A review on the impact of SO_2 on the oxidation of NO, hydrocarbons, and CO in diesel emission control catalysis

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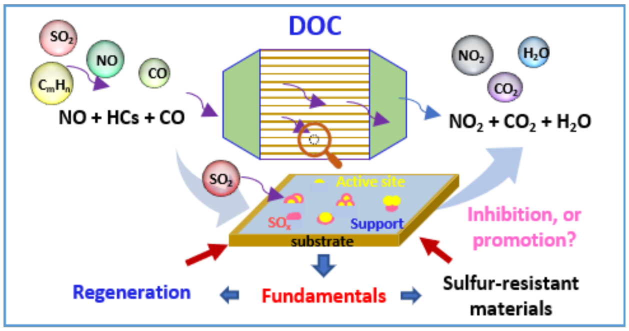

Abstract

A high-efficiency after-treatment technology has been required to meet the increasingly stringent regulations on the emissions of nitrogen oxides (NO_x), hydrocarbons (HCs) and carbon monoxide (CO) exhausts from diesel engine vehicles throughout the world. The diesel oxidation catalyst (DOC) is an indispensable part of diesel fueled exhaust system, which mainly functions in the oxidation of unburned HCs and CO to CO_2 and H_2O (in the case of HCs), and a proportion of NO to NO_2. However, the DOC will unavoidably be poisoned by trace gaseous SO_2 or accumulated sulfur on the catalyst under real operational conditions and hence impair the overall purification efficiency of the aftertreatment system. There have been significant research efforts from both academia and industry involving sulfur-relevant diesel oxidation chemistry and development of robust sulfur-resistant oxidation catalysts. This review focuses on recent advances in the study of SO_2 effects on the catalytic oxidation of NO, HCs, and CO over DOCs, with particular attention to the fundamentals beneath apparent observations of sulfur influence on PGM-based and non-noble metal-based catalysts in the different oxidation reactions. Regeneration methods and design rationale for sulfur-resistant catalysts are also covered. Several challenges in the future research regarding microscopic insights into SO_2 influencing mechanism and next-generation sulfur-resistant DOC design are highlighted towards the real-world practice.

Keywords: Diesel oxidation catalysts, sulfur dioxide effect, Pt-group metals, non-noble metal catalysts, regeneration, sulfur-resistant materials

1. Introduction

Air pollution is closely associated with vehicle emissions which have caused growing burden on environment and public health.[1] Diesel engines delivers high thermal efficiency with low fuel consumption, low CO_2 output and long durability and reliability.[2] These advantageous characteristics drive diesel engines to continuously expand in current vehicle market, and will remain so to become one of the largest contributors to air pollution.[3] Typically, diesel fuel under high pressure is injected into the diesel cylinder where it mixes with excess air to incite combustion. While due to incomplete combustion of fuel, a wide range of gaseous and solid compounds are discharged in the exhaust, mainly including carbon monoxide (CO), unburned hydrocarbons (HCs), particulate matter (PM, mostly soot) and nitrogen oxides (NO_x) emissions.

Since 1990s, more stringent regulations have been put into practices worldwide to hit the increasing emissions of NO_x, CO, HCs and PM, regardless of diesel, gasoline or natural gas engines.[4-7] As shown in **Figure 1**, the CO, HCs, NO_x and PM emissions for heavy-duty diesel engines are required to decrease by 66, 76, 95 and 98%, respectively, in Euro VI standards compared with Euro I.[7] Such reductions rely on the advances in diesel after-treatment technologies that heterogeneous catalytic process is proven as the most efficient solution. Because diesel exhaust is lean in that CO and HCs emitted from the end of pipe are in low concentration levels yet NO_x and PM are not, one being reduced at the expense of the increase of the other, traditional three-way technology used near stoichiometric burn is unable to efficiently operate in the high air/fuel (A/F) ratio diesel engine.[3, 5] The state-of-the-art technology in diesel engine has to be adapted for current practice: i.e., the development of diesel oxidation catalyst (DOC) and diesel particle filter (DPF) to control HCs, CO and soot; and the closely coupled selective catalytic reduction (SCR) and ammonia slip catalyst (ASC) units targeting at the abatement of NO_x. Specifically, DOC remains a key in the overall aftertreatment system, which is responsible for the oxidation of HCs, CO and NO, and assists DPF and SCR units to remove soot and NO_x emissions.

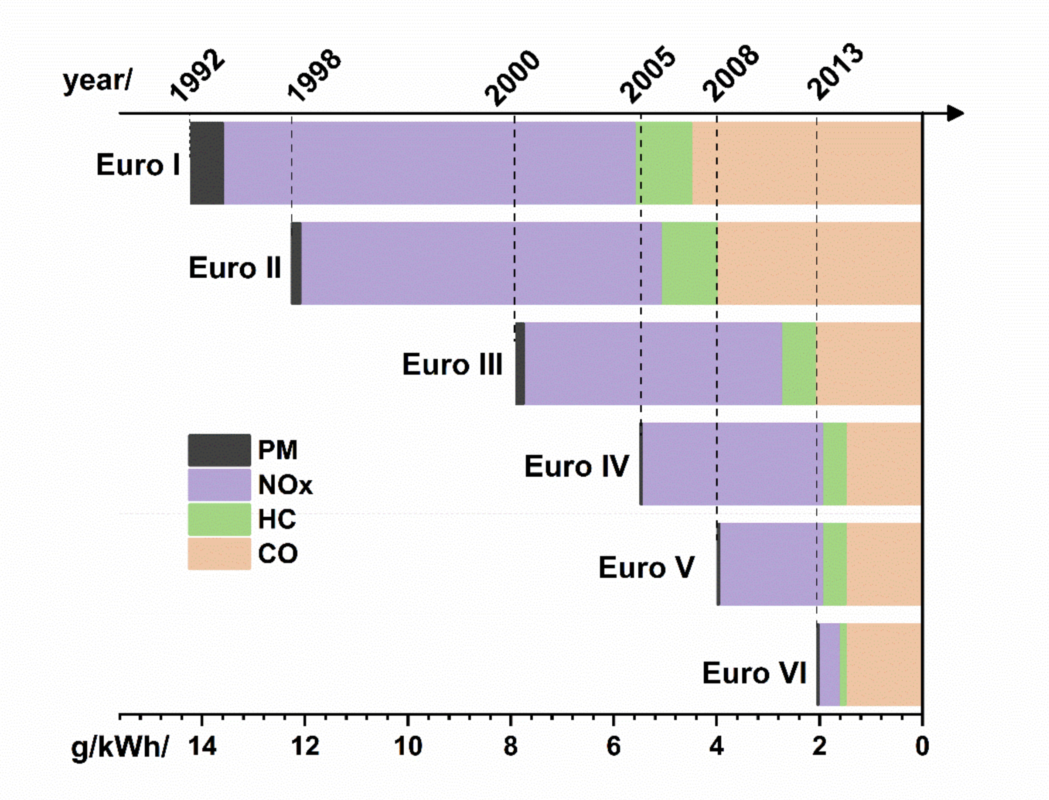

Figure 1. Standard evolution for heavy-duty vehicles in European union.

Sulfur species from fuel and lubricating oil are one of the major chemical contaminants contributing to catalysts degradation while the upstream DOCs unavoidably claim the first impact from sulfur poisoning.[8-9] It is found that the NO conversion over commercial DOCs decreases from ca. 27% for zero-S fuel to ca. 16% for fuel containing 37ppm S but sharply to ca. 5% when the sulfur content increases up to 706 ppm. This is a representative example for the positive correlation of pollutant emissions with increasing fuel sulfur content, implying the loss of efficiency of the DOCs.[10-11] The major part of the sulfur in the engine exhaust is in the form of sulfur dioxide (SO_2), which increases in proportion to the fuel sulfur content.[12-13] It undergoes oxidation into SO_3 when encountering with oxidizing catalysts in the DOC systems.[13] The resulting SO_3 may further react with water vapor to form sulfuric acid (H_2SO_4), which is harmful to the after-treatment system and to the atmosphere as an important component in $PM_{2.5}$ aerosols.[14] Therefore, lowering fuel sulfur content has been an urgent trend and it even becomes mandated over sulfur-free ($\leqslant$15 or 10 ppm S) fuel in US, Europe and China.[1, 14] Although a low-sulfur fuel has been put in use, the accumulation of sulfur can be as high as high-content sulfur fuel used in amount owing to considerable consumption of fuel as well as long-term exposure to vehicle.[13]

The most active components used in DOCs are Pt-group metals (PGM), particularly Pt and Pd-based noble metals.[15-16] For a long time, the single Pt catalyst dominates the market due to its high reactivity while it has some drawbacks in poor thermal stability and notable propensity to yield SO_4^{2-} in the contact of SO_2.[17] In this context, the addition of Pd or Rh is found to stabilize Pt species and helps to reduce SO_2 conversion relative to all-Pt catalysts.[18] Research efforts on catalyst formulation has been constantly pursued in order to develop cheaper and high-efficiency catalysts, yet those catalysts still undoubtedly suffer from sulfur poisoning.[17, 19] Further, in the real practice the composition of a typical commercial DOC is more complicated in comparison to the widely studied model catalysts in academia, as the former also contains various stabilizers and additives on alumina to ensure high catalytic activity and durability. Combining with the changing operating conditions (including temperature, gas composition and air-fuel ratio etc.), all these toss up great concerns for researchers to address sulfur poisoning issue in the reality. A pursuit of deep understanding of SO_2 poisoning is hence anticipated to bridge the gap between academia research and industrial applications to advance the efficient emission control.

There have been a wide range of literature reviews dealing with the emission regulations, catalyst materials, reaction mechanisms, inhibition reactions or reactor configurations for DOCs during the past two decades.[3, 5, 7, 16, 20-22] But very few have been specifically concerned with the sulfur influence. An early review by Sharm et al. has given excellent description of SO_2 interaction with PGM-based DOC catalysts in terms of microkinetic modeling.[11] Recent reviews also involve sulfur poison in the regard of CH_4 combustion,[22-23] or NO oxidation.[21] Yet CH_4 oxidation is not the working focus of DOCs. Most sulfur-related reviews to date disregard the fundamental understanding of SO_2 poisoning, i.e., the role of SO_2 played from atomic level and the common issues it triggers across various oxidation reactions from macroscopic view. Under urgent call for the development of highly sulfur-tolerant DOCs in the emerging markets, an update from recent advances in both academia and industrial research is needed to provide new insights for researchers in this field to be better informed with current requirements and research challenges upon the stringent regulations.

In this review, we survey currently existing *academia and industry* research on the SO_2 influence on HCs, NO and CO oxidation in diesel engines. The paper starts with a brief introduction of DOC functionalities in the aftertreatment system as well as the discussion scope based on the relevance of different oxidation reactions to practical DOCs. An analysis of the fundamentals of SO_2 interaction with noble metals and typical oxide supports is followed. Emphasis is given to the review of latest understanding of SO_2 function mechanism on typical DOCs (particularly PGM-based ones) during various oxidation reactions. The strategies to mitigate sulfur poisoning, including regeneration methods of sulfated DOCs and development of sulfur-resistant materials, are then surveyed. In the end, we put forward opportunities and challenges where future research on sulfur-resistant DOCs could advance.

2. DOC working architecture/ functionalities.

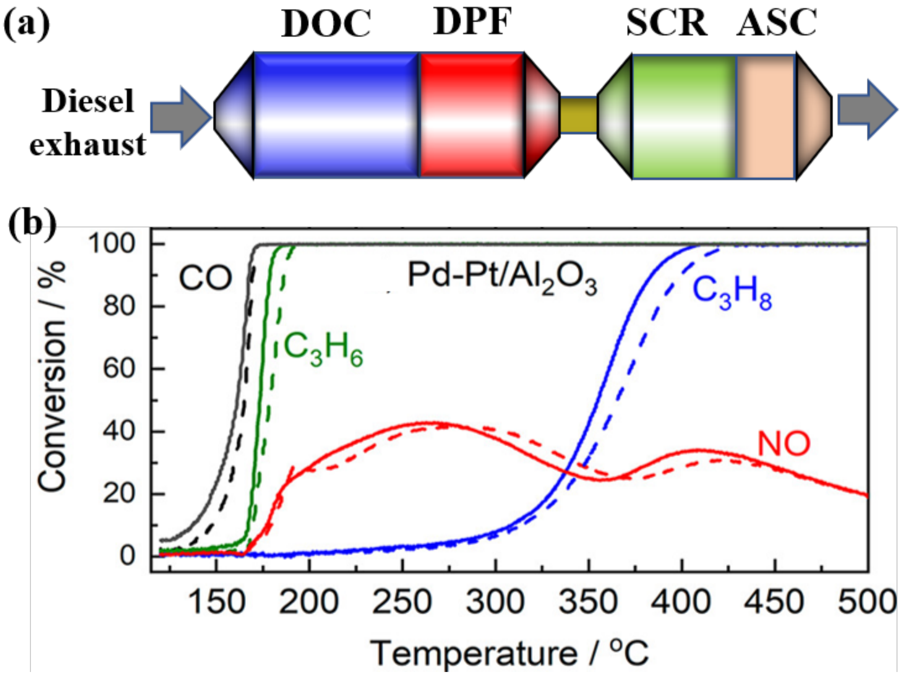

Figure 2. (a) Current diesel exhaust aftertreatment system architecture and the structure of DOC cordierite monolith (side and end views). (c) Light-off curves of HCs (e.g., C_3H_6 and C_3H_8) and CO, and conversion of NO oxidation on Pd and Pt based catalysts. Reprinted with permission from ref [24]. Copyright 2021 American Chemistry Society. Further permissions related to the material excerpted should be directed to the ACS.

Before reviewing the sulfur impact on DOCs, it is necessary to clarify the role of DOCs in the diesel aftertreatment control system and the relevance of different oxidation reactions studied in academia labs to the real-world practice. As presented in the layout of current diesel exhaust aftertreatment system architecture **(Figure 2a)**: DOC meets the exhaust in the first place, closely followed by DPF, combined with downstream coupled SCR and ASC assembles. Within this working architecture, DOC functions to 1) oxidize unburned HCs and CO into CO_2 or/and H_2O, and especially a portion of NO to NO_2 with excess air input; and 2) boost PM and NO_x purification efficiency in downstream working cells by generating heat and NO_2.[6-7, 25-28] The principal role of DPF is to trap soot while at much lower temperatures when O_2 dose is unable to combust soot, the NO_2 generated over DOC acts as an oxidant (called "passive" regeneration). As a relatively high temperature is required for DPF to enabling soot combustion, DOCs also involve heating the exhaust by exothermic oxidation of HCs (either coming from exhaust or additionally injected fuel). After passing through DPF, the remaining portion of NO_2 produced in DOC will reach SCR to kick-off "fast" SCR reaction to improve NO_x control, followed by removal of NH_3 residue by ASC.[4, 26, 29] Obviously, the performance of DOC determines the overall efficiency of the whole diesel aftertreatment system.

Currently, despite intense academic research interest, *the catalytic oxidation of CO is not a real challenge in the diesel after-treatment system* due to its lower light-off temperature relative to those of other coexisting gaseous pollutants, as shown over typical PGM DOCs in **Figure 2b**.[30-31] Therefore, the inclusion of SO_2 influence on CO oxidation in the following text is taken more as an academic probe reaction rather than its industrial relevance. Regarding HCs, there exist various kinds of light and heavy HCs compounds, among which short-chain propane and propylene are studied the most in academia, either in isolation or in conjunction with other gaseous species, as the model saturated and unsaturated alkane and alkene, respectively (e.g. in **Figure 2b**).[7, 32-41] In contrast, long-chain like iso-octane or n-dodecane which are liquid at ambient conditions, are often neglected though most real-world HCs in the exhaust are present in such a long-chain form. A recent study has introduced diesel fuel into a plug flow reactor to simulate the realistic diesel oxidation process in a DOC catalyst whereas it was challenging to analyze the variation of oxidation products.[42] In this context, knowledge is lacking regarding SO_2 influence on heavy-HCs (C_4 and beyond) oxidation and our discussion will be more based on light HCs-relevant studies in this review. It should be noted that methane combustion is not even an issue in the diesel exhaust oxidation; however, the case of sulfur influence on CH_4 oxidation cannot be completely excluded in the following text (especially in the section of mitigation strategies for sulfur poisoning) in the sense that it could act as a reference for missing studies on other kinds of HCs in the diesel exhaust.

As with HCs oxidation, NO oxidation is the other challenge facing DOC application in the real world. In DOC function, one has to mention that the oxidation of NO to NO_2 plays a key role in soot and NO_x removal in diesel aftertreatment system. The NO oxidation reaction is kinetically controlled at low temperature and thermodynamically constrained at high temperature while the temperature window in between varies with catalysts.[43] Typically, the evolution of NO_2 from NO oxidation usually tends towards the exit of the catalyst bed, which increases until the oxidation of CO and propylene (C_3H_6) is almost complete but occurs prior to the oxidation of propane (C_3H_8) (**Figure 2b**).[24, 44-45] Of great significance to $DeNO_x$ efficiency in industry, there is much research available for sulfur-related NO oxidation over DOCs, but still it deserves extended study under more realistic conditions.

3. The impact of SO_2 on DOCs.

3.1. Fundamentals of SO_2 interaction with typical noble metals/oxides

In order to better understand the nature of SO_2 influence on the oxidation of NO, HCs and CO over DOC catalysts, we will start with reviewing fundamental insights obtained on the interaction of SO_2 with the widely studied PGM-based noble metal catalysts and different types of oxide supports in the absence of reaction atmosphere.[11, 46-51] Typically, the oxidation of SO_2 to SO_4^{2-} over catalysts follows either Eley-Rideal (ER), Langmuir-Hinshelwood (LH) or Mars-van Krevelen (MvK) pathway: LH and ER mechanisms are involved with the oxidation of SO_2 (either adsorbed or from gas phase) by surface activated O_2 while MvK mechanism is closely linked to the surface lattice O, which generates O vacancy upon production of SO_3 and SO_4^{2-}.[50, 52-53] The left O vacancy can be refilled by gas-phase O_2 which initiates the next oxidation circle. Taking SO_2 oxidation over PdO surface as an example, it was calculated that on the surface of PdO (101) ER and LH mechanisms are kinetically limited by higher activation barrier of O_2 while MvK mechanism is more kinetically feasible although the former two mechanisms are exothermic under more realistic condition (400°C).[53] However, SO_2 oxidation path would differ with different reaction systems, the discussion of which is beyond our focus given the very limited data on surface experiments and modeling for DOCs.[11] Instead, we devote our main efforts to discussing the sensitivity of SO_2 oxidation towards different types of catalysts in the following text.

SO_2 interaction with noble metals. The reactivity of Pt and Pd towards the oxidation of SO_2 varies greatly based on different chemical states of the metals and the gas environment. Metallic Pt tends to chemisorb O_2 and acquires enhanced uptake and oxidation capability towards SO_2 in the presence of O_2. Yet Pt is unable to be sulfated wherein the oxidized SO_x sits around Pt particles forming "$Pt^{\delta+}$-SO_3/SO_4" like species.[54] By comparison, Pd would convert to stable $PdSO_4$ in contact with SO_2 and the presence of O_2 stabilizes the formation.[50] The decomposition temperature of $PdSO_4$ can be beyond 600°C. Therefore, $PdSO_4$ could act as an inhibitor for further sulfation of PdO in the presence of SO_2.[50] When comparing with monometallic, bimetallic catalysts like Pt-Pd, Pt-Rh, and Pd-Rh are found more active than individual Pt, Pd or Rh for the uptake and oxidation of SO_2 possibly caused by a synergistic effect existed between alloyed metals.[49, 55-56] The SO_2 adsorption/desorption characteristics are greatly related to metal particle size: mono- and bimetallic Pt/Pd particles supported on Al_2O_3 with smaller sizes contribute to the formation of stable sulfate species; while those with larger sizes are in favor for the formation of low thermally stable species (e.g. physically SO_2 and adsorbed sulfite species).[49]

The interaction of sulfur compounds with noble metals not only gives rise to sulfur deposit on the surface but also facilitates rearrangement of crystal structure and modifies the electronic properties of noble metals. Previous studies have found that SO_2 adsorption induces recrystallization of Pt(111) facet to Pt(100) via surface diffusion driven by lowered surface free energy; and this even occurs for Al_2O_3 supported Pt catalyst.[57-58] Notably, for those reactions which are sensitive to surface structure of the catalyst, such as ring opening of methyl-cyclopentane, hydrogenolysis and isomerization, they are sensitive to sulfur poisoning as well.[57] The sulfur species can decrease the electronic density of Pt clusters as a result of its electronegative character, thus weakening the adsorbing ability of Pt towards other adsorbates.[59-60]

SO_2 interaction with supports. Typically, Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2 and their combinations are popular support materials for the state-of-the-art DOCs. Except SiO_2, other oxide supports typically behave like a reservoir for sulfates. Al_2O_3 is considered as the most common support due to its high surface area and thermal stability. Taking Pt/Al_2O_3 DOC as a model catalyst, the richness of OH on the catalyst surface (mainly support surface) enables the adsorption of SO_2

(Eq. 1) besides those directly adsorbed on the noble metal (Eq. 2), which can react with activated oxygen on noble metals (Eqs. 3, 4) and the resulting SO_3 transports onto the support (Eq 5) (possibly as highly stable $Al_2(SO_4)_3$ with decomposition temperature beyond 700°C).[11, 51, 61-62] Under more realistic condition with humid exposure, the excess water vapor accelerates the formation of $Al_2(SO_4)_3$ or H_2SO_4 (Eqs. 5, 6) owing to the increased number of surface-OH groups that react with SO_2 or faster combination of SO_3 with adsorbed H_2O.[63-64] The equations are shown below:

$$SO_2 + OH^- (s) \rightarrow SO_3H^- (s) \quad (1)$$

$$SO_2 + * \rightarrow SO_2* \quad (2)$$

$$SO_3H^- (s) + O* \rightarrow SO_4H^- (s) + * \quad (3)$$

$$SO_2* + O* \rightarrow SO_3* + * \quad (4)$$

$$SO_3* + 2OH^- (s) \rightarrow * + SO_4^{2-} + H_2O \quad (5)$$

$$SO_3* + H_2O (s) \rightarrow * + H_2SO_4 \quad (6)$$

where * indicates vacant sites on noble metals and (s) indicates catalyst surface. However, the resulting oxidation products, i.e., SO_3 or H_2SO_4 have inhibition effect on further oxidation of SO_2, especially H_2SO_4 that owns enhanced poisoning ability to the active sites.[64-65] From another point of view, H_2O competes with SO_2 for the adsorption sites on Al_2O_3, which promotes spillover of sulfur from the support to PdO or the reverse in the case of Pt.[11] Both end up with fast deactivation of catalysts, particularly for PdO/Al_2O_3 due to accelerated formation of $PdSO_4$.[11, 66-69]

TiO_2 and SiO_2 are another popular acidic supports studied in academia.[70-71] Compared to Al_2O_3, TiO_2 is known to be more resistant towards sulfur poisoning because the sulfates formed on TiO_2 is thermally unstable.[72-74] In contrast, SiO_2 is very inert towards the adsorption of acidic SO_2 due to its high acidic nature.[75-76] As a result, the use of non-sulfating SiO_2 favors rapid migration of SO_2 onto Pt, followed by oxidation and facile desorption of SO_3.[77] This allows for a high reactivity of Pt/SiO_2 towards SO_2 oxidation but instead a faster sulfation of some active components (e.g. PdO) due to incapability of sulfur storage in the support.[11] ZrO_2 is an amphoteric support, which has both acidic and basic sites on the surface.[75] Thus, ZrO_2 is more in favor for the adsorption of SO_x. It is found that the sulfur deposit can be three times higher on ZrO_2-supported NO_x storage reduction (NSR) catalyst than on TiO_2-supported one.

In fact, SO_2 oxidation can take place in the absence of O_2, where supports provide oxygen species to form sulfates.[50] This is especially true for CeO_2 on account of its high oxygen storage and release capacity.[77-79] The formation of $Ce_2(SO_4)_3$ is predominant in a slightly reduced atmosphere coupled with the reduction of Ce^{4+} to Ce^{3+}.[80-81] While in the presence of excess O_2, stable $Ce(SO_4)_2$ takes the majority form on the surface as the surface carries rich reactive oxygen species.[80-81] It is reported that both sulfite and sulfate formation, including transformation of sulfite to sulfate, occurs more efficiently on CeO_2 than on Al_2O_3.[81-82] The formed sulfates on CeO_2 is thermally more stable than on the other supports, dissociating into SO_2 and O_2 at a higher temperature span of 800 to 900ºC.[78, 83] Due to preferential sulfation of CeO_2 over other supports and higher stability of ceria sulfate, it is much easier for, such as Pt/CeO_2, to get irreversibly deactivated than Pt/SiO_2.[77] Whereas on the other hand, the remarkable sulfur storage capacity of CeO_2 also helps prevent sulfate accumulation on the active metal components.

Besides directly interacting with SO_2, the acid-base properties of the supports may indirectly influence the sulfur interaction with noble metals by affecting the chemical state of the active components. Acidic supports like Al_2O_3-SiO_2 and low Si/Al ratio siliceous zeolite supports with higher amounts of acidic sites are able to maintain metallic or less oxidized Pt or Pd species (or highly dispersed Pd^{2+}) even at high oxygen concentration while basic supports and zeolites with high Si/Al ratios result in large PdO_x clusters/particles etc.[66, 84-87] The former, such as Al_2O_3-SiO_2, gives rise to higher CO and propane oxidation activity than basic CeO_2 or ZrO_2 supports by keeping high oxidation-resistance ability of metallic Pt and reducibility of Pt oxide, even in the presence of SO_2.[88-89] Yet it is also argued that the high-dispersion Pd species on low Si zeolite would degrade to large particles with enhanced mobility over the support.[90] The controversy could arise from discrepancies in reaction conditions, where the latter contains CH_4 and large amounts of steam in the feed; and also from the distinct support constructure (such as mono or bimetallic/acidic-basic compositions, oxide or zeolite etc.). Clearly, it still remains largely unknown about the role of supports in determining the nature of active phase when SO_2 is involved under typical DOC reaction regime.

In essence, the interaction of SO_2 with either single metal oxides or composites can be seen as an epitome of heterogeneous reaction of SO_2 wherein the rich hydroxyl groups, active oxygen species as well as defects (e.g. exposed lattice oxygen or metals) on solid surfaces provide important sites for the adsorption and transformation of SO_2.[61, 91] Nonetheless, the reactivity varies with distinct catalyst structure, composition, and especially reaction environment, as below illustrated in the oxidation of NO, HCs and CO over DOCs.

3.2. SO_2 effects on PGM-based diesel oxidation reactions.

As presented in the side and end views in **Figure 3a**, the current DOC cell is based on a monolith honeycomb cordierite coated with PGM catalyst, having open channels in both ends parallel to the exhaust flowing direction so as to minimize the gas resistance.[7] The main active components contained in washcoat are Pd, Pt and possibly small amounts of Rh if present, besides oxide carriers including CeO_2, ZrO_2 and Al_2O_3. When gas flows through the channels, HC, NO and CO react with O_2 on the catalyst. An early review by Russell and Epling has offered in-depth coverage in relation to the reaction models of HCs, NO and CO oxidation over PGM-based DOCs, and towards precious metal characteristics (oxidation state, particle size/dispersion, active site location) and O_2 variation, which we will not expand here.[3] A common feature appeared for HCs, NO and CO oxidation is that all proceed via interfacial or superficial reactions, where trapping of HCs, NO and CO on metals serves as the precursor for total oxidation (which is secondary to C-H bond cleavage in the case of HCs).[33, 53, 92-100] Those adsorbed molecules reacts with neighboring activated lattice oxygen (route i), or oxygen adsorbed in the support vacancies (route ii), or with oxygen species adsorbed on metals (route iii) , as shown in **Figure 3b**.

No doubt these reactions compete for the same active sites (i.e., the metals) and the oxygen species. As previously displayed in **Figure 2**, the onset of NO oxidation begins after complete oxidation of C_3H_6 since the latter prevents sufficient oxygen coverage for NO to reach O-adatoms or the resulting NO_2 can be consumed by C_3H_6 during the early stages of C_3H_6 conversion. But it occurs conversely for C_3H_8 because of the lower ability of C_3H_8 towards the removal of surface O_2 that allows for high active sites for oxidation of NO.[52] A competition between HCs on CO oxidation can also be found over PGM catalysts whereas the light-off of HCs oxidation consistently follows that of CO due to the stronger inhibition by CO.[16, 101-102] It should be noted that the highly sticking NO_2 on Pt sites would dissociate into gas-phase NO and O, forming an oxidized Pt surface of less activity; and that NO_2 residing on PdO reduces the number of vacancies, in turn decreasing the mobility of surface oxygen and thus NO oxidation.[77, 97] A similar selfpoisoning is popular for CO oxidation at relatively low temperatures in that CO preoccupies the precious metal sites and blocks the adsorption of O_2.[77, 97] Unlike NO_2, the inhibition effect will be removed with the increase of temperature and causes no obvious postpone of activity. Such phenomenon can be more complex in terms of HCs oxidation concerning the varying chain length and multiple oxidation intermediates over PGM catalysts but there are very few studies to refer.[3]

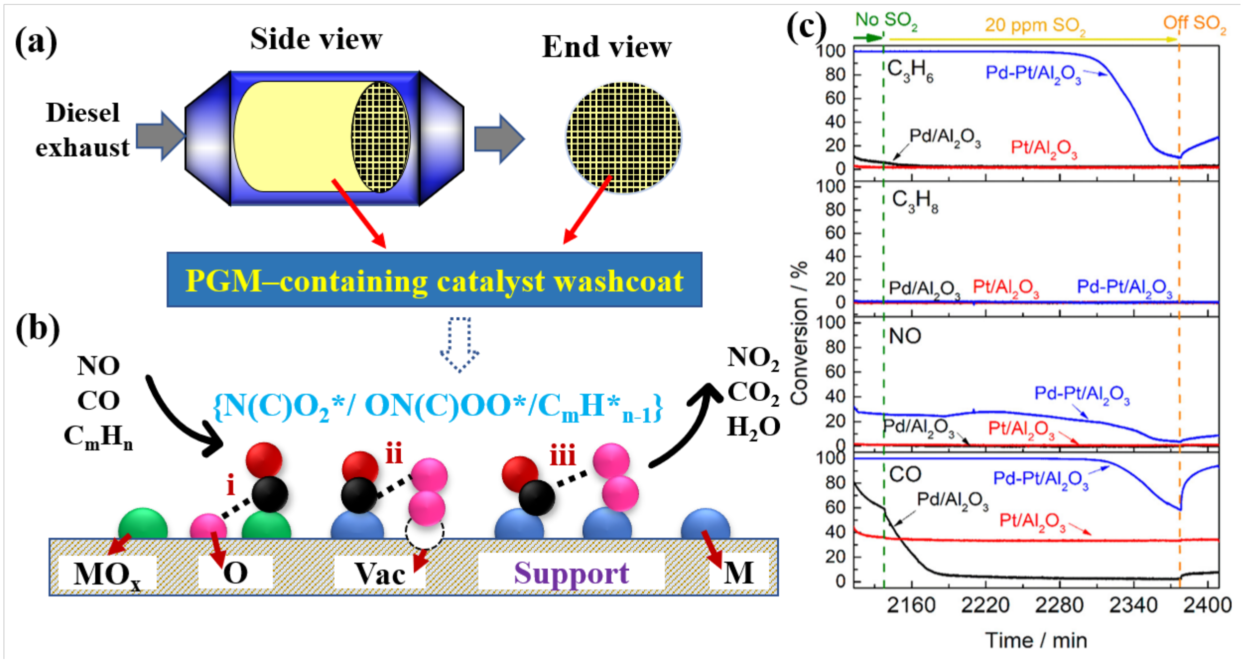

Figure 3. (a) Current DOC cordierite cell in the diesel aftertreatment system; (b) Possible reaction routes (including i, ii, iii) of NO, CO, or HCs on the surface of catalyst, where the black ball represents N, C or C_mH_{n-1} while the red one represents O or H. Since C-H bond cleavage serves as a prerequisite step for the total oxidation, herein we simplify the cleavage model of HC molecule. (c) gas conversions (CO, NO, C_3H_8, and C_3H_6) during the sulfur poisoning at 200°C for 4 h; total flow rate of 2600 mL min^{-1} containing 1000 ppm of CO, 500 ppm of NO, 500 ppm of C_3H_6, 500 ppm of C_3H_8, 10vol % O_2, and 5 vol % H_2O balanced in Ar. Reprinted with permission from ref [24]. Copyright 2021 American Chemistry Society. Further permissions related to the material excerpted should be directed to the ACS.

Combining abovementioned interaction of SO_2 with DOCs (in Section 3.1), one can see that SO_2 would block the oxidation pathways of HCs, NO and CO by occupying the noble metal sites and consuming O_2 species due to competition effect.[70-71, 103] Just as observed in the simultaneous oxidation of HCs, NO and CO **(Figure 3c)**, the presence of sulfur results in lower conversions of all reactants over PGM catalysts. No effect is shown for propane because of the lack of activity at the test temperature of 200°C. This inhibition impact is more pronounced with high SO_2 dose.[47, 62-63, 72, 76, 100, 103-116] Compared to HCs and NO, the negative impact of sulfur is less significant for CO in the practical application of DOCs.

However, kinetic models on sulfur impact are difficult to build given that a series of reactant-SO_2-O_2 dynamic behaviors is involved even for a single oxidation process. For instance, the inhibition effect of SO_2 on the conversion of HCs (especially unsaturated HCs) below light-off is proposed to be the blocking of active Pt sites by sulfur deposits, whereas it is unable to track which step (such as HC activation, decomposition, O incorporation, desorption etc.) is accounting for the sulfur poisoning.[110-111] As for the much simpler NO and CO oxidation systems, the poisoning process may vary from inhibition of NO or CO adsorption to O_2 dissociation, or to the formation or decomposition of intermediates (e.g. nitrate for the case of NO oxidation).[60, 71, 103] Especially the equilibrium of SO_2-O_2-reactant adsorption waves with reaction conditions when the reactions compete with each other or the dominant reaction mechanism changes. Based on the uncertainty in kinetic model, we extract major fundamentals underlying the apparent observation (inhibition vs promotion) of SO_2 effects on the three oxidation reactions, as is discussed below.

3.2.1 Inhibition. Depending on the different oxidation subject under a specific condition, the inhibition effect includes blockage of noble metals and restriction of oxygen exchange as a result of different forms of sulfur species. At relatively low temperatures, SO_2 molecules linger on the metal sites to prevent adsorption of other reactants.[110, 117] At high temperatures, SO_2 on the noble metals tends to be oxidized into SO_3/sulfuric acid (H_2SO_4) which possibly transports onto the oxide supports (except SiO_2) as stabilized sulfate or in part, desorbs as gaseous SO_3 (in the case of SiO_2 as support or from the decomposition of H_2SO_4).[64, 91, 109-110, 115, 117-120] Under typical diesel exhaust gas conditions containing excess water vapor, the surface of commercial DOC (such as 0.1% Pt on Al_2O_3 and SiO_2 washcoat) can be quickly saturated with H_2SO_4, followed by slower sulfation of the bulk washcoat.[121] By comparison, the freshly formed H_2SO_4 on/nearby the metals is considered as a major poison for NO oxidation below 400°C in contrast to the negligible influence of more stable sulfate species, e.g., $Al_2(SO_4)_3$ in washcoat. Notably, such a deactivation could be removed upon heating to 400°C as H_2SO_4 desorbed between 350 and 400°C; In the case of CO oxidation, a high ratio of larger pores in Pt/TiO_2 catalyst is found to ease the poisoning and enables a stable conversion of CO within 250-300°C by accommodating liquid H_2SO_4.[120-121]

The behavior that the freshly formed sulfates undergoes displacement to interfacial sites/ supports or kinetically irrelevant sites allows for the redistribution of sulfates on non-noble sites.[100, 122-124] Some possible ways to redistribute sulfates, i.e., catalyst "baking", include a treatment of the catalyst in its sulfated state under moderately high temperatures and net oxidizing conditions, and field-aging (e.g., commercial DOCs used after vehicle or engine aging in different types and times of S fuel duration).[100, 104, 122, 124] For instance, the NO oxidation activity decreases linearly in response to the amount of freshly deposited sulfur, until it reaches a plateau.[124] While the catalyst after baking or the as-received DOC from vehicle or engine-aging demonstrates no sign of poisoning albeit with high sulfur loading.[123-124] Obviously, the redistribution of sulfate helps to free active sites and delay the negative effect of sulfur on noble metals. Even so, an early study found that the associative adsorption of propylene and CO on Pt sites is still restricted due to the repulsive force from the accumulated sulfate on Al_2O_3, as well as from the increased coverage of propylene on Al_2O_3.[30] Moreover, the abundance of C_3H_6 or CO promotes reduction of SO_x to S solids, the bounding of which to Pt sites limits the availability of Pt to reactants as well.[110, 117, 125-126]

Except blockage of reactant adsorption over the noble metals, another reason behind the catalytic activity loss is the restricted availability of oxygen species to the oxidation of the target adsorbate. For example, the dissociative adsorption of O_2 on Pt site is forbidden due to weakened electron transfer from Pt to O_2 as a result of sulfur coordinated onto Pt with high coverage; and beyond which, the inertization of O in sulfates (both for sulfated metals and supports) limits oxygen transfer. [60, 127] For some supports that govern oxygen transfer between active sites and supports (e.g., CeO_2, Ce-Zr and perovskite), they are flexible in donating/withdrawing oxygen to/from Pt/Pd to supplement consumed O or prevent overoxidation of Pt. Thus they work better initially but would fail eventually like Al_2O_3 when the supports are saturated with stable sulfate etc.[128-133] Different from the cases of NO and HCs (especially unsaturated alkenes), H_2O could also act as an O supplier in the case of CO oxidation by dissociating into active OH, such as at Pt-Ti interface, to initiate CO oxidation by forming COOH intermediate.[134] However, the formation of $TiOSO_4$ on TiO_2 surface in the presence of SO_2 hinders the dissociation of H_2O and oxygen transfer at the interface. Furthermore, H_2O can react with oxidized SO_2 to form H_2SO_4 liquid which aggravates this process, as is discussed over typical PGM-based DOCs in Section 2 and above. Irrespective of H_2SO_4 or stable sulfate poisoning, a high sulfur storage capacity of catalyst is capable of postponing complete activity loss.[60, 135] Whereas structural degradation cannot be avoided by strongly bounded sulfur deposit or sintering of support under repeated thermal impact within operational temperature regime. The structure variation as a function of environmental factor further hampers mass transfer of reactants/products (including redistribution of sulfates) in the exterior/interior of catalyst.[60, 88, 121]

Table 1. A summary of SO_2 impact on various oxidation reactions and relevant reaction conditions over typical PGM catalyst systems.

Catalyst	Gas feed composition (balanced with inert gas)	WHSV (L g-cat^{-1} h^{-1})	Oxidation reaction	$X_{conversion}$ (%) / T_{50} (°C)			Ref
				SO_2-free [i]	With SO_2 [ii]	SO_2-aged [iii]	
2 % Pt/Al_2O_3 monolith [α]	(*a*) SO_2 aging: 630 ppm NO, 8 vol% O_2, 30 ppm SO_2; 200°C for 22h. (*b*) 630 ppm NO, 8 vol% O_2; heating, at 200°C	~444	NO	27%	-	92%	136
1.21 % Pt/Al_2O_3+1.54%SiO_2	(*a*) SO_2 aging: 20 ppm SO_2, 10%H_2O, 5%CO_2, 10%O_2, at 300°C for 5h. (*b*) 500 ppm NO, 100 ppm CO, 100 ppm C_3H_6, 5% CO_2, 3% H_2O, 10% O_2; heating, at 300°C	30	NO	~80%	-	~80%[†]	54
1.47wt%Pt-0.41wt%Mn/Al_2O_3	1000 ppm NO, 10 vol% O_2 and 300 ppm SO_2 (if used); heating.	120,000 [*]	NO	~98% [‡]	60% [‡]	-	103
1%Pt/Al_2O_3	(*a*) SO_2 aging: 50 ppm SO_2, 5 vol% O_2, 10h at 500°C. (*b*) 4.5 vol% C_3H_8, 15 vol %O_2, 50 ppm SO_2 (if used); heating.	30	C_3H_8	260	290	230	117
1wt%$Pt/Ce_{0.67}Zr_{0.33}O_2$	(*a*) Presulfation: sulfuric acid impregnation, calcination at 500°C for 3h. (*b*) 800 ppm C_3H_8, 2 vol %O_2; heating.	300	C_3H_8	343	-	282	137
1 % Pt/Al_2O_3 monolith [β]	(*a*) SO_2 aging: 500 ppm NO, 30ppm SO_2, 8 vol% O_2, 5 vol% H_2O at 250°C for 22h. (*b*) 500 ppm C_3H_6, 8 vol% O_2, 5 vol% H_2O; heating.	360	C_3H_6	~197	-	~173	138
1 wt%Pt/Ce-Zr	(*a*) Pre-loading of 10 wt% SO_4^{2-} over Ce-Zr support via H_2SO_4 impregnation, followed by loading of 1wt% Pt. (*b*) 1000ppm CO, 500ppm NO, 500ppm C_3H_6, 200 ppm SO_2 (if used), 10 vol%O_2; heating.	24	C_3H_6	214	~237	178	139
			CO	225	~255	176	
1wt%Pt/TiO_2 (rutile)	1vol %CO, 40 ppm NO, 20 vol %H_2O, 40 ppm SO_2 (if used), 10 vol %O_2; steady-state test at 250°C for 6h.	600	CO	>90%	~60%	-	120
2wt%Pd/CeO_2	1 vol% CO, 1 vol % O_2, 100 ppm SO_2 (if used); steady-state test at 150°C for 30h	120	CO	> 95%	0	-	140
1.2 wt% Pd/Al_2O_3 monolith [γ]	(*a*) SO_2 aging: 1000ppm CO, 500ppm NO, 500ppm C_3H_6, 500ppm C_3H_8, 10 vol%O_2, 10 vol % H_2O, 20ppm SO_2 at 200°C for 4h. (*b*) Same as SO_2-free gas mixture presented in (*a*), steady-state test at 400°C for 30 min	22520 [*]	NO	~12%	-	0	24
			C_3H_8	> 90%	-	~40%	

4wt% Pd/ZrO_2	(*a*) SO_2 aging: 100ppm SO_2, 10 vol% air at 400°C for 5h. (*b*) 500ppm CO, 300ppm C_3H_6, 12 vol% O_2; heating.	240	C_3H_6	118	-	176	109
			CO	60	-	162	
0.7wt% Pt-1 wt% Pd/Al_2O_3 monolith $^\gamma$	(*a*) SO_2 aging: 1000 ppm CO, 500 ppm NO, 500 ppm C_3H_6, 500 ppm C_3H_8, 10 vol%O_2, 10 vol% H_2O, 20 ppm SO_2 at 200°C for 4h. (*b*) Same as SO_2-free gas mixture presented in (*a*), steady-state test at 200°C for CO, NO and C_3H_6 while at 400°C for C_3H_8.	22520*	NO	~37%	-	~ 13%	24
			C_3H_8	100%	-	~80%	
			C_3H_6	100%	-	~50%	
			CO	100%	-	~98%	

Catalyst was dispersed into a cordierite ceramic monolith: $^\alpha$ diameter (*Φ*) 22mm, length (*L*) 15mm, with a channel density of 400 cpsi containing washcoat 499 mg; $^\beta$ *Φ* = 20 mm, *L*=22 mm, with a channel density of 400 cpsi, containing washcoat ~500 mg; and $^\gamma$ *Φ* = 21 mm, *L*=20 mm, with a channel density of 400 cpsi, containing washcoat ~500 mg. ^{i} Fresh sample in SO_2-free gas feed. ^{ii} Fresh sample in SO_2-containing gas feed. ^{iii} Sulfur-aged catalyst after being treated under Condition *a* was exposed to Condition *b* except for the one in Ref [117] that was exposed to SO_2-containing gas feed. * Here is GHSV (h^{-1}). ‡ Maximal conversion obtained at 330°C and 375°C without and with SO_2, respectively. † For 3rd-cycle evaluation.

3.2.2. Promotion. As exhibited above, the sulfated DOCs generally show decreased performance due to limited availability of noble metals and restricted oxygen transfer. These resulting features can be interpreted as negative modification of sulfates to the noble metals or to the support-metal interface. However, there appears a reverse phenomenon on the other side that an unexpected benefactory effect of sulfates is found in the oxidation of saturated alkanes (such as propane) over Pt-based catalysts.[11, 114, 136-138, 141-148] Similar occurrence to NO, propylene or CO oxidation is also reported by a few studies.[52, 77, 136, 139, 146-150] In light of SO_2-involved performance of typical PGM DOCs provided by Table 1, most positive observations are related to SO_2-aged Pt-based catalysts. The origin of such a promotion effect can be attributed to the sintering of noble metals and modification of electronic properties at the support-metal interface, as discussed below.

Sintering of noble metals. Typically, Pt-only catalyst is superior towards HCs and NO oxidation while higher PdO content lowers the CO light-off temperature than Pt-only ones, but high temperature cause activity degradation for both due to evaporation of Pt and decomposition of PdO into less active metallic Pd and sintering.[44, 101, 151-153] A popular observation is that larger Pt or PdO clusters (i.e., lower Pd dispersion) at high loading exhibit higher NO and HCs (mainly reported for propane and propylene oxidation) activity than small ones because of attenuated oxygen binding with noble metals.[123, 154-155] This feature allows for moderate O_2 adsorption-activation-desorption dynamics over active metallic Pt or less oxidized PdO species.

Many studies have found that sulfur can induce surface reconstruction and particle agglomeration by lowering the surface energy. In doing so, the sintering of Pt in Pt-only catalysts turns out to promote the oxidation of NO or propane despite limited accessible sites.[52, 77, 89, 123, 136, 144, 146, 149] For example, the maximum NO conversion is observed to increase with the decreasing dispersion of Pt after aging of Pt/Al_2O_3 in SO_2/SO_2+O_2 mixture at varying temperatures (**Figure 4a**).[136, 138, 146] One possible explanation is that the adsorbed SO_2 helps to remove strongly bonded oxygen species on Pt by irreversibly reducing highly dispersed PtO_2 clusters to partially sintered active metallic Pt, as shown in the electron microscopy image in **Figure 4b**.[89, 136, 146] The resultant large metallic Pt particles, resembling the case of NO oxidation, exhibit higher reactivity to propane oxidation provided that metallic Pt serves to dissociate chemically adsorbed O_2, forming comparatively weakly bounded $Pt^{\delta+}$-$O_a^{\delta-}$ pairs (rather than fully oxidized PtO_2) that are efficient for the polarization and cleavage of C-H bond (the C-H activation, as already mentioned before, is the perquisite for the complete oxidation of HCs.).[144] For other type of HCs, relevant research is still missing. Compared to the findings for propane and NO oxidation, the sintered Pt particles caused by sulfation are found less active for the oxidation of CO.[120, 134] Especially the “oxygen-scavenging” ability of SO_2 may hurt the contribution of surface metal oxide phase to the catalytic CO oxidation.[97, 156] Yet controversies can be found in different literature reports about the role of PGM particle size and oxidation state in the oxidation of CO with postulated active forms ranging from metallic atom, oxides, clusters, to nanoparticles or mixed phases etc.[157-159]

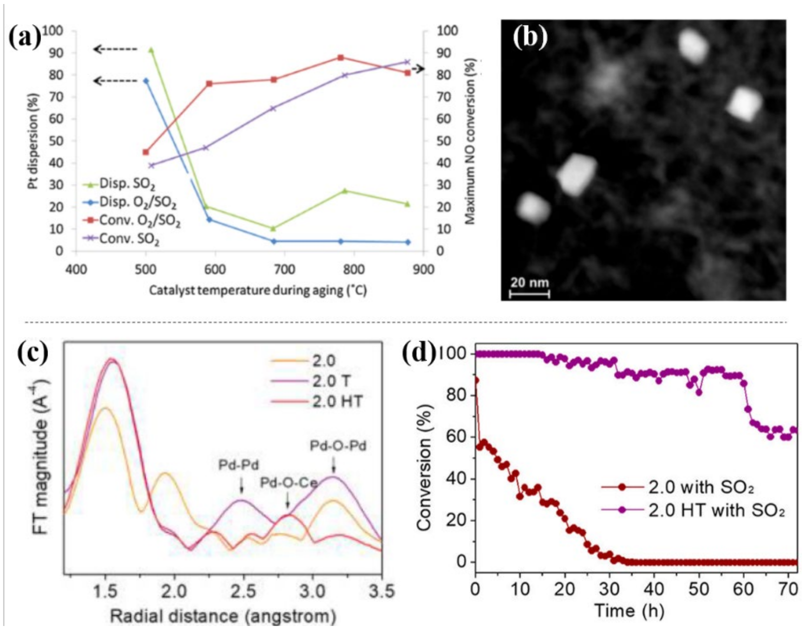

Figure 4. (a) Platinum dispersion and maximum NO conversion versus aging temperature for the sample aged in 30 ppm SO_2 + 10% O_2 and comparison with the sample aged in SO_2 alone; (b) STEM images of large Pt particles appeared in the SO_2+O_2-900ºC-aged Pt/Al_2O_3 catalyst. Reprinted with permission from ref [146]. Copyright 2012 Elsevier. (c) Overlapping of the FT-EXAFS spectra of 2 wt % as-made (2.0), thermally treated (2.0 T), and hydrothermally treated Pd/CeO_2 (2.0 HT), and (d) CO oxidation results of 2.0 and 2.0 HT in the presence of 100 ppm of SO_2 flow. Reprinted with permission from ref [140] (https://pubs.acs.org/doi/10.1021/acscatal.7b01810). Copyright 2017 American Chemical Society. Further permissions related to the material excerpted should be directed to the ACS.

As for Pd-only catalysts, there are insufficient investigations to discuss S-induced redistribution of Pd, partially because Pd tends to transform into stable $PdSO_4$ which is unfavorable for diesel oxidation (Table 1). Moreover, the sulfur-relevant studies on Pd catalysts basically have focused on CO oxidation given the superior activity of Pd-dominating materials towards CO rather than HCs and NO oxidation. Whereas different from what was found over Pt catalysts for the oxidation of HCs and NO, CO oxidation exhibits worse performance at low Pd dispersion. For instance, the T_{50} was found to increase with decreasing Pd dispersion over sulfur-aged Pd/Ce-Zr-Al catalyst because of limited oxygen adsorption and activation.[127] In another instance, the surface hydroxylated Pd/CeO_2 via hydrothermal treatment (with 10% H_2O at 750ºC) allows redispersion of Pd nanoparticles into reduced domain size in an increased numbers of oxidized state through migration of Pd^{2+}-OH along ceria surface with a strong Pd-O-Ce interaction **(Figure 4c)**.[140] During the CO oxidation with 100 ppm SO_2 for the first 14h, the catalyst obtained 100% CO conversion by hindering sulfate and carbonate accumulation **(Figure 4d).** One can tell that SO_2 in this case is taken as a probe to evaluate the overall catalytic outcome rather than the reverse, i.e., the force to drive the change of Pd chemical state. Actually, in both academia and industrial fields, most researchers follow the former protocol to explore sulfur influence on DOCs while ignoring SO_2-induced dynamic change of chemical characteristics (oxidation state, particle size/ dispersion) of PGM in the atmosphere of HCs, NO or CO.

The combination of Pt and Pd bimetallic catalyst has been chosen as the most desirable one applied in real practice based on a good balance between HCs/NO/CO oxidation and stability towards hydrothermal aging and sulfur poisoning.[24, 135, 151, 160] An optimum ratio of Pd:Pt provides sufficient Pd surface for CO oxidation and Pt surface for HCs oxidation by the formation of PtPd clusters, albeit with decreased NO oxidation by decreased Pt size and Pt relative content on the surface.[52] The PtPd alloy prevents SO_2 adsorption on PdO and Pt species through a subtle electronic interaction within the alloy phase.[161-162] However, the effects of PtPd alloy dispersion/size in the resistance towards SO_2 poisoning are seldomly studied in the area of DOCs, but rather in methane oxidation.[163-164] For the latter, the PtPd alloy catalyst with reduced size is found to perform better than its large-sized monometallic counterparts that have suffered from sintering, despite that both Al_2O_3 supported mono- and bimetallic Pt/Pd catalysts with large particle size are adverse to the deposit of sulfur species.[49, 56, 123, 164] This result somewhat contrasts to the previous finding in the individual reaction of SO_2 with PdPt/Al_2O_3 catalysts that small-sized noble metals are in favor for the formation of stable sulfate, regardless of Pt:Pd ratio.[49] Obviously, not only the size (or dispersion) and composition, other factors including metal-support interaction (as mentioned in the following) and especially reactants/reaction conditions also have a great effect on the catalytic behaviors of DOCs in the presence of SO_2.

Electronic modification of support-metal interface. Besides the size effect of Pt particles, the sulfates either through loading of SO_4^{2-} or presulfation could significantly promote the reactivity of Pt/Al_2O_3 or Pt/Ce-Zr towards HCs (especially propane and propylene), CO and NO oxidation as a result of increased acidity.[117, 138-139, 141-142, 144, 165-167] For example, the loading of 10wt%SO_4^{2-} on Pt/Ce-Zr enables a 75°C decrease of T_{90} of the oxidation of propylene and CO relative to the fresh catalyst. Moreover, the conversion of Pt/Ce-Zr-10wt%SO_4^{2-} exceeds 95% at

240°C even after 0.02% SO_2 poisoning for 20 h in simulated diesel exhaust stream.[139] Also, it is found that SO_4^{2-}-aged Pt/Al_2O_3 catalyst shows the best activity for NO oxidation among the fresh and aged samples.[138] A reasonable explanation is that the enhanced surface acidity by the presence of SO_4^{2-} inhibits further adsorption of SO_x on the catalyst, regardless of HCs, NO or CO oxidation. For the case of NO oxidation, another possible mechanism is that the enhanced acidity upon SO_2 exposure over Pt/Al_2O_3 is likely a way to protect active metallic Pt from forming oxide phase by weakening the Pt-adsorbate (possibly including NO_2) bond.[138, 168] Differently from the finding above, this may reflect an non-sintering possibility for Pt to resist oxidation due to electron-attracting property of sulfate group, but it still needs further investigation since the change of oxidation state of Pt can be subtle under different reaction conditions, as seen in the conflicting result in the case of CO oxidation (as mentioned below).

As explained in the case of HCs oxidation, it is not the overall acidity of the catalyst but that the Pt-support interface is the key factor, therefore over loading of SO_4^{2-} would result in less promotional effect and even inhibition.[117, 141-142, 144, 165-166] The buildup of electronegative sulfate deposit on the support which lies in close proximity to the edge of Pt particles induces the withdrawal of electrons from Pt to SO_4^{2-}, leading to the formation of $(SO_4^{2-})^{\delta-}$-$Pt^{\delta+}$ couples.[137, 166] The stronger acidity of $Pt^{\delta+}$, the easier activation of C-H bond through $Pt^{\delta+}$-H^- interaction.[146, 166] An early study found that the pre-coverage of SO_2+O_2 on single Pt (111) could directly involve C-H activation of propane by abstraction of H from propane ($SO_x+C_3H_8 \rightarrow C_3H_y+HSO_x$) in which preadsorbed oxygen is a necessary condition.[169] Notably, for a fresh Pt/γ-Al_2O_3 catalyst, the propane oxidation is inhibited at the beginning of SO_2 feed until the catalyst has been sulfur-aged, and then the inhibition effect becomes a promoting effect.[117, 142, 166] Although rarely common, the sulfates bring the same benefits to Rh/Al_2O_3 catalysts as to the Pt catalysts in the oxidation of propane and propylene, i.e., the large Rh ensembles (or sintering) forms as a result of sulfation while sulfates mediate propane and propylene activation/spillover at the metal-support interface.[150]

The electronic modification of sulfur varies as a function of catalyst system in the case of CO oxidation. For typical Pt-based catalysts, the sulfur adsorbates weaken Pt-CO binding by reducing the back donation of *d*-electrons of Pt to CO, and such perturbation may last over long-range distances, thus decreasing the formation rate of CO_2.[60] The change of metallic Pt to Pt^{2+} via Pt-S interaction is considered as the main reason for activity loss because Pt^{2+} may not be active for dissociation of O_2.[60] Different from Pt catalysts, the sulfate-induced interface effect is positive over Au-supported catalysts, especially over Au/TiO_2 catalyst.[114, 147-148, 170-174] Besides directly interacting with Au to positively charged Au, SO_4^{2-} ions develops unbalanced charge on Ti as well as defects in the TiO_2 network.[172] The changed electronic environment further influences the charge distribution on Au.[173-174] Structurally, SO_4^{2-} anchored on TiO_2 suppresses particle growth through intense interaction of SO_4^{2-} with TiO_2.[173-174] All these profiting from the modest SO_4^{2-} deposit moderately strengthens CO adsorption on Au (arisen from enhanced back donation) and O_2 activation (in defects) at the interface. However, heavy S deposit suppresses migration of CO to the Au-TiO_2 perimeter to react with activated O because of strong adsorption of CO on Au.[114, 147-148]

In brief, loading of SO_4^{2-} or presulfation acts as a short-term "baking" of catalysts at lab scale to deliberately modify the interface (**Table 1**).[54, 123, 138, 146-147] However, the promotion effect of acidity due to the presence of SO_4^{2-} at the Pt-support interface is not applicable for Pd-based catalysts in the diesel oxidation although it works in lean-burn CH_4 oxidation (which is not relevant to DOCs).[129, 175] For a Pt-Pd bimetallic catalyst, it is more sulfur-resistant than its monometallic counterparts in the oxidation of propane, propylene and CO (while not for NO oxidation) through the synergy effect of Pd-Pt alloy, as previously mentioned.[24] Whereas there still remains a large unexploited domain regarding the influence of SO_2 on chemical features of active components in diesel oxidation.

It should be highlighted that the promotion effect of SO_2 on NO, unsaturated alkene (e.g., propylene) and CO is not as universal as on saturated alkane oxidation. Such different functions of SO_2 on them may lead to a different reaction path in the presence of SO_2 when compared to that without SO_2. For example, if there is no SO_2 being involved, the oxidation of propane proceeds consecutively as propane → propylene→ ethane→ CO→CO_2 on Pt/Al_2O_3.[141] Since the presence of SO_2 inhibits the conversion of propylene and CO under this condition, propane tends to crack C-C bond consecutively, leading to the formation of ethane and C_1 fragments. While the oxidation of ethane is also promoted by SO_2 profiting from the acidic effect at the SO_4^{2-}-Pt/Al_2O_3 perimeter.[110, 141] This new reaction path can be an additional reason for the promoting effect of SO_2. Research also found that the promotion effect of SO_x is not confined to saturated HCs but is also found for oxygenates such as ethyl acetate and ethanol over Pt/Al_2O_3.[110] Besides abovementioned reasons, the sulfates promote the decomposition of partially oxidized intermediates that are most likely caused by newly created reaction pathways.

Findings from above indicate that the presence of sulfur compounds fundamentally perturbs where electron flow within adsorbates-metal-support or affects the geometric match between reactants with active sites, thus causing an apparent effect on DOC activity. However, the nature of such process remains unclear with varying catalyst formulation and under different reaction conditions due to limited studies. Despite that sulfation brings about activity increase to some degree, the catalyst would eventually evolve towards an unfavored electronic/geometric condition (e.g., fully oxidized, sintering, structural loss etc.) with long-term sulfur exposure, where its reactivity and sensitivity to diesel HCs/NO/CO becomes worse. In order to resist this process, mitigation strategies have been developed and will be reviewed in a later part of this paper.

3.3. SO_2 influence on non-noble metal-based diesel oxidation reactions

In the pursuit of non-noble metal-based DOCs, low cost transition metal oxides (TMOs), including perovskites and Mn/Ce/Co/Cr oxide composites have been studied as potential alternatives. Perovskite-type oxides with a general ABO_3 stoichiometry (A and B are cations with different sizes) have been studied mostly in lean CH_4 and CO oxidation (with little involvement in HCs oxidation) owing to their good oxidation activity, low cost and thermo-chemical stability at high temperatures (900-1100°C).[176-182] Although CH_4 oxidation is not directly relevant to DOCs, the features perovskites exhibited towards sulfur poisoning in this reaction could help to weigh its possibility in the application of DOCs. To date, most studies focus on La-Mn/La-Co perovskite catalysts by substituting Mn/Co with Mg, Cr, Cu, Fe etc. in the B site or partial substitution of La by Ce, Ag Sr, etc. in the A site to modify oxygen mobility and reducibility, or to provide a shield for La such that it helps to increase the oxidation activity and SO_2 durability.[176-189] For example, the introduction of alkaline Mg, both as substitution for B site inside perovskite framework ($LaMn_{1-x}Mg_xO_3$) and as MgO active phase on the external surface ($LaMn_{1-x}Mg_xO_3 \cdot yMgO$), acts as a shield for La sites due to its preferential adsorption towards SO_2.[185-187] For the redox dopants such as Ag, it guards perovskite from sulfation when staying in extra-framework while the inserted one in the lattice could increase the acidity of Mn^{4+} ions to weaken the interaction with SO_2 as well as improve the oxygen mobility.[178, 182] The combination of noble metals with perovskite structure also attracts much attention in HC and CO oxidation while the effects on catalysis and

SO_2 poisoning depend on the nature of the noble metals and the perovskite type.[180, 190-191] In either way, the perovskite catalyst tends to end up with structure collapse when encountering with SO_2 by detachment of phases into lanthanum sulfate and other oxide phases due to the basic character of La.

As for the other group of non-noble metal materials, MnO_x, CeO_2, CoO_x, CuO or their binds usually excel in the oxidation of NO and CO, especially in NO oxidation.[192-194] Catalyst formulation in this regard mainly centers on Mn-based and Ce-based catalysts, in the form as single MnO_x oxide of different shapes (e.g., α-, β-, γ-, hollow tunnel structure etc.) and valences,[195-199] single CeO_2[200], binary or trimetallic Mn-Ce[201-205], Mn-Co[201, 206], Ce-Co[207-208], MnCeM (M=Co, Fe, Sn etc.) mixtures,[202, 209-211] as well as supported Mn/TiO_2 (or ZrO_2, Al_2O_3).[95, 212-214] For example, the unique hollow or tunnel structure, and redox cycles between Mn and its partners (e.g., $Ce^{4+} + Mn^{3+} \leftrightarrow Ce^{3+} + Mn^{4+}$ for Mn-Ce, or $Co^{2+}+Mn^{4+} \leftrightarrow Mn^{3+}+Co^{3+}$; $Co^{3+}+Mn^{2+} \leftrightarrow Mn^{3+}+Co^{2+}$ for Mn-Co etc.) contribute to the NO oxidation activity by facilitating mass/electron exchange and enriching chemisorbed oxygen species at the interface. Once in contact with SO_2, sulfation of Mn can poison the catalyst.[194-195, 198, 201, 206] Whereas the strong interaction existing between some of those couplings (e.g. Mn-Co-Ce-O_x) renders formation of unstable sulfate/sulfite specie that can be decomposed at relatively low temperatures (e.g. 190°C), or that dopants help to protect active metal sites or to retain parts of undestroyed nitrates intermediate for conversion into NO_2.[192, 202-203, 205, 210, 215-218] Those features allow for a partial or full recovery of catalyst performance when SO_2 is removed from gas feed but cannot resist sulfation of metals in the duration of SO_2.[209] In some cases, the co-presence of H_2O eases SO_2 poisoning possibly by competitive adsorption effect, but it may also inhibit the transformation of nitro to NO_2.[195, 198, 211] It is notable that CrO_x/mesoporous TiO_2-pillared clay (TiO_2-PILC) or Ce doped Cr-Ce/TiO_2-PILC or $Cr/Ce_xZr_{1-x}O_2$ catalysts exhibit high sulfur resistance due to the absence of Cr sulfation during the oxidation process.[219-221]

Little research attention has been paid to the intrinsic properties of SO_2 influence on non-noble metals. Sulfur tends to break the electronic distribution and induce more oxygen vacancies in metal oxide surface, as observed for Mn, Ce-based materials.[196] While there is no report to demonstrate the positive role of this behavior in diesel oxidation because of more significant sulfation of metal oxides. An exceptional instance regarding the promotion effect of high-valence $S^{6+/4+}$ modification in the lattice of perovskite $La_{2-x}Sr_xCuO_4S_y$ can be analogous to the case of S in the metal-support interface over SO_2-aged PGM catalyst. Except for induction of more reducible Cu species effective for C_3H_6 via charge compensation, the more important feature is to enhance catalytic C_3H_6 oxidation in the presence of SO_2 with excess O_2.[222] It will be interesting to explore if such positive roles of S-containing compounds are present in other non-noble metal catalyst systems.

The superiority of non-noble metals over PGM catalysts in sulfur resistance was noticed in an early study of CH_4 oxidation.[223] Relative to the rapid deactivation of Pd/Al_2O_3, perovskite $La_{0.9}Ce_{0.1}CoO_3$ and Cr_2O_3 oxide (especially the latter) showed unappreciable activity decrease during long-term SO_2 exposure in a real industrial emission. Later study also observed a comparable activity of NO oxidation over Mn mixed-phase material to commercial Pt-based catalysts in simulated diesel exhaust.[224] Whereas it should count on more attempts to rationalize the promising application of noble-metal free replacements in DOC field given limited researches in both academia and industry. At least for most perovskites and commonly studied metal oxides, the preferential sulfation in the presence of SO_2 is still an obstacle for practical consideration in the near future, not to say their stability under harsh diesel oxidation conditions.

3.4. SO_2 impact on DOCs under real operation condition.

As noted above, the various oxidation reactions compete with each other for active sites on DOCs, a situation surely occurring in the real diesel exhaust where the mixtures of CO-HCs-NO-O_2 are present. The presence of SO_2 further intensifies such complexity by triggering or suppressing relevant reactions. The impact of SO_2 is not only characterized by its function on a specific reaction but also could result in multiple processes as the coexisting gases and intermediates (or byproducts) disturb one another.[225-227] When HCs and CO coexist, SO_2 adsorbs preferentially on the sites most important for HCs oxidation but less for CO oxidation.[31, 227-228] While the resulting CO_2 from either CO oxidation or HCs oxidation inhibits HCs oxidation by spillover from the support to the noble metal sites or residing on the support as stabile carbonates in the presence of H_2O.[31, 229] If NO is further added, the resulting NO_2 from NO oxidation could, as a stronger oxidant than O_2, oxidize HCs and CO, and meanwhile promotes the conversion of SO_x into sulfates.[230] These mixed reactions blur the influencing process of SO_2 on DOC performance.

Different from the light HCs as studied in the academia research, the real diesel exhaust contains heavy HCs. Such oxidation reactions can be rather complex involving a series of intermediates. Taking toluene oxidation as an example, the reaction proceeds consecutively as partial oxidation of toluene to benzyl alcohol, followed by transformation into benzoic acid and benzaldehyde and then the opening of benzene ring to form maleic anhydride, finally converting into CO_2 and H_2O etc.[38, 40, 214]Although suppression of benzaldehyde oxidation by SO_2 is proposed to be the rate-determining step for retarding the entire reaction in this system, no further evidence was provided to conceive what would happen if the study is put in a more real environment containing NO and CO, other kinds of HCs and water.[38, 40] It would involve a series of dynamics that may arrive at a quasi-equilibrium of multi-behaviors before leading to an apparent effect, depending on the kinetics of surface adsorption, transformation, transition state, desorption, catalyst and even the reactor used.[60] However, establishment of such information remains an open question, due not only to the absent knowledge of inclusion of SO_2 into the kinetic modeling but also to the involvement of multiple gases in the diesel exhaust.[11]

Furthermore, the real settings to which DOC is subjected may keep changing as the vehicle works in different circumstances, such as temperature and gas exposure doses.[231] The major impact of sulfur on DOCs is found at cold-start conditions, under which the exhaust gas temperature is low for oxidation. Moreover, with increasingly lowered exhaust temperature in the future by optimized combustion recipe (such as low temperature diesel combustion (LTDC)), low-temperature DOCs with stronger sulfur resistance should be an urgent need.[232] On the other hand, the concentration of SO_2 plays a significant role in the catalytic performance. An early report observes a full recovery of HCs oxidation in the simulated exhaust feed stream (containing propylene/propane mixture, CO, NO_x) when SO_2 is increased from 1 to 5 ppm and then returned to 1 ppm; but a partial recovery shows when SO_2 is reduced to 1 ppm from 30 ppm, unless the catalyst is operated at or above 700°C.[116] Another study regarding lean-burn CH_4 oxidation over bimetallic $Pd/Pt/Al_2O_3$ shows that low SO_2 concentration leads to more stable bulk $PdSO_4$, while high-concentration SO_2 tends spillover onto the support to form less stable $Al_2(SO_4)_3$.[233] Although the former gathers a lower total sulfur amount, it acquires equal activity to the latter due to lower desorption rate of sulfur and limited spillover ability, ending up with saturation of active sites.[131, 233] Currently, the mandate over ultra-low sulfur fuel (ULSD) makes DOCs possible to exhibit good performance for an extended time while continuous accumulation of sulfur species in DOCs can still result in degraded catalytic performance in the long run in reality.[91]

A last but not least concern associated with the real-world operation is that catalyst aging is a combination of hydrothermal aging and chemical contaminations (which are not only limited to S poison, but also include non-S contaminants such as P and minor metal impurities). But deactivation from such treatment (aging) is quite difficult to simulate under laboratory conditions due to the fact that multiple deactivation modes may occur simultaneously in the real world and it is challenging to distinct which poison dominates with the change of reaction conditions.[234-235] Obviously, concerted efforts from various aspects are required to unveil SO_2 dynamics on DOCs in the above-mentioned real-world context, including a solid feedback loop between academia and industry and advanced transient state simulation/capturing techniques. Especially, the combination of computational modelling and *in situ/operando* characterization techniques can be powerful in picturing sulfur poisoning process. Whereas some limitations in computation speed/amount, time/space resolution in responding to the real-world parameter settings would determine the efficacy of those techniques.

4. Mitigation strategies for sulfur poisoning

4.1. Regeneration of sulfated DOCs

One of the challenges of applying DOCs on the engine is catalyst regeneration. An effective regeneration or desulfation strategy should be able to remove the sulfur from the catalyst and recover the catalyst performance. However, relevant research is still limited on sulfated DOCs and mostly falls in the area of lean-burn CH_4 oxidation that is not directly relevant to DOCs. [54, 162, 179, 215, 225, 236-239] Given the similar catalyst formulation used for both reactions (diesel oxidation and CH_4 oxidation), the thermal and chemical regeneration protocols may also fit in with DOCs, such as high-temperature treatments under air/inert atmosphere or with the injection of reductants (such as H_2, CO, HCs).[183]

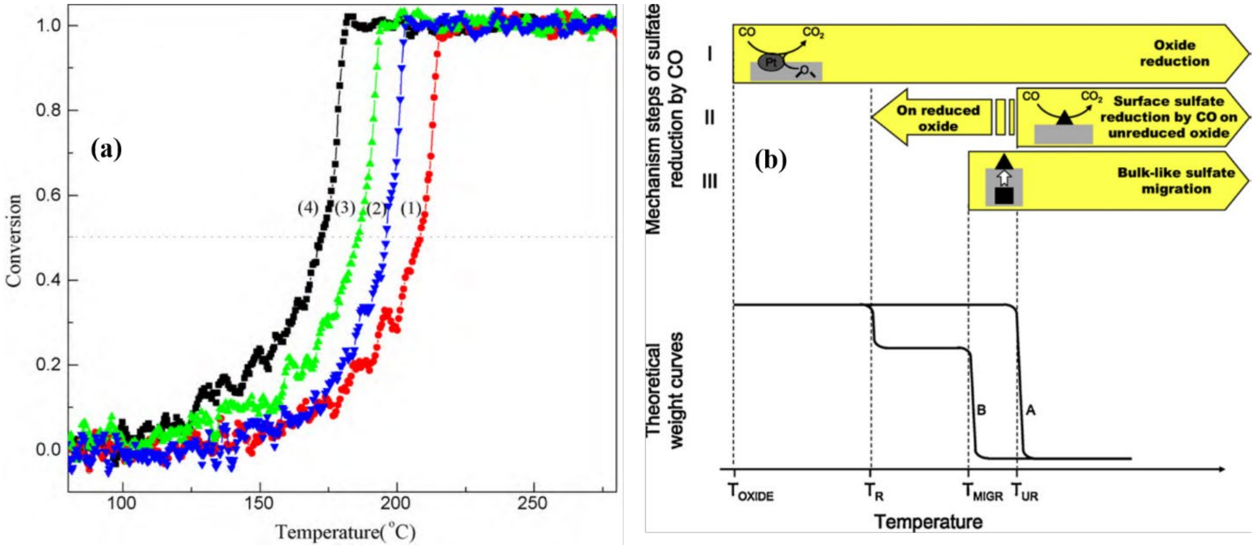

Figure 5. (a) Propylene total oxidation activity over Pt/Al_2O_3: (1) after sulfation (2 g/L S), (2) after sulfation and TPO to 700 °C in 5%O_2, 2.5% H_2O, 5% CO_2 and a He balance, (3) after sulfation and TPD to 700 °C in 2.5% H_2O and 5% CO_2 and a He balance and, (4) after sulfation and TPR to 700 °C in 1% H_2, 2.5% H_2O and 5% CO_2 and a He balance. (b) Schematic representation of a proposed mechanism for sulfates reduction by CO, in which black triangle: surface sulfates; black square: bulk-like sulfates; (A) Pt free, Ce-containing sample; (B) Pt loaded, Ce-containing sample. TOXIDE stands for oxide reduction temperature, TR for surface sulfate reduction temperature on reduced samples, TMIGR for bulk-like sulfate migration temperature and finally, TUR for surface sulfate reduction temperature on unreduced samples. Reprinted with permission from ref [240] and ref [241]. Copyright 2010 and 2012 Elsevier.

Thermal decomposition is the most common method to regenerate used catalysts. As previously described, the sulfur species formed on the catalysts include physio-chemically adsorbed SO_2/SO_3, sulfite species, H_2SO_4, surface and bulk sulfate coordinated onto OH, lattice oxygen or active oxygen species present in defects. The molecularly adsorbed SO_2 desorbs below 400ºC while surface and bulk sulfates like aluminum sulfate, cerium sulfate or $PdSO_4$ can maintain up beyond 600ºC and even above 800ºC.[119, 163, 242] Obviously, high temperature (at least 500°C) is a necessity to recover some catalyst performance.[194] Generally, the decomposition of sulfate in the active phase or in support undergoes stepwise release of oxygen from SO_4^{2-} to SO_3^{2-} and finally to SO_2, as found in the case of decomposition of $PdSO_4$ via $PdSO_4 \rightarrow PdSO_3 + 0.5O_2 \rightarrow Pd + SO_2 + 0.5O_2$ or in that Co_3O_4 substrate to CoO for sulfated Pd/Co_3O_4.[31, 69, 194, 243-245] The resulting metallic component or reduced oxide tends to sinter, probably accompanied with the shrink or collapse of catalyst structure, which is not in favor for activity recovery.[31, 69, 194, 243, 246-248]

An increased desulfation efficiency can be achieved at a lower temperature in the *reducing atmosphere* containing H_2, CO or HCs in comparison to air/inert atmosphere.[163, 178, 183, 240, 249-251] As found for a deactivated Pt/Al_2O_3 DOC for C_3H_6 oxidation (**Figure 5a**), reductive removal of the sulfur from $Al_2(SO_4)_3$ via H_2 at 700°C leads to most effective reactivation of the catalyst than via oxidizing or inert gas. This can be due to the enhanced SO_2 release, facilitating the recovery of the original acidic properties of the support and the electronic properties of the Pt particles.[240, 252] In this case, the activation energy decreases with the increased temperature and sulfur release since it is mass transfer-limited by the diffusion of bulk sulfates to surface/to active Pt sites or by H_2 diffusion to sulfur sites.[240] Interestingly, the presence of Pt favors reduction of sulfates since the dissociated atomic H on Pt site, followed by spillover to the support surface, is more reactive to sulfates at lower temperatures.[253-254] The imbalance created by the elimination of surface sulfate renders migration of bulk sulfate to the surface and reduces the sulfur deposit.[253] As similarly observed with H_2, Pt promotes the reduction of Ce-containing oxide (e.g. in sulfated $Pt/Ce_xZr_{1-x}O_2$) by CO at the interface, and then surface sulfates start to decompose to provide oxygen to the reduced oxide (as shown in **Figure 5b**).[119, 241] Whereas with excess H_2 or dry CO, the stepwise reduction of sulfate will lead to the yield of H_2S/COS or sulfur species adsorbed on Pt and oxides (e.g. in the form of cerium oxysulfur).[233, 249, 255-256] Moreover, the presence of H_2O promotes SO_2 and H_2S releases where surface hydroxyls may get involved in the formation of H_2S even when H_2O is absent.[240] For Pd-rich CH_4 oxidation catalysts, the regeneration may eventually result in the formation of Pd_4S species (via $PdSO_4 + 4H_2 \rightarrow PdS + 4H_2O$).[115, 257-259]

Treatment of S-poisoned catalysts in the SO_2-free *reaction atmosphere* also causes effective decomposition of sulfur species and reactivate the catalysts. This has been found for S-poisoned Pd-rich catalysts under rich fuel pulses (e.g. CH_4+H_2O) or with alternate CH_4-reducing/lean combustion treatments or close to stoichiometric conditions.[236, 238, 260] Also for sulfated Pt/Al_2O_3 DOC, in the coexisting gas feed of $NO + CO + C_3H_6 + O_2 + CO_2 + H_2O$, NO oxidation could drive converse decomposition of sulfates into unstable SO_x, which is the key intermediate to both sulfation and regeneration processes.[54, 149] As a result, the activity is almost restored to the initial level for the activated catalyst after three oxidation cycles. However, the catalyst cannot be completely recovered for long-term sulfated one, possibly due to that NO oxidation cannot move the sulfur species away from the Pt sites and they reappear near the Pt sites under oxidizing conditions.[149]

SO_2 prefers to adsorb on the kinked Pt, followed by the edge and finally terrace Pt sites due to the electron-donating nature of SO_2 molecule.[54] Long-term SO_2 exposure leads to more irreversibly bound sulfur species at the edge and kinked Pt sites which are hardly removed in the regeneration process. This phenomenon occurs in most cases of CH_4 oxidation catalysts even with the most effective regeneration treatments, combined with other causes, such as structural loss and active phase transformation.[31, 179, 194, 237, 251, 261] It should be mentioned that H_2O has a promoting effect on the desulfation of sulfated CH_4 oxidation catalysts in the reducing CH_4 atmosphere, resembling the findings for sulfated DOC or NSR when H_2 is used as the dominant reductant.[240, 249-250] It is proposed that the destabilizing effect of water on aluminum sulfate (which transforms into instable $Al_2O_2SO(OH)$ owning lower desorption energy) or on rhodium sulfate (for Rh/ZSM-5) facilitates sulfate removal.[260, 262] However, it remains uncertain whether this feature caused by H_2O is applicable to all cases of sulfated DOCs due to the limited studies and the lack of in-depth knowledge in this field.

Washing catalysts with distilled water or with alkaline NH_3 solution can easily cope with sulfates that stay at the surface in small amount. This method is observed effective for perovskite-type catalysts. It is observed no significant decrease in NO oxidation activity for sulfated $LaCoO_3$ DOC even after five regeneration cycles with distilled water wash.[183] Likewise, the $La_2(SO_4)_3$ or $MgSO_4$ formed on $LaMnO_3$ and Mg-doped $LaMn_{1-x}Mg_xO_3{\cdot}yMgO$ etc. can be dissolved into insoluble $La(OH)_3$ or $Mg(OH)_2$, respectively in basic solution /water, balanced by H^+ and HSO_4.[185] Then the former two can decompose into La and MgO to remain on the catalyst upon heating while the latter two are easily removed by rich OH^- as well as water leaching, thus restoring the CH_4 oxidation activity.[185, 187, 228] However, this method may wash away some components of the catalysts, which is not suitable for those soluble in water/basic media and also PGM catalysts containing low content of precious metals.[183, 187, 228] Additionally it costs additional efforts to unload catalyst module from aftertreatment system for regeneration in the real application.

4.2.2 Development of sulfur-resistant catalytic materials

After regeneration, the sulfur residue and the resulting deterioration of catalyst morphology, such as sintering, structural loss and phase transformation, will cause unreversible loss of activity.[243] Therefore, development of sulfur-resistant and regeneration-friendly catalysts has been an urgent need in the field of DOCs.[140, 159, 192, 218, 263-264] Approaches to alleviate sulfur poisoning include reducing sulfur budget on noble metals and creating new adsorption sites for target reactants.

In the reduction of sulfur budget on noble metal sites, the sulfating supports, doped with rare earth metals (such as Ce, La or their oxide CeO_2, La_2O_3) or alkaline metals (such as Mg, Ba or their oxides) with preferential reactivity towards SO_2 can be taken as sulfur sink to protect the noble metals.[125-126, 174, 265] Combining the sintering caused by sulfur and hydrothermal aging under harsh operational conditions of DOCs, sintering barriers like La_2O_3, ZrO_2 and CeO_2 or highly stable/acidic supports like SiO_2, Al_2O_3 or their mixtures are favored.[194, 236, 261, 266] Specifically, ZrO_2 is a necessary component to strengthen support robustness via Zr-O-M (M=Ce, Al, Si etc.) bond formation with CeO_2, Al_2O_3 and SiO_2.[88-89, 127, 261, 265, 267] For popular Ce-Zr solid support or the ones they modified (e.g., Al_2O_3/Ce-Zr), it has been established that the appropriate content of Zr modification into CeO_x creates defects that promote the reduction of surface sulfate at lowered temperatures, allowing the Ce-Zr-supported Pt catalyst with better regeneration ability than pure oxide like CeO_2. Similarly, the introduction of CeO_2 into Pd/Al_2O_3/$Ce_{0.6}Zr_{0.4}O_2$ decreases the decomposition temperature of sulfate by 50-100°C.[241, 253, 266, 268] Besides, the inclusion of non-sulfating SiO_2, siliceous zeolite framework supports, TiO_2 or their blends in response to decreasing sulfur adsorption and destabilizing formed sulfate on support are alternative ways to free noble metals and hence improve the regenerability of catalyst.[269] [11, 52, 66, 74, 270-273] Finally, the acid-base property of those supports carrying electro-attracting groups (e.g. SO_4^{2-}) acts to tune/ maintain the chemical state of PGM (as is discussed in sections 3.1, and 3.2.). More details regarding the support effect on sulfate formation and decomposition can be referred to Section 2.[88-89, 127, 261, 265, 267, 274]

To add additional adsorption and activation channels for target reactants and oxygen, doping transition metals such as Fe, Mn, Cu, V, W, Co etc. to modify PGM active components or supports are popularly applied in academic research.[98-99, 275] The charge imbalance resulting from the multi-valence metal dopants yields oxygen vacancies in the oxide support, which is in favor for the adsorption and dissociation of O_2 and hence the oxidation activity, such for compensating the loss caused by SO_2 poisoning.[80, 201, 210, 264, 270, 276] Note that the dopant may work in crossing roles, which involves protecting noble metals from sulfation and hindering sintering and enriching oxygen vacancies etc. at the same time.[153, 277] For instance, the Ti aimed at modifying the support acidity can also enhance oxygen mobility by Ti-O-Si linkage when incorporated into the Si matrix in Pd/SBA-15 and Pd/hollow mesoporous silica (HMS) catalysts. But the real sulfur-resistance effect is associated with the distribution form of Ti. The uniformity of Ti distribution in Pd/HMS doesn't work well in CH_4 combustion as its segregated phase in Pd/SBA-15, because the higher acidity resulting from the uniform distribution of Ti promotes spillover of SO_2 to active Pd sites as well as disables active PdO due to the formation of $Pd(OH)_2$ by enhanced surface hydrophilicity.[74, 270] This example may not cover the cases of diesel oxidation reaction but at least hints us the importance of the distribution form of dopants.

Apart from doping, morphology control, such as crystal facet fabrication or special structure constructing is also adopted to tune the adsorption sites for SO_2 vs. HCs/NO/CO and O_2 despite unknown effectiveness in the real-world practice.[196, 230, 263, 278-284] Though overlapping in adsorption sites for SO_2 and diesel exhaust gas under O_2-rich condition, a subtle local arrangement of atoms in specific crystal facet may determine its sensitivity towards SO_2 and target reactant, and hence to the degree of sulfur poisons.[78, 98-99, 230, 284] As popularly found over CeO_2 and TiO_2 oxides for NO oxidation, the low coordination status in CeO_2 (100) /(110) facet and in TiO_2 (001) facet renders the CeO_2 rod and TiO_2 nanosheet more tolerant to SO_2 oxidation than their high-coordinated counterparts, i.e., (111) facet dominated CeO_2 octahedra and (101) dominated TiO_2.[78, 200, 230, 282-283, 285] On the one hand, the high-coordination structure like CeO_2 (111) doesn't have as many adsorption sites as the low-coordinated ones to satisfy both adsorption and oxidation of SO_2 and NO adsorption. The residing of sulfite due to the lack of active O_2 species in CeO_2 octahedra may retard the transformation of sulfite to sulfate, and further redistribution of sulfur deposit. On the other hand, as in TiO_2 (101) facet, its tendency to condensing water creates an acidic aqueous environment, which favors transformation of sulfite ions to sulfate ions especially by the presence of nitrate ions resulting from the oxidation of NO, thus cause overwhelming of sulfate over the surface.[230] Both of these results explain the differences of facets towards SO_2 affinity but it may differ when involving different active components, as well as with different reaction conditions.[282]

The fabrication of specific morphology not only modifies adsorption property but also serves as a physical architecture to protect active components from SO_2 poisoning. Encapsulation of metal active components into a nanoporous shell to assemble a core-shell structure or adoption of an inverse support/metal structure with sulfur-resistant oxide (such as, SiO_2 or TiO_2 that either has non-sulfating ability or enables low thermal stability of sulfate) as a shield, has been effectively applied.[128, 215, 263, 286-287] For instance, the confinement effect of SiO_2 shell layer in the Pd-Ce nanowire@SiO_2 core-shell catalyst or in Pd@silicalite-1 catalyst is found to prevent the sintering of active Pd phase as well as the formation of large-sized $PdSO_4$ clusters.[263, 287] Both perform well for lean-burn methane combustion in the presence of SO_2 (even under harsh conditions, e.g. 800°C, water vapor, and SO_2 for the former catalyst) due to the maintenance of enough active sites and facile desorption of sulfur species. Other kinds of structural designs include the use of hollow cavity and mesoporous framework or zeolite structure.[66, 196, 270, 275, 288-289] Actually in most cases, doping and morphology control are combined to ameliorate the catalyst performance towards sulfur poisoning.[196, 290-291] Although these solutions are aimed for mitigating sulfur influence on lean-burn CH_4 oxidation, they may provide insights into improving sulfur resistance for DOCs in diesel oxidation.

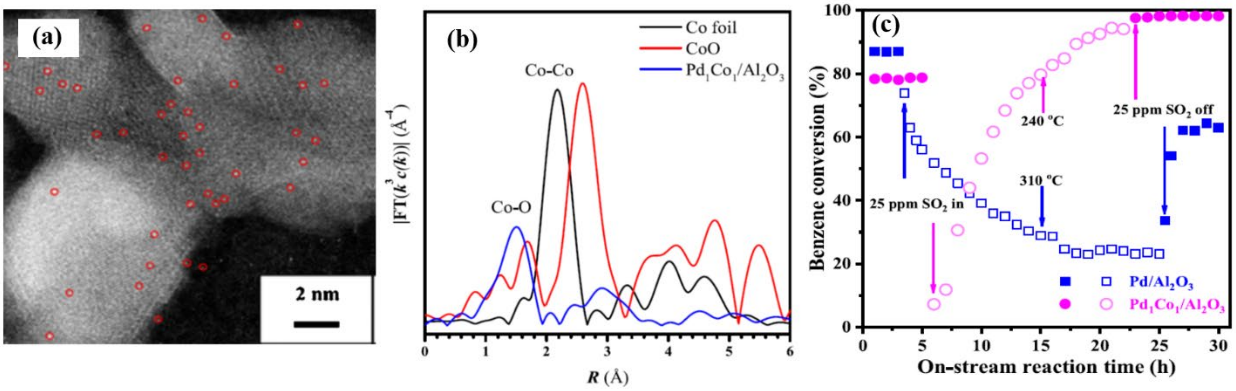

Figure 6. (a) Single atom Pd distribution and (b) Fourier transformed EXAFS spectra of Pd_1Co_1/Al_2O_3 catalyst. (c) Benzene conversion as a function of on-stream reaction time in the presence or absence of SO_2 over the as-obtained samples. Reprinted with permission from ref [292]. Copyright 2021 Elsevier.

Recently, a witness of maximum atom economy for single-atom catalysts (SACs) in achieving reactivity/selectivity has prompted its potential use in reactions relevant to diesel oxidation.[158, 293-

[295] The single metal atoms are fixed on the supports by keeping enough distance after sophisticated treatment, as confirmed for the atomically dispersed Pd and Co in PdCo/Al_2O_3 catalyst (**Figures 6a and b**). This feature makes the SO_2-poisoned PdCo/Al_2O_3 catalyst restored its benzene oxidation activity and even to a higher value than the fresh one (**Figures 6c**) because the strongly anchored Pd reacts with SO_2 to form PdO-SO_3 complex which is metastable and can decompose at low temperature for releasing the active sites and reactive oxygen species. In addition, SACs fabrication via a strong bonding between metals and supports can increase the diffusion barriers and slow down the sintering rate.[159] Nigam et al. theoretically calculated that alloying of single Ag into Pt cluster@Al_2O_3 lowers the activation barrier of S-O bond in SO_3 and weakens the binding of SO_2 with Pt cluster while also strengthens the metal cluster-Al_2O_3 interaction, hence inhibiting sulfur accumulation and Pt sintering.[161]

Despite the shown promise in sulfur resistance, there are certain deficiencies associated with SACs involving poor stability and rigorous synthesizing requirement. The single atom metals can enter the matrix of oxide complex and be lost inside the bulk phase or tend to agglomerate into nanoparticles/clusters if undergoing thermal aging or other reaction conditions.[292, 296] Especially under the reactions of HCs or NO with the presence of SO_2, there is nothing known yet about the performance of SACs. Another concern with SACs is its scale-up production due to limited use of some atomic dispersion technologies as well as characterization approaches, since it is hard to insure an even heat/mass transfer in a large-scale synthesis.[296] Such a big vacuum in the HCs/NO-relevant DOCs research and unmature scale-up production bring a challenge for SACs to be considered for industrial application in the near future.

Overall, regeneration of catalysts designed with sintering/sulfur-resistant quality in reducing atmosphere seems like an advantageous strategy to ensure longevity of DOCs. Nevertheless, understanding the choice of regeneration methods and its relation to catalyst composition and reaction conditions is highly complex and challenging. Predictable models are still lacking for the regeneration of sulfated DOCs that bridge academia investigations and real automobile application.

5. Conclusion and future directions

Sulfur dioxide in the exhaust is one of the major factors contributing to the degradation of DOCs. Current investigations and understanding of SO_2 impact on the oxidation of NO, HCs and

CO has been reviewed in this work from both academic and industrial perspectives. The preferential adsorption SO_2 over NO, HCs and CO reactants on the active sites is the main reason for the catalyst deactivation. It blocks the access of reactants to noble metals and restricts oxygen exchange between the metals and the supports. Besides, SO_2 could induce sintering of Pt species, and the sulfate deposit would modify the metal-support interface physically and electronically (e.g., exhibiting $Pt^{\delta+}$-SO_4^{2-} perimeter effect). Such changes sometimes can temporarily improve the activity in the HCs and NO oxidation, especially in the case of alkene oxidation. However, the presence of sulfur in the long run eventually leads to an unfavored electronic/geometric condition for the DOCs (e.g., fully oxidized, sintering, structural loss etc.) and thus deactivation. In the real-world practice, the complexity of gas compositions, SO_2 concentration and different working circumstances of diesel vehicles add great difficulty in revealing the influence of SO_2 on DOCs.

Regeneration of sulfated catalysts in reducing atmosphere or in SO_2-free reaction atmosphere is preferred to renew the catalyst, but it hardly recovers the activity due to irreversibly bounded sulfur residues on the catalysts regardless of morphology change and active phase transformation during regeneration process. Overall, formulation of DOCs involving metal/support composition and structure construction remains a current trend in weakening SO_2 poisoning.

Despite advances in the investigation of DOC sulfation chemistry, there are still several formidable challenges to be addressed in developing robust DOCs that are more sulfur-resistant and easy to regenerate: (1) fundamental understanding is needed on how the local coordination environment or the active phase geometry changes as function of the time-on-stream of SO_2. Insights can be obtained into the interaction modes of SO_2 and the corresponding structural evolution of catalysts, thereby catalyst design strategies could be made to minimize the sulfur interactions and maintain catalyst integrity. (2) *In situ/operando* characterization and theoretical modeling techniques are needed to understand the transient physical and chemical changes of DOCs in the multiple physical-chemical processes involved in diesel oxidation reactions, thereby helping to predict the deactivation curves and develop sulfur resistance strategy for the real-world application. (3) Simulating the deactivation of DOCs in academia laboratory in well-controlled conditions is suggested with a closed loop input from the industrial know-how knowledge in real-world aging. Such a feedback loop between academia and industry is essential in transferring fundamental knowledge to solve applied problems and will ensure that real-world aged catalysts are able to meet tightening emissions till the end of their use life. (4) Efforts should also be devoted to establishing DOC regenerability-structure relationship to achieve effective regeneration of catalysts. (5) Development of sulfur-resistant materials for DOC applied for a wide operational window should be encouraged since engine exhaust temperature tends to go lower due to the advances in engine development and turbo application. Overall, considering the strong application nature of DOCs, more efforts are needed to devise a systematic protocol filling the gap between laboratory research and industrial applications in enabling the design and development of next generation sulfur-tolerant DOCs.

Notes

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