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Cooperativity between atoms in supported "Single-Atom Catalysts" and metal clusters

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1. Introduction

Following pioneering work by Gates, Thomas, Muetterties, Sintfelt, Basset and others, the race to understand single metal atoms and small metal clusters in catalysis remains vivid. Supported molecular metal species started as a concept to close the gap between solution and solid catalysts [1–4]. These catalysts comprise uniform, simple metal centers, like in enzymes and organometallic compounds, but incorporate a second catalyst component, the support, often inorganic in nature, aimed at enhancing the stability of the active species. As a result, a door to straightforward structure-performance correlations and the use of rigorous theory opens [5], following postulations that are almost 100 years old [6]. Near atomically dispersed metals have also become the target of researchers seeking breakthrough discoveries, based on the realization that relevant physical–chemical properties of these types of sites are fundamentally different relative to those of common metal nanoparticles. In these fields, Prof. Gates has been an inspiration to the catalysis community for over 4 decades, leading to numerous exciting results that will remain part of a magnificent legacy.

Because several comprehensive reviews on single-atom catalysts and metal clusters have recently compiled multiple examples of catalysis performed by these types of species [7–12], this contribution aims at triggering a critical debate on the opportunities, limitations and potential misconceptions around these systems.

The first part of this *Review* briefly introduces supported molecular metal catalysts as model catalysts to build sound structure-performance correlations. The second half discusses recent examples of outstanding catalysis by supported molecular metal catalysts.

1.1. General considerations

Literature loosely uses the terms "single-site", "single-atom", "metal complex", "single organometallic metal complex", "atomically dispersed metals", or "mononuclear metal complexes" to refer to catalysts where the active sites lack metal–metal bonds between atoms of the same element (as either M−M, M−O−M or, more generally, M−X−M). These terms, however, are not inter-exchangeable, and denote relevant aspects of the active sites beyond the metal nuclearity (number of metal atoms that each catalytic unit comprises) that are important to understand [7,13]. Particularly, a central idea of the present *Review* is that most catalysts that strictly meet the definition of a "single-atom catalyst" (SAC) rarely operate as single-site catalysts, taking into account that other catalyst components often actively participate in the reaction. Describing solid catalysts only (or mainly) as per the metal nuclearity of the active sites oversimplifies the problem and limits, thus, our ability to tackle new challenges.

On the other hand, sites comprising at least one metal–metal bond between atoms of the same element, and where the diameter of the metal ensemble does not exceed 1 nm, approximately, are commonly referred in the literature as metal clusters, in opposition to particles larger than 1 nm, which are called nanoparticles. The boundary between metal clusters and metal nanoparticles is fuzzy, corresponding to a transition from well-defined molecular orbitals to plasmonic d-bands that is not always easy to delineate.

Atomically dispersed supported metals, that is, solid catalysts where the active sites comprise only one metal atom, and supported metal clusters, with nuclearities between 2 and a few dozen atoms, are often referred, more generally, as supported "molecular" metal catalysts. This term is used to emphasize that chemical reactions occur here upon interaction between reactants and metal species that behave, in essence, like molecules bonded to ligands dynamically changing during the course of the chemical transformation. A remarkable singularity of supported molecular metal catalysts is that the support can, indeed, be regarded as a metal macro-ligand with well-defined electron-withdrawing/electron-donating characteristics. Prof. Gates has made significant contributions to the popularization of these concepts, and has critically influenced various generations of researchers to conceive solid catalysts in molecular terms.

Table 1 summarizes a series of events that help to understand the evolution of this field for near a century now. Fig. 1 shows the evolution of citations since 1950 for various interconnected topics.

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Table 1
Compilation of historical events on the catalysis by single metal atoms and metal clusters.

Year	Correspond. Authors	Event/Relevance	Ref.
1925–1926	Taylor	100 years old contributions by Taylor on the heterogeneity of solid catalysts	[6,14]
1964	Jasinski	First report on M−NC (metals on nitro-doped carbons) for fuel cell applications, which set the pace to later work on Fe and Co SAC catalysts for the ORR reaction	
1971–1975	Montrasi, Baetzold, Muetterties	Publication of first papers on (unsupported) metal clusters in catalysis	[15–17]
1974	Robertson	First thesis on supported metal complexes for catalysis	[18]
1976–1978	Gates, Ichikawa	First papers on supported metal clusters in catalysis	[19,20]
1980	Schwartz, Ward	Early examples of silica-supported zirconium hydrides as olefins isomerization and hydrogenation catalysts	[21]
1985–1987	Haruta, Hutchings	First papers on supported Au catalysts. Au showed unprecedented sensitivity to particle size, with drastic activity boost at < 2 nm	[22,23]
1986	Iwamoto	First paper on Cu^{2+} inside zeolites for the selective catalytic reduction of NO_x with ammonia, which signified a revolution for automotive emissions control	[24]
1987–1991	Taramasso, Perego, Notari	First contributions on the use of isolated Ti atoms in zeolites for selective oxidations. Isolated Lewis acids, including Zr, Ti, and Sn, later became a prominent class of single-atom catalysts	[25,26]
1995	Gates	One of the first comprehensive reviews on the catalysis by supported metal clusters	[4]
1997	Haruta	Highly cited review (>5500)[a] on supported gold catalysts, with unquestionable impact on following cluster catalysis	[27]
2006	Zelenay	Publication of non-precious metal catalysts (SACs in N-doped carbon materials) for fuel cells application. Foundational work on SACs for the Oxygen Reduction Reaction	[28]
2011	Liu, Li, Zhang	Publication of Pt_1/FeO_x catalyst for the CO oxidation reaction, with > 5500 citations.[a] The term SAC was coined. Undoubted impact over future works on single metal atoms.	[29]
2016	Dinca	Unusually active Ni atoms inside a MOF for the ethylene dimerization reaction	[30]
2018	Corma	Highly cited (~3500)[a] recent review on the catalysis by supported single metal atoms and metal clusters	[8]
2018	Wang, Li, Zhang	Highly cited (~3000)[a] recent review on the catalysis by supported single metal atoms	[10]

[a] Citation search done on April 2024.

2. Supported molecular metal catalysts as model catalysts

Single-atoms and small noble metal clusters have probably always existed as minority species in common supported metal catalysts. However, their role in catalysis remained elusive for decades as a result of challenges to detect these species within the surface of highly complex materials that host, very predominantly, metal particles larger than 2 nm under practical reaction conditions. Visionary work by Gates and others led to the preparation of solid samples with only one type of active site, with properties that could be tuned one by one, including the exact metal nuclearity and the metal electron density [4,31,32]. To attain this goal, common ill-defined supports such as SiO_2 or Al_2O_3 were replaced by highly crystalline, uniformly terminated materials, such as zeolites, and synthesis methods proper to organometallic chemistry were adopted. The work opened the door to precise quantification of the role of various structural descriptors on the catalysis [33,34], and drew a path for many of us to follow. For example, through a series of $Ir(C_2H_4)_2$ complexes on various supports, it was later demonstrated that the activity of Ir_1 in the ethylene hydrogenation reaction correlates with the position of the IR CO stretch in CO-probed materials, used as a marker of the metal electron-density [35,36](Fig. 2). The correlation exists because the rate-determining step is, in this case, a reaction, the H_2-dissociation, that is strongly inhibited on single Ir atoms when olefins are present, more so if the metal is electron-rich. Accordingly, the activity of single Ir atoms increases more than 20 times when replacing the electron-donating MgO by the electron-withdrawing HY zeolite [35]. Interestingly, the activity boost far exceeded that observed when the metal nuclearity was increased from 1 to 4 in alternative experiments to quantify the role of the metal–metal bond [35](Ir_4 clusters on MgO, more specifically, are about 6 times more active than Ir_1 on this support; and Ir_4 on HY is barely more active than Ir_1/HY). Nevertheless, the magnitude of these effects appears to be element specific, and is affected by subtle differences in the final catalytic structures. For example, single Rh atoms on MgO drastically benefit by the formation of a first metal–metal bond in dimeric Rh structures, with an outstanding activity increase of more than 60 times for the ethylene hydrogenation reaction [37]. These and other examples of pronounced changes in performance as a result of minimal changes in the catalyst structure [38–44] have encouraged researchers to seek disruptive technology based on atomically (or *quasi* atomically) dispersed metals on supports (see below).

3. Supported molecular metal species with unique catalytic characteristics

The following section reviews a number of recent supported molecular metal catalysts (SAC and metal clusters) with intriguing catalytic characteristics. For clarity, activity, selectivity, and stability, common performance metrics in catalysis, are evaluated separately. Comparison across the different datasets is challenging, given the variability of experimental conditions, characterization techniques and interpretability of certain results, using catalytic data that, sometimes, lacks kinetic rigor. This scenario leads, at times, to apparent incoherence, contradiction and noise that obscure structure/performance correlations, and makes more difficult to identify critical catalyst attributes.

3.1. Activity

3.1.1. Supported vs unsupported metal complexes and clusters

Generally, the activity of single-atom organometallic compounds in

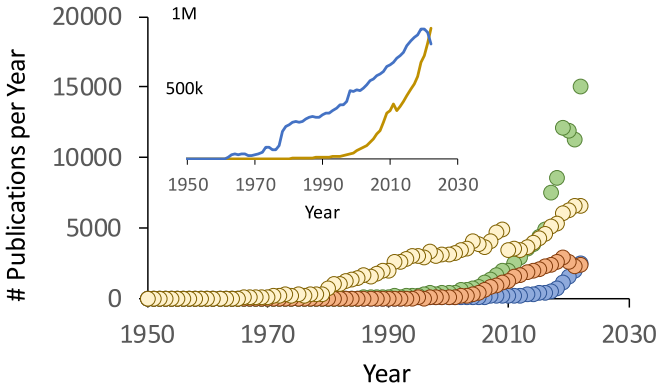

Fig. 1. Number of peer-reviewed publications per year since 1950 according to Web of Knowledge, using the following entries in the search engine: "Zeolites" (yellow); "Clusters Catalysis" (green); "Gold Catalysis" (orange); "Single Atom Catalysis" (blue). Insert shows the number of total peer-reviewed publications per year by USA (blue line) and China (golden line) institutions according to this database (in all research fields). Search done on July 2023. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

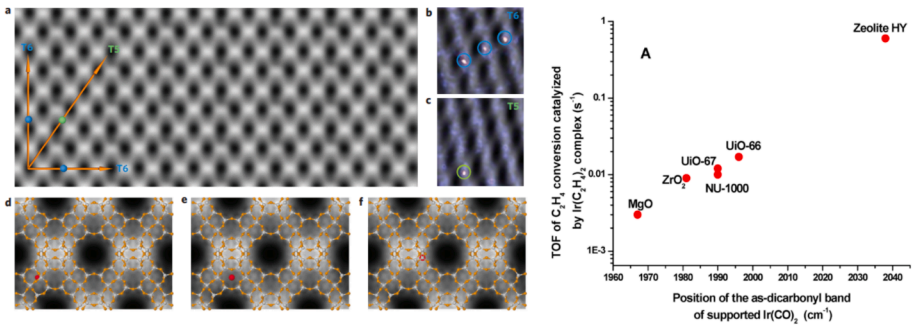

Fig. 2. (A) One of the earliest examples to show the location of isolated metal atoms (Ir) inside a zeolite (DAY), taken by the Gates and Browning's group. Adapted with permission from [45]; (B) Correlation between the activity of single Ir atoms and its electronic properties, approximated by the position of dicarbonyls bands in the IR spectra of $Ir(CO)_2$ species on various supports [35,36]. Reproduced with permission from [36].

solution slows down when the active site is grafted to a solid surface. This result is often associated with problems to adopt optimal 3D configurations when the metal complex is bonded to a rigid structure, with a consequent raise of the transition state energy. Heterogenized Ziegler-Natta catalysts exemplify this general principle, as discussed in excellent reviews [46,47]. Accordingly, active metal complexes tethered to the support through long, flexible ligands (e.g. an alkyl chain) tend to better retain their unsupported activity, as most of their rotational freedom is retained.

Nonetheless, some grafted metal complexes compete, or even improve, the activity of their unsupported analogues. For instance, Ni (II) in $[Tp^{Mes}Ni]^+$ (Tp^{Mes} = HB(3-mesitylpyrazolyl)$_3$) grafted to the MFU-4 (a Metal Organic Framework) is as active as the free metal complex in solution for the dimerization of olefins [48], both systems sharing the same Cossee-Arlman reaction mechanism [30]; olefin metathesis, on the other hand, occurs faster on single-atom rhenium, molybdenum or tungsten alkylidines that are bonded to partially dehydroxylated silica, due to the formation of alkoxide species that are more stable than the unsupported counterparts [49–51]; and isolated Sn or Ti in the framework of zeolites are highly active for oxidation reactions using H_2O_2 [52–54], and for the skeletal isomerization of glucose to fructose (on Sn) [55,56], thanks to promotional confinement effects inside the zeolite pores [57].

Moreover, single metal atoms often become more stable when supported, and high stability is a door to faster catalysis by running the chemistry at harsher reaction conditions. Note that although the intrinsic activity of the active site may not be improved by supporting the metal, the catalyst productivity may be increased, in practice, by operating at higher temperature. This is exemplified by MMO enzymes, which are able to convert CH_4 to CH_3OH in air at room temperature, in sharp contrast to dimeric Cu-O-Cu species in CHA zeolite, which are inactive under identical conditions, despite similarities in the active site nuclearity. The inorganic system, however, can run the chemistry at 200 °C, at rates several orders of magnitude higher than those by the biological analogue, which collapses at this high temperature [58].

3.1.2. Supported single metal atoms vs supported metal clusters

3.1.2.1. SAC alloys. Single-atom catalysts are, usually, less active than catalysts made to include metal–metal bonds (i.e. metal clusters and nanoparticles) in reactions that involve H_2 and/or O_2 (i.e. in most redox chemistry, as discussed next). This obeys the rather general principle that neighboring metal atoms cooperate to activate reactants and scramble their bonds. Accordingly, most "highly active" SACs that have been reported in the literature comprise, in reality, active sites made of single-atoms of one element that work in concert with a second metal function. In these cases, the use of the terms SAC and "single site" are, to a large degree, misleading.

Hydrogenation reactions with H_2, using metals where the H_2 dissociation activity is strongly limited, illustrate this controversy. In these cases, the incorporation of impurity levels of a fast H_2 activator, often a noble metal, has been shown to improve the hydrogenation activity via a H_2-spillover mechanism from one metal species to the other. Recent literature has rebranded these systems as "SAC alloys" [59] after the realization that metals such as Pt tend to arrange as single Pt atoms on top of other metal surfaces when their concentration is sufficiently low. Single Pt or Pd atoms embedded in bulk Cu are representative examples [59–61]). The Pt_1/Cu catalysts show high activity in the hydrogenation of 1,3-butadiene [62], for instance, and when the activity is reported on a per Pt basis, high Turnover Frequencies (TOF) can be inferred. However, the "non-SAC" component of this catalyst (the Cu particle) is a co-catalyst that actively participates in the reaction. The observed H_2 spillover cooperative mechanism has, indeed, ruled the performance of other precedents in the literature, before the terms SAC or SAC-alloy were coined. The promotional role of Pt on the catalysis by Au nanoparticles is, for example, well-documented for multiple hydrogenation reactions [63,64], after the realization that Au struggles to activate H_2 in the presence of other compounds [63].

Following this concerted mechanism, activities normalized by the amount of Pt give, in these examples, the (false) impression that single atoms in SAC alloys are more active relative to each catalyst component alone. For example, the hydrogenation rate of 3-nitrostyrene on 1.5 wt% Au/TiO_2, 0.01 wt% Pt/TiO_2, and 1.5 wt%-0.01 wt Pt/TiO_2 are 70, 2994, and 550 mol converted/(mol metal. h), respectively, at 70 °C and 8 bar, on a total metal basis (Au + Pt) [63], a result that corresponds to more than one order of magnitude activity raise by the bimetallic formulation if the rate was referred to Pt only (neglecting the fact that Au is a co-catalyst). In other examples, i.e. isolated Pt on Cu surfaces, SACs alloys show more active relative to the bulk component alone, but less active than highly dispersed Pt species outside the Cu matrix [62]. Both PtAu and PtCu systems, on the other hand, take advantage of enhanced selectivities towards the desired product, with greater overall productivities when compared to each catalyst component alone. Fig. 3 shows the parallelism between these two systems.

3.1.2.2. Supported SACs. Supported SAC is the preferred term to refer to single metal atoms found on top of bulk metal oxides, rather than on reduced metal particles. Supported SACs differ from SAC alloys, thus, on the oxidation state of the non-SAC component. The support, in these cases, can bring redox activity, or not, depending on its reducibility. Supports that include elements able to shuttle between oxidation states, such as TiO_2, CeO_2, and Fe_2O_3, are called reducible supports, in opposition to non-reducible supports, which include SiO_2, Al_2O_3, ZrO_2, and zeolites.

The use of non-reducible supports prevents the direct participation of the support as a redox co-catalyst. This is helpful to interrogate the redox performance of the supported metal species. As a consequence of the elimination of some, but not all, of the potential cooperative

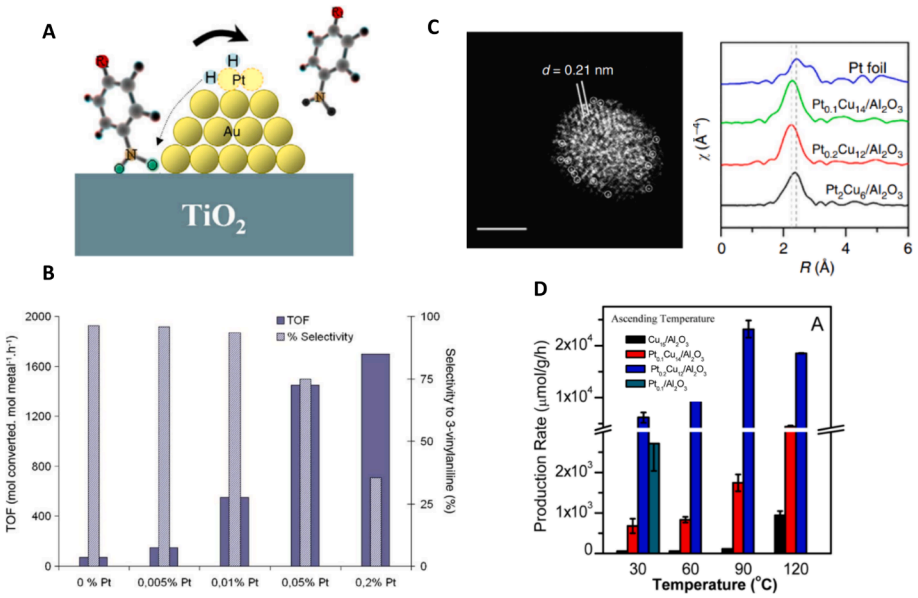

Fig. 3. (A) Proposed cooperative mechanism of PtAu/TiO_2 catalysts with impurity levels of Pt (0.01 wt%) for the hydrogenation of nitroaromatics. Due to extremely low Pt loadings, the exact nuclearity of Pt could not be determined, and was represented as pseudo atomically dispersed species on top of the Au nanoparticles. Adapted with permission from [63]; (B) Activity on a total metal basis, and selectivity to 3-vinylaniline, of pure Au/TiO_2, pure Pt/TiO_2 and PtAu/TiO_2 mixtures. Adapted with permission from [63]; (C) STEM and EXAFS characterizarion of PtCu/Al_2O_3 catalysts showing isolated Pt atoms in a SAC alloy. Adapted with permission from [62]; (D) Productivity of butenes from 1,3-butadiene using pure Cu/Al_2O_3, pure Pt/Al_2O_3, and bimetallic PtCu/Al_2O_3 catalysts. Pure Pt/Al_2O_3 shows the highest rate on a per Pt basis, provided that the temperature is sufficiently low to mitigate unselective paths towards butane. Adapted with permission from [62]; In both PtAu and PtCu examples, highest productivity to the desired product is attained compared to the monometallic counterparts thanks, primarily, to enhanced selectivity when Pt is atomically dispersed.

mechanisms between the metal and the support (see Fig. 4), the activity of single atoms is, in these cases, often low when compared to a) metal clusters [65–68], and b) single atoms on redox active materials, such as CeO_2 [69–71] or FeO_x [72]. For example, the vast majority of single Pt atoms reported in the literature require the temperature to exceed 80–100 °C, when CeO_2 is the support [70,73], and 160–180 °C, when Al_2O_3 is the support [74], to reach TOFs greater than 0.025 s^{-1} for the CO oxidation reaction, something that Pt clusters and small

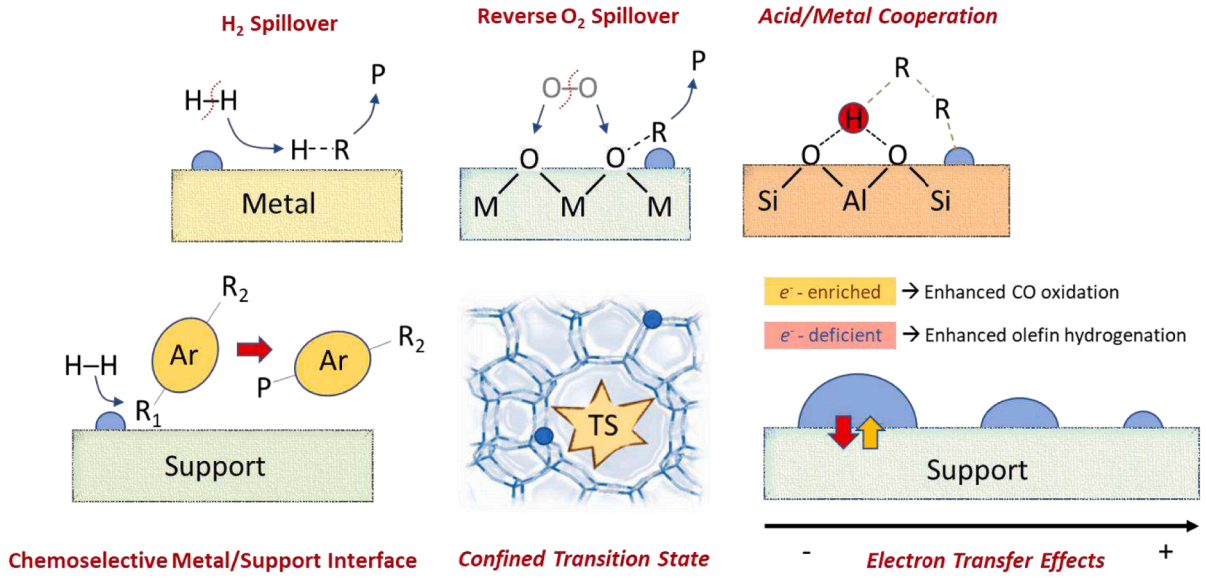

Fig. 4. Schematic representation of the cooperation between single atoms and supports that often results in enhanced catalytic performance. H_2 spillover (in hydrogenation reactions), reverse O_2 spillover (in oxidation reactions), acid/metal cooperation, and chemoselective activation of specific functional groups at the metal/metal support interface are examples of bifunctional catalysis with critical participation of the support as a co-catalyst. Confinement effects in microporous materials (stabilization of the reaction transition state, TS, via Van-der-Waals interactions) and electron-transfer phenomena between the metal and the support are also prominent mechanisms to boost the activity of single metal atoms and small metal clusters. Blue circles in these pictures represent the supported metal species; "Ar" is an aryl group, as in the chemoselective hydrogenation of nitroaromatic compounds. "R" represents a reactant, and "P" a product. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nanoparticles can accomplish below 50 °C [68]. Accordingly, it has been shown that the key to highly active Pt on CeO_2 for the CO oxidation reaction is to avoid ceria terminations that are particularly good at the stabilization of single atoms under the selected reactive conditions [69]. This result is in agreement with previous reports showing that Pt and Pd catalysts deactivate in other oxidation reactions (e.g. combustion of methane) if clusters and/or small nanoparticles undergo oxidative fragmentation into single atoms [75,76].

Nevertheless, the general observation that redox processes accelerate when cooperation between several metal atoms can take place (Fig. 4) does not preclude the possibility that single metal atoms see their activity enhanced, to a substantial degree, via alternative promotional mechanisms (Fig. 4). For example, the activity of single Pt atoms for the CO oxidation reaction is high using KLTL zeolite as a non-reducible support [77], with K potentially playing a promoting role [77,78]. And the CO oxidation activity of single Pt-atoms benefits from interactions with mesoporous Al_2O_3, through metal sites that bind strong enough to the support at unsaturated pentahedral Al^{3+} centers, to prevent metal aggregation, and weak enough to the CO to mitigate chemical poisoning [74]. The activity of these systems relative to those using reducible supports [29,68] is, however, still low.

On the other hand, although notable efforts were done in all these investigations to evidence the presence of single Pt atoms before, sometimes after, and rarely during the reactions, using several complimentary microscopic and spectroscopic techniques, this type of analyses faces its own challenges and limitations [79,80]. In this sense, it must be noted that the stability of single atoms on non-reducible supports is relatively low in atmospheres that include reactive species such as H_2, O_2, and CO, or H_2O [65,67,81]. The use of reducible supports mitigates this problem, but does not completely eliminate it. These phenomena constrain the reactions and reaction conditions that can be investigated without the in-situ formation of other highly active species, such as clusters or nanoparticles. A major concern in this area is that a small fraction of species in the form of small clusters or nanoparticles may be contributing significantly to the catalysis, as discussed in Section 4 of this *Review*.

The stability of metal molecules on supports tends to improve on reducible metal oxides, as they are more prone to accommodate various types of defects and oxidation states to properly charge balance extra-framework cations. The roles of these supports to a) alter the structure of the metal; b) its electronics; and/or c) contribute to the catalysis via cooperation at the metal/support periphery are well-known in catalysis, and can be described in terms of Strong Metal Support Interactions [82]. The effect of the support becomes increasingly more relevant as the size of the supported metal species decreases [9]. Accordingly, single metal atoms and clusters are particularly sensitive to changes in their chemical environment [35,44], and attempts to use the metal nuclearity as a standalone structural descriptor have shown very limited success. Interesting work by the Christopher's group clearly demonstrates the critical roles that other factors play in the catalysis by single metal atoms when supported on reducible supports [71]. This work, more specifically, correlated the activity of isolated Pt species for the CO oxidation reaction with the activation energy needed to abstract oxygen from various supports, in cases where the oxygen abstraction rate from the support, via reserve spillover, is limiting. Accordingly, isolated Pt atoms on non-reducible supports, such as Al_2O_3, showed at the bottom of the activity rank (being also 5 times less active than Pt clusters on the same solid surface) [71]. Key to ensure that Pt stays as a single atom throughout the reaction in these examples was the development of an interesting synthesis method to deposit ~1 precious metal atom per support particle [71].

The potential critical role of reducible supports in the activity of single metal atoms is also illustrated in CO oxidation reactions by Pt on CeO_2 [69,73] or FeO_x [29], after the realization that these supports can act as co-catalysts following a Mars-van-Krevelen mechanism (Fig. 6) [83–85]. This cooperative mechanism is reminiscent of that previously reported for the CO oxidation reaction by Au on CeO_2, where nanocrystalline (i.e. defective) CeO_2 acts as a strong activity promoter [86]. Similarly, single Pt atoms on FeO_x appear to be highly active for the hydrogenation of nitroaromatic compounds [72], in a reaction that benefits from the presence of this support to facilitate the activation of the $–NO_2$ group [87,88].

In summary, SACs and SAC alloys have been reported as highly active redox catalysts, but only in cases where effective cooperation between the single atom and the support is facilitated via bifunctional catalysis that occurs at the metal/support interface. Fig. 4 compiles most relevant mechanisms to promote the activity of atomically dispersed supported metal atoms. Fig. 5, on the other hand, qualitatively benchmarks the activity and selectivity of prototypical catalyst configurations in several reactions of interest.

3.1.2.3. Supported metal clusters. As discussed above, most active redox catalysts often involve more than one metal atom to carry out the chemical reaction. This can be inferred using model catalysts in low temperature hydrogenation reactions [66], as well as in high temperature oxidations [65,68,76].

In addition to CO oxidation examples in section 3.1.2.2 (see also Fig. 7), it has been demonstrated that the combustion of methane by single Pt and Pd atoms on CHA zeolite and Al_2O_3, respectively, happens at lower rates relative to nanoparticles on these same supports [75,76]. Indeed, the *in-situ* formation of single atoms, from small clusters that undergo oxidative fragmentation in O_2 at high temperatures [81], is a form of catalyst deactivation [75,76]. In agreement, isolated Pd is also less active than 2D Pd rafts on CeO_2 for this reaction [89].

On the other hand, it has been also observed that Cu dimers are more active than isolated Cu for the partial oxidation of methane to methanol in CHA zeolite [90], and more active for the SSR reaction according to recent reports, where Cu-O-Cu moieties that form under reaction conditions and are, thus, hard to identify, revealed as the true active sites (Fig. 8) [91].

Literature also reports multiple examples of hydrogenation, oxidation, and coupling reactions that occur faster on small metal clusters compared to not only single metal atoms, but also metal nanoparticles. These examples may not follow classical structure-sensitivity correlations obtained with nanoparticles larger than 2 nm (related to differences in crystallographic planes, or ratio of coordinated to uncoordinated sites step or corner sites). For example, the activity of Au clusters for the oxidation of styrene and cyclohexane peaks at < 100 Au atoms on SiO_2 and HAP (hydroxyapatite), respectively [40,41]; the TOF of SiO_2-supported Pt_{13} is at least 3 times higher than that of a Pt (1 1 1) surface for the hydrogenation of ethylene [42]; and Pt dimers on graphene are several times more active than Pt nanoparticles on SiO_2 in the dehydrogenation of ammonia borane [43]. Moreover, subnanometric Pt clusters in Pt/CHA and Pt-K-MFI catalysts are more than 2 orders of magnitude more active than single Pt atoms and 2 nm Pt nanoparticles in O_2 scrambling reactions, leading to a singular case of ultra-sensible catalytic response to the metal nuclearity [76].

It is worth noting that outstanding cluster catalysis has been also observed in solution (with unsupported metal species) for a number of C-C, C-N and C-O bond formation reactions that take place at low temperature. Low temperature and extremely low metal concentration in the solution (in the order of ppm levels) [38,39] are key to promote the formation of clusters that benefit from high flexibility to adopt optimal 3D configurations, the ability to engage several metal atoms to cooperate throughout the catalytic cycles and, probably, the possibility to change the metal nuclearity at various points of the catalytic cycle, so extraordinary activity can be delivered [38,39].

For more comprehensive recent reviews of catalysis by metal clusters, see [8,92,93].

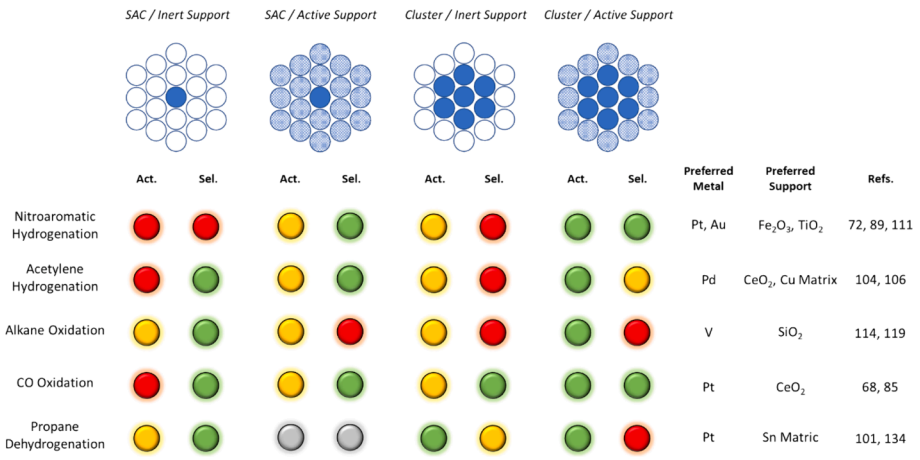

Fig. 5. Top: Schematic representation of various catalyst configurations. Solid blue circles represent atoms of a catalytically active metal. Empty circles are neighboring atoms of elements that can be considered inert for the reaction in hands. Patterned blue circles are neighboring atoms of elements that act as co-catalysts for the reaction in hands; Bottom: Qualitative raking of activity and selectivity for several reactions of interest, as a function of the catalyst structure. Green circles denote highest activity and/or selectivity on a relative basis. Yellow denotes intermediate activity and/or selectivity. Red denotes lowest activity and/or selectivity. Gray denotes insufficient information available to make an assessment. (See above-mentioned references for further information.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

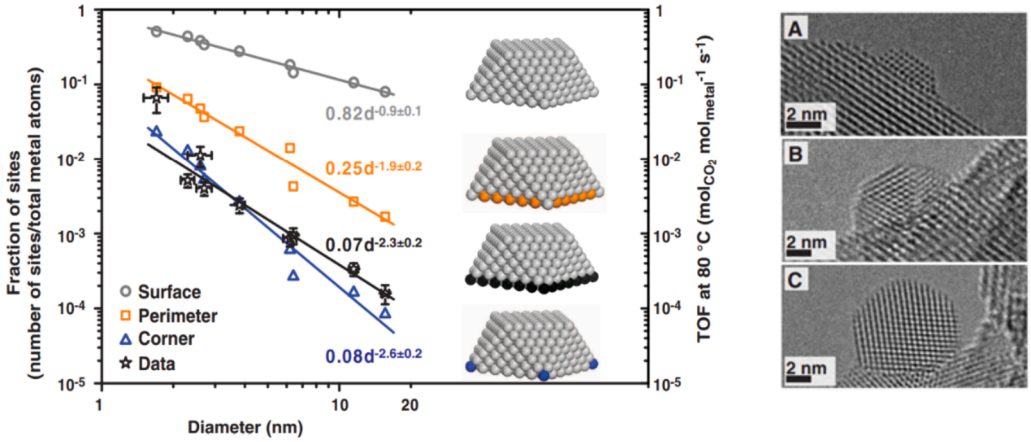

Fig. 6. (Left) Calculated number of sites for various particle geometries (surface, perimeter, or corner atoms in contact with the support) as a function of the diameter and TOF for the CO oxidation reaction [84]. Experimental data indicates that Pt atoms in direct contact with the support (periphery) are the active species under the selected reaction conditions, consistent with a reverse O spillover mechanism from the CeO_2 support; (Right) HRTEM images of supported Pt nanoparticles of variable geometry. Adapted with permission from [84].

3.2. Selectivity

Downsizing the nuclearity of the active site to one or only a few metal atoms often results in selectivity benefits. This generalization finds roots in the orbitals theory, by which geometric (crystallographic) factors and band gap properties determine the interactions between adsorbates and metals in extended metal surfaces, whereas the interactions with single atoms and small clusters occur throughout well-defined molecular orbitals, which are more sensitive to subtle changes in the structure of the active site (basically, the transition state of the various possible reactions is more likely to be different, raising a selectivity difference). Additionally, uniformity in catalysts made with all active sites identical, when accomplished, further enhances the selectivity compared to catalysts made of a variety of species. These concepts are empirically backed-up by literature examples, as discussed next.

Many reactions necessitate a critical dimensionality (i.e. a minimum size of uninterrupted metal–metal bonds) to proceed at a meaningful rate. This principle regulates the chemistry of relevant processes, for example, hydrogenolysis and coking reactions of alkanes on Pt surfaces [94–96], or the hydrogenation of aromatics and double bonds [87,97,98]. As a result, pure Pt nanoparticles show low selectivity and fast deactivation in alkane dehydrogenation reactions, because coke accumulates faster on the catalyst surface. This problem has been traditionally mitigated by including a second *inert* element such as Sn to disrupt the Pt-Pt periodicity [95,99]. A boundary condition is found when all Pt atoms are fully isolated within the Sn matrix, which leads to high selectivity and low time-on-stream deactivation for the propane dehydrogenation reaction [100]. Similar results have been obtained with other Pt-SAC alloys with Cu [60] or Ga [101] as the periodic matrix. Although the dehydrogenation activity of a fresh single Pt atom (i.e. at time ~ 0) is inferior to that of a fresh Pt atom bonded to other Pt atoms, the selectivity is certainly superior due to the mitigation of hydrogenolysis and coking reactions. In agreement with this structure-performance correlation, Zhang et al. recently reported that single Pt atoms supported on Al_2O_3, without any Sn, deactivate less, and are more selective than Pt nanoparticles for the PDH reaction [94]. The difference in the deactivation rate can, moreover, cause that single atom catalysts (or single alloy catalysts) appear more active at long TOS, once steady-state conditions have been reached.

On the other hand, the lower affinity between certain functional

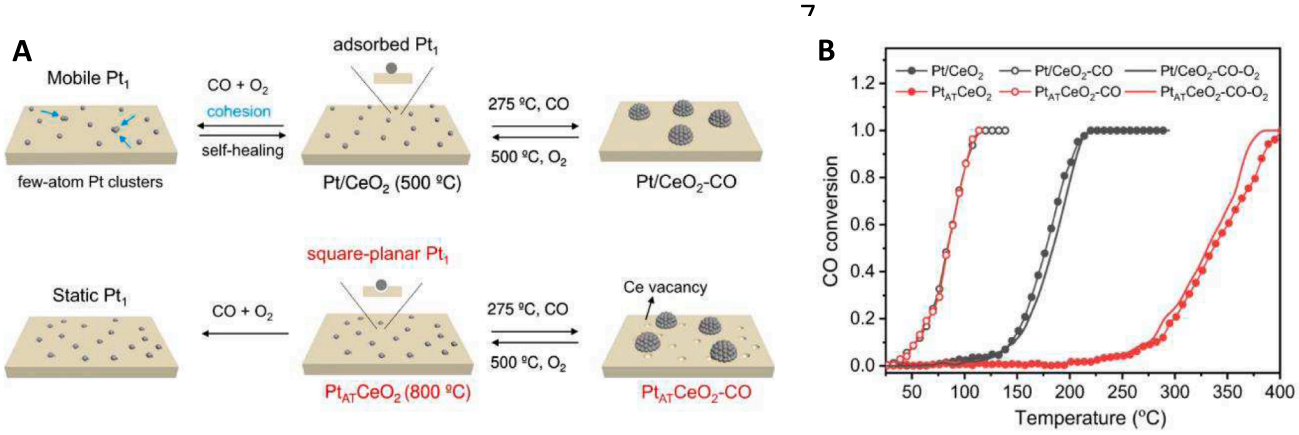

Fig. 7. (A) Schematic representation of Pt species on the surface of CeO_2 as a function of the gas composition. Reproduced with permission from [68]. (B) CO conversion in CO + O_2 mixtures as a function of the reaction temperature for catalysts with variable Pt speciation. Reproduced with permission from [68]. Activity shows highest after pre-treatment in CO due to the formation of Pt clusters and nanoparticles, and catalyst deactivates upon high temperature treatment in O_2 due to reversible formation of (less active) single Pt atoms.

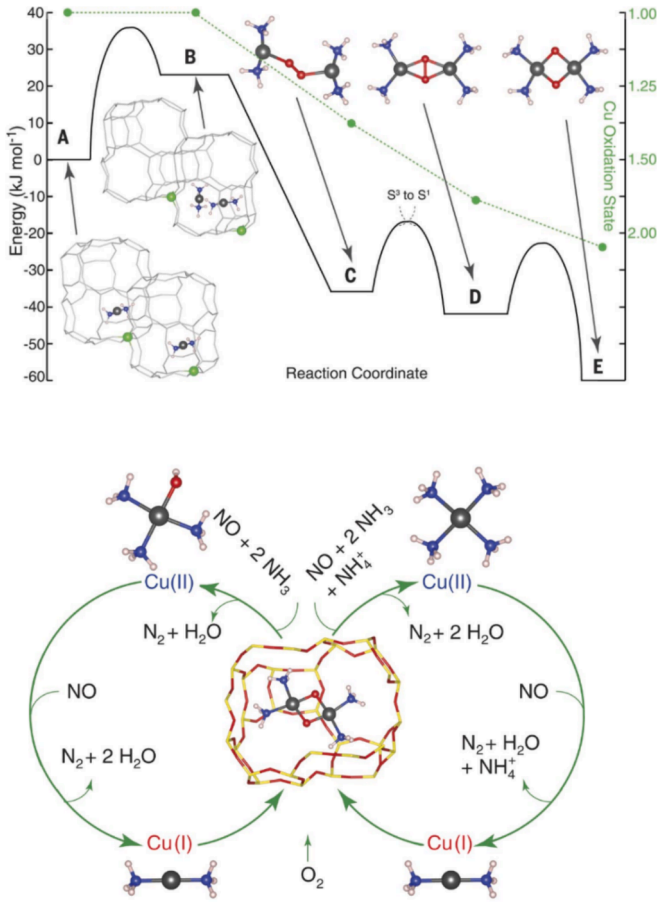

Fig. 8. (Top) Energy profile in the transformation of isolated Cu cations into dimeric Cu clusters inside CHA zeolites, in the presence of O_2 and NH_3; (Bottom) Proposed catalytic cycle for the SCR reaction using the Cu/CHA system, involving the participation of dimeric Cu sites. Adapted with permission from [91].

groups and metal particles of decreasing size is the basis for the high selectivity recently reported with several SACs. For example, while typical Pd nanoparticles are rather selective in semi hydrogenations of acetylene and 1,3-butadiene, being commercially practiced [102], recent studies have revealed that the selectivity becomes maximum if direct Pd-Pd bonds are avoided, either through Pd-SAC alloys (e.g. Pd embedded in Cu [103], or Ag [104]), or single Pd atoms on CeO_2 [105]. This inference is well-aligned with theoretical DFT studies on intermetallic Pd compounds demonstrating that Pd-Pd-Pd sites are responsible for the loss of selectivity (to ethane) in the acetylene hydrogenation, and that the ethylene-to-ethane transformation does not occur at a measurable rate on Pd-Zn-Pd ensembles [106]. The effect of the metal nuclearity becomes even more apparent when the catalyst is based on elements traditionally regarded as unselective, such as Pt [74,107] or Rh [108,109], which may see their selectivity improved from less than 50 % to greater than 98 %, in the case of Rh.

Another reaction whose selectivity improves with the presence of single metal atoms is the chemoselective hydrogenation of nitroaromatic compounds [72]. The mechanism to turn unselective Pt, Ni or Ru into highly selective catalysts was first elucidated using large metal nanoparticles [110], based on the observation that moieties such as C = O, C = C, or C≡C bonds are more (negatively) affected by the loss of terrace sites in particles of decreasing size, relative to the $–NO_2$ group. Accordingly, protocols to selectively eliminate those highly coordinated metal positions, without affecting uncoordinated species at corners and steps of the nanoparticles, showed successful to control the selectivity. Control of the particles size, and the incorporation of surface modifiers were the first reported methods to boost the nitro reduction selectivity [110–112] and, more recently, catalysts made to restrict the size of the metal–metal ensemble to a single-atom, as in the case of the Pt_1 on Fe_2O_3, have been also demonstrated to obey this general catalyst design principle [72].

The second big block of reactions whose selectivity benefits from the nuclearity of single-metal atoms and small clusters are aerobic oxidations. For example, supported single site V species are more selective than polymeric V for the oxidative dehydrogenation (ODH) of alkanes [113]; Cu dimers inside zeolites are more selective for the catalytic partial oxidation of methane to methanol compared to Cu nanoparticles [90]; and Cu cations [114–116], or dimers [91], inside zeolites selectively catalyze the SRC reaction in mixtures of NH_3, NO_x and O_2, under conditions where CuO_x particles favor the combustion of NH_3 [117]. In these systems, the lack of multiple neighboring metal sites limits the number of O atoms locally available to run consecutive hydrogen abstractions and/or oxygen insertions before the desired reaction intermediate can be released. Accordingly, one can turn polymeric VO_x species, unselective for the propane ODH reaction, into more selective sites by using N_2O instead of O_2 as the oxidant, because then a) the concentration of neighboring surface oxygen atoms throughout the vanadium reduction/oxidation cycle is diminished, given the lower

oxidation potential of N_2O vs O_2; and b) only one, instead or two, O atoms are engaged in each oxidation event [118]. Nonetheless, arguments like these only explain selectivity loses that happen via primary reaction routes, that is, at low conversion of the reactant, and the battle to turn down the overoxidation of valuable, but unstable, products such as propylene or methanol remains unsettled when the conversion is high.

Finally, it must be clarified that the metal nuclearity is not a standalone selectivity performance descriptor either. Other factors, such as the active site electron-density, and roles that the support itself may play in the catalysis, can also induce fundamental changes to the reaction mechanisms and, thus, the selectivity. For example, in the above Pt_1/Fe_2O_3 example for the hydrogenation of 3-nitrostyrene, it is expected that the selectivity to react the nitro group is enhanced by the support, taking into account that the catalysis likely occurs at the metal/support interface [110,111]. On the other hand, in comparisons between Ru $(C_2H_4)_2$ and $Rh(C_2H_4)_2$ species, grafted to either HY zeolite or MgO, and reacted with ethylene and H_2 at low temperature (<60C), the Gates group demonstrated that electron-rich isolated metal species (on MgO) catalyze the C = C bond hydrogenation with a selectivity of 100 %, whereas electron-deficient, structurally analogous, sites on the zeolite yield butenes via dimerization with selectivities greater than 70 % under otherwise identical reaction conditions [119,120]. Whether the unusual olefin dimerization behavior of Rh and Ru, in the presence of H_2, is due to an electronic-effect [121,122] or a concerted action between single-atoms and nearby acidic Al-OH centers [123,124] is still under debate.

3.3. Stability

Today, a handful of samples are able to maintain single atoms and/or subnanometric clusters of noble metals in reactive atmospheres such as O_2, H_2, H_2O or CO at elevated temperatures. This stability issue has largely limited our capacity to understand these types of species in multiple reactions of interest. Recent successes to synthesize, and hold, subnanometric noble metal sites on solid supports are the outcome of years of research to unravel the mechanisms behind complex surface chemistries. Even then, the general principles that would allow full control of supported metal molecules, very particularly with nuclearities between 2 and ~ 100, remain elusive. Here, we summarize a journey that many of us had to take to tame active species that persevered to misbehave.

3.3.1. Stability in O_2

Most supported metal catalysts incorporate single noble metal atoms after their synthesis, when they are still bonded to ligands from the corresponding metal precursors. Supported metal catalysts, however, are usually treated at high temperature prior to reaction to a) eliminate these ligands, which can poison the active site and/or speed up side reactions, and b) stabilize the active sites under conditions close to the reaction conditions. Most commonly, activation protocols involve a first activation step in O_2, air, or diluted O_2, through a process that consolidates large (reduced or oxidized) metal aggregates for elements in groups VIII to XI (e.g. Pt, Rh, Pd, Au, Ir, Ru, Ag). Sintering in O_2 denotes the lack of stable structures conformed by a *bare*, isolated metal cation bonded to oxygen atoms of the support. Oxophilic elements such as V, Mo, Cr, W, Fe or W are, in contrast, more prone to stabilize as single atoms in O_2 on most supports, including non-reducible supports, provided that the metal loading is sufficiently low (relative to the availability of surface anchoring sites). It is worth noting that these metals, in general, can adopt more oxidation states compared to noble metals, and can directly ligate to oxygen via oxo bonding (noble metals cannot [125]). Accordingly, supported single atoms of elements such as V [113,126], Mo [127], or Fe [128] are a prolific research area in oxidation catalysis.

To stabilize single atoms and tiny clusters of elements like Rh, Cu, Pt, Ag or Au, the support must be designed carefully to accommodate the corresponding metal cation favorably. Because oxo ligands are prohibited in most of these cases, all charge compensation in O_2 must be provided by the support (although the presence of water and hydroxyl ligands bonded to metals add another layer of complexity). Typically, redox active supports are the preferred choice for stabilization of cations of noble metals, because their atoms can shuttle between oxidation states, and they can host different defects to neutralize surface charge. Nevertheless, the surface termination of metal oxides is complex, and hard to control, and optimization of their properties has been mostly empirical. For example, treatment of Pt/CeO_2 ⟨1 0 0⟩ in O_2 at 800C leads to square-planar Pt species within 4-oxygen pockets that hold the single atoms more tightly than other ceria surfaces [70]. The process by which CeO_2 rearranges around Pt at 800C to deliver these pockets is not fully understood yet. At lower activation temperatures, the surface of ceria is less likely to rearrange, and the amount of single metal atoms that a given surface can host is a function of the specific surface area and the degree of defectiveness. Single atoms can be obtained when the metal-to-binding site ratio is below 1. Higher metal loadings typically lead to small metal clusters, or metal rafts [89]. Further growth is usually hindered by virtue of SMSI effects that favor wettability of the surface over the formation of large 3D structures [82]. Also, while single atoms of noble metals on reducible metals oxides appear rather stable in O_2, they are less stable in reducing atmospheres (e.g. in the presence of H_2 or CO), which tends to lead to mixtures of single atoms and small clusters on the catalyst surface (see Section 3.3.2).

On non-reducible supports such as silica, Al_2O_3 or zeolites, alternative charge compensation mechanisms must be stimulated to stabilize cationic species of elements such as Pt, Rh or Pt. To introduce negative charges on these supports, framework atoms of a specific valence can be replaced by elements of another valence, creating the need for an extra-framework counterion charge compensation. This case is well-known in zeolites made to incorporate 3 + valence elements (e.g. Al, Ga, Fe) replacing Si^{4+}, which leads to negatively charged binding sites that can host monocationic species such as Na^+, H^+, or NH^{4+}. A breakthrough discovery was made when the amount and proximity of tri-valent elements such as Al was controlled to maximize the presence of Al pairs [129], bringing two negative charges close enough to stabilize isolated dicationic metal sites such as Pt^{2+} and Pd^{2+} [130], as well as other multimetal dicationic species such as $(Cu\text{-}O\text{-}Cu)^{2+}$ dimers [129].

Controlling the nuclearity of noble metal clusters in O_2 is, on the other hand, an even greater challenge, because small clusters tend to evolve into either single atoms or larger nanoparticles when subjected to moderate temperatures. Ostwald ripening sintering, a process by which metal particles grow at the expense of small clusters, is indeed the result of single atoms spilling over supports that cannot intercept and stabilize metal cations before finding large particles. For Pt on CHA zeolite, the re-dispersion temperature is lower than 100 °C when the cluster size is lower than 1 nm [130]. To attain stable metal–metal bonds at higher T in O_2, the metal cluster size must increase. It is believed that 500 °C is sufficient to re-disperse particles of, at least, 2 nm [130]. Looking at the catalytic properties of noble metal active sites with nuclearities between 2 to a few dozens of atoms is, thus, challenging, more so when the reaction temperature is high. The observation that small metal clusters of Pt, for example, show distinct (enhanced) oxidation activity relative to single Pt atoms and > 1 nm nanoparticles boost the motivation to further investigate this field.

3.3.2. Stability in H_2

Supported single noble metal cations (e.g. Pt^{2+}, Pd^{2+}, Rh^+, Ir^+) typically reduce at temperatures below 150 °C in H_2. This can be demonstrated in Temperature Programmed Reduction (TPR) or in situ XANES experiments that look at changes in the metal oxidation state, and microscopy or EXAFS experiments that evidence the formation of metal–metal bonds. The temperature (or rate) at which a particular noble metal cation reduces in H_2 depends on various factors, most importantly, the types of ligands bonded to it, including the support. In

general, it is accepted that H_2 weakens the interaction between noble metals and supports, promoting collisions that yield reduced clusters and/or nanoparticles (more stable from a thermodynamic standpoint, at least in H_2). The sintering process is a direct consequence of the incapacity of that metal/support combination to form any stable single-atom species upon reaction with the H_2. The stability of a single metal atom in H_2 is closely related to the strength of the metal/support interaction, but also the reactivity of other labile ligands that might be present. For example, CO ligands bonded to isolated Rh atoms on HY or MgO do not react with H_2 before $Rh(CO)_2$ fragments migrate and form clusters at temperatures that correlate well with the metal/support binding energy (e.g. stronger on electron-withdrawing HY zeolite than on electron-donating MgO) [131]. In this case, HY imparts stability to $Rh(CO)_2$, more so than MgO. In contrast, $Rh(C_2H_4)_2$, a 16 e^- species, readily reacts with H_2 to form $Rh(C_2H_6)_2$, a less stable 14 e^- species, through a process that is accelerated on HY zeolite compared to MgO [131]. Consequently, $Rh(C_2H_4)_2$, a different single Rh atom species, is more stable on MgO than on HY zeolite.

For high temperature hydrogenations (e.g. > 400 °C), however, most single atoms of noble metals evolve into metal clusters. As a result, most research discussing the catalytic behavior of single noble metal atoms in H_2 refers to low temperature reactions such as acetylene, 1,3-butadiene, and nitroaromatic compounds hydrogenations (*vide supra*). SAC-alloy catalysts (e.g. single Pt atoms at terrace positions of Cu [60] or Sn [100] crystals) are a notable exception, which have been shown stable at > 500 °C for alkane dehydrogenation reactions, as discussed above.

Metals stop sintering once they reach a critical size at a given temperature. That critical size is highly dependent on the interaction with the support, being, in general, smaller on reducible metal oxides thanks to *SMSI* effects. Rising the temperature in H_2 tends to increase the particle size, as forces that prevent Brownian motion (i.e. coalescence) are overcome. Luckily, supports can be engineered to boost the metal/support interaction, so the sintering degree can be controlled. Besides SMSI effects, on supports such as CeO_2, TiO_2, or Fe_2O_3, the use of alkali promoters [132,133] and encapsulation strategies [81,134,135] have been successfully applied to limit the metal growth. Nevertheless, limiting the cluster size to < 1 nm at high temperatures (i.e. > 600 °C) is still extremely challenging. A notable exception are subnanometric Pt nanoparticles inside K-MFI zeolite, which do not only retain low nuclearity in H_2 at high temperature, but continue to do so after consecutive oxidation/reduction cycles at 600 °C [133,136]. A key to resist harsh cyclic redox treatments is the ability of the sample to undergo reversible cluster formation/cluster fragmentation transformations. This performance relies on a dual role of the support to limit both Ostwald-ripening (in O_2) and coalescence (in H_2) mechanisms Fig. 9 [81,130]. Pt/CHA, Pt/CeO_2, and Pt-K-MFI exemplify this behavior, attending to distinct properties. On the one hand, small cage-like zeolites limit the H_2 sintering process due to effective encapsulation of small nanoparticles, whereas the sintering in O_2 is limited thanks to the presence of Al pairs [76,130]. CeO_2, on the other hand, promotes SMSI effects in H_2 and traps single Pt atoms at surface defects [69,70]. And K-MFI uses alkali to promote the formation of silanol/siloxy nests that can trap metal atoms and subnanometric clusters in H_2 and O_2, respectively [136,137].

4. Catalysis by supported molecular metal catalysts: Open challenges

4.1. Challenges in the identification of the active site (Characterization Challenges)

To prove, beyond reasonable doubt, that a particular type of species is the main contributor to the catalysis of a given reaction is challenging with supported molecular metal catalysts. This is a natural consequence of a) the large variability in performance that can occur as a result of subtle changes in the structure of the active sites; b) the lack of uniformity in common supported catalysts, including the lack of uniformity of the support; and c) the lack of precise characterization to describe all key structural properties in a quantitative manner. Following these arguments, Prof. Gates championed the idea that well-defined model catalysts, and probe reactions, are most useful to build-up unambiguous structure-performance correlation [4,5,9,31,33,66,93].

Recently, notable efforts have been done to explore the catalytic properties of single atoms of elements that are otherwise highly active when in the form of conventional metal nanoparticles. Examples of these are Pt and Pd [8,10]. The problematic to discern what type of species (i.e. single atoms vs clusters) is most adequate in a given reaction is slippery. Arguments can be found in the literature to support either hypothesis, even when other catalyst parameters, such as the support, are kept constant (see, for example, Pt on CeO_2) [68,69]. A legitimate question is whether those cases where outstanding reactivity is observed are truly the result of exceptional single-atom/support architectures or, otherwise, are a strong indication of other highly active sites present, such as metal clusters, that may form as hard-to-detect minority species under reaction conditions. Authors are sometimes cautious enough to acknowledge that unconventional metal arrangements "similar" to single atoms of an element, but not quite, might be behind the high activities reported. For example, Wei et al describe their highly active nitroaromatic hydrogenation Pt_1/Fe_2O_3 catalyst as a single or *pseudo*-single atom catalyst, and they define the term 'pseudo-single-atom catalyst' as "a special structure composed of a few to tens of atoms that are loosely and randomly associated with each other, but do not form strong metallic bonds, and thus show structure and function similar to that of isolated single atoms" [11].

Detection of "impurity" levels of highly active species is, and has historically been, a big problem in catalysis. This is, in part, because of obvious limitations to work near the detection limit of the corresponding characterization techniques, and the difficulty to deconvolute small from large spectroscopic signals. Moreover, nuances around single atoms and small metal clusters complicate the creation of standardized characterization protocols exempt of over- or mis-interpretation.

In general, several complimentary techniques are needed to rule out

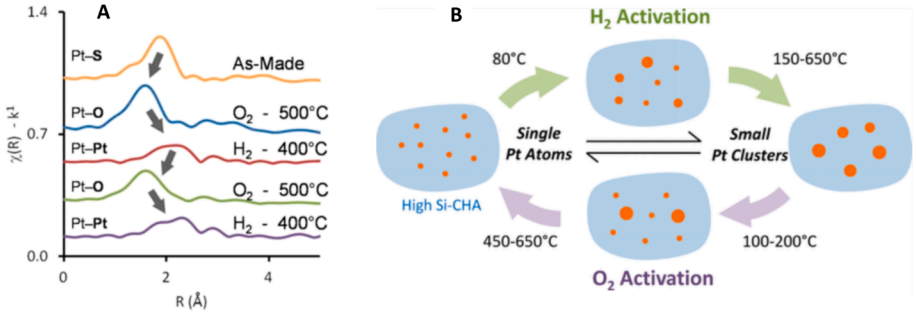

Fig. 9. (A) EXAFS results in the R-space obtained at the Pt LIII-edge characterizing single metal atoms (in O_2) and small metal clusters (in H_2) at high temperature; (B) Schematic representation of the reversible transformation of single atoms into clusters inside Al-paired CHA zeolite. Adapted with permission from [81].

the presence of clusters in a sample, and only when *all* data is fully consistent, a prudent inference can be made (reasons for prudence depicted below). For example, in the case of Pt on nanoCeO_2 as a highly active CO oxidation catalyst [73], it was reported that the activity boost occurs after reduction of the metal in H_2 at 300 °C, showed by XANES, through a process that did not lead to the formation of metal–metal bonds, according to EXAFS, HAADF-STEM, and FT-IR. Arguments to claim that the observed activity is due to isolated Pt atoms are, thus, as solid as the combination of these state-of-the-art characterization techniques is. The observation simply has to co-exist with the other general inferences from the literature, more specifically, that a) the stabilization of single Pt atoms in H_2 at these rather high temperatures is rather exceptional; and b) clusters and small nanoparticles of Pt are usually more active than single atoms, as discussed above.

Another illustrative example of unanticipated catalytic behavior by single metal atoms was reported in [76], where Pt atoms on non-reducible supports, including CHA and K-MFI zeolites, were shown active in isotopic O_2 exchange experiments. After a high temperature treatment in O_2, these samples showed the lack of metal–metal bonds by EXAFS and STEM microscopy, within the limitations of the techniques [81,133], being active in the O_2 scrambling reaction at 400 °C. How the activation of two O_2 molecules happens on a highly oxidized, isolated Pt cation, or even whether the catalysis truly occurs on a single Pt atom, remains uncertain. The possibility that hard-to-detect, minority Pt clusters (or short-lived clusters that arise from collisions of O-carrying species) are responsible for the isotopic exchange cannot be completely ruled out.

To understand the challenges in the identification of the active site in supported molecular metal catalysts, it is also important to understand the limitations and challenges of most common characterization techniques. On the one hand, microscopies, such as STEM or TEM, only provide local information of a minuscule subset of particles in the material, being thus susceptible to sampling biases. EXAFS, on the other hand, can miss up to 5 % of the metal due to detection sensitivity issues. Bare et al., more specifically, have nicely demonstrated that metal–metal signals in catalysts with less than 5 % nanoparticles (in weight) are hardly distinguishable from the noise, giving the appearance that only single atoms are present [80]. And analyses of FTIR spectra of CO-probed catalysts sometimes overlook tails around main absorption peaks, ignoring that a plethora of active sites are in reality present. For example, peaks centered at > 2090 cm^{-1} are often invoked to evidence the presence of single cationic species in Pt catalysts, without taking into consideration that tails below 2075 cm^{-1} likely denote the co-existence of Pt nanoparticles [69,74]. Moreover, IR peaks of CO bonded to single metal atoms are extremely sensitive to electronic effects beyond the metal nuclearity, with changes in the wavenumber as large as $\sim$ 40c [124], which makes the resolution of electronic vs geometric difficult.

X-Ray electron-beam damage and other modifications of the catalyst during the experiment are also common challenges in the characterization of metal clusters and single atoms, given their highly mobile nature. The sole exposure of the sample to the ambient (i.e. O_2 and moisture at room temperature) after a particular activation or reaction treatment may induce structural rearrangement of the active sites prior to the characterization measurement. This complication can be avoided by *in-situ* or *operando* characterization methods, or following air-tight transfer protocols (e.g. use of glove boxes, Schlenk lines, etc.). Even then, probe molecules used to characterize the metal with some techniques, e.g. CO in FTIR analyses, can promote undesired metal–metal bond formation [130] or metal–metal bond scissoring [138]. For instance, small Rh or Ir clusters supported on HY zeolite oxidatively fragment under a pulse of CO at room temperature, leading to Rh_1 *gem*-dicarbonyl species and, thus, the wrong impression that the catalyst consists of single metal atoms [138]. While measures to prevent these phenomena can be put in place (e.g. low temperature dosing), protocols are not always rigorously applied, and/or have simply not been stablished for all cases of study.

The challenge to characterize molecular metal sites toughens under working conditions, because most techniques do not allow to properly replicate the atmospheres present in common reactors, particularly at high temperatures or pressures, or with liquids. Variations in the performance of molecular metal catalysts with time (as a reaction takes place, or after catalyst regeneration) are clear indicators of dynamic changes in the active site structure. Particular care should be placed to rule out changes in the nuclearity of molecular metal species in these cases before unanticipated activity descriptors are invoked.

Table 2 compiles a few indicators and best practices that authors and readers can use to assess the strength of the experimental evidences.

4.2. Challenges in the industrial implementation of supported molecular metal catalysts

From a practical standpoint, the number of commercial processes that use supported single metal atoms and/or metal clusters as catalysts is still very limited. Although these types of sites are likely present in commercial supported metal catalysts, as minority species, very few examples rely exclusively on atomically or *quasi* atomically dispersed metals to attain commercial success. Notable exceptions can be found, including site-isolated Ti atoms in framework positions of zeolites and porous silicates, applied commercially in epoxidation processes [140], and Cu_1/zeolites, used for the abatement of NO_x in diesel vehicles [141]. It must be noted, however, that the discovery of these systems date back to the late 80 s [24,26], happening thus more than 20 years before the term SAC was coined [29]It is indeed generally agreed that SACs and supported metals clusters, as such, are in their infancy, and that it will take years before they are broadly applied in industrial processes [142–144]. Not without reason, the typical timeline to commercialize technology in the energy and commodity chemicals sectors is greater than 30 years [145]and the commercialization of Ti-silicates and Cu/zeolites for olefin epoxidation and NO_x abatement reactions needed, more specifically, between 20 to 30 years after the initial discoveries were made. Moreover, the acceptance of single-atoms and metal clusters as industrial catalysts is not exempt of risk aversion challenges to enter spaces where conventional supported metal catalysts and classical unsupported metal catalysts perform already reasonably well, in high temperature, gas-phase processes and solution chemistry, respectively. Incremental improvements over existent (mature) technology will be likely disregarded by the industry in the short- and mid-term in light of multiple risks associated with the scale-up and long-term stability of the technology. Tolerance to risk would improve, in contrast, in the event of breakthrough discoveries able to unlock disruptive technologies.

With regards to catalyst manufacturing scalability, some of the methodologies used to produce atomically dispersed metal catalysts in the laboratory are, simply, too costly or unfeasible for large-scale catalyst productions. Catalyst cost is a hard-to-recuperate capital expense in projects with narrow annual returns, for example in the commodity chemicals business. In this sector, aqueous wetness impregnation is the gold standard metal deposition method, which uses relatively affordable metal salts (relative to methods that require elaborated ligands) and generates very little waste water as a by-product. Any alternative that increases the cost of production cost, such as atomic-layer deposition, mass-selected soft-landing methods, or photochemical syntheses, sometimes employed to prepare well-defined SACs and supported metal clusters, will need to attain beyond marginal improvement of the long-term returns before they can be industrially adopted. Specialty chemicals and pharmaceutical sectors, in contrast, are less sensitive to the catalyst cost, as they produce high added-value molecules, but are at the same time less receptive to the replacement of their classical well-defined organometallic catalysts by supported metal systems, and the reality is that the latter have not become widely spread in this sector yet.

On the other hand, long-term stability is a major challenge for the industrial application of supported metal molecules (single atoms and clusters), in cases where the targeted performance truly requires high

Table 2
Tips in the evaluation of common techniques for the characterization of supported single metal atoms and small metal clusters.

Technique	Scenario	Challenge	Risk	Recommendations
All	Lack of characterization after reaction	Single metal atoms and small metal clusters have been shown unstable in a number of atmospheres (typically at high temperature and/or pressure).	Misrepresentation of catalytic structures present during catalysis. Wrong structure-performance correlations.	Run always post-mortem characterization. Run isothermal reactivity tests to rule out changes in performance over time. Compare light-off activity curves of fresh vs spent samples
HRTEM/STEM	Microscopy is the only or main technique to support conclusions	Statistically meaningful STEM/TEM analysis is time consuming. Atomically supported metal species are prone to electron beam damage.	Possible unconscious sampling biases. Formation of new active sites under the microscope. Wrong structure-performance correlations.	Include FESEM images and TEM at low magnification, to estimate the density of large nanoparticles. Use low dosing techniques, and other complimentary characterization.
Vacuum techniques, including HRTEM/STEM, and XPS	Lack of in situ/*operando* characterization	Environmental cells are still relatively rare in catalysis. Attenuation of signals under pressure makes the detection of certain species challenging. Treatments inside sample holders deviate from conditions inside a typical flow reactor	Recent literature shows that *meta*-stable species may form under reaction conditions, thus, only observable if those conditions are reproduced inside the characterization cells	Seek self-consistency using alternative *operando* techniques (e.g. EXAFS and IR spectroscopy). Plan *operando* efforts as standalone, multidisciplinary research projects (in collaboration with experts in different fields)
FTIR of adsorbed CO	The center of a broad IR band is used to identify single atoms in the sample. Use of literature data to infer the metal nuclearity.	Broad bands denote complex mixtures of active sites. The position of carbonyls strongly depends on the geometry, but also the electronics of the metal species. Changes in the wavelength greater than 40 cm^{-1} are possible without a change in the active site nuclearity.	Underestimation of the roles of sites represented by those IR peaks tails. Over-emphasis of the metal nuclearity role.	Increase efforts to improve the uniformity of the sample. Confirm that trends hold true for samples with varied gradient of nuclearities. Restrict assignments to reasonably similar cases, such as those where the support is held constant.
FTIR of adsorbed CO	Contact of the sample with CO causes the active site to change	SACs and metal clusters are particularly mobile under CO, and may undergo oxidative fragmentation (clusters than convert into single atoms) or reductive sintering (atoms that convert into clusters)	Wrong assignment of the active sites nuclearity. Wrong structure-performance correlation.	Compare IR results after CO dosing at various temperatures (including < room temperature). Use other techniques to check for internal consistency.
XAS	Absence of strong metal–metal signals as the main evidence of the lack of metal clusters	M−O−M EXAFS signals are often weak (see, for example, PtO_2 spectra). Long-distance signals from several elements often lead to deconstructive wave events that mask the presence of multiple backscatterers. Intrinsic limitations of EXAFS impede to fit multiple shells with statistical significance. The coordination number and bond distance of first shell M−O bonds is often similar in single metal atoms and small metal clusters (for Pt, for example, between 4 and 6, at ~ 2 Å)	Small metal clusters mistakenly characterized as single metal atoms, or *vice versa.* In mixtures of single atoms and small metal clusters, sensitivity problems arise if less than 5 % of the metal is forming metal–metal bonds.	Use complimentary techniques. Report raw EXAFS data to evaluate quality of the obtained spectra, and follow standardized fitting protocols [139]

specificity of the active sites to remain atomically dispersed throughout the whole catalyst lifetime. In the long-term, these catalysts face strong driving forces to consolidate other thermodynamically more stable larger metal structures, following surface-mediated reactions and kinetics that are not fully understood.

As these and other uncertainties that surround SACs and supported metal clusters reduce over time with more fundamental work to unravel their idiosyncrasy, it is expected that the risk/reward ratio for industrial implementation of the technology relaxes, leading to greater adoption rates.

5. Conclusions and perspectives

The interest on single metal atoms and metal clusters for catalysis is greater than ever. The raise of examples showing distinct (often advantageous) performance relative to conventional metal nanoparticles comes hand in hand with step-up improvements in characterization methods and the incorporation of rigorous theory during the last decade. Understanding the specific mechanisms behind the mode of action of supported metal molecules is essential to ensure progress towards the resolution of long-lasting challenges in catalysis.

Although the term “single atom catalyst” was conceived to accentuate one particular property of the active site on the support, the metal nuclearity, chemical reactions rarely proceed faster on single metal atoms unless those atoms work in concert (i.e. cooperate) with other elements of the catalyst for efficient activation of the reactants and stabilization of the corresponding transition state. As a result, the outstanding catalysis observed with certain single atom catalysts is often the result of (also) outstanding co-catalysis by the support at the metal/support interface. Many of these phenomena are not exclusive of supported single atoms, but are also applicable to conventional supported nanoparticles, albeit to a lesser degree, given the decreased metal/support interaction there. Fig. 4 summarizes relevant mechanisms of the cooperation between metals and supports that affect most notably to single-atom catalysts.

On the other hand, reduced active site nuclearity does not only promote the concurrence of bifunctional activation at the metal/support interface, but can be important to avoid chemical transformations that require a critical dimensionality to proceed. In these cases, it is not what single metal atoms can do, but what they do not do, what yields a competitive advantage in the form of enhanced selectivity.

An intrinsic challenge in the investigation of supported molecular

metal catalysts is the high mobility that these species manifest when contacted with reactants at temperature and/or pressure. Consequences are not only practical (i.e. loss of the desired molecular attributes over time), but introduce fundamental challenges in the determination of the precise metal speciation that drives the catalysis under working conditions. In the case of SACs, more particularly, ruling out the presence of small amounts of other highly active species, such as metal clusters, is often difficult, due to intrinsic limitations of state-of-the-art characterization techniques.

It must not be forgotten that pioneers such as Prof. Bruce Gates broke the ice more than 40 years ago to investigate these systems under well-controlled conditions. For decades, he investigated "simple" model catalysts in "simple" model reactions, to unravel straightforward correlations between the catalyst structure and the catalyst performance. The resulting work sets the ground for several future generations of researchers, based on a series of fundamental pillars and directions [4,5,9,13,66,93]:

- Uniform materials (i.e. catalyst that avoid complex mixtures of active species) are cornerstones to improve our understanding of catalysis.
- The catalyst uniformity starts with high uniformity of the support to provide a well-defined chemical environment. In this sense, supports should be considered macro-ligands of the metal species.
- Single metal atoms and metal clusters show distinct, molecular properties that traditional nanoparticles do not show, opening the door to unanticipated catalysis.
- The catalytic behavior of single metal atoms and metal clusters is very sensitive to subtle changes in the active sites electronics and nuclearity.
- The support in molecular metal catalysts is often an active catalyst component (i.e. a co-catalyst), with distinct redox or acid/base characteristics.
- Supported SACs and metal clusters often re-structure under reaction conditions. *Operando* characterization is called to play gradually greater roles in the build-up of precise structure-performance correlations.
- Well-characterized, simple, and uniform catalysts open the door to the application of rigorous theory as part of the catalyst design workflow.

CRediT authorship contribution statement

Pedro Serna: Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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

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