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Review

Structure-activity relationship in Pd/CeO₂ methane oxidation catalysts

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ARTICLE INFO

Article history:

Received 30 July 2019

Accepted 4 September 2019

Published 5 June 2020

Keywords:

Palladium

Ceria

Methane catalytic oxidation

Pd-ceria interaction

Nanostructure

ABSTRACT

Palladium based catalysts are the most active for methane oxidation. The tuning of their composition, structure and morphology at macro and nanoscale can alter significantly their catalytic behavior and robustness with a strong impact on their overall performances. Among the several combinations of supports and promoters that have been utilized, Pd/CeO₂ has attracted a great attention due to its activity and durability coupled with the unusually high degree of interaction between Pd/PdO and the support. This allows the creation of specific structural arrangements which profoundly impact on methane activation characteristics. Here we want to review the latest findings in this area, and particularly to envisage how the control (when possible) of Pd-CeO₂ interaction at nanoscale can help in designing more robust methane oxidation catalysts.

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1. Introduction

The engineering and optimization of metal-oxide units for catalytic applications have always received enormous interest. Currently, the research is focused mainly on the tailoring of metal-support interaction at nanoscale [1,2]; this is particularly true for palladium-ceria formulations, which show in general very interesting catalytic properties for different reactions [3–6]. The synergy between Pd and CeO₂ is widely exploited for the catalytic oxidation of methane, a topic that is object of increasing attention due to the global warming potential of methane (~30 times that of CO₂) associated with the spreading of natural gas fueled vehicles (NGVs). NGVs have more than doubled their number worldwide in the years 2010–2019 (<http://www.iangv.org/current-ngv-stats/> accessed on August 29th, 2019), thanks to their lower pollutant emissions compared to traditional diesel or gasoline engines [7]. A vehicle running on natural gas can be equipped with a lean burn or a

stoichiometric engine, the first technology being mostly applied to heavy duty vehicles (i.e. buses and trucks) and stoichiometric operation preferred for passenger cars. In this second configuration, the exhaust aftertreatment catalyst should be able to abate efficiently also nitrogen oxides (NO_x) and CO together with unburned methane. Despite their wide application and the significant amount of research papers dedicated to Pd-based catalysts for methane abatement [8–10] some important issues are still open, the most critical being those related to the undesirable PdO decomposition at high temperature, the poor CH₄ oxidation activity at low temperature of the existing catalysts and the still modest catalyst stability. Palladium presents a peculiar redox behavior during heating-cooling cycles, in which PdO decomposition and Pd re-oxidation take place with a large thermal hysteresis [11]. Palladium oxide, which is believed to be the active phase for methane oxidation at high temperature, decomposes into poorly active Pd metal above ~973 K, the threshold tempera-

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DOI: S1872-2067(19)63510-2 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 41, No. 6, June 2020

ture depending mainly on oxygen partial pressure. This is reflected negatively on catalytic activity, with a significant loss in methane conversion particularly during cooling, when the temperature is not high enough to self-sustain the homogeneous gas phase reaction. The activity can be recovered, but only when the temperature reaches about 823 K (again depending on oxygen partial pressure) where the re-oxidation of metallic Pd takes place. Fig. 1 describes this effect, both in terms of oxygen release/uptake profile and of methane conversion for a model Pd/alumina catalyst.

Clearly this behavior is detrimental for NGV applications, due to the temperature oscillations experienced by the exhaust gases. The low temperature activity is also a fundamental requirement for efficient methane abatement catalysts, in order to minimize the emissions of unburned methane at tailpipe during cold start, together with the stability and durability in presence of steam and sulfur compounds present in the exhausts, which can deactivate the catalyst [12].

Several authors have tried over the years to optimize Pd-based formulations in order to overcome these issues, and the addition of ceria as a promoter or its use as an active support has been found very promising for all of them or even, in some cases, the best solution for optimal catalyst design. Ceria has been reported to promote Pd re-oxidation at higher temperature, increasing the thermal stability window of PdO, as well as the overall catalytic activity of Pd-based catalysts. Moreover, the use of ceria, often in combination with zirconia, has been shown to improve the catalysts stability in presence of water and/or sulfur compounds [13–17].

As a rule of thumb, the redox properties of ceria are indicated as the main responsible for the improved catalyst stability, whereas a strong Pd-ceria interaction, possibly obtained by the insertion of Pd into ceria lattice, is regarded as necessary to provide high catalytic activity. This last assumption is made on the basis of both experimental results and theoretical calculations, which suggest that a low methane activation barrier can be achieved over Pd-substituted ceria surfaces. Beside these general remarks, though, the situation is rather complex, and the picture highlighted by a careful literature survey indicates that the synergy between Pd and CeO₂ can give rise to a range of unique properties for catalytic methane oxidation. There are several reasons behind the enhanced performances of Pd-ceria

catalysts, and many of them are still under investigation or present some critical points which need to be addressed more in depth. Purpose of this review is to give an overview of the past and recent results on Pd-ceria systems for the catalytic oxidation of methane mainly in lean conditions (if not otherwise stated), considering both experimental and theoretical works and providing some tools to understand which important factors should be taken into account when designing efficient Pd-ceria formulations for catalytic methane abatement.

2. Effect of ceria on PdO stabilization and redox behavior

The thermal hysteresis between PdO decomposition and Pd re-oxidation reported in Fig. 1 was mostly studied in the 1990s and early 2000, when methane catalytic combustion was investigated also for energy production, a process typically requiring higher temperatures compared to exhaust methane abatement. In this respect, Pd was usually supported on high surface area carriers, to overcome thermal stability issues, and ceria was added as a promoter.

The first literature study describing a beneficial effect of CeO₂ on Pd-PdO transformation in Pd-based methane combustion catalysts dates back to 1995, when Farrauto and coworkers observed the decrease of the thermal hysteresis between PdO decomposition and Pd re-oxidation for Pd supported on ceria with respect to the conventional Pd/Al₂O₃ system [18]. In their work, the authors compared the thermal hysteresis of Pd supported on different oxides measured by thermogravimetric analysis, finding that the smallest gap was that of Pd/CeO₂. A literature screening for Pd-oxide catalytic systems confirms that Pd/CeO₂ shows always the lowest temperature difference between the onset of PdO decomposition and the onset of Pd re-oxidation, irrespective of the experimental technique and oxygen partial pressure (Fig. 2(A)) [18–22]. The same decrease of the thermal hysteresis is observed also when ceria is added as a dopant on Pd/Al₂O₃ (Fig. 2(B)) [23–29].

Indeed, in earlier papers it was already reported that Pd and ceria had a strong influence on the reciprocal redox behavior with palladium promoting low temperature CeO₂ reduction and CeO₂ promoting Pd oxidation [30,31], a situation confirmed also in more recent works [32–34]. The effect of ceria in the promotion of Pd oxidation, as suggested by Farrauto et al. [18], has substantial implications for the high temperature methane oxidation activity of Pd-based catalysts and, if in the past this was mainly studied for energy production applications, at present it should be taken into account when considering for example close coupled three-way catalysts for methane abatement. Primavera et al. [35] investigated the catalytic behavior of Pd-containing ceria-zirconia catalysts observing a higher methane conversion at high temperature for the sample with about 60 mol% CeO₂, a composition which gives rise to faster oxygen diffusion compared to other formulations, suggesting that the transfer of oxygen from the support to the metal could be beneficial to preserve Pd in an oxidized state. The increased conversion during the cooling branch of the light-off cycle on Pd-based catalysts containing CeO₂ is reported in several pa-

Fig. 1. Lean methane conversion (black profile) and Pd-PdO redox behavior (red profile) of a model Pd/Al₂O₃ catalyst (solid line: heating; dashed line: cooling).

Fig. 2. (A) Thermal hysteresis for Pd-oxide systems; (B) Thermal hysteresis for Pd-alumina and Pd/ceria-alumina systems (ΔT calculated as the difference between the onset of PdO decomposition and the onset of Pd re-oxidation).

pers, and in most of them is correlated experimentally with Pd-PdO redox behavior [24,26,29,36–40]. Groppi et al. [24] observed that the improvement in conversion was in good agreement with the dynamics of Pd-PdO transformation emerging from thermogravimetric analysis, showing a stabilization of PdO and an increase in the Pd re-oxidation temperature on Ce-doped (11.5 wt% Ce) Pd/Al₂O₃ and Pd/La-Al₂O₃ catalysts. The same promoting effect of ceria on Pd/Al₂O₃ catalysts was described by Haneda et al. [23] and Thevenin et al. [25], who followed PdO-PdO transition by temperature programmed oxidation (TPO) experiments in which peaks of oxygen release due to PdO decomposition and of oxygen uptake due to Pd re-oxidation can be observed. Interestingly, for Ce-doped samples two oxygen uptake peaks were detected, the first one being at higher temperature with respect to the ceria-free catalysts, thus reducing the thermal hysteresis in Pd-PdO transformation (Fig. 3). In the work by Thevenin et al. [25] it is reported that the amount of oxygen uptake in the first peak varied depending on catalyst composition and preparation method, but its temperature remained unchanged. In this case though, the promoting effect of ceria on the high temperature portion of the catalytic activity was not straightforward, likely due to the particular setup employed in the tests which

gives rise to very high space velocities. The presence of the two oxygen uptake peaks on Pd/Ce-Al₂O₃ catalysts was reported also in a paper from our group, in which we proposed the association of the high temperature peak with Pd in contact with ceria [26].

The confirmation of this hypothesis came a few years later by coupling TPO experiments with *ex-situ* HRTEM characterization. The HRTEM images of a Pd/Ce-Al₂O₃ catalyst quenched in nitrogen in the middle of the two oxygen uptake peaks during the cooling part of TPO experiment (Figure 4) showed that Pd particles in contact with CeO₂ were re-oxidized to PdO, whereas Pd clusters on alumina were still retained in metallic form [37].

To the best of our knowledge, this was the first experimental evidence of a structural Pd-ceria interplay during Pd-PdO transformation with ceria likely acting as an oxygen buffer capable to speed up the process of Pd oxidation, according to Scheme 1. Other rare earth oxides (REOs) were also found to increase the temperature for the onset of oxygen uptake in TPO experiments [21,26], as well as ceria-zirconia alone [27,28] or in combination with rare earths or yttrium [36]. When single REOs are added to the Pd/alumina catalyst, the extent of Pd re-oxidation in the high temperature step is always much smaller than with ceria [21,26], indicating a unique role of CeO₂ on the promotion of Pd oxidation. It should be emphasized that also the way Pd and ceria are put in contact with each other affects the extent of the activity loss at high temperature during the cooling part of the light-off cycle. This can be

Fig. 3. TPO profiles for Pd/CeO₂/Al₂O₃ catalysts (adapted with permission from references indicated in the Figure). Ref [23] solid line: heating; dashed line: cooling; copyright (1998) American Chemical Society. Ref [25]: copyright (2003), reprinted with permission from Elsevier. Ref [37]: copyright (2007), reprinted with permission from Elsevier.

Fig. 4. HRTEM image of a Pd/CeO₂/Al₂O₃ catalyst quenched in nitrogen during TPO experiment (point A of the cooling branch, dashed line). Adapted from Ref. [37], copyright (2007), with permission from Elsevier.

Scheme 1. Reaction scheme for promoted oxidation of Pd particles in contact with ceria on an alumina support.

inferred from the studies that compare catalysts prepared following different synthesis procedures leading to different degrees of Pd-ceria interaction [17,22,25,40–43]. For samples showing a strong Pd-CeO₂ reciprocal interplay the loss in methane conversion is less pronounced, indicating a more efficient oxygen transfer between the two components.

The action of ceria is not limited to the boosting of Pd re-oxidation during heating/cooling cycles, with the consequent reduction of the thermal hysteresis between PdO decomposition and re-formation. Evidences that the presence of CeO₂ as support or dopant stabilizes palladium in oxide form and promotes Pd oxidation in fact can be found in the literature, also not specifically referred to methane catalytic oxidation. For example, X-ray photoelectron spectroscopy (XPS) reveals that the oxidation state of Pd in Ce-containing catalysts is higher than on ceria-free supports [16,28,31,32,44–50]. The binding energies (measured as Pd 3d_{5/2}) of the different forms of palladium lie in the ranges 334.4–336.2 eV for Pd⁰, 335.7–337.6 for PdO and 335.5–336.4 eV for PdO_x, which is indicated as a surface or interfacial non-stoichiometric palladium oxide. Some authors measured also higher binding energies (337.5–338.5 eV) which were attributed to PdO₂ or Pd^{δ+} (2 < δ ≤ 4) inserted into ceria lattice [4,40,43,44,46,51–55]. The variation and overlapping of the ranges are due to different experimental conditions and composition of the samples [56], the common feature being that binding energies of Pd when ceria is present are higher with respect to the ceria-free samples. Other experimental techniques corroborate XPS results, showing a beneficial effect of ceria in maintaining Pd in oxidized form and/or shifting PdO decomposition to higher temperature [14,16,38,43,49,57]. The stabilization of oxidized palladium by ceria is often observed also after aging or reducing treatments [14,16,28,45,46,50,52,53,58–61], post reaction [22,44,62,63], or during *in situ* or *operando* experiments [14,32,38,52,64–66] even in oxygen deficient atmosphere typical of stoichiometric (or rich) operation [14,38,66].

There are some hints in the literature that the extent of the promotion of Pd oxidation by ceria can be tuned by varying ceria oxidation state and structural properties. Haneda et al. [23] observed that the presence of partially reduced ceria on alumina is beneficial to speed up Pd oxidation in TPO experiments, as well as to increase the amount of oxygen exchange with respect to stoichiometric CeO₂. Satsuma et al. [67] observed highly dispersed PdO particles on high surface area ceria, and bigger particles partly in metallic form on crystalline, low surface area CeO₂. Also Craciun et al. [68], who investigated the activity of Pd/CeO₂/Al₂O₃ catalysts for methane steam reforming, detected Pd in a more oxidized state on the sample containing amorphous ceria compared to that containing crys-

talline CeO₂. These two works suggest an influence of ceria crystal structure (and surface area) not only on Pd dispersion but also on Pd oxidation state, an effect that should be taken into account when designing Pd/CeO₂ catalysts supported on ceria with different surface area. An opposite situation was observed by Hoflund et al. [44], who reported that Pd supported on polycrystalline CeO₂ (BET S.A. of 7.5 m²/g) did not show any Pd metal after reaction, whereas a feature of metallic Pd was detected on the XPS spectrum of palladium deposited on nanocrystalline CeO₂ (BET S.A. of 179 m²/g) [44]. In this last case, though, a substantially different Pd loading was present on the two samples, which might account for the discrepancies with the papers mentioned previously.

The exposure of different facets of ceria can also affect the degree of Pd oxidation as well as PdO and CeO₂ reducibility [69–71]. A recent paper by Zhu et al. [72] provides a method to evaluate the strength of metal-ceria interaction, and according to their results not only the adsorption energy of Pd on CeO₂ varies depending on ceria exposed planes, but also there are preferential adsorption sites on each plane. This aspect is very important and deserves further investigation, as it is known that ceria morphology can undergo restructuring under operating conditions and thermal treatments [73] thus potentially affecting palladium electronic/oxidation state and Pd-ceria interaction. Moreover, also the mutual interplay and physical arrangement of Pd entities and ceria support, which can be tuned by opportune tailoring of the synthesis procedure [20,22,41,46,74,75], has a strong influence on the chemical state of Pd nanoparticles. For example, palladium can be present as Pd²⁺ in the form of PdO nanoparticles on the surface of CeO₂, or as Pd^{δ+} (2 < δ ≤ 4) inserted into ceria lattice [4,20,40,43,54,55]. Palladium stabilized into ceria lattice seems less prone to take part in redox cycles compared to Pd nanoparticles on ceria surface [20] and it is also more stable in a highly oxidized form after reaction with respect to PdO nanoparticles [22]. It would be useful to carry out specific experiments to shed some light on the influence of surface area (and degree of crystallinity), of the exposure of different planes and of Pd-Ce arrangements in order to better understand which are the parameters that have the strongest effect on Pd oxidation state and on palladium species present on the catalyst, as these properties appear to be crucial for the catalytic performance of Pd-based catalysts.

3. Role of ceria on catalytic activity

While the effect of ceria in preserving Pd in oxidized form is well established and can be ascribed to its unique oxygen exchange properties, its role on the catalytic activity for methane oxidation is more complex. Low temperature methane activation has been long debated in the past and recent literature due to the uncertainty regarding the real active phase, even if now on the basis of kinetic and theoretical studies it is proposed that an easy methane activation is not a matter of Pd or PdO but should rather be attributed to a mixture of different palladium species (Pd, PdO, undercoordinated Pd-sites and ionic Pd entities, Pd^{δ+}) and/or Pd-PdO exposed planes [76–78]. The trans-

formations experienced by the active phase with temperature under reaction atmosphere, together with other factors such as metal dispersion, mechanism of molecular activation, PdO exposed facets, lean or rich reaction conditions etc. add further complexity to the analysis of the support effect on the overall catalytic activity.

When ceria is added as a promoter in the catalyst formulation, there is a general agreement that it enhances Pd dispersion [19,45,48,50,51,58,64,79–81], apart from some discrepancies due to different Pd and ceria loadings [82] and to the presence of ceria in oxidized or reduced form [23,68]. Nevertheless, despite the promotion of palladium dispersion, in the studies in which the low temperature activity can be compared some authors do not observe a real improvement upon the addition of ceria [25,83–85]. However, it should be considered that the introduction of ceria as promoter was usually finalized to the stabilization of PdO in the high temperature range, where indeed palladium in oxide form shows the highest activity.

Regarding the use of pure ceria, or of ceria-based supports, a distinction should be made between its role on the low temperature methane activation and on the overall catalytic activity. Past and recent experimental results obtained for unsupported palladium seem to indicate that the support has negligible or no effect on methane conversion at low temperature, which depends solely on the intrinsic activity of Pd [22,86,87]. A recent paper by Willis et al. [88] compares the activity below 673 K of Pd nanoclusters of uniform sizes supported on different oxides (Al_2O_3 , SiO_2 , $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and MgO). Their screening reveals that there is a moderate size effect, with medium size nanoparticles (4–5 nm) showing slightly higher turnover frequencies for lean methane oxidation with respect to smaller (2–4 nm) or bigger (5–9 nm) particles, irrespective of the support provided that it is not basic (MgO having the lowest turnover frequencies). This work thus clarifies that, when considering Pd nanoclusters, methane activation at low temperature depends uniquely on the nature of the Pd active sites and not on the support, the mild size sensitivity being tentatively ascribed to a different proportion of exposed PdO facets. The authors in fact did not observe significant differences in Pd oxidation states, which might account for different reactivity [76,77,89–91]. The interesting findings by Willis et al. [88] are obtained in a low temperature range and involve conventional systems where Pd is present as supported clusters. When considering a wider temperature range the support becomes important in anchoring the noble metal, and when the support and the metal are in strong physical and/or electronic interaction with each other again the effect of the support can be relevant in determining the catalytic activity. This is particularly true for many Pd-ceria systems in which palladium is not present in the form of clusters on ceria surface but assumes more complex configurations.

There are several papers, mostly published in the last decade, which report that catalysts showing a strong Pd- CeO_2 interaction possess unique properties for methane oxidation and in general outperform conventional samples. Pd-based catalysts in which Pd and ceria are in strong physical contact

and/or Pd is embedded into ceria lattice are nowadays regarded as the most active formulations for methane oxidation [20,22,41,75,92,93], also on the basis of repeated reaction cycles and exposure to high temperature which are important factors in light of practical applications. Cargnello et al. [41] described the superior activity of a catalyst in which Pd-ceria core-shell nanoparticles were deposited on Si-functionalized hydrophobic alumina. According to their findings, the porous ceria shell maximizes the contact between Pd and CeO_2 itself and stabilizes the active phase particularly at high temperature since the loss in conversion normally observed on Pd-based catalysts is not present unless at very high space velocities (1,000,000 $\text{mL}/(\text{g}\cdot\text{h})$) (Fig. 5).

Despite the careful material design, some structural modifications are observed at high temperature by environmental TEM, even if very small Pd-ceria units are retained thanks to the reciprocal interaction, with possible involvement of silica as well [94].

The same group reported that the reaction rate for methane oxidation on samples calcined at 773 K can be further improved (more than twice) by high temperature calcination (1073 K) due to the modifications occurring on the ceria shell and affecting its interaction with Pd [95]. The role of ceria on methane oxidation performance in core-shell nanoparticles has been further confirmed by the comparison of Pd@CeO_2 with Pd@TiO_2 both supported on $\text{SiO}_2/\text{Al}_2\text{O}_3$, with the latter showing a much lower catalytic activity (~35% methane conversion at 573 K for Pd-Ce system against ~15% conversion for Pd-Ti; $\text{CH}_4/\text{O}_2 = 2$ and $\text{GHSV} \approx 170000 \text{ mL}/(\text{g}\cdot\text{h})$) [39]. A similar configuration with Pd@CeO_2 core-shell units, in this case without support, has been recently described by Cai et al. [92]. Ceria shell helps to avoid the aggregation of Pd particles as well as to maintain them in oxidized state. The catalytic results show that this units possess a good activity for methane conversion and are also very stable (99% methane conversion for 50 h on stream at 773 K). Pd-ceria entities in which ultra-small PdO nanoclusters are deeply inserted into CeO_2 colloidal spheres supported on alumina have also been found active and stable for methane oxidation (~100% methane conversion at 713 K maintained for 60 h; $\text{GHSV} = 60000 \text{ mL}/(\text{g}\cdot\text{h})$) [93]. In some cases, though, these units have been found unable to maintain

Fig. 5. Activity of $\text{Pd@CeO}_2/\text{H-Al}_2\text{O}_3$ core-shell catalyst (A), and $\text{Pd/CeO}_2\text{-IWI}$ (B), and $\text{Pd/CeO}_2/\text{Al}_2\text{O}_3\text{-IMP}$ impregnated reference catalysts (C). From Ref. [41], reprinted with permission from AAAS.

Fig. 6. (A) SEM-EDX mapping of Pd and ceria integrated into porous glass (reprinted with permission of Elsevier from Ref. [98]); (B) schematic representation of PdO-supported CeO₂ nanosheets@ZSM-5 membrane (republished with permission of RSC Pub, from Ref. [99]; permission conveyed through Copyright Clearance Center, Inc.); (C) Pd/PrCeO₂ nanospheres and related elemental profiles (republished with permission of RSC Pub, from Ref. [33]; permission conveyed through Copyright Clearance Center, Inc.).

their good performances in presence of water, as it will be reported in the following section.

Other formulations involving close coupled Pd and ceria have been proposed in the literature, with Pd and ceria in separate domains interacting with each other [33,64,96–101] or in which Pd is inserted into the lattice of ceria [17,20,22,40,43,46,54,102]. Regarding the first class of materials, it should be highlighted that in many cases from the characterization it is not clear whether they also might include Pd-Ce solid solutions, and the various catalyst configurations (nanosheets, nanospheres, Pd and ceria confined into porous supports etc.) make a common discussion of the results quite difficult (Fig. 6).

Nevertheless, as a general remark it can be observed that, when a comparison between the engineered Pd-ceria formulations and conventional catalysts with the same composition is reported, the first ones are always more active, indicating an important role of optimized Pd-ceria interaction in promoting the overall reactivity for methane oxidation. This appears more clearly when looking at catalysts in which palladium enters into the lattice of ceria, that are much more active with respect to samples where Pd(PdO) clusters are supported conventionally on CeO₂ [20,22,40,46,54]. The configurations explored in the literature include the formation of a solid solution between Pd and ceria by solution combustion synthesis [20,40,54] (Fig. 7), the presence of highly dispersed cationic PdO⁺ sites on ceria obtained by deposition precipitation [46] and a unique arrangement in which Pd and ceria are mixed to form an amorphous layer surrounding ceria nanoparticles realized by dry mechanical milling of Pd and CeO₂ powders [22,75].

A recent paper by Ma and coworkers [43] proposes that the role of Pd_xCe_{1-x}O₂ is that of transferring active oxygen species

from bulk CeO₂ to surface PdO species which are the real active sites, suggesting also that if the Pd-O-Ce intermixed layer is too thick the effect can be the opposite with a hindering of oxygen transfer and a decrease in catalytic activity. This point is particularly important and deserves further investigations aiming to fully understand the modifications of surface and subsurface Pd-Ce arrangements occurring during the reaction.

Whichever the role of Pd-ceria entities with tight intermixing, the experimental evidence of a higher activity of these Pd-CeO₂ formulations is supported by different theoretical works demonstrating in general that the activation of CH₄ is favored on Pd-substituted ceria surfaces. The group of Janik deeply investigated the issue of vacancy formation and methane activation on ceria, observing that the presence of Pd into the lattice increases the reducibility of CeO₂ assisting in the dissociative adsorption of methane [103,104], and that ceria in turn can favor the insertion of Pd in its structure and the stabilization of palladium oxide species in different oxidation states depending on ceria plane [105]. This latter result is functional to the lowering of methane activation barrier which is found to be lowest on Pd⁴⁺ sites that are stabilized at the interface be-

Fig. 7. Side and 3D views of the Pd-O-Ce superstructure predicted by DFT calculations for 2 wt% Pd/CeO₂ catalyst prepared by solution combustion synthesis. Reproduced from Ref. [20] copyright (2009) with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

tween CeO_2 and partially embedded PdO_x clusters [106–108]. Other authors provide further theoretical evidences that the substitution of Pd into ceria lattice increases the oxygen storage capacity of ceria [109] and that the substitutional Pd ions favor CH_4 adsorption, C–H bond cleavage and oxygen removal over these surfaces [110,111]. It is interesting to note that the predicted configuration with active Pd ionic entities originating from embedded PdO_x clusters is very similar to the observed real structure where Pd nanoparticles dissolve at the interface with CeO_2 following mechanical milling, resulting in highly active methane oxidation catalysts, as schematically shown in Fig. 8.

A general survey of the literature involving catalysts with an enhanced Pd-ceria interaction offers different examples on how to maximize this interplay by suitable treatments and synthesis methods [6,55,59,65,74,112,113]. This indicates on one side that Pd- CeO_2 systems are highly promising also for other catalytic reactions, i.e. they are intrinsically very active materials, and on the other gives some hints for the further optimization of these catalysts in the specific field of methane oxidation.

The influence of ceria on the activity of Pd-based catalysts for methane abatement should be considered also from the point of view of CeO_2 exposed facets, because different ceria planes can act differently on Pd oxidation states and on catalytic activity in general (see also the paragraph on Pd-PdO redox behavior) [105,114,115]. Up to now, only a few papers address this issue and there seems to be general agreement that the most favorable surface is the $\text{CeO}_2(110)$ or, alternatively, an agglomeration of different facets [69–71,116]. A couple of papers consider ceria nanorods as support for Pd-based catalysts, but without providing a comparison with other morphologies [43,117]. Since this topic can be particularly relevant, it would be desirable in the future to carry out a systematic investigation of the effect of different ceria planes on catalyst activity and stability, as it is known that specific ceria morphologies can change dramatically upon exposure to high temperature and can also undergo faceting and restructuring under reaction conditions [73,118].

By putting together all the past and recent experimental results, there are clear indications that the role of the support on low temperature methane activation should not be overestimated, provided that palladium is present with its most active species. These species could be identified as a mixture of Pd,

PdO and ionic Pd entities (PdO_x , Pd^{2+}), which are likely more prone to exchange or activate oxygen (and consequently methane) compared to bulk PdO. In this scenario the role of ceria appears to be that of stabilizing these species into the lattice preserving or even improving their oxygen mobility and exchange capability. In this respect, it would be interesting to check whether the insertion of Pd in ionic form into other non-redox active supports would guarantee a high catalytic activity at low temperature as well, and if these supports are capable of maintaining an appreciable methane conversion after repeated thermal cycles and in the presence of steam, as it has been reported for Pd inserted into ceria.

Ceria plays its part also in the high temperature range where PdO is the most active phase. In this case its effect is unique in stabilizing PdO and in promoting Pd re-oxidation after PdO decomposition, so that, in general, Ce-containing systems outperform other oxide-supported Pd-based catalysts for methane oxidation as discussed previously. These evidences result in the overall indication that CeO_2 is an extremely promising support for Pd-based methane abatement catalysts.

4. Poisoning and deactivation of Pd-based catalysts

The application of Pd-based catalysts for the aftertreatment of the emissions from natural gas fueled vehicles must face important challenges due to the exposure to deactivants and contaminants present in the exhausts, particularly steam (10–15 vol%) and sulfur compounds (in the ppm range [119]). If on one side the effect of SO_2 is less debated in the literature, being assessed the adsorption and consequent formation of stable sulfates on the active sites and on the support, the effect of water on Pd-based methane abatement catalysts is still more controversial. The mechanisms proposed for the deactivation observed in presence of steam include the formation of inactive $\text{Pd}(\text{OH})_2$ species as well as hydroxyl accumulation on the surface, sintering of Pd particles and inhibition of oxygen exchange with the support [120]. Within this framework, the role of ceria as a potential stabilizer for Pd-based catalysts has been investigated with respect to both sulfur compounds and water, whose effects have been considered either combined or separately. Here, for sake of clarity, the poisoning by sulfur compounds and by steam will be addressed in separate paragraphs.

Ceria is known to be a sulfating compound, due to the easy

Fig. 8. Schematic representation of the origin of highly active Pd embedded species in theoretical simulation and in real Pd/ CeO_2 catalyst. Adapted with permission from Refs. [108], copyright (2017) American Chemical Society, and [22], copyright (2018) Wiley-VCH Verlag GmbH & Co. KGaA.

formation of bulk and surface sulfates in presence of SO_2 [121]. The addition of ceria on alumina and zirconia Pd-based methane oxidation catalysts was observed to increase their deactivation in presence of SO_2 both in transient [13,51] and steady state experiments [13,122], whereas sulfation with H_2S was reported to be more severe for $\text{Pd}/\text{Al}_2\text{O}_3$ with respect to $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$ [123]. Interestingly, no deactivation was detected over Ce-doped $\text{Pd}/\text{Co}_3\text{O}_4$ catalyst during a light-off test with 10 ppm of SO_2 in the feed gas, even if a deposit of sulfates was supposed to take place because in a subsequent sulfur-free light off an increase in the temperature to achieve 50% CH_4 conversion was observed and ascribed to spillover of sulfates from Co_3O_4 to Pd [124]. The deactivation of ceria-containing methane oxidation catalysts in presence of sulfur compounds is a common finding in the literature [125–127], both in absence and in presence of water co-fed in the reaction mixture. Nevertheless, it was also reported that a sulfated $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst can be reactivated at lower temperature following a CH_4 -reducing pulse compared to non-doped $\text{Pd}/\text{Al}_2\text{O}_3$, and this was attributed to the effect of ceria in preserving some PdO from sulfation [128,129], in agreement with the observation that the overall amount of SO_2 adsorbed is lower on $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$ compared to $\text{Pd}/\text{Al}_2\text{O}_3$ when sulfation is carried out under lean reaction conditions [122]. A decrease of the sulfates decomposition temperature in inert atmosphere is reported also when ceria or ceria-zirconia are added to $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst [130]. This protecting role of ceria was tentatively related to a physical contact between CeO_2 and part of Pd nanoparticles, with sulfates forming preferentially on ceria (Scheme 2).

In this respect it should be mentioned that a comprehensive TPD-FTIR study of Pd/CeO_2 sulfation did not report any Pd-related sulfate species [131], somehow supporting the hypothesis that ceria can “attract” sulfur thus protecting the palladium particles in close vicinity.

The mechanism seems to be different when the catalyst formulation (and reaction atmosphere) is more complex. The formation of sulfates on Pd at temperatures below 723 K has been recently described for core-shell $\text{Pd@Ce}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles deposited on alumina, with spillover of sulfur species onto the support detected only above 773 K [132]. Moreover, the easier regeneration of a $\text{Pd-Pt}/\text{CeO}_2\text{-ZrO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$ methane oxidation catalyst compared to $\text{Pd-Pt}/\text{Al}_2\text{O}_3$ was found to be canceled when nitrogen oxides were added to the reaction, due to the presence of more stable PdO phase capable to link sulfates that could not be reduced during regeneration in rich conditions [133]. This should be kept in mind, since the presence of NO_x is ubiquitous in automotive exhaust gases.

A recent theoretical work by Arevalo et al. investigates the formation of SO_x ($x = 2,4$) species on the surface of $\text{PdO}(101)$,

Scheme 2. Proposed protecting action of ceria on PdO in presence of sulfur compounds.

showing that SO_2 adsorption involves both the Pd_{3f} and Pd_{4f} sites on the $\text{PdO}(101)$ surface whereas methane activation takes place only on the Pd_{3f} site [134]. The authors propose to overcome the sulfur poisoning issue by replacing the Pd_{4f} atoms with less sulfating elements or to block selectively these sites with an adsorbate that does not compromise the activity of the Pd_{3f} sites. These last findings indicate that, despite the agreement on the easy formation of sulfates on methane oxidation catalysts and tentative regeneration treatments, there are still fundamental aspects that would deserve some further investigation, particularly related with the effect of the contact between Pd and ceria and their mutual interaction. This last point is relevant also in light of the possible tuning of exposed Pd sites by a suitable Pd-ceria interplay.

When dealing with the presence of steam, a positive effect of ceria-containing support was firstly reported by Ciuparu et al. [135] who investigated the rate of hydroxyls accumulation and of de-hydroxylation of the surface for $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ catalysts. The authors observed that the deactivation of $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst at low temperature strongly correlates with the rate of surface coverage with hydroxyl groups, thus suggesting a cause-effect relationship between the two phenomena. On the ceria-zirconia supported catalyst, the rate of surface hydroxyls removal was higher with respect to alumina (Fig. 9) and this was attributed to the easier oxygen mobility of the support.

Other authors reported the stability of palladium catalysts after hydrothermal aging or during methane oxidation in wet atmosphere in presence of CeO_2 (or ceria-zirconia) as support or dopant [15,17,22,51,85,136,137]. A link with the properties of ceria is not always investigated in these papers, but in some of them a correlation between this benefit and the type of interaction between Pd and ceria is proposed. For example, in our group we have observed that when the catalyst formulation involves Pd entities embedded into ceria lattice the overall stability in presence of water is very good and higher with respect to the impregnated analogues containing Pd nanoclusters, both in transient and in steady state conditions, the loss in

Fig. 9. Rates of decrease of the Gram-Schmidt infrared relative response for Pd-based catalysts on different supports during hydroxyl desorption from the surface. Reprinted from Ref. [135] copyright (2004 with permission from Elsevier.

conversion during time on stream experiments being comprised between 10% and 20% against 75% of impregnated catalysts [17,22]. The same does not hold for core-shell Pd@CeO₂ units, supported [42] or unsupported [92], for which the formation of stable OH groups on ceria is proposed to inhibit the oxygen exchange with PdO and its accessibility to the gas phase [42]. For the alumina-supported core-shell units an additive deactivation in presence of water and phosphorus has also been observed, and ascribed to the agglomeration of CeO₂ nanoparticles with subsequent incorporation of Pd active phase [138]. The opposite behavior of these two configurations in presence of water, in both of which Pd and ceria are in strong interaction with each other, indicates clearly that the interaction itself is not enough to guarantee good stability, and emphasizes once more the role of the reciprocal physical position of the two components and, likely, of their mutual electrochemical interaction.

The tailoring of the physical environment in which Pd-ceria ensembles are located seems indeed to be crucial in enhancing their stability against deactivation in presence of water and/or sulfur. Very recent papers consider the encapsulation of Pd-ceria entities in protecting shells that are found to be effective to stabilize their behavior (Fig. 10) [99,102,139]. The interaction between Pd and ceria, considered as the responsible of the catalytic activity, is preserved by a shell or a layer that prevents the deactivation of the catalyst keeping Pd-ceria units free from contaminants present in the gas stream. This novel approach appears to be very promising in light of the design of more stable and durable methane abatement catalysts because, even if these materials have not yet being tested in a full exhaust mixture, the experimental conditions reported in these works are intended to mimic real operating atmosphere especially regarding the presence of steam and sulfur.

5. Conclusions

Pd/CeO₂ catalysts for methane oxidation appear to be complex systems in which the mutual nanoscale interaction of the

two materials can alter significantly the structural characteristics together with redox properties and reactivity of the single components. One of the first things to be assessed in the literature, and that is now well accepted, is that the synergy between Pd and ceria improves the stability of palladium oxide at high temperature and promotes the re-oxidation of metallic Pd, resulting in higher methane conversion in the high temperature range compared to other Pd-supported materials. Despite this result, there is still some work to be carried out, because only few of the most recent papers consider catalyst testing at high temperature (i.e. above 973 K), where the decomposition of PdO becomes relevant. Due to the temperature oscillations experienced by the exhaust gases and considering the kinetically hindered re-oxidation of metallic Pd, this aspect should not be overlooked and repeated heating/cooling cycles should be performed up to ~1100 K in order to evaluate the overall catalytic performances.

The effect of ceria on the low temperature methane activation is more debated, essentially because there are still some uncertainties on the real Pd active phase under operating conditions, and on the role of the support. The analysis of the literature, especially the most recent one, seems to indicate that bulk PdO is less active than a combination of Pd in different oxidation states (Pd⁰, Pd²⁺, Pd⁴⁺, substoichiometric PdO_x etc.), and that the support has a minor effect on the intrinsic catalytic activity. In this respect, the role of ceria appears to be that of promoting the oxygen mobility of Pd ions which, in turn, are likely to be stabilized by the direct interaction with CeO₂. To better clarify this point, it would be interesting to carry out specific studies aimed at understanding the influence of palladium electronic configuration and morphology, independently from the presence of ceria, as there are indications in the recent literature towards an effect of different Pd-PdO exposed planes and electronic state on methane activation.

Over the years, the researchers have evidenced that the synergy between Pd and ceria can be tuned by specific synthesis approaches that favor the nanoscale interaction, for example by embedding Pd species into ceria lattice (more active configuration), over the formation of less active PdO clusters in which most of the palladium is not in direct contact with ceria. The physical contact between the two components is indeed a key factor, as observed also for the high temperature stabilization of PdO and for the resistance to sulfur poisoning of Pd/CeO₂/Al₂O₃ materials. Moreover, the presence of ceria as a promoter of oxygen mobility has been demonstrated to improve the stability of catalysts in presence of water, a crucial issue for the application in the abatement of methane emitted from natural gas fueled vehicles. Regarding this aspect, more work is needed in order to assess the practical feasibility of such systems with Pd and ceria in strong interaction, both in terms of sustainable synthesis routes (for example limiting the number of steps to obtain the final product and the use of solvents, considering the possibility of scale up of the synthesis etc.) and of catalyst robustness and durability that should be evaluated in realistic reaction atmosphere. At present, many of the papers describing close-coupled Pd-ceria configurations involve quite complex preparation methods that are not easily

Fig. 10. Schematic representation of Pd-Ce catalysts obtained by confinement into SiO₂ nanowires. Reprinted with permission from Ref. [102], copyright (2018) Wiley-VCH Verlag GmbH & Co. KGaA.

scalable. If on one side this has been and still is necessary to understand the fundamentals of Pd-CeO₂ entities, on the other needs somehow to be overcome in perspective of their practical application.

The future research should then be addressed both towards the fundamental understanding of the low temperature methane activation mechanism on Pd/CeO₂ systems, that is essential to move forward in the design of effective catalysts, and to the development of sustainable approaches to obtain these materials. The increased availability of advanced *in situ* and *operando* characterization techniques should be exploited in order to better understand which are the parameters that govern the mutual nanoscale Pd-CeO₂ interaction under reaction atmosphere and the nature of the active sites. A systematic approach considering the effect of the single properties, such as for example the exposure of different Pd and/or ceria facets, would be desirable due to the many variables involved. Regarding the preparation methods, more efforts should be devoted to the exploring of solvent free (or solventless) routes, and to the evaluation of the stability of the recently proposed encapsulated Pd-Ce ensembles in more realistic reaction conditions (for example by including NO_x and CO in the testing mixture).

Pd/CeO₂ catalysts constitute an exciting challenge in the field of environmental catalysis, and the great attention raised nowadays by the topic of methane activation makes them very attracting also beyond the application in natural gas fueled vehicles, pushing the research towards a deeper investigation of the issues that remain still open.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 938–950 doi: 10.1016/j.cjcat.2020.06.010

Structure-activity relationship in Pd/CeO₂ methane oxidation catalysts

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Pd/CeO₂ methane oxidation catalysts show good performances, associated with the unusually high degree of interaction between the two components. This review summarizes some recent advances in this area, with a focus on Pd-ceria interaction at nanoscale.

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Pd/CeO₂甲烷氧化催化剂的构效关系

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摘要: 钯基催化剂是甲烷氧化活最具活性的催化剂。在宏观和纳米尺度上, 它们的组成、结构和形态的调整可以显著改变其催化行为和稳定性, 对催化剂的整体性能有很大的影响。在已经应用的几种载体和促进剂组合中, Pd/CeO₂由于其活性

和耐用性以及Pd/PdO载体之间较强的相互作用而引起了人们的极大关注. 这使得人们可在纳米尺度上创建特定的结构, 从而对甲烷活化特性产生重大的影响. 本文综述了该领域的最新发现, 特别是设想如何在纳米尺度上尽可能控制Pd-CeO₂相互作用, 从而有助于设计更强劲的甲烷氧化催化剂.

关键词: 钯; 二氧化铈; 甲烷催化氧化; Pd-CeO₂相互作用; 纳米结构

收稿日期: 2019-07-30. 接受日期: 2019-09-04. 出版日期: 2020-06-05.

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