Applied Catalysis A, General 723 (2026) 121035

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Leaching, redistribution, and dynamic heterogeneity in supported catalysts

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ARTICLE INFO

Keywords:
Heterogeneous catalysts
Supported transition metal catalysts
Catalyst leaching
Elemental leaching
Active species
Catalyst poisoning

ABSTRACT

Supported metal catalysts are often regarded as purely heterogeneous systems, yet under liquid-phase reaction conditions many undergo elemental leaching, leading to the loss of active species, catalyst deactivation and product contamination. Beyond deactivation, leached metal and non-metal species can affect turnover numbers and modify surface active sites. In some cases, a transition from solid catalysts to active species in the liquid phase is observed, or coupled "release and capture" mechanisms operate. These effects blur the boundaries between heterogeneous and homogeneous catalysis and complicate structure-activity relationships. Herein we summarize the most common elemental leaching pathways in supported metal catalysts and critically evaluate the diagnostic tools used to determine the true nature of the active species. Diagnostic approaches are organized into three categories: reaction progress-based diagnostics (e.g., hot filtration test, poisoning experiments, three-phase test, kinetic signatures), spectroscopy-based diagnostics (e.g., ICP-OES/MS, UV-Vis, NMR, IR/Raman, and *in-situ/operando* X-ray absorption spectroscopy), and theory-based (indicative) diagnostics (e.g., density functional theory, Pourbaix-type diagrams). We highlight key benefits and limitations, and emphasize the need for converging evidence from complementary diagnostic techniques. Finally, we discuss strategies to mitigate leaching and propose a structured workflow to reduce ambiguity regarding catalyst heterogeneity and guide the design of leaching-resistant supported catalysts.

1. Introduction

Heterogeneous catalysis plays a central role in modern chemical technology and industrial processes, where robustness, scalability, and ease of catalyst handling are essential. Compared to homogeneous systems, heterogeneous catalysts are often favored due to their straightforward separation from the reaction mixture and their potential for reuse and recycling, features that are critical for large-scale applications. [1–5] As a result, extensive efforts have been devoted to the development of solid-state catalytic materials using a wide range of synthetic approaches with the aim of enhancing activity, selectivity, and stability. Within this broad landscape, supported catalysts, in which the catalytically active species is dispersed on a solid support, have emerged as a particularly important class, due to the enhanced metal dispersion, the potential for low metal loadings, improved resistance to sintering, and the opportunity to modulate catalytic behavior through interactions between the active phase and the support. [6,7]

Despite these advantages, a major challenge in the application of heterogeneous catalysts is maintaining the active elements firmly immobilized on the support, particularly in liquid-phase reactions. It is well established that heterogeneous catalysts operating in solution-based processes, are frequently affected by so-called "catalyst leaching", often referred to as "metal leaching". In this Perspective, we use the broader term "elemental leaching", as it also includes the dissolution of non-metallic species from the solid support. For example, when supported rhodium sulfides are employed as catalysts in the hydroformylation of styrene, we observed that not only rhodium but also sulfur species can leach into the reaction medium. [8] Elemental leaching thus describes the loss of any elemental species from the solid catalyst into the surrounding liquid phase. [9,10] Such processes undermine key advantages of heterogeneous catalysis, as the removal of dissolved elemental species can compromise catalyst activity and selectivity, complicate separation procedures, and ultimately limit catalyst recyclability. In addition, leached species can contaminate the product stream, which is particularly critical in fine chemical and pharmaceutical applications. In these fields, stringent purity

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https://doi.org/10.1016/j.apcata.2026.121035
Received 13 April 2026; Received in revised form 13 May 2026; Accepted 14 May 2026
Available online 15 May 2026

requirements often require demanding and costly purification steps. [11–14]

Beyond practical considerations, shown in Fig. 1, elemental leaching also complicates the fundamental interpretation of catalytic reaction mechanisms. The presence of soluble elemental species in the reaction medium introduces ambiguity regarding the true nature of the catalyst, since leached species may contribute as homogeneous catalysts. Even trace concentrations of dissolved metal can raise questions about the genuinely heterogeneous character of the system, since such species may be sufficient to drive the reaction. [15–17] This challenge becomes even more pronounced when both surface-bound and homogeneous metal species contribute simultaneously to the observed activity. In such cases, so-called "cocktail" systems arise, in which heterogeneous and homogeneous pathways operate in parallel, further obscuring any mechanistic interpretation. [18–20] Consequently, the combined implications of elemental leaching, including catalyst deactivation, product contamination, and uncertainty regarding the identity of the active species, have motivated extensive investigations into leaching phenomena in solid-state catalysts.

A variety of strategies have been reported in the literature to minimize or even prevent elemental leaching from supported catalysts, ranging from the rational design of catalysts to the careful optimization of reaction conditions. [21–23] From our own work in the field of heterogeneous and heterogenized catalysts, however, we have repeatedly encountered elemental leaching as a persistent and often challenging issue. This ongoing challenge has been a key motivation for writing this Perspective, which is not intended to provide a comprehensive literature review, but rather to offer selected insights and a practical, experience-based guide applicable to day-to-day laboratory work. Elemental leaching is particularly significant from an economic standpoint, when rare and costly transition metals, such as platinum-group metals, are employed. Addressing this challenge requires the careful collection of diagnostic evidence and, based on this evidence, a clear understanding of both the nature and the catalytic contribution of species that have "disappeared" from the support. Accordingly, two key objectives have emerged in the catalysis community: (i) minimizing or preventing the loss of elemental species to enable straightforward catalyst separation, while ensuring product contamination remains within regulatory limits, and (ii) identifying the nature and catalytic role of any leached species. Although these objectives are conceptually clear, their practical realization remains challenging due to the diversity of leaching pathways. Moreover, the varying complexity and reliability of experimental approaches used to distinguish between truly heterogeneous catalysis and catalysis mediated by molecularly dissolved species complicate this task. In this Perspective article, we examine different types and consequences of elemental leaching in liquid-phase reactions using supported heterogeneous catalysts. We highlight effective strategies to mitigate leaching and briefly review methods for identifying catalytically active species. Our aim is to provide practical guidance for the design, execution, and interpretation of supported transition metal catalyzed liquid-phase reactions, with particular attention to the often underestimated impact of catalyst leaching phenomena.

2. Types of catalyst leaching

The loss of elemental species from supported solid-state catalysts during liquid-phase reactions can broadly be categorized into chemical, physicochemical, and mechanical pathways, depending on the underlying mechanism and origin of the leaching phenomenon (Fig. 2). In the context of this Perspective, chemical and physicochemical losses are referred to as leaching and, according to widely accepted definitions, are defined as the dissolution of catalytically active species from a heterogeneous catalyst into the liquid reaction medium. [9,18] In contrast, mechanical pathways are defined in this Perspective as processes that mainly result from physical forces, including attrition, shear forces, pressure pulses, or the detachment of nanoparticles from the support, where no true dissolution into the reaction medium occurs. [24,25] Nevertheless, from a broader and practically relevant perspective, any process that leads to the release of catalytically active species from a supported catalyst into the reaction medium, particularly when catalyst recovery is compromised, may reasonably be regarded as catalyst leaching. Accordingly, in this work we treat all forms of detachment or loss of active elemental species from the original catalyst under a unified framework, although their origin might differ substantially.

A widely reported pathway for elemental detachment from solid supports under catalytic reaction conditions involves the formation of soluble molecular metal species. This phenomenon is particularly pronounced in liquid-phase reactions conducted under conditions that mimic hydrothermal and solvothermal environments, such as elevated pressure and temperature. In reactions such as olefin hydroformylation, high CO pressures favor the formation of thermodynamically stable metal carbonyl complexes, thereby promoting elemental leaching through dissolution of metallic nanoparticles. [26] A classic example of this behavior was demonstrated by Beller and co-workers, who investigated cobalt nanoparticles supported on carbon, titania, silica, ceria, and alumina in the liquid-phase hydroformylation of *n*-butyl acrylate. During the reaction, molecular cobalt complexes were generated *in-situ* from the supported cobalt nanoparticles and were shown to be mainly responsible for product formation *via* a homogeneous catalytic pathway. [27] Similarly, a theoretical study by Chang *et al.* demonstrated that a

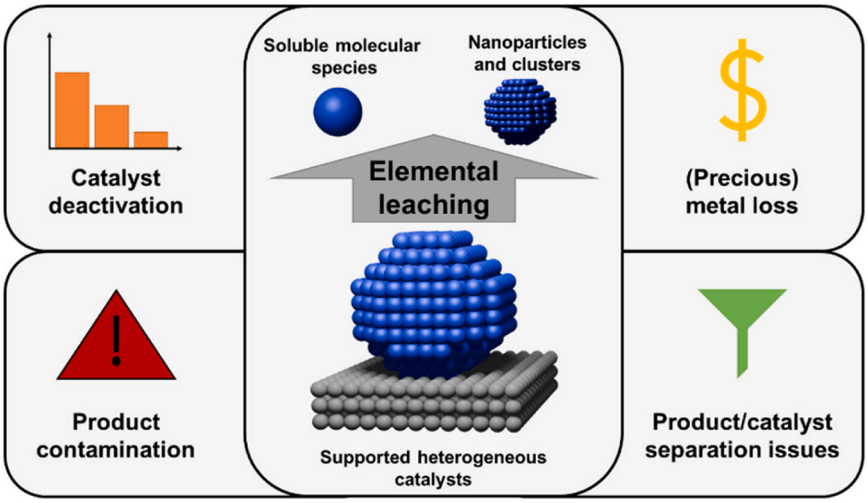


Fig. 1. Schematic illustration of key consequences of elemental leaching in supported heterogeneous catalysts.

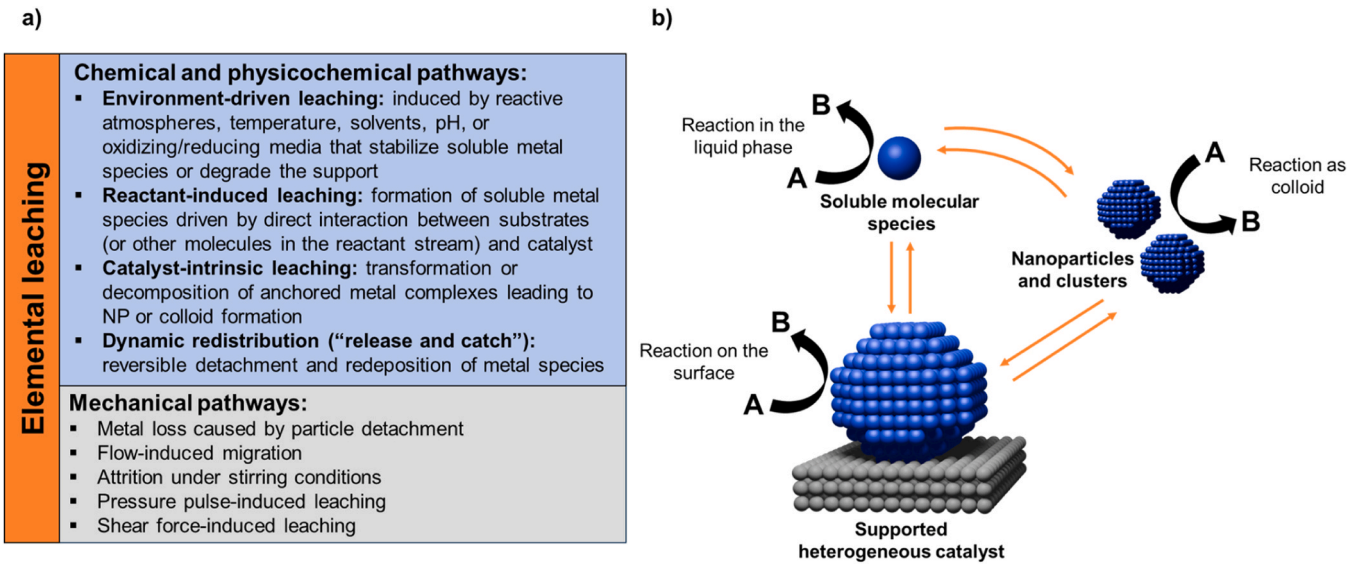


Fig. 2. a) Classification of pathways leading to the loss of active species from a supported catalyst in liquid-phase reactions and b) simplified schematic representation of possible reaction pathways when using supported catalysts. NP = nanoparticle.

high-pressure CO atmosphere can induce palladium leaching from solid catalysts *via* the formation of $Pd(CO)_x$ (x = 2, 3) subcarbonyl species, effectively removing active metal species from the solid phase. [28] Consequently, it is reasonable to hypothesize that such leached species may also form under typical carbonylation and CO hydrogenation reaction conditions, where they could directly participate in the catalytic cycle.

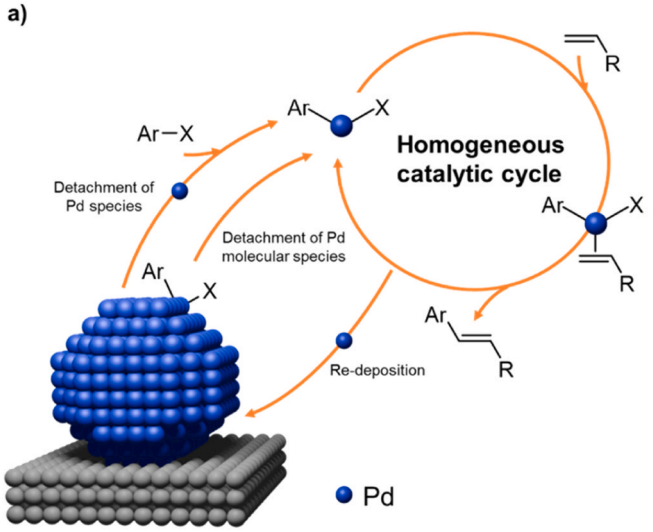
Beyond the effects of absolute and partial pressure and reactive atmospheres, the chemical nature of the reaction medium itself plays a critical role in promoting elemental leaching. Solvents and additives including acids, bases, alcohols, or oxidants/reductants (e.g., hydrogen peroxide, hydrides, etc.) can dissolve or digest active metal species and may additionally degrade the support, thereby releasing metal particles into solution. [29–31] For instance, the direct dissolution of titanium-based species into methanol at elevated temperatures has been reported as a major deactivation pathway during biodiesel production *via* transesterification of vegetable oils using silica-supported TiO_2 catalysts. [32] Likewise, heterogeneous catalysts employed in peroxymonosulfate (PMS)-activated Fenton-like reactions for the degradation of organic contaminants have been shown to suffer from significant leaching of supported transition metals (e.g., iron, cobalt, and nickel on carbon-based supports) under acidic conditions. [33] Similarly, in one of our studies, silica-supported palladium phosphide nanoparticles employed in the Wacker-Tsuji oxidation of styrene were found to undergo dissolution (digestion) in the reaction medium under harsh reaction conditions using piranha solution (H_2O_2 and H_2SO_4). [29]

As mentioned, elemental leaching can also be driven by support degradation, where dissolution of the catalyst support leads to the detachment and release of active species into the reaction medium. [34,35] For instance, dissolution of the widely used support γ-Al_2O_3 in water has been reported and is attributed to chemical reactions at the oxide/water interface. [34] Likewise, silica supports are known to dissolve in aqueous media, particularly under neutral and basic pH conditions. [36] Beyond dissolution, oxidic supports may also undergo structural transformations under hydrothermal reaction conditions, often accompanied by a pronounced loss of surface area. [35,37] As an example, γ-Al_2O_3 can transform into boehmite at temperatures around 200 °C, resulting in a marked reduction in surface area. [37] Such changes weaken metal-support interactions and can further facilitate the detachment and loss of active species from the support. Collectively, these observations underscore the limited stability of conventional oxide supports in aqueous reaction environments, where support dissolution and hydrothermal restructuring can promote elemental leaching and ultimately catalyst deactivation.

In addition to environment-driven leaching, interactions between organic reactants or other molecules in the liquid phase and the catalyst surface can directly induce the formation of molecular species. This behavior is well documented in Pd-catalyzed C–C coupling reactions, where one commonly discussed leaching pathway involves the generation of catalytically active, soluble palladium species from supported Pd nanoparticles following the oxidative addition of aryl halides. [38–41] Another example in this context is the leaching of nickel from supported Ni catalysts (e.g., on Al_2O_3 or silica gel) during the hydroprocessing of products derived from the Fischer-Tropsch process. One reported cause of this phenomenon is the presence of carboxylic acids in the feed stream, which can react with the catalyst to form soluble nickel carboxylates. [42,43] A related but conceptually distinct pathway occurs in single-site solid-state (heterogenized) catalysts, where metal complexes anchored to a support undergo a chemical transformation under reaction conditions. [44–46] For example, in Pd-catalyzed coupling reactions operating *via* a Pd(0)/Pd(II) redox cycle, anchored complexes, such as immobilized imine-based palladacyclic catalysts, [47] palladium (II)-SCS-pincer complexes [48] and tridentate diphosphinoaryl palladium(II) complexes [49] may undergo decomposition, releasing Pd nanoparticles that can subsequently form stable colloidal species. [45,50,51]

An important manifestation of catalyst dynamics associated with catalyst leaching, especially in the context of Pd catalyzed cross-coupling reactions, is the so-called "release and catch" mechanism (Fig. 3). [52] In this scenario, soluble species or colloidal nanoparticles formed during the reaction from a supported catalyst serve as the active catalytic species and subsequently redeposit partially or completely onto the support upon completion of the reaction. [16,40,52–54] Zhao *et al.* investigated the Heck coupling reaction of iodobenzene and methyl acrylate using Pd nanoparticles supported on carbon and silica. Significant Pd leaching was observed under the reaction conditions, with the leached species being identified as the catalytically active form. After reaction completion, Pd was found to redeposit onto the support, consistent with a "release and catch" mechanism. Notably, the use of a mixed base system (triethylamine and sodium carbonate) and elevated temperature promoted re-deposition, with carbon supports facilitating this process more effectively than silica. [54] While such a process can be beneficial, for catalyst separation and minimizing metal contamination in the liquid phase, catalyst recyclability often remains challenging.

a)



b)

Initial heterogeneous catalyst	Soluble metal species	Catalytic reaction
Pd/C, Pd/SiO_2, bulk Pd nanoparticles	ArPdX , $ArPdXL_n$ (L: organic base), $Pd(Et_3N)_2$	C–C coupling
Rh/SiO_2, Rh/C, Rh/Al_2O_3, bulk Rh nanoparticles	$H_nRh(CO)_m$, $Rh(CO)_m$	Hydroformylation
Co/SiO_2, bulk Co nanoparticles	$H_nCo(CO)_m$, $Co(CO)_m$	Hydroformylation
Pd/C, Pd/SiO_2, bulk Pd nanoparticles	$Pd(CO)_n$, ArPdX , $ArPdXL_n$ (L: organic base)	Carbonylation
Ni/SiO_2, Ni/Al_2O_3	Nickel carboxylates: $Ni(CH_3COO)_2$, $Ni(C_2H_5COO)_2$	Fischer-Tropsch, hydroprocessing

Fig. 3. (a) Schematic illustration of the "release and catch" mechanism for supported Pd nanoparticles in C–C coupling reactions, using the Heck reaction as example. (b) Overview of representative heterogeneous transition metal catalysts and the corresponding soluble species that may form under reaction conditions. [23,28,42,43,55–58].

Repeated release and redeposition can substantially alter the catalyst surface, ultimately leading to decreased activity and/or selectivity.

Similar challenges regarding catalyst identity and dynamic heterogeneity also arise in immobilized asymmetric catalytic systems. [59,60] In such systems, immobilization of the catalytically active species can be achieved through encapsulation, covalent attachment, electrostatic interactions, adsorption, or self-support *via* coordination. [61] In particular, heterogenized chiral transition metal complexes and organocatalysts have frequently been proposed to operate through partially leached or "release and catch" mechanisms, in which catalytically active molecular species are reversibly transferred between the support and the liquid phase. [52] One representative example is the enantioselective arylation of aryl bromides employing BozPhos (1,2-bis [(2 *R*,5 *R*)-2,5-dimethylphospholano]benzene monooxide) as the bisphosphine ligand in combination with a supported *N*-heterocyclic carbene-based Pd(II) catalyst. Mechanistic investigations indicated that the heterogeneous carbene catalyst acts as a reservoir for catalytically active homogeneous Pd(0) species. [62] Beyond coupling reactions, similar behavior has also been observed for a Rh(I) complex containing a pyrene-modified Pyrphos (2-(diphenylphosphino)pyridine) ligand adsorbed on carbon nanotubes and applied in the asymmetric hydrogenation of α-dehydroamino esters. In this system, the "release and catch" behavior was found to be strongly influenced by the choice of solvent and the reaction temperature. [63] Several strategies have been proposed to influence "release and catch" performance and the associated elemental leaching in such systems, including modification of the support material to increase its ionic character, optimization of the tether ligand structure and length, enhancement of host–guest interactions between the immobilized complex and the support, and minimization of reaction times. [59,64] Establishing the true nature of the active species in these systems is often particularly challenging because even low concentrations of dissolved chiral catalysts may dominate the observed catalytic activity and stereoselectivity. These effects can become even more pronounced under continuous-flow conditions, where non-equilibrium operation may continuously influence catalyst speciation, redistribution, and catalyst leaching phenomena. [65–67]

In addition to the chemical leaching pathways discussed above, elemental leaching from supported systems can also occur *via* mechanical mechanisms. Under reaction conditions, supported nanoparticles may detach from the support (erosion) and disperse into the liquid phase, forming colloidal species. In flow reactions, the continuously moving mobile phase can further facilitate such particle migration. [10,13] Similarly, in single-site catalysts, insufficient stabilization of anchored complexes can lead to their transfer into the liquid phase. [44–46] A less frequently discussed but technically important leaching pathway involves mechanical grinding or attrition of the catalyst under stirring conditions, where intense mixing and associated shear forces can promote structural degradation and fragmentation of the catalyst material. [24,68,69] Catalyst attrition refers to the degradation of catalyst particles during operation, which often makes it difficult to separate the catalyst from liquid products. [70,71] The main attrition mechanisms include erosion or abrasion, where surface layers or particle edges are gradually removed, and fracture, which causes particles to break into smaller fragments. These processes result from mechanical and chemical stresses acting on the catalyst, such as pressure, temperature fluctuations, particle-particle contact, and interactions with reactive species under operating conditions. [71] Catalyst attrition has been reported in slurry reactors, such as bubble column and stirred-tank slurry reactors, particularly at industrial scale. It was primarily attributed to mechanical mechanisms, including interparticle collisions and interactions with reactor internals. [25,71] For instance, Lin *et al.* reported severe attrition of an Fe–Cu–K–SiO_2 catalyst in a pilot-scale stirred-tank slurry reactor during Fischer-Tropsch synthesis. Particle size analysis and electron microscopy imaging indicated that fracture was the dominant attrition mechanism, underscoring the critical relevance of this phenomenon in industrial processes. [25] In operations susceptible to pressure fluctuations or pressure pulses, such as those caused by depressurization events or process surges, the frequency of particle-wall and particle-particle collisions increases, promoting the formation of fine particles. A prominent example is continuous catalyst regeneration (CCR) units, which are widely used in the petrochemical industry. In these systems, rapid changes in hydrogen pressure intensify particle collisions and consequently accelerate catalyst attrition. [72] Furthermore, during industrial reactor loading, the potential detachment of active components from the catalyst surface should not be overlooked.

Beyond mechanistic interpretation and catalyst stability, elemental leaching can also have important implications for reactor operation, catalyst lifetime, and process modelling. From a reactor-engineering perspective, elemental leaching can also be regarded as a catalyst deactivation process in which the concentration of catalytically active sites changes dynamically during operation. In simplified kinetic descriptions, catalyst activity is commonly treated as a time-dependent

parameter that decreases due to the continuous dissolution of active species from the solid support. [73] The catalyst activity a(t) at a given time can thereby be expressed as the ratio between the reaction rate at time t and the initial reaction rate of the fresh catalyst, [74] as shown in Equation 1.

$$a\ (t) = \frac{\text{Reaction rate at time } (t = t)}{\text{Reaction rate at time } (t = 0)} \quad (1)$$

Different theoretical, empirical, and semi-empirical models have been proposed in the literature to describe catalyst deactivation as a function of parameters such as the time-on-stream (TOS) of hydrocracking catalysts, [74] the operating conditions of Fischer-Tropsch catalysts, [75] or the composition of the reaction mixture in systems exhibiting reversible and irreversible two-step deactivation pathways. [76] Such deactivation models are highly relevant for reactor simulation and process optimization, particularly for predicting catalyst lifetime and long-term reactor performance under reaction conditions.

All of these described challenges have important implications for reactor operation and reactor modelling. In systems affected by elemental leaching, dissolved species may remain catalytically active and thereby introduce parallel homogeneous pathways. Consequently, the observed catalytic rate may arise from both surface-bound and dissolved species, resulting in dynamically evolving "cocktail" systems, as discussed previously. [18–20] Classical heterogeneous reactor models generally assume stationary active sites, constant catalyst composition, and negligible catalyst transport. [73,77] In systems undergoing elemental leaching, however, these assumptions may no longer hold, since the catalyst may continuously dissolve, redistribute, redeposit, aggregate, or undergo attrition during operation. Leaching can even occur through different pathways simultaneously. [10] In fixed-bed reactors, elemental leaching may lead to axial redistribution of active metals, concentration gradients along the catalyst bed, and non-uniform catalyst aging. [13] In slurry and fluidized-bed reactors, particle collisions, shear forces, and enhanced mass transport can further accelerate catalyst attrition and metal redistribution. [25] Consequently, accurate reactor modelling may require coupling reaction kinetics with catalyst deactivation kinetics, transport phenomena, hydrodynamics, and dissolution/redeposition processes to realistically describe catalyst behavior under practical operating conditions. [73]

3. Strategies to prevent catalyst leaching

A central strategy for resolving uncertainties surrounding the true nature of the catalytically active species is the suppression of elemental leaching, and a wide range of approaches to achieve this goal have been reported in the literature (Fig. 4). [78,79] Because elemental leaching is highly sensitive to the reaction environment, the most straightforward mitigation strategy involves the careful control of the reaction conditions. Parameters such as solvent polarity, pressure, temperature, and pH strongly influence catalyst stability. Polar solvents and solvothermal reaction conditions are known to promote metal dissolution and consequently the use of less polar or nonpolar solvents can significantly reduce leaching. [9] Likewise, extreme temperatures, high pressures, and strongly acidic or basic environments tend to accelerate metal loss, which underscores the need for highly stable and active heterogeneous catalysts. [32,80]

Beyond operational control, the use of chemical additives or complexing agents represents an effective strategy to suppress leaching during catalysis. A notable example is the addition of citric, oxalic, or formic acid, which has been reported to suppress cobalt leaching from a silica-supported Co catalyst (Co/SiO_2) during the hydroformylation of 1-hexene. These acids competitively adsorb on cobalt sites, and thereby reduce CO adsorption, thereby limiting metal carbonyl formation and ultimately suppresses the dissolution of active cobalt species. [22]

Beyond the reaction conditions, the reactor in which the catalytic reaction is performed, can also strongly influence elemental leaching behavior. Parameters such as mixing intensity, flow regime, residence time, pressure fluctuations, and hydrodynamic shear affect both chemical dissolution and mechanical attrition processes. [10,71] For example, excessive stirring or strong particle collisions in slurry and fluidized-bed reactors may accelerate catalyst fragmentation and metal release, whereas milder flow conditions and controlled hydrodynamics can improve catalyst stability. [71] Consequently, careful reactor design and process optimization represent additional strategies to mitigate catalyst degradation and elemental leaching, particularly in continuous processes and large-scale applications. [81]

A more fundamental and increasingly adopted approach to leaching mitigation is the rational design of supported catalysts that are intrinsically resistant towards elemental detachment under reaction conditions. In this context, catalyst encapsulation has emerged as a particularly effective strategy. [82] One successful example was demonstrated by O'Neill *et al.*, who employed atomic layer deposition (ALD) to mitigate leaching from Cu nanoparticles supported on γ-Al_2O_3. In their approach, an alumina overcoat was deposited onto the supported Cu nanoparticles *via* ALD. Upon subsequent thermal treatment, the overcoat partially opened to expose catalytically active sites while simultaneously stabilizing leaching-prone regions during the hydrogenation of furfural. [83] Related to encapsulation, strategies in which the support partially migrates onto the metal surface to form a thin overlayer can enhance leaching resistance by providing additional anchoring of the metal species. Moreover, electron transfer between the support and the metal under these conditions can further stabilize the active

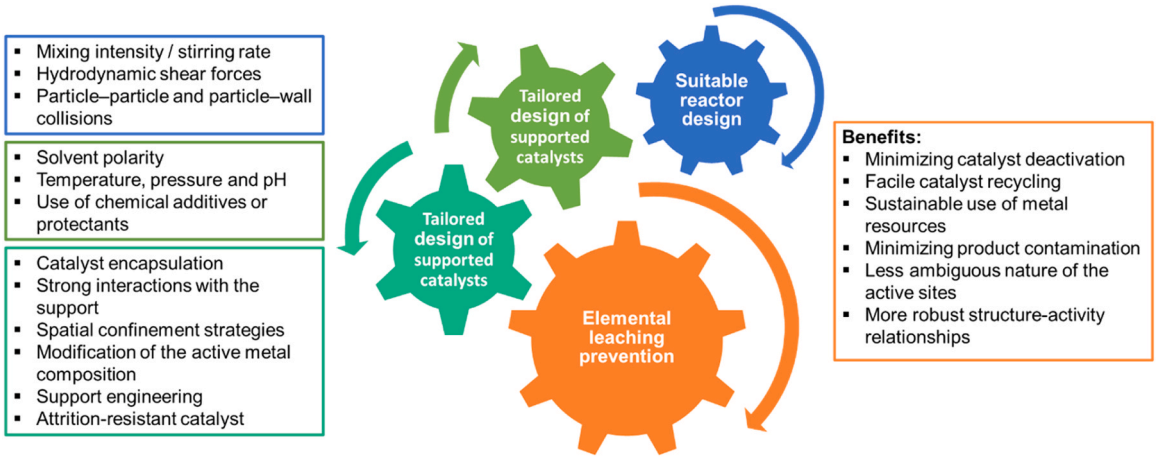


Fig. 4. Schematic representation of major factors to reduce elemental leaching and associated key benefits of these approaches.

phase and contribute to a reduced metal dissolution. [82,84]

Alternative catalyst design strategies rely on spatial confinement to limit metal mobility. For example, Lai and co-workers substantially reduced cobalt leaching during peroxymonosulfate activation by employing a deliberately engineered yolk-shell structure. In this system, cobalt was anchored within a hollow void and confined by a porous N-doped carbon shell, resulting in a fourfold reduction in leaching compared to a reference catalyst lacking any shell confinement. [85] Another promising approach to suppress leaching involves the modification of the chemical composition of the active metal itself. Incorporation of a secondary element into the metal lattice can significantly alter adsorption properties and enhance metal stability. For instance, Zhao *et al.* demonstrated that introducing gallium into cobalt to form silica-supported CoGa intermetallic nanoparticles (CoGa IMC/SiO_2) substantially reduced metal leaching compared to pure Co nanoparticles (Co/SiO_2) during liquid-phase hydroformylation. Gallium atoms, which are unfavorable for CO adsorption, act as anchoring sites for cobalt, thereby enhancing resistance to carbonyl formation and metal dissolution. Using this strategy, the authors reported a leaching reduction of up to 96% during the hydroformylation of 1-hexene conducted at 60 bar syngas pressure. [26] Similarly, in one of our previous studies, incorporation of phosphorus into palladium to form silica-supported Pd_3P nanoparticles (Pd_3P/SiO_2) resulted in nearly a 60% reduction in Pd leaching during the Heck coupling reaction compared to Pd/SiO_2, which served as a reference catalyst. [21]

Catalyst stability can also be enhanced through the deliberate choice of support materials. As mentioned before, the stability of supports can differ greatly under varying reaction conditions, and therefore careful selection is required. Along these lines, the modification of the support itself, often referred to as support engineering, can be employed as an additional strategy. Hereby, the incorporation of heteroatoms, such as phosphorus or nitrogen, into the support framework has been shown to strengthen metal-support interactions, thereby improving resistance to metal detachment and leaching under liquid-phase reaction conditions. [21,23,86–89] Also the tuning of the supports porosity and pore structure can significantly influence the extent of metal leaching by governing both confinement and mass transport processes. [90,91] For example, the heterogenization of a palladium(II) complex in functionalized 2D-hexagonal mesoporous silica has proven to be a very effective strategy to access efficient and stable catalysts for Suzuki cross-coupling reactions. [92]

Finally, from an industrial perspective, the development of attrition-resistant catalysts is crucial. Several strategies can be employed to improve their mechanical durability, including the design of uniform particle morphologies (e.g., spherical particles), the selection of appropriate binders and promoters, and the optimization of key properties, such as density, pore size, and microstructure. [93]

4. Identification of leaching processes and related diagnostic tools

Even when mitigation strategies are applied, complete suppression of catalyst leaching is rarely achievable under practical reaction conditions. Given that dissolved metal species may participate directly in catalysis, the mechanistic interpretation depends on establishing the presence of catalyst leaching, resolving its pathway, identifying the solution-phase species generated (molecular complexes, clusters, nanoparticles), and assessing their impact on catalytic turnover. Leaching also introduces dynamic catalyst speciation, which blurs the boundary between homogeneous and heterogeneous catalysis. Supported transition metal catalysts may operate through surface-bound sites, through soluble species generated during the reaction, or through coupled pathways in which dissolved species re-deposit, aggregate, or continuously exchange with the support (so-called “release and capture” behavior). Consequently, assigning the identity of the active catalyst requires more than detecting elemental leaching. It also requires determining whether leached species are merely inactive spectators, transient intermediates, or catalytically relevant homogeneous contributors.

A broad toolbox of analytic techniques has therefore been developed to probe the catalyst identity and to investigate leaching phenomena in-depth. These approaches range from simple diagnostic tests, such as hot filtration and poisoning experiments conducted in standard laboratories, to advanced *in-situ* and *operando* techniques, including X-ray absorption spectroscopy (XAS), often performed at synchrotron facilities. In addition, comprehensive catalyst characterization before and after the catalytic reaction represents one of the most fundamental and essential steps, providing a readily accessible means to assess structural, morphological, and electronic changes associated with leaching and catalyst transformation. However, when applied individually, these techniques typically provide only tentative indications and do not allow conclusive interpretation. Robust conclusions about catalyst leaching and the relative contributions of homogeneous and heterogeneous pathways generally require a combination of complementary methods, ideally linking catalytic performance with quantitative dissolved-metal analysis and time-resolved characterization. In this Perspective, the available approaches are classified into three broad categories: reaction-progress-based, spectroscopy-based, and theory-based investigations, and critically evaluated with respect to their scope, limitations, and practical implementation.

4.1. Reaction progress-based diagnostics

Reaction-progress-based techniques provide a practical first assessment of catalyst leaching by monitoring reaction performance under constrained conditions or by analyzing kinetic regimes. The hot filtration test is a widely used diagnostic to probe the operative nature of a catalyst. [94] In a typical experiment, the reaction is first conducted in the presence of the supported transition metal catalyst and interrupted at low conversion (commonly $<$20%). The solid catalyst is then removed, usually by filtration through a syringe filter, at or near the reaction temperature to minimize cooling-induced changes and to reduce the likelihood of re-deposition of dissolved species onto the support. The resulting filtrate is subsequently allowed to react further under identical reaction conditions. The continued formation of product (i.e., increasing conversion) in the absence of the solid catalyst is generally taken as evidence that soluble metal species contribute to the catalytic activity. [94–96] From a practical standpoint, the hot filtration test is straightforward and can be implemented in most catalyst testing laboratories. However, the interpretation based on this test alone can be misleading. Colloidal nanoparticles or sub-nanometer clusters detached from the support may pass through the filter and remain catalytically active in the filtrate, leading to a false indication of homogeneous catalysis. Conversely, genuinely soluble active species may be removed or deactivated during filtration, for example by adsorption onto the filter membrane or by changes in coordination environment upon exposure to air or temperature gradients. Additionally, metal carbonyl species formed under high-pressure hydroformylation conditions may decompose upon depressurization, leading to precipitation and subsequent removal during filtration. In such cases, an inactive filtrate may falsely suggest an exclusively heterogeneous catalyst, even when molecular catalysis occurs under reaction conditions. Best practice therefore includes appropriate controls, such as a filter blank experiment, varying the nature of the filter medium and the filter pore size to probe any colloid passage, quantifying dissolved species in the filtrate by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analysis, and re-adding fresh support or catalyst to test for re-deposition (“release and catch”) effects. Moreover, the application of ultracentrifugation can improve the separation of nanoparticles from the liquid medium to provide more reliable test results.

Another widely applied approach to probe elemental leaching and catalyst speciation involves poisoning experiments, in which selective

inhibitors are added to the reaction mixture with the aim of selectively inhibiting either surface-bound sites or soluble molecular species. Common poisons include elemental mercury, carbon disulfide (CS_2), and dibenzo[*a*,*e*]cyclooctene (DCT). In the classical mercury drop test, a large excess of Hg(0), relative to the metal content, is introduced. Mercury can suppress the catalytic reaction by adsorbing on metallic surfaces and/or forming amalgams. Strong inhibition is often interpreted as evidence for a heterogeneous, metal-surface-based reaction mechanism. However, independent studies have shown that mercury can also interact with molecular complexes, leading to inhibition even when molecular species contribute to turnover. [97,98] In addition, the high toxicity of mercury makes its use undesirable in standard laboratory practices, and the test should be applied with caution and appropriate safety measures. Beyond Hg, strongly coordinating ligands, such as CS_2, and related sulfur- or phosphorus-containing additives (e.g., thiophene, PPh_3) are frequently employed. When sub-stoichiometric amounts of CS_2 (relative to the total metal present) induce pronounced inhibition, this behavior is interpreted as consistent with heterogeneous catalysis, because only a fraction of the total atoms in a nanoparticle are present at the surface and provide accessible binding sites. Nevertheless, interpretation remains system-dependent, since ligand binding can be reversible, and dissociation at elevated temperatures (often above ~50 °C) can limit the applicability. [99–101] Moreover, CS_2 is highly toxic, volatile, and flammable, which restricts its routine use and motivates the search for safer and thermally robust catalyst poisons. As a complementary strategy, Anton and Crabtree introduced DCT as a selective poison for molecular species in platinum-group-metal catalysis. [102] While DCT can provide valuable mechanistic insight, its inhibitory effect is frequently modest and may require prolonged contact times to achieve a reliable suppression of the catalytic reaction. In addition, DCT binding and poisoning efficiency strongly depend on the identity of both the soluble metal species and the metal center, which restricts its generality to a narrower set of reactions and catalyst systems. [99,102] Overall, poisoning experiments provide useful qualitative evidence but rarely yield definitive conclusions on their own. Because poisoning efficacy depends sensitively on the nature of the metal and the metal species, as well as the reaction conditions, applying multiple poisons with distinct selectivities, alongside complementary leaching analyses, is recommended to arrive at a robust mechanistic assessment. [99,103]

A more reliable insight into the presence of soluble catalytically active species comes from the three-phase test developed by Rebek and Gavina. [104] In this approach, one reactant is covalently immobilized on an inert solid support, whereas the second reactant remains in the liquid phase. The heterogeneous catalyst is then added, and the reaction is allowed to proceed. The formation of product bound to the immobilized reactant is typically interpreted as evidence that soluble catalytic species resulting from the heterogeneous catalyst diffuse into solution and mediate turnover at the solid-bound substrate. [46,104] Despite its conceptual strength, the three-phase test has important limitations. The non-immobilized reactant(s) must remain fully soluble in the reaction medium to ensure meaningful mass transport and avoid competing surface processes. [50] Moreover, the immobilization must be sufficiently robust under the applied conditions to prevent leaching of the tethered reactant, which would otherwise lead to false-positive indications of homogeneous activity.

The methods discussed above either require the addition of external reagents (e.g., poisons) or involve interrupting the reaction (e.g., filtration). An alternative, non-invasive strategy probes the reaction kinetics itself. In particular, sigmoidal reaction profiles and prolonged induction periods are often associated with changes in the nature of the catalyst and have been linked to the gradual formation of catalytically active soluble species. [99] However, such kinetic signatures are not uniquely diagnostic, since induction periods can also arise in purely heterogeneous systems, for example due to surface restructuring, reduction/activation steps, or slow formation of the active surface state under reaction conditions. Consequently, kinetic observations provide valuable hints but require corroboration by complementary evidence.

A major advantage of the above-mentioned reaction-progress-based approaches is their accessibility. The experiments can typically be implemented in standard catalyst-testing laboratories without specialized instrumentation beyond equipment routinely used for catalytic evaluation and product analysis (e.g., autoclaves, GC-MS/FID or HPLC systems). Nevertheless, reaction mixtures in which multiple interconnected homo- and heterogeneous catalytic pathways arise from species released from the solid catalyst, including transient soluble intermediates, re-deposition processes, and evolving surface states, remain difficult to deconvolute using these methods.

4.2. *Spectroscopy-based diagnostics*

The spectroscopic analysis of both the solid supported catalyst and the reaction solution can provide valuable insight into catalyst stability, active species, and leaching behavior. Among the most widely used methods, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or ICP-MS enables the quantitative determination of elemental leaching during catalysis. Comparing the elemental content of the supported catalyst before and after reaction, together with the corresponding element concentration in the liquid phase, reveals the extent of elemental leaching. In addition, time-dependent ICP measurements, correlated with the reaction progress, can provide mechanistically relevant information. A classic example is the palladium-catalyzed C–C coupling reaction, where an initial increase in dissolved Pd concentration concurrent with conversion, followed by a decline, has been interpreted as evidence for a “release and catch” mechanism. [53] Importantly, ICP-based analyses only give the total element content in the analyzed liquid sample and do not distinguish between truly molecular and colloidal/particulate metal species. For this reason, it is advisable to assess the reaction solution for the presence of nanoparticles (e.g., by dynamic light scattering or electron microscopy) to complement any elemental quantification. Furthermore, the presence of leached species does not necessarily imply catalytically relevant homogeneous turnover, since in many systems, leached species may be inactive spectators or off-cycle decomposition products and thus contribute little, if at all, to the observed catalytic activity.

More specific information concerning the catalytically active species and underlying mechanisms can be gained from *in-situ* and *operando* XAS. [16,105] *In-situ* XAS can track metal dissolution by monitoring changes in the intensity and spectral features of the corresponding absorption edge (e.g., the Ag K-edge) in the liquid phase as a function of time. [106] Analysis of X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) features provides element-specific structural information (oxidation state, coordination environment, interatomic distances) and can thereby support mechanistic assignments regarding homogeneous versus heterogeneous contributions. A notable example is the study by Reimann *et al.*, [16] who investigated Al_2O_3-supported Pd catalysts in C–C coupling reactions using quick-scanning EXAFS (QEXAFS). The authors monitored the solid catalyst and the liquid reaction medium separately using a custom-made *in-situ* EXAFS cell with two beam paths, while studying the coupling of styrene and bromobenzene. These measurements revealed the coexistence of palladium colloids and molecular Pd species in the liquid phase. The mechanistic interpretation suggested that the catalysis proceeds primarily *via in-situ* generated molecular species, with the dissolution of Pd from colloids being the rate-determining step. [16] Similarly, Lee and co-workers applied *operando* liquid-phase XAS in the Suzuki cross-coupling reaction on poly(vinylpyrrolidone) (PVP)-stabilized Pd nanoparticles and reported evidence consistent with a surface-catalyzed mechanism. [107] While these advanced methods provide powerful mechanistic insights, their application requires access to specialized facilities (e.g., synchrotrons), which can represent a significant bottleneck. In addition, the design and operation of

in-situ/operando EXAFS cells can be technically challenging, particularly for reactions conducted at elevated temperature or high pressure, thereby limiting the generality of these approaches.

Beyond XAS, additional spectroscopic tools can support the detection and characterization of soluble metal species, including Ultraviolet-Visible (UV-Vis), Nuclear Magnetic Resonance (NMR), infrared (IR), and Raman spectroscopy. For example, Gaikwad *et al.* combined mass spectrometry with NMR and UV-Vis spectroscopy to study palladium catalysts in cross-coupling reactions and concluded that the catalytic activity originates from Pd(0) atoms and leached Pd(II) species, rather than from the nanoparticles themselves. [108] A key limitation of many spectroscopic methods (with XAS as a notable exception) is their detection sensitivity, which may be insufficient for species present at very low concentrations that can nevertheless be catalytically relevant.

4.3. Theory-based diagnostics

The experimental methodologies discussed above rely on laboratory experiments and access to analytical infrastructure. Theoretical investigations can complement these experimental studies by providing mechanistic insight that is difficult to obtain experimentally. In particular, computational methods allow the examination of trace species that are difficult to detect experimentally but play crucial roles in the catalytic cycle. [109]

A central application involves assessing the thermodynamic driving forces for leaching processes. Density functional theory (DFT) calculations can estimate the favorability of elemental dissolution from surfaces or nanoparticles and the stabilization of the resulting species in solution. [39] Such analysis can provide evidence for the formation of soluble species even at extremely low concentrations, which may still contribute to catalytic activity. In addition, DFT can compare the energetics of competing pathways (surface-bound turnover *versus* leaching-mediated mechanisms) and thereby support mechanistic assignments. [109]

A detailed example is given by Polynski *et al.*, who used DFT studies to model palladium nanoparticle catalyzed reactions involving aryl halides (ArX), where the oxidative addition is a key elementary step. Since the oxidative addition to Pd is widely considered a trigger for leaching, the authors evaluated alternative scenarios by computing (i) the oxidative addition followed by oligomerization of the resulting Pd species and (ii) the detachment of Pd species from the nanoparticle surface and stabilization by ligands, such as trimethylamine, as a model for amine bases in the catalytic system. [109] In a related study, Rösch and co-workers examined Pd leaching under CO atmosphere from Pd(111) surfaces with different structural defects. DFT calculations compared the energetic cost of Pd detachment from bare and CO-covered surfaces over a range of CO coverages and indicated that leaching becomes thermodynamically feasible for defective Pd surfaces under high CO pressure. [28] Together, these theoretical investigations highlight the value of integrating computational and experimental evidence when evaluating leaching pathways and identifying the true catalytically relevant species in supported metal systems.

Another interesting strategy involves the use of Pourbaix diagrams to assess the thermodynamic likelihood of metal dissolution in a given reaction medium. [13,110,111] Such diagrams map electrochemical potential as a function of pH and provide information concerning the stability, solubility, and equilibria of metals, oxides, and ionic species in aqueous environments. Because leaching involves the release of ionic species from a metal surface into a polar medium, or the reverse process of reduction followed by migration and aggregation, its behavior mirrors key concepts in corrosion science. Consequently, Pourbaix diagrams can offer a useful framework to anticipate whether a metal remains in its elemental form, becomes passivated by oxide formation, or enters solution as ionic species. Such catalyst stability assessments using Pourbaix diagrams have been widely reported in the context of electrocatalysis. [111,112] A key limitation, however, is that classical Pourbaix diagrams are defined for aqueous media, which restricts their direct applicability to the aprotic organic solvents commonly used in liquid-phase catalysis. [13] Looking forward, computational strategies could generate solvent-specific analogues of Pourbaix diagrams for relevant metal/solvent/ligand systems, thereby enabling a more systematic prediction of leaching tendencies. One possible framework is inspired by the Materials Project, [113] which constructs Pourbaix diagrams for multicomponent systems by combining DFT calculations with experimental data. A similar approach could be adapted to develop transition metal leaching "maps" for catalytically relevant solvent environments, thereby providing practical guidance for selecting reaction conditions and designing leaching-resistant supported catalysts.

Despite their promise, theory-based approaches face practical limitations. Capturing realistic experimental conditions, such as solvent effects, ligand exchange, particle size distributions, dynamic surface restructuring, and concentration-dependent speciation, remains challenging, and the resulting mechanistic predictions may depend sensitively on model assumptions. Moreover, advanced DFT studies require expertise and computational resources that may not be readily available in laboratories focused primarily on experimental catalysis.

4.4. Summary of diagnostic tools

As mentioned before, the existence of diverse elemental leaching phenomena complicates the interpretation of structure-activity relationships due to the presence of a heterogeneous "cocktail" of catalytic species distributed across both the solid and liquid phases. Moreover, multiple pathways may operate in parallel or sequentially, further increasing the complexity of any mechanistic analysis (Figs. 2 and 3). For example, nanoparticles released from the support, as a result of weak metal-support interactions, may undergo surface reactions with substrates to generate soluble molecular species, which subsequently dissolve into the reaction medium. These dissolved species can then be reduced to zero-valent metal species, agglomerate into new nanoparticles, and ultimately redeposit onto the support. Simple quantification of metal content on the support before and after reaction, or in the product solution, is therefore insufficient to capture such multistep processes, as no net metal loss may be detected despite extensive metal redistribution. Importantly, not all metal species released from the parent catalyst necessarily participate in the catalytic cycle. In many cases, they transform into catalytically inactive forms. [114] Therefore, a critical and comprehensive analysis of the reaction system is essential to identify the true active species and to elucidate the dynamic transformations undergone by the catalyst during liquid-phase reactions. In Table 1 we therefore provide a summary of commonly used diagnostic tools as well as their strengths, weaknesses and some improvement methods.

5. Practical guidelines

The discussion above highlights the broad toolbox available to probe elemental leaching and to clarify the true nature of the catalytically active species. In essence, a rigorous heterogeneity investigation requires two key steps: (i) detecting leaching and identifying its form (e.g., molecular complexes, clusters, nanoparticles) and (ii) determining whether the leached species contribute to any catalytic turnover, and if so, to what extent. It is important to keep in mind that no single method can provide definitive evidence for both aspects. However, combining multiple complementary approaches can yield robust insights into the extent of leaching and the relative contributions of surface-bound and solution-phase species to the catalytic cycle. Ideally, reaction-progress-based diagnostics should be combined with *in-situ/operando* spectroscopic methods and supported by computational studies. Together, this convergent strategy provides the most reliable framework for disentangling leaching pathways, catalyst speciation, and the operative catalytic regime. In practice, however, such comprehensive investigations can be time-intensive and limited by access to specialized

Table 1
Key diagnostic tools, strengths, weaknesses and proposed improvement strategies.

Diagnostic tool	Strengths	Weaknesses	Improvement strategy
Catalyst characterization before and after reaction	▪ Reveals structural, morphological, and electronic changes after catalytic reaction ▪ Enables identification of sintering, leaching, or phase transformations	▪ *Ex-situ* characterization may not reflect true active state under reaction conditions ▪ Sample handling can introduce artefacts (e.g., oxidation, aggregation)	▪ Combine *ex-situ* with *in-situ/ operando* techniques ▪ Apply time-resolved studies to capture dynamic changes
Hot filtration test	▪ Straightforward to implement in laboratory setups ▪ Applicable across a broad range of reaction systems	▪ High risk of misinterpretation ▪ Active species may deactivate during filtration ▪ Very small nanoparticles may pass through filter	▪ Implementation of efficient particle removal techniques ▪ Analysis of filtrate for molecular species and nanoparticles
Poisoning experiments	▪ Straightforward to implement in laboratory setups ▪ Applicable across a broad range of reaction systems	▪ Results may be biased by the choice of poison ▪ Strongly condition-dependent: poison stability and coordination behavior may lead to misleading conclusions	▪ Selection of appropriate poison under relevant reaction conditions ▪ Conducting multiple tests using different poisons
Three-phase test	▪ Requires comparatively simple experimental setup ▪ More reliable than hot filtration and poisoning experiments	▪ Non-immobilized reactant(s) must remain soluble in reaction ▪ Insufficient immobilization may lead to misleading results	▪ Enhance immobilization using suitable linkers ▪ Evaluate immobilization stability under real reaction conditions
Kinetic investigations	▪ Straightforward to implement in laboratory setups ▪ No interruption of the reaction or addition of external reagents	▪ Extended induction periods due to surface-generated active species may be misinterpreted as homogeneous catalysis	▪ Compare kinetics of catalyst-containing system and filtrate ▪ Asses metal concentration dependence and reaction order
ICP analysis	▪ Provides quantitative information about leaching ▪ Time-dependent analysis combined with kinetic evaluation enables comprehensive assessment of leaching	▪ ICP alone cannot distinguish between leaching pathways or catalytic relevance ▪ Improper sample preparation may lead to inaccurate results	▪ Ensure complete particle removal prior to the filtrate analysis ▪ Analyze fresh and recovered catalysts as well as the filtrate to gain comprehensive insights

instrumentation.

Accordingly, we provide a comparative assessment of the methods discussed herein based on four key criteria: popularity (frequency of use in literature), simplicity (feasibility in a standard catalysis laboratory), reliability (confidence in deducing the catalyst's true nature), and adaptability (applicability across diverse reaction systems). This comparative assessment, shown in Fig. 5b, provides practical guidance for elemental leaching and heterogeneity investigations. Depending on the research question and available resources, studies may combine several methods that rank highly in simplicity and adaptability and are well suited for routine laboratory implementation, or rely on highly reliable but less accessible techniques, such as *in-situ* or *operando* XAS, which provide atomic-level insight at the cost of specialized instrumentation. When access to high-reliability methods is limited, prioritizing approaches that score highly in simplicity, adaptability, and popularity can still enable reasonable mechanistic assignments. In such cases, conclusions should be strengthened through convergent evidence from multiple complementary tests. This strategy also supports efficient catalyst screening, where readily accessible methods identify candidate systems for deeper investigation using more sophisticated techniques.

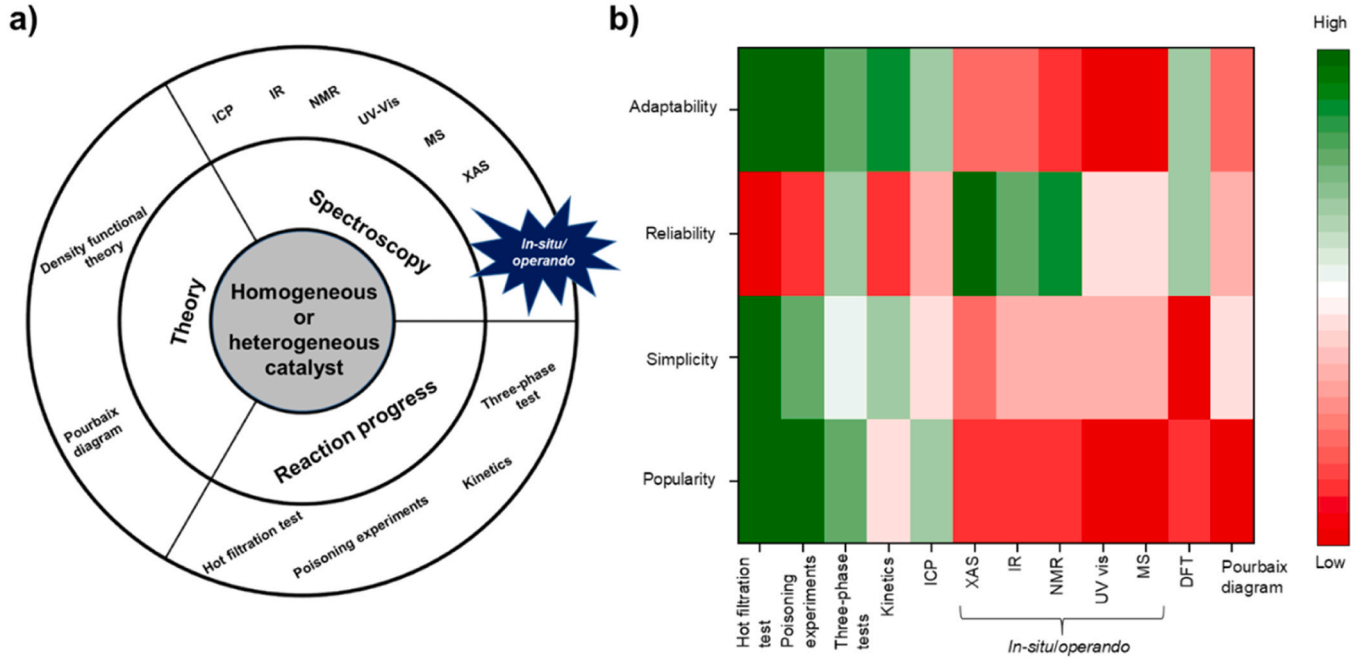


Fig. 5. Methods used for the investigation of elemental leaching processes and b) a heat map classifying these methods according to their popularity, simplicity, reliability, and adaptability.

Importantly, the reliability of lower-confidence tests can often be improved by targeted follow-up analyses. For example, hot filtration results become more robust when the filtrate is examined for particulate species by electron microscopy, or more accessibly by DLS, followed by appropriate particle-removal steps (e.g., centrifugation or ultrafiltration) prior to activity testing. Finally, spectroscopic characterization of catalytically active species in the filtrate (e.g., through NMR or IR) can provide direct information about dissolved molecular species and further refine the assignment of the operating catalytic species.

An example workflow is outlined in Fig. 6 to support a systematic assessment of elemental leaching and, ultimately, the true nature of the catalytically active species. The investigation may begin with catalyst recovery and reuse tests, performed both at low (to estimate initial activity and turnover frequency) and at high conversion (to probe stability under demanding reaction conditions). These readily accessible experiments provide an initial indication of catalyst deactivation processes and help to determine whether performance loss is linked to catalyst instability. At this stage, the recovered catalysts (post-reaction) can be further characterized using powder X-ray diffraction, electron microscopy, ICP analysis and further spectroscopic techniques, such as XAS and X-ray photoelectron spectroscopy (XPS), to gain insights into the structural, morphological and electronic changes occurring in the catalyst. For example, an increase in particle size of the recovered catalyst, as observed by electron microscopy, may indicate a possible "release and catch" mechanism. [16,115]

Next, elemental analysis (e.g., ICP) can be used to detect and quantify leached species in the reaction solution. If ICP confirms elemental leaching, the workflow proceeds to (i) implement mitigation measures tailored to the leaching phenomenon and (ii) assess whether the leached metal fraction contributes to catalysis. For this purpose, reaction progress-based investigations can be performed to evaluate whether the observed activity is consistent with homogeneous molecular complexes, mixed species, or a genuinely heterogeneous catalyst. If a homogeneous component is indicated, advanced spectroscopic studies can be employed to identify relevant solution-phase species and follow their evolution under reaction conditions. If leached species are found to be catalytically active, theoretical analysis can further elucidate the driving forces for catalyst leaching and the operative catalytic pathways, thereby providing a mechanistic basis for redesigning the supported transition metal catalyst. Importantly, even when elemental analysis does not detect significant elemental leaching, reaction progress-based tests still remain essential. Leached species may be present below

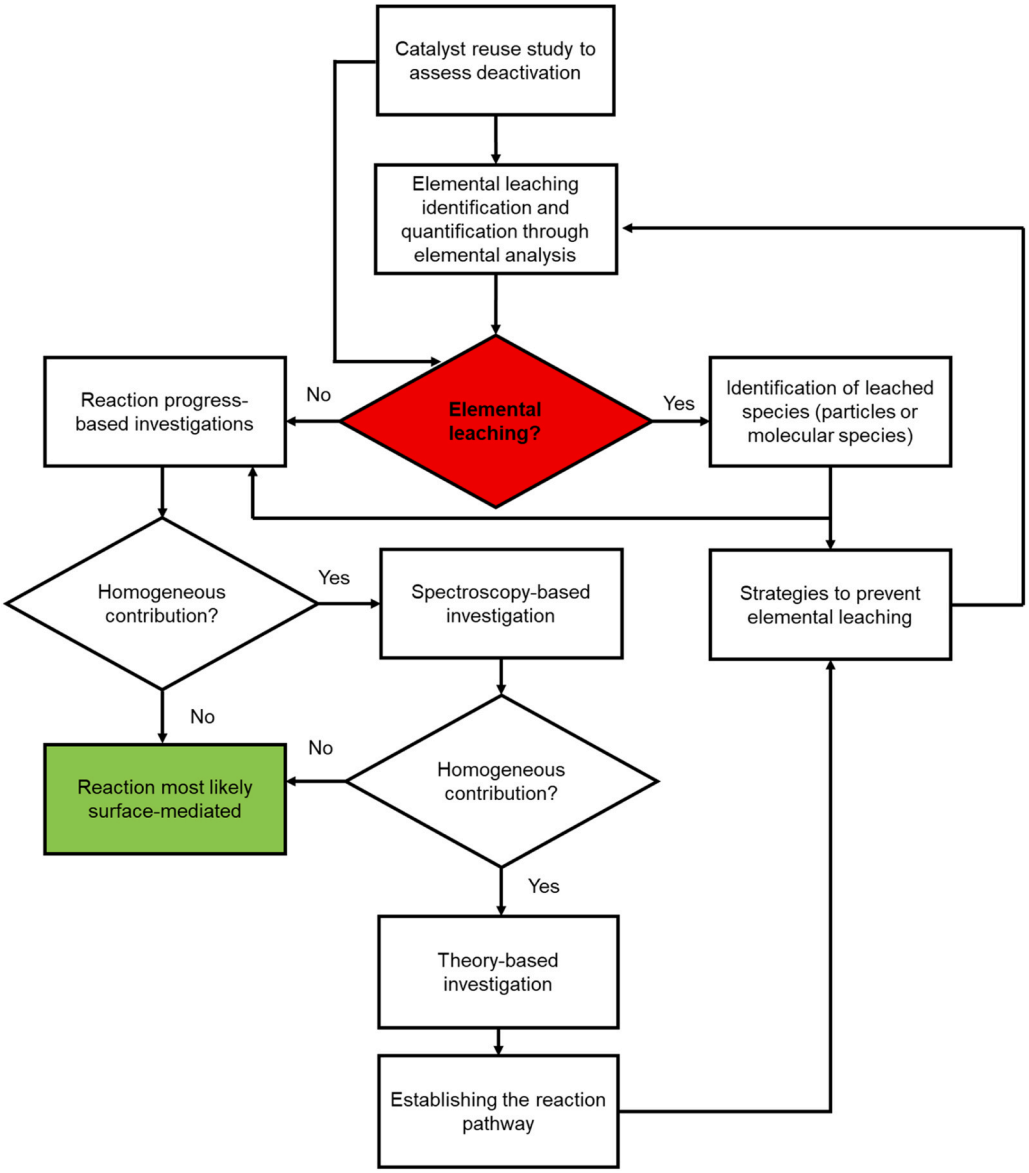


Fig. 6. Proposed workflow for elemental leaching investigations and for determining the true nature of the catalytically active species.

detection limits, or a "release and catch" process may operate, such that the catalyst repeatedly dissolves and redeposits without an obvious net metal loss. In such cases, kinetic signatures and reaction-regime analysis can still reveal whether the active species is truly heterogeneous.

Overall, the workflow shown in Fig. 6 is deliberately iterative. Evidence obtained at each stage guides whether the next priority is to improve stability and suppress elemental leaching, to clarify the active species, or to pursue both in parallel. The workflow can be tailored to specific catalyst systems and practical constraints, while accounting for the strengths and limitations of the available diagnostic methods.

6. Conclusions

Elemental leaching is a phenomenon with consequences ranging from the loss of catalytic activity and product contamination to the more fundamental question of which species actually catalyzes the reaction. Although rational catalyst design and careful control of the reaction conditions can mitigate elemental losses from supported transition metal catalysts, leaching (and re-deposition) often remains difficult to eliminate entirely. A rigorous interpretation of structure-activity relationships therefore requires explicit consideration of species released from the solid catalyst, including their speciation, persistence, and potential catalytic relevance.

The methods discussed in this Perspective provide a pragmatic framework for navigating this complexity. In most cases, mechanistic interpretations and structure-activity correlations should rely on multiple laboratory-accessible diagnostic tests selected for simplicity and broad applicability. These first-line experiments can identify systems in which leaching or dynamic speciation is likely and help prioritize catalyst candidates for more in-depth investigations. When higher confidence is required, particularly for catalysts suspected to operate *via* coupled heterogeneous-homogeneous pathways, *in-situ/operando* spectroscopic tools and computational analyses offer powerful complementary evidence and can substantially refine the assignment of the operative catalytic regime.

CRediT authorship contribution statement

Arjun Neyyathala: Writing – original draft, Investigation, Data curation. **Schunk Stephan Andreas:** Writing – review & editing, Supervision, Conceptualization. **Schirin Hanf:** Writing – review & editing, Writing – original draft, Methodology, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT (OpenAI) in order to assist with English language polishing. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Arjun Neyyathala reports financial support was provided by German Research Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for funding through the National research data infrastructure for catalysts-related sciences (NFDI4Cat - Project-ID 441926934) for A.N. We also thank the members of the SFB 1441, funded by the Deutsche Forschungsgemeinschaft (DFG, SFB 1441, Project-ID 426888090) for valuable discussions.

Data Availability

No data was used for the research described in the article.

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