Perovskite-supported Palladium for Methane Oxidation – Structure–Activity Relationships

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Abstract: Palladium is the precious metal of choice for methane oxidation and perovskite-type oxides offer the possibility to stabilize it as PdO, considered crucial for catalytic activity. Pd can adopt different oxidation and coordination states when associated with perovskite-type oxides. Here, we review our work on the effect of perovskite composition on the oxidation and coordination states of Pd and its influence on catalytic activity for methane oxidation in the case of typical Mn, Fe and Co perovskite-based oxidation catalysts. Especially X-ray absorption near edge structure (XANES) spectroscopy is shown to be crucial to fingerprint the different coordination states of Pd. Pd substitutes Fe and Co in the octahedral sites but without modifying catalytic activity with respect to the Pd-free perovskite. On LaMnO₃ palladium is predominantly exposed at the surface thus bestowing catalytic activity for methane oxidation. However, the occupancy of B-cation sites of the perovskite structure by Pd can be exploited to cyclically activate Pd and to protect it from particle growth. This is explicitly demonstrated for La(Fe,Pd)O₃, where catalytic activity for methane oxidation is enhanced under oscillating redox conditions at 500 °C, therefore paving the way to the practical application in three-way catalysts for stoichiometric natural gas engines.

Keywords: Automotive catalysis · Octahedral coordination · Methane · Palladium · Perovskite

Introduction

Perovskite-type oxides of general formula AB₉O₃ₓ where A is typically a lanthanide or alkaline-earth element in twelvefold coordination and B a transition metal in sixfold coordination (BO₆ octahedra), are mixed-oxide oxidation catalysts with intriguing properties.[1] Substitution of either the A- or B-site cation is considered a suitable strategy to tune both the stability to exposure to high temperature and the efficiency for various catalytic reactions. For some practical applications like car exhaust aftertreatment where reductive operation periods are periodically applied, addition of a precious metal by the partial substitution of B-site cation[2] or by mixing the perovskite-type oxide with a conventional non-perovskitic formulation[3] results in suitable conversion efficiencies of pollutants. The former situation is the subject of this contribution. The protective function of the perovskite-type oxide towards particle growth of precious and transition metals was already recognized in the early studies.[4] However, the structural redox ‘breathing’ of a perovskite-type oxide has provided renewed interest for the combination with a precious metal, especially where the precious metal is required for low-temperature activity and for reduction activity. Addition of Pd to LaFeO₃ generates a promising three-way catalyst for the exhaust aftertreatment of gasoline engines that was commercialized in Japan.[5] Under the oscillating redox conditions and after exposure to high temperature, LaFeO₃ is able to avoid extensive Pd particle growth observed on the conventional catalyst, a major source of efficiency loss of automotive catalysts with mileage. Pd can reversibly enter the perovskite lattice under oxidizing conditions and exsolve under reducing conditions. This strong interaction was also exploited to develop a PdO/LaFeO₃ catalyst for NO and N₂O reduction.[5]

The scarce global oil reserves together with the increasing number of vehicles worldwide and the progressively severe emission regulations call for alternative fuels and as a consequence for targeted exhaust after-treatment technologies. In this context, the Swiss Federal Laboratories for Materials Science and Technology (Empa) are developing mid-class passenger vehicles based on the use of natural gas (composed of >90% CH₄). The current commercial after-treatment technology for stoichiometric natural gas fuelled engines is based on three-way catalysts (TWC) enriched in Pd, recognized as the major active precious metal for CH₄ oxidation. Beside CO and NOx pollutants, engine CH₄ emissions need to be treated catalytically because of its larger global warming potential than CO₂.[6] Since perovskite-type oxides are excellent CH₄ oxidation catalysts[7] and are promising TWC of natural gas engines when modified with palladium,[8] we have initiated a research line directed towards the systematic understanding of the structure of precious metal-substituted perovskite-type oxides and its influence on catalytic activity for the specific case of CH₄ oxidation as model reaction. Against the background provided by the work on LaFeₓPd₃₋ₓO₄ for gasoline vehicles, we have started to consider the influence of the structure of Pd in the same catalyst formulation but for CH₄ oxidation under steady state and oscillating redox conditions. Since LaFeO₃ is not very active for CH₄ oxidation, the major questions are whether the protective function exerted by the perovskite-type structure is a general feature of typical oxidation catalysts (ferrate, cobaltate and manganate) and whether it can be exploited in the case of natural gas operation. In this contribu-
tion, we review our results obtained over the past five years.

Where is Palladium?

Determination of the oxidation- and coordination state of palladium in perovskite-type oxides by XRD is difficult because of the fine dispersion of the Pd-containing phase and especially because of the overlap of the perovskite reflexes with those of PdO. The oxidation and coordination states of palladium are better investigated using X-ray absorption near edge structure (XANES) spectroscopy, which is also excellently suited for in situ studies. The XANES spectra of two samples are presented in Fig. 1(a). La(Fe,Pd)O$_3$ was prepared by the amorphous citrate method[9] by directly mixing La, Fe and Pd precursors and citric acid, followed by drying on the rotary evaporator and in the vacuum oven at 70 °C and by calcination at 700 °C for 2 h.[9] On the other hand, a second sample designated as PdO/LaFeO$_3$ was prepared by impregnation of LaFeO$_3$ by keeping the Pd loading at 2 wt%. Both spectra show that palladium is oxidized. However, the spectrum of PdO/LaFeO$_3$ is very similar to that of dispersed PdO on Al$_2$O$_3$. Therefore, Pd in this sample is present on average as Pd$^{2+}$ in square planar coordination as is the case of Pd in PdO particles. This conclusion is strongly supported by XPS.[9] Pd exhibits different oxidation and coordination states in La(Fe,Pd)O$_3$. The high energy edge position of the corresponding XANES spectrum suggests that the oxidation state is higher than in PdO/LaFeO$_3$ and typical supported PdO. XPS results indicate that Pd is in a higher oxidation state than 2+. Additionally, the whiteline of the XANES spectrum is very different from that of PdO and presents a doublet (ΔE = ca. 11 eV) that can be taken as the fingerprint of Pd occupying octahedral Fe sites and therefore in octahedral coordination inside the LaFeO$_3$ framework.[9] The following evidence supports this conclusion. The simulated spectrum of La(Fe,Pd)O$_3$, based on full multiple scattering theory[9] clearly shows the doublet observed in the experimental spectrum (Fig. 1(a)). Further, a similar XANES spectrum with the characteristic doublet is observed for LaPdO$_3$. The origin of the peak 11 eV higher than the whiteline was associated by Kim et al. to a shake up process involving 1s→5p transitions in the octahedral system[12] but still deserves deeper investigation. Additionally, the doublet is also observed in the XANES spectra of the self-regenerative catalyst (LaFe$_{0.95}$Pd$_{0.05}$)$_2$O$_3$,[13] though the interpretation of the reversible change of structure of Pd in oxidizing and reducing environments was based mainly on the shift of the Pd edge energy. The observation that also other elements in distorted octahedral coordination display a doublet in the whiteline of the XANES spectrum supports our interpretation.[14]

The nature of the different Pd species identified using XANES can be further verified by probing their stability under reducing conditions, i.e. using hydrogen temperature programmed reduction (H$_2$-TPR). Under H$_2$-TPR conditions, PdO/LaFeO$_3$ partly reduces already at room temperature, which is typical of supported Pd nano-particles (Fig. 2). At 300 °C, the spectrum resembles that of metallic Pd supported on conventional oxide supports. In strong contrast, La(Fe,Pd)O$_3$ reduces slowly and at 300 °C the XANES spectrum does not present any evident feature of metallic Pd. Reduction occurs as indicated by the shift of the edge energy to lower values (arrows in Fig. 2). The different reduction behaviour of La(Fe,Pd)O$_3$ is associated with the slow segregation of Pd and
the formation of small Pd domains that do not yet show the typical EXAFS oscillations of structured Pd nano-particles at this temperature. The in situ XANES data well reflect conventional H₂-TPR experiments showing a single reduction peak at 86 °C and a broad one at 270 °C for PdO/LaFeO and La(Fe,Pd)Oₓ, respectively.[9]

The characterization data show that Pd adopts at least two different oxidation and coordination states in LaFeO₃, depending on the different synthesis routes. When the Pd salt is added to the precursor solution of the perovskite-type oxide, a solid solution between LaFeO₃ and PdO is formed, where Pd is in distorted octahedral coordination and as a result of charge neutrality in higher oxidation state than 2+. The formal formula of this sample is LaFe₁₋ₓPdxO₃. On the other hand, when LaFeO₃ is impregnated with the Pd salt, calcination generates supported PdO nano-particles and therefore, Pd in the oxidation state 2+. Actually, we have shown by XANES analysis that both Pd states populate PdO/LaFeO₃.[9] Thermal aging of PdO/LaFeO₃ causes variations of the ratio between the two observed Pd species.[15]

The observed Pd species demonstrate different effects on the catalytic activity of the two LaFeO₃-based materials.[9] It is immediately evident from Fig. 3(a) that PdO/LaFeO₃ is more active at lower temperature than La(Fe,Pd)Oₓ for methane oxidation (O₂/CH₄ = 4) during a full heating-cooling cycle (200–900 °C). PdO exposed on LaFeO₃ is obviously the active phase. In contrast, the activity of La(Fe,Pd)Oₓ is almost identical to that of LaFeO₃. Therefore, octahedral Pd cannot sustain catalytic activity in this temperature regime. Typically, the activity of a perovskite-type oxide above 500 °C is dictated by the oxygen supplied by the perovskite lattice (intracrystalline mechanism).[16] Hence, Pd does not modify this property upon incorporation in the LaFeO₃ structure.

The cooling segment of the activity run of Fig. 3(a) is indicative of strong structural modifications upon attaining high temperature. The activity profile of PdO/LaFeO₃ exhibits a loss of ca. 25% between 700 and 550 °C that is typical of the formation of metallic Pd. At high temperature, PdO thermodynamically reduces to Pd⁰ even under oxidizing conditions, a process that is well-known on conventional Pd-based methane oxidation catalysts.[17] Pd re-oxidation upon cooling regenerates the catalytic active PdO phase below 600 °C thus explaining the activity rise before extinction. Interestingly, the same activity profile is observed in the case of LaFe(Pd)O₃. Assuming that the same reduction/re-oxidation process described for PdO/LaFeO₃ is valid, we conclude that during heating at temperatures above 700–800 °C octahedrally coordinated Pd segregates at the LaFeO₃ surface as Pd⁰ thus causing the activity loss during cooling. At lower temperature Pd⁰ re-oxidation causes a similar activity increase observed for PdO/LaFeO₃, but the gained activity is lower than for PdO/LaFeO₃ because of the partial re-incorporation of Pd into the LaFeO₃ structure. The process may be partial because restoration of the LaFe(Pd)O₃-like structure upon reduction and re-oxidation is temperature dependent: the lower the re-oxidation temperature the lower the fraction of octahedral Pd.[12]

Methane oxidation under lean conditions is a suitable probe reaction for the different Pd states. It allows structural information to be drawn during the reaction and it is a measure of the reactivity of different precious metal species. Fig. 3(a) reveals that if the activity profile of PdO/LaFeO₃ is compared to that of PdO/Al₂O₃, a tenfold higher surface area catalyst (Table 1), PdO/LaFeO₃ can be considered a good high temperature catalyst, but still inferior to PdO/ceria-zirconia, for example.[18] LaFeO₃ retards the spontaneous reduction of PdO: the temperature range in which the activity drop occurs is narrower and the activity loss is reduced compared to PdO/Al₂O₃. This function can be easily attributed to the strong interaction between palladium and LaFeO₃ that is reflected in the small fraction of octahedral Pd present in the sample. It can be speculated that PdO particles obtained after calcination are anchored to LaFeO₃ through the PdOₐ/-containing phase.[5] LaFeO₃ providing a reservoir for oxidized Pd in the high temperature regime where re-incorporation is still feasible.

Table 1. Physico-chemical properties of Pd-free and Pd-substituted LaMnO₃, LaFeO₃ and LaCoO₃.

| sample     | SSA [m²/g] | Pd content [wt %]¹ | XRD² |
|------------|------------|---------------------|------|
| LaMnO₃     | 20         | –                   | pr   |
| La(Mn,Pd)O₃ | 12         | 1.86                | pr   |
| LaFeO₃     | 14         | –                   | po   |
| La(Fe,Pd)O₃ | 14         | 1.95                | po   |
| PdO/LaFeO₃ | 13         | 1.98                | po   |
| LaCoO₃     | 6          | –                   | pr   |
| La(Co,Pd)O₃ | 9          | 1.90                | pr   |
| PdO/Al₂O₃  | 135        | 2                   | PdO, γ-Al₂O₃ |

¹Determined by ICP-OES.[9,10] ²p, perovskite; r, rhombohedral; o, orthorhombic.
Oscillating Reaction Conditions

LaFeO$_3$ is not very active for methane oxidation and improved catalytic activity was found only upon addition of palladium in the form of PdO particles. However, it has been shown above that we have been able to prepare a LaFe$_{0.95}$Pd$_{0.05}$O$_3$-like solid solution that is homogeneous with respect to the oxidation and coordination states of Pd. The apparent activation pathway shown in Fig. 3 indicates that it would be of Pd. The apparent activation pathway modulation (Fig. 4(a)). However, the spectral changes are more important for La(Fe,Pd)O$_3$. In PdO/Al$_2$O$_3$, the spectrum obtained at the end of each O$_2$ pulse does not coincide with the fully oxidized state indicating that during the experiment the oxidation state of Pd reduces. This is confirmed by the data obtained after treatment using phase sensitive detection (PSD) to improve the S/N ratio and to enhance the subtle spectral changes induced by the repeated redox pulsing.[19,20] The phase-resolved spectra of both samples (Fig. 4(b)) show that the amplitude of the signal arising in correspondence with the Pd edge (24.350 keV) of LaFe$_{0.95}$Pd$_{0.05}$O$_3$ is twice that of PdO/Al$_2$O$_3$. The amplitude of this signal is proportional to the oxidation state of the sample, its intensity coinciding with the energy shift indicated by arrows in Fig. 2. The larger the difference between initial and final oxidation state achieved during the experiment, the larger the amplitude change in the phase-resolved spectra. In the case of PdO/Al$_2$O$_3$, this amplitude change must correspond to the change from reduced Pd to partially oxidized Pd, the highest achievable oxidation state being 2+. However the time-resolved spectra indicate that re-oxidation is not complete. On the other hand, the intense edge energy signal for LaFe$_{0.95}$Pd$_{0.05}$O$_3$ can be associated with the periodic reduction to Pd$^0$ and re-oxidation to an oxidation state that is larger than 2+ and that possibly corresponds to 3+ as indicated for LaFe$_{0.95}$Pd$_{0.05}$O$_3$.[21] This observation is considered the evidence that the protective function of the perovskite is at work under these conditions. Under oxidizing conditions, metallic Pd is re-oxidized and the strong interaction between the perovskite and the precious metal is restored. The absence of such interaction in the case of the alumina support prevents Pd from returning to the original oxidized state after every reduction pulse, thus causing the continuous reduction that at higher temperature induces particle sintering.

The mass spectrometry (MS) data also demonstrate that such reversible periodic reduction/re-oxidation has positive effects on catalytic activity for methane oxidation. In correspondence with each pulse the concentration of methane is transiently reduced to a larger extent than at the end of each pulse, which represents steady state reaction conditions (Fig. 4(c)). This is confirmed by the corresponding transient increase of the CO$_2$ concentration at each pulse, which is not observed for PdO/Al$_2$O$_3$. Hence, the transient reduction and re-oxidation of Pd in La(Fe,Pd)O$_3$ evident from the QEXAFS data is associated with a transient enhancement of catalytic activity. The data obtained under periodic reaction conditions indicate the need to perform operando time-resolved measurements under representative reaction conditions in order to try to disclose the nature of the possible transient species responsible for this behaviour.

Typical Perovskite-type Oxidation Catalysts

In contrast to LaFeO$_3$, LaMnO$_3$ and LaCoO$_3$ are excellent oxidation catalysts.[16] LaMnO$_3$ was shown to surpass Pt/Al$_2$O$_3$ for methane oxidation.[23] The addition of Pd to the perovskite structure can generate active materials with similar properties to those of LaFe$_{0.95}$Pd$_{0.05}$O$_3$. Pd- and Pt-substituted LaCoO$_3$ is promising for example for NO reduction by H$_2$[24] and for the water gas shift reaction.[25] respectively. Synthesis of LaFeO$_3$ and LaMnO$_3$ using ultrasonic spray combustion (USC) indicated that the oxidation and coordination states of Pd might be different from those proposed for LaFe$_{0.95}$Pd$_{0.05}$O$_3$.[24] Nishihata et al. reported the solubility regimes of Pd, Pt and Rh in a number of perovskite-type formulations.[25] They also demonstrated that the self-regenerative property observed for LaFe$_{0.95}$Pd$_{0.05}$O$_3$ was not valid for LaMnO$_3$ and LaCoO$_3$ because of the irreversible reduction of the perovskite lattice at high temperature.[26] Based on the acquired knowledge on the possible Pd species present on LaFe$_{0.95}$Pd$_{0.05}$O$_3$ using XANES, La(Mn,Pd)O$_3$ and La(Co,Pd)O$_3$ were prepared by the amorphous citrate method and were characterized with respect to the oxidation and coordination state of Pd (Table 1). The XANES spectra of fully oxidized La(Mn,Pd)O$_3$ and La(Co,Pd)
LaCoO₃ in the same temperature range. Because of contradiction with the incorporation of Pd in La(Mn,Pd)O₃, it is very similar (Fig. 5). Reduction of La(Co,Pd)O₃ demonstrates that PdO and LaCoO₃ reduce, thus confirming the inactivity of Pd buried in the perovskite lattice for this reaction.


dispersed palladium on perovskite-type mixed oxides is a potential catalyst for three-way catalysis, where the oxidation activity of the support is completed by the reduction and the oxidation activity of the precious metal. Our work shows that the structure of the precious metal-based catalysts needs to be carefully ascertained, which is dependent on the nature of the selected metal cations, including Pd.

Finally, it should be emphasized that the intimate interaction between a perovskite matrix and Pd is not a characteristic of Pd only but can be associated with transition and coinage metals in a broader view. Therefore, the "self-regenerative" property can be used in a wider application range where other elements than precious metals are used.[11] It certainly represents a fascinating strategy to prepare catalysts with new and unusual properties.

Conclusions

Dispersed palladium on perovskite-type mixed oxides is a potential catalyst for three-way catalysis, where the oxidation activity of the support is completed by the reduction and the oxidation activity of the precious metal. Our work shows that the structure of the precious metal-based catalysts needs to be carefully ascertained, which is dependent on the nature of the selected metal cations, including Pd.

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