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Opportunities and challenges in the development of advanced materials for emission control catalysts

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Advances in engine technologies are placing additional demands on emission control catalysts, which must now perform at lower temperatures, but at the same time be robust enough to survive harsh conditions encountered in engine exhaust. In this review, we explore some of the materials concepts that could revolutionize the technology of emission control systems. These include single atom catalysts, 2-D materials, 3-D architectures, core@shell nanoparticles derived via atomic layer deposition and via colloidal synthesis methods and microporous oxides. While these materials provide enhanced performance, they will need to overcome many challenges before they can be deployed for treating exhaust from cars and trucks. We assess the state-of-the art for catalyzing reactions related to emission control and also consider radical breakthroughs which could potentially completely transform this field.

Overview

The technology of emissions control is driven by regulations [1], which dictate the allowable limits on the emission of pollutants such as CO, NOx, hydrocarbons (HC). In parallel, CO_2 emissions from transportation systems (cars, buses & trucks, railway, marine) need to be reduced, which leads to lower exhaust temperatures and new challenges for catalytic exhaust control. Hence, exhaust emission catalysis is an active field of research for the development of advanced materials since the number of vehicles is increasing, demanding even more stringent regulations to meet air quality goals [2]. There are many reviews that describe current emission control standards and how changes in the regulatory framework could impact the technologies being developed [2-4]. This manuscript seeks to identify challenges in the catalytic transformation of pollutants that could lead to revolutionary breakthroughs in technology. Materials concepts have been proposed in recent years that promise far superior performance compared to current industry practice. Are these materials ready for deployment? What would be needed to make these materials easy to manufacture, keeping an eye on cost and the environmental impacts of the synthesis techniques? What are the challenges in making these materials suitable for withstanding real world aging conditions? We focus on identifying promising new materials synthesis routes and materials concepts and assess their prospects for integration into current industrial practice. While material costs and scalable synthesis routes are important for the deployment of advanced materials, they have not been considered here since our focus is on performance. The review will also try to sketch out some radical breakthroughs that could be enabled if new materials are developed to catalyze these reactions. Our hope is to guide researchers in these promising directions.

Figure 1 shows an ideal emission control system for gasoline and diesel engines that transforms all pollutants into CO_2, N_2 and water vapor [5]. Not shown are contaminants that come from fuels, such as S and P. To gain a perspective on the current state of technology, a good starting point is the yearly reviews by Tim Johnson, the latest one was published in 2018 [3]. Martin Twigg [6] provides an excellent account of the development of exhaust emission systems for cars, and the treatment of particulate matter from diesel exhaust [7]. Zhang et al. [8] provide a detailed account of the challenges in selective conversion of nitrogen-containing exhaust gases. Wang and Olsson [9]describe the impact of emission control catalysts on UN sustainable development goals. An excellent historical account of automobile emissions control catalysts is presented by Farrauto et al. [1]. There are other reviews that should be consulted to get a comprehensive view of recent developments in the field of emission control catalysts [10-13].

Hydrothermal aging – a necessary step for emission control materials development

As engines get more efficient, the exhaust temperature decreases, so low-temperature active catalysts are required. Typically, it is expected that conversions > 90% should be achieved by 150°C – the DOE "150 °C challenge". But the catalysts that need to be active at low temperature must also survive the harsh conditions expected during high speed driving. In recent years we see many reports of materials that demonstrate superior performance, for example in CO oxidation. However, these materials must be able to handle all the components in exhaust, at an economical price (per unit volume of catalyst, not per atom) and be thermally robust and resistant to poisons. To aid researchers, a consortium of industry and national lab researchers in the US has developed protocols for testing catalysts so their performance can be validated across multiple laboratories [14]. This reference provides specifications for how catalysts must be aged, tested in reactors and exposed to poisons such as sulfur, so that materials that are ready for deployment in exhaust systems can be developed. While academic researchers will likely not possess all of the necessary hardware to perform these tests, it is important to be cognizant of the demands that will be placed on the materials being developed.

Any new materials must be subjected to hydrothermal aging before they can be considered for further development. The first step is degreening, which involves heating to 700 °C in 10% CO_2 and 10% H_2O for gasoline engines, and the inclusion of 10% O_2 for diesel engines, with the CO_2 and H_2O contents dropped to 5 vol% [14]. This is the first level to which all catalysts should be subjected before testing for activity. Next they are subjected to aging at elevated temperatures which depend on the specific engine configuration (800 °C for 50 hours for diesel exhaust). For three-way catalysts (TWC) used in gasoline engines current industrial practice requires aging temperatures up to 1050 °C. To avoid missing out on interesting candidates, and assuming that further stability improvements will be achieved during industrial optimization, an aging temperature of 900 °C is recommended for an initial screening of new catalyst concepts [14]. It is in this context that we explore materials concepts that have been proposed in recent years. Our goal is to identify which of them might potentially meet the demands of hydrothermal aging imposed by industry protocols and provide enhanced performance.

Advanced synthesis routes for emission control catalysts

Encapsulation of catalytically active nanoparticles to avoid sintering and to maximize metal-support interfacial area

A general approach to increase stability of a catalyst is to encapsulate the catalytically active nanoparticles in an inert material so that agglomeration and sintering are avoided. Different encapsulation approaches have been proposed [15, 16]. A major challenge is to preserve the thermal stability of the encapsulating layer at the high temperatures encountered in emission control catalysts, since the layer not only should maintain its structural stability but also its porosity. Dai et al. [17] showed that the encapsulation by a SiO_2 layer improves the aging resistance of Pt nanoparticles supported on TiO_2 nanofibers. By using Pd-Ce nanowires in a SiO_2 shell, Peng et al. [18] demonstrated thermal and SO_2 aging stability for methane oxidation. Another approach is to encapsulate active metal particles in a hollow oxide sphere yielding a yolk-shell geometry [19]. However, such hollow sphere geometries result in extremely low-density materials leading to lower overall reactivity per unit volume of catalyst, which may limit application in catalytic converters.

Besides preventing sintering, nanoscale-design can also be applied to optimize the contact of different phases in cases where catalysis happens at the interface of different materials. A prototypical example of such a nano-design is shown in Figure 2a where Pd@CeO_2 catalysts were developed for CH_4 oxidation [20, 21]. Here the Pd-ceria interface is optimized by depositing Ce nanoparticles on the Pd particles. Since the reaction is believed to proceed at the Pd-ceria interface, increased methane oxidation activity is obtained (Figure 2b). Unfortunately, the ceria particles in this design proved to be insufficiently thermally stable for automotive applications and sulfur poisoning presents an additional issue. The thermal stability of the Pd@CeO_2 clusters can be improved, if the individual clusters are anchored on an inert support like Al_2O_3, so that the agglomeration of the clusters is avoided [22].Enhanced thermal stability of Pd@CeO_2, Pd@$Ce_{0.5}Zr_{0.5}O_2$ and Pd@ZrO_2 can also be achieved by using thicker surface layers (Figure 2c) [23] . The catalysts were aged at 1050 °C in 10% H_2O for 5 hours. The porous coating can be clearly seen in TEM images, and the improvement in reactivity of the aged catalysts suggests that this approach could be promising for emission control catalysts. Recently, a facile one-pot synthesis based on a novel metalorganic cerium precursor has been proposed that results in thermally stable Pd@CeO_2 [24] and Pd@SiO_2 [25] core@shell structures.

Encapsulation via Atomic Layer Deposition (ALD) and Solution Atomic Layer Deposition (SALD)

Stair and coworkers [26] demonstrated the encapsulation of supported metal nanoparticles by Atomic Layer Deposition (ALD), a technique originally developed for the semi-conductor industry. Here catalytically active nanoparticles are first deposited on a support oxide and then the entire ensemble of support and metal oxide is encapsulated by a thin layer obtained by ALD (Figure 3a). Directly after the application of the ALD layer, catalyst efficiency is reduced by the diffusion resistance in the protective layer, but after appropriate thermal treatments the formation of cracks (Figure 3b) in the ALD layer leads to improved mass transfer. A coking- and sinter-resistant catalyst was reported using this approach by depositing alumina on Pd/Al_2O_3 [26]. This initial work exposed the catalyst to 700 °C in air, which is not sufficient to demonstrate durability in the context of emission control catalysts. The application of the ALD encapsulation approach to automotive catalysis was demonstrated by Onn et al. [27] who showed that a ZrO_2 protective layer on a Pd/CeO_2 catalyst leads to improved thermal- and SO_2 resistance of the catalyst. A more recent study [28] explored this synthetic approach for methane oxidation catalysts tested up to 850 °C in air. These authors deposited alumina thin films on Pd/SiO_2. The authors suggest that the alumina helps to moderate the redox properties of Pd, improving the thermal stability of the catalyst for methane oxidation (see figure 3c).

ALD has also been used to modify a support before deposition of the active metal (Figure 3d). Mao et al. [29] (Figure 3e) deposited cerium oxide via ALD followed by Pd impregnation. The resulting catalyst was aged at 900 °C demonstrating the ability of the catalyst to preserve the dispersion and reactivity of the Pd for methane oxidation. ALD requires volatile precursors and the synthesis is not compatible with conventional liquid phase synthesis routes used in industry. For this reason researchers at Ford suggested solution atomic layer deposition (SALD) as an alternative for ALD that is more compatible with industrial catalyst synthesis procedures [30]. They deposited thin layers of titania on a conventional alumina support used for three-way catalysts. The authors propose that the titania forms an epitaxial layer that is strongly bonded to the alumina but does not have long range order, so it is amorphous. This titania layer helps maintain the dispersion of Rh at near-atomic levels and provides significant improvement in emission control of all the pollutants seen in typical automotive exhaust. The underlying mechanism by which the titania overlayer enhances catalytic performance is not fully understood, but this is a very promising development suggesting that ultrathin amorphous layers of oxides may help to enhance the performance of emission control catalysts (Figure 3f).

Advanced materials for emission control catalysts

Composite materials aggregated into a secondary structure

Composite materials that combine different nanoparticles into a common secondary structure represent industry-compatible variants of the previously discussed encapsulation and nano- interface design. Conventional exhaust catalysts consist of micrometer scale secondary particles obtained by agglomeration of primary particles of a single material. Recently, composite materials have been developed that combine different primary particles such as alumina and ceria/zirconia in a common secondary structure. An early example (Figure 4a) of this approach is the work by Morikawa and coworkers who suggested the use of alumina nanoparticles as a spacer to avoid sintering of CeO_2/ZrO_2 nanoparticles [31, 32]. Such composite architectures can be obtained either by co-agglomeration of the different primary particles or by supporting a colloidal solution of one particle within the structure of a support oxide. An example of the latter approach is provided by Toops et al. [33], who deposited CeO_2/ZrO_2 nanoparticles in an alumina framework and demonstrated improved performance of this catalyst. Since these structures are compatible with existing catalyst synthesis techniques, they are being applied for exhaust after treatment, with promising results (Figure 4b) [32].

Maintaining catalyst activity by exsolution of the active phase

A classical approach to maintain catalytic activity at high temperatures is the in-situ generation of the active phase by exsolution from a homogeneous solid solution. The best known example of this approach to automotive catalysis is the ‘intelligent catalyst’ by Daihatsu and Toyota, which consists of a Pd-containing perovskite that generates finely dispersed Pd in a reducing atmosphere [34, 35]. During aging in oxidative atmospheres, the Pd is reintegrated into the perovskite lattice so that it can again be exsolved during the next rich phase. Later work has questioned the efficiency of the Pd exsolution in the original ‘intelligent catalyst’ since Pd is dissolved not only at the surface but also in the bulk [36]. Recently Onn et al. [37] applied ALD to produce thin supported perovskite layers. Due to the short diffusion paths in the thin layers, Pd is dissolved mainly on the surface, improving the accessibility of the formed Pd nanoparticles. Future studies will need to show whether the perovskite layers produced by ALD can be made sufficiently thermally robust to withstand the harsh aging requirements of a three-way catalyst. Most work on the exsolution approach in exhaust catalysis focuses on achieving periodic catalyst regeneration by a reversible solution-dissolution cycle. Irvine and coworkers [38] demonstrated that exsolution of active metal nanoparticles from perovskites holds promise also in the absence of such a regeneration cycle, since exsolution can generate nanoparticles that are strongly anchored to the position from where they are exsolved.

Nanostructured (2-D and 3-D) architectures

Altering the morphology of the catalyst can provide improved performance. Nanoparticles present a convex surface, which results in a higher surface energy and a tendency to ripen via Ostwald ripening. If the surface had a negative curvature, for example through holes created in a 2-D metal sheet, the stability of the catalyst could be improved. This was demonstrated by Song et al. [39] who created dendritic nanosheets via a wet chemistry approach using multi lamellar vesicles as templates. The holey nano-sheets resisted surface area loss due to ripening. But translating this idea to emission control catalysts is not possible since the effective surface area per unit mass of Pt is limited. There are other 2-D materials that are attracting interest for catalytic applications. Free-standing, hierarchical, ultrathin, and two-dimensional (2D) polycrystalline Co_3O_4 flowers were synthesized by a hydrothermal and topotactic transformation process [40]. The hierarchical Co_3O_4 flowers contain many grain boundaries, pockets, surface steps, and other types of surface defects (Figure 5a). CO oxidation on the as-synthesized hierarchical Co_3O_4 flowers showed a specific activity (normalized to the surface area) about 5 times that of the most active Co_3O_4 reported in the literature.

While 2D materials provide improved catalytic performance, their thermal stability may be limited. By integrating them into 3D structures via interconnections into *nanoflowers*, it may be possible to provide sinter resistance and improved mass transfer. Yang et al. [41] reported enhanced sinter resistance for Pd catalysts through a compartmentalization strategy where nanosheets were assembled into three dimensional structures (Figure 5b). The unique flowerlike morphologies efficiently suppress the lamellar aggregation and irreversible phase transformation of γ-Al_2O_3 nanosheets at elevated temperatures. Furthermore, these structures exhibit significant structural advantages for heterogeneous reactions, such as fast mass transport and easy access to active sites. This is a facile stabilization strategy that can be further extended to improve the thermal stability of other Al_2O_3-supported nanocatalysts for industrial catalytic applications, in particular for those involving high-temperature reactions.

High Entropy Alloys

High entropy alloys represent a new class of material where multiple alloying elements are combined into a single nanoparticle. They provide the opportunity to maximize interfacial contact between different components, hence achieving enhanced catalytic properties. A general route for alloying up to eight dissimilar elements into single-phase solid-solution nanoparticles was presented by Yao et al. [42]. Xie at al. reported high reactivity for decomposition of ammonia using a high entropy alloy [43]. Many of the applications of these materials are in electrocatalysis [44], where the electrical conductivity is important, and the materials do not have to survive high temperatures. In the context of emission control, mixed oxides have shown promise for low temperature oxidation [45].

Single atom catalysts

Single atom catalysts promise the ultimate in atom efficiency, making it possible to lower the demand for platinum group metals [46]. The field of single atom catalysts for CO oxidation was recently reviewed by Beniya and Higashi [47]. These authors point out the need for an “atomically dispersed, dense catalyst layer” to provide the necessary performance for future automotive applications. Indeed, most single atom catalysts are prepared at very low metal loadings (<0.05 wt%) [48]. This is, in part, to separate the atoms and prevent formation of nanoparticles. However, the harsh conditions encountered during typical aging protocols [14] may make it difficult to maintain atomic dispersion. Not surprisingly, most conventional synthesis of single atom catalysts also contain metal nanoparticles and elaborate methods have to be used to sort out the relative contributions from single atoms and the nanoparticles [49, 50]. It is commonly assumed that the single atom form of the catalyst is the more active one, and nanoparticles would lead to a loss in catalytic activity. But this is not always true. A recent example comes from a study of Pd/Al_2O_3 catalysts by Goodman et al. [51] who showed that heat treatment at 750 °C caused the dispersion of Pd into isolated single atoms, leading to a drop in catalytic activity for methane oxidation (Figure 6a). Likewise, Gänzler et al. reported a loss of CO oxidation activity when Pt/CeO_2 was heated to high temperatures (~600 °C) under oxidizing conditions, because the Pt is redispersed to form single atoms [52].

The formation of atomically dispersed PGM species after heating to high temperatures is seen in many other metal/support combinations [53]. Peterson et al. [54] showed that atomically dispersed Pd was formed on alumina when heated in air at 750 °C. Yao et al. [55] dispersed a catalyst powder on a carbon nanofiber, by heating it electrically for short pulses of 50 milliseconds up to 2000K. The formation of stable Pt single atoms when Pt/ceria catalyst is heated at 800 °C in air was termed atom trapping [56] and provides a viable route for synthesis of thermally stable single atom catalysts with a high metal loading (1 atom/nm^2) of thermally stable single atoms [57]. It appears therefore that a counterintuitive, but practical, approach to improve catalyst durability is to synthesize the catalysts at high temperatures [58] since only the most strongly bound species will survive.

Unfortunately, the most stable Pt single atom catalysts prepared using high temperature synthesis do not yield the highest activity for CO oxidation [55, 56]. Ceria supported catalysts require an additional activation step. Activation in steam at 750 °C was shown to be successful [59] while retaining single atoms. Subjecting the Pt/CeO$_2$ to reducing environments yields vastly improved reactivity for CO oxidation at low temperatures [60, 61]. While nanoparticles are formed when the catalyst is reduced, it was argued that the improved activity in both these studies [59, 60] was due to the ability of the ceria support to transfer oxygen to interfacial sites (Figure 6b). Due to the mobility of PGMs at high temperatures, significant sintering can occur during the exotherm encountered during the so-called “fuel-cut” protocol, where residual fuel gets combusted under strongly oxidizing conditions [62]. For a catalyst to survive under these conditions, the atoms must be covalently bonded to an oxide support. Ceria supports provide suitable sites for bonding platinum group metals to surface oxygens [63]. A practical strategy to retain the benefits of atomic dispersion and thermal stability along with the higher reactivity of nanoparticles was proposed by Betz et al. [64] (Figure 7a). A combination of longer reducing pulses to generate medium sized Pt particles and short reducing pulses to rejuvenate the catalyst help achieve improved low temperature activity and high temperature stability [64]. Such catalyst activation by reductive pulses is possible in-situ using existing engine control system protocols (desulfation and Lean NOx trap regeneration), suggesting this is a practical way to combine the benefits of single atom catalysts in emission control systems.

Since it has been shown that single atoms are generated in-situ during high temperature treatments [65], it is possible that these structures play a role in current industrial emission control catalysts. A major challenge is that stable single metal atoms are generally in an oxidized ionic state, which does not correspond to the highest activity state of the catalyst. One strategy to improve the performance of single atom catalysts is the generation ensembles, for example Pt-O-Pt ensembles by Yang et al. [66]. Another approach that appears to be very successful was demonstrated recently by Jeong et al. [67] who created stable islands of ceria on which the PGMs were deposited (Figure 7b). In these ensembles, the precious metal atoms achieve 100% dispersion while preserving a metallic state and hence show an increased turn-over frequency for three-way catalysis. Despite the small size of the metal ensembles, the catalysts show surprising thermal stability with negligible deactivation after hydrothermal aging at 900 °C.

Microporous Materials

Small pore zeolites demonstrate how the discovery of new catalyst materials can have an immediate impact on the design of exhaust emission control systems. Just a few years after they were proposed as more thermally stable catalysts for selective catalytic reduction (SCR), with better low-temperature activity, copper exchanged chabazite catalysts have become the state-of-the-art catalyst for the selective reduction of NO by NH_3. Initially, small pore structures based on alumina-silica as well as silico-alumino-phosphates (SAPO) had been used and showed promising behavior after standard high temperature aging procedures. However, during real world applications, the SAPO variants showed unexpected aging phenomena during low temperature exposure to water vapor [68, 69]. This is a good example of the necessity of testing new materials for exhaust catalysis under a variety of realistic operating conditions. The focus of recent work has been on understanding of the mechanism of the unusual low-temperature activity of the copper exchanged zeolites and a detailed picture now has emerged from a combination of DFT, in situ characterization and kinetics studies [70, 71]. Based on this understanding, further improvements of the technology can be expected. One important finding from this mechanistic work is that through common gas phase species such as HONO, the SCR chemistry on the zeolites is coupled with the NOx storage chemistry on barium- and other oxides. This opens up the possibility of bifunctional catalyst systems that combine SCR- and NOx storage chemistry in a single device [72]. In parallel, the search for even more thermally stable zeolites is ongoing, a recent example being the LTA proposed by Jo et al. [73].

Due to the need to inject a liquid urea solution, SCR only works at temperatures above ~180°C. To eliminate any NOx emitted at lower temperatures, when the exhaust system has not yet reached the temperature threshold for urea dosing, the concept of the passive NOx adsorber has been proposed. The goal is to store NO and NO_2 at low temperatures below 200°C and then thermally desorb these molecules at higher temperatures when the urea-SCR is operational [74]. Most precious metals on oxide supports show some level of low temperature adsorption of NO, one example being Pt or Pd on alumina [75]. Much better adsorption is observed if Pd is supported on reducible oxides such as ceria [76]. The major challenge that limits the use of Pd/ceria as a passive NOx adsorber is the affinity of ceria for sulfur which causes poisoning of the catalyst [77, 78].

One approach to improve sulfur tolerance is the use of Pd-exchanged zeolites as low-temperature NOx adsorbers [77]. According to current understanding, NO is adsorbed mainly on ionic single Pd species within the zeolite framework, which show negligible sulfur poisoning [74]. The mechanism of low temperature adsorption as well as thermal desorption is currently under intensive investigation and it is understood that for efficient desorption in the desired temperature range of 200°C to 300°C, a good catalyst should favor the formation of nitrites over the formation nitrates [78]. It has further been observed that the presence of CO in the exhaust results in increased NO adsorption [79]. Only recently Gu et al [80] reported that the same CO concentrations that lead to increased adsorption in the short term, cause severe degradation of the storage capacity in the long term [80]. The CO-induced degradation currently presents the biggest challenge for the practical application of zeolite-based passive NOx adsorbers. This is another example that shows how important effects can be overlooked if new materials are tested under simplified exhaust conditions.

Zeolite-based hydrocarbon adsorbers have been investigated for a long time [81]. Current interest is directed at combining NOx and HC adsorbers in a single device. HC adsorption requires a match of the zeolite pore size and the size of the hydrocarbons. For this reason, the small pore zeolites currently preferred for passive NOx adsorption are not optimally suited to capture all hydrocarbons, especially the long chain alkanes. Therefore, in all likelihood, a combined NOx-and hydrocarbon adsorber will contain a mixture of different zeolites [82].

Grand Challenges/Radical Breakthroughs

It is possible to create a wish-list of reactions which if possible, could completely transform the technology for emissions control. We present our list here, recognizing that catalytic materials for these reactions have not yet been developed. Our goal is to highlight promising candidates and suggest targets for future research.

Splitting NO

Splitting NO into N_2 and O_2 is the dream reaction of exhaust catalysis since this would eliminate the need for a reductant, i.e. no ammonia and no need to run the engine rich. With a heat of formation for NO of ΔH^0_f= 90 kJ/mol, the decomposition reaction is thermodynamically downhill, but despite a lot of research effort no suitable catalyst has been found to date. While reasonable conversion has been demonstrated under lab conditions in the absence of oxygen, the main challenge is that NO decomposition is inhibited by O_2, so that negligible conversion is obtained under realistic operating conditions [83, 84]. Nørskov and coworkers [85] investigated NO decomposition on different transition metals using DFT derived Brønsted–Evans–Polanyi relations. They show that for the metals, due to the linear relationship between oxygen adsorption energy and the activation barrier for NO decomposition, good catalytic activity for the NO decomposition is intrinsically linked to oxygen inhibition. This makes it difficult to circumvent the problem of oxygen inhibition for this class of catalysts. Recent research has focused on metal oxide and on Cu exchanged zeolite catalysts. The limited success achieved so far might indicate that like the transition metals, other catalyst classes also show an intrinsic coupling of oxygen adsorption and NO decomposition. A systematic understanding of these intrinsic couplings might provide a way to map out those compositions that allow decoupling of oxygen inhibition and NO decomposition. Recently microwave assisted catalytic NO decomposition has been proposed [86], however, reaction rates are still orders of magnitude below those required for a practical application in the vehicle.

Activation of CH_4

CH_4 as a fuel offers the potential for the reduction of CO_2 emissions, in the short term due to its more favorable H/C ratio, and in the longer term since it can be produced from renewable resources, either from biomass, bio-waste or from hydrogen obtained by electrolysis or photocatalytic water splitting. Unfortunately, catalytic activation of CH_4 in the exhaust catalyst is difficult since it is a stable molecule with limited ability to bind to any catalytic surface. Currently the only technically feasible solution is the application of very high Pd metal loadings. Industrial development focuses on CH_4 oxidation under stoichiometric conditions which is feasible since Pd catalysts can be activated by periodic rich operation. Even better fuel efficiency could be obtained by lean (with oxygen excess) combustion of CH_4 but this technology is currently not practiced because of the lack of a catalyst showing stable activity in the presence of excess oxygen. The major challenge is deactivation by water vapor and SO_2. Given the potential of lean CH_4 combustion and the dimension of the challenge, it is not surprising that lean methane oxidation is one of the major target reactions for the recent development of new catalyst design strategies [87]. Many of the catalytic materials discussed in this review have been tested for methane oxidation. Other approaches include the confinement of Pd clusters in the framework of a mordenite zeolite. Sodium exchange of the zeolite acid sites prevents Pd mobility in the framework an hence prevents sintering [88]. Periodic reductive pulses activate the Pd nanoparticles and allow stable CH_4 conversion at ~400°C in the presence of water.

A new concept is the application of amorphous phases for CH_4 oxidation. The ability of amorphous Pd/ceria to catalyze lean CH_4 oxidation was reported by Trovarelli and coworkers using high energy milling of Pd and ceria [89]. Likewise Zhang et al. found that in their Pd@ceria catalyst supported on silica doped alumina, the actual catalytically active phase is an amorphous Pd/ceria formed during the thermal aging of the catalyst [90]. This finding suggests that amorphous phases might indeed play an important role in many more catalytic systems, but might have been overlooked so far since they are harder to characterize and since the focus is on the nano-design of well-defined crystalline systems. Amorphous phases are high entropy in nature which might make their on-purpose design a versatile strategy to obtain high temperature stable catalysts, especially for reactions that require the combination of different catalytic sites that otherwise can only be obtained at the interface of different materials. Amorphous phases could be created directly during catalyst preparation or catalysts need to be designed, so that the active amorphous phases evolve during high temperature operation.

Catalysts free of Platinum Group Metals (PGMs)

Currently the highest (not only economic but also environmental) cost of exhaust aftertreatment comes from the use of precious metals. Driven by the cost and amount of the applied precious metals, recent research has been focused on noble metal free catalysts [91]. Promising results under lab conditions have been obtained with perovskites [92, 93]. Kang et al. [94] developed new oxygen storage material based on a Mn/Fe spinel that can reversibly be reduced to metallic iron nanoparticles and manganese oxide. Researchers at GM demonstrated that lanthanum-based perovskite catalysts show NO oxidation activity comparable to conventional precious metal catalysts [95]. New material combinations with improved activity continue to be discovered, a recent example being the Cu/Co/Ce ternary oxides discovered by Binder et al. [96]. The so-called CCC catalyst contains a mixture of cobalt, copper and cerium oxides. The authors suggest that cobalt oxide forms an isolated phase (not dissolved into the CeO_2 lattice), which gives rise to a separate active site for hydrocarbon oxidation. This isolation of active sites for CO and HCs is the key to catalyst design and prevents the inhibition of CO oxidation by the hydrocarbons. However, the research to date has not yet adequately addressed the need to survive high aging temperatures. There is no known PGM-free catalyst system that meets industry requirements, especially the ability to withstand poisoning (in particular by SO_2) and survive high temperature aging.

Achieving Low light-off temperatures

Newer engine designs aim for lower exhaust temperatures due to improved fuel efficiency, since less heat is wasted in the exhaust. Hence the catalyst now needs to become active at low temperature, preferably room temperature, but it must also be stable at high temperatures. Many of the new materials and synthesis strategies discussed in this review aim in this direction. Achieving catalytic activity at drastically lower temperatures (for example 70°C) will allow placement of the catalyst further downstream in the exhaust system, reducing the aging requirements. Since the major shortcoming of most of the more revolutionary concepts discussed in this review is their insufficient aging stability, development of catalysts with ultra-low-temperature activity could be an enabler for many of the other concepts, leading to a complete redesign of the exhaust system. Here we focus on progress in achieving low temperature conversion of the three main regulated pollutants: CO, hydrocarbons and NOx.

NOx: NOx reduction has made a large step forward by the introduction of small pore zeolites. Improvements in mechanistic understanding may lead to materials that perform well at operating temperatures above the urea dosing limit of ~180 °C while meeting the demands for activity as well as thermal stability. A remaining challenge will be to control aging and poisoning effects over catalyst lifetimes [97]. For temperatures below the urea dosing limit, the most promising approach is passive NOx adsorption. Besides the recently discovered CO-induced aging phenomena [80], a more fundamental problem is to ensure sufficient conversion under all possible driving conditions. In addition to further developments in materials, this will require the development of model-based operating strategies derived from a thorough mechanistic understanding.

CO and hydrocarbons: The current technology for emission treatment is based on Pt/Pd alloy nanoparticles supported on inert oxides such as alumina. After aging, CO light-off temperatures around 200°C are achieved. Since CO inhibits the oxidation of other species, hydrocarbon and NO light-off is observed only after CO is fully converted. Therefore, the focus today is on CO oxidation. Catalysts for the next generation of fuel-efficient engines will require CO- and hydrocarbon light-off below 150°C. This cannot be achieved by current Pt/Pd catalysts so that more efficient catalysts need to be developed. Low temperature CO oxidation has been extensively studied and there are reports of CO conversion even at room temperature [98]. Unfortunately, most of these catalysts are not stable after undergoing the aging conditions required for automotive applications. A promising system is Pd supported on ceria [99-101]. In these catalysts, the presence of an amorphous Pd-ceria mixed phase seems to improve the activity. Similar positive effects of ceria on CO oxidation on Pd are possible with nano-designed Pd@CeO_2 catalysts where each Pd nanoparticle is surrounded by a shell of CeO_2 nanoparticles. The improved CO oxidation performance of these Pd@CeO2 catalysts was attributed to a redispersion of Pd into the encapsulating ceria shell [102]. Single atom Pt catalysts with suitable activation [59-61, 64], or ensembles of Pt single atoms [66, 67], also demonstrate low temperature light off for CO oxidation. Sulfur poisoning remains a severe constraint on the practical applicability of ceria-based catalysts. More efforts should be spent on investigating catalyst performance in the presence of sulfur, as well as on the discovery of new materials that are not affected by sulfur.

Concluding Remarks

In this review we have described materials synthesis technologies and materials concepts that have potential for major impact on emission control catalysts. Academic research emphasizes fundamental understanding, modeling and kinetic studies. Table 1 lists material concepts that show promise after aging under conditions approaching those relevant for industrial practice. This is a very limited list and is based on those materials that were highlighted in Figures 2-7. Very few of these materials have been exposed to poisons such as S and P and aging is often done for short durations. The major bottleneck in translating these materials into industrial practice is the gap between aging conditions applied during academic research versus those used in industry. The differences not only reflect different incentives in academic and industrial work, but there are concrete technical challenges associated with testing the stability of new materials at the small scale powder level (as opposed to monoliths). Especially for three-way catalysts, transient rich/lean steps and the exotherms generated during these steps are important ingredients of realistic aging. Such transient aging conditions are nearly impossible to simulate in small scale reactors at the scale of milligrams. The large surface to volume ratio in micro-reactors leads to high heat losses and catalytic reactions taking place on the reactor walls when temperatures exceed >1000°C. To date, there has been very little work on the validation of small-scale powder reactor aging procedures. The development of such validated procedures would increase the likelihood that academic research on advanced materials could be translated into industrial practice.

From the standpoint of an industry practitioner, almost all the studies included in this review use overly mild aging conditions. Furthermore, it is common practice to only report on the performance of a catalyst that is still working after being subjected to certain prescribed aging procedures. Our recommendation is that each material should be pushed until it fails. Knowing where these materials fail helps researchers in the field investigate the failure mechanisms and to develop methods to overcome limitations. It is also possible for industry to develop operating conditions that keep the materials within their operating limits.

Our review focused on emerging materials concepts such as single atoms and amorphous phases. In both cases the most active form of the catalyst is developed during operation, sometimes very different from the initial structure created during synthesis. Hence, it is important to characterize the working catalyst, which can be done via in-situ techniques but also via careful passivation after the catalyst is used. It is clear that the as-prepared catalyst is altered significantly after it has been subjected to working conditions. Our hope is that the future focus of catalyst development might shift from simply describing the initial nano-architecture, but rather treat the catalyst design as the first step in the evolution of the precursor into the active working catalyst. Once the dynamic changes of the catalyst in response to different operating and aging conditions are recognized, the design of the precursor can move forward in a more rational manner.

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Author contributions

Both authors contributed equally to this manuscript.

Competing Financial Interest

The authors declare no competing financial interest.

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Figure Captions

Fig. 1 | Typical configurations of a modern gasoline and diesel emission catalysts. For gasoline aftertreatment **a**, the HC, CO and NOx are removed in the three-way catalyst (TWC), which may be followed by a gasoline particulate filter (GPF) or a catalyzed gasoline particulate filter (cGPF) for removing particulates. For diesel aftertreatment **b**, the HC and CO are removed in the diesel oxidation catalyst (DOC) the particulates are removed in the diesel particulate filter (DPF) and the NOx in the selective catalytic reduction (SCR) catalyst using addition of urea. The ammonia slip catalyst (ASC) oxidizes any residual ammonia that remains in the exhaust. The DPF will frequently contain a catalytic functionality, for example an SCR coating. This idealized representation ignores the contaminants in fuel such as S and P which can also be emitted in the exhaust. Courtesy of Umicore AG.

Fig. 2 | Encapsulation of the active phase via colloidal synthesis. a, Pre-formed colloidal Pd nanoparticles are embedded within CeO_2 crystals [21]. **b**, The Pd@CeO_2 shows enhanced low temperature reactivity for methane oxidation [21]. **c**, TEM images showing core@shell particles where the core is Pd and the shell is composed of (A-B) CeO_2, (C-D) $Ce_{0.5}Zr_{0.5}O_2$ and (E-F) ZrO_2 [23].

Fig. 3 | Atomic Layer Deposition (ALD) for for overcoating and surface modification. a, Schematic showing how an oxide can be deposited on a supported metal catalyst *after* nanoparticles have been deposited on a support. **b,** After calcination and high temperature treatments, micropores develop in the oxide overcoat allowing transport of reactants and products [26]. **c,** HAADF-STEM images, and EDS elemental maps of Al_2O_3/c-Pd/SiO_2 (A1, A2)) and Al_2O_3/o-Pd/SiO_2(B1, B2) showing how the dense alumina layer blocks access to the Pd, but suitable thermal treatments allow Pd to become active for methane oxidation [28]. **d,** Schematic showing an alternative approach where ALD is used to modify the surface of an oxide support *before* deposition of nanoparticles. **e**, High angle annular dark field STEM image and EDS maps of Al, Ce, and Pd on ALD Pd/CeO_2/Al_2O_3 after calcination to 900 °C, taken from the region indicated by the green box [29]. The scale bars correspond to 10 nm. The image shows uniform deposition of the cerium oxide on alumina which helps to preserve the dispersion of Pd. **f**, The temperature to achieve 90% conversion of various pollutants on catalysts where the surface of alumina was modified by titania through solution based ALD. The 12% TiO_2/Al_2O_3 provides the best performance [30].

Fig. 4 | Composite materials aggregated into a secondary structure. a, Schematic illustration of a "diffusion barrier concept" where the alumina particles serve as a barrier that prevents the sintering of the ceria-zirconia [31]. **b**, Light-off activity of a Al_2O_3/CeO_2/ZrO_2 mixed oxide and the (Al_2O_3 + CeO_2/ZrO_2) mixture supported Pd catalysts after 1050 °C/36 h redox aging [32]. The mixed oxide support allows the catalyst to achieve higher reactivity, with T_{90} lowered by 50 °C.

Fig. 5| 2-D and 3-D nanostructures for emission control catalysts. a, SEM images of the as-prepared CoO_x (left panel) (a, b) and Co_3O_4 (d, e) powders show the flower-like morphology [40]. Bright-field STEM images of an individual CoO_x (c) and Co_3O_4 (f) flower, respectively, show that the 2D CoO_x and Co_3O_4 nanosheets (the building blocks of the individual flowers) are extremely thin. These materials demonstrate excellent activity for CO oxidation. **b**, Nanosheet alumina assembled (NA-Al_2O_3) via cross-linking (bottom) retains high surface area and a porous structure, while the nanosheet alumina (NA, top) collapses like a deck of cards [41]. The Pd phase can be stabilized by NA-Al_2O_3 even after heating in air to 1000 °C

Fig. 6 | Deactivation by formation of single atoms and their *in-situ* reactivation. **a,** At elevated temperatures and on suitable supports, nanoparticles can transform into single atoms [51]. This leads to lower catalytic activity for methane oxidation and also for CO oxidation [54]. **b**, CO reduction at 275 °C leads to enhanced reactivity due to the formation of Pt nanoparticles [57] and facile oxygen transport from the CeO_2 support [60].

Fig. 7 | Strategies to achieve high reactivity in single atom catalysts. a, The low CO oxidation reactivity of a Pt single atom catalyst (A) can be enhanced by reduction at 250 °C (down arrow in B), but these catalysts are susceptible to activity loss after oxidation at $T > 400$ °C (up arrow in B). The optimal strategy is reduction at 400 °C leading to slightly larger particles (C). Upon oxidation, these larger particles lose some activity (blue curve in D), but the high activity state can be restored by short reducing pulses (green curve in D). This approach allows achieving high reactivity and stability starting from Pt single atoms in an operating diesel oxidation catalyst [64]. **b,** By creating stable islands of ceria on pre-reduced alumina, the deposited Pt forms ensembles that preserve 100% dispersion of metal atoms in a zero valent state [67]. The ceria nano-islands help to keep the catalyst stable during redox cycling at 900 °C.

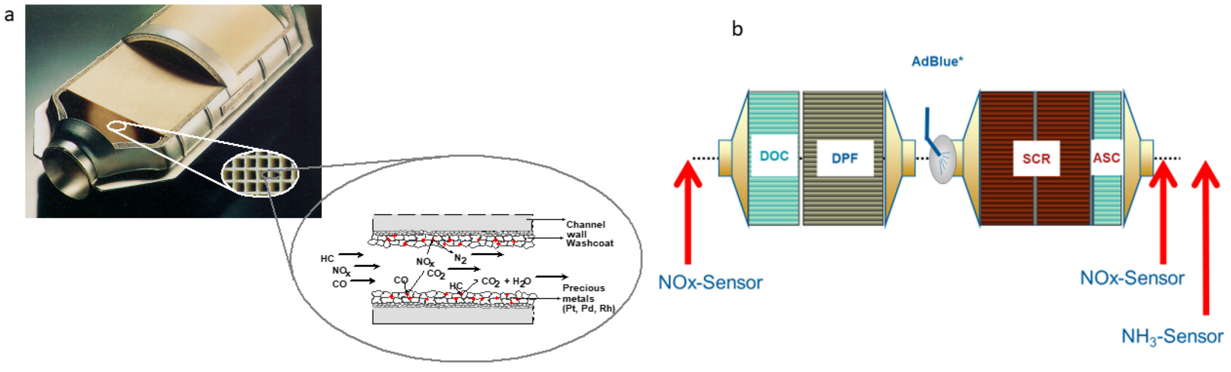

Fig. 1 | Typical configurations of a modern gasoline and diesel emission catalysts. For gasoline aftertreatment **a**, the HC, CO and NOx are removed in the three-way catalyst (TWC), which may be followed by a gasoline particulate filter (GPF) or a catalyzed gasoline particulate filter (cGPF) for removing particulates. For diesel aftertreatment **b**, the HC and CO are removed in the diesel oxidation catalyst (DOC) the particulates are removed in the diesel particulate filter (DPF) and the NOx in the selective catalytic reduction (SCR) catalyst using addition of urea. The ammonia slip catalyst (ASC) oxidizes any residual ammonia that remains in the exhaust. The DPF will frequently contain a catalytic functionality, for example an SCR coating. This idealized representation ignores the contaminants in fuel such as S and P which can also be emitted in the exhaust. Courtesy of Umicore AG.

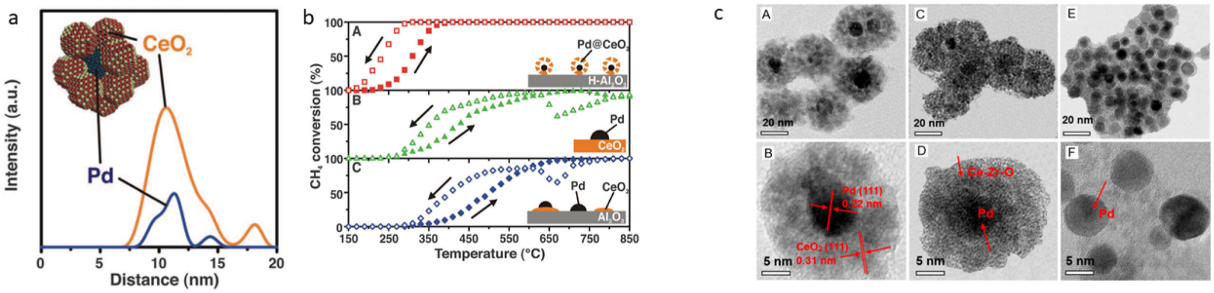

Fig. 2 | Encapsulation of the active phase via colloidal synthesis. a, Pre-formed colloidal Pd nanoparticles are embedded within CeO_2 crystals [21]. **b**, The $Pd@CeO_2$ shows enhanced low temperature reactivity for methane oxidation [21]. **c**, TEM images showing core@shell particles where the core is Pd and the shell is composed of (A-B) CeO_2, (C-D) $Ce_{0.5}Zr_{0.5}O_2$ and (E-F) ZrO_2 [23].

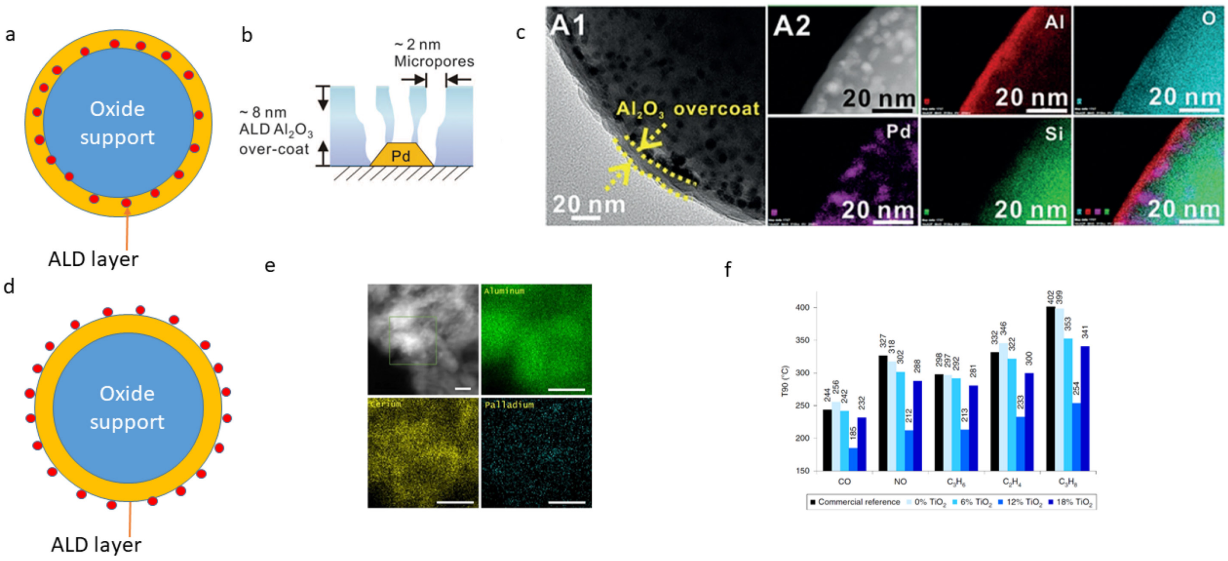

Fig. 3 | Atomic Layer Deposition (ALD) for for overcoating and surface modification. a, Schematic showing how an oxide can be deposited on a supported metal catalyst *after* nanoparticles have been deposited on a support. **b**, After calcination and high temperature treatments, micropores develop in the oxide overcoat allowing transport of reactants and products [26]. **c**, HAADF-STEM images, and EDS elemental maps of Al_2O_3/c-Pd/SiO_2 (A1, A2)) and Al_2O_3/o-Pd/SiO_2(B1, B2) showing how the dense alumina layer blocks access to the Pd, but suitable thermal treatments allow Pd to become active for methane oxidation [28]. **d**, Schematic showing an alternative approach where ALD is used to modify the surface of an oxide support *before* deposition of nanoparticles. **e**, High angle annular dark field STEM image and EDS maps of Al, Ce, and Pd on ALD Pd/CeO_2/Al_2O_3 after calcination to 900 °C, taken from the region indicated by the green box [29]. The scale bars correspond to 10 nm. The image shows uniform deposition of the cerium oxide on alumina which helps to preserve the dispersion of Pd. **f**, The temperature to achieve 90% conversion of various pollutants on catalysts where the surface of alumina was modified by titania through solution based ALD. The 12% TiO_2/Al_2O_3 provides the best performance [30].

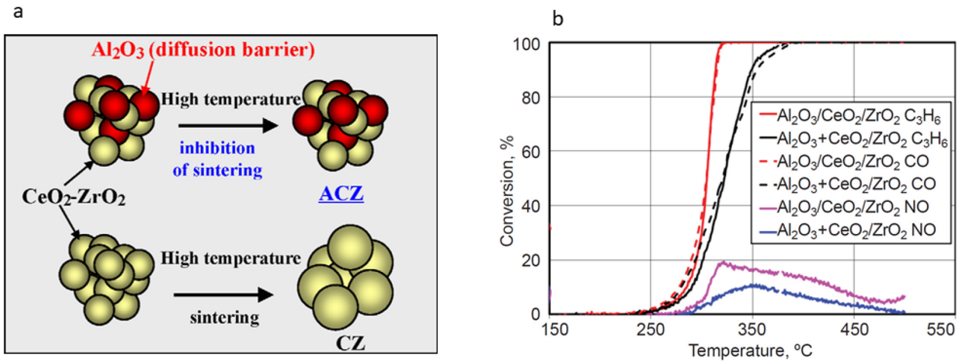

Fig. 4 | Composite materials aggregated into a secondary structure. a, Schematic illustration of a “diffusion barrier concept” where the alumina particles serve as a barrier that prevents the sintering of the ceria-zirconia [31]. **b**, Light-off activity of a $Al_2O_3/CeO_2/ZrO_2$ mixed oxide and the (Al_2O_3 + CeO_2/ZrO_2) mixture supported Pd catalysts after 1050 °C/36 h redox aging [32]. The mixed oxide support allows the catalyst to achieve higher reactivity, with T_{90} lowered by 50 °C.

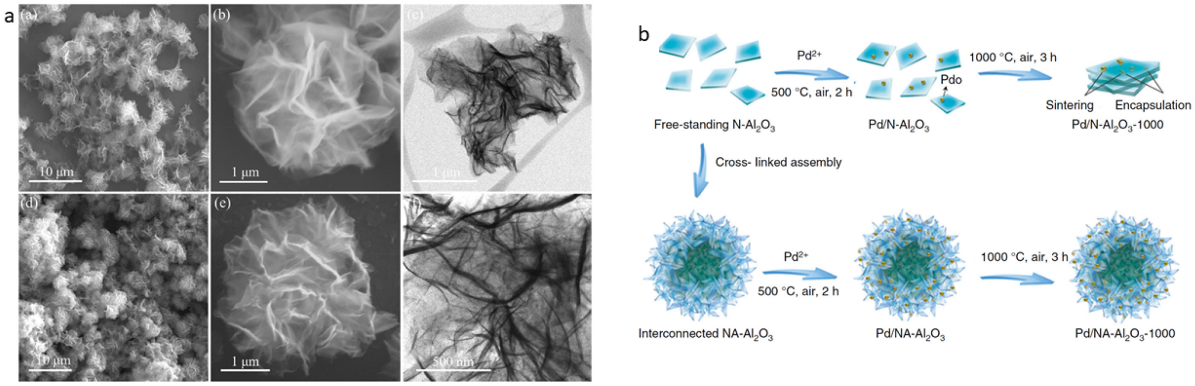

Fig. 5| 2-D and 3-D nanostructures for emission control catalysts. a, SEM images of the as-prepared CoO_x (left panel) (a, b) and Co_3O_4 (d, e) powders show the flower-like morphology [40]. Bright-field STEM images of an individual CoO_x (c) and Co_3O_4 (f) flower, respectively, show that the 2D CoO_x and Co_3O_4 nanosheets (the building blocks of the individual flowers) are extremely thin. These materials demonstrate excellent activity for CO oxidation. **b**, Nanosheet alumina assembled (NA-Al_2O_3) via cross-linking (bottom) retains high surface area and a porous structure, while the nanosheet alumina (NA, top) collapses like a deck of cards [41]. The Pd phase can be stabilized by NA-Al_2O_3 even after heating in air to 1000 °C

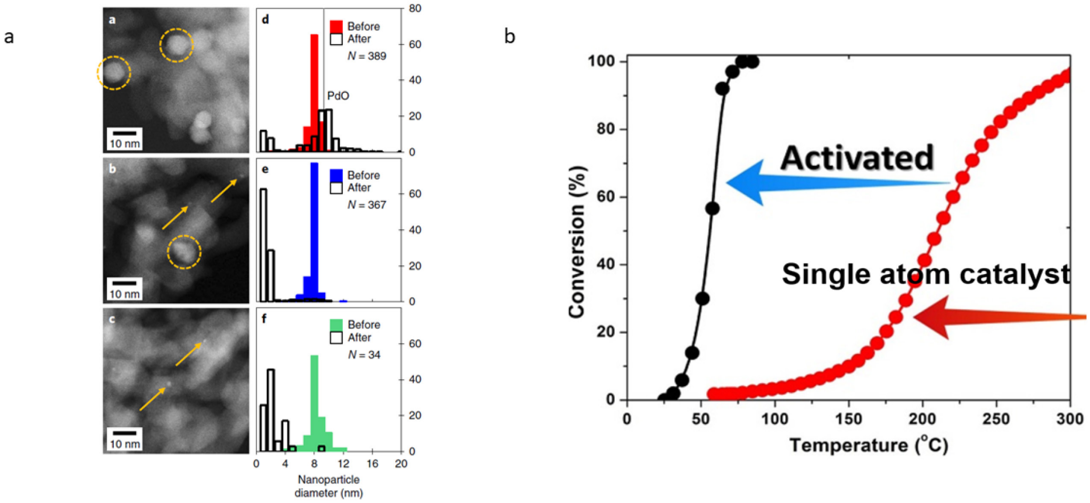

Fig. 6 | Deactivation by formation of single atoms and their *in-situ* reactivation. a, At elevated temperatures and on suitable supports, nanoparticles can transform into single atoms [51]. This leads to lower catalytic activity for methane oxidation and also for CO oxidation [54]. **b**, CO reduction at 275 °C leads to enhanced reactivity due to the formation of Pt nanoparticles [57] and facile oxygen transport from the CeO_2 support [60].

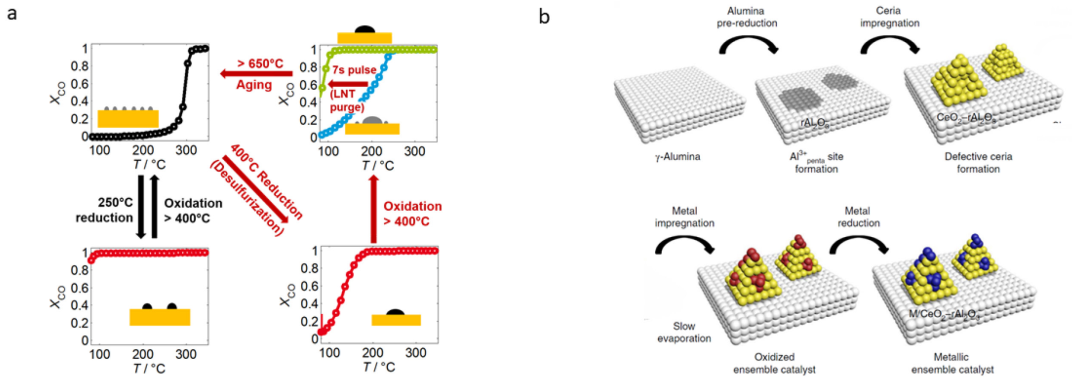

Fig. 7 | Strategies to achieve high reactivity in single atom catalysts. a, The low CO oxidation reactivity of a Pt single atom catalyst (A) can be enhanced by reduction at 250 °C (down arrow in B), but these catalysts are susceptible to activity loss after oxidation at T > 400 °C (up arrow in B). The optimal strategy is reduction at 400 °C leading to slightly larger particles (C). Upon oxidation, these larger particles lose some activity (blue curve in D), but the high activity state can be restored by short reducing pulses (green curve in D). This approach allows achieving high reactivity and stability starting from Pt single atoms in an operating diesel oxidation catalyst [64]. **b,** By creating stable islands of ceria on pre-reduced alumina, the deposited Pt forms ensembles that preserve 100% dispersion of metal atoms in a zero valent state [67]. The ceria nano-islands help to keep the catalyst stable during redox cycling at 900 °C.