Summary

In this perspective, I highlighted the role of defects in metal exsolution catalysts. Imperfections in the crystal lattice of exsolution-active host oxides are linked to phase stability, mass transport dynamics of reducible cations, nanoparticle nucleation and coarsening dynamics, shaping the properties of exsolved nanoparticles under reaction conditions. While defect engineering of exsolution-active host oxides opens new routes to tailor key nanoparticle properties in exsolution catalysts, it impacts the functional properties of oxide supports and associated nanoparticle–support interactions. For instance, high oxygen vacancy concentrations may promote fast oxygen exchange reactions through the oxide backbone and accelerated metal exsolution dynamics, initially correlated to large nanoparticle densities. However, at the same time high surface oxygen vacancy concentrations might result in a limited thermal stability of exsolved nanoparticles promoting degradation of nanoparticle properties by coarsening over time. While improving morphological nanoparticle parameters is typically a main objective of defect-engineering approaches, and highly relevant for catalysis, the impact of the oxide defect structure evolving under reaction conditions, needs to be considered in the design of exsolution-active oxides. Defects may directly affect the catalytic properties of the functional oxide, beyond their influence on particle–support interactions. In particular, modulations in the electronic structure localized at defect sites can alter the catalytic landscape at the catalyst surface, thereby influencing interactions with reaction intermediates and charge transfer across the electrochemical interface. Moreover, driving metal exsolution in host oxides that contain considerable amounts of reducible cations, and which exhibit low redox stability, may lead to partial decomposition of the chemical, structural and physical properties of oxide supports, driving degradation in the catalytic functionality.

Therefore, the design of exsolution catalysts with optimized electrochemical performance will require controlling material characteristics with respect to both the nanoparticle properties and the functional oxide support in anticipation of dynamic changes under reaction conditions. Here, considerable improvements in catalytic performance may be achieved by moving beyond simplified morphological descriptors such as the nanoparticle density or nanoparticle size, while instead focusing on a holistic material design strategy that considers nanoparticle–support interactions decisive for activity and the durability of supported nanoparticle catalysts under demanding reaction conditions. The desired defect types and concentrations for an effective functionalization of the electrochemical interface will strongly depend on the targeted electrochemical reaction and the specific reaction environment (e.g. solid–gas vs solid–liquid interfaces; room temperature vs high-temperature applications). If defect engineering of exsolution catalysts is employed with the goal of tuning not only nanoparticle properties but also support functionalities and particle–support interactions, considerable advances in the control of catalytic properties may be achievable.

Data availability statement

No new data were created or analysed in this study.

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